The Twenty-eighth Session of the Intergovernmental Meeting (IG28)
on the Acid Deposition Monitoring Network in East Asia (EANET)
24-26 November 2026, Niigata, Japan

FINAL REVIEW OF TECHNICAL TRAINING GUIDANCE FOR AMBIENT VOCS MONITORING UNDER EANET

I. INTRODUCTION

1. VOCs are noteworthy substances in achieving co-control of $PM_{2.5}$ and ozone as the common precursors of both. In terms of VOCs related activities, there is a huge disparity among the participating countries of Acid Deposition Network in East Asia (EANET) in capacity of monitoring methodologies, instruments, human resources, etc., and this disparity is much bigger than other substances. Some EANET participating countries are still under way of establishing or developing in VOCs related activities.

2. Considering such different status among the EANET Participating Countries, the EANET project "Promotion of VOCs Related Capacity Building in EANET" (hereinafter referred to as the EANET VOCs Project) starts from the feasibility study in 2023 and implement full-scale activities from 2024 to 2026 in line with its plans approved by the Intergovernmental Meeting (IG) of the EANET in respective years.

3. The purpose of the EANET VOCs project including:
   - Understand the VOCs monitoring and analysis status in EANET;
   - Enhance necessary capacity building for the VOCs monitoring and analysis in EANET;
   - Suggest policy implication to improve the VOCs management in coordinately controlling $PM_{2.5}$ and O_3 and mitigate health impacts;
   - Conduct other activities including VOCs related research requested by the EANET Participating Countries.

II. DRAFT COMMITTEE

4. To support the development of comprehensive Guidance on VOCs Monitoring and Measurement Technology under the EANET VOCs Project, we propose the establishment of a Draft Committee. This committee and Advisory Group experts are responsible for drafting the guidance, ensuring that it reflects the latest scientific knowledge, best international practices, and practical experiences from EANET participating countries. The guidance will incorporate original data obtained from capacity-building activities conducted in pilot cities, making it a valuable resource to EANET participating countries.
5. Key Tasks of the Draft Committee:
   - Develop the Structure and Scope of the Guidance – Define key topics, methodologies, and technical requirements for VOCs monitoring and measurement, incorporating

experiences learned from pilot cities.

- Review Existing Standards and Best Practices – Analyze international guidelines and align the document with globally accepted approaches while considering regional contexts.
- Utilize Original Data from Capacity-Building Activities – Integrate data collected from pilot cities to ensure the guidance is based on practical experiences and challenges.
- Facilitate Stakeholder Engagement – Consult with participating countries, institutions, and field technicians to incorporate diverse perspectives and operational insights.
- Draft and Revise the Guidance – Prepare a comprehensive draft and refine it based on feedback from advisory group members, technicians, and stakeholders.
- Finalize and Endorse the Guidance – Ensure the document is validated by experts and stakeholders, making it ready for implementation by EANET participating countries.
- By considering both scientific expertise and hands-on experience, the Draft Committee will ensure that the guidance is not only technically sound but also practical and applicable to VOCs monitoring activities of EANET participating countries.

III. ACTIONS REQUIRED

6. The Session of SAC26 adopted the Technical Training Guidance for Ambient VOCs Monitoring under EANET (Attachment 1) from the scientific and technical viewpoint and to be further endorsed at IG28.

Attachment 1

Technical Training Guidance for Ambient VOCs Monitoring under EANET

Network Center for Acid Deposition Monitoring Network in East Asia (EANET)

AUTHORS LIST

Advisory Group Members:

- Dr. Toshimasa Ohara, Director General, Asia Center for Air Pollution Research (ACAP), the Network Center for the EANET (NC)
- Dr. Junya Hoshi, Researcher Manager, Tokyo Metropolitan Institute of Environment Protection, Japan
- Dr. Le Ngoc Cau, Deputy Director General, Institute of Meteorology, Hydrology, Environment and Marine Sciences (IMHEMS), Ministry of Agriculture and Environment, Vietnam
- Prof. Fan Meng, Visiting researcher, former DDG of the NC for the EANET
- Prof. Hong Li, Professor, Institute of Atmospheric Environment, Chinese Research Academy of Environmental Sciences (CRAES), China
- Prof. Gangwoong Lee, HANKUK University of Foreign Studies, the Republic of Korea
- Dr. Kessinee Unapumnak, Ministry of Natural Resources and Environment, Thailand
- Dr. Yujiro Ichikawa, Researcher, Center for Environmental Science in Saitama (CESS), Japan

Drafting Committee members:

- Mr. Sammy L. Aytona, Senior Science Research Specialist, Environmental Research and Laboratory Services Division, Environmental Management Bureau, Department of Environment and Natural Resources (DENR), the Philippines
- Mr. Joel Michael A. Tugano, Senior Science Research Specialist, Environmental Research and Laboratory Services Division, Environment Management Bureau, Department of Environmental and Natural Resources (DENR), the Philippines
- Mr. Barkhasragchaa Baldorj, Head, Environmental Laboratory, Central laboratory for Environment and Metrology, National Agency for Meteorology and Environmental Monitoring (NAMEM), Ministry of Environment and Tourism, Mongolia
- Mr. Dyveasna Nath, Ministry of Environment, Cambodia
- Ms. Jimin Lee, Korea University, the Republic of Korea
- Dr. Mingqun Huo, Chief Senior Researcher, ACAP, the NC for the EANET
- Dr. Pham Kim-Oanh, Researcher, ACAP, the NC for the EANET
- Ms. Azusa Sakue, Senior Researcher, ACAP, the NC for the EANET

Acknowledgements

This Technical Training Guidance was prepared under the EANET VOC Project through the collaborative efforts of experts from EANET participating countries.

Sincere appreciation is extended to the members of the Advisory Group and the Drafting Committee for their invaluable technical guidance, expertise, and dedicated contributions throughout the preparation of this guidance. In particular, special thanks are extended to Dr. Yujiro Ichikawa for preparing the chapters on canister sampling, sorbent tube sampling, and charcoal tube sampling; Dr. Junya Hoshi for preparing the chapter on passive sampling; Ms. Jimin Lee for her contributions to the chapters on passive sampling and photoionization detector (PID); Mr. Sammy L. Aytona and Mr. Joel Michael A. Tugano for preparing the chapter on Differential Optical Absorption Spectroscopy (DOAS); and Prof. Hong Li for preparing the chapter 4 on VOC data analysis and interpretation, supported by the international collaboration project of CRAES. The authors would also like to express their sincere appreciation to Mr. Xiaoshuai Gao, Mr. Qi Jiang, Ms. Shudan Wei, Ms. Yuanyuan Ji, Ms. Xiaoyu Yan, and Mr. Zhengyang Liu for their valuable contributions to Chapter 4, which covers systematic analytical methods, data auditing, pollution characteristic analysis, photochemical reactivity analysis, contribution assessment to ozone and secondary organic aerosol formation, source apportionment, and the formulation of control strategies based on VOC data. Special appreciation is extended to Mr. Xiaoshuai Gao and Mr. Zhengyang Liu for their efforts in coordinating and editing the chapter, and to all contributors for their technical expertise and dedicated efforts in preparing the various sections of Chapter 4.

The authors also wish to express their sincere gratitude to Dr. Gantuya Ganbat (Mongolia), Mr. Chandath Him (Cambodia), Ms. Ma. Fatima Anneglo R. Molina (the Philippines), Mr. Jundy Tigley Del Socorro (the Philippines), and Mr. Roger Cayaban Evangelista Jr. (the Philippines) for their invaluable support in organizing and conducting the field training activities under the EANET VOC Project. Their enthusiastic participation and practical assistance greatly contributed to the successful implementation of the project and the development of this guidance.

Finally, the authors gratefully acknowledge the valuable contributions of all Advisory Group members, Drafting Committee members, participating countries, and experts who contributed to the technical discussions, pilot monitoring activities, field training, and review process. Their constructive comments, continuous support, and commitment have greatly enhanced the scientific quality, technical value, and practical applicability of this guidance.

Disclaimer:

This publication may be reproduced as a whole or in part and in any form for educational or non-profit purposes without special permission from the copyright holder, provided that the sources are acknowledged.

This report has been prepared based on available reports, scientific data from the EANET monitoring, assessment, and research activities, supplemented by information obtained from various sources which are duly acknowledged. The contents of the report do not necessarily reflect the views, policies, or opinions of any Participating Country and organization.

The term East Asia in this report refers to the Northeast Asia and Southeast Asia regions unless otherwise stated.

This document serves as supporting material for EANET activities and includes data from the EANET Project 2025/11. The activities described herein are not compulsory for EANET participating countries.

Abbreviation in this document

ACSM	Aerosol Chemical Speciation Monitors	NIOSH	National Institute for Occupational Safety and Health
ADT	(Roadway) Average Daily Traffic	NMVOCs	Non-methane volatile organic compounds
AERMOD	Air Pollutant Dispersion Model	NO_2	Nitrogen Dioxide
AMS	Aerosol Mass Spectrometers	NO_x	Nitrogen Oxides
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes	O_3	Ozone
CAMx	Comprehensive Air Quality Model with Extensions	OBM	Observation-Based Model
CCD	Charge-coupled devices	OC	Organic Carbon
CCV	Continuing Calibration Verification	OFP	Ozone Formation Potential
CF	Correction Factor	OSAT	Ozone Source Apportionment Technology
CFC	Chlorofluorocarbon	OVOCs	Oxygenated Volatile Organic Compounds
CIMS	Chemical Ionization Mass Spectrometry	Pa; kPA	Pascal; kilopascal
CMAQ	Community Multiscale Air Quality Modeling System	PAMS	Photochemical Assessment Monitoring Stations
CMOS	Complementary metal-oxide semiconductor	PAN	Peroxyacetyl Nitrate
CMS	Carbon Molecular Sieve	PCA	Principal Component Analysis
CO_2	Carbon Dioxide	PFTBA	Perfluorotributylamine
CS_2	Carbon Disulfide	PIC	Photochemical Initial Concentration
CV	Coefficient of Variation	PID	Photoionization Detector
CWT	Concentration-Weighted Trajectory	PLOT	Porous Layer Open Tubular
DE	Desorption Efficiency	PM	Particulate Matter
DNPH	2,4-dinitrophenylhydrazine	PMF	Positive Matrix Factorization
DOAS	Differential Optical Absorption Spectroscopy	ppbv	parts per billion by volume
EANET	Acid Deposition Monitoring Network in East Asia	PPE	Personal Protective Equipment
EC	Elemental Carbon	ppmv	parts per million by volume
ECTD	Extended Cold Trap Dehydration	pptv	parts per trillion by volume
EI	Electron Ionization	Prop-Equiv	Propylene-Equivalent Concentration
EIA	Environmental Impact Assessment	PSAT	Particulate Source Apportionment Technology

EKMA	Empirical Kinetic Modeling Approach	PSCF	Potential Source Contribution Function
FAC	Fractional Aerosol Coefficient	PTR	Proton-Transfer-Reaction
FID	Flame Ionization Detector	QA/QC	Quality Assurance/Quality Control
FOAM	The Framework for 0-D Atmospheric Modeling	RIR	Relative Incremental Reactivity
GC	Gas Chromatography	RMS	Root-Mean-Square
GCB	Graphitized carbon black	RO_2	Peroxy Radicals
HCHO	Formaldehyde	RPD	Relative Percent Difference
HONO	Nitrous Acid	RSD	Relative Standard Deviation
HPLC	High-performance Liquid Chromatography	S/IVOCs	Semi/Intermediate Volatile Organic Compounds
HSE	Health and Safety Executive	SAR	Structure-Activity Relationship
ICH	International Council for Harmonisation	SIFT-MS	Selected Ion Flow Tube Mass Spectrometry
ISO	International Organization for Standardization	SIM	Selective Ion Monitoring
IUPAC	International Union of Pure and Applied Chemistry	SO_2	Sulfur Dioxide
KMO	Kaiser–Meyer–Olkin	SOA	Secondary Organic Aerosols
LOD	Limit of Detection	SOAFP	Secondary Organic Aerosol Formation Potential
L_{OH}	Hydroxyl Radical Consumption Rate	SOC	Secondary Organic Carbon
LOQ	Limit of Quantification	TD	Thermal Desorption
LPG	liquefied petroleum gas	TIC	Total Ion Chromatogram
MAD	Mean Absolute Difference	TOC	Total Organic Carbon
MCM	Master Chemical Mechanism	TVOC	Total Volatile Organic Compounds
MDL	Method Detection Limit	TWA	Time-Weighted Average
MIR	Maximum Incremental Reactivity	U.S. EPA	United States Environmental Protection Agency
MS	Mass Spectrometry	VOCs	Volatile Organic Compounds
NAQPMS	Nested Air Quality Prediction Modeling System	WRF-Chem	Weather Research and Forecasting Model coupled with Chemistry
NASA/JPL	NASA Jet Propulsion Laboratory	WSOC	Water-Soluble Organic Carbon
NH_3	Ammonia		

Table of Contents

Preface 9
1. Introduction....1
1.1 Importance of Ambient VOCs Monitoring....1
1.2 Challenges of VOC Monitoring....2
1.3 Purpose of this Guidance....4
2. Off-line Method....7
2.1 Sites Selection and Sampling Time....8
2.1.1 Regional Background Air Quality....8
2.1.2 Urban Air Quality....9
2.1.3 Environmental Impact Assessment (EIA) and Near-Source Monitoring....10
2.2 Canister Sampling Method....12
2.2.1 Overview....12
2.2.2 Equipment and Materials....12
2.2.3 Sample Collection....16
2.2.4 Preparation of Working Standard Gas....18
2.2.5 Sample Measurement....21
2.3 Active Sorbent Tube Sampling....26
2.3.1 Overview....26
2.3.2 Equipment and Materials....26
2.3.3 Sample Collection....29
2.3.4 Sample Measurement....30
2.4 Active Charcoal Tube Sampling....33
2.4.1 Overview....33
2.4.2 Reagents....33
2.4.3 Equipment and Materials....34
2.4.4 Sample Collection....36
2.4.5 Sample Measurement....38
2.5 Passive Charcoal-Based Diffusive Sampling....40
2.5.1 Overview....40
2.5.2. Reagents....41
2.5.3 Equipment and Materials....41
2.5.4 Sample Collection....43
2.5.5 Sample Measurement....45
2.6 Passive Sorbent-Based Diffusive Sampling....47
2.6.1 Overview....47
2.6.2 Equipment and Materials....48
2.6.3 Sample Collection....50
2.6.4 Sample Measurement....51
2.7. Analytical Methods....53
2.7.1 Overview of Analytical Methods....53
2.7.2 GC-MS Analysis....53
2.7.3 GC-FID Analysis....60
2.8 Calculation of Concentration....64
2.8.1 General Calculation Principles....64
2.8.2 Correction for Desorption Efficiency....65
2.8.3 Calculation of Concentration for Passive Sampling....65

2.8.4 Detection and Quantification Limits 69
2.9 Quality Assurance and Quality Control (QA/QC)....70
2.9.1 Precision 71
2.9.2 Recovery Assessment 72
2.9.3 Data Validation 72
2.9.4 Documentation and Traceability....72
3. Online Methods 74
3.1 Photoionization Detector (PID) 74
3.1.1 Overview....74
3.1.2 Instrument Configuration and Types 75
3.1.3 Field Deployment and Operation....75
3.1.4 Calibration 76
3.1.5 Interferences and Limitations 77
3.1.6 Quality Assurance / Quality Control 77
3.1.7 Data Reporting and Interpretation 78
3.2 Open-Path Differential Optical Absorption Spectroscopy (DOAS)....80
3.2.1 Overview....80
3.2.2 Apparatus and Equipment for Active Long Path DOAS....82
3.2.3 Sitting Criteria and Installation of DOAS 86
3.2.4 Measurement Procedure 88
3.2.5 Calibration 90
3.2.6 Routine Maintenance 93
3.2.7 Safety Considerations 94
4. Systematic Data Analysis Methods for Ambient Air VOCs 95
4.1 Framework of Systematic Analytical Methods for Ambient Air VOCs 95
4.2 Data Auditing Methods for Ambient Air VOCs....95
4.2.1 Workflow 96
4.2.2 Quality Control Methods for VOCs Monitoring Data....96
4.2.3 Methods for Achieving Quality Control of All Species Using Limited VOC Species 100
4.3 Pollution Characteristic Analysis Methods for Ambient Air VOCs 103
4.3.1 Workflow and Data Requirements 103
4.3.2 Characterization of Ambient-Air VOC Concentration Levels 104
4.3.3 Characterization of Chemical Composition....105
4.3.4 Characterization of Temporal Variations 107
4.3.5 Characterization of Spatial Distribution 108
4.4 Photochemical Reactivity Analysis Methods for Ambient Air VOCs 110
4.4.1 Workflow 110
4.4.2 Data Processing Methods for Photochemical Reactivity Analysis....111
4.4.3 Selection Principles for Reactivity Analysis Species 112
4.4.4 Photochemical Loss Compensation for Reactive VOC Species....114
4.4.5 Reactivity Assessment Based on OH-Radical Consumption Rate (L_{OH}) 115
4.4.6 Reactivity Assessment Based on Propylene-Equivalent Concentration (Prop-Equiv)....115
4.4.7 Reactivity Assessment Based on Ozone Formation Potential (OFP)....116
4.5 Contribution Assessment and Analysis Methods of Ambient Air VOCs to Ozone Formation 117
4.5.1 Workflow 117
4.5.2 Assessment of the Potential Contribution of Ambient VOCs to Ozone Formation Based on Observational Data 118
4.5.3 Assessment of VOCs Contribution to Ozone Formation Based on Observation-Based

Modeling....119
4.5.4 Assessment of VOCs Contribution to Ozone Formation Based on 3D Air Quality Modeling....121
4.6 Contribution Assessment Methods of Ambient Air VOCs to Secondary Organic Aerosol Formation....121
4.6.1 Workflow....122
4.6.2 Formation Potential Assessment....123
4.6.3 Formation Concentration Estimation....123
4.6.4 Combination of Multiple Methods....125
4.6.5 Comparative Analysis of Assessment Methods....125
4.7 Sources Apportionment Methods for Ambient Air VOCs....130
4.7.1 Workflow....130
4.7.2 Sources Analysis Methods for Ambient Air VOCs Based on Observation- Diagnostic ratios....130
4.7.3 Sources Analysis Methods for Ambient Air VOCs Based on Observation- Exploratory methods+ Quantitative source apportionment Industrial Source Apportionment....131
4.7.4 Sources Analysis Methods for Ambient Air VOCs Based on Three-Dimensional Air Quality Modeling-Quantitative source apportionment....133
4.8 Insights on Formulating Control Strategies Based on VOCs Data Findings....133
5. Conclusion....135
References....139
ANNEX A Principle of Photoionization Detection....1
ANNEX B Comparison of VOC Sampling Methods....4

Preface

The Acid Deposition Monitoring Network in East Asia (EANET) has played an important role in promoting regional cooperation on air quality monitoring and environmental protection since its establishment in 2001. Through harmonized monitoring methodologies, technical capacity building, and scientific collaboration, EANET has supported participating countries in understanding the status and long-term trends of atmospheric pollutants across the region.

In recent years, the importance of volatile organic compounds (VOCs) has received increasing attention because of their significant roles in atmospheric chemistry and regional air pollution. VOCs participate in complex photochemical reactions with nitrogen oxides (NOx), leading to the formation of ground-level ozone (O_3) and secondary organic aerosols (SOA), both of which are major components of photochemical smog and fine particulate matter ($PM_{2.5}$). As many countries in East Asia continue to experience rapid urbanization and industrial development, understanding VOCs emissions and ambient concentrations has become increasingly important for developing effective air quality management strategies.

Recognizing these needs, EANET launched the VOC Project to strengthen technical capacity for VOCs monitoring among participating countries. Through expert meetings, technical workshops, pilot monitoring campaigns, inter-laboratory discussions, and collaborative research activities, the project has facilitated the exchange of knowledge and practical experience among experts from the region. These activities have also highlighted the diversity of monitoring objectives, technical capabilities, and available resources across participating countries, emphasizing the need for practical and flexible technical guidance (Fig. 1).

This Technical Training Guidance has been prepared based on the experiences accumulated during the EANET VOC Project, while also drawing upon established VOCs monitoring practices, methodologies, and technical references from various countries and international sources. Rather than prescribing a single standardized monitoring approach, the guidance introduces commonly used VOCs monitoring techniques, discusses their principles, advantages, limitations, and suitable applications, and provides recommendations for selecting appropriate methods under different monitoring objectives and resource conditions.

The guidance covers off-line sampling techniques, including canister sampling, sorbent tube sampling, charcoal tube sampling, and passive sampling, as well as selected online monitoring approaches suitable for rapid screening or continuous observation of ambient VOCs. It also introduces essential considerations for data evaluation and interpretation to support the generation of reliable and comparable monitoring results.

It is expected that this guidance will serve as a practical technical reference for scientists, engineers, laboratory personnel, and environmental agencies involved in ambient VOCs monitoring within EANET participating countries and beyond. Through continued technical cooperation, capacity building, and methodology comparison, EANET will continue to strengthen the capacity building on VOC monitoring and contribute to improved scientific understanding on ozone and $PM_{2.5}$ pollution across East Asia. By providing flexible and broadly applicable technical information, this guidance may also be referred to and utilized by organizations, institutions, and practitioners outside the

EANET region.

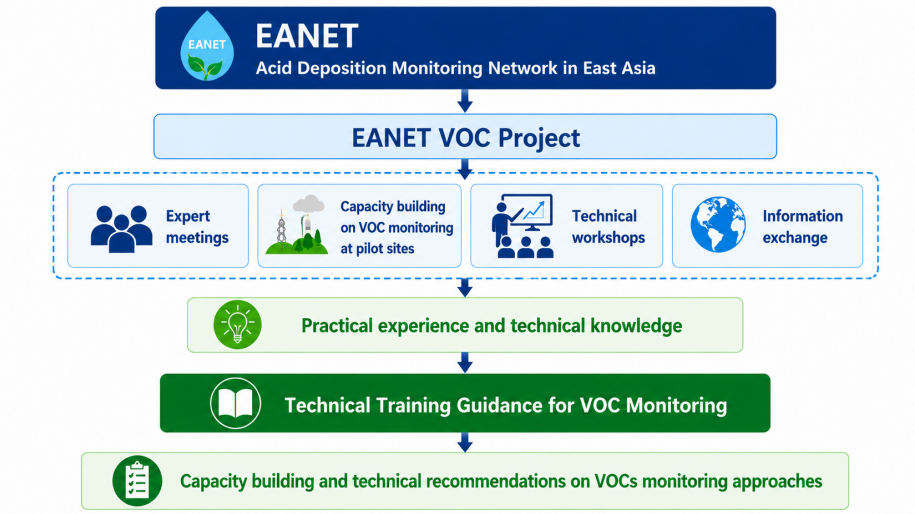


Figure 1 Development Framework of the Technical Training Guidance for Ambient VOCs Monitoring under the EANET

Note: The guidance provides technical options and recommendations to support capacity building for VOC monitoring and data analysis in participating countries.

Dr. Toshimasa Ohara
Chair of the Advisory Group
EANET VOC Project
(Promoting VOCs related Capacity Building in the EANET, 2024-2026)
Network Center for Acid Deposition Monitoring Network in East Asia
October 2026

1. Introduction

1.1 Importance of Ambient VOCs Monitoring

Non-methane volatile organic compounds (NMVOCs) comprise a large and diverse group of carbon-containing organic chemicals that readily evaporate into the atmosphere under ambient conditions. NMVOCs originate from numerous anthropogenic and natural sources, including industrial processes, vehicle exhaust, fuel evaporation, solvent use, biomass burning, and biogenic emissions from vegetation. Owing to their diverse chemical properties, atmospheric lifetimes, and emission sources, VOCs play multiple roles in atmospheric chemistry and environmental pollution (Fig. 1.1). In this guidance, the term "VOCs" refers to NMVOCs unless otherwise specified.

One of the most important reasons for monitoring VOCs is their involvement in photochemical ozone formation. In the presence of sunlight, VOCs react with nitrogen oxides (NOx) through a series of complex oxidation processes that generate ground-level ozone. Unlike stratospheric ozone, which protects the Earth from ultraviolet radiation, ground-level ozone is a harmful air pollutant that adversely affects human health, agricultural productivity, and natural ecosystems (Fig. 1.1). Elevated ozone concentrations have become an increasingly important environmental issue in many urban and suburban areas throughout East Asia.

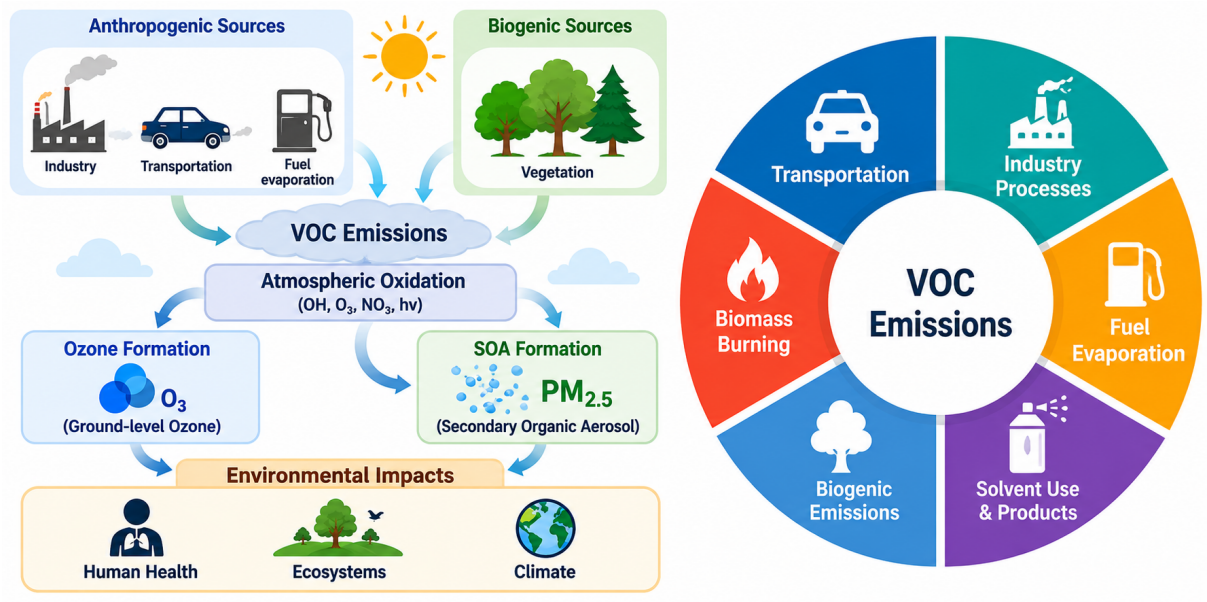


Figure 1.1 Atmospheric Chemistry and Sources of VOCs

VOCs are also important precursors of secondary organic aerosols (SOA), which constitute a substantial fraction of fine particulate matter ($PM_{2.5}$). Atmospheric oxidation of VOCs produces low-volatility compounds that partition into the particulate phase, contributing to SOA formation. Since $PM_{2.5}$ has been associated with adverse health effects, reduced visibility, and climate impacts, understanding VOCs contributions to SOA formation is essential for effective particulate matter management.

In addition to their indirect effects on atmospheric pollution, several VOC species are themselves hazardous air pollutants. Compounds such as benzene, formaldehyde, and 1,3-butadiene have been associated with carcinogenicity or other toxic health effects. Monitoring ambient VOCs

concentrations therefore provides valuable information for assessing human exposure and supporting public health protection.

Furthermore, ambient VOCs measurements provide useful information for identifying emission sources and evaluating emission control policies. Different emission sources exhibit characteristic VOCs compositions, allowing source apportionment analyses to distinguish contributions from traffic, industrial activities, solvent use, biomass burning, and biogenic emissions. Long-term ambient VOCs observations also enable the evaluation of temporal trends and the effectiveness of emission reduction measures.

1.2 Challenges of VOC Monitoring

Despite its importance, VOCs monitoring remains considerably more challenging than monitoring many conventional air pollutants (Fig. 1.2.1).

First, VOCs represent a highly diverse class of compounds. Hundreds of individual VOC species exist in the atmosphere, covering a wide range of chemical structures, volatilities, polarities, and atmospheric reactivities. No single sampling or analytical method can adequately measure all VOC species with equal performance. Consequently, monitoring methods must be selected according to the target compounds and monitoring objectives.

Second, ambient VOCs concentrations vary substantially among locations and species. Some compounds occur at sub-parts-per-billion (ppb) or even parts-per-trillion (ppt) levels, while others may reach much higher concentrations near emission sources. Achieving sufficient analytical sensitivity while maintaining acceptable accuracy and precision requires appropriate sampling strategies, calibration procedures, and quality assurance practices.

Third, VOCs measurements are susceptible to sampling artifacts. Losses during sample collection, adsorption onto sampling surfaces, chemical reactions during storage, contamination from sampling equipment, and breakthrough of highly volatile compounds may all introduce significant uncertainties. Proper selection of sampling materials, storage conditions, and analytical procedures is therefore essential for obtaining representative measurements.

Fourth, VOCs analysis generally requires sophisticated analytical instrumentation, including gas chromatography coupled with flame ionization detection (GC-FID) or mass spectrometry (GC-MS), together with certified calibration standards and well-established quality assurance and quality control (QA/QC) procedures. These technical requirements may present practical challenges for laboratories with limited analytical resources.

The diversity of technical capacity among EANET participating countries further increases the complexity of implementing VOC monitoring programs. While some countries possess advanced laboratory facilities and continuous monitoring systems, others are still developing their monitoring infrastructure. Financial resources, availability of analytical instruments, access to calibration standards, and technical expertise vary considerably across the region. Consequently, a monitoring strategy that is appropriate for one country may not be feasible for another.

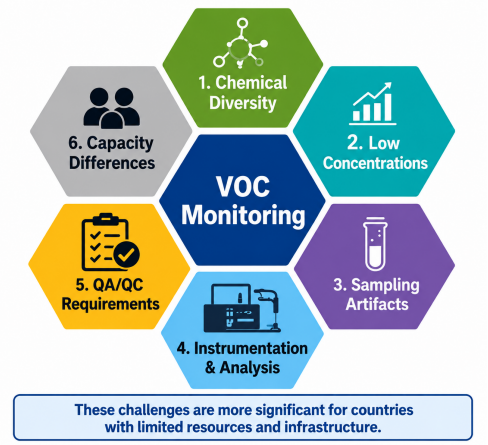


Figure 1.2.1 Challenges of VOC monitoring

VOC monitoring requires a fit-for-purpose approach. Because VOCs are chemically diverse and no single method can effectively measure all compounds and applications, monitoring methods should be selected according to the objectives of the monitoring program, target VOC species, data requirements, and available resources. Users are encouraged to adopt approaches that are technically feasible and appropriate for their local circumstances rather than applying a single standardized methodology. Examples of monitoring approaches for different VOC monitoring objectives are shown in Table 1.2.1.

Table 1.2.1. Recommended VOC Monitoring Approaches for Different Monitoring Objectives

Monitoring Objective	Information Needed	Recommended Sampling / Measurement Approaches	Typical Sites
Background Monitoring	Regional VOC levels, seasonal variation, long-term trends	Passive sampler; Sorbent tube + GC-MS or GC-FID (where quantitative data are needed)	Remote, rural, regional background sites
Trend Monitoring	Temporal changes in VOC concentrations	Passive sampler; Sorbent tube + GC-MS or GC-FID	Regional, urban, suburban monitoring sites
Routine Ambient Monitoring	Concentration levels of selected or priority VOCs; compliance and assessment data	Canister + GC-MS (where comprehensive speciation is needed); Sorbent tube + GC-MS or GC-FID	Urban, suburban, industrial influence sites
Spatial Distribution Assessment	Comparison of VOC concentrations among locations	Passive sampler; Sorbent tube + GC-MS or GC-FID	Monitoring sites, community monitoring locations
Hotspot Identification	Areas with elevated VOC concentrations or potential source impacts	Sorbent tube + GC-MS or GC/FID; Canister + GC-MS; PID for preliminary screening	Roadside, industrial, commercial, port areas

Monitoring Objective	**Information Needed**	**Recommended Sampling / Measurement Approaches**	**Typical Sites**
Source Identification and Characterization	VOC fingerprints, dominant emission sources	Canister + GC-MS; Sorbent tube + GC-MS	Source-oriented and industrial sites
Source Apportionment	Quantification of source contributions using receptor models	Canister + GC-MS (preferred); high-quality Sorbent tube + GC-MS datasets may also be applicable	Urban research and reference sites
Ozone Precursor Assessment	Reactive VOC species, O_3 formation potential	Canister + GC-MS; Online GC-FID; PTR-MS	Urban and regional O_3 monitoring sites
Photochemical Studies	VOC speciation and atmospheric transformation processes	Canister + GC-MS; Online GC-FID; PTR-MS; DOAS for selected compounds	Research and supersites
Screening and Preliminary Surveys	Rapid identification of VOC presence and concentration hotspots	PID screening; follow-up sampling by Canister or Sorbent tube methods	Industrial facilities, complaint areas, field surveys
Episodic Event / Incident Investigation	Short-term releases, abnormal emission events	Canister sampling; Online GC-FID or GC-MS; PID screening	Accident sites, industrial areas, emergency investigations

Note: Canister sampling and GC-MS analysis methods are based on U.S. EPA Compendium Method TO-15, while sorbent tube sampling methods are based on U.S. EPA Compendium Method TO-17.

1.3 Purpose of this Guidance

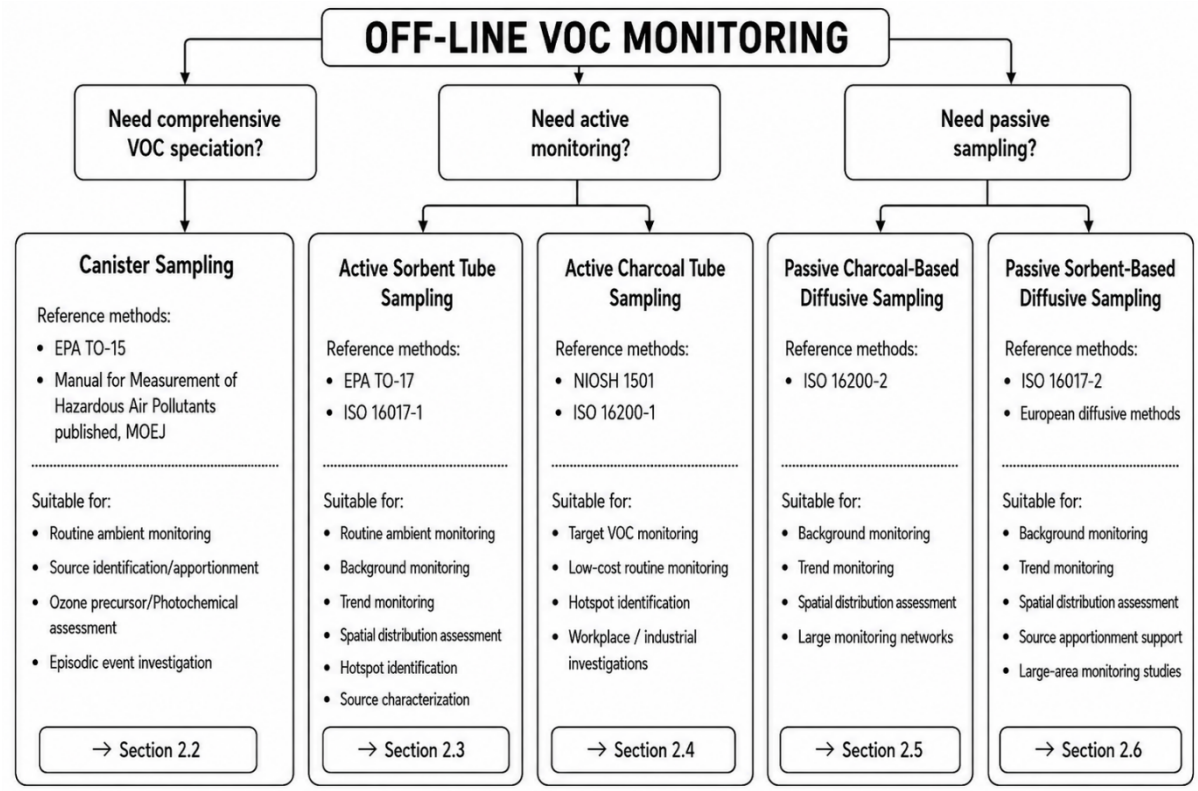
Considering these challenges, this Technical Training Guidance has been developed to support EANET participating countries in capacity building programs for VOCs monitoring and data analysis.

The guidance introduces practical sampling and analytical techniques that have been widely applied in ambient air monitoring, together with their advantages, limitations, and recommended applications. Rather than recommending a single monitoring approach, it provides flexible technical options that can be adapted according to monitoring objectives, available resources, and technical capacity.

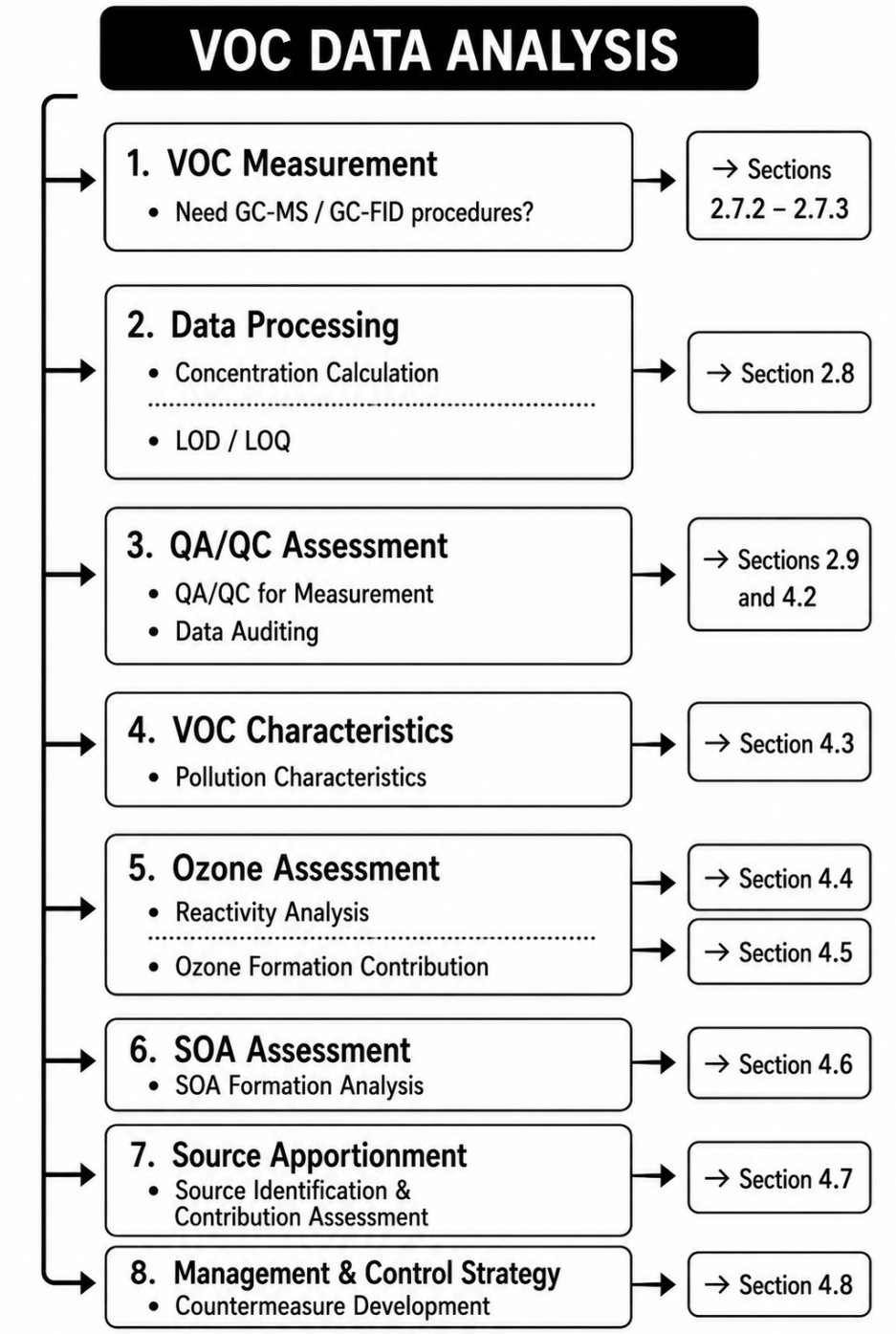
This document is intended primarily as a technical training reference for environmental monitoring agencies, research institutes, and laboratories within EANET. It is expected to provide practical technical guidance for VOC monitoring, improve data quality and comparability, strengthen regional technical capacity, and promote scientific cooperation and experience sharing among participating countries.

Figures 1.3.1-1.3.2 are provided as a navigation tool to help users quickly identify the VOC monitoring, measurement, and data analysis approaches most appropriate for their objectives. **Figure**

1.3.1 provides guidance for selecting appropriate VOC monitoring methods, including both off-line and on-line approaches, according to monitoring objectives and operational requirements. **Figure 1.3.2** serves as a roadmap for VOC data analysis and interpretation, guiding users from VOC measurement and data processing through data validation, pollution characterization, ozone and SOA assessment, source apportionment, and the development of management and control strategies. Once the appropriate method or analytical objective has been identified using these figures, users may proceed directly to the corresponding section for detailed technical guidance.



157 **Figure 1.3.1 Decision Framework for Selecting VOC Monitoring Methods**



158
159 **Figure 1.3.2 Roadmap for VOC Data Analysis and Interpretation**
160
161

2. Off-line Method

Off-line sampling methods are widely used for ambient VOC monitoring because they provide reliable measurements and can be implemented with relatively simple equipment and laboratory analysis. This chapter introduces five commonly used off-line sampling methods: canister sampling, active sorbent tube sampling, active charcoal tube sampling, passive sampling using charcoal-based adsorbents, and passive sampling using sorbent-based adsorbents.

Among these methods, active sampling techniques collect ambient air using a sampling pump, whereas passive samplers collect VOCs by molecular diffusion without the use of a pump. Canister sampling is a whole-air sampling technique in which ambient air is collected directly into an evacuated canister. The selection of an appropriate method should be based on monitoring objectives, target VOC species, available resources, and technical capacity. The principles, procedures, advantages, limitations, and typical applications of each method are described in the following sections.

Table 2.1.1 provides a comparative overview of the five off-line sampling methods described in this chapter, including the requirement for a sampling pump, typical sampling period, relative precision, range of applicable VOCs, key advantages and limitations, and relative cost. The table is intended to help users understand the main characteristics of each method at a glance and to support the selection of an appropriate sampling approach according to their monitoring objectives and available resources.

Table 2.1.1 Comparison of off-line sampling methods for ambient VOC monitoring

Off-line Method	Pump	Sampling period	Precision*	VOC coverage**	Key advantages	Key limitations	Cost***
Canister sampling	No	12 h to 1 week	★★★★★	Very broad	Multi-component suitable for highly volatile VOCs	High cost; limited large-scale deployment	$$$$$
Active (sorbent-based)	Yes	Several hours (1–10 L total sampling volume)	★★★★★	Broad	High sensitivity; flexible sorbents	Breakthrough; moisture effects	$$$$
Active (charcoal-based)	Yes	Approximately 24 h	★★★☆☆	Moderate	Simple; low cost; re-analysis possible	Solvent extraction; blank/recover tests	$$
Passive (charcoal-based)	No	Several weeks	★★☆☆☆	Limited-moderate	Simple; long-term, multi-site use	TWA only; extraction; uptake rate validation required	$
Passive (sorbent-based)	No	Several weeks	★★★☆☆	Moderate–broad	Flexible sorbents; long-term monitoring	Uptake rate validation required	$$$

* Precision: qualitative relative comparison under QA/QC conditions.
** VOC coverage: qualitative range of measurable VOCs.

*** Cost: relative scale ($ to $$$$$).

The measurement method of the off-line sampling is usually GC-MS or GC-FID. GC-MS provides both quantitative measurements and compound-specific identification, making it the preferred method for detailed VOC speciation and source characterization. In contrast, GC-FID is a simpler and more cost-effective technique that offers robust quantification of many hydrocarbons but limited compound identification capability. Therefore, the choice between GC-MS and GC-FID should be based on the monitoring objectives, required level of chemical speciation, available technical capacity, and budget.

2.1 Sites Selection and Sampling Time

Selection of monitoring sites and sampling schedules for VOC measurements should be based on the objectives of the monitoring program. International air monitoring frameworks recommend selecting sites that are representative of the target environment while minimizing interference from nearby emission sources, buildings, vegetation, and other physical obstructions that may affect airflow and pollutant measurements (U.S. EPA, 2026; European Commission, 2026; EEA, 2024). Site selection should consider the intended spatial representativeness of the measurements, whether the objective is to assess regional background conditions, urban population exposure, traffic-related pollution, or source-specific impacts (EEA, 2024; European Commission, 2026). These principles are consistent with EANET monitoring concepts, which emphasize representative monitoring locations and harmonized observations across remote, rural, and urban environments (EANET, 2022).

2.1.1 Regional Background Air Quality

Objective: To characterize baseline VOC concentrations and assess regional trends.

Site Selection:

- **Location:** Monitoring sites should be located in remote or rural areas with minimal influence from local emission sources and should be representative of regional background air quality (EANET, 2022; EEA, 2024). For example, EANET background monitoring stations located tens of kilometers away from major urban or industrial areas to minimize direct local influences.
- **Height:** Sampling inlets should be installed at a height appropriate for ambient air monitoring and in accordance with applicable monitoring protocols (EANET, 2022; U.S. EPA, 40 CFR Part 58, Appendix E). For example, U.S. EPA ambient monitoring guidance specifies inlet heights generally between 2 and 15 m above ground level for many monitoring applications.
- **Requirements:** Monitoring sites should be located in open areas with adequate airflow and be sufficiently distant from buildings, trees, and other obstructions that may affect pollutant dispersion or create localized influences on measured concentrations. In accordance with U.S. EPA ambient monitoring siting criteria, sampling inlets should generally have unrestricted airflow through an arc of at least 270° and should be located away from nearby structures. For example, EPA recommends that the distance between a monitoring inlet and nearby trees should generally be at least twice the height of the trees to minimize interference with ambient measurements (U.S. EPA, 40 CFR Part 58, Appendix E). If the objective is to characterize anthropogenic VOCs, consideration should also be given to minimizing the influence of biogenic VOC emissions from surrounding vegetation.

Sampling Time:

- **Duration:** The sampling duration should be selected according to the monitoring objective and sampling method. Twenty-four-hour integrated samples are commonly used to characterize daily average VOC concentrations and temporal variability. For long-term assessment of ambient air quality, seasonal trends, or chronic health risk evaluation, longer integrated sampling periods may be appropriate. For example, passive diffusive samplers are often deployed for periods of approximately 1 to 2 weeks, and EPA Method 325A for VOC monitoring uses a typical sampling duration of 14 days.
- **Frequency:** Monitoring should be conducted at a frequency sufficient to characterize temporal variability and achieve the objectives of the monitoring program. For regional background assessments, measurements should preferably cover multiple seasons to account for seasonal changes in emissions, meteorological conditions, atmospheric chemical processes, and VOC lifetimes.

2.1.2 Urban Air Quality

Objective: To identify urban dominant VOC sources

- **Site Selection:**

  - **Location:** Urban monitoring stations should be located in areas representative of population exposure, such as residential, commercial, educational, or public-service areas. Urban background sites should characterize the general urban atmosphere and should not be dominated by emissions from a single nearby source (EEA, 2024; European Commission, 2026). Monitoring stations may be installed in suitable public buildings or other secure locations provided that the measurements remain representative of ambient conditions and comply with applicable siting requirements.

  - **Distance from Roads:** The distance from major roads should be determined according to the monitoring objective.

    - *For General Exposure:* Monitoring sites are often located away from major roads so that measurements represent the urban background atmosphere rather than a single roadway emission plume. For example, some urban monitoring programs use distances of approximately 100 m or greater from major motorways for urban background monitoring.

    - *For Traffic Hotspots:* Sites may be located immediately adjacent to roadways to characterize vehicle emission impacts and roadside exposure (EEA, 2024; European Commission, 2026). For example, roadside monitoring stations are sometimes installed within 2-5 m of the road edge, with inlet heights of approximately 1.5-3 m above ground level to characterize human exposure.

  - **Requirements:** Monitoring sites should be located in open areas with minimal interference from nearby buildings, trees, or other obstacles. Sampling inlets should have largely unrestricted airflow (e.g., at least 270° around the inlet under U.S. EPA siting criteria). Street-canyon locations (narrow streets with high buildings) should generally be avoided for urban background monitoring because restricted airflow and nearby sources may affect the representativeness of measurements. Such locations may be appropriate when the objective is

to assess roadside exposure, traffic impacts, or pollutant accumulation (EANET, 2022; European Commission, 2026; U.S. EPA, 40 CFR Part 58, Appendix E;).

- **Sampling Time:**
  - **Duration:** Sampling duration should be selected according to the monitoring objective and method. Twenty-four-hour integrated samples are commonly used to characterize daily average VOC concentrations, while longer integration periods (e.g., 1-2 week passive sampling) may be used to estimate seasonal or annual average concentrations and chronic exposure. (U.S. EPA Method 325A).
  - **Frequency:** Sampling should be conducted during multiple seasons to capture temporal variations in emissions, meteorological conditions, atmospheric chemistry, and VOC concentrations. For health risk assessment and long-term exposure evaluation, monitoring should preferably be distributed throughout the year to improve the representativeness of annual average concentrations and population exposure (EANET, 2022; European Commission, 2026).

2.1.3 Environmental Impact Assessment (EIA) and Near-Source Monitoring

Objective: To evaluate the impacts of specific emission sources, verify compliance with regulatory requirements, and estimate source contributions.

- **Site Selection:**
  - **Location:** Monitoring locations should be selected based on the expected impact area of the emission source, nearby receptors, prevailing meteorological conditions, and project objectives. Where appropriate, dispersion models (e.g., AERMOD) may be used to identify areas of elevated concentrations and potential maximum ground-level impacts (U.S. EPA, 2018; European Commission, 2026).
  - **Upwind/Downwind:** Where feasible, monitoring should include at least one upwind site to characterize background conditions and one or more downwind sites to assess source impacts. This approach is commonly used to distinguish source contributions from ambient background concentrations in environmental impact assessments and source-oriented monitoring studies (U.S. EPA, 2018; European Commission, 2026).
  - **Requirements:** Site selection should consider prevailing wind direction, terrain characteristics, source operating conditions, and the location of sensitive receptors (e.g., residential areas, schools, hospitals, and workplaces) to ensure representative assessment of source impacts. Monitoring locations should be situated where source-related impacts are expected to occur and where measurements can effectively support the monitoring objectives (EANET, 2022; European Commission, 2026).
- **Sampling Time:**
  - **Duration:** Sampling duration should be selected according to the monitoring objective and the temporal characteristics of source emissions. Short-term measurements may be used to characterize peak concentrations or episodic emission events, while longer-term measurements may be required to assess average impacts and regulatory compliance (U.S. EPA, 2019a; EANET, 2022).

- **Meteorological Conditions:** Sampling should be conducted under meteorological conditions relevant to the monitoring objective, particularly when emissions are likely to be transported from the source toward the monitoring location. When the objective is to assess maximum source impacts, monitoring may be conducted during conditions associated with limited atmospheric dispersion and favorable transport from the source to the receptor (U.S. EPA, 2018; European Commission, 2026).

- **Frequency:** The frequency and duration of monitoring should be sufficient to capture temporal variability in emissions, source operations, and environmental conditions, and should comply with applicable regulatory or project-specific requirements. Monitoring is often scheduled during representative operating periods of the source and, where appropriate, under different meteorological conditions to characterize variability in source impacts (EANET, 2022; European Commission, 2026).

2.2 Canister Sampling Method

2.2.1 Overview

The canister sampling method described in this section was developed based on the authors' practical experience in ambient VOC sampling and analysis, together with information and procedures described in established reference methods. In particular, the U.S. EPA Method TO-15A and the Manual for Measurement of Hazardous Air Pollutants published by the Ministry of the Environment, Japan, were used as major references in preparing this section.

Purpose and scope

This method provides guidance for the measurement of volatile organic compounds (VOCs) in ambient air using stainless-steel canisters. It is suitable for the simultaneous measurement of multiple VOCs, including benzene, toluene, ethylbenzene, and xylenes (BTEX). The method is based on whole-air sampling and can be applied to ambient air monitoring over different sampling durations by selecting an appropriate canister size and sampling flow rate.

Measurement principle

Ambient air is collected directly into a cleaned and evacuated stainless-steel canister through a flow controller at a constant flow rate. After sampling, the collected air is pressurized with VOC-free air or high-purity nitrogen as necessary, and a fixed volume of the sample is introduced into a preconcentrator. The target VOCs are concentrated in a cooled trap while interfering components such as excess moisture and carbon dioxide are removed. The concentrated VOCs are then thermally desorbed and introduced into a GC-MS (or GC-FID) for separation, identification, and quantification. Although both GC-MS and GC-FID can be used for VOC analysis, this guidance focuses on GC-MS because of its applicability to a broad range of VOCs and its capability for both compound identification and quantitative analysis.

Advantages and limitations

A major advantage of canister sampling is that a whole-air sample is collected, allowing multiple VOCs to be determined from the same sample. Evacuated canister sampling can also be performed without an external sampling pump, and the sampling duration can be adjusted by controlling the canister size and/or sampling flow rate. In addition, cleaned canisters can be reused.

The principal limitations are the need for careful cleaning, evacuation, and leak control of the canisters and associated sampling equipment. High-boiling-point and polar VOCs may be lost by adsorption onto the inner surfaces of the canister or sampling lines, particularly when these surfaces are contaminated. Appropriate inert materials, short sampling lines, and careful quality control are therefore required. Sample handling, pressure dilution, preconcentration, and GC-MS analysis also require specialized equipment, and samples should be analyzed within the specified storage period.

2.2.2 Equipment and Materials

Canisters

Stainless-steel canisters are commercially available in a variety of sizes, differing in capacities (volumes), shapes (e.g., spherical, oblong, oval), valve specifications and the inert treatment applied to the inner walls. Photos of the canisters in different sizes and shapes are shown below (Picture

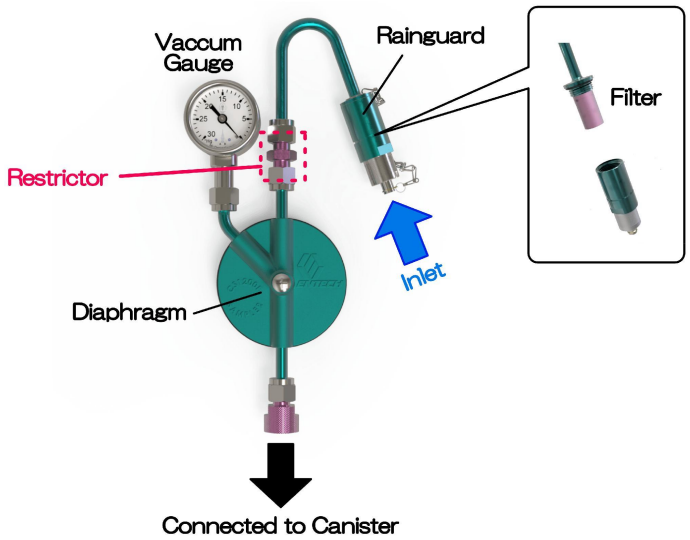
2.2.1). You can select the appropriate type depending on the intended application, such as the required sample volume and sampling duration. The most commonly used size for atmospheric VOCs sampling is 6 L. Inert treatments for inner walls include electropolishing and silica coating, amongst others, and vary depending on the manufacturer. The canister must be leak-free and capable of withstanding a pressure of approximately 300 kPa and a vacuum of 13 Pa or less at atmospheric pressure.



Picture 2.2.1 Photos of canisters by size and shape
(Source of the photograph: Entech Instrument official web site)

Flow Controllers

The photo and components of the flow controller are shown below in Picture 2.2.2. Typically, the inlet section of a flow controller is equipped with a filter (the standard mesh size is approximately 2 μm) to remove particles and a rain guard to prevent rainwater ingress. The flow controller regulates the air flow by combining the restrictor with a diaphragm. The restrictor provides coarse control of flow rate, while the diaphragm provides finer control. A vacuum gauge (pressure range displayed from approximately -100 kPa to 300 kPa) is then used to measure the pressure inside the canister. This allows the user to verify how many atmospheric samples have been collected in the canister. A key advantage of this device is that it does not require an external power source. The flow controller must be leak-free, and the materials used in the parts in contact with the gas should be stainless-steel or inert treated aluminum, or materials offering equivalent or superior performance. Furthermore, it must have a pressure resistance of approximately 300 kPa and be capable of withstanding a pressure drop of 13 Pa or less under atmospheric pressure. It must be capable of controlling the flow rate within ±10% of the set value.



Picture 2.2.2 A photograph of the flow controller components
(Source of the photograph: Entech Instrument website)

Canister Cleaner

The canister must be capable of being cleaned for reuse through a pressurization and venting cycle multiple times (at least three times) using humidity VOC-free air or high-purity nitrogen, followed by high-vacuum evacuation. It is important to humidify the cleaning gas because moisture helps prevent VOCs, particularly those containing oxygen, from adsorbing onto the inner walls of the canister and keeps them in the gas phase. Heating is effective for desorbing VOCs remaining on the inner walls of the canister and around the valve. Some commercially available systems use heating jackets or ovens as standard or optional features, with a recommended temperature of around 80°C. The ultimate vacuum should be at least less than 0.027 kPa, and the vacuum level of the canister should be monitorable. The gas-contacting parts must be made of stainless steel or an inert material of equivalent or higher quality, and the structure must be designed to minimize VOCs adsorption. It is desirable that the cleaned canister blank achieve a concentration of less than 0.2 ppbv for the target VOCs.

Prior to field deployment, the cleanliness of the canister should be verified by confirming that target VOC concentrations in the blank canister meet the established acceptance criteria. To verify the cleanliness of the canister, a blank test should be performed after the cleaning procedure by filling the canister with humidified VOC-free air or high-purity nitrogen and analyzing it under the same analytical conditions as those used for ambient air samples. The blank level should be sufficiently low so that it does not significantly affect the quantification of VOCs in actual samples. If the concentration of any target VOC exceeds 0.2 ppbv, the canister should be cleaned again and re-evaluated before use. Repeatedly high blank levels may indicate contamination of the canister interior, valve, fittings, or cleaning system, and these potential sources should be inspected as necessary.

Pressure Diluter

A pressure diluter performs quantitative pressure dilution based on a pressure ratio by introducing VOC-free air or high-purity nitrogen into a canister that has collected VOCs from the atmosphere. The absolute pressure in the canister before and after dilution must be measured and recorded using a pressure gauge or similar instrument, and the dilution factor must be calculated based on these absolute pressures (The pressure display range should be at least 0 to 250 kPa absolute). The gas-contacting parts must be made of stainless steel or an inert material of equivalent or higher quality, and the structure must be designed to minimize VOCs adsorption.

Preconcentrator System

The preconcentrator system is required to measure samples collected from canisters containing atmospheric VOCs. It must be capable of removing moisture, carbon dioxide (CO_2), and other matrix gases from the samples; concentrating VOCs using trap tubes (such as Tenax) and cooling with liquid nitrogen or an electric cooler; and introducing the VOCs into the GC via thermal desorption. For the target VOCs, there must be no breakthrough at the set injection volume, and good recovery rates and reproducibility must be achieved for components ranging from low-boiling-point to high-boiling-point compounds. Although contaminants such as moisture and CO_2 in the sample are removed as they interfere with the measurement, the system must be designed to minimize the loss of the target VOCs during this removal process. The system must be capable of controlling and recording the sample injection volume, injection flow rate, pressure, trap temperature, desorption temperature, and internal standard addition conditions. It is desirable for the system to have a leak check function for

the canister connection, a line purge function, and a trap bake function.

Analytical equipment

Canister sampling is most commonly coupled with gas chromatography-mass spectrometry (GC-MS), which enables the analysis of a broad range of VOCs at trace atmospheric concentrations while providing both compound identification and quantification. Following sample collection, a fixed volume of air is typically concentrated using a preconcentrator prior to GC-MS analysis. This approach is widely used for ambient VOC monitoring, source characterization, ozone precursor assessment, and source apportionment studies. Although gas chromatography-flame ionization detection (GC-FID) may also be applied for the quantification of selected VOCs, its use with canister samples is less common. Therefore, this Technical Guidance focuses on canister sampling coupled with GC-MS. Detailed information on instrument configuration, analytical procedures, calibration, and QA/QC requirements is provided in Section 2.7-2.9.

Standards

Stock Standard Gas

It is recommended to use commercially available standard gas supplied in cylinders with attached certificates of target VOCs (0.1–1 ppmv). For components for which standard gases are not commercially available, a standard solution of the component should be introduced into an evacuated canister and vaporized. As commercially available standard gases are calibrated in terms of volumetric concentration (ppmv, μL/L), to convert to mass/volume concentration (μg/L), multiply by 273.15・M /［22.4・(273+T)］ (where M is the molecular weight of the component and T is the temperature in degrees Celsius).

Working Standard Gas

Prepare approximately five levels of humidified mixed working standard gas ranging from 0 to 2000 pptv by diluting the stock standard gas with humidified VOCs-free air or high-purity nitrogen gas using methods such as pressure dilution, volumetric mixing, or flow-ratio mixing, depending on the quantification range of each target VOCs. However, since some VOCs must be prepared in a higher concentration range, this should be determined based on the atmospheric concentration conditions. The humidified mixed working standard gas should be prepared under a pressure of approximately 200 kPa.

Internal Standard Gas

Generally, substances such as toluene-d_8, fluorobenzene, and chlorobenzene-d_5 are used as internal standards. Dilute internal standard gases with humidified VOCs-free air or high-purity nitrogen gas to the desired concentration before use (0.1–1 ppmv). Commercially available standard calibration gases in cylinders, accompanied by certificates of analysis, are also sold for internal standard gases.

2.2.3 Sample Collection

Ambient Air Sampling

To collect samples, connect a flow controller to a canister that has been pre-evacuated (to 13 Pa or less) and collect the sample at a constant flow rate. There are two following methods:

(1) Evacuated Canister Sampling Method, in which collection is completed at atmospheric pressure or below. This Technical Guidance focuses on this method, which is currently the most common method for VOCs sampling using canisters.

(2) Pressurized Canister Sampling Method, in which a pressurization pump is used to collect the sample up to approximately 200 kPa.

All parts of the sample collection system that come into contact with the sample should be made of stainless-steel or a material with equivalent or superior performance. If non-metallic components are used, it must be confirmed in advance that they will not affect the VOCs to be measured.

Particular care must be taken regarding the adsorption of high-boiling-point and polar substances into the sample collection system; even if the material is metallic, there is a risk of loss due to adsorption if the parts in contact with the VOCs to be measured are contaminated. In addition to regularly cleaning or replacing piping and other components, measures such as direct sampling and keeping piping as short as possible are necessary.

The pressure at the end of canister sampling must remain sufficiently below the ambient atmospheric pressure to ensure that the flow controller can maintain a constant sampling flow rate throughout the sampling period. As a general guidance, the final canister pressure may be set at approximately 80% of the local atmospheric pressure. Because atmospheric pressure varies with altitude and meteorological conditions, the appropriate final pressure should be determined based on the atmospheric pressure at the sampling site and the operating specifications of the flow controller. For example, at a site where the atmospheric pressure is approximately 100 kPa, a final canister pressure of approximately 80 kPa is typically appropriate. When using a 6 L canister for a 24-hour collection, the sampling flow rate should be adjusted according to the desired final pressure and the local atmospheric pressure. Under conditions where the atmospheric pressure is approximately 100 kPa and the target final pressure is approximately 80 kPa, the sampling flow rate is approximately 3.3 mL/min.

Note: At higher elevations, where atmospheric pressure is lower, the corresponding target final pressure should be determined as a proportion of the local ambient pressure rather than using a fixed value. The sampling system manufacturer's specifications should also be consulted to confirm the acceptable operating pressure range of the flow controller.

The following is a step-by-step overview of the VOCs sampling procedure using the evacuated canister sampling method.

a) Prepare a canister that has been cleaned and evacuated to the specified vacuum level.

b) Inspect the canister valve, flow controller, fittings, and other equipment to ensure there is no contamination, damage, or loose connections. After assembling the sampling system, check all connections for leaks before starting sample collection. The leak check should be performed using

an appropriate procedure recommended for the sampling equipment. If a leak is detected or suspected, tighten or replace the affected connection or component and repeat the leak check before sampling.

c) Verify and record the canister ID number, flow controller ID number, initial pressure, sampling location, sampling date and time, weather conditions, and other relevant information. A field data sheet should be used to ensure that all necessary information is recorded consistently during each sampling event. Table 2.2.1 shows an example of a field data sheet for canister sampling. The format may be modified as appropriate according to the monitoring program and local requirements.

Table 2.2.1 Example of a field data sheet for ambient VOC sampling using a canister

Sampling ID	Location	Canister ID Flow Controller ID	Date	Time	Pressure	Temp (°C)	Weather	Field Blank	Duplicate Measurement	Operator	Comment
ACAP 1	Niigata station	Canister No. 14 Flow controller No. 6	Start Nov. 21, 2024	10:00	-0.1 MPa	16.7	Sunny	Yes/No	Yes/No	AAA	Painting work was being done on a nearby building
			End Nov. 22, 2024	10:00	-0.020 MPa	15.8	Sunny			AAA	
CESS 2	Saitama City Hall	Canister No. 51 Flow controller No. 11	Start Nov. 21, 2024	11:14	-75 cmHg	20.4	Cloudy	Yes/No	Yes/No		
			End Nov. 22, 2024	11:14	-13 cmHg	20.1	Cloudy			BBB BBB	A field burning was observed on nearby farmland
Tokyo A	Asakusa station	Canister No. 30 Flow controller No. 1	Start Nov. 21, 2024	15:23	-100 kPa	20.7	Cloudy	Yes/No	Yes/No		
			End Nov. 22, 2024	15:23	-18 kPa	20.1	Cloudy			XXX XXX	

d) To start sampling, record the sampling start time and open the canister valve. Ambient air is introduced into the canister through the flow controller by the negative pressure inside the canister.

e) During sampling, the flow rate, canister pressure, and surrounding conditions should be checked as necessary to confirm that there are no abnormal pressure changes or flow fluctuations.

f) When the specified sampling time has elapsed, close the canister valve to stop sampling. Record the sampling end time and the final canister pressure. After sampling, the canister should be checked for leaks by measuring and recording the canister pressure.

Note: Canister pressure should be measured after sample collection and again upon receipt at the laboratory. Any significant pressure changes during storage or transport may indicate leakage and should be investigated in accordance with laboratory QA/QC procedures. EPA Method TO-15A recommends that canisters exhibiting excessive leakage, defined as a vacuum or pressure change greater than 0.69 kPa/day (0.1 psi/day) during leak testing, be removed from service and repaired. Samples collected in canisters showing evidence of leakage should be carefully evaluated and, where appropriate, considered invalid.

Operational Blank Preparation

The operational blank consists of humidified VOC-free air or high-purity nitrogen pressurized to the same level as the atmospheric sample and introduced into a cleaned canister. Conduct an operational blank test to verify that there is no contamination attributable to the equipment, or laboratory environment used in the measurement process.

Field Blank Preparation

Using the same method as for the sampling canister, pressurize the field blank canister with humidified VOCs-free air or high-purity nitrogen gas to approximately 80 kPa. This field blank canister is handled in the same manner as the sampling canister, except that no sampling operations are performed.

During sample collection, place the field blank canister next to or near the sampling canister. After the sampling period has elapsed, transport the field blank canister in the same manner as the sampling canister, and then pressurize it with VOCs-free air or high-purity nitrogen gas to approximately twice the pressure (approximately 160 kPa).

Field blank test is recommended to prevent contamination and should be performed for a series of sample collections at the same sampling locations and time periods, using the same transport methods and distances, and under the same other conditions. This test should generally be conducted for approximately 10% of the total number of sampling sites when a large number of sites are included in the monitoring program (i.e. at least three field blank canisters per campaign). When the number of sampling sites is limited to one or two, it is recommended that the field blank test be conducted at each sampling site (i.e. at least one field blank per site).

Duplicate Measurement

For duplicate measurements, two or more duplicate measurement canisters must be collected under the same conditions as the sampling canisters. It is recommended that duplicate measurement canisters be collected at a frequency of approximately 10% of the total number of samples.

2.2.4 Preparation of Working Standard Gas

Working standard gas may be prepared using following methods:

・Pressure dilution method

・Dynamic flow dilution method

・Syringe injection method

In all methods, the concentration of the stock standard gas or standard solution shall be accurately known and traceable to a reliable reference, such as a certified concentration provided by the manufacturer or a concentration determined from the preparation procedure using calibrated equipment. Before preparing the working standard gas, the dilution gas and all components that contact the standard, including the canister, tubing, valves, fittings, and humidification system, if used, shall be checked to confirm that they do not contribute significant contamination of the target VOCs. This verification may be performed by preparing and analyzing a blank using the same dilution gas and preparation system without introducing the stock standard gas or standard solution. If target VOCs are detected at levels that may affect the accuracy of the working standard, the source of contamination should be identified and removed by appropriate cleaning, replacement of contaminated components, or use of a cleaner dilution gas before standard preparation is continued.

The prepared working standards should be measured under the same preconcentrator-GC-MS conditions as the actual atmospheric samples. The following sections describe the procedures for each method and how to calculate the concentration of the working standard gas produced by that method.

Pressure Dilution Method

a) Evacuate the canister to achieve the specified initial vacuum level.

b) Thoroughly purge the gas line with the stock standard gas to displace any air or residual gas within the line.

c) Record the initial pressure (absolute pressure) of the canister.

d) Introduce the stock standard gas into the canister and pressurize it to the specified partial pressure.

e) Record the canister pressure (absolute pressure) after introducing the stock standard gas.

f) Calculate the partial pressure of the introduced stock standard gas based on the difference between the pressure after the stock standard gas is introduced and the initial pressure (P_P).

g) Introduce humidified VOC-free air or high-purity nitrogen and pressurize to the specified final absolute pressure.

h) Record the final pressure after dilution in absolute pressure (P_F).

i) Calculate the concentration of the prepared working standard gas (C_W) based on the stock standard gas concentration (C_S), the partial pressure of the gas introduced (P_P), and the final pressure (P_F).

$$C_W = C_S \times \frac{P_P}{P_F} \qquad (2\text{-}1)$$

C_W: Concentration of target VOCs in the working standard gas (ppbv)

C_S: Concentrations of target VOCs in the stock standard gas (ppbv)

P_P: Internal pressure in the canister after introducing stock standard gas (kPa)

P_F: Internal pressure of the canister after dilution (kPa)

Dynamic Flow Dilution Method

a) Evacuate the canister to achieve the specified initial vacuum level.

b) Verify that there are no leaks in the stock standard gas line, dilution gas (humidified VOC-free air, high-purity nitrogen) line, mixing section, valves, and canister connections.

c) Thoroughly purge the stock standard gas line with stock standard gas.

d) Thoroughly purge the dilution gas line with dilution gas.

e) Set the flow rates of the stock standard gas (Q_1) and dilution gas (Q_2) according to the target concentration of the working standard gas (C_W).

f) Verify that each flow rate has stabilized.

g) The stock standard gas and the dilution gas are continuously mixed in the mixing section.

h) Vent the mixed gas for a set period of time to stabilize the gas composition in the mixing section and piping.

i) Once the gas mixture has stabilized, transfer it to a canister.

j) Fill the canister to the specified pressure.

k) After filling, close the canister valve and record the final pressure.

l) Calculate the concentration of the prepared working standard gas (C_W) based on the stock standard gas concentration (C_S), the flow rate of the stock standard gas (Q_1) and the flow rate of the dilution gas (Q_2).

$$C_W = C_S \times \frac{Q_1}{(Q_1+Q_2)} \qquad (2\text{-}2)$$

C_W: Concentration of target VOCs in the working standard gas (ppbv)

C_S: Concentrations of target VOCs in the stock standard gas (ppbv)

Q_1: Flow rate of stock standard gas (mL/min)

Q_2: Flow rate of dilution gas (mL/min)

Syringe Injection Method

a) Evacuate the canister to achieve the specified initial vacuum level.

b) Rinse the syringe several times with the standard solution or standard gas.

c) When using a standard solution, accurately measure out the specified amount using a micro syringe. When using a standard gas, measure out the specified volume using a gas-tight syringe.

d) Connect the syringe to the canister inlet (using a commercially available septum stopper or similar).

e) Promptly inject the standard solution or standard gas into the canister.

f) When injecting a standard solution, heat the canister as necessary to ensure that the injected liquid completely vaporizes inside the canister. However, the temperature must remain within a range that does not cause decomposition of the target component or affect the surface treatment of the canister.

g) Introduce humidified VOC-free air or high-purity nitrogen to pressurize the canister to the specified final pressure.

h) Record the final pressure (absolute pressure).

i) Calculate the injection volume of the standard solution or standard gas, the standard concentration, the canister capacity, the final pressure, and the concentration of the working standard gas.

When injecting the standard solution

$$C_W = \frac{n_W \times 8.314 \times T}{P_{Final} \times V_{Can}} \times 10^9 \quad (2\text{-}3)$$

C_W: Concentration of target VOCs in the canister (ppbv)

n_W: The amount of the target VOCs injected into the canister (mol)

P_{Final}: Final pressure inside the canister (kPa)

V_{Can}: Capacity of the canister (L)

T: Temperature (K)

When injecting the stock standard gas

$$C_W = C_S \times \frac{V_{inj} \times 101.3}{P_{Final} \times V_{Can}} \quad (2\text{-}4)$$

C_W: Concentration of target VOCs in the canister (ppbv)

C_S: Concentration of the injected stock standard gas (ppbv)

V_{inj}: Injection volume for stock standard gas in gas-tight syringes (L)

P_{Final}: Final pressure inside the canister (kPa)

V_{Can}: Capacity of the canister (L)

2.2.5 Sample Measurement

The procedures for concentration calculation, determination of detection and quantification limits (LOD and LOQ), and QA/QC requirements are described in Section 2.6

Pressure Dilution of Canister Samples

Since sample collection must be performed under reduced pressure, the collected sample must be diluted with VOCs-free air or high-purity nitrogen gas as quickly as possible and pressurized to approximately twice the pressure at the time of collection. When pressurizing the sample, be sure to record the pressure before and after pressurization. The dilution ratio is calculated from this pressure

difference. Sample analysis must be performed within one week of collection.

Preconcentrator System

The preconcentrator is operated according to the following procedure.

a) Purge the sample inlet line of the preconcentrator with VOCs-free air, high-purity nitrogen, or helium to remove residual compounds from previous samples and to prevent contamination by room air.

b) Connect the canister to the sample inlet line of the preconcentrator (ensure that sufficient sample pressure remains for measurement).

c) Check the canister connection, tubing, valves, and sample inlet line for leaks.

d) Introduce a specified volume of the sample into the preconcentrator while controlling the flow rate using a mass flow controller or an equivalent flow-control device. Note to set an appropriate amount of sample to prevent the concentration section from becoming saturated.

e) Introduce a fixed amount of internal standard gas for correction of analytical variability.

f) The target VOCs are trapped and concentrated using liquid nitrogen or an electrically cooled trap. In this step, trace-level VOCs contained in a relatively large volume of air are concentrated in a small trap volume.

g) Remove interfering components, such as nitrogen, oxygen, carbon dioxide, and excess water, to the extent possible. If required, dry or purge the trap while retaining the target VOCs, in order to remove residual water vapor and other unwanted gases.

h) Rapidly heat the trap to thermally desorb the trapped VOCs.

i) Refocus the desorbed VOCs before introduction into the GC column to obtain sharp chromatographic peaks.

j) Transfer the thermally desorbed VOCs to the GC using a carrier gas such as helium.

k) After sample injection, bake and purge the trap, valves, and sample lines to remove residual VOCs.

Gas Chromatographic-Mass Spectrometric Measurement

GC-MS analysis shall be performed in accordance with the procedures described in Section 2.6.2, including instrument calibration, data acquisition, compound identification, and analytical conditions.

Calibration Curve

Calibration curves shall be prepared using working standard gases containing the target VOCs at known concentrations. The working standard gas is introduced into the preconcentrator in the same manner as the actual atmospheric sample and analyzed through a series of operations, including dry purging, cooling and trapping, thermal desorption, and GC-MS measurement. This allows for the creation of a calibration curve based on the entire analytical process, which includes the sample injection volume, cooling and trapping efficiency, moisture control, desorption efficiency, and GC-

MS response.

The concentration range of the calibration curve shall be set to include the concentrations of VOCs expected to be present in actual atmospheric samples. When targeting low-concentration VOCs, multiple concentration points shall be set to include the area near the limit of quantification (LOQ); for high-concentration VOCs, additional standard points on the high-concentration side shall be added as necessary.

Calibration curve may be established using either “Individual Standards Method” or “Effective Dilution Method”.

Figure 2.2.1 shows a schematic diagram of the Individual Standards Method. In this method, calibration standards are prepared at multiple concentration levels in separate canisters. The same sample volume is introduced from each calibration canister into the preconcentration system. In this method, the amount of sample gas, water vapor, and matrix gases introduced into the system is kept constant at each calibration level, while the concentrations of the target VOCs are varied. This method is preferred when establishing a new measurement method, measuring low-level VOCs, analyzing highly volatile compounds, or when strict quality control is required.

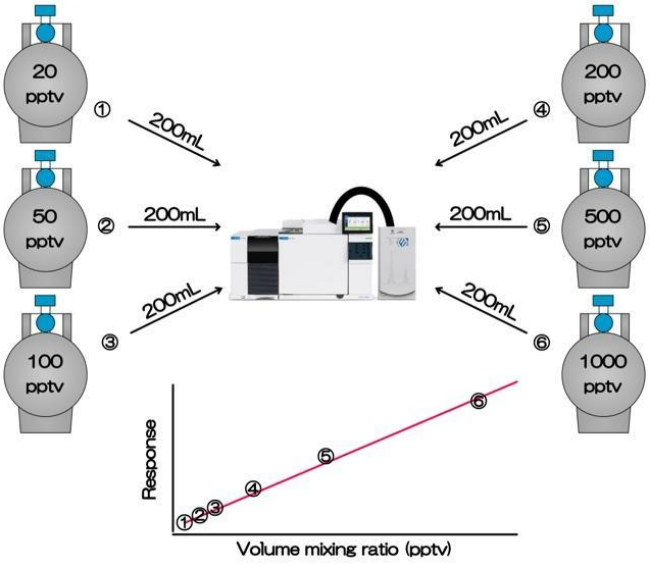


Figure 2.2.1 Schematic diagram of the Individual Standards Method

Figure 2.2.2 shows a schematic diagram of the Effective Dilution Method. In this method, a calibration standard, typically the highest-level and middle-level calibration standard, is introduced into the preconcentration system at different volumes. The effective calibration concentration is calculated by multiplying the concentration of the standard gas by the ratio of the introduced volume to the actual sample introduction volume. For example, if the actual sample introduction volume is 400 mL and 80 mL of a 5 ppbv standard gas is introduced, the effective calibration concentration is 1 ppbv.

When the Effective Dilution Method is used, the accuracy and reproducibility of the sample introduction volume shall be verified. Because different introduction volumes may change the amount of water vapor, carbon dioxide, matrix gases, and the behavior of target compounds in the trap, the

applicability of this method should be verified by comparison with a calibration curve prepared using the Individual Standards Method.

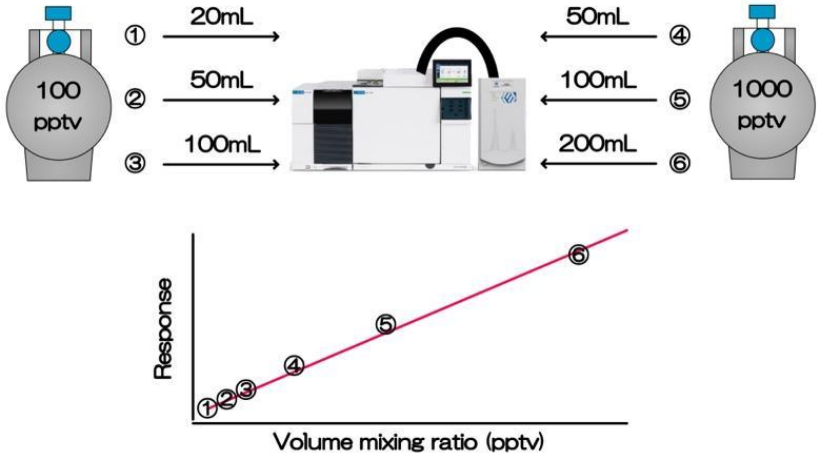


Figure 2.2.2 Schematic diagram of the Effective Dilution Method

A fixed amount of internal standard gas shall be added to each calibration standard, blank, and sample. The peak area of each target compound shall be corrected using the peak area of the corresponding internal standard, and calibration curves shall be prepared from the relationship between concentration and response ratio.

Operational Blank

Perform GC-MS measurement on the operational blanks to determine the operational blank values for each target VOC component. If target VOC compounds are detected in the operational blank, assess the stability and reproducibility of the blank values through replicate measurements. When the blank values are demonstrated to be stable and reproducible, apply the quality control procedures described in Section 2.9, including appropriate blank correction where applicable, and proceed with sample quantitation. If the blank values are unstable, unusually high, or indicate contamination, re-clean the canister or adjust the associated equipment (e.g., canister cleaner, dilutor, GC-MS) and repeat the blank measurements to confirm acceptable blank performance before proceeding with atmospheric sample collection and analysis.

Sample Analysis

Perform GC-MS measurement on the collected samples. The weight (As) of each target VOC component will be calculated using a calibration curve based on the peak area ratios of the target VOC components and the internal standard compound. The calculation of final concentration is described in detail in Section 2.8

Field Blank

Perform GC-MS measurement on the field blank canisters, and determine the weight of each target VOC component. For this test, measure at least three samples and use the average value as the field blank value (At).

Duplicate Samples

Perform GC-MS measurement on duplicate samples to determine the weight of each target VOC component. Verify that the difference between two or more measurements is 30% or less, or that each individual measurement falls within ±15% of the average. If the difference is significant, that VOC component is generally considered invalid.

2.3 Active Sorbent Tube Sampling

2.3.1 Overview

The active sorbent tube sampling method described in this section was developed based on the authors' practical experience in ambient VOC sampling and analysis, together with information and procedures described in established reference methods. In particular, the U.S. EPA Method TO-17 and the Manual for Measurement of Hazardous Air Pollutants published by the Ministry of the Environment, Japan, were used as major references in preparing this section. The methodology is further aligned with the principles and requirements specified in ISO 16017-1:2000.

Purpose and scope

This method provides guidance for the measurement of volatile organic compounds (VOCs) in ambient air using sorbent tubes and active sampling. Ambient air is drawn through a tube packed with one or more adsorbent materials, allowing target VOCs to be collected and concentrated directly from the atmosphere. The applicable range of VOCs depends on the type and combination of sorbents used, and appropriate sorbents should therefore be selected according to the target compounds and sampling conditions.

Measurement principle

Ambient air is drawn through a sorbent tube at a controlled flow rate using a sampling pump. The target VOCs are retained on the adsorbent material, with dehumidification performed as necessary. After sampling, the sorbent tube is connected to a thermal desorption unit and heated while helium flows through the tube. The desorbed VOCs are transferred to and re-concentrated in a cooled trap. The trap is subsequently heated rapidly, and the target VOCs are introduced into a GC-MS (or GC-FID) for separation, identification, and quantification. Although both GC-MS and GC-FID can be used for VOC analysis, this guidance focuses on GC-MS because of its applicability to a broad range of VOCs and its capability for both compound identification and quantitative analysis.

Advantages and limitations

An advantage of sorbent tube sampling is that VOCs are collected and concentrated directly on the sorbent during sampling. Different sorbent materials, or combinations of sorbents in multi-bed tubes, can be selected to cover a wide range of VOCs. Thermal desorption also enables the collected VOCs to be transferred directly to the analytical system without solvent extraction.

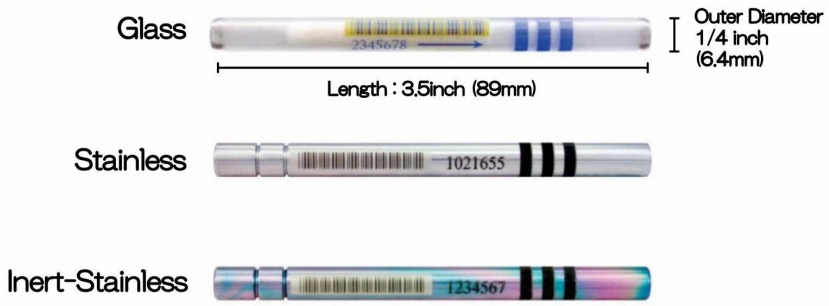
The principal limitations are that sampling conditions must be carefully selected according to the target VOCs and the characteristics of the sorbent. Excessive sampling volumes may cause breakthrough, particularly for highly volatile compounds. Moisture can also affect sampling and analysis, especially when hydrophilic sorbents are used, and dehumidification may therefore be necessary under high-humidity conditions. The sorbent tubes must also be properly cleaned and stored to minimize blank contamination, and thermal desorption requires dedicated instrumentation.

2.3.2 Equipment and Materials

Sorbent Tube

As shown in Picture 2.3.1, there are three types of outer materials for sorbent tubes: glass, stainless steel, and inert stainless steel. They are 3.5 inches (89 mm) long and have an outer diameter of 1/4 inch (6.4 mm). While the glass type allows for visual inspection of the condition of the packed

adsorbent materials, it has the disadvantage of being fragile. On the other hand, stainless steel and inert stainless steel are highly rigid and resistant to breakage, making them easy to handle.



Picture 2.3.1 Photo showing the outer material and dimensions of the sorbent tube
(Source of the photograph: Camsco official web site)

As illustrated in Fig. 2.3.1, sorbent tubes packed with a single type of adsorbent are referred to as "single-bed", whereas those packed with multiple types of adsorbents are referred to as "multi-bed" tubes. The sorbent tube has a specific orientation; the atmospheric sample is introduced with the side featuring the indentation (the "corset" side) facing upstream, and carrier gas is introduced from the downstream side during measurement and cleaning. Types of adsorbent materials suitable for measuring trace gas components in the atmosphere include porous polymers (ex. Tenax TA), graphitized carbon black (ex. Carbotrap), and carbonized molecular sieves (ex. Carboxene, Carbosieve); the choice depends on the target component and the observation environment. In general, porous polymers, graphitized carbon black, and carbonized molecular sieves are considered to cover VOCs with approximate carbon number ranges of C5–C30, C3–C20, and C2–C8, respectively. Porous polymers and graphitized carbon black tend to be hydrophobic, while carbon molecular sieves tend to be hydrophilic. Therefore, when sampling in high-humidity environments, it is recommended to use hydrophobic sorbent tubes, such as those made of porous polymers or graphitized carbon black, or to install a dehumidification tube upstream of the sorbent tube to prevent problems caused by moisture.

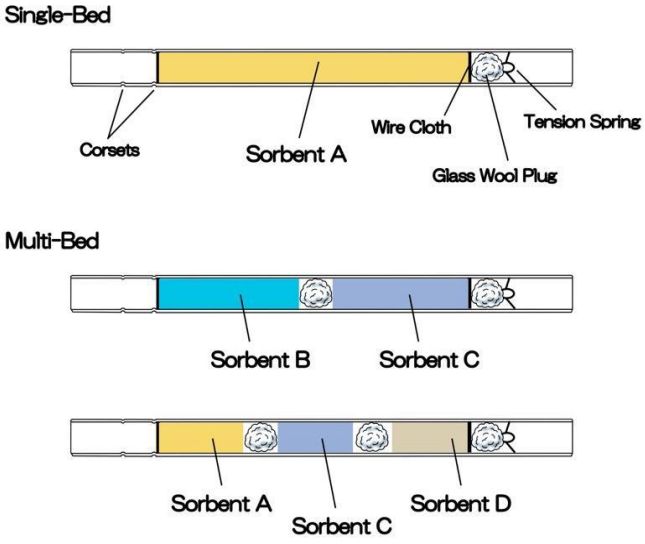


Figure 2.3.1 Schematic illustration of sorbent tube configurations: a single-bed tube packed with one type of adsorbent and a multi-bed tube packed with multiple types of adsorbents

Dehumidification Tube

A glass tube filled with approximately 15 g of magnesium perchlorate, with both ends sealed with quartz wool. Seal both ends tightly and store in an airtight container containing activated carbon until use.

Pump

A sealed pump (such as a diaphragm pump) capable of maintaining the specified collection flow rate, or a pump with equivalent or superior performance.

Mass Flow Controller

A device capable of controlling flow rates within the range of 10–500 mL/min, with a control accuracy of ±10% of the set flow rate, or a device with performance equivalent to or better than this. The mass flow controller should be calibrated and verified at regular intervals using a flow calibration device or equivalent standard (e.g., soap bubble flow meter) to ensure that the actual flow rate remains within the specified accuracy. Calibration frequency should be established as part of the laboratory QA/QC program and should be performed after maintenance or repair, and whenever performance checks indicate possible flow deviations.

Integrating Flow Meter

A device capable of measuring down to 10 mL/min using a mass flow meter or a similar instrument, and capable of operating accurately within the control range of a flow control device.

Analytical equipment

Sorbent tube sampling may be coupled with either GC-MS or GC-FID, depending on the monitoring objectives, target compounds, and available resources. After sampling, VOCs retained on the sorbent are transferred to the analytical system by thermal desorption or solvent extraction. This guidance primarily describes the use of **thermal desorption (TD)** in conjunction with chromatographic analysis. Detailed information on GC-MS and GC-FID instrumentation, analytical procedures, calibration, and QA/QC requirements is provided in Section 2.7-2.9.

Standards

Standard Gas

In general, it is recommended to use commercially available standard reference gas supplied in cylinders with attached certificates of analysis (approximately 1 ppmv). For components for which standard gases are not commercially available, a standard solution of the VOC component should be introduced into an evacuated canister and vaporized. As commercially available standard reference gases are calibrated in terms of volumetric concentration (ppmv, μL/L), to convert to mass/volume concentration (μg/L), multiply by 273.15・M /［22.4・(273+T)］ (where M is the molecular weight of the component and T is the temperature).

Internal Standard Gas

Purchase from the manufacturer or prepare in-house individual or mixed internal standard gas containing suitable substances such as toluene-d_8 of fluorobenzene, dilute with high-purity nitrogen gas to a concentration of approximately 1 ppmv.

2.3.3 Sample Collection

The entire volume of the sample collected in the sorbent tube is used for measurement. To ensure that the sample load on the GC column does not become excessive, the total sampling volume, sample injection method (split ratio), and detection method (scan mode, SIM mode) should be taken into account. Generally, it is desirable to keep the sample load on the column at 100 ng or less. Furthermore, since highly volatile substances may cause breakthrough in the sorbent tubes, the sample collection volume must be adjusted based on the target VOCs atmospheric concentration (generally within the range of 1–10 L). If continuous collection for 24 hours is not possible, perform repeated short-term collections and calculate the 24-hour average. After sampling, the sorbent tubes should be stored under refrigerated or frozen conditions in an environment where they are protected from contamination. It is recommended that the collected samples be analyzed within one month after sampling.

Cleaning the Sorbent Tube

While flowing approximately 50 mL/min of high-purity nitrogen or high-purity helium from the downstream side of the trap tube (the side without the collar), thoroughly displace the air inside the sorbent tube. Then, heat it at approximately 300°C for at least one hour, allow it to cool to room temperature, and seal both ends tightly. Note that some types of sorbents exhibit increased blank values when heated in the presence of oxygen; therefore, ensure the air inside is thoroughly purged with high-purity nitrogen or high-purity helium before performing the heating operation. Also, be cautious, as prolonged heating at temperatures exceeding 300°C may cause carbon oxidation and result in a change in performance. After cleaning, it is recommended that the sorbent tube be analyzed to confirm that the blank levels of the target VOCs have been reduced sufficiently so that they do not significantly affect the measurement of actual samples.

Ambient Air Sampling

Remove the caps from the sorbent tube, connect the downstream end (the end without the corsets) to the pump, and attach a sample tube, a dehumidification tube, and a rain guard to the upstream end (the end with the corsets) as necessary. Note that the material of the sampling tube shall be glass, passivated stainless-steel, or an equivalent material. In particular, avoid using materials other than fluororesin and polyimide whenever possible. It is necessary to verify in advance that the material of the sampling tube used does not affect the measured values of the target VOCs. After confirming that there are no leaks along the entire sample line, adjust the flow rate so that the total sampling volume is approximately 1–10 L, and then start the pump.

If the total sampling volume or sampling flow rate is excessive, breakthrough of VOCs from the sorbent tube may occur. Therefore, appropriate precautions shall be taken. Breakthrough may be checked by the following methods. In the first method, two identical sorbent tubes are connected in series, and an atmospheric sample is collected. If the target VOCs are not detected in the downstream

tube, it is considered that breakthrough has not occurred. In the second method, two adsorption tubes are operated in parallel with different total collection volumes, and the analytical results are compared. If there is no difference in the measured values between the two, it can be confirmed that breakthroughs have not occurred even under the condition with the higher collected volume.

After sampling is complete, cap both ends of the sorbent tube tightly and store it in a sealed container containing activated carbon. Whenever possible, use sorbent tubes that have been cleaned within the past week.

Operational Blank Preparation

Conduct an operational blank test to verify that there is no contamination attributable to the equipment, reagents, or laboratory environment used in the measurement process.

Field Blank Preparation

Use unused, tightly sealed sorbent tubes intended for field blank testing; do not perform any sample collection procedures, but transport and handle them in the same manner as sorbent tubes used for sample collection. While preparing for sampling (the period between removing the cap from the sampling tube and starting the sampling process), keep the field blank tube uncapped; reseal it tightly once the preparation is complete. During sampling, keep the field blank tube close to the sampling tube. After sampling is complete, open the cap again, reseal it at the same time as the sampling tube, and store it in a cooled, sealed container containing activated carbon until measurement.

Field blank testing should be conducted at a frequency of approximately **10% of the total number of samples**, with at least **one field blank per sampling event** and a minimum of **three field blank tubes** for larger monitoring campaigns conducted under similar conditions (e.g., location characteristics, transport procedures, and sampling periods).

Duplicate Measurement

For duplicate measurements, collect two or more samples simultaneously under the same conditions. Sample collection for duplicate measurements should be performed at a frequency of approximately 10% of the total number of samples in a given sampling series.

2.3.4 Sample Measurement

Thermal Desorption and Sample Introduction

The sorbent tube is attached to the thermal desorption unit, and the following procedure is performed.

1) Perform leak checks on all flow lines.

2) Perform a dry purge by flowing high-purity helium from the downstream side of the sorbent tube (the side without the corsets) to remove any residual moisture from the sorbent tube and displace the gas within the flow path.

3) The sorbent tube is heated to desorb VOCs. Through inlet splitting, a portion of the sample gas is

re-adsorbed and concentrated in a built-in trap tube cooled by a Peltier element or similar device.

4) The trap tube is rapidly heated to facilitate secondary desorption. A portion of the sample gas is injected into the GC-MS or GC-FID via the transfer line.

Chromatography Analysis

Analysis of the thermally desorbed VOCs may be performed using GC-MS or GC-FID, as appropriate. Instrument configuration, calibration procedures, analytical conditions, compound identification, and QA/QC requirements are described in Section 2.6.

Calibration Curve

The procedure for creating a calibration curve is as follows:

(1) While passing approximately 10–30 mL/min of high-purity nitrogen or helium gas through a cleaned sorbent tube, add a fixed volume (several mL) of the mixed standard and the internal standard gases to allow sufficient adsorption of VOCs. Prepare at least five sorbent tubes for calibration curve by varying the volume of the mixed standard gas. Various manufacturers sell equipment for preparing sorbent tubes used to create calibration curves, as shown in Fig. 2.3.2 below.

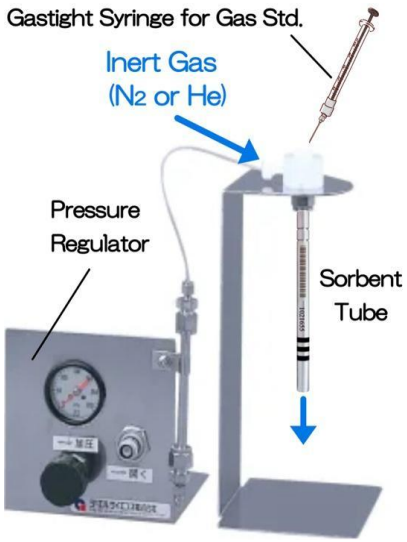


Figure 2.3.2 Examples of equipment for introducing a standard gas (standard solution) into a sorbent tube (Source of the photograph: GL Science official web site)

(2) Place the sorbent tube prepared in (1) for the calibration curve into the thermal desorption unit and perform GC-MS measurement. Record the chromatograms for each target VOCs according to the method described in Section 4.3.

(3) Calculate the intensity ratio of the quantifier and the qualifier for each VOC component in the working standards.

(4) Calculate the peak area ratio of the quantifier for each VOC component and the internal standard, and plot a calibration curve using these peak area ratios and the weights of each VOC component.

Operational Blank

Perform extraction and GC-MS measurement on the operational blanks to determine the operational blank values for each target VOC component. If target VOC compounds are detected in the operational blank, assess the stability and reproducibility of the blank values through replicate measurements. When the blank values are demonstrated to be stable and reproducible, apply the quality control procedures described in Section 2.9, including appropriate blank correction where applicable, and proceed with sample quantitation. If the blank values are unstable, unusually high, or indicate contamination, re-clean the sorbent tube or adjust the analytical equipment (e.g., thermal desorption unit, GC-MS) and repeat the blank measurements to confirm acceptable performance before proceeding with sample analysis.

Sample Analysis

Perform thermal desorption and analysis of the collected samples are performed using a GC-MS or GC-FID equipped with a TD, as appropriate. Using a calibration curve based on the peak area ratio of the qualifiers for each target VOC component and the internal standard substance, the weight (*As*) of each target VOC component in the injected sample is determined. Calculation of the final VOC concentration is described in Section 2.8

Field Blank

Perform GC-MS or GC-FID measurement on the field blank tubes and determine the weight of each target VOC component. For this test, measure at least three samples and use the average value as the field blank value (*At*).

Duplicate Samples

Perform GC-MS or GC-FID analysis on duplicate samples to determine the weight of each target VOC component. Verify that the difference between two or more measurements is 30% or less, or that each individual measurement falls within ±15% of the average. If the difference is significant, that VOC component is generally considered invalid.

2.4 Active Charcoal Tube Sampling

2.4.1 Overview

The active charcoal tube sampling method described in this section was developed based on the authors' practical experience in ambient VOC sampling and analysis, together with information and procedures described in established reference methods. In particular, the Manual for Measurement of Hazardous Air Pollutants published by the Ministry of the Environment, Japan, were used as major references in preparing this section. The methodology is further aligned with the principles and requirements specified in ISO 16017-1:2000.

Purpose and scope

This method provides guidance for the measurement of VOCs in ambient air using charcoal-based adsorbent tubes and active sampling. It is suitable for the simultaneous measurement of VOCs such as benzene, toluene, ethylbenzene, and xylenes (BTEX). The method is particularly applicable when relatively large volumes of ambient air need to be collected, and the target VOCs can be efficiently retained on the selected adsorbent and recovered by solvent extraction.

Measurement principle

Ambient air is drawn at a controlled flow rate through a collection tube packed with an adsorbent material, such as a carbon molecular sieve, using a sampling pump. Moisture is removed as necessary before the air reaches the collection tube. The target VOCs retained on the adsorbent are subsequently extracted with an appropriate solvent, such as carbon disulfide. The resulting extract is then measured by GC-MS (or GC-FID) for separation, identification, and quantification of the target VOCs.

Advantages and limitations

A major advantage of this method is that relatively large volumes of ambient air can be collected by using an adsorbent with sufficient retention capacity. In addition, because the collected VOCs are transferred into an extract solution, the same extract can be used for repeated measurements when necessary. The sampling equipment is also relatively simple and is based on a collection tube, flow-control device, and sampling pump. A principal limitation is that the collected VOCs are diluted during solvent extraction, which may reduce analytical sensitivity and therefore require a relatively large sampling volume. Blank contamination originating from the adsorbent material or extraction solvent may also affect the detection limit. In addition, collection efficiency and solvent recovery can vary depending on the target VOC and sampling conditions. These factors should therefore be evaluated in advance, and appropriate quality control should be carried out.

2.4.2 Reagents

Carbon Disulfide (CS_2)

Use as an extraction solvent. When injecting this solvent into a GC-MS or GC-FID system, it must not interfere with the chromatograms of the target VOCs or the internal standard substances. Use high-purity products with low VOC levels, such as workplace environmental monitoring grade.

Carbon disulfide is toxic and highly flammable and should therefore be handled with appropriate precautions. All procedures involving CS_2, including preparation of standards and extraction of samples, should be performed in a well-ventilated laboratory, preferably in a chemical fume hood, to minimize inhalation exposure. Appropriate personal protective equipment (PPE), including suitable protective gloves and safety glasses, should be worn to prevent skin and eye contact. Because CS_2 has a very low flash point and its vapor can readily form flammable or explosive mixtures with air, it must be kept away from open flames, sparks, hot surfaces, and other ignition sources. Containers should be kept tightly closed when not in use and stored in an appropriate location for flammable solvents. Users should consult and follow the relevant Safety Data Sheet (SDS) and applicable institutional or national safety regulations before handling CS_2.

Magnesium Perchlorate

This is used when dehumidifying atmospheric samples. An elemental analysis grade is desirable. A particle size of 300–700 μm is appropriate; if the particles are too fine, the pressure loss becomes large.

Stock Standard Solution

Use reagents with a purity of 98% or higher for the VOCs used to prepare stock standard solutions. While it is acceptable to prepare mixtures of individual component standard solutions using CS_2 as the solvent, commercially available VOC mixture standard solutions are also available; the concentration should be approximately 10–20 μg/mL.

Working Standard Solution

Dilute the stock standard solution with CS_2 to prepare working standard solutions for creating a calibration curve. Although the concentrations of VOCs (such as benzene, toluene, ethylbenzene, and xylene) must be adjusted on a case-by-case basis depending on ambient VOC concentrations, prepare at least five mixed standard solutions within the range of 0–500 ng/mL. When stored frozen, the working standard solution remains usable for about two weeks.

Internal Standard Solution

Toluene-d_8, which is readily available, is commonly used as an internal standard substance. It is advisable to select an appropriate internal standard substance based on the specific purpose. Dilute it with CS_2 to a concentration of approximately 50–100 μg/mL.

2.4.3 Equipment and Materials

Extraction Vial

Use glass vials with screw caps. Select vials of an appropriate volume based on the amount of extraction solvent.

Micro Syringe

It is used for preparing standard solutions and adding internal standards to sample solutions; selecting

an appropriate size based on the intended volume.

Sampling Apparatus

To collect a sample, connect the equipment in the following order: dehumidification tube, charcoal tube, mass flow controller, pump, and integrating flow meter. Currently, many pumps are commercially available that combine a mass flow controller and an integrating flow meter into a single unit.

It is desirable that the sample be collected directly by the charcoal tube, however, if the samples cannot be taken directly due to unavoidable circumstances, use a sampling tube for sample collection. The material of sampling tube shall be glass, passivated stainless steel, or an equivalent material. In particular, avoid using materials other than fluororesin and polyimide whenever possible. It is necessary to verify in advance that the material of the sampling tube used does not affect the measured values of the target VOCs.

Clean all equipment used in the sampling system to minimize contamination. After assembling the system for sampling, check for leaks, and purge and replace the system with sample air to minimize contamination as much as possible.

Charcoal Tube

The charcoal tube is prepared by packing approximately 200 mg and 100 mg of carbon molecular sieve into two layers in a glass tube with an inner diameter of about 3–4 mm, and plugging both ends of each layer with quartz wool (Pic. 2.4.1). Some models feature a high fill volume of 400 mg in the front stage and 200 mg in the rear stage, making them particularly suitable for sampling highly volatile organic compound vapors.



Picture 2.4.1 Photo of charcoal tube
(Source: Sibata Scientific Technology Ltd. official web site)

Dehumidification Tube

A glass tube filled with approximately 15 g of magnesium perchlorate, with both ends sealed with quartz wool. Seal both ends tightly and store in an airtight container containing activated carbon until use.

Pump

A sealed pump (such as a diaphragm pump) capable of maintaining the specified collection flow rate, or a pump with equivalent or superior performance.

Mass Flow Controller

A device capable of controlling flow rates within the range of 10–500 mL/min, with a control accuracy of ±10% of the set flow rate, or a device with performance equivalent to or better than this. The mass flow controller should be calibrated and verified at regular intervals using a flow calibration device or equivalent standard (e.g., soap bubble flow meter) to ensure that the actual flow rate remains within the specified accuracy. Calibration frequency should be established as part of the laboratory QA/QC program and should be performed after maintenance or repair, and whenever performance checks indicate possible flow deviations.

Integrating Flow Meter

A device capable of measuring down to 10 mL/min using a mass flow meter or similar instrument, and capable of operating accurately within the control range of a flow control device.

Analytical equipment

Charcoal tube sampling may be coupled with either GC-MS or GC-FID, depending on the monitoring objectives, target compounds, and available resources. After sampling, VOCs retained on the charcoal adsorbent are recovered by solvent extraction, typically using carbon disulfide (CS_2) or another suitable extraction solvent, and the resulting extract is introduced into the analytical system. This guidance primarily describes the use of solvent extraction in conjunction with chromatographic analysis. Detailed information on GC-MS and GC-FID instrumentation, analytical procedures, calibration, and QA/QC requirements is provided in Section 2.7-2.9.

2.4.4 Sample Collection

Ambient Air Sampling

The sample is collected over a 24-hour period at a flow rate of 50–100 mL/min from the upstream end of the charcoal tube (the end containing the larger amount of adsorbent material) fitted with a dehumidifying tube. During sampling, shield the charcoal tube from light using aluminum foil or similar material. After collecting the sample, securely cap both ends of the tube and store it in a freezer until analysis.

Tube labeling

Each passive sampler shall be identified by a unique identification number corresponding to the sampling location, date and time, and other relevant information. To avoid contamination, no markings of any kind using ink shall be made on clean samplers, and adhesive labels shall not be affixed to the samplers. When labeling is necessary, a **pencil may be used for writing on the sampler holder or associated documentation**, as appropriate. Identification information for each passive sampler shall be recorded on the storage bag used to hold the sampler. After sampling, special

care shall be taken to prevent any mix-up of the samplers.

Operational Blank

Conduct an operational blank test to verify that there is no contamination attributable to the equipment, reagents, or laboratory environment used in the extraction process.

Field Blank

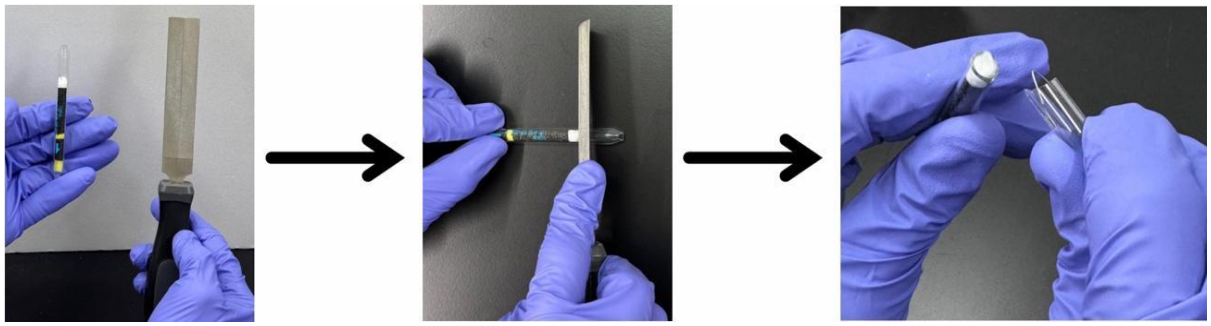
Use unused, tightly sealed charcoal tubes intended for field blank testing; do not perform any sample collection procedures, but transport and handle them in the same manner as charcoal tubes used for sample collection, with the exception. While preparing for sampling (the period between removing the cap from the sampling tube and starting the sampling process), keep the field blank tube uncapped; reseal it tightly once the preparation is complete. During sampling, keep the field blank tube close to the sampling tube. After sampling is complete, open the cap again, reseal it at the same time as the sampling tube, and store it in the freezer until measurement. This field blank testing shall be performed on at least three samples, at a frequency of approximately 10% of the total number of samples, in a series of sampling operations that are considered equivalent in terms of location characteristics, transport procedures, or distance. When the monitoring program includes only one or two sampling sites, it is recommended that at least one field blank be prepared for each sampling site.

Duplicate Samples

For duplicate measurements, collect two or more samples simultaneously under the same conditions. Sample collection for duplicate measurements should be performed at a frequency of approximately 10% of the total number of samples in a given sampling series.

Extraction Procedure

Cut the collection tube with a glass cutter as shown in the Picture below (Pic. 2.4.2), and transfer both layers of adsorbent into a vial. Add an appropriate volume of CS_2 sufficient to completely immerse the adsorbent and extract the collected VOCs. A volume of 2 mL CS_2 may be used as a nominal extraction volume; however, the volume may be adjusted according to the expected VOC concentrations and the calibration range of the analytical method. The actual extraction volume shall be recorded and incorporated into the concentration calculations. Immediately seal the vial and shake until no visible bubbles remain. Add an appropriate amount of internal standard solution and allow the extract to stand for at least 1 hour prior to analysis. The volume of internal standards should be adjusted, where necessary, to maintain a consistent internal standard-to-extraction solvent ratio. For example, when 2 μL of internal standard solution (50 μg/mL) is added to a 2 mL CS_2 extract, the internal standard volume should be adjusted proportionally if a different extraction volume is used. Perform the extraction procedure in the same manner for the field blank, operational blank and the duplicate measurement sample.



Picture 2.4.2 A scene of cutting off the charcoal tube

2.4.5 Sample Measurement

Chromatographic Analysis

Analysis of the solvent extracted VOCs may be performed using GC-MS or GC-FID, as appropriate. Prior to chromatographic separation, a measured volume of the extract is introduced into the gas chromatograph through a liquid injection port, typically using a microsyringe or autosampler. Instrument configuration, calibration procedures, analytical conditions, compound identification, and QA/QC requirements are described in Section 2.6.

Calibration Curve

The procedure for creating a calibration curve is as follows.

(1) Accurately measure 1 mL of each working standard solution from the concentration series and transfer it to a vial. Then, add 1 μL of the internal standard solution to each vial.

(2) Inject 1 μL of the working standard solutions prepared in (1) into the GC-MS or GC-FID, as applicable. Perform the GC-MS or GC-FID measurement and record the chromatograms for each target substance.

(3) Calculate the intensity ratio of the quantifier and the qualifier for each VOC component in the working standard solution.

(4) Calculate the peak area ratio of the quantifier for each VOC component and the internal standard and plot a calibration curve using these peak area ratios and the weights of each VOC component.

Operational Blank

Perform extraction and GC-MS measurement on the operational blanks to determine the operational blank values for each target VOC component. If target VOC compounds are detected in the operational blank, assess the stability and reproducibility of the blank values through replicate measurements. When the blank values are demonstrated to be stable, apply the quality control procedures in Section 2.9 and proceed with sample quantitation. If contamination or unstable blank values are observed, re-clean or re-prepare the equipment and repeat the blank measurements before sample analysis.

Sample Analysis

Perform extraction and analysis of the collected samples using GC-MS or GC-FID, as appropriate. Using a calibration curve based on the peak area ratio of the qualifiers for each target VOC component and the internal standard substance, the weight (*As*) of each target VOC component in the injected sample is determined. Calculation of the final VOC concentration is described in Section 2.8

Field Blank

Perform extraction and GC-MS or GC-FID measurement on the field blank solution and determine the weight of each target VOC component in the injected solution. For this test, measure at least three samples and use the average value as the field blank value (*At*).

Duplicate Samples

Extract and perform GC-MS or GC-FID analysis on the duplicate samples to determine the weight of each target VOC component. Verify that the difference between two or more measured values is 30% or less, or that each individual measured value is within 15% of the average. If the difference is significant, that VOC component is generally considered invalid.

2.5 Passive Charcoal-Based Diffusive Sampling

2.5.1 Overview

The passive sampling method using charcoal-based samplers described in this section was developed based on the authors' practical experience in ambient VOC monitoring, together with information and procedures described in established reference methods. In particular, the Manual for Measurement of Hazardous Air Pollutants published by the Ministry of the Environment, Japan and U.S. EPA Method 325A were used as major references in preparing this section. The methodology is further aligned with the principles and requirements specified in ISO 16200-2:2000.

Purpose and scope

This method describes the collection and determination of VOCs in ambient air using passive samplers containing activated charcoal as the adsorbent medium enclosed within a porous polymeric diffusion barrier. VOCs are transported into the sampler by molecular diffusion and are retained on the charcoal sorbent (ISO 16017-2, 2003; U.S. EPA, 2019a). Following sample collection, VOCs retained on the sorbent are extracted with an appropriate solvent and quantitatively determined by GC-MS or GC-FID.

This method is applicable to the simultaneous determination of benzene, toluene, ethylbenzene, and xylenes (BTEX), and may also apply to a broad range of other VOCs, provided that the sampler configuration, sorbent material, and analytical conditions are appropriately selected and validated for the compounds of interest. Owing to its simplicity and relatively low cost, charcoal-based passive sampling is widely used for spatial monitoring, screening studies, and long-term trend assessment.

This section describes the principles, applicability, sample collection procedures, extraction procedures, analytical procedures, concentration calculations, and QA/QC quality assurance/quality control considerations for passive sampling of VOCs in ambient air.

Measurement Principle

Passive samplers collect VOCs from ambient air at a monitoring location by molecular diffusion into the sampler. The collected compounds are adsorbed onto activated charcoal and subsequently recovered by solvent extraction for laboratory analysis. Ambient air concentrations are calculated from the mass of each compound collected by the sampler.

This method provides time-integrated average concentrations over a specified sampling period. For ambient air monitoring, a sampling period (exposure period) of at least 24 hours is generally required to obtain adequate measurement sensitivity. The amount of analyte collected by a passive sampler is fundamentally governed by Fick’s first law of diffusion, and the appropriate uptake rate should be obtained from the manufacturer or determined experimentally for the target analytes and sampler configuration.

Advantages and Limitations

Passive charcoal sampler requires no sampling pump or other external power sources. Because the samplers are small and lightweight, they are easy to handle and are well suited for simultaneous

monitoring at multiple locations. However, their performance depends on validated uptake rates and sufficient exposure duration. As a result, the method is generally more suitable for long-term monitoring than for short-duration or real-time measurements.

2.5.2. Reagents

The extraction solvent, calibration standards, and internal standard solutions used for passive sampling with charcoal-based adsorbents are the same as those described for active charcoal tube sampling.

Carbon Disulfide (CS_2)

Use as an extraction solvent. When injecting this solvent into a GC-MS system, it must not interfere with the chromatograms of the target VOCs or the internal standard substances. Use high-purity products with low VOC levels, such as workplace environmental monitoring grade.

Carbon disulfide is highly flammable and toxic. It should be handled in a fume hood with appropriate personal protective equipment (PPE), and all waste should be disposed of according to relevant safety regulations and laboratory procedures.

Stock Standard Solution

Use reagents with a purity of 98% or higher for the VOCs used to prepare stock standard solutions. While it is acceptable to prepare mixtures of individual component standard solutions using carbon disulfide as the solvent, commercially available VOC mixture standard solutions are also available; the concentration should be approximately 10–20 μg/mL.

Working Standard Solution

Dilute the stock standard solution with CS_2 to prepare working standard solutions for creating a calibration curve. Although the concentrations of VOCs (such as benzene, toluene, ethylbenzene, and xylene) must be adjusted on a case-by-case basis depending on ambient VOC concentrations, prepare at least five mixed standard solutions within the range of 0–1000 ng/mL. When stored frozen, the working standard solution remains usable for about two weeks.

Internal Standard Solution

Toluene-d8 or chlorobenzene-d5, both of which are readily available, are commonly used as internal standard substances. It is advisable to select an appropriate internal standard substance according to the specific purpose. Dilute the selected substance with CS_2 to a concentration of approximately 50–100 μg/mL.

2.5.3 Equipment and Materials

Extraction Vial

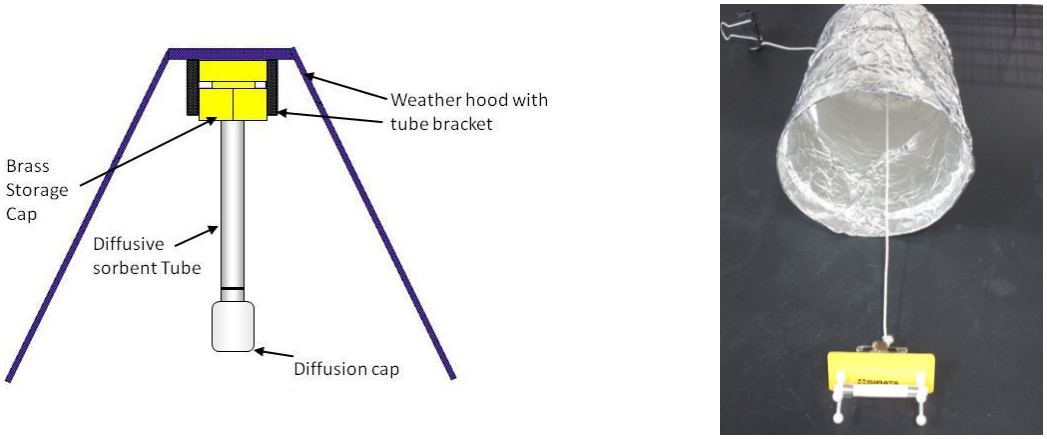
Use glass vials with screw caps. Select vials of an appropriate volume based on the amount of extraction solvent.

Micro Syringe

It is used for preparing standard solutions and adding internal standards to sample solutions; select an appropriate size based on the intended volume.

Passive sampling tube protective shelter

A simple weatherproof hood, suitable for protecting passive sampling tubes from the worst of the weather, consists of an inverted cone/funnel constructed of an inert, non-outgassing material that fits over the diffusive tube, with the open (sampling) end of the tube projecting just below the cone opening. An example is shown in Pic 2.5.1.



Picture 2.5.1 Example of passive sampling tube protective shelter
(Left: Described in EPA Method 325A; Right: Shelter designed by the Tokyo Metropolitan Research Institute for Environmental Protection)

Note: Passive samplers collect gaseous compounds by allowing them to diffuse through the pores on the sampling surface and contact the sorbent. Therefore, airflow across the diffusion surface may affect the measured values. In general, higher wind speeds tend to lower ambient concentrations; however, they also increase the amount of gas contacting the passive sampler, which may increase the sampled amount and result in overestimation of the ambient concentration. Accordingly, a protective shelter shall be used to minimize the influence of airflow at the sampling site.

Passive Sampling Tube

Commercially available passive samplers include cylindrical radial samplers and badge-type axial samplers (Fig. 2.5.1). These samplers shall be packed with a sorbent such as coconut-shell activated carbon and covered with a porous polymer material having fine pores, such as PTFE. Target substances in ambient air are collected on the sorbent by natural diffusion. As an example, a radial sampler consists of a tube with an outer diameter of approximately 0.27 inches (7.0 mm) and an inner diameter of approximately 0.19 inches (4.8 mm). As an example, an axial sampler has a circular diffusion surface with a diameter of 35 mm.

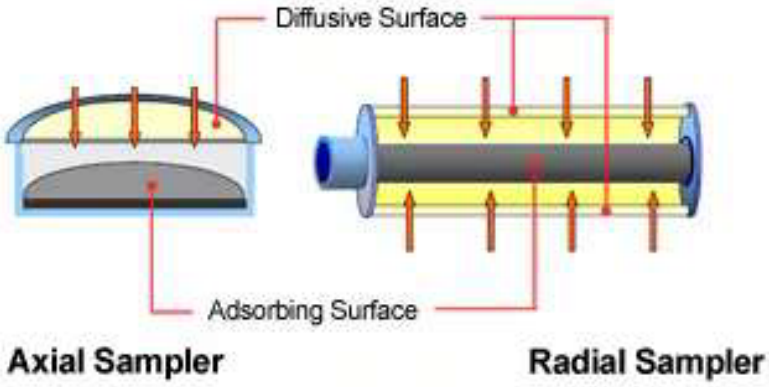


Figure 2.5.1 Configuration of passive samplers
(Source: Merck KGaA, Darmstadt, Germany. official web site)



Picture 2.5.2 Examples of passive samplers
(Left: Merck KGaA, Darmstadt, Germany; Center: SIBATA Scientific Technology Ltd.; Right: SKC, Inc.)

Analytical equipment

Charcoal tube sampling may be coupled with either GC-MS or GC-FID, depending on the monitoring objectives, target compounds, and available resources. After sampling, VOCs retained on the charcoal adsorbent are recovered by solvent extraction, typically using CS_2 or another suitable extraction solvent, and the resulting extract is introduced into the analytical system. This guidance primarily describes the use of solvent extraction in conjunction with chromatographic analysis. Detailed information on GC-MS and GC-FID instrumentation, analytical procedures, calibration, and QA/QC requirements is provided in Section 2.7-2.9.

2.5.4 Sample Collection

Ambient Air Sampling

Sampling is initiated at the monitoring site by removing the sampling tube from the storage/transport bag and placing it in the protective shelter. The sampling start time is the time at which the tube is removed from the bag at the sampling site or the time at which the caps are removed from the tube. During the sampling period, care must be taken to ensure that the tube is not directly exposed to airflow.

After sample collection, the tube is placed in an airtight storage bag and stored frozen until analysis.

Tube labeling

Each passive sampler shall be identified by a unique identification number corresponding to the sampling location, date and time, and other relevant information. To avoid contamination, no markings of any kind using ink shall be made on clean samplers, and adhesive labels shall not be affixed to the samplers. When labeling is necessary, a **pencil may be used for writing on the sampler holder or associated documentation**, as appropriate. Identification information for each passive sampler shall be recorded on the storage bag used to hold the sampler. After sampling, special care shall be taken to prevent any mix-up of the samplers.

Operational Blank

Conduct an operational blank test to verify that contamination attributable to the equipment, reagents, passive samplers, or laboratory environment used in the extraction procedure does not affect the measured values.

Field Blank

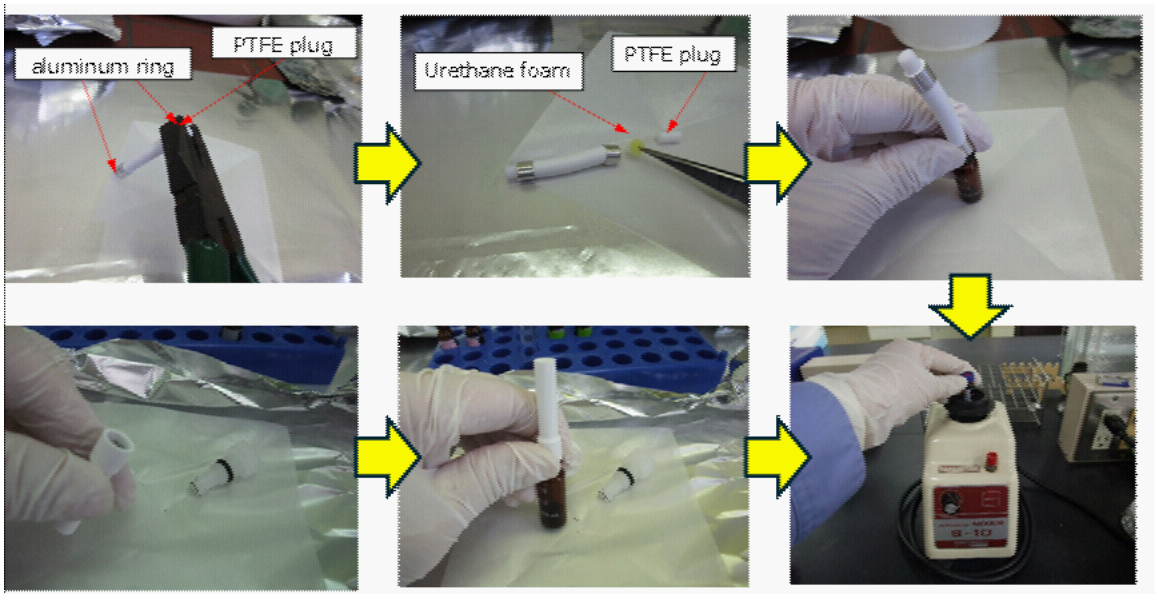
Use an unused passive sampler as a field blank. Do not expose the field blank sampler for sample collection. In all other respects, transport and handle the field blank sampler in the same manner as the passive samplers used for sample collection. During sampling preparation, remove the sampler from the storage bag once and immediately return it to the bag. During the sampling period, keep the field blank sampler near the protective shelter. After sampling, return the field blank sampler to the laboratory with the exposed passive samplers, seal it, and store it frozen until analysis. Perform field blank testing on a minimum of three samples at a frequency of approximately 10 percent of the total number of samples for each set of sampling operations considered equivalent in terms of site characteristics, transport procedures, or distance.

Duplicate Samples

For duplicate measurements, collect two or more samples simultaneously under the same conditions. Sample collection for duplicate measurements should be performed at a frequency of approximately 10% of the total number of samples in a given sampling series.

Extraction Procedure

As shown in Pic. 2.5.3, remove the sorbent from the passive sampler and transfer it to a vial. Add 1 mL of CS_2 to the vial and seal the vial tightly. Shake the vial until any bubbles disappear, then add 1 to 2 μL of the internal standard solution (50 to 100 μg/mL) and allow the vial to stand for at least 1 hour. Perform the extraction procedure in the same manner for the field blank, operational blank, and duplicate measurement samples.



Picture 2.5.3 Preparation of Passive Samplers
(Upper: SIBATA Scientific Technology Ltd.; Lower: Merck Merck KGaA, Darmstadt, Germany)

2.5.5 Sample Measurement

The analytical procedures for passive samplers using charcoal-based adsorbents are generally the same as those used for active charcoal tube sampling.

Chromatographic Analysis

Analysis of the solvent extracted VOCs may be performed using GC-MS or GC-FID, as appropriate. Prior to chromatographic separation, a measured volume of the extract is introduced into the gas chromatograph through a liquid injection port, typically using a microsyringe or autosampler. Instrument configuration, calibration procedures, analytical conditions, compound identification, and QA/QC requirements are described in Section 2.6.

Calibration Curve

The procedure for creating a calibration curve is as follows.

(1) Accurately measure 1 mL of each working standard solution from the concentration series and transfer it to a vial. Then, add 1 µL of the internal standard solution to each vial.

(2) Inject 1 µL of the working standard solutions prepared in (1) into the GC-MS or GC-FID, as applicable. Perform the GC-MS or GC-FID measurement and record the chromatograms for each target substance.

(3) Calculate the intensity ratio of the quantifier and the qualifier for each VOC component in the working standard solution.

(4) Calculate the peak area ratio of the quantifier for each VOC component and the internal standard and plot a calibration curve using these peak area ratios and the weights of each VOC component.

Operational Blank

Perform extraction and GC-MS measurement on the operational blanks to determine the operational blank values for each target VOC component. If target VOC compounds are detected in the operational blank, assess the stability and reproducibility of the blank values through replicate measurements. When the blank values are demonstrated to be stable, apply the quality control procedures in Section 2.9 and proceed with sample quantitation. If contamination or unstable blank values are observed, re-clean or re-prepare the equipment and repeat the blank measurements before sample analysis.

Sample Analysis

Perform extraction and analysis of the collected samples using GC-MS or GC-FID, as appropriate. Using a calibration curve based on the peak area ratio of the qualifiers for each target VOC component and the internal standard substance, the weight (*As*) of each target VOC component in the injected sample is determined. Calculation of the final VOC concentration is described in Section 2.8

Field Blank

Perform extraction and GC-MS or GC-FID measurement on the field blank solution and determine the weight of each target VOC component in the injected solution. For this test, measure at least three samples and use the average value as the field blank value (*At*).

Duplicate Samples

Extract and perform GC-MS or GC-FID analysis on the duplicate samples to determine the weight of each target VOC component. Verify that the difference between two or more measured values is 30% or less, or that each individual measured value is within 15% of the average. If the difference is significant, that VOC component is generally considered invalid.

2.6 Passive Sorbent-Based Diffusive Sampling

2.6.1 Overview

The passive sampling method using sorbent-based samplers described in this section was developed based on the authors' practical experience in ambient VOC monitoring, together with information and procedures described in established reference methods. In particular, ISO 16017-2:2003, and U.S. EPA Method 325A were used as major references in preparing this section.

Purpose and scope

This method describes the collection and determination of VOCs in ambient air using passive samplers containing **engineered sorbent materials**, such as graphitized carbon black (Carbopack), Tenax TA, Carbograph, or other suitable sorbents. VOCs migrate from ambient air into the sampler by molecular diffusion and are retained on the sorbent bed without the use of pumps or electrical power (Lee et al., 2024; ISO 16017-2, 2003; U.S. EPA, 2019a).

Compared with charcoal-based passive samplers, sorbent-based passive samplers generally provide greater flexibility for monitoring a wider range of VOCs. Depending on the sorbent material and analytical requirements, collected analytes may be recovered by thermal desorption (TD) or solvent desorption (Woolfenden, 2010). The procedures described in this section focus on tube-type diffusive samplers suitable for thermal desorption, followed by analysis using GC-MS or GC-FID, as appropriate (ISO 16017-2, 2003).

This section describes the principles, applicability, sampling procedures, sample preparation methods, analytical procedures, concentration calculations, and QA/QC requirements for sorbent-based passive VOC monitoring.

Measurement principle

A diffusive sampler is exposed to ambient air for a measured period. Analyte vapor migrates down a stationary air layer of defined geometry and is retained on the sorbent; the mass collected is governed by Fick’s first law of diffusion (ISO 16017-2, 2003). Because the diffusion path length and cross-sectional area are fixed by the sampler design, the mass accumulated is proportional to the airborne concentration and the exposure time. The result is a time-weighted average (TWA) concentration over the exposure period. Validated exposure durations may range from several hours to several weeks, depending on the sampler design, sorbent–analyte combination, expected ambient concentration, analytical sensitivity, and sorbent capacity. (ISO 16017-2, 2003).

Advantages and limitations

Passive sorbent samplers offer several advantages: they are inexpensive, silent, require no external power, and allow dense spatial monitoring networks to be deployed with relatively simple field operations. They are particularly useful for characterizing spatial variability, assessing long-term trends, and supporting source-apportionment studies. (Lee et al., 2024; ISO 16017-2, 2003; U.S. EPA, 2019a).

However, the method provides a time-integrated rather than a real-time concentration, and

measurement accuracy depends on the availability of validated, compound- and sampler-specific uptake rates. Uptake rates may also be influenced by environmental factors such as temperature, humidity, and face velocity, with the magnitude of these effects depending on the sorbent and sampler design. Method performance may also vary among compound classes; for example, olefins were reported to be approximately 24% higher than corresponding online measurements in the Seoul field study (Lee et al., 2024).

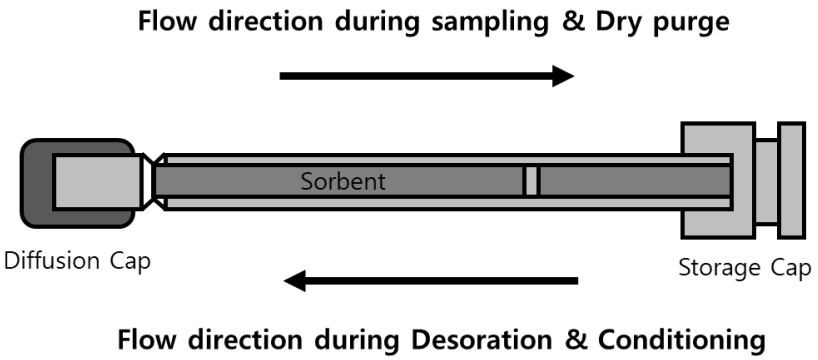


Figure 2.6.1 Structure of automated thermal desorption tube passive air sampler

2.6.2 Equipment and Materials

Reagents and Materials

1) Conditioned sorbent tubes: inert-coated stainless-steel TD tubes packed with the selected sorbent (e.g., Carbopack X), thermally conditioned and blank-verified before deployment (see Section 2.5.3).

2) Calibration standard: a certified VOC reference mixture (e.g., a BTEX or PAMS-component standard gas) used to calibrate the analytical response by loading known masses onto conditioned tubes (U.S. EPA, 2019c).

3) Internal / reference standard (optional): a stable compound loaded at a constant level to monitor desorption and injection performance.

4) Gases: high-purity carrier gas (helium or nitrogen) and FID fuel/oxidant gases (hydrogen and zero-grade air), all filtered and hydrocarbon-free.

Diffusive sampler

The sampler consists of a tube or cartridge with a defined diffusion path length (L) and cross-sectional area (A), and a sampler-specific diffusive end-cap or other diffusion barrier that defines the diffusion face (ISO 16017-2, 2003). Both ends are sealed with appropriate storage caps before and after exposure (ISO 16017-2, 2003; US EPA, 2019a). For outdoor deployment, a weather or turbulence shield should be used where required by the sampler design to reduce the influence of precipitation and excessive air movement (US EPA, 2019a).

Sorbent

Graphitized carbon black (GCB), including Carbopack grades, is a non-porous, relatively hydrophobic carbon sorbent with a specific surface area of roughly 5–100 m^2/g, in which analyte retention is dominated by dispersive interactions. Depending on the specific grade, GCB sorbents can be used for a range of VOCs, including aromatic compounds such as benzene, toluene, and xylenes. The applicable volatility range and uptake characteristics depend on the sorbent grade, sampler configuration, sampling conditions, and target compounds. The choice of sorbent and the associated uptake rate must therefore be appropriate for the target compound list; guidance on sorbent selection is provided in ISO 16017-2 (2003), Annexes B–D.

Table 2.6.1 Common sorbent families used for VOC sampling and their approximate volatility ranges and applications.

Sorbent family	Example trade names	Volatility range	Typical use
Graphitized carbon black (GCB)	Carbopack, Carbotrap, Carbograph	C_4–C_{12} (grade-dependent)	BTEX, C_5–C_{10} hydrocarbons
Carbon molecular sieve (CMS)	Carboxen, Carbosieve	C_1–C_5	Very volatile / light hydrocarbons
Porous organic polymer	Tenax TA, Porapak	C_6–C_{26}	Higher-boiling VOCs / SVOCs
Activated charcoal	coconut-shell charcoal	broad; solvent desorption	Classic BTEX (NIOSH 1500/1501)

Analytical and ancillary equipment

1) Thermal desorption (TD) unit coupled with GC-MS or GC-FID, suitable for direct desorption of the selected sorbent tubes and quantitative transfer of the target VOCs to the GC system.

2) Capillary column appropriate to the analyte range (e.g., a non-polar 100 % dimethylpolysiloxane or 5 %-phenyl phase; a PLOT column for light hydrocarbons) (U.S. EPA, 2019c).

3) Tube conditioner / oven with inert-gas purge for cleaning reusable sorbent tubes prior to deployment (ISO 16017-2, 2003).

4) Glassware and consumables: volumetric flasks, gas-tight microsyringes, autosampler vials with PTFE-lined septa, tweezers for handling sorbent inserts.

5) Analytical balance (for gravimetric standard preparation), and field instruments to record ambient temperature, relative humidity and wind, plus a GPS receiver for site coordinates (U.S. EPA, 2019a).

6) Clean storage containers (e.g., metal cans with activated-carbon sachets) and cool, dark, contaminant-free storage/refrigeration for conditioned and exposed tubes (U.S. EPA, 2019b).

Calibration and Quantification

The analytical response shall be calibrated using certified VOC standard gas mixtures, such as PAMS or BTEX standards, introduced onto conditioned sorbent tubes and analyzed using the same TD-GC-FID procedure applied to field samples. Using identical TD and chromatographic conditions for standards and samples minimizes bias associated with sample introduction and desorption efficiency (Healy et al., 2018; U.S. EPA, 2019c).

Multi-level calibration standards should be prepared across the working concentration range. Calibration curves are constructed from the relationship between the analyte mass loaded onto the sorbent tube and the corresponding peak area (or peak area ratio relative to an internal standard). Calibration performance should be verified using an independent calibration check standard during each analytical batch.

For compounds lacking individual calibration standards, the approximately carbon-proportional response of the FID may provide an estimate of analyte response. However, whenever possible, quantification should be based on authentic reference standards for the target compounds.

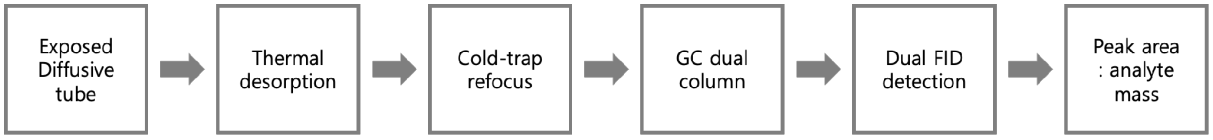


Figure 2.6.2 Analytical workflow from an exposed diffusive tube to quantified analyte mass under thermal-desorption GC-FID.

2.6.3 Sample Collection

Tube conditioning and blank verification

Before deployment, reusable sorbent tubes shall be conditioned by heating under a flow of inert gas to remove adsorbed artifacts, following the sorbent manufacturer's temperature limits and a validated conditioning procedure consistent with ISO 16017-2 (2003). After conditioning, a representative tube from each batch shall be analyzed as a blank, and the batch shall be released for use only when artifact levels meet the predefined method-specific acceptance criterion. Conditioned tubes shall be capped immediately with storage caps and kept in clean, sealed containers until deployment.

Field deployment

1) Siting: Select locations representative of the intended spatial coverage. Mount samplers at a standard height (commonly ~1.5–4 m), sheltered from precipitation and direct sun but with free air movement, and use the weather shield specified for the sampler (U.S. EPA, 2019a).

2) Face velocity: Diffusive uptake requires a minimum air movement across the sampler face (of the order of $\geq$10 cm s^{-1} for many samplers) to avoid a starvation (reduced-uptake) effect; the shield is designed to maintain this while damping turbulence (NIOSH, 2003; U.S. EPA, 2019a).

3) Exposure: Record the start and stop times to the nearest minute; the exposure duration (e.g., one to four weeks for ambient concentrations) must be within the validated range for the

sorbent and expected concentration so that the sorbent is neither under-loaded nor saturated (ISO 16017-2, 2003).

4) Replication and blanks: Deploy field duplicates at a defined fraction of sites, and expose/return field blanks (a capped tube taken to the site and returned unopened) and travel/transport blanks with each batch (U.S. EPA, 2019b).

5) Recovery: At the end of exposure, immediately reseal the tube with storage caps, log the sampler, and transport it cool and upright in a sealed, contaminant-free container. Analyze within the validated storage-stability holding time (U.S. EPA, 2019b; NIOSH, 2003).

2.6.4 Sample Measurement

The analytical procedures for passive samplers using sorbent-based adsorbents are generally the same as those used for active sorbent tube sampling employing TD.

Thermal Desorption and Sample Introduction

The sorbent tube is attached to the TD unit, and the following procedure is performed.

1) Perform leak checks on all flow lines.

2) Perform a dry purge by flowing high-purity helium from the downstream side of the sorbent tube (the side without the corsets) to remove any residual moisture from the sorbent tube and displace the gas within the flow path.

3) The sorbent tube is heated to desorb VOCs. Through inlet splitting, a portion of the sample gas is re-adsorbed and concentrated in a built-in trap tube cooled by a Peltier element or similar device.

4) The trap tube is rapidly heated to facilitate secondary desorption. A portion of the sample gas is injected into the GC-MS or GC-FID via the transfer line.

Chromatography Analysis

Analysis of the thermally desorbed VOCs may be performed using GC-MS or GC-FID, as appropriate. Instrument configuration, calibration procedures, analytical conditions, compound identification, and QA/QC requirements are described in Section 2.6.

Calibration Curve

The procedure for creating a calibration curve is as follows:

1) While passing approximately 10–30 mL/min of high-purity nitrogen or helium gas through a cleaned sorbent tube, add a fixed volume (several mL) of the mixed standard and the internal standard gases to allow sufficient adsorption of VOCs. Prepare at least five sorbent tubes for calibration curve by varying the volume of the mixed standard gas. Various manufacturers sell equipment for preparing sorbent tubes used to create calibration curves.

2) Place the sorbent tube prepared in (1) for the calibration curve into the TD unit and perform GC-MS measurement. Record the chromatograms for each target VOCs according to the method described in Section 4.3.

3) Calculate the intensity ratio of the quantifier and the qualifier for each VOC component in the working standards.

4) Calculate the peak area ratio of the quantifier for each VOC component and the internal standard and plot a calibration curve using these peak area ratios and the weights of each VOC component.

Operational Blank

Perform extraction and GC-MS measurement on the operational blanks to determine the operational blank values for each target VOC component. If target VOC compounds are detected in the operational blank, assess the stability and reproducibility of the blank values through replicate measurements. When the blank values are demonstrated to be stable and reproducible, apply the quality control procedures described in Section 2.9, including appropriate blank correction where applicable, and proceed with sample quantitation. If the blank values are unstable, unusually high, or indicate contamination, re-clean the sorbent tube or adjust the analytical equipment (e.g., thermal desorption unit, GC-MS) and repeat the blank measurements to confirm acceptable performance before proceeding with sample analysis.

Sample Analysis

Perform extraction and analysis of the collected samples using GC-MS or GC-FID, as appropriate. Using a calibration curve based on the peak area ratio of the qualifiers for each target VOC component and the internal standard substance, the weight (As) of each target VOC component in the injected sample is determined. Calculation of the final VOC concentration is described in Section 2.8

Field Blank

Perform GC-MS or GC-FID measurement on the field blank tubes and determine the weight of each target VOC component. For this test, measure at least three samples and use the average value as the field blank value (A_t).

Duplicate Samples

Perform GC-MS or GC-FID analysis on duplicate samples to determine the weight of each target VOC component. Verify that the difference between two or more measurements is 30% or less, or that each individual measurement falls within ±15% of the average. If the difference is significant, that VOC component is generally considered invalid.

2.7. Analytical Methods

2.7.1 Overview of Analytical Methods

Following sample collection, VOCs are quantified using a series of analytical procedures, including sample preparation, instrumental analysis, calibration, concentration calculation, and quality assurance and quality control (QA/QC). Although sampling methods differ among canister, sorbent tube, charcoal tube, and passive samplers, many of the subsequent analytical procedures are common.

This section summarizes the analytical approaches commonly applied in ambient VOC monitoring, including GC-MS and GC-FID analysis, thermal desorption, solvent extraction, concentration calculation, determination of detection and quantification limits, and QA/QC procedures. Detailed analytical conditions should be established according to the monitoring objectives, target compounds, sampling methods, and instrumentation used.

2.7.2 GC-MS Analysis

Gas chromatography coupled with mass spectrometry (GC-MS) is one of the most widely used techniques for ambient VOC monitoring due to its ability to identify and quantify a wide range of VOC species with high selectivity and sensitivity. The method is applicable to samples collected using canisters, sorbent tubes, charcoal tubes, and passive samplers following appropriate sample preparation and introduction procedures. GC-MS is particularly useful for the determination of target VOCs in complex atmospheric mixtures and for confirmation of compound identity when multiple species are present. General guidance on GC-MS operation, calibration, analytical conditions, and compound identification is provided in the following sections.

Principle

GC-MS combines the separation capability of gas chromatography (GC) with the identification and quantification capability of mass spectrometry (MS). VOCs introduced into the GC system are separated according to their physicochemical properties and interaction with the chromatographic column. The separated compounds are subsequently ionized in the mass spectrometer, and the resulting ions are detected according to their mass-to-charge ratio (m/z). Compound identification is based on retention time and mass spectral characteristics, while quantification is performed using calibrated responses of the target compounds. GC-MS can be operated in scan mode for compound identification and screening purposes or in selective ion monitoring (SIM) mode for enhanced sensitivity and quantitative analysis.

Instrument Configuration and Analytical Conditions

The GC-MS system configuration and analytical conditions shall be suitable for the selected sampling and sample preparation method. A typical GC-MS analytical system consists of a sample introduction unit, a gas chromatograph, a mass spectrometer, a carrier gas supply system, and a data acquisition system.

The analytical conditions should be optimized to achieve adequate separation, identification, and quantification of the target VOCs.

Sample Introduction Unit

The sample introduction unit transfers VOCs from the sampling device or sample extract into the GC-MS system and shall be compatible with the selected sampling and sample preparation method. Common sample introduction approaches include:

- **Preconcentration systems** for canister samples, where VOCs are concentrated from a known volume of air prior to GC-MS analysis.
- **Thermal desorption (TD) units** for sorbent tube samples, where VOCs collected on the sorbent are thermally desorbed and introduced directly into the GC-MS system.
- **Liquid injection systems** for solvent extracts obtained from charcoal-based active or passive samplers, or other sampling media specifically designed for solvent extraction.

The selected sample introduction system shall provide adequate recovery, reproducibility, and sensitivity for the target VOCs and concentration range of interest.

GC Column Oven

The GC column oven temperature control range shall be 35–300°C, and the oven shall be capable of temperature control by a temperature-increase program so that the optimum separation conditions for the target VOCs can be achieved.

GC Capillary Column

The GC capillary column shall be a fused-silica based column with an inner diameter of 0.25–0.32 mm and a length of 30–60 m, coated internally with a layer of methyl silicone, phenylmethyl polysiloxane, or cyano-propylmethyl polysiloxane, etc., having a film thickness of approximately 0.25–3 μm, or a product with separation performance equivalent to or better than that described above.

Mass Spectrometer Detector

While there are various types of MS detectors, such as quadrupole, ion trap, and time-of-flight detectors, the quadrupole type is the most widely used for general-purpose analysis of atmospheric VOCs. If the detector is a quadrupole type, it must be compatible with electron ionization (EI) and support both scan mode and SIM mode.

Carrier Gas

The carrier gas shall be helium with a purity of 99.999% by volume or higher.

Interface Section

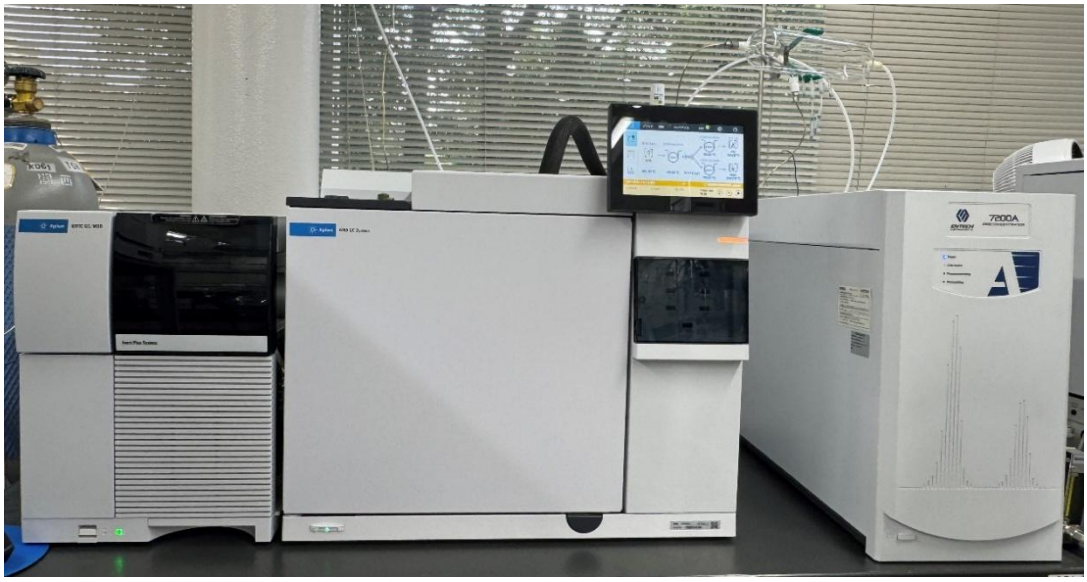
The interface section between GC and MS shall be capable of being maintained at approximately 200–300°C.

Ion Source

The ion source shall be capable of being maintained at approximately 200–300°C, and the ionization voltage shall be 70 eV.

(1) Canister Sampling with Preconcentration-GC-MS

Canister samples are typically introduced through a preconcentration system to remove moisture and concentrate VOCs prior to GC-MS analysis (Pic 2.7.1). Typical instrument configurations and operating conditions are summarized in Table 2.7.1. These conditions allow for the measurement of multiple VOCs, including major VOCs such as benzene, toluene, ethylbenzene, and xylene. Adjust this setting appropriately depending on the purpose of the measurement and the target VOCs.



Picture 2.7.1 Example of Preconcentrator connected with GC-MS system

Table 2.7.1 Example of preconcentrator system and GC-MS conditions

Preconcentrator system	**7200A (Entech Instruments)**
Concentration mode	Extended Cold Trap Dehydration (ECTD)
Sampling Flow Rate	50 mL/min
Trap Flush	200 mL
Module 1 (M1)	Empty Trap
Trap Temp.	-40°C
Desorption Temp.	10°C
M1 to M2 Vol.	40 mL
M1 to M2 Flow Rate	100 mL/min
Module 2 (M2)	Tenax TA
Trap Temp.	-40°C
Desorption Temp.	210°C
Module 3	Cryo Focus
Trap Temp.	-160°C
Desorption Temp.	80°C

Injection Time	0.2 min
GC-MS	**5977C (Agilent Technologies)**
Carrier Gas	High-purity helium gas
Carrier Gas Flow Rate	1.5 mL/min (Constant Flow)
Column	DB-1 (Agilent Technologies)
Column Size	Inner diameter: 0.32 mm Length: 60 m Film thickness: 1.00 µm
Oven Temp.[1)]	35°C (hold for 4 minutes) → 5°C/min → 140°C → 20°C/min → 220°C (11 minutes)
Transfer Line Temp.[2)]	220°C
Ion Source Temp.	250°C
Quadpole Temp.	150°C
Ionization Voltage	70 eV
Detection Mode	SIM or Scan

1) Note that the temperature must be within the maximum temperature range of the column being used.
2) Recommended to set to the maximum temperature of the column oven during measurement.

(2) Sorbent-Based Adsorbents with Thermal Desorption (TD)-GC-MS

Sorbent tube samples are typically analyzed using a thermal desorption (TD) unit coupled to GC-MS (Pic 2.7.2). VOCs collected on the sorbent are thermally desorbed, focused onto a trap, and subsequently transferred to the GC-MS system. Typical instrument configurations and operating conditions are summarized in Table 2.7.2. This condition allows for the measurement of multiple VOCs, including major VOCs such as benzene, toluene, ethylbenzene, and xylene. Adjust this setting appropriately depending on the purpose of the measurement and the target VOCs.



Picture 2.7.2 Example of Thermal Desorption Unit for sorbent tube connected with GC-MS system

Table 2.7.2 Example of measurement condition for Thermal Desorption unit and GC-MS

Thermal Desorption Unit	**TurboMatrix 650 ATD (Perkin Elmer)**
Sample Tube Temp.	280°C
Valve Temp.	240°C
Transfer Temp.	280°C
Trap Tube Temp.	280°C
Purge Time	7 min
Sample Tube Desorption Flow Rate	50 mL/min
Inlet Split Flow Rate	30 mL/min
Trap Tube Desorption Flow Rate	1 mL/min
Outlet Split Flow Rate	10 mL/min
GC-MS	**GCMS-QP2010 Plus (Shimadzu)**
Carrier Gas	High-purity helium gas
Carrier Gas Flow Rate	1 mL/min (Constant Flow)
Column	Aquatic-2 (GL Science)
Column size	Inner diameter: 0.25 mm Length: 60 m Film thickness: 1.4 μm
Oven Temp.[1)]	35°C (hold for 8 minutes) → 5°C/min → 170°C → 15°C/min → 230°C (9 minutes)
Interface Temp.[2)]	230°C
Ion Source Temp.	210°C
Ionization voltage	70 eV
Detection mode	SIM or Scan

1) Note that the temperature must be within the maximum temperature range of the column being used.

2) Recommended to set to the maximum temperature of the column oven during measurement.

(3) Charcoal-Based Adsorbents with Solvent Extraction-GC-MS

For charcoal tube active and passive sampling, VOCs are extracted from the sorbent material using an appropriate solvent and analyzed by GC-MS using a liquid injection system. Typical instrument configurations and operating conditions are summarized in Pic. 2.7.3 and Table 2.7.3. For analyses involving liquid sample extracts, the injection port shall be capable of heating to at least 200°C and shall support both split and splitless injection modes. This condition allows for the measurement of multiple VOCs, including major VOCs such as benzene, toluene, ethylbenzene, and xylene. Adjust this setting appropriately depending on the purpose of the measurement and the target VOCs.



Picture 2.7.3 Example of Injection Port connected with GC-MS system for solvent extraction

Table 2.7.3 Example of GC-MS measurement condition

Injection Port Unit	**Auto Injection AOC-20i Plus (Shimadzu)**
Injection Port Temp.	200℃
Sample Injection method	Splitless (Splitless time：1 min)
GC-MS System	**Trace 1310-ISQ LT (Thermo Fisher Scientific)**
Carrier Gas	High-purity helium gas
Carrier Gas Flow Rate	1.2 mL/min (Constant flow)
Pressure	9.14 psi
Column	InertCap Aquatic-2 (GL Sciences)
Column Size	Inner diameter: 0.32 mm Length: 60 m Film thickness: 1.8 μm
Oven Temp.[1)]	40°C (hold for 3 min) → 5°C/min → 170°C → 10°C/min → 250°C (10 min)
Interface Temp.[2)]	250℃
Ion Source Temp.	230℃
Ionization Voltage	70 eV
Detection Mode	Scan or SIM

1) Note that the temperature must be within the maximum temperature range of the column being used.
2) Recommended to set to the maximum temperature of the column oven during measurement.

Compound Identification

Prior to analysis, the mass spectrometer should be calibrated using an appropriate mass calibration standard (e.g., PFTBA) to verify mass accuracy, mass resolution (mass range of approximately 18–300 m/z with a resolution of at least 1 amu), and instrument performance. The calibration results should be documented and retained as part of routine instrument performance monitoring.

Compound identification shall be based on a combination of chromatographic retention time and mass spectral information. Identification may be performed by comparison with certified reference standards, reference chromatograms, or validated mass spectral libraries.

GC-MS may be operated in either **Scan mode** or **SIM mode**, depending on the analytical objectives. Generally, because scan mode allows for the confirmation of mass spectra, it provides higher accuracy in identifying the components of peaks detected by total ion chromatogram (TIC). On the other hand, SIM mode enables low bassline noise, high-sensitivity detection by selectively detecting mass spectra, making it suitable for quantitative analysis; however, it provides limited information regarding substance identification.

Scan Mode

It is important to assign each peak on TIC obtained by measuring the working standard solution in scan mode to a specific VOC component. Peaks are identified by displaying the mass spectra for each peak and performing a library search using the GC-MS software. Since the mass spectra in standard libraries are typically generated at an ionization energy of 70 eV, ensure that the ionization energy in your measurement conditions is set to 70 eV.

When unknown compounds are encountered, scan mode data and library matching may be used for tentative identification. Confirmation should be performed using reference standards when compound-specific identification is required.

SIM Mode

In SIM mode, you must set the mass-to-charge ratio (m/z) for quantification and the m/z for identification for each VOC component to be measured; the former is called the quantifier, and the latter is called the qualifier. For reference, Table 2.7.4 lists the quantifier and qualifier values for VOCs.

Table 2.7.4. Example of quantitative and qualitative ions for GC-MS analysis of VOC components

VOC component	Quantifier	Qualifier
Benzene	78	77
Toluene	91	92
Ethyl benzene	91	106
m, p-Xylene	91	106
o-Xylene	91	106
Toluene-d_8	98	100
Chlorobenzene-*d5*	117	119

For SIM analysis, at least one quantitative ion (quantifier) and one or more confirmation ions (qualifiers) should be monitored for each target compound. The measured ion ratios and retention times should be within the acceptance criteria established by the laboratory QA/QC procedures.

2.7.3 GC-FID Analysis

Gas chromatography coupled with flame ionization detection (GC-FID) is one of the most widely used techniques for the quantitative determination of VOCs in ambient air due to its simplicity, robustness, and relatively low operating cost. The method is applicable to samples collected using canisters, sorbent tubes, charcoal tubes, and passive samplers following appropriate sample preparation and introduction procedures. GC-FID provides high sensitivity and a wide linear dynamic range for hydrocarbons and many VOC species, making it suitable for routine monitoring and trend assessment. However, compared with GC-MS, GC-FID has limited capability for compound identification and relies primarily on chromatographic retention time for compound confirmation. General guidance on GC-FID operation, calibration, analytical conditions, and quality assurance and quality control (QA/QC) is provided in the following sections.

Principle

GC-FID combines the separation capability of gas chromatography (GC) with the quantitative detection capability of a flame ionization detector (FID). VOCs introduced into the GC system are separated according to their physicochemical properties and interactions with the chromatographic column. The separated compounds are then introduced into a hydrogen-air flame, where organic molecules are ionized during combustion. The resulting ions generate an electrical current that, for hydrocarbons, is approximately proportional to the amount of carbon entering the detector and can be used for quantitative determination following calibration with appropriate standards.

Instrument Configuration and Analytical Conditions

A typical GC-FID system for ambient VOC analysis consists of a sample introduction unit, a gas chromatograph, a FID, carrier gas, hydrogen, and air supply systems, and a data acquisition system. The analytical conditions should be optimized to achieve adequate separation, identification, and quantification of the target VOCs.

Sample Introduction Unit

The sample introduction unit transfers VOCs from the sampling device or sample extract into the GC-FID system and shall be compatible with the selected sampling and sample preparation method. Common sample introduction approaches include:

- **Thermal desorption (TD) units** for sorbent tube samples, where VOCs collected on the sorbent are thermally desorbed and introduced directly into the GC-FID system.
- **Liquid injection systems** for solvent extracts obtained from charcoal-based active or passive samplers, or other sampling media designed for solvent extraction. In this approach, a measured volume of extract is introduced into the GC-FID system through a heated injection port using a microsyringe or autosampler. For analyses involving liquid sample extracts, the injection port shall be capable of heating to at least 200°C and shall support both split and splitless injection modes.

The selected sample introduction system shall provide adequate recovery, reproducibility, and sensitivity for the target VOCs and concentration range of interest.

GC Column Oven

The GC oven shall support temperature-programmed operation over a range sufficient to achieve adequate separation of the target VOCs (e.g., 35–300 °C).

GC Capillary Column

Column dimensions and stationary phase shall be selected according to the volatility range and chromatographic separation requirements of the target compounds. For example, a fused-silica based column with an inner diameter of 0.25–0.32 mm and a length of 30–60 m, coated internally with methyl silicone or phenylmethyl polysiloxane, may be used.

Flame Ionization Detector (FID)

The flame ionization detector shall be supplied with high-purity hydrogen and air and operated under conditions that provide stable flame combustion and detector response. The detector temperature should be maintained at a sufficiently high temperature to prevent condensation of target compounds.

Carrier Gas

The carrier gas shall be helium, nitrogen, or another suitable high-purity gas compatible with the analytical system.

Example: Sorbent-Based Adsorbents with Thermal Desorption (TD)-GC-FID

Sorbent tube samples may be analyzed using a TD unit coupled to GC-FID (Pic. 2.7). VOCs collected on the sorbent are thermally desorbed and transferred to the GC-FID system, no solvent is used. Typical instrument configurations and operating conditions are summarized Table 2.7.5.

In a two-stage thermal desorption system, the sorbent tube is heated under a flow of inert carrier gas using validated conditions that provide adequate recovery of the target compounds without exceeding the temperature limits of the sorbent or analytical system. For example, in this method, the sorbent tube is heated to approximately 360 °C, and desorbed VOCs are refocused on a cooled secondary trap held at approximately −20 °C. The secondary trap is subsequently heated rapidly to approximately 360 °C to transfer the analytes into the GC. Desorption and focusing conditions shall be optimized and documented for the sorbent, target compounds, and instrument used. (Healy et al., 2018; Woolfenden, 2010).

For analysis of VOCs included in the PAMS ozone-precursor target list, a dual-column configuration may be used to cover the broad volatility range of the target compounds. In such systems, a Dean-switch (or equivalent) can direct the light and heavier fractions to two complementary columns feeding dual FIDs, for example, a PLOT-type column (e.g., Al_2O_3/PLOT, 50 m × 0.32 mm × 5 μm) for C_2–C_6 hydrocarbons and a non-polar capillary column (e.g., a dimethyl/5 %-phenyl-polysiloxane column such as CP-Sil 5 CB, 60 m × 0.25 mm × 1.00 μm) for the C_6–C_{12} fraction. This configuration can allow most PAMS ozone-precursor species to be determined in a single run. Representative TD and GC-FID conditions are given in Table 2.7.5; each laboratory should optimize and document the conditions for its own instrument, columns, and target compound list.



Picture 2.7.4 Example of TD-GC/FID instruments for VOCs analysis

Table 2.7.5 Example of measurement conditions for TD-GC/FID

Thermal desorption	**TurboMatrix ATD series (PerkinElmer)**
Injector	Split/Splitless, heated
GC-FID System	**7890 Series Gas Chromatograph (Agilent)**
Column	Non-polar capillary column (e.g., 5 %-phenyl-methylpolysiloxane) or PLOT column for light hydrocarbons
Carrier gas	Helium (or nitrogen), constant flow
Oven	Temperature-programmed (low initial hold, ramped to elute C_{12})
Detector	FID with H_2/air, at elevated temperature

Calibration of GC-FID Response

Calibration of GC-FID response should be performed using certified reference standards appropriate to the target compounds and sample-introduction method. For thermal-desorption analysis, known amounts of the target compounds should be loaded onto conditioned sorbent tubes and analyzed using the same TD-GC-FID procedure applied to field samples. For solvent-extract methods, calibration standards should be introduced through the same liquid-injection pathway used for samples. A multi-level calibration covering the working range should be established and verified using continuing calibration checks in accordance with the laboratory QA/QC procedure.

Compound Identification

Since GC-FID does not provide mass spectral information, compound identification is generally based on comparison of chromatographic retention times with those obtained from certified reference

standards analyzed under the same analytical conditions. Care should be taken to ensure adequate chromatographic separation of compounds with similar retention characteristics.

Where confirmation of compound identity is required, GC-FID measurements may be supplemented by GC-MS analysis or other appropriate analytical techniques. For routine monitoring of well-characterized target VOCs, quantification by GC-FID using retention time matching and calibration standards is generally sufficient.

2.8 Calculation of Concentration

2.8.1 General Calculation Principles

The atmospheric concentration of each target VOC compound shall be calculated using the measured sample amount, blank correction value, and sampling parameters appropriate to the sampling method employed. The calculation procedure varies according to the sampling technique used, such as canister sampling, active sorbent sampling, charcoal tube sampling, or passive sampling. Method-specific equations and parameters are provided in the corresponding sections of Chapter 2.

In general, the concentration of a target VOC is determined from the blank-corrected analyte mass and the sampled air volume. For sampling methods in which the actual air volume is measured at ambient temperature and pressure and concentrations are reported at standard conditions (20°C, 1 atm), the following equation may be used:

$$C = \frac{n\times(A_s - A_t)}{Vair} \times \frac{(273+T)}{293} \times \frac{101.3}{P} \qquad (2\text{-}5)$$

C: Concentrations (μg/m³) of the target VOC in ambient air at standard conditions (20°C, 1atm)

n: Sample preparation or dilution factor

A_s: Amount of the target VOC measured in the sample (μg when V_{air} is expressed in m^3; ng when V_{air} is expressed in L)

A_t: Amount of the target VOC measured in the field blank (μg when V_{air} is expressed in m^3; ng when V_{air} is expressed in L)

V_{air}: Sampled air volume measured at the sampling temperature and pressure (m^3 or L, consistent with the analyte mass)

T: Temperature (°C) during sampling or measurement, as applicable

P: Atmospheric pressure (kPa) during sampling or measurement

The calculated concentration may be expressed in μg/m³ or converted to a volume mixing ratio (ppb) using the appropriate reference temperature and pressure conditions. The reference conditions used for reporting concentrations shall always be stated. The definitions of $n$and V_{air}vary according to the sampling method are summarized in Table 2.8.1.

Table 2.8.1 Definitions of n and V_{air} for Different Sampling Methods

Sampling method	n	V_{air}
Canister sampling	Dilution ratio	Volume of sample introduced into the analytical system
Active Sorbent tube sampling	1	Total sampled air volume
Active Charcoal tube sampling	Extraction factor = $E \times 1000/v$* E: extract volume (mL)	Total sampled air volume

Sampling method	n	V_{air}
	v*: injection volume (µL)	
Passive sampling using charcoal-based adsorbents	Method-specific extraction/sample-preparation factor	Equivalent sampled air volume calculated from the validated sampler-specific sampling rate and exposure time
Passive sampling using sorbent-based adsorbents (TD)	1	Equivalent sampled air volume calculated from the validated uptake rate and exposure time

Where applicable, the measured analyte mass should be corrected for desorption efficiency, extraction recovery, or dilution factors before concentration calculation. The correction procedures should be documented and consistently applied to calibration standards and field samples.
The final reported concentration shall be accompanied by the applicable reference conditions, units, and any corrections applied during data processing.

2.8.2 Correction for Desorption Efficiency

Where applicable, the measured analyte mass should be corrected for desorption efficiency (DE) to account for extraction losses.

$$m_{corr} = \frac{m_{meas}}{\frac{DE}{100}} = \frac{A_S - A_t}{\frac{DE}{100}} \qquad (2\text{-}6)$$

where:

- **m_{corr}**: recovery-corrected analyte mass (µg when V_{air} is expressed in m^3; ng when V_{air} is expressed in L)
- **m_{meas}**: blank-corrected measured analyte mass (µg when V_{air} is expressed in m^3; ng when V_{air} is expressed in L)
- **DE**: desorption efficiency (%)
- **A_s:** Amount of the target VOC measured in the sample (µg when V_{air} is expressed in m^3; ng when V_{air} is expressed in L)
- **A_t:** Amount of the target VOC measured in the field blank (µg when V_{air} is expressed in m^3; ng when V_{air} is expressed in L)

Desorption efficiency should be determined by analyzing spiked sorbent tubes using the same sample preparation and analytical procedures applied to field samples. The corrected mass should be used for concentration calculations.

2.8.3 Calculation of Concentration for Passive Sampling

For passive (diffusive) samplers, the time-weighted average (TWA) concentration may be calculated using the diffusive uptake approach (Healy et al., 2018). The concentration calculation requires the

sampling rate (SR) or uptake rate (U), which is specified for individual compounds and samplers, and the sampling (exposure) duration (*t*).

$$C = \frac{m_{meas}}{V_{eq}} = \frac{A_s - A_t}{V_{eq}} \qquad (2\text{-}7)$$

where:

- **C**: time-weighted average concentration in ambient air (μg/m³)
- $\mathbf{m_{meas}}$: blank-corrected mass of analyte recovered from the sampler (μg when Veq is expressed in m^3; ng when Veq is expressed in L)
- $\boldsymbol{V_{eq}}$**:** Equivalent sampled air volume (m^3 or L, consistent with the analyte mass)
- $\boldsymbol{A_s}$**:** Amount of the target VOC measured in the sample, expressed in the same mass unit as m_{meas}
- $\boldsymbol{A_t}$**:** Amount of the target VOC measured in the applicable blank, expressed in the same mass unit as m_{meas}
- **SR:** sampling rate (m^3/h) or uptake rate (mL/min)
- **t**: exposure time (h or min, consistent with the units of SR or U)

Conceptually, the ideal sampling rate (uptake rate) follows Fick's first law, *SR* or $U = D \times A / L$, where *D* is the analyte's diffusion coefficient in air, *A* is the cross-sectional area, and *L* is the diffusion path length. Because sampling rates (uptake rates) depend on sampler design, sorbent material, target compound, and deployment conditions, values shall be obtained from validated sources such as manufacturer specifications, published studies, relevant standards, or laboratory validation data. Examples of uptake rates for passive samplers are shown in Tables 2.8.2 and 2.8.3. Because uptake rates vary among passive sampler designs and sorbent materials, values from one sampler configuration shall not be applied to another configuration unless their equivalence has been demonstrated. In practice, validated uptake rates should be used and reported their sources.

Blank correction should normally be based on the average analyte mass measured in field blanks, as these best represent contamination associated with sampler preparation, transport, storage, and field handling. Transport blanks and sorbent blanks should primarily be used for QA/QC evaluation of contamination sources. The blank correction procedure and blank type used shall be documented.

For passive sampling using charcoal-based adsorbents, when SR is expressed in m^3/h and t in h, V_{eq} (m^3) = SR × t, and m_{meas} should be expressed in μg. For passive sorbent samplers analyzed by thermal desorption, when U is expressed in mL/min and t in min, V_{eq} (L) = U × t / 1000, and m_{meas} should be expressed in ng. An additional temperature or pressure correction should not be applied when the validated sampling or uptake rate already incorporates the applicable sampling or reference conditions.

(1) Example of Sampling rate (SR) of Passive Sampling Using Charcoal-Based Adsorbents

For benzene, toluene, ethylbenzene, and xylene, sampling rate, also referred to as the uptake rate,

determined by the respective manufacturers (Table 2.8.2).

Table 2.8.2 Example of Sampling Rate for Passive Charcoal Diffusive Sampling (m^3/h)

VOC component	SIBATA Scientific Technology Ltd.	Merck KGaA, Darmstadt, Germany,	SKC, Inc.
Benzene	0.00329	0.00218	0.00099
Toluene	0.00282	0.00281	0.00087
Ethyl benzene	0.00176	0.00227	0.00077
m-Xylene	0.00252	0.00222	0.00083
p-Xylene	0.00252	0.00222	0.00077
o-Xylene	0.00252	0.00212	0.00085

Note. 1 Express the published values from each manufacturer after converting them to m^3/h.

(2) Example of Uptake rate (U) of Passive Sampling Using Sorbent-Based Adsorbents

Table 2.8.3 gives the diffusive sampling rates (uptake rates) applied in the Seoul study as an example of a validated set (Lee et al., 2024, Supplement S2). They were determined for a specific low-uptake Carbopack X diffusive tube and deployment; many species share a common nominal value (0.29 mL min^{-1}), while aromatics (benzene 0.38, toluene 0.39, ethylbenzene and the xylenes 0.36 mL/min) and selected compounds carry compound-specific values. These values are illustrative, because the uptake rate depends on the sampler geometry, sorbent and deployment conditions, any other configuration must use uptake rates from a correspondingly validated source (e.g., U.S. EPA Method 325B, ISO 16017-2, or an in-house determination) (U.S. EPA, 2019b; ISO 16017-2, 2003).

Table 2.8.3 Example diffusive uptake rates (U_{NTP}, mL/min) for the 52 PAMS species quantified in the Seoul study, corrected to the mean sampling temperature in use.

Species	U (mL/min)	Species	U (mL/min)
Propylene	0.29	2,2,4-Trimethylpentane	0.29
iso-Butane	0.29	n-Heptane	0.27
n-Butane	0.29	Methylcyclohexane	0.29
trans-2-Butene	0.29	2,3,4-Trimethylpentane	0.15
1-Butene	0.29	Toluene	0.39
cis-2-Butene	0.29	2-Methylheptane	0.27
Cyclopentane	0.29	3-Methylheptane	0.15
iso-Pentane	0.29	n-Octane	0.33
n-Pentane	0.29	Ethylbenzene	0.36
trans-2-Pentene	0.29	p,m-Xylene	0.36
1-Pentene	0.29	Styrene	0.29

Species	U (mL/min)	Species	U (mL/min)
cis-2-Pentene	0.29	o-Xylene	0.36
2,2-Dimethylpentane	0.29	n-Nonane	0.29
2,3-Dimethylbutane	0.29	Isopropylbenzene	0.29
2-Methylpentane	0.29	n-Propylbenzene	0.29
3-Methylpentane	0.29	m-Ethyltoluene	0.29
Isoprene	0.29	p-Ethyltoluene	0.29
1-Hexene	0.29	1,3,5-Trimethylbenzene	0.29
n-Hexane	0.24	o-Ethyltoluene	0.29
Methylcyclopentane	0.29	1,2,4-Trimethylbenzene	0.29
2,4-Dimethylpentane	0.27	Decane	0.31
Benzene	0.38	1,2,3-Trimethylbenzene	0.29
Cyclohexane	0.29	m-Diethylbenzene	0.29
2-Methylhexane	0.27	p-Diethylbenzene	0.29
2,3-Dimethylpentane	0.27	n-Undecane	0.29
3-Methylhexane	0.27	n-Dodecane	0.21

Source: Lee et al., 2024, Supplement S2

Influence of Meteorological Variables on Passive Sampling

Environmental conditions may affect the uptake rate of passive diffusive samplers, and the magnitude of these effects depends on the sampler design, sorbent, target compound, and exposure conditions. Validated uptake rates should therefore be used under conditions consistent with those for which the sampler has been evaluated, and environmental corrections should be applied where required by the applicable method or validated uptake-rate procedure (ISO 16017-2, 2003; Plaisance, 2011).

- **Wind/face velocity:** Air movement around the sampler can affect diffusive uptake. Very low air velocities may reduce uptake because of increased external mass-transfer resistance, whereas higher air velocities may increase uptake for some sampler designs. The magnitude of this effect is sampler-specific; therefore, an appropriate diffusive end-cap and, where applicable, a weather or turbulence shield should be used in accordance with the validated sampler configuration (Plaisance, 2011).
- **Temperature:** Temperature can affect molecular diffusion and sorbent retention and may therefore influence the uptake rate. Temperature-dependent corrections should be applied where specified by the validated uptake-rate method or sampler calibration. For the sampler used in the Seoul study, a 20 K difference in mean sampling temperature resulted in a change of up to 3.6 % in the calculated concentration, illustrating that the magnitude of the effect can be sampler- and method-specific (Lee et al., 2024).

- **Relative humidity:** The influence of relative humidity depends on the sorbent, target compound, and sampler design. Hydrophobic sorbents such as graphitized carbon black are generally less sensitive to humidity than more hydrophilic sorbents; however, humidity effects should be evaluated for the specific sampler and analytical method, and corrections should be applied where required by the validated procedure (Healy et al., 2021).

- **Pressure:** The effect of atmospheric pressure should be considered where it is included in the uptake-rate formulation or in conversion to the stated reference conditions. Any pressure correction should be applied consistently with the validated sampling-rate calculation and the concentration-reporting procedure.

2.8.4 Detection and Quantification Limits

The limit of detection (LOD) and limit of quantification (LOQ) are used to evaluate the sensitivity of the analytical method. They shall be determined from repeated analyses of low-concentration standards and/or blank samples, with at least five replicate measurements recommended for estimating the standard deviation. When operational blanks are included, the larger standard deviation obtained from either the low-concentration standards or the operational blanks should be used for calculating the LOD and LOQ. The calculation approach should be selected in accordance with the applicable standard, regulatory requirement, or laboratory QA/QC protocol.

Option 1: Signal Variability Approach (Commonly Used in Japanese Methods)

LOD and LOQ may be estimated from replicate measurements of low-concentration standards or blanks:

$$LOD = 3S \qquad (2\text{-}8)$$

$$LOQ = 10S \qquad (2\text{-}9)$$

where S is standard deviation obtained from at least five replicate measurements of low-level standards. This approach is commonly adopted in Japanese environmental monitoring methods because of its simplicity and direct relationship to analytical variability.

Option 2: Calibration Curve Approach (ICH and International Guidelines)

Alternatively, the LOD and LOQ may be calculated from the standard deviation of the response and the slope of the calibration curve (ICH, 2005):

$$LOD = \frac{3.3\sigma}{S}\ (10) \qquad (2\text{-}10)$$

$$LOQ = \frac{10\sigma}{S}\ (11) \qquad (2\text{-}11)$$

where:

- σ: standard deviation of the analytical response obtained from replicate low-level standards, blanks, or regression residuals;

- S: slope of the calibration curve.

This approach is widely used in international analytical guidelines because it incorporates calibration sensitivity and allows comparison among analytical methods with different detector responses. Where regulatory reporting is required, the method detection limit (MDL) may instead be determined from replicating low-level spikes using the procedure of U.S. EPA 40 CFR Part 136, Appendix B.

Selection of the Approach

Either approach may be used provided that the calculation method is clearly documented and consistently applied throughout the monitoring program.

- The **3S/10S approach** is recommended when the objective is routine environmental monitoring and consistency with existing Japanese monitoring practices.
- The **3.3σ/S and 10σ/S approach** is recommended when method validation, interlaboratory comparison, regulatory reporting, or compliance with international analytical guidelines is required.

For passive samplers, the air-concentration detection limit depends not only on the analytical mass detection limit but also on the validated sampling or uptake rate and the exposure duration. The calculation shall be performed using consistent units. When LOD_{mass} is expressed in μg, U in mL/min, and t in minute:

$$LOD_{air}(\mu g/m^3) = \frac{10^6 \times LOD_{mass}(\mu g)}{U(mL/min) \times t(min)} \qquad (2\text{-}12)$$

When the sampling rate, SR, is expressed in m^3/h and the exposure time in h:

$$LOD_{air}(\mu g/m^3) = \frac{LOD_{mass}(\mu g)}{SR\left(\frac{m^3}{h}\right) \times t(h)} \qquad (2\text{-}13)$$

Consequently, a longer exposure generally lowers the achievable air-concentration detection limit. For sorbent-based passive samplers, blank artefact levels may also influence the practical detection and quantification limits; therefore, blank performance should be evaluated in accordance with the applicable method-specific QA/QC criteria (ISO 16017-2, 2003; US EPA, 2019b).

2.9 Quality Assurance and Quality Control (QA/QC)

A structured QA/QC program is essential to ensure the accuracy, precision, representativeness, and traceability of VOC measurement data. QA/QC procedures should cover all stages of monitoring, including sample collection, transportation, storage, preparation, instrumental analysis, data processing, and reporting.

The minimum QA/QC elements should include:

- Calibration and calibration verification;
- Operational, media, field, and transport blanks, as applicable;

- Duplicate analyses and co-located sampling, where appropriate;
- Internal standard monitoring;
- Recovery assessment (e.g., extraction recovery or desorption efficiency);
- Instrument performance verification;
- Sample holding time and storage condition control; and
- Documentation and data validation.

Typical QA/QC checks and acceptance criteria are summarized in Table 2.9.1 (adapted from U.S. EPA Method 325B (2019b), ISO 16017-2 (2003) and NIOSH (2003)).

Table 2.9.1 Examples of QA/QC Elements for VOC Monitoring

QA/QC element	Purpose	Frequency/Criteria
Calibration standards and continuing calibration verification (CCV)	Verify instrument response and calibration performance	≥5–6 point curve; daily CCV, RPD
Operational blank/ Media blank	Assess contamination during sample preparation and analysis/ originating from sorbents or sampling media	Each batch; artefacts < LOD
Field blank/ Transport blank	Assess contamination during handling, deployment, and transport/ storage and shipment	With every deployment batch; artefacts < LOD
Internal standard monitoring	Evaluate analytical stability and instrument performance	Every injection
Duplicate analysis/ Co-located sampling	Assess analytical/sampling precision	Defined fraction of sites; precision (RSD, CV)
Reference-method comparison	Method validation/bias	Periodic (e.g., vs active/pams)
Recovery assessment or desorption efficiency (DE)	Evaluate extraction or desorption efficiency	Meet the recovery/desorption-efficiency criterion specified by the applicable analytical method (e.g., DE ≥ 75 %).
Holding time verification	Ensure sample integrity during storage	Validated; within holding time
Data validation	Verify completeness and acceptability of reported data	Before final data reporting

2.9.1 Precision

Analytical precision should be assessed through replicate analyses, duplicate samples, or co-located samplers, as appropriate for the sampling method. Precision may be evaluated using statistical

measures such as relative percent difference (RPD), coefficient of variation (CV), root-mean-square (RMS) difference, and mean absolute difference (MAD) (Hyslop & White, 2009). Acceptance criteria should be established by the monitoring program or laboratory QA/QC procedures. Significant discrepancies between replicate or duplicate measurements should be investigated before data reporting. Where applicable, systematic bias may be assessed through comparisons with reference methods or co-located measurements. Well-characterized passive samplers have been reported to achieve coefficients of variation ranging from a few percent to approximately 10%, with overall uncertainties influenced by environmental conditions and sampler characteristics (Plaisance, 2011).

2.9.2 Recovery Assessment

For methods involving solvent extraction or thermal desorption, recovery should be periodically evaluated using appropriate recovery standards. Measured concentrations may be corrected for extraction recovery or desorption efficiency when required by the analytical method.

2.9.3 Data Validation

Data should be reviewed for compliance with method performance requirements, including calibration acceptance criteria, blank contamination, recovery performance, duplicate precision, and instrument quality control checks. Data failing predefined acceptance criteria should be flagged, qualified, or excluded in accordance with the laboratory QA/QC procedures. Where feasible, method performance should be evaluated through comparison with co-located measurements or established reference methods. Statistical assessments of agreement, precision, and bias may be used to support data validation. For example, Lee et al. (2024) reported good agreement between passive samplers and reference measurements for most VOC species, while identifying a positive bias for olefins, highlighting the importance of method-specific performance evaluation.

2.9.4 Documentation and Traceability

Complete records should be maintained for all monitoring activities, including sampling information, analytical conditions, calibration and blank results, QA/QC records, meteorological data, and data processing procedures. Information such as site metadata, sample identifiers, chain-of-custody records, batch/lot numbers, and, where applicable, uptake rates and correction factors should also be documented. All reported VOC concentrations should be fully traceable to the original measurements and QA/QC records (U.S. EPA, 2019a, 2019b). Another example for QA/QC is presented here (Fig. 2.9.2). This flowchart was developed in accordance with the Japanese Manual for the Measurement of Hazardous Air Pollutants.

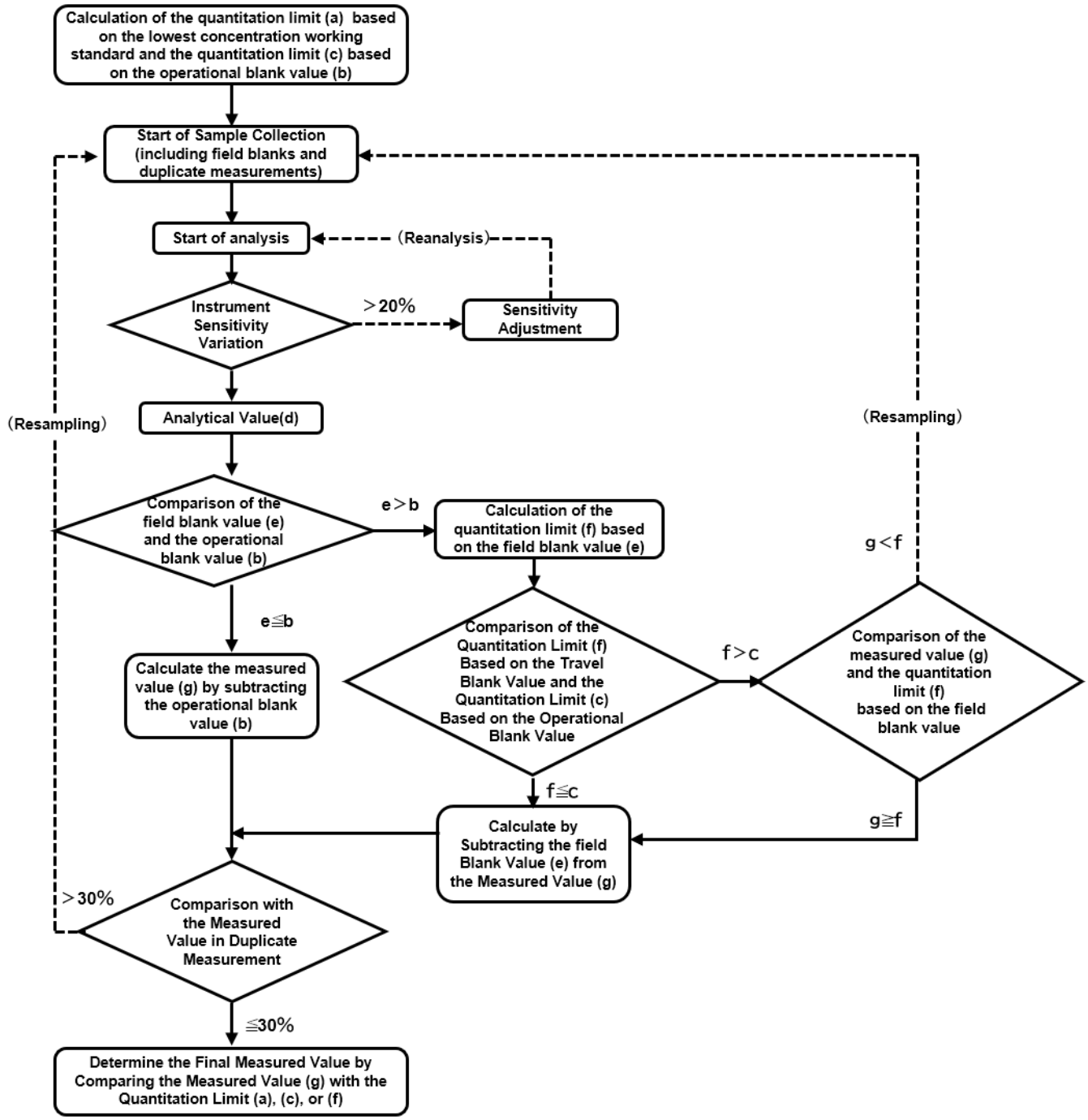


Figure 2.9.2 Flowchart of Quality Control Procedures

(Source: Japanese Manual for the Measurement of Hazardous Air Pollutants)

3. Online Methods

A variety of on-line techniques are available for ambient VOC monitoring, providing continuous or near real-time measurements with different analytical capabilities. This chapter introduces two on-line methods that were applied during the implementation of the EANET VOC Project: the photoionization detector (PID) and differential optical absorption spectroscopy (DOAS). These methods were selected based on their practical applications in the project and are presented to demonstrate their principles, operational procedures, and typical uses. Other advanced on-line monitoring techniques are briefly discussed in the Conclusion as future developments and potential options for VOC monitoring.

3.1 Photoionization Detector (PID)

3.1.1 Overview

Purpose

This chapter provides technical guidance for the real-time, direct-reading measurement of VOCs using a PID. A PID is a portable (hand-held or fixed) instrument that provides a continuous response to ionizable VOCs, typically reported as concentration equivalents of the calibration gas over the parts-per-billion (ppb) to parts-per-million (ppm) range (Ion Science, 2021; US EPA, 2017). The principle of photoionization detection is described in Annex Text A1. The PID is used principally for rapid spatial screening, for locating and delineating VOC hotspots, and for providing an immediate, semi-quantitative indication of the overall PID-responsive VOC burden that complements the speciated, time-integrated methods (passive samplers, canisters, sorbent tubes/GC) described elsewhere in this guidance.

The chapter describes the general operating principle, instrument types, field operation, calibration, interferences, and quality control common to PIDs. A single common configuration is used as an illustrative example; no specific brand or model is endorsed or required, and the guidance applies to any PID meeting the relevant performance requirements.



Picture 3.1.1. PID instrument used for VOC screening
(Source: RAE Systems/Honeywell, 2013)

Advantages and limitations

The main advantages of the PID are that it provides real-time measurements, is generally non-destructive, portable, sensitive to low concentrations of many VOCs, and responsive to a broad range of ionizable compounds using a common calibration gas, although compound-specific responses may

differ (Ion Science, 2021). Its principal limitations are that it does not provide compound-specific identification; that readings for compounds other than the calibration gas may require an appropriate correction factor; that the response may be influenced by humidity, temperature, lamp ageing, and window contamination; and that compounds whose ionization energy exceeds the photon energy of the lamp cannot be detected (US EPA, 2017; RAE Systems/Honeywell, 2013). Because of these limitations, the PID is best used as a rapid screening and mapping tool alongside speciated analytical methods rather than as a replacement for them.

3.1.2 Instrument Configuration and Types

Components

A PID comprises: a sample inlet (either diffusion-based or actively pumped); the UV lamp and its window; the ionization chamber and electrodes; the signal amplifier; and a display with data-logging. Some instruments include an integral moisture/humidity compensation feature and interchangeable lamps (Blackline Safety, 2025).

Types

1) Portable (hand-held) vs. fixed: hand-held units are used for surveys and personal/area screening; fixed units provide continuous point monitoring (Ion Science, 2021).
2) Pumped vs. diffusion sampling: a pump gives a defined, faster response and allows remote/probe sampling; diffusion mode is simpler and lower-maintenance (Blackline Safety, 2025).
3) Single-sensor vs. multi-gas: the PID may be a stand-alone sensor or one channel within a multi-gas instrument.
4) Measurement range and resolution: typical instruments span from ~1 ppb (or a few ppb) up to several thousand ppm, with the low end and resolution depending on the sensor and lamp (Ion Science, 2021; Blackline Safety, 2025).

3.1.3 Field Deployment and Operation

1) **Warm-up and zeroing:** Allow the instrument to complete the manufacturer-specified warm-up period before use. Check and, where necessary, adjust the instrument zero using clean air or an appropriate zero gas in accordance with the applicable method, manufacturer's instructions, or monitoring QA/QC procedure (US EPA Method 21, 2017).
2) **Sampling mode:** For mobile or walk-through screening surveys, move through the survey area at a consistent pace and observe real-time changes in PID response to identify spatial gradients and localized enhancements. For fixed-point monitoring, select an appropriate logging and averaging interval according to the monitoring objective and expected variability.
3) **Probe handling:** Avoid drawing liquid water, excessive dust, or aerosols into the instrument. Where required, use the manufacturer-recommended particulate filter, sampling probe, or moisture-management accessory. The inlet, filter, and sampling line should be kept clean and checked regularly for blockage or contamination (RAE Systems, 2013).
4) **Ancillary records:** Record the sampling location, date and time, ambient temperature and relative humidity, instrument identification, lamp energy, and relevant operating settings. For mobile surveys, GPS coordinates or equivalent location information should be recorded where available to support spatial interpretation of the measurements.
5) **Field application:** PID surveys may be used to identify spatial concentration gradients and potential VOC hotspots, support the selection of locations for subsequent integrated or

speciated sampling, and provide rapid screening information during field investigations. Because PID response is non-specific, elevated readings should be interpreted as screening information and, where necessary, confirmed using an appropriate speciated analytical method.

3.1.4 Calibration

Zero and span

PIDs should be checked and calibrated in accordance with the applicable method and manufacturer's instructions. A typical calibration procedure includes a zero check using clean air or an appropriate zero gas and a span check using a certified reference gas. Isobutylene is commonly used as the calibration gas for general PID measurements because it provides a convenient reference response for many VOCs (RAE Systems/Honeywell, 2013; US EPA Method 21, 2017). If the instrument response does not meet the applicable calibration acceptance criteria, the cause should be investigated and corrected before measurement.

Correction (response) factors

A PID calibrated with isobutylene reports a response relative to isobutylene. For a known individual compound, an appropriate compound- and lamp-specific correction factor (CF) may be applied to estimate its concentration (RAE Systems/Honeywell, 2013; Ion Science, 2021):

$$\text{Estimated concentration of compound} = \text{PID Reading (isobutylene-equiv.)} \times \text{CF} \qquad (3\text{-}1)$$

The correction factor depends on the compound, lamp energy, and instrument response. Current instrument-specific correction factors should therefore be obtained from the manufacturer or another validated source. A compound-specific correction factor should not be applied to an unknown or complex VOC mixture unless the composition is sufficiently characterized to justify its use.

Table 3.1.3 Illustrative correction factors for selected compounds using a 10.6 eV PID lamp

Compound	Illustrative CF (10.6 eV)	Interpretation of a 10-ppm reading
Isobutylene (reference)	1.0	10 ppm
Benzene	≈ 0.5	≈ 5 ppm
m-Xylene	≈ 0.43	≈ 4.3 ppm
Trichloroethylene	≈ 0.54	≈ 5.4 ppm
Butyl acetate	≈ 2.6	≈ 26 ppm

Worked calibration example

For example, if a PID calibrated with isobutylene gives a reading of 20 ppm in an atmosphere known to be dominated by benzene, and the applicable benzene correction factor for the instrument and lamp is 0.5, the estimated benzene concentration would be:

$$20 \text{ ppm} \times 0.5 = 10 \text{ ppm benzene}$$

If the identity or composition of the VOCs is unknown, the reading should instead be reported as a PID response expressed in isobutylene equivalents, rather than as the concentration of a specific compound or as a true total VOC concentration (RAE Systems/Honeywell, 2013).

Detection limit, range and response check

The detection capability, measurement range, resolution, response time, and linear range of a PID depend on the instrument design, lamp energy, target compound, operating conditions, and instrument condition. Manufacturer-specified or method-validated performance characteristics should therefore be used for the intended application. Where low-concentration measurements are required, an appropriate low-level response check may be performed to confirm that the instrument response is adequate for the monitoring objective. Relevant performance information should be documented as part of the measurement QA/QC record (Ion Science, 2021; Blackline Safety, 2025).

Frequency and traceability

Zero checks, span checks, functional response checks, and full calibrations should be performed at frequencies specified by the applicable method, manufacturer, or monitoring QA/QC procedure, and should also be repeated following maintenance, lamp cleaning or replacement, or when instrument performance is in question. Certified or otherwise traceable calibration gases should be used where required, and calibration and response-check records should be retained (US EPA Method 21, 2017; Ion Science, 2021).

3.1.5 Interferences and Limitations

1) **Humidity**: PID response may be affected by high relative humidity, with the magnitude and direction of the effect depending on the instrument design and condition. Where applicable, use manufacturer-recommended humidity compensation or moisture-management measures and record RH (RAE Systems/Honeywell, 2013).
2) **Temperature and pressure**: Response may vary with temperature and pressure; operate the instrument within the manufacturer-specified environmental conditions and perform calibration or performance checks as required.
3) **Non-speciation**: The PID provides a non-specific response to ionizable compounds and cannot identify individual VOCs. Speciation requires an appropriate separation or compound-specific analytical method.
4) **High-ionization-energy compounds**: Compounds with ionization energies above the lamp photon energy are not detected. Compounds with ionization energies below the lamp energy may be detected, but response sensitivity varies among compounds (Ion Science, 2021).
5) **Lamp ageing and window contamination**: UV output may decrease and the lamp window may become contaminated with use, causing drift or loss of sensitivity; regular inspection, cleaning, and lamp replacement should follow the manufacturer's recommendations (Ion Science, 2021).
6) **High-boiling compounds and dust**: Less-volatile compounds may show slower or reduced response, while particulates can contaminate the inlet, chamber, or lamp window.

3.1.6 Quality Assurance / Quality Control

1) **Bump test / functional check:** before each use to confirm response to span gas.
2) **Calibration precision test**: Following the approach of U.S. EPA Method 21, make repeated alternating zero and span measurements and confirm the calibration precision is within

tolerance (Method 21 specifies agreement within about ±10 % of the calibration-gas concentration) (U.S. EPA, Method 21).

3) **Zero-drift and span-drift checks:** at the start and end of a survey to bracket the data.
4) **Response-factor verification:** for the target compound where a specific CF is applied.
5) **Data logging integrity**: verify time synchronization and logging interval; retain raw logs.
6) **Method validation / cross-check**: Where appropriate, co-locate the PID with a speciated reference method, such as canister or sorbent-tube GC, over the same sampling period to evaluate PID performance and the relationship between the PID response and speciated VOC measurements. The frequency of cross-checks should be defined in the monitoring QA/QC plan and repeated after significant instrument maintenance or repair, substantial changes in operating conditions, or when data-quality concerns arise.
7) **Documentation**: record instrument ID, lamp energy, calibration gas and lot, calibration results, ambient T/RH, and operator for full traceability.

The minimum QA/QC elements for field PID use are summarized in Table 3.1.4.

Table 3.1.4 Minimum QA/QC requirements for field use of a PID

QA/QC element	Purpose	Typical frequency / criterion
Bump (functional) test	Confirm response to span gas	Before each day's use
Zero check / zero-air	Verify baseline in clean air	Start of each survey
Span calibration	Set response to isobutylene	Per schedule; after lamp service
Calibration precision	Verify repeatability	Alternating zero/span; within ~±10 % (method 21)
Zero-/span-drift bracket	Bound the survey data	Start and end of survey
Correction-factor check	Verify factor for target compound	When a compound-specific cf is used
Lamp / window inspection	Detect drift from ageing/fouling	Per manufacturer; clean/replace as needed
Reference co-location	Verify PID performance against a reference method and evaluate the relationship between PID response and speciated VOC measurements	As specified in the monitoring QA/QC plan (e.g., at least annually); after major maintenance or repair, substantial changes in operating conditions, or when data-quality concerns arise; co-locate over the same sampling period.
Records / traceability	Full documentation	Every deployment

3.1.7 Data Reporting and Interpretation

To ensure PID data are interpreted correctly and remain comparable across sampling points/sites, each reported value should be accompanied by: the lamp energy used; the calibration gas (normally

isobutylene) and its concentration; whether a correction factor was applied and, if so, the compound and factor used; the averaging interval; and the ambient temperature and relative humidity. For unknown or mixed VOC atmospheres, PID measurements should be reported as PID response expressed in isobutylene equivalents, with any compound-specific conversion clearly identified. Because the PID does not speciate, elevated readings should be treated as screening information and, where necessary, confirmed and quantified using an appropriate speciated analytical method.

3.2 Open-Path Differential Optical Absorption Spectroscopy (DOAS)

3.2.1 Overview

Open-Path Differential Optical Absorption Spectroscopy (DOAS) provides continuous, path-integrated measurements of selected volatile VOCs and other gaseous pollutants in ambient air. Unlike conventional offline sampling methods, such as canister-based sampling followed by GC/MS or GC/FID analysis, which characterize pollutant concentrations at a specific sampling point, DOAS measures the average concentration of target compounds across a defined optical path.

The DOAS method is not intended to replace canister-based or other offline analytical methods. Rather, these approaches are considered complementary because each provides different types of information and has its own strengths and limitations. DOAS offers continuous and spatially integrated measurements that can provide information on temporal variations and pollutant behavior across a monitoring area, while offline methods generally provide greater compound specificity and sensitivity for a wider range of VOCs at individual sampling locations. The combined use of these techniques, where appropriate, can therefore provide a more comprehensive characterization of ambient VOC concentrations.

Scope and Application

This method describes the procedures for the continuous determination of selected VOCs in ambient air using DOAS. The method utilizes ultraviolet (UV) and visible (Vis) absorption spectroscopy to measure the average concentration of target gaseous compounds over a defined atmospheric optical path without physically extracting an air sample. Measurements are based on the wavelength-specific absorption characteristics of individual gaseous species and the application of the Beer-Lambert law through differential spectral analysis.

Typical compounds measurable by DOAS include benzene, toluene, p-xylene, formaldehyde (HCHO), and selected aromatic hydrocarbons, provided that the instrument possesses adequate spectral resolution, optical path length, and sensitivity. Depending on the instrument configuration and selected wavelength interval, the method may also be applied to other gaseous pollutants including sulfur dioxide (SO_2), nitrogen dioxide (NO_2), ozone (O_3), nitrous acid (HONO), ammonia (NH_3), and additional compounds possessing suitable absorption spectra.

The DOAS technique determines the average concentration of pollutants along the entire optical path rather than at a single point. Consequently, the measured concentration represents the integrated atmospheric concentration between the transmitting and receiving optical assemblies. The technique is particularly suitable for ambient air quality monitoring, industrial perimeter monitoring, roadside air quality assessments, urban background monitoring, and environmental research applications where representative path-averaged measurements are required.

This method is intended for use in continuous ambient air monitoring programs and shall be implemented only by trained personnel familiar with spectroscopic instrumentation, atmospheric monitoring principles, quality assurance procedures, and applicable safety requirements. Instrument installation, operation, calibration, maintenance, and data validation shall be performed in accordance with this method, the manufacturer's operating instructions, and the quality assurance procedures established by the implementing organization or monitoring agency.

Because DOAS relies upon optical absorption within the ultraviolet and visible regions of the electromagnetic spectrum, the applicability of this method is limited to compounds exhibiting measurable differential absorption features within the selected wavelength interval. Volatile organic compounds lacking suitable absorption characteristics or present at concentrations below the instrument detection capability may require alternative analytical methods such as GC/MS or GC/FID.

Principle of Measurement

The DOAS method is founded upon the Beer-Lambert law, which describes the attenuation of monochromatic radiation as it passes through an absorbing medium. When ultraviolet or visible radiation traverses the atmosphere, molecules possessing absorption features within the transmitted wavelength interval selectively absorb photons according to their characteristic electronic transitions. The resulting reduction in light intensity is proportional to the concentration of the absorbing species, the molecular absorption cross-section, and the optical path length.

The DOAS is based on Beer-Lambert law, which expresses the attenuation of radiation passing through an absorbing medium (Platt & Stutz, 2008):

$$I(\lambda) = I_0(\lambda) \cdot exp\ exp\ (-\sigma(\lambda) \cdot C \cdot L) \qquad (3\text{-}2)$$

where:

$I(\lambda)$is the measured light intensity at wavelength λ;
$I_0(\lambda)$is the incident light intensity;
$\sigma(\lambda)$is the molecular absorption cross-section;
C is the atmospheric concentration of the absorbing species; and
L is the optical path length.

In practical atmospheric measurements, the observed attenuation includes contributions from broadband scattering processes caused by air molecules, aerosols, clouds, optical contamination, and fluctuations in source intensity. The DOAS technique overcomes these effects by separating slowly varying broadband extinction from the narrow-band molecular absorption structures that uniquely characterize individual gases. This mathematical separation is achieved through differential spectral analysis, whereby polynomial fitting or high-pass filtering techniques remove broadband spectral components while preserving the differential absorption features of the target analytes.

The processed differential spectrum is compared with high-resolution reference absorption spectra using nonlinear least-squares fitting algorithms. Simultaneous fitting of multiple molecular absorption cross-sections permits the determination of several gaseous species from a single measured spectrum, provided that spectral overlap can be adequately resolved. The resulting concentrations represent path-integrated average concentrations along the monitored atmospheric path and are subsequently converted to engineering units such as parts per billion (ppb), parts per million (ppm), or micrograms per cubic meter (μg/m³), as required by the monitoring program.

The overall accuracy and reliability of the measurement depend on the quality of the reference absorption spectra, wavelength calibration, optical alignment, instrument stability, spectral resolution, signal-to-noise ratio, atmospheric visibility, and the implementation of appropriate quality assurance and quality control (QA/QC) procedures. Such procedures include routine instrument calibration, wavelength verification, optical alignment checks, performance verification, preventive maintenance, and data validation to ensure that measurement results meet the data quality objectives of the monitoring

program.

Method Limitations

The DOAS method provides continuous, path-integrated measurements of selected gaseous pollutants under a wide range of ambient atmospheric conditions. However, measurement quality and reliability may be affected by environmental conditions, instrument performance, and the spectral characteristics of the target analytes. Adverse meteorological conditions, such as dense fog, heavy rainfall, snowfall, blowing dust, or other conditions that significantly reduce atmospheric visibility, may attenuate the transmitted optical signal, reduce measurement sensitivity, and degrade data quality. Likewise, physical obstructions within the optical path, including vegetation, construction activities, vehicles, birds, insects, or contamination of optical components, may reduce optical throughput and adversely affect instrument performance.

The accuracy of concentration measurements may also be influenced by spectral interferences arising from atmospheric constituents with overlapping absorption features, particularly when spectral resolution is insufficient or unexpected absorbing species are present. Measurements obtained at very low analyte concentrations may exhibit increased uncertainty due to reduced signal-to-noise ratio, with overall measurement capability depending on factors such as optical path length, atmospheric visibility, integration time, instrument sensitivity, and the absorption characteristics of the target analytes. Since the DOAS method determines the average concentration along the established optical path, the reported results represent path-averaged concentrations and do not provide spatially resolved concentration measurements at individual locations along the optical path. Consequently, localized concentration gradients or short-term emissions occurring within only a portion of the optical path may not be distinguishable from the reported path-averaged concentration. Measurement performance further depends on proper instrument installation, wavelength calibration, optical alignment, routine maintenance, and satisfactory completion of calibration and performance verification activities. Additional operational limitations and performance requirements specified by the instrument manufacturer shall be observed where applicable, and where such requirements are more stringent than the minimum requirements specified in this method, the manufacturer's specifications shall take precedence.

3.2.2 Apparatus and Equipment for Active Long Path DOAS

Open-Path DOAS Monitoring System

The monitoring system shall consist of an open-path DOAS analyzer capable of continuously measuring gaseous pollutants by transmitting UV and/or Vis radiation through the atmosphere and analyzing the differential absorption spectra of target compounds. The system shall be capable of simultaneously determining the concentrations of one or more gaseous pollutants with sufficient sensitivity, spectral resolution, and measurement stability to meet the objectives of the monitoring program.

The monitoring system shall include, at a minimum, a broadband light source, transmitting optics, receiving optics, spectrometer, detector, data acquisition system, and associated software for spectral analysis and concentration calculations

Equipment Performance and Certification Criteria for VOC Applications

The Open-Path DOAS monitoring system shall hold formal certification, designation, or performance approval (such as European Standard EN 15267 / TÜV, UK MCERTS, U.S. EPA Equivalent Method designation, or an equivalent national formal approval program) specifically covering the target VOCs species to be monitored.

The scope of certification shall explicitly list the target VOC analytes (e.g., benzene, toluene, xylenes, or other specific target hydrocarbons) and demonstrate that the instrument meets established performance criteria for ambient air quality monitoring

Broadband Light Source

The light source shall provide stable broadband radiation covering the wavelength range appropriate for the target analytes. The emitted radiation shall possess sufficient intensity to maintain an adequate signal-to-noise ratio over the selected optical path length under normal operating conditions. Xenon arc lamps are commonly employed because they provide continuous ultraviolet and visible radiation suitable for atmospheric absorption measurements. Alternative light sources may be used provided that they satisfy the spectral and stability requirements of the monitoring application.

The light source shall exhibit minimal intensity drift during operation and shall be protected from excessive temperature fluctuations, vibration, and moisture.

Transmitting Optical Assembly

The transmitting optical assembly shall direct the emitted radiation toward the measurement path while maintaining beam collimation and optical stability. The assembly may consist of lenses, mirrors, beam-shaping optics, or equivalent components designed to maximize optical throughput and minimize beam divergence.

The optical assembly shall be securely mounted to prevent misalignment caused by vibration, wind loading, or thermal expansion. Protective windows shall be installed to prevent contamination of optical components by dust, precipitation, insects, and other environmental factors.

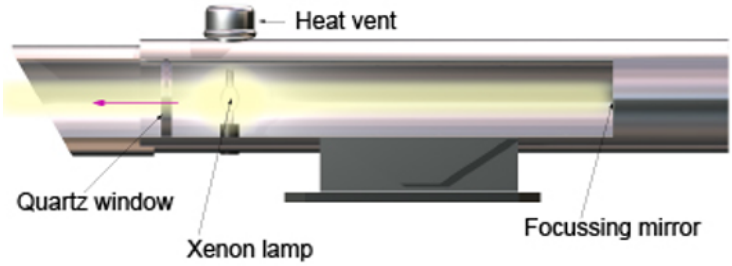


Figure 3.2.1 Typical Transmitting Optical Assembly Unit
(retrieved from Measuring multiple pollutants (DOAS system) - qld.gov.au)

Receiving Optical Assembly

The receiving optical assembly shall collect the transmitted radiation after passage through the

atmospheric optical path and focus the light into the spectrometer. The receiving system shall provide sufficient light-gathering capability to maintain stable measurements throughout the intended monitoring distance.

The receiving optics shall minimize stray light, optical distortion, and reflection losses while maintaining stable alignment with the transmitting system. Optical components shall be routinely inspected and cleaned to ensure optimum performance.

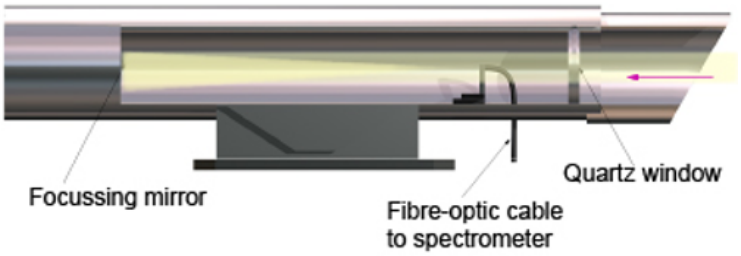


Figure 3.2.2 Typical Receiving Optical Assembly Unit
(retrieved from Measuring multiple pollutants (DOAS system) - qld.gov.au)

Retroreflector

For monostatic open-path systems (see Fig. 3.2.3), a retroreflector shall be installed at the opposite end of the monitoring path to return the transmitted radiation to the receiving optics. The retroreflector shall maintain high reflectivity throughout the operational wavelength range and shall be resistant to weathering, ultraviolet radiation, corrosion, and other environmental influences.

The retroreflector shall be rigidly mounted to minimize movement resulting from wind, vibration, or ground settlement. For bistatic systems (see Fig. 3.2.4), a separate receiving optical assembly may be employed in lieu of a retroreflector.

Spectrometer

The spectrometer shall separate the received radiation into its constituent wavelengths with sufficient spectral resolution to resolve the characteristic absorption structures of the target gaseous species. The instrument shall provide stable wavelength calibration and shall exhibit low stray-light characteristics throughout the operational wavelength range.

The spectrometer shall be capable of repeated spectral acquisition at intervals appropriate for the desired measurement frequency while maintaining wavelength stability during continuous operation.

Detector

The detector shall convert the dispersed optical spectrum into electrical signals suitable for digital processing. Charge-coupled devices (CCD) or complementary metal-oxide semiconductor (CMOS) array detectors are commonly employed because they permit simultaneous acquisition of multiple wavelengths with high sensitivity and rapid response.

The detector shall exhibit low electronic noise, high linearity, and stable performance under anticipated environmental operating conditions.

Data Acquisition and Processing System

The monitoring system shall include a computer-based data acquisition and processing system capable of controlling instrument operation, recording spectral data, performing differential optical absorption analysis, calculating pollutant concentrations, and storing measurement results.

The software shall provide automated instrument diagnostics, wavelength calibration verification, spectral fitting, quality control evaluation, alarm generation, data validation, and generation of monitoring reports. The system shall retain raw spectral data and process concentration data for subsequent review and quality assurance purposes.

Meteorological Monitoring Instruments

Meteorological measurements should be performed concurrently with DOAS monitoring to facilitate interpretation of pollutant concentrations and atmospheric dispersion conditions. The monitoring station should include instruments capable of measuring ambient temperature, relative humidity, atmospheric pressure, wind speed, and wind direction. Additional parameters such as solar radiation, precipitation, and visibility may be monitored where required by the objectives of the monitoring program.

Meteorological sensors shall be installed in accordance with recognized siting criteria and shall be calibrated at intervals specified by the manufacturer or the quality management system.

Calibration Equipment

Calibration equipment shall be available for routine verification of instrument performance and may include wavelength calibration standards, certified reference gas cells, optical density filters, neutral density filters, alignment targets, optical power meters, and other devices necessary to evaluate instrument performance.

Where certified gas cells are used, the concentration and optical path length shall be traceable to NIST or recognized national or international measurement standards. Calibration accessories shall be maintained under conditions that prevent deterioration or contamination.

Communication and Power Supply

The monitoring system shall be provided with a stable electrical power supply meeting the instrument manufacturer's requirements. Where continuous operation is required, an uninterruptible power supply (UPS) or equivalent backup power source should be provided to minimize data loss during temporary power interruptions.

Communication equipment shall permit local or remote instrument control, data retrieval, software updates, and system diagnostics. Appropriate cybersecurity measures should be implemented where remote communication is employed.

Ancillary Equipment

Ancillary equipment necessary for routine operation and maintenance may include alignment telescopes, optical cleaning materials, environmental enclosures, mounting structures, weather protection devices,

maintenance tools, and personal protective equipment. Such equipment shall be maintained in good working conditions and used in accordance with the manufacturer's recommendations and established laboratory procedures.

3.2.3 Sitting Criteria and Installation of DOAS

Establishment of the Measurement Path

There are two primary instrumental configurations for open-path UV-DOAS systems: bistatic and monostatic configurations (U.S. Environmental Protection Agency, 2018).

In a monostatic open-path system, the transmitting and receiving optics are combined into a single transceiver unit at one location. A retro-reflector (such as a corner-cube reflector array) is mounted at the far end of the monitoring path to reflect the emitted light beam 180° back to the origin. This design simplifies installation and alignment by consolidating power supply and detection hardware at a single station.

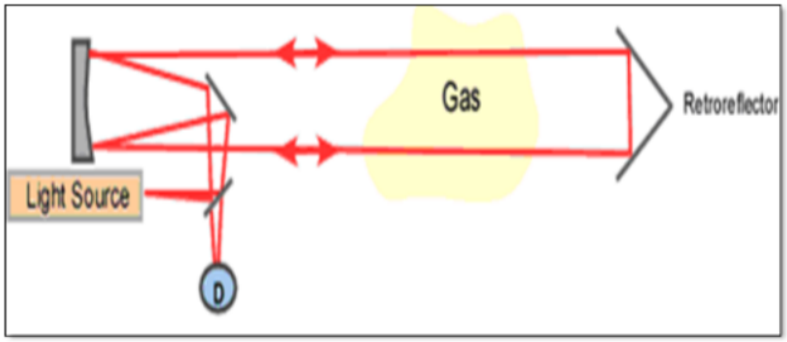


Figure 3.2.3 Monostatic Open-path DOAS setup
(U.S. Environmental Protection Agency, 2018)

In a bistatic open-path system, the transmitter (light source) and the receiver (detector) are housed in separate units installed at opposite ends of the monitoring path. The transmitter projects a light beam across the measurement path directly to the receiver. Both units must be fixed and precisely aligned with one another, requiring independent electrical power supply at each end.

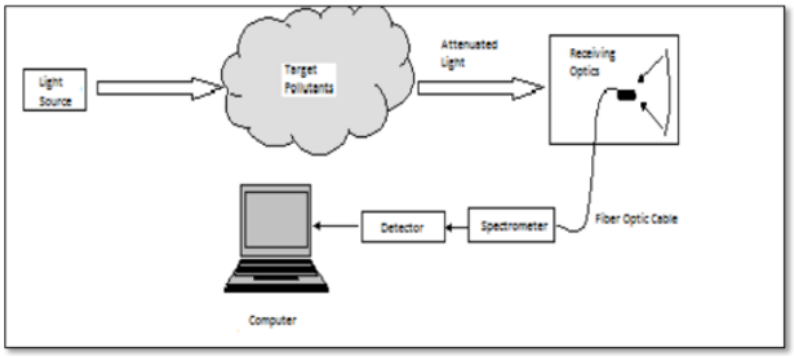


Figure 3.2.4 Bistatic Open-path DOAS setup
(U.S. Environmental Protection Agency, 2018)

Site selection criteria

The optical path length shall be selected based on the monitoring objectives, expected pollutant concentrations, instrument sensitivity, and local site characteristics. Longer optical paths generally improve measurement sensitivity for low-concentration pollutants but may also increase susceptibility to signal attenuation caused by adverse meteorological conditions such as fog, heavy rainfall, or dense aerosols.

The measurement path shall be representative of the monitoring location and should avoid permanent obstructions, localized emission sources not representative of the monitoring objective, and surfaces that may produce excessive reflection or optical interference.

To ensure uniform collection of comparable ambient air monitoring data, open-path DOAS monitoring station must adhere to these siting criteria (U.S. Environmental Protection Agency, 2024):

(1) Path Length Restrictions

- Neighborhood and Urban Scales: The maximum optical path length must not exceed 1.0 km.
- Middle Scale: The maximum optical path length must not exceed 300 m.
- Environmental Considerations: In areas prone to fog, rain, dust, or snow, a shorter path length should be selected to prevent data loss resulting from temporary optical beam attenuation.

(2) Height and Horizontal Separation

- Vertical Elevation: At least 80% of the monitoring path length must be situated between 2.0 and 15 meters above ground level.
- Separation from Trees: To minimize scavenging and surface deposition effects, at least 90% of the path length should be ≥ 20m from the dripline of trees and must be ≥10m from the dripline.
- Separation from Obstacles: The horizontal distance from any obstacle (e.g., buildings) to 90% of the monitoring path must be at least twice the height that the obstacle protrudes above the path height. Sites failing this requirement must be classified as microscale or middle scale.

(3) Airflow and Airway Obstructions

- Unrestricted Airflow: Unrestricted airflow is required across at least 90% of the monitoring path in a continuous arc of 270°.
- Street Canyons: If the path is deployed along a wall or building side for street canyon monitoring, an unobstructed arc of 180° is permitted.
- Minimum Distance from Roadways

(4) Minimum Distance from Roadways

The minimum separation distance required between the monitoring path and the nearest edge of traffic lanes depends on the Roadway Average Daily Traffic (ADT) volume (U.S. EPA, 2024, Appendix E, Table E-1), see Table 3.2.1.

Table 3.2.1: Minimum Separation Distance Between Roadways and Monitoring Paths for Monitoring Neighborhood and Urban Scale

Roadway Average Daily Traffic (Vehicles per Day)	Minimum Distance (Meters)	Minimum Distance (Meters)
≤ 1,000	10	10
10,000	10	20
15,000	20	30
20,000	30	40
40,000	50	60
70,000	100	100
≥ 110,000	250	250

3.2.4 Measurement Procedure

The DOAS method performs continuous, in situ measurements of gaseous pollutants by transmitting ultraviolet and/or visible radiation through an open atmospheric path and measuring the wavelength-dependent absorption of the target analytes. Unlike conventional extractive sampling methods, no physical air sample is collected or transported to an analyzer. Instead, pollutant concentrations are determined directly from the absorption of light over the defined optical path, providing a path-averaged concentration representative of the monitored atmosphere.

Prior to initiating measurements, the monitoring system shall be inspected to ensure that all components are operating properly and that the instrument has achieved thermal and operational stability. The optical path shall be free from permanent obstructions, and all optical surfaces shall be clean and free from contamination that could adversely affect measurement quality.

Instrument Preparation

Before each monitoring period, the instrument shall be powered on and allowed to stabilize in accordance with the manufacturer's recommendations. Instrument diagnostics shall be reviewed to verify the operational status of the light source, detector, spectrometer, communication system, and data acquisition software.

The wavelength calibration, detector response, optical signal intensity, and instrument diagnostics shall be verified before routine measurements commence. Any abnormal instrument condition shall be corrected prior to data acquisition.

Optical Alignment

The transmitting and receiving optical assemblies shall be aligned to maximize the received optical signal while maintaining a stable optical path. For systems employing retroreflectors, the retroreflector

shall be positioned such that the transmitted beam is returned efficiently to the receiving optics. Alignment shall be verified whenever the instrument is installed, relocated, subjected to maintenance, or whenever a reduction in received signal strength is observed.

The received optical signal shall remain within the operating range specified by the instrument manufacturer throughout the monitoring period. Significant reductions in signal intensity caused by optical misalignment, contamination of optical components, or atmospheric conditions shall be investigated and corrected before valid measurements are reported.

Establishment of the Measurement Path

The optical path length shall be selected based on the monitoring objectives, expected pollutant concentrations, instrument sensitivity, and local site characteristics. Longer optical paths generally improve measurement sensitivity for low-concentration pollutants but may also increase susceptibility to signal attenuation caused by adverse meteorological conditions such as fog, heavy rainfall, or dense aerosols.

The measurement path shall be representative of the monitoring location and should avoid permanent obstructions, localized emission sources not representative of the monitoring objective, and surfaces that may produce excessive reflection or optical interference.

Meteorological Observations

Meteorological conditions shall be monitored concurrently with atmospheric measurements whenever practicable. Ambient temperature, atmospheric pressure, relative humidity, wind speed, wind direction, precipitation, and visibility provide valuable information for interpreting pollutant concentrations and evaluating the influence of atmospheric conditions on measurement quality.

Periods of dense fog, heavy precipitation, or severe atmospheric instability that significantly reduce optical transmission should be identified during data review.

Data Acquisition

The data acquisition system shall continuously record raw spectra, processed spectra, calculated pollutant concentrations, instrument status indicators, quality assurance flags, and meteorological observations, where applicable. Measurement data shall be stored in a secure electronic format that preserves the original analytical results and provides complete traceability for subsequent review and quality assurance activities.

The data acquisition system should automatically assign time and date stamps to all recorded measurements using synchronized system clocks.

Data Validation

Measurement results shall be reviewed following each monitoring period to verify data completeness, instrument performance, and measurement quality. Data validation shall include evaluation of optical signal intensity, wavelength calibration status, spectral fitting residuals, instrument diagnostic

information, and environmental conditions that may have affected measurement quality, in accordance with the manufacturer's specifications and recommendations.

Measurements obtained during instrument malfunction, calibration activities, maintenance operations, severe optical interference, or other conditions that compromise data integrity shall be identified and excluded from routine reporting in accordance with the manufacturer's specifications and recommendations and the established quality assurance program.

3.2.5 Calibration

The purpose of calibration is to verify that the DOAS system is capable of accurately measuring the concentrations of target gaseous pollutants within the specified operating range. Calibration shall establish the accuracy of wavelength assignment, verify instrument stability, confirm the integrity of the optical path, and ensure that the spectral fitting algorithm correctly identifies and quantifies the target analytes.

Unlike extractive analytical methods, the DOAS technique does not require routine multipoint calibration using calibration gases introduced into the sampling system. Quantification is based on the Beer-Lambert law and the comparison of measured atmospheric spectra with certified molecular absorption cross-sections or validated reference absorption spectra. Consequently, calibration primarily consists of wavelength calibration, optical alignment verification, instrument performance verification, and periodic validation of the spectral analysis.

In addition to the requirements specified in this method, calibration shall be performed in accordance with the instrument manufacturer's operating manual and maintenance instructions. Manufacturer-recommended calibration procedures, verification routines, acceptance criteria, and maintenance intervals shall be followed whenever they are more stringent than the minimum requirements specified herein.

Initial Calibration

Prior to routine operation, the monitoring system shall undergo an initial calibration following installation, relocation, major maintenance, replacement of critical optical components, or software modifications that may affect measurement performance.

The initial calibration shall include:

(1) Verification of wavelength calibration;

(2) Verification of optical alignment;

(3) Confirmation of detector performance and light source stability;

(4) Verification of spectrometer performance;

(5) Validation of reference absorption spectra used for spectral fitting;

(6) Functional verification of the data acquisition and processing system; and

(7) Additional calibration or verification procedures required by the instrument manufacturer.

Routine monitoring shall not commence until all calibration requirements have been satisfactorily completed.

Calibration Standards

Calibration and performance verification shall utilize reference materials, calibration standards, or certified reference devices that are appropriate for the measurement principle and traceable, where applicable, to recognize national or international standards. The selected standards shall be suitable for verifying the performance of the spectrometer, optical system, wavelength scale, and spectral analysis software.

Calibration and verification may include, but are not limited to, the following:

(1) **Certified wavelength reference sources**, such as spectral emission lamps or equivalent optical wavelength standards, used to verify the wavelength accuracy and stability of the spectrometer.

(2) **Certified optical reference filters**, neutral density filters, or other optical attenuation devices used to verify detector linearity, optical throughput, and instrument response.

(3) **Certified gas reference cells** containing known concentrations of one or more target analytes or other suitable reference gases used to verify spectral identification, concentration calculations, and overall analytical performance.

(4) **Validated molecular absorption cross-sections or reference absorption spectra** obtained from recognized scientific databases, published literature, or certified reference libraries appropriate for the target analytes and the operating wavelength range (as applicable).

(5) **Internal reference standards or built-in verification systems**, where incorporated into the instrument design, that automatically evaluate wavelength stability, optical alignment, detector performance, or other critical operating parameters.

(6) **Other calibration standards, reference materials, or verification devices** recommended by the instrument manufacturer and demonstrated to be suitable for the intended application.

Reference materials shall be maintained, handled, stored, and replaced in accordance with the manufacturer's recommendations to prevent contamination, deterioration, or degradation that may affect calibration accuracy. Calibration standards shall be periodically inspected and verified to ensure continued suitability for use. Where expiration dates or recertification intervals are specified by the manufacturer or certifying body, such requirements shall be observed.

When manufacturer-specific calibration accessories or proprietary reference standards are required for instrument performance verification, their use shall be permitted provided that they are maintained in accordance with the manufacturer's specifications and satisfy the quality assurance requirements established by this method.

Acceptance Criteria

Calibration and performance verification shall be considered acceptable only when all applicable acceptance criteria listed in Table 3.2.2 have been satisfied. Measurements obtained when the

acceptance criteria are not met shall be considered invalid and shall not be reported until the instrument has been restored to acceptable operating conditions and satisfactory performance has been verified.

Table 3.2.2 Acceptance Criteria for Calibration and Performance Verification of DOAS

Performance Parameter	Acceptance Criteria
Wavelength Calibration	Wavelength accuracy and stability shall comply with the manufacturer's specifications or the acceptance criteria established by the implementing organization or monitoring agency
Optical Alignment	Optical alignment shall provide sufficient optical throughput and received signal intensity to support reliable measurements. The received signal shall meet or exceed the minimum operating level specified by the manufacturer.
Light Source Performance	Light source intensity and stability shall remain within the manufacturer's specified operating limits.
Detector Performance	Detector response, linearity, and signal-to-noise ratio shall satisfy the manufacturer's specifications.
Spectrometer Performance	Spectral resolution, wavelength stability, and optical performance shall comply with the manufacturer's specifications and be adequate to resolve the differential absorption features of the target analytes.
Spectral Analysis	Spectral fitting residuals shall remain within the acceptance limits specified by the manufacturer or established by the implementing organization.
Reference Standards Verification	Verification using wavelength standards, gas reference cells, optical reference devices, internal reference systems, or other approved reference materials shall produce results within the manufacturer's specified tolerances.
Instrument Diagnostics	All instrument self-tests, communication systems, internal diagnostics, and operational status indicators shall indicate normal operation without critical faults.
Environmental Operating Conditions	Instrument operating temperature, humidity, and other environmental conditions shall remain within the manufacturer's specified operating limits.
Automatic Verification Functions (if applicable)	Automatic calibration, wavelength verification, or performance verification routines shall complete successfully without error.
Additional Manufacturer Requirements	All additional calibration and verification procedures specified by the manufacturer shall be successfully completed before routine monitoring.

When continuous monitoring is conducted, the frequency of calibration and performance verification shall be determined in accordance with the instrument manufacturer's recommendations. If none is available, conduct these activities at least annually or as the need arises (e.g. after repairing the equipment).

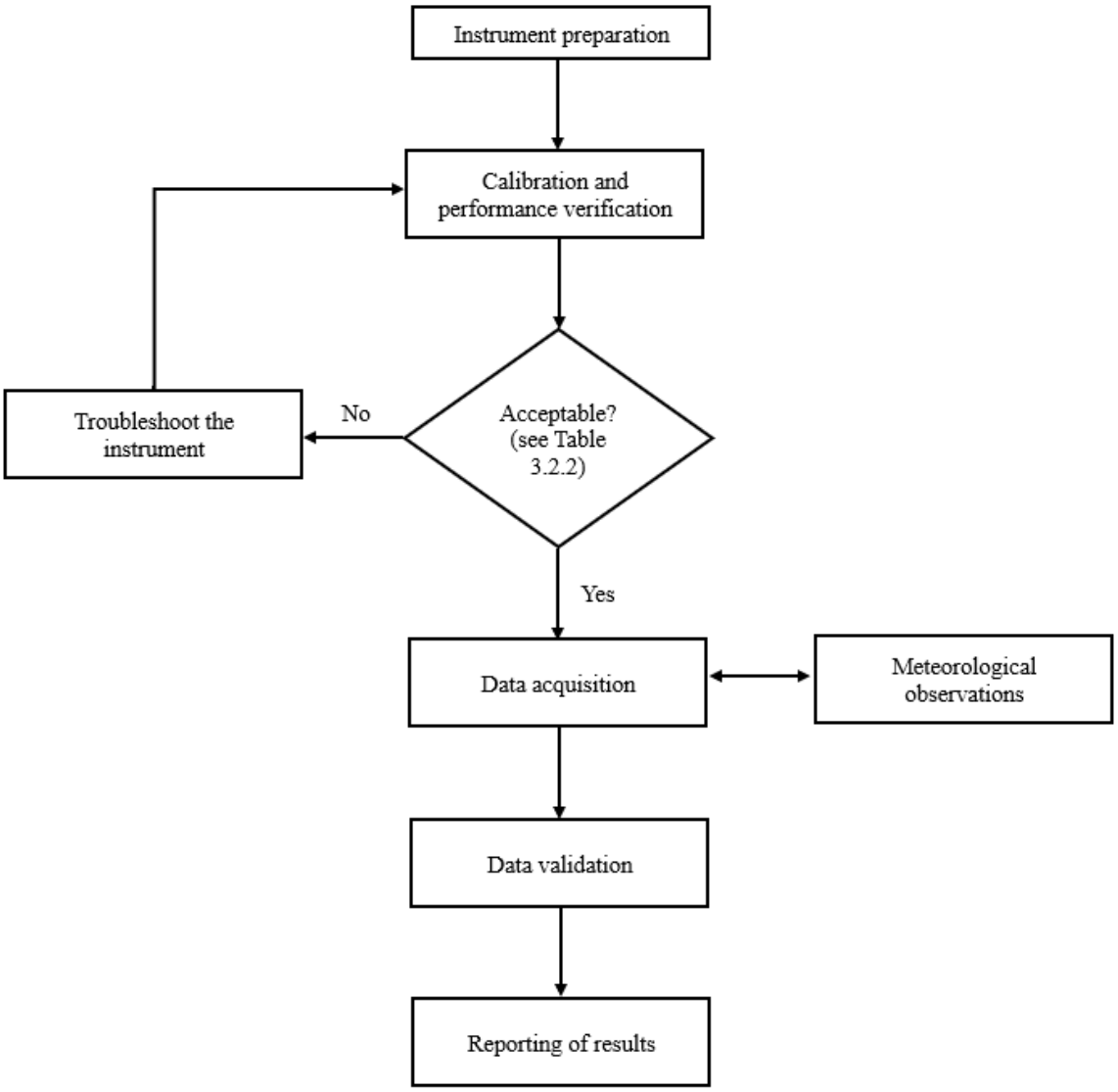


Figure 3.2.5 Schematic workflow for measurement of VOCs using DOAS

3.2.6 Routine Maintenance

Routine maintenance shall be performed at intervals specified by the instrument manufacturer or the implementing organization to ensure continued instrument reliability, measurement accuracy, and compliance with the data quality objectives of the monitoring program. Maintenance activities shall be documented and performed only by qualified personnel familiar with the operation of the monitoring system.

Routine maintenance may include inspection and cleaning of transmitting and receiving optical assemblies, retroreflectors (where applicable), protective windows, and other optical components to remove dust, moisture, insects, or other contaminants that may reduce optical throughput. The condition and alignment of optical components shall be verified periodically to ensure stable signal intensity and optimum measurement performance.

The performance of the broadband light source, spectrometer, detector, communication systems, environmental enclosures, and power supply shall be routinely inspected in accordance with the

manufacturer's recommendations. Components exhibiting deterioration, instability, or abnormal operation shall be repaired or replaced prior to continued monitoring.

Instrument diagnostics, wavelength calibration, optical alignment, detector response, signal intensity, and other performance verification checks shall be performed following routine maintenance, replacement of critical components, relocation of the instrument, or any activity that may affect measurement performance. Routine monitoring shall not resume until satisfactory instrument performance has been verified in accordance with the calibration and acceptance criteria specified in this method.

Maintenance activities, repairs, replacement of components, calibration results, performance verification records, and any corrective actions taken shall be documented and retained as part of the monitoring records in accordance with the quality management system established by the implementing laboratory or monitoring agency.

3.2.7 Safety Considerations

Installation, operation, calibration, maintenance, and servicing of the DOAS monitoring system shall be performed in accordance with applicable occupational health and safety regulations, the implementing organization's safety procedures, and the instrument manufacturer's safety instructions.

Personnel shall be aware that DOAS monitoring systems may utilize high-intensity ultraviolet and visible light sources, electrical equipment operating at hazardous voltages, elevated mounting structures, and outdoor installations exposed to adverse environmental conditions. Direct viewing of energized light sources or optical beams shall be avoided unless specifically permitted by the manufacturer and appropriate protective measures are implemented.

During installation and maintenance activities, appropriate personal protective equipment (PPE) shall be worn as required by the work being performed. Personnel shall exercise caution when working at elevated locations, near roadways, around energized electrical equipment, or during adverse weather conditions. Maintenance involving electrical components shall be performed only after the equipment has been isolated from the electrical supply in accordance with established lockout/tagout procedures or equivalent safety practices, where applicable.

Monitoring equipment installed outdoors shall be adequately protected against lightning, moisture intrusion, excessive heat, flooding, and other environmental hazards that may compromise equipment integrity or personnel safety. Maintenance activities should not be performed during severe weather conditions when such activities may present unacceptable safety risks.

All maintenance chemicals, cleaning materials, compressed gases, and other ancillary materials used during instrument servicing shall be handled, stored, and disposed of in accordance with the manufacturer's recommendations and applicable environmental, occupational health, and safety regulations.

4. Systematic Data Analysis Methods for Ambient Air VOCs

4.1 Framework of Systematic Analytical Methods for Ambient Air VOCs

Ambient air volatile organic compounds (VOCs) are crucial precursors for secondary organic aerosols (SOA) and ozone (O_3). Certain toxic and hazardous VOC species pose risks to human health. Therefore, precise source tracing and management of VOC pollution not only contribute to air quality improvement but also directly help eliminate air pollutants with potential hazards to human health. The systematic analysis method system for ambient air VOCs comprises data auditing, pollution characteristic analysis, photochemical reactivity analysis, ozone formation contribution assessment, SOA formation contribution assessment, and source apportionment methods. On this basis, countermeasure recommendations for the prevention, control, and management of ambient air VOC pollution can be formulated.

The framework of the systematic analytical methods for ambient air VOCs is shown in Fig. 4.1, in which basic analyses are denoted by hollow squares and advanced analyses by solid squares. Researchers may choose among the methods based on their individual needs.

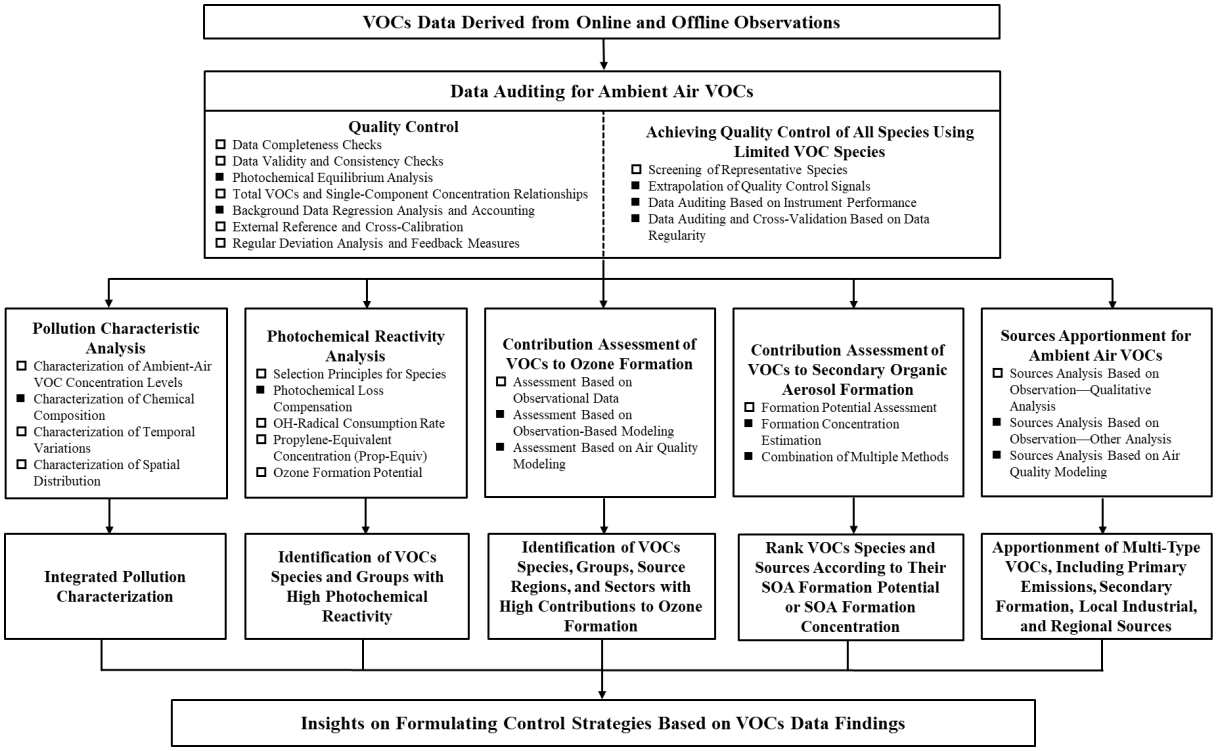


Figure 4.1 Schematic Diagram Illustrating the Framework of the Systematic Analytical Methods for Ambient Air VOCs

(□-Basic Analyses; ■-Advanced Analyses)

4.2 Data Auditing Methods for Ambient Air VOCs

Ambient air VOCs data audit is a systematic quality assessment and screening process conducted throughout the entire chain—from sample collection and laboratory analysis to final data reporting—in accordance with technical monitoring specifications and quality control requirements. The specific methods include: instrument performance verification, calibration curve validity testing, internal standard response monitoring, blank sample limit determination, relative percent difference calculation for duplicate samples, and logical plausibility checks based on atmospheric chemical mechanisms, such as characteristic species ratios and diurnal variation trends. The core purpose of this rigorous audit is to

eliminate invalid data caused by instrument anomalies, operational errors, or environmental interferences, thereby ensuring the accuracy, comparability, and integrity of monitoring data to the greatest extent. This robust foundation supports the precise identification of reactive VOCs species, facilitates coupled mechanistic analysis of ozone and secondary organic aerosol formation, enables refined source apportionment, and provides reliable evidence for scientifically evaluating the actual effectiveness of emission reduction measures.

4.2.1 Workflow

Ambient air VOC data auditing is carried out step-by-step following the principle of "instrument first, data second":

- Perform data completeness checks and instrument performance audits to screen out invalid time periods.
- Manually recheck raw chromatograms and complete re-integration to ensure qualitative and quantitative accuracy.
- Conduct cross-validation using laws such as mass conservation, characteristic ratios, and photochemical equilibrium, and confirm rationality by combining background data and external references.

Quality control for all species is achieved through response extrapolation of representative species throughout the entire process, ultimately classifying data into three tiers: valid, reference, and invalid, resulting in a traceable quality control report.

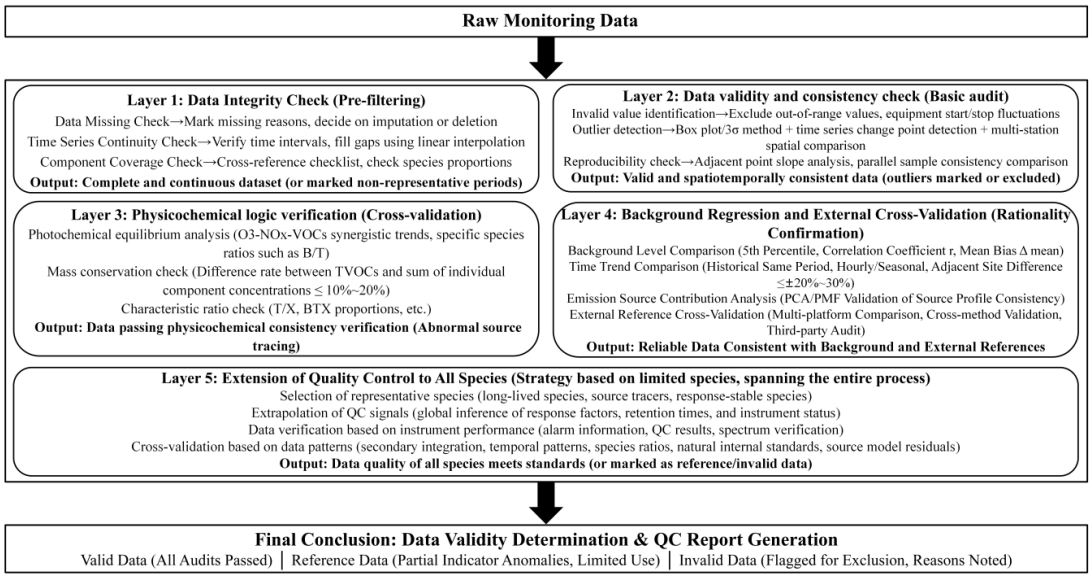


Figure 4.2 Workflow for the Quality Control and Review Methodology System for Ambient Air VOCs Data

4.2.2 Quality Control Methods for VOCs Monitoring Data

Volatile organic compounds (VOCs) in ambient air are diverse, and monitoring data must go through multiple stages from collection to reporting. Deviations at any stage can affect the final data quality. Therefore, establishing a systematic data auditing and quality control system is the core guarantee to ensure the scientific validity, accuracy, and reliability of VOC monitoring data.

Data quality control and auditing should follow the basic principle of "instrument first, data second." For online monitoring systems, hierarchical quality control frequencies—including daily checks, weekly checks, monthly inspections, quarterly calibrations, and annual tests—should be strictly followed. Quality control and quality assurance procedures such as zero-air blanks, system blanks, single-point checks, flow checks, leak checks, recalibration of standard curves, and target compound testing must be implemented to ensure instruments remain in optimal operating condition. For offline manual monitoring, key quality control steps such as blanks, parallel samples, internal standard tracking, and calibration curve management must be strictly performed in accordance with specified method requirements.

When auditors receive a batch of raw monitoring data, conducting data-driven audits is essential. The entire quality control system covers multiple levels, including data completeness checks, data validity and consistency checks, photochemical equilibrium analysis, mass conservation validation, background data regression analysis, and external reference cross-calibration, forming a closed-loop quality control and auditing process from sampling to data reporting.

Data Completeness Checks

Data completeness is the primary step in quality control, aimed at checking and identifying missing or abnormal values in the data.

- Missing Data Checks: Check for missing values in time series data. Retain records of missing values and mark the reasons (e.g., technical issues, power failure, sampling failure). If missing values are few, study whether to perform interpolation fitting (e.g., linear interpolation); if there are too many missing values, they can be marked as non-representative periods and considered for exclusion.
- Time Series Continuity Checks: Check whether data collection time intervals are consistent. For discontinuous time series parts, combine with station monitoring records to judge whether the data have practical significance. For abnormal interval data, filling can be done via linear interpolation or neighboring point values, supplemented by calculating the concentration gradient change rate between the linearly interpolated data and adjacent periods to verify interpolation rationality.
- Component Coverage Checks: Check whether VOCs are sampled completely; if certain target species are missing, analyze the reasons and record them. Introduce a reference list as a judgment basis, such as the target VOC analyte list specified in US EPA Method TO-15. Check whether target compound concentrations under specific environmental conditions (e.g., stable nighttime meteorological conditions) conform to reasonable proportional relationships. For example, the proportional relationship among alkanes, alkenes, and aromatics is approximately 3: 2: 1; if any category is out of balance, sample collection and analysis methods must be re-verified.

Data Validity and Consistency Checks

One of the cores of data quality control is ensuring data consistency across time and space while eliminating invalid and abnormal values.

- Invalid Value Identification: Eliminate meaningless values caused by human factors or special events, such as short-term fluctuations before and after equipment startup or shutdown, or values exceeding the upper instrument detection limit or falling below the lower detection limit. Upper and lower limits are defined in accordance with ambient air quality monitoring standards (GB/T 37822-2019), setting the single-species concentration upper limit at 90% of the detection limit; values excessively high or low are eliminated. Real-time flow and dilution factor dynamic monitoring are employed to assist judgment when identifying invalid values.

- Anomaly Checks: Anomalies can comprehensively affect data credibility and are typically identified through the following methods:
  - *Statistical Methods:* Utilize box plots or the 3-standard-deviation method to identify anomalies deviating from distribution extremes. For instance, use box plots to locate suspicious data exceeding 3 times the interquartile range. When peaks occur between 12:00 and 16:00 (typical VOC photochemical formation periods), focus on checking whether time accumulation of downwind observations exhibits step-like changes.
  - *Time Series Anomaly Detection:* Analyze continuous time series data from the same area to detect sudden spikes or fluctuation points significantly deviating from regional background values.
  - *Multi-site Spatial Comparison:* When multiple monitoring points exist, compare whether data variations across adjacent sites in the same region are consistent to identify anomalies at a single site. Background concentration weight factors are incorporated into spatial-temporal comparisons.
- Repeatability Checks: Perform slope analysis on concentration changes at adjacent time points (e.g., if the concentration change rate is too high, monitoring bias may exist). Check whether repeated analysis results of samples under similar conditions during the same period (e.g., parallel samples or concurrent measurement results) are consistent.

Photochemical Equilibrium Analysis

VOCs frequently participate in atmospheric oxidation reactions, and their concentration levels hold a logical relationship with photochemical equilibrium, which can validate data rationality.

- Specific Species Equilibrium Checks: Analyze the intrinsic logic of typical VOC species, such as relative variation ratios of benzene to toluene (B/T). If compound ratios are abnormal (e.g., suddenly extremely high or low B/T values), it may indicate abnormal emissions, sampling flaws, or measurement errors.

Total VOCs and Single-Component Concentration Relationships

Perform equilibrium validation on the relationship between total target compound concentrations (TVOCs) and all single-component concentrations. Discover potential anomalies and data deviations via mass conservation and characteristic ratio analysis.

- Mass Conservation Verification: TVOCs are explicitly defined as the sum of concentrations of all detected VOC components, including alkanes, alkenes, alkynes, aromatics, and oxygenated compounds. Check component breakdown of TVOCs to ensure consistency between the total sum and individual chemical components. If the sum of single-component concentrations is much lower than total TVOCs, it may indicate missed reporting of certain characteristic components. This can be verified by checking the discrepancy rate between TVOCs and the sum of single-component concentrations, which typically should remain below 10%–20%. Excessively high discrepancies indicate component omission or TVOC overestimation, necessitating specific checks on instrument calibration, detection methods, and whether key compounds were un-desorbed or undetected (e.g., low-boiling VOCs not being captured).

The discrepancy rate formula is expressed as:

$$Discrepancy\ Rate = \frac{TVOCs - \sum_{i=1}^{n} c_i}{TVOCs} \times 100\% \quad (4\text{-}1)$$

where c_i is the concentration of each single component, and $TVOCs$ is the total concentration.

- Characteristic Ratio Verification: Certain chemical components maintain relatively stable environmental ratios. Typical chemical component ratios can be utilized to validate proportional relationships among components. For instance:

- *Toluene/Xylene Ratio (T/X):* According to domestic and international research, atmospheric toluene/xylene ratios generally range between 0.5 and 1.0 (with variations closely tied to source characteristics). If measured T/X ratios far exceed the normal range, specific emission sources or detection biases may be responsible.
- *Aromatic Proportion Verification:* Total aromatics (benzene, toluene, xylenes, BTX) generally account for 10%–20% of TVOCs; proportions that are too low suggest omission, while those too high suggest single-component overestimation.

Background Data Regression Analysis and Accounting

Compare observational data with background or historical values to verify rationality.

- Background Level Comparison: Determine regional background values using historical monitoring data or typical periods with similar meteorological conditions. Background values can be calculated via wind direction filtering methods or clean wind direction selection. For instance, at manual sampling sites, the 5th percentile concentration value divided across annual background wind directions defines the background level. Routine quantitative statistical indicators, such as correlation coefficient (r) and mean bias (Δ_{mean}), are employed during data comparison.
- Temporal Trend Comparison: If concentrations of certain species fluctuate abnormally in the short term, compare contemporaneous data or cross-validate different data sources (e.g., manual sampling vs. online monitoring). Segmented time comparisons and seasonal comparisons can be considered to judge whether abnormal fluctuations significantly deviate. Generally, VOCs concentration differences between adjacent stations should not exceed $\pm 20\% - 30\%$.
- Emission Source Contribution Analysis: Simple source apportionment methods (such as Principal Component Analysis, PCA, and Positive Matrix Factorization, PMF) can verify whether VOC emission sources align with regional characteristics. For example, if no industrial activity surrounds a site, yet concentrations of industrial marker compounds (such as vinyl chloride) are high, it may suggest data errors (e.g., mistakenly capturing emissions from other areas) or calibration biases.

External Reference and Cross-Calibration

To further confirm data accuracy, external reference data can be introduced for comparison.

- Multi-platform Data Comparison: When conditions permit, field online monitoring data can be compared with laboratory manual analysis results to verify consistency.
- Cross-calibration Between Different Methods: For example, compare determination results of the same target compound using different analytical methods (such as gas chromatography and mass spectrometry).
- Third-party Testing Recheck: Entrust samples from specific time periods to authoritative or independent third-party laboratories for testing to inspect data deviations.

Regular Deviation Analysis and Feedback Measures

- Long-term Trend Checks: Conduct regular monthly or quarterly trend analyses on monitoring data to check for systematic biases.
- Quality Control Reporting and Traceability: Formulate complete quality control reports for operations such as data elimination and interpolation post-quality control to ensure traceability. Indicate reasons and bases for any manual modifications, providing potential reverse backtracking.

Quality control of ambient air VOC data is not merely a technical tool but a systematic workflow. From data completeness checks and anomaly screening to component balancing and external

reference validation, every step requires strict execution and detailed quality control log maintenance. Applying these methods ensures high scientific validity, accuracy, and reliability of VOC data, offering robust support for subsequent research and policy formulation.

4.2.3 Methods for Achieving Quality Control of All Species Using Limited VOC Species

Volatile organic compounds (VOCs) in ambient air are highly diverse, with known species reaching up to several hundred. However, constrained by expensive reference materials, limited analytical channels, and high operation and maintenance costs, it is difficult for any laboratory or monitoring network to equip full-process quality control for hundreds of substances individually. Therefore, utilizing representative species for quality control and extending quality control effectiveness to all species through systematic data auditing methods is a pragmatic choice to pursue data credibility under limited resources.

Addressing this critical issue, domestic and international research and practice mainly construct methodological strategies from three dimensions: representative species screening, quality control signal extrapolation, and data auditing and cross-validation.

Screening of Representative Species

The screening of representative species is the foundation of the entire quality control strategy, typically following three major principles:

- Selecting Species with Weaker Photochemical Activity and Longer Atmospheric Lifetimes: Compounds such as benzene and ethane can be selected as quality control benchmarks. During transport from emission sources to receptor points, photochemical reactions do not significantly alter the mass balance of such species, rendering concentration data high comparability and stability. Long-lived VOC components possess distinct background concentrations in the atmosphere, and regional background values are relatively close, making them useful for diagnosing abnormally low or high concentration phenomena.
- Screening Marker Species (Tracers) for Various Emission Sources: For example, use aromatics to trace traffic source emissions, carbon tetrachloride to trace industrial source emissions, and isopentane to trace oil and gas evaporation. Concentration variations of these species sensitively reflect changes in emission intensity of specific source categories, and their quality control status can represent data quality for corresponding source-related species.
- Selecting Compounds That Are Easy to Detect and Have Stable Instrument Responses: Choose compounds that exhibit good responses in GC-MS/FID systems, low detection limits, symmetrical chromatographic peaks, and stable retention times as daily quality control "benchmark" species. Such species should be resilient to interference under routine analytical conditions and exhibit good quantitative repeatability, serving to monitor system stability daily.

Extrapolation of Quality Control Signals

After screening representative species, quality control methods extend from limited species to all species via system response extrapolation.

- Response Factor Extrapolation: Determine the response stability of the entire chromatographic system by monitoring response factor changes of benchmark species during daily or weekly calibrations. If response factor fluctuations of benchmark species remain within $\pm 20\%$, the entire GC-MS/FID system response to all species is considered within a controllable range.
- Retention Time and Chromatographic Separation Extrapolation: Based on the regularity of chromatographic retention times, retention times and peak shapes of a few known species can be extended to evaluate the separation performance of other uncalibrated species. In

chromatographic analysis, retention times of homologues and isomers follow predictable patterns. If retention time drift of benchmark species is within acceptable limits ($\leq \pm 0.1\ min$), qualitative identification of all analytical species can be inferred as reliable.

- Global Estimation of Instrument Performance Status: Various alarm information generated during instrument operation (such as carrier gas pressure anomalies, detector signal saturation, temperature control deviations) represents important bases for judging data validity. If no alarm information affecting data quality occurs during a specific period and all quality control indicators of benchmark species pass, monitoring data for all species during that period can be presumed valid.

Data Auditing Based on Instrument Performance

Data auditing serves as the final gateway to guarantee data quality across all species. In accordance with technical documents such as *Technical Specifications for Continuous Automated Monitoring of Volatile Organic Compounds in Ambient Air*, data auditing should prioritize performance-based audits.

- Alarm Information Auditing: Check whether alarm information affecting data quality exists based on instrument operation during the audited time period. Common alarms requiring attention include: low or fluctuating carrier gas pressure, detector signal overflow, temperature control failure, flow control anomalies, and autosampler failure. Data during periods with alarm information should be directly labeled as invalid.
- Quality Control Result Auditing: Audit based on single-point check quality control results from the most recent daily or weekly checks. If quality control results fail to meet quality control targets (e.g., relative error exceeding 20%), data between the two quality control periods should be labeled as reference data; monitoring data following single-point checks that fail quality control targets must be labeled as invalid data until trouble is cleared, normal operation is restored, or recalibration is completed.
- Chromatogram Auditing: For monitoring data with analytical chromatograms, audits must incorporate chromatogram conditions, focusing on:
    - Check whether chromatogram baselines exhibit abnormal drift and fluctuation.
    - Check whether chromatographic peak shapes of target compounds are symmetrical and whether fronting or tailing phenomena exist.
    - Identify and evaluate unknown peaks or abnormal high peaks in chromatograms.
    - Check resolution of critical species pairs to ensure qualitative and quantitative accuracy remains undisturbed.

Data with distinct baseline disturbances and abnormal chromatograms must be labeled as invalid.

Data Auditing and Cross-Validation Based on Data Regularity

Following instrument performance-based audits, data regularity-based audits are required. This level of auditing targets data quality across all species directly, serving as the ultimate test of the "limited quality control extrapolation to all species" strategy.

- Secondary Integration and Qualitative/Quantitative Confirmation: For monitoring data with analytical chromatograms, perform secondary integration to ensure accuracy of qualitative and quantitative results. Specific actions include: checking whether integration start and end points of target compound chromatographic peaks are reasonable one by one; checking whether internal standard integration areas are stable (typically requiring internal standard area fluctuations not to exceed $\pm 50\%$); manually re-integrating chromatographic peaks with unreasonable automatic integration.
- Absolute Concentration and Temporal Variation Regularity Auditing: Audit in combination

with absolute concentrations and temporal variations of monitoring results. Examples include: checking whether time series of total VOC concentrations exhibit sudden increases/decreases; comparing with historical contemporaneous data to judge whether concentration levels fall within reasonable ranges; checking whether diurnal variation patterns match expected patterns of pollution source emissions and meteorological dispersion.

- Inter-species Correlation and Ratio Auditing: Inter-species correlations and characteristic ratios serve as powerful tools to validate data quality. Owing to advantages like convenience and speed, ratio methods hold high practical value in VOC data auditing. Common VOC species pairs utilized for data auditing include:

Table 4.1 Common VOC species pairs

Species Pair	**Auditing Purpose**	**Anomaly Judgment Reference**
n-Butane & i-Butane	Traffic / gas source tracing	Ratios deviating from typical ranges suggest interference or quality control issues
n-Pentane & i-Pentane	Oil/gas evaporation tracing	Abnormal ratios suggest sampling or analytical problems
2-Methylpentane & 3-Methylpentane	Isomer audit	Abnormal ratios suggest qualitative errors or co-elution
Ethylbenzene & m/p-Xylene	Traffic source tracing	Ratios deviating suggest source changes or data anomalies
m/p-Xylene & o-Xylene	Isomer separation effect check	Abnormal ratios suggest insufficient resolution or interference

- Natural Internal Standard and Tracer Auditing: Utilize natural internal standards and tracer gases to validate data rationality:
  - *CFC-113 as a Natural Internal Standard:* CFC-113 possesses extremely stable chemical properties in the atmosphere and relatively uniform concentrations, serving as a natural internal standard source. If CFC-113 concentrations exhibit abnormal fluctuations during a period, it suggests systematic issues in sampling, analysis, or data transmission.
  - *VOC-to-Tracer Gas Ratio Verification:* Utilize emission ratios of VOCs to tracer gases like CO to compare inventory estimated values with measured regression values, verifying monitoring data rationality.
- Cross-Validation in Source Apportionment Models: Within source apportionment models (such as PMF), test input data quality via model diagnostic indicators and residual analysis. Abnormal data are identified and eliminated during iteration. If residuals of a certain species in the model remain persistently large or goodness-of-fit (Q value) is abnormal, it suggests potential data quality problems for that species, requiring retrospective checks on its quality control status.

Achieving quality control of all species via limited VOC species is not a simple oversimplification, but a systematic methodology built upon rigorous scientific logic. Its core lies in: determining quality control "anchors" via "representative species screening"; extending limited quality control signals to all species via "system response extrapolation"; ensuring reliability during data acquisition via

"instrument performance-based data auditing"; and conducting ultimate inspections on data quality across all species via "data regularity-based auditing and cross-validation." The four links interlock tightly to form a complete quality control closed loop, effectively guaranteeing data quality for all VOC species under limited monitoring resource conditions.

4.3 Pollution Characteristic Analysis Methods for Ambient Air VOCs

Pollution-characteristic analysis is the foundation of systematic ambient-air VOC data analysis. It describes the measured pollution level, chemical composition, temporal variation, and spatial distribution and interprets these characteristics together with meteorological conditions and site context. The analysis is intended to identify dominant measured species, high-value periods and areas, characteristic composition patterns, and preliminary emission or transport influences. Its outputs could provide a consistent data basis for subsequent photochemical-reactivity, ozone-formation, secondary-organic-aerosol, and quantitative source-apportionment analyses.

Pollution characteristics are determined jointly by emissions, atmospheric chemistry, dilution, deposition, and transport. Accordingly, descriptive statistics should not be interpreted in isolation. The analytical method must be selected according to the monitoring approach, time resolution, species coverage, number and representativeness of sites, data completeness, and study objectives. Methods whose data requirements are not satisfied should not be applied mechanically, and exploratory results must not be presented as quantitative source contributions.

4.3.1 Workflow and Data Requirements

The primary input is a quality-controlled VOC dataset containing species names, concentrations, units, timestamps, validity flags, detection limits, sampling or analytical method information, and instrument-quality-control records. Site coordinates, sampling height, site classification, nearby land use, and known changes in site environment or instrumentation should also be compiled. The species list and chemical grouping used in the analysis must be traceable to the monitoring method and should remain consistent throughout the study period.

Where available, VOC observations should be combined with concurrent O_3, NO, NO_2 or NO_x, CO, $PM_{2.5}$, and other relevant pollutant data. Meteorological inputs may include temperature, relative humidity, wind speed and direction, atmospheric pressure, precipitation, solar radiation, and boundary-layer height. Co-located, directly observed data with a time resolution compatible with the VOC data are preferred. If co-located observations are unavailable, nearby regulatory stations, radiosonde or remote-sensing products, meteorological reanalysis, or model outputs may be used after their spatial and temporal representativeness has been evaluated (U.S. EPA, 2018, 2023).

Where relevant, land-use data, road networks, industrial-facility information, emission inventories, and regional-background information may be used to support interpretation. These auxiliary data must not be treated directly as quantitative source-contribution results.

For every auxiliary dataset, the report must identify the data provider, station or product name, coordinates or grid resolution, measurement height when relevant, time zone, averaging period, quality-control status, and access or processing date. A practical priority is: co-located observation; nearby observation demonstrated to be representative; validated remote-sensing or reanalysis product; and model-derived variable. Lower-priority sources are not necessarily unusable, but their additional uncertainty and intended analytical role must be stated.

Before analysis, all datasets must be synchronized to a common time zone and averaging period. Species names, concentration units, missing-value codes, and validity flags must be harmonized. Duplicate records, clock shifts, calibration periods, instrument downtime, values below the detection limit, and physically implausible observations should be processed using predefined and documented rules. Data capture should be evaluated by species and by reporting period so that a mean or

percentile is not dominated by a small or seasonally biased subset.
Temporal matching should use the finest common interval justified by the measurements. If a VOC sample covers several hours, auxiliary variables should normally be aggregated over the same interval rather than matched to a single timestamp. Spatial matching should consider distance, terrain, elevation, surface type, and local emission influence rather than distance alone. When instruments, sites, or species lists change, overlap periods and comparability checks should be used where possible. The final analysis dataset should preserve links to the original records and processing flags.

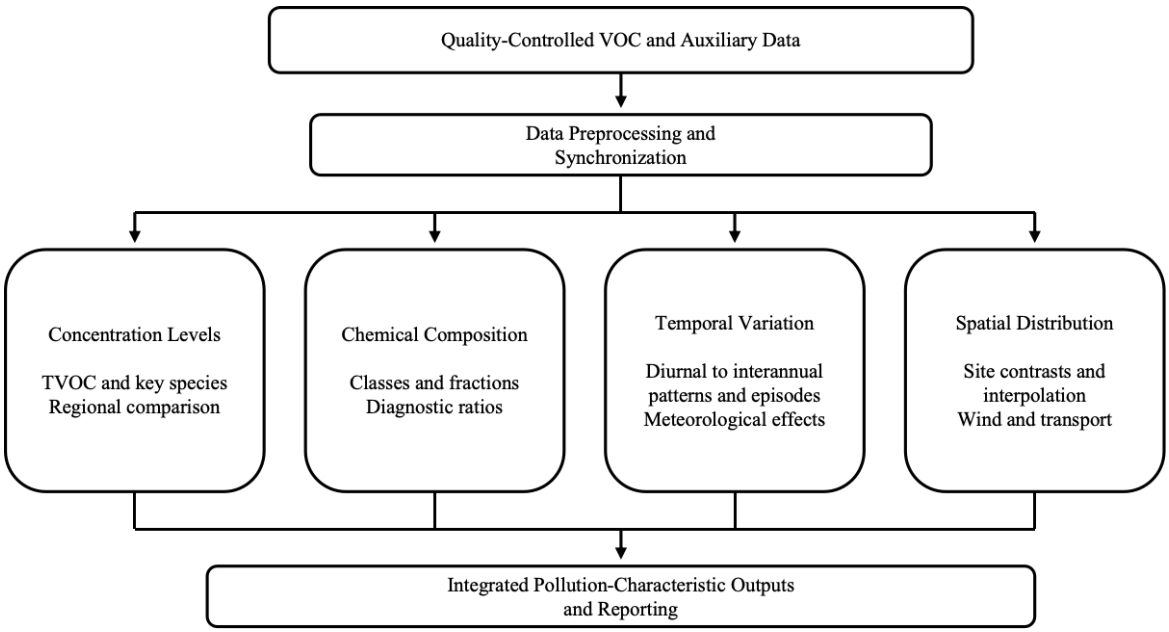


Figure 4.3 Workflow for pollution-characteristic analysis of ambient-air VOCs

4.3.2 Characterization of Ambient-Air VOC Concentration Levels

Concentration Units and Conversion

VOC concentrations are commonly expressed as volume mixing ratios (ppbv) or mass concentrations (μg/m^3). Volume mixing ratios are suitable for gas-phase abundance, diagnostic ratios, and atmospheric-chemistry calculations, whereas mass concentrations are required for mass-based composition, ozone-formation-potential, secondary-organic-aerosol-potential, and health-risk calculations. The selected unit should match the purpose of the analysis and must be stated in every table and figure.

Conversion must be performed separately for each species using its molecular mass. At 298.15 K and 101.325 kPa, $C_i\ (\mu g/m^3) = \frac{\chi_i(ppbv) \times M_i(g/mol)}{24.465}$, where C_i is the mass concentration, χ_i is the volume mixing ratio, and M_i is the molecular mass. For other conditions, the ideal-gas expression $C_i = \frac{\chi_i \times P \times M_i \times 10^{-3}}{R \times T}$ may be used, where P is pressure in Pa, T is absolute temperature in K, and R is 8.314462618 J mol^{-1} K^{-1}. Concurrent temperature and pressure are preferred; if standard or fixed conditions are used, they must be reported.

A single conversion factor must not be applied to all VOCs because molecular masses differ. Quality checks should verify molecular formulas, molecular masses, unit prefixes, and standard-condition definitions. Values reported on a dry or wet basis, or referenced to different standard conditions, must be harmonized before comparison.

Total Measured VOC Concentration Statistics

For a defined set of n measured VOC species, the total measured VOC concentration, denoted as C, may be calculated as $C = \sum_{i=1}^{n} C_i$. This quantity represents the sum of concentrations of the explicitly reported measured species rather than the total concentration of all organic compounds in the atmosphere. The report must list the included species, chemical classes, concentration unit, detection-limit treatment, and minimum completeness criterion. If the species set changes over time, a stable common-species sum should be used for trend comparison, while the full-species sum may be reported separately.

For the total measured VOC concentration, chemical-class concentrations, and selected individual species, the analysis should report the number of valid observations, data capture, arithmetic mean, median, standard deviation, 25th and 75th percentiles, and, where useful, the 5th and 95th percentiles, minimum, and maximum. VOC concentrations often have right-skewed distributions, so the mean and median should normally be presented together. Values below the method detection limit should be treated using a predefined rule appropriate to the purpose and detection frequency, and sensitivity to that rule should be examined for species with a large censored fraction.

Statistics should be stratified only when the subgroup has adequate and reasonably balanced coverage. A period mean should not be reported as representative if most expected observations are missing or if the retained data cover only a particular time of day or season. Cross-period and cross-site comparisons must use consistent species sets, statistics, and completeness criteria.

Key Species Ranking and Identification

Individual species may be ranked by mean or median mass concentration, volume mixing ratio, or their fraction of the total measured VOC concentration. The top-ranked species and their cumulative fraction provide a transparent description of the components dominating measured abundance. Heatmaps, rank plots, and cumulative-contribution curves may be used, provided that units and the denominator are clear.

Concentration ranking alone does not define photochemical importance, health significance, source specificity, or control priority. A low-concentration alkene may be highly reactive, and a low-abundance toxic or source-diagnostic species may remain important. Therefore, the species carried forward to subsequent analyses should be selected using multiple criteria, including concentration, detection frequency, chemical reactivity, toxicological relevance, and diagnostic usefulness.

Comparisons with Other Cities or Regions

External comparisons should use cities or regions with reasonably comparable climate, season, site classification, monitoring method, time resolution, study period, and species scope. A comparison table should identify the location, site type, monitoring period, sampling and analytical method, averaging time, number of measured species, concentration unit, and statistical metric. Differences in these factors should be discussed before environmental explanations are proposed.

When complete species-list harmonization is not possible, comparisons should be limited to common species or consistently defined chemical classes. Unadjusted sums of measured VOC concentrations derived from substantially different species sets must not be ranked as if they represented the same quantity. Published values should be checked against the original source, and conversion between units should use species-specific molecular masses and clearly stated temperature and pressure conditions.

4.3.3 Characterization of Chemical Composition

Chemical-Class Concentrations and Fractions

Measured species should be grouped into chemically meaningful classes, such as alkanes, alkenes, alkynes, aromatics, halocarbons, oxygenated VOCs (OVOCs), and other groups relevant to the

monitoring method. The classification scheme must be reported and applied consistently. Isomers should remain separate when they are analytically resolved and have different reactivity or diagnostic value.

For chemical class k, the class concentration is $C_k = \sum_{i \in k} C_i$, and its measured composition fraction is $F_k = \frac{C_k}{\sum_j C_j} \times 100\%$. Both absolute concentration and relative fraction should be reported. The denominator and treatment of missing or below-detection-limit species must be stated. Stacked bars, composition profiles, or heatmaps may be used, but a percentage plot should not replace the absolute-concentration information.

Composition Changes across Time, Sites, and Pollution Scenarios

Chemical composition may be compared among hours of day, weekdays and weekends, seasons, sites, and predefined pollution scenarios. The comparison should use a consistent species set and display both concentration and fraction, because a larger fraction may result either from an increase in that class or from preferential removal of other classes. Sample size and data capture should be shown for each group, and the same averaging method should be used across groups.

Changes in alkane, alkene, aromatic, or OVOC fractions may reflect different mixtures of emissions, chemical processing, and dilution. OVOCs may have both primary and secondary origins; consequently, an increase in OVOC concentration or fraction cannot by itself be interpreted as secondary formation. Interpretation should be checked against oxidant levels, radiation, temperature, wind, co-pollutants, and known emission conditions.

Diagnostic Ratios and Photochemical Aging

Ratios such as toluene/benzene, i-pentane/n-pentane, and xylenes/ethylbenzene may provide preliminary information on source mixture or photochemical aging when the paired species have compatible measurement quality, adequate detection frequency, and a plausible relationship in local emissions. The ratio should normally be calculated for paired observations rather than from two separately averaged concentrations, and the distribution and sample size should be reported.

Diagnostic ratios are affected by source mixing, dilution, transport time, chemical loss, analytical uncertainty, and changing background concentrations. Literature thresholds or source signatures from another region should therefore not be treated as universal. Ratios close to the detection limit or with an unstable denominator require particular caution.

When a pair of co-emitted species reacts at different rates with OH and dilution is assumed to affect both similarly, a relative photochemical age may be estimated as $\Delta t = \frac{ln(X/Y)_0 - ln(X/Y)}{[OH](k_X - k_Y)}$, where $(X/Y)_0$ is the emission ratio, X/Y is the observed ratio, [OH] is the assumed OH concentration, and k_X and k_Y are the corresponding reaction-rate constants. Because the emission ratio and OH exposure are often uncertain and source mixing violates the simple model, the result should be reported as an indicator with sensitivity analysis, not as an exact air-mass age.

For VOC species i, the approximate atmospheric lifetime against OH oxidation may be estimated as $\tau_i = \frac{1}{k_{OH,i}[OH]}$, where $k_{OH,i}$ is the reaction-rate constant and [OH] is the assumed OH-radical concentration. Because actual OH concentrations vary substantially in time and space and other oxidants may also contribute to VOC loss, the result should be used only as a relative aging indicator.

Correlation, Clustering, and Preliminary Source Clues

Pearson correlation may be used for approximately linear, normally distributed relationships, whereas Spearman rank correlation is generally more robust for skewed VOC data and monotonic relationships. The analysis should specify data transformation, outlier treatment, sample size, significance criterion, and multiple-testing control when many pairs are examined. Correlation should

be evaluated by relevant time period or meteorological regime if aggregation could conceal changing relationships.

Hierarchical clustering, principal-component analysis, or related exploratory methods may be used to identify groups of species with similar variation. Input scaling, missing-data treatment, distance metric, linkage method, retained components, and stability checks must be reported. Similar variation may arise from a common source, common meteorological control, or common chemical behavior; therefore, these results provide hypotheses and supporting evidence rather than quantitative source attribution.

4.3.4 Characterization of Temporal Variations

Diurnal and Weekly Variation

For hourly or finer online observations, diurnal variation should be evaluated for the total measured VOC concentration, major chemical classes, and selected species using hourly means or medians together with an interquartile range or confidence interval. The number of valid observations in each hour should be checked, and time should be reported in local standard time or another explicitly stated time basis. Separate profiles may be prepared for seasons or pollution regimes when sufficient data are available.

Weekday–weekend or workday–holiday contrasts can help evaluate activity patterns, but the locally applicable calendar and holiday definition must be used. Differences in season, weather, and sample coverage should be controlled or disclosed. Morning and evening peaks may coincide with traffic or other time-dependent emissions, while daytime decreases may reflect dilution and chemical loss; these interpretations should be checked using co-pollutants and meteorological variables.

Monthly, Seasonal, and Interannual Variation

Monthly and seasonal statistics should be based on reasonably balanced coverage and consistent species sets. Seasons must be defined for the local climate and hemisphere, with the included months reported. Box plots or distribution plots are preferable to bar charts alone because they show variability and extreme values. Changes in heating, fuel use, vegetation, industrial activity, solar radiation, mixing height, and monsoon or synoptic circulation may all contribute to seasonal patterns.

Group differences may be evaluated with Kruskal–Wallis or another suitable test. If the overall test is significant, a post hoc comparison with multiplicity adjustment may be used to identify the differing groups. Statistical significance should be interpreted together with effect size and data coverage so that a small difference in a very large dataset is not overstated as environmentally important.

When several complete years are available and the site, instruments, calibration strategy, and species list are sufficiently continuous, monotonic trends may be tested with the Mann–Kendall method and quantified with the Sen slope (Mann, 1945; Sen, 1968). Seasonality and temporal autocorrelation should be considered. Site relocation, instrument replacement, detection-limit change, and other discontinuities must be evaluated before a change is interpreted as an environmental trend.

Pollution Scenarios and Typical Episodes

Data may be divided into high-O_3, high-particle, combined-pollution, background, or other scenarios using the air-quality standards applicable to the study region or scientifically justified criteria defined before the comparison. Thresholds, averaging periods, seasonal scope, data-completeness rules, and sample sizes must be reported. Reference periods should preferably come from the same season and a comparable meteorological background.

The total measured VOC concentration, together with chemical-class and key-species concentrations and fractions, may be compared among scenarios. A relative change may be expressed as $\Delta C = \frac{C_{scenario} - C_{reference}}{C_{reference}} \times 100\%$, provided that the reference definition and its uncertainty are clear.

When samples are few or uneven, distributions and confidence intervals should be presented rather than relying on a single percentage change.

A typical pollution episode should be examined using synchronized time series of VOCs, O_3, NO_x, CO, particles, and meteorological variables. Wind shifts, stagnation, boundary-layer changes, precipitation, and known emission events should be annotated when supported by data. Episode analysis is used to form a mechanism hypothesis, and conclusions should rely on coordinated changes in multiple variables.

Meteorological Effects on Temporal Variation

Temporal changes in VOCs are controlled jointly by emissions, chemistry, and meteorological dispersion. Temperature may influence fuel evaporation and biogenic emissions; solar radiation affects photochemistry; relative humidity and precipitation may affect removal processes; and wind speed and boundary-layer height regulate dilution and accumulation. Meteorological variables should be matched to the VOC observations at a time scale consistent with their physical role.

Meteorological effects may first be explored using stratified distributions, scatterplots, correlation, or multivariable regression. For example, VOC distributions may be compared across temperature, wind-speed, or boundary-layer-height ranges after controlling for season and time of day. Because meteorological variables are often intercorrelated, a bivariate association should not be interpreted as an independent causal effect. Nonlinear relationships and interactions should be considered where physically plausible.

For long-term trend or intervention evaluation, multiple regression, generalized additive models, or random-forest meteorological normalization may be used to estimate concentrations under comparable meteorological conditions. The model should have separate training and validation data and should report predictors, performance metrics, residual behavior, extrapolation limits, and uncertainty. Time-blocked or otherwise leakage-resistant validation is preferable for multi-year data.

Meteorologically normalized concentrations are model estimates and must be presented with the original observations. If model performance is poor during extreme weather, site change, or an abrupt shift in emission structure, the normalized series should not replace the observed evidence.

4.3.5 Characterization of Spatial Distribution

Multi-Site and Functional-Zone Comparisons

Multi-site comparisons require harmonized species lists, monitoring methods, time windows, averaging periods, and validity criteria. The total measured VOC concentration should be compared together with chemical-class and selected-species concentrations and composition. Site type, coordinates, sampling height, surrounding land use, terrain, and known nearby activities must be documented. If coverage differs among sites, a common observation window should be analyzed before results from the full site-specific records are compared.

Sites may be grouped as traffic, industrial, residential, commercial, urban background, or regional background according to the local monitoring-network definition. The classification basis must be stated and should not be inferred from the site name alone. Spatial differences can reflect emissions, terrain, wind field, boundary-layer structure, or sampling height; meteorology and site context should therefore be evaluated together with concentration and composition.

Spatial Mapping and Interpolation

A geographic information system may be used to map site locations and observed concentrations. When the number, density, and representativeness of sites support spatial prediction, inverse-distance weighting, kriging, natural-neighbor interpolation, or another justified method may be used. Method selection should be based on the sampling design, spatial autocorrelation, terrain, and analytical scale rather than a universal minimum number of sites.

The coordinate system, temporal aggregation, interpolation algorithm, search neighborhood, parameters or variogram model, and cross-validation results must be reported. Prediction should be checked for undue influence from a small number of high observations. Greater uncertainty should be indicated for sparse areas, network edges, or terrain not represented by the sites, and extrapolation beyond the monitoring domain should be avoided.

Mobile measurements can increase spatial resolution, but route and time are strongly coupled. Mobile or uncrewed-aircraft surveys should document route, speed, instrument response time, repeat coverage, and temporal-adjustment method. A short-lived plume must not be interpolated as a stable long-term hotspot. When fixed-site and mobile data are combined, temporal differences must be addressed before mapping.

Wind Dependence and Potential Source Direction

VOC concentrations may be stratified by wind direction and wind speed and examined using pollution roses or bivariate polar plots. High concentrations at low wind speed may indicate local accumulation, whereas directional high values at moderate or high wind speed may suggest upwind transport. These interpretations must be checked against topography, site exposure, wind-measurement representativeness, and known activity patterns.

A conditional probability function may be calculated as $CPF_\theta = \frac{m_\theta}{n_\theta}$, where m_θ is the number of samples above a selected concentration threshold in wind sector θ and n_θ is the total number of valid samples in that sector. The threshold may be selected as a study-relevant percentile. Wind-sector width, minimum sample count, low-wind treatment, missing-data rule, and threshold must be reported, and sensitivity to reasonable alternative thresholds and sectors should be evaluated.

Nonparametric wind regression or a smoothed polar model can estimate concentration patterns in wind-speed and wind-direction space when a sufficiently large and representative dataset is available. Kernel, smoothing, and validation choices influence the shape of apparent hotspots. A polar hotspot is a potential directional clue and must not be equated directly with a specific facility or emission source.

Regional-Transport Analysis

When regional transport is relevant, back trajectories may be calculated with HYSPLIT or an equivalent model, and trajectory clustering may be used to compare VOC concentrations among air-mass pathways. The receptor coordinates and starting height, trajectory duration and launch frequency, meteorological driver, model version, and vertical-motion option must be reported. Alternative starting heights or other key settings should be tested to evaluate pathway stability.

If trajectory number and spatial coverage are adequate, potential source contribution function (PSCF) or concentration-weighted trajectory (CWT) analysis may be used to identify grid cells associated with high observed concentrations. Grid size, concentration threshold, residence-time calculation, and weighting of cells with few trajectory endpoints can substantially affect the result and must be reported with sensitivity analysis.

Trajectory, PSCF, and CWT results are affected by the resolution of the meteorological field, starting height, and accumulated trajectory error. They indicate potential transport pathways or influence regions, not an emission inventory, and they do not quantify the contribution of a source. Quantitative source contributions must be determined using the receptor-model or three-dimensional modeling methods in Section 4.7.

Integrated interpretation and reporting requirements: Pollution-characteristic conclusions should consider concentration level, chemical composition, temporal variation, spatial contrast, meteorological conditions, and site context together. Preliminary source or transport interpretations should be based on multiple mutually consistent indicators, such as marker-species combinations,

diagnostic ratios, species correlations, high-value periods, site contrasts, wind dependence, and trajectory results. A single species, ratio, correlation coefficient, polar plot, or trajectory must not be used to identify a pollution source.

The report must document data sources, monitoring methods, study period, time zone, species list, unit conversion, data-completeness rule, below-detection-limit treatment, statistical tests, meteorological matching, spatial-analysis parameters, and model versions. Uncertainty arising from species coverage, site representativeness, time resolution, auxiliary meteorological data, analytical assumptions, and exploratory source indicators must be discussed to ensure comparability, traceability, and reproducibility.

4.4 Photochemical Reactivity Analysis Methods for Ambient Air VOCs

Photochemical reactivity of ambient air VOCs refers to the relative capacity and reaction rate of VOCs participating in oxidation reactions in the atmospheric environment. Owing to differences in molecular structures and chemical properties, distinct VOC species exhibit significant discrepancies in reaction rates with atmospheric oxidants (particularly $\cdot OH$ radicals) and capacities to generate O_3.

Photochemical reactivity analysis quantitatively assesses the reactivity of each VOC species in atmospheric photochemical processes and its contribution potential to O_3 formation, identifying key reactive species contributing most heavily to regional O_3 pollution, thereby providing a scientific basis for targeted formulation of VOC emission reduction strategies.

4.4.1 Workflow

This section first describes the analytical workflow, data-processing requirements, and species-selection principles for photochemical-reactivity analysis. It then presents optional photochemical-loss compensation and three commonly used reactivity metrics: the hydroxyl-radical consumption rate (L_{OH}), propylene-equivalent concentration (Prop-Equiv), and ozone formation potential (OFP). L_{OH} and Prop-Equiv characterize kinetic reactivity toward OH, whereas OFP characterizes relative ozone-forming potential using Maximum Incremental Reactivity (MIR). When these metrics are used to assess ozone-formation contributions under actual atmospheric conditions, the nonlinear and model-based methods in Section 4.5 should also be considered.

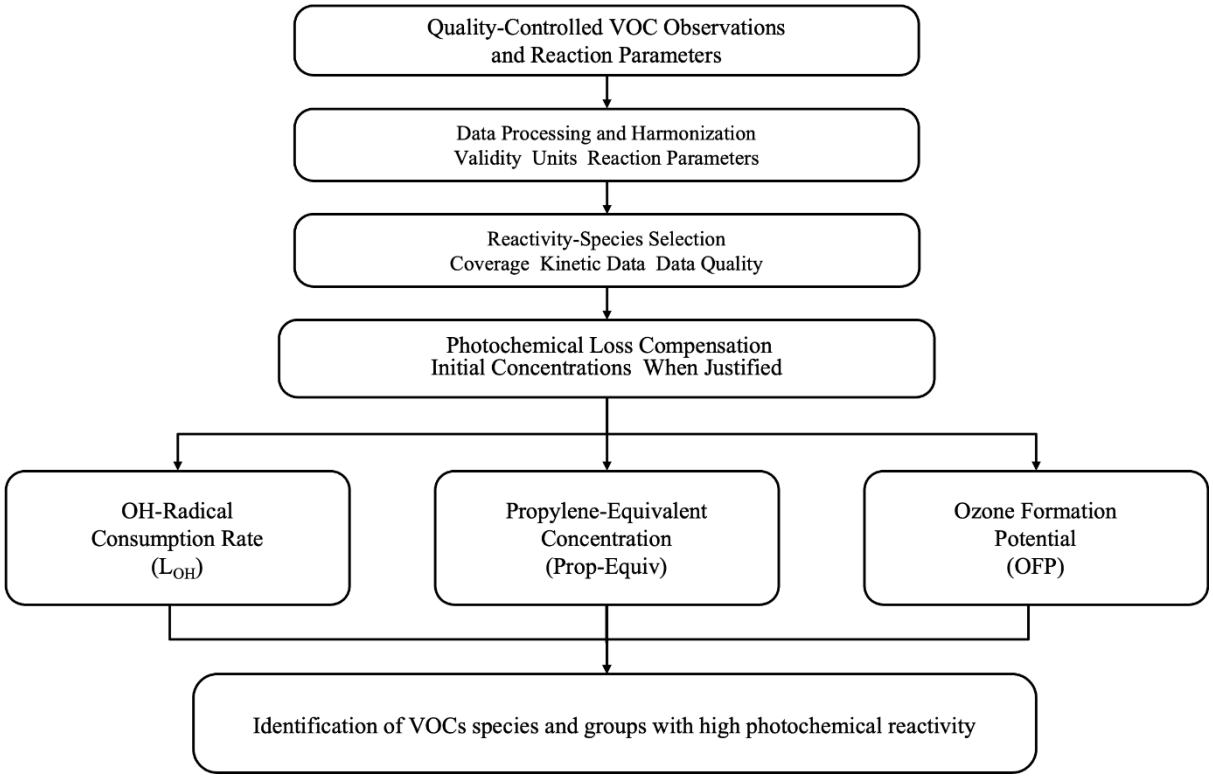


Figure 4.4 Workflow for photochemical reactivity analysis of ambient air VOCs

4.4.2 Data Processing Methods for Photochemical Reactivity Analysis

Data processing for photochemical reactivity analysis is the prerequisite for conducting reactivity evaluations. Work primarily encompasses the following links.

Clarify the data sources and time resolutions of VOC concentration data utilized for reactivity analyses

Online continuous monitoring data (such as online GC-MS/FID systems, typically with 1-hour resolution) and offline sampling analysis data (such as SUMMA canister sampling-GC-MS methods, DNPH derivatization-HPLC methods, etc.) are both applicable for reactivity analysis. Online data support hourly calculations of reactivity indicators (L_{OH}, Prop-Equiv, OFP, etc.), subsequently analyzing diurnal and seasonal variation characteristics of reactivity; offline data typically correspond to sampling periods ranging from several hours to 24 hours, yielding reactivity indicators representing average reactivity levels during sampling periods.

Perform quality control on concentration data

Eliminate outliers resulting from instrument faults, calibration biases, or sampling contamination. Detection rates should be calculated for each species over the monitoring period. Values below the method detection limit (MDL) must be handled according to a predefined method appropriate to the analytical objective and censoring fraction. Simple substitution with 1/2 MDL may be used only when justified, and sensitivity to the selected method should be evaluated. Species with low detection rates should be included or excluded based on data quality, analytical purpose, and sensitivity analysis, with the criteria and effects reported.

Harmonize concentration units

L_{OH} calculations require concentrations expressed in molecular concentrations (molecules/cm^3); OFP calculations require mass concentrations (μg/m^3); Prop-Equiv calculations utilize volume mixing ratios (ppbv). Conversion methods among units are detailed in Section 4.3.2.

Prepare reaction kinetic parameters for each species

Key parameters required for reactivity analysis include: reaction rate constants of each VOC species with $\cdot OH$ radicals (k_{OH}, units: $cm^3 \cdot molecule^{-1} \cdot s^{-1}$). When conducting ozone formation potential analyses, Maximum Incremental Reactivity coefficients (MIR, units: g O_3/g VOC) must also be prepared.

Primary data sources for k_{OH} values include the VOC-$\cdot OH$ reaction rate constant dataset compiled by Atkinson and Arey (2003), IUPAC chemical kinetics data evaluation reports, and NASA/JPL chemical kinetics data evaluation reports; MIR values primarily reference the updated MIR value database by Carter (2010), which covers nearly 600 VOC species. For species lacking measured k_{OH} or MIR values, Structure-Activity Relationship (SAR) methods can be adopted for estimation, calculating based on additive contributions of functional groups (such as C-H bonds, C=C double bonds, -OH groups) to total reaction rate constants. The k_{OH} and MIR values of each species must be listed in tabular format within analysis reports.

When the equation $OFP_i = MIR_i \times VOC_i$ (see Sections 4.4.7 and 4.5.2) is used, VOC_i must be expressed as a mass concentration ($\mu g/m^3$), and MIR_i must be expressed as the mass of additional ozone formed per unit mass of the VOC added (g O_3/g VOC). Each measured VOC species must be matched to the corresponding entry in a single, clearly identified MIR scale and chemical-mechanism version. The resulting OFP_i has units of $\mu g\ O_3/m^3$, and the total OFP for the measured species set is obtained by summing OFP_i across the included species. Concentrations used for comparison must have a consistent averaging period and measurement basis. For species without a published MIR value, substitution with the value of a structurally similar species should not be made unless the estimation method and its uncertainty are explicitly documented.

This calculation is applicable to screening and comparing the relative ozone-forming potentials of VOC species or chemical groups under a consistent reference framework. MIR values are model-derived incremental reactivities calculated for prescribed atmospheric mixtures and conditions selected to maximize the ozone response to an incremental VOC addition, generally representing NO_x-saturated (VOC-limited) conditions (Carter, 1994, 2010). Therefore, the product $MIR_i \times VOC_i$ is a theoretical ozone-formation-potential indicator; it is not an observed ozone concentration, a net ozone production rate, or an absolute source contribution. Linear summation of species-level OFP values also does not explicitly represent nonlinear chemical interactions or the effects of local NO_x levels, background VOC composition, photolysis, meteorology, dilution, transport, and photochemical loss. When actual ozone sensitivity or the effectiveness of precursor controls is being evaluated, MIR-based results should be interpreted together with observation-based box modeling or three-dimensional air quality modeling (see Sections 4.5.3 and 4.5.4).

Determine whether to perform photochemical loss compensation

Observed VOC concentrations in ambient air represent residual concentrations following photochemical reaction consumption; observed concentrations of highly reactive species (such as alkenes, reactive aromatics) may fall significantly below initial concentrations from emission sources. Calculating reactivity directly using observed concentrations may underestimate concentration levels and reactivities of high-reactivity species prior to photochemical consumption.

Based on data conditions, reactivity indicators may be calculated using both observed concentrations and photochemical initial concentrations (PIC), and the two sets of results may be compared to quantify the influence of photochemical consumption on reactivity evaluations. The calculation methods, applicability conditions, assumptions, and uncertainty requirements for photochemical-loss compensation are specified in Section 4.4.4.

4.4.3 Selection Principles for Reactivity Analysis Species

Ambient air VOC observation species typically encompass dozens to over a hundred compounds, yet

not all species need to be incorporated into photochemical reactivity analysis. Species selection directly impacts the accuracy and completeness of reactivity evaluation results, requiring adherence to the following principles.

- Inclusion of Reactive Non-Methane Organic Compounds: VOC species incorporated into reactivity analysis are non-methane organic compounds possessing clear atmospheric photochemical reactivities, including alkanes, alkenes, alkynes, aromatics, and oxygenated volatile organic compounds (OVOCs) participating in atmospheric photochemical reactions. Methane is excluded because this analysis focuses on non-methane organic compounds and because methane reacts with ·OH radicals much more slowly than most NMOCs (k_{OH}=6.4×10^{-15} cm^3 · molecule^{-1} · s^{-1} at 25°C), with an atmospheric lifetime of approximately 9–12 years; however, it should not be regarded as chemically inert.
- Exclusion and Inclusion of Halocarbons: Most halocarbon species (such as methyl chloride, dichloromethane, chloroform, carbon tetrachloride, 1,1,1-trichloroethane) possess extremely low photochemical reactivities, with MIR values close to zero or negative, and are typically omitted from reactivity analyses. However, a minor subset of halocarbons exhibit high reactivity, such as vinyl chloride (MIR=2.83 g O_3/g VOC) and 1,3-dichloropropene (cis MIR=3.70, trans MIR=5.03), and must be incorporated when environmental concentrations are elevated.
- Availability of Kinetic Parameters: Reaction rate constants with ·OH radicals (k_{OH}) and maximum incremental reactivity coefficients (MIR) are key parameters for screening active species. Species incorporated into photochemical reactivity analysis should possess concentration data meeting quality requirements alongside traceable reaction kinetic parameters. When conducting OH reaction reactivity analyses, incorporated species must possess reliable k_{OH} values; when conducting multi-oxidant loss analyses, corresponding parameters like k_{O3} should be supplemented according to research objectives; when conducting OFP analyses, incorporated species must also possess reliable MIR values. Species excluded owing to concentration data or parameter omissions must be listed with stated reasons. Reaction rate constant or MIR thresholds can be utilized for result categorization and sensitivity analysis.
- Data Quality Requirements: Species incorporated into reactivity analysis must satisfy data quality criteria. Detection rates should be calculated for each species over the monitoring period. Inclusion criteria and treatment of values below detection limits must be predefined according to the analytical objective, censoring fraction, and data quality; no universal 50% detection-rate threshold or 1/2-MDL substitution rule should be applied mechanically. Sensitivity analyses should be conducted when the treatment may affect species rankings or aggregate reactivity. Concentration data are applied to reactivity calculations only after quality control and documented treatment of invalid observations.
- Special Treatment for OVOCs: Special care is required when incorporating OVOC species. Formaldehyde (MIR=9.46), acetaldehyde (MIR=6.54), acetone (MIR=0.36), butanone (MIR=1.48), methyl vinyl ketone/MVK (MIR=9.65), and methacrolein/MACR (MIR=6.01) possess high photochemical reactivities and ozone formation potentials, serving as important active species. However, the complexity of OVOC sources (coexistence of primary emissions and secondary formation) renders their treatment in reactivity analyses unique. When calculating reactivity based on observed concentrations, observed OVOC concentrations encompass both primary emissions and secondary formation, reflecting the potential contribution of actually existing atmospheric OVOCs to O_3 formation. When conducting source-oriented reactivity analyses (such as evaluating O_3 formation contributions from

various emission sources), primary and secondary formation contributions of OVOCs must be differentiated (see Section 4.7.2 for details).

- The final list of species incorporated into reactivity analysis, alongside k_{OH} values, MIR values, and detection rates for each species, must be completely presented in tabular format within analysis reports to ensure traceability and reproducibility.

4.4.4 Photochemical Loss Compensation for Reactive VOC Species

Ambient-air VOC concentrations are residual concentrations after chemical loss during transport rather than direct measurements of initial source emissions. Reactive alkenes and aromatics may have atmospheric lifetimes of only several hours, so calculations based only on observed concentrations can systematically underestimate their pre-reaction concentrations and reactivities. When the required assumptions and data conditions are satisfied, photochemical-loss compensation may be used to reconstruct a photochemical initial concentration (PIC) and to evaluate how chemical decay affects the identification of key reactive species.

Under a first-order approximation in which VOC loss is dominated by reaction with OH, the concentration consumed during transport may be estimated as:

$$VOC_{i,consumed} = VOC_{i,t} \times \{exp(k_i[OH]\Delta t) - 1\} \quad (4\text{-}2)$$

where VOC_i,consumed is the concentration of species i consumed during transport; VOC_i,t is its observed concentration at receptor time t; k_i is its reaction-rate constant with OH (cm^3 $molecule^{-1}$ s^{-1}); [OH] is the OH-radical concentration (molecules cm^{-3}); and Δt is the reaction time (s). The product [OH]Δt is the OH exposure, commonly used as a measure of photochemical age.

OH exposure may be estimated from the ratio of two strongly co-emitted species B and C whose OH reaction-rate constants differ substantially. If C is the more reactive species, the relationship is:

$$[OH]\Delta t = \frac{ln(C/B)_0 - ln(C/B)_t}{k_C - k_B} \quad (4\text{-}3)$$

The selected pair should have a stable initial emission ratio and a sufficiently large difference in k_{OH}, preferably at least a factor of two. Common examples include m/p-xylene relative to ethylbenzene and 1,2,4-trimethylbenzene relative to benzene. The initial ratio $(C/B)_0$ may be obtained from a representative local source profile or from a justified high percentile of fresh-air observations, such as the 95th or 99th percentile. The choice of pair, initial ratio, percentile, and screening rules must be reported and tested for sensitivity.

The reconstructed photochemical initial concentration is calculated as:

$$PIC_i = VOC_{i,t} + VOC_{i,consumed} = VOC_{i,t} \times exp(k_i[OH]\Delta t) \quad (4\text{-}4)$$

When observations or defensible parameterizations of additional oxidants are available, loss by OH, O_3, and NO_3 may be considered together:

$$VOC_{i,consumed} = VOC_{i,t} \times \{exp[\sum_j k_{i,j}[Ox_j]\Delta t] - 1\} \quad (4\text{-}5)$$

where j represents the included oxidants, $k_{i,j}$ is the reaction-rate constant of species i with oxidant j, and $[Ox_j]$ is the oxidant concentration. An OH-only approach is generally appropriate when only VOCs and routine pollutant observations are available. A multi-oxidant approach is appropriate only when the additional kinetic parameters, photolysis information, and oxidant constraints are sufficiently complete and traceable. Results based on observed concentrations and PIC should be reported side by side.

Photochemical-loss compensation assumes a sufficiently coherent air mass, a representative and stable initial species ratio, limited fresh-emission input during transport, and adequately characterized oxidant exposure. These assumptions are often violated in urban areas. Nighttime OH exposure is especially uncertain and can produce negative or unrealistically large ages; nighttime data should therefore be treated separately or excluded, and reasonable upper bounds should be applied. PIC

results are approximate reconstructions rather than direct source concentrations, and their uncertainty must be evaluated through alternative species pairs, initial ratios, oxidant assumptions, and photochemical-age limits.

4.4.5 Reactivity Assessment Based on OH-Radical Consumption Rate (L_{OH})

The OH-radical consumption rate (L_{OH}), also termed VOC-related OH reactivity, is a direct kinetic indicator of how rapidly measured VOCs react with OH. It represents the contribution of VOCs to the atmospheric OH sink and the initiation of radical-propagation chemistry. A higher L_{OH} indicates faster consumption of OH and greater kinetic photochemical reactivity, but it does not by itself quantify ozone production.

The contribution of VOC species i is calculated as:

$$L_{OH,i} = k_{OH,i} \times [VOC_i] \quad (4\text{-}6)$$

where $L_{OH,i}$ has units of s^{-1}, $k_{OH,i}$ is the second-order reaction-rate constant with OH (cm^3 $molecule^{-1}$ s^{-1}), and $[VOC_i]$ is the molecular concentration (molecules cm^{-3}). When the measured concentration is reported in ppbv, it may be converted as:

$$[VOC_i] = C_i(ppbv) \times \frac{PN_A}{RT} \times 10^{-15} \quad (4\text{-}7)$$

where P is atmospheric pressure (Pa), N_A is Avogadro's constant, R is the ideal-gas constant, and T is air temperature (K). At 298.15 K and 101325 Pa, 1 ppbv is approximately 2.46×10^{10} molecules cm^{-3}. The total OH reactivity attributable to the measured VOC species is:

$$L_{OH,total} = \sum_i L_{OH,i} \quad (4\text{-}8)$$

Species-level L_{OH} values should be ranked to identify key reactive compounds, and class-level contributions should be calculated for alkanes, alkenes, aromatics, OVOCs, and other study-relevant groups. Concentration fractions and L_{OH} fractions should be compared because low-concentration species with high k_{OH} values can dominate reactivity. Diurnal, seasonal, episode, and inter-site variations in $L_{OH,total}$ and class contributions may be analyzed when data coverage is adequate.

If PIC is available, L_{OH} should be calculated using both observed and reconstructed concentrations to determine whether photochemical decay changes the ranking of key species or chemical classes. The reported quantity covers only the included VOCs; total atmospheric OH reactivity also includes CO, NO_2, CH_4, and unmeasured reactive compounds. L_{OH} is therefore a kinetic reactivity metric rather than a complete ozone-production metric. Its use within ozone-formation contribution assessment is described further in Section 4.5.2.

4.4.6 Reactivity Assessment Based on Propylene-Equivalent Concentration (Prop-Equiv)

Propylene-equivalent concentration (Prop-Equiv) expresses the OH reactivity of each VOC as the concentration of propylene that would produce the same OH reaction rate. The method places VOC species on a common and intuitive concentration scale and was introduced for comparing hydrocarbon reactivity in ambient air.

For VOC species i, Prop-Equiv is calculated as:

$$Prop-Equiv_i = C_i \times \frac{k_{OH,i}}{k_{OH,propylene}} \quad (4\text{-}9)$$

where C_i is the observed volume mixing ratio of species i (ppbv), $k_{OH,i}$ is its OH reaction-rate constant, and $k_{OH,propylene}$ is the OH reaction-rate constant of propylene, taken as 2.63×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K. Prop-$Equiv_i$ is the amount of propylene, in ppbv, required to provide the same OH reaction rate as the observed concentration of species i.

$$Prop-Equiv_{total} = \sum_i Prop-Equiv_i \quad (4\text{-}10)$$

Prop-Equiv and L_{OH} use the same concentration and k_{OH} information and are related by a constant conversion factor when consistent units and conditions are used. Consequently, they produce the same relative species ranking. Prop-Equiv is useful when a concentration-like unit is easier to communicate or compare directly with measured mixing ratios, whereas L_{OH} provides the physically direct first-order loss-rate unit.

Results should include species rankings, chemical-class contributions, concentration-versus-reactivity comparisons, and temporal or spatial patterns. When PIC is used, observed-concentration and compensated Prop-Equiv results should be reported together. Prop-Equiv describes relative OH kinetic reactivity; it does not represent an observed ozone concentration, a net ozone-production rate, or an absolute source contribution.

4.4.7 Reactivity Assessment Based on Ozone Formation Potential (OFP)

Ozone formation potential (OFP) combines the mass concentration of a VOC with its Maximum Incremental Reactivity (MIR) to compare relative ozone-forming potential under a consistent model-derived reference condition. Unlike L_{OH} and Prop-Equiv, which quantify reaction speed toward OH, OFP incorporates the modeled influence of the subsequent radical and NO-to-NO_2 reaction chain represented in the selected MIR scale.

For VOC species i, OFP is calculated as:

$$OFP_i = MIR_i \times C_i \quad (4\text{-}11)$$

where C_i is the mass concentration of species i (μg m^{-3}), MIR_i is the mass of additional ozone formed per unit mass of the VOC added (g O_3 g^{-1} VOC), and OFP_i has units of μg O_3 m^{-3}. The total for the included measured species is:

$$OFP_{total} = \sum_i \quad OFP_i \quad (4\text{-}12)$$

All species must be matched to one clearly identified MIR scale and chemical-mechanism version, and concentrations must use the same measurement basis and averaging period. Species without a published MIR value should be excluded or estimated only through a documented method with explicit uncertainty. The report must list the included species, concentration units, MIR values, data source and version, excluded species, and the effect of incomplete species coverage.

Species-level OFP values should be ranked, chemical-class contributions should be calculated, and concentration fractions should be compared with OFP fractions to identify compounds whose ozone-forming potential is disproportionate to their abundance. Temporal, episode, and spatial variations may be evaluated when the underlying concentration data are comparable. If PIC is available, OFP based on observed concentrations and PIC should be compared to quantify the influence of photochemical consumption on key-species identification.

MIR values are model-derived incremental reactivities for prescribed mixtures and conditions selected to maximize the ozone response to an incremental VOC addition, generally corresponding to NO_x-saturated, VOC-limited conditions. OFP is therefore a theoretical comparative indicator and must not be interpreted as an observed ozone concentration, a net ozone-production rate, or an absolute source contribution. Linear summation does not explicitly resolve nonlinear chemistry, local NO_x, background VOC composition, photolysis, meteorology, dilution, transport, or photochemical loss. When the objective is to assess actual ozone sensitivity, precursor-control regimes, or emission-reduction effectiveness, OFP results should be interpreted together with observation-based box modeling or three-dimensional air-quality modeling.

L_{OH}, Prop-Equiv, and OFP should be viewed as complementary. L_{OH} and Prop-Equiv describe OH kinetic reactivity and normally yield identical relative rankings when consistent inputs are used. OFP represents relative ozone-forming potential under the selected MIR framework. Agreement among the three metrics strengthens the identification of priority reactive species, whereas differences should be

explained through concentration, k_{OH}, MIR, species coverage, and photochemical-loss effects.

4.5 Contribution Assessment and Analysis Methods of Ambient Air VOCs to Ozone Formation

The assessment of ambient VOCs contributions to O_3 formation encompasses three primary components: (1) the ozone formation potential (OFP) analysis of VOCs species, groups and sectors; (2) the sensitivity analysis of O_3 formation to VOCs species, groups and sectors; and (3) the quantitative contribution analysis of VOCs groups, source regions, and sectors to O_3 formation. This assessment is primarily conducted based on observational data, observation-based models (OBM), and air quality model driven by emission inventories, with the objective of identifying the VOCs species, chemical groups, source regions, and sectors that rank highest in their contribution to O_3 formation.

4.5.1 Workflow

Based on the analytical framework for assessing the contribution of ambient VOCs to ozone formation, the following approaches are typically employed:

- **Hydroxyl Radical Consumption Rate and Ozone formation potential (OFP) calculations** can be performed using observational data alone to provide a rapid estimation of the potential contribution of VOC species, group**s** and sectors to ozone generation;
- **Observation-based models (OBM)** enable further analysis of ozone formation sensitivity and the relative contribution of VOCs species, groups and sectors to ozone production;
- **Three-dimensional air quality models** allow for comprehensive assessments of both ozone formation sensitivity and the contribution of VOCs emissions from different regions or sectors to ozone formation.

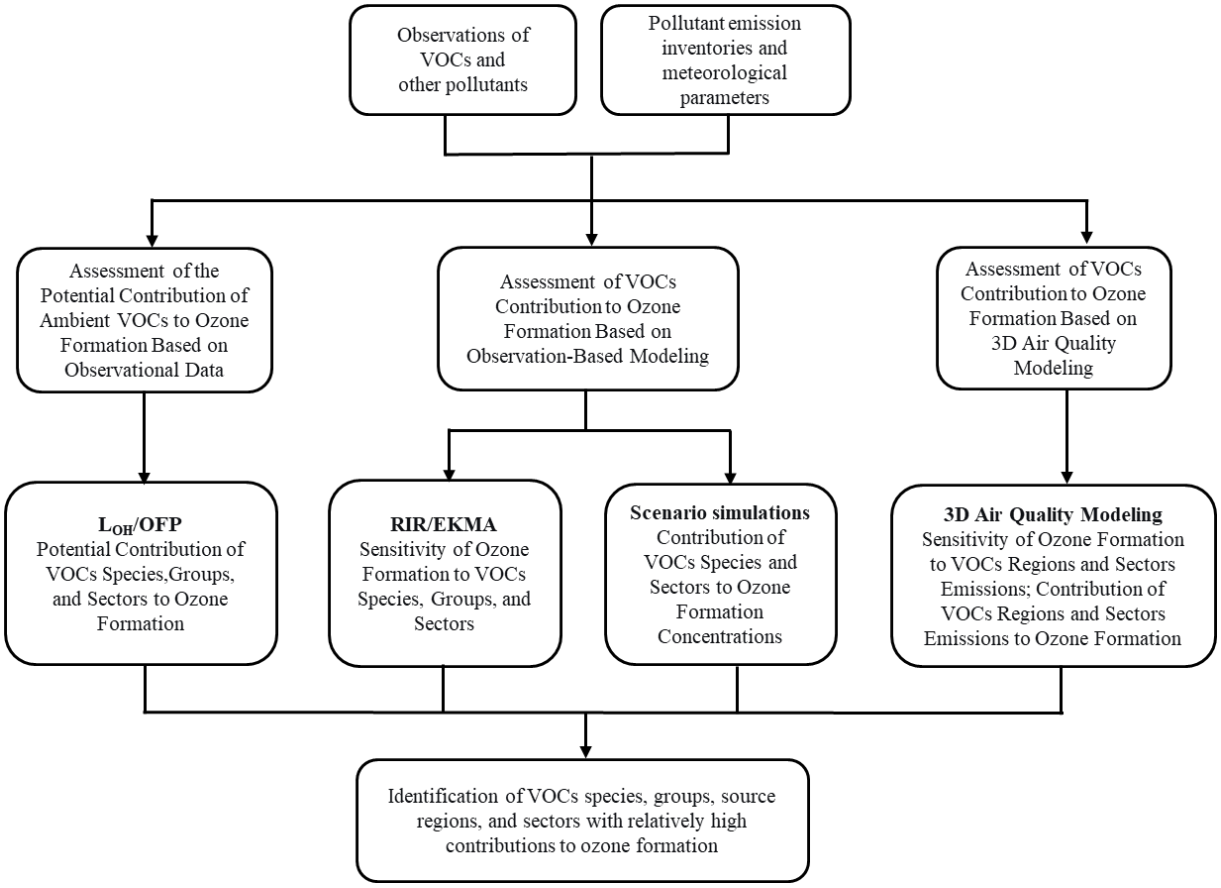


Figure 4.5 Workflow for Evaluating the Contribution of Volatile Organic Compounds to Ozone

Formation

4.5.2 Assessment of the Potential Contribution of Ambient VOCs to Ozone Formation Based on Observational Data

Potential Contribution of VOCs Species and Groups to Ozone Formation

Hydroxyl Radical Consumption Rate

VOCs react with OH radicals in the atmosphere to generate corresponding peroxy radicals ($RO_2 \cdot$). This reaction constitutes the rate-determining step for atmospheric ozone generation and contributes significantly to ozone formation.

Higher L_{OH} values indicate higher VOC reactivity and greater contributions to O_3 formation. Although this method cannot explain all atmospheric reaction processes in which measured species participate, it provides a simple indicator for studying the relative contributions of specific VOC species to daytime photochemical reactions. k_{OH} values for various VOCs are listed in the appendix. The L_{OH} calculation formula is expressed as:

$$L_{OH_i} = \sum \quad k_{OH,i} \times [VOC_i] \quad (4\text{-}13)$$

$$L_{OH_{group}} = \sum_i \quad L_{OH_i} \quad (4\text{-}14)$$

where:

- L_{OH}: Hydroxyl radical consumption rate (s^{-1});
- $k_{OH,i}$: OH radical reaction rate constant for the i-th VOC ($cm^3/molecule/s$);
- $[VOC_i]$: Concentration of the i-th VOC ($molecule/cm^3$).
- $L_{OH_{group}}$: Total L_{OH} of VOCs species by chemical groups.

Ozone Formation Potential (OFP)

The chemical reactivity calculated via the hydroxyl radical consumption rate method only applies to reactions between VOCs and OH, failing to estimate subsequent photochemical reaction processes. Incremental reactivity (IR) of VOCs refers to the change in O_3 concentration generated by adding or removing a unit of measured VOC within a given air mass. IR relates to the nature of the given air mass and the $VOCs/NO_x$ ratio; altering the $VOCs/NO_x$ ratio maximizes IR, yielding the Maximum Incremental Reactivity (MIR), at which point VOC species play their largest role in ozone formation. MIR serves as one of the important criteria for measuring VOC contributions to ozone formation. Ozone formation potential (OFP) can be calculated utilizing the maximum incremental reactivity (MIR) of VOCs to assess VOC contributions to ozone formation. MIR values for various VOCs are listed in the appendix. The OFP calculation formula is expressed as:

$$OFP_i = MIR_i \times VOC_i \quad (4\text{-}15)$$

$$OFP_{group} = \sum_i \quad OFP_i \quad (4\text{-}16)$$

where:

- OFP_i: Ozone formation potential ($\mu g/m^3$);
- MIR_i: Maximum incremental reactivity of the i-th VOC ($g\ O_3/g\ VOC$);
- VOC_i: Mass concentration of the i-th VOC ($\mu g/m^3$).
- OFP_{group}: Total OFP of VOCs species by chemical groups.

Potential Contribution of VOCs Sectors to Ozone Formation

Based on the results of VOCs source apportionment, L_{OH} and OFP for each source category were calculated using the contribution of each source factor to individual VOCs species concentrations, combined with the species-specific K_{OH} and MIR values. These

calculations were performed to evaluate the potential contribution of each VOCs source sector to ozone formation, and thereby to further identify the priority sectors for emission control.

$$\eta_{OFPj} = \frac{OFP_j}{\sum_{j=1}^{n} OFP_j} = \frac{\sum_{i=1}^{m} F_{ij} \cdot S_i \cdot MIR_i}{\sum_{j=1}^{n} OFP_j} \quad (4\text{-}17)$$

$$\eta_{L_{OH}j} = \frac{L_{OH_j}}{\sum_{j=1}^{n} L_{OH_j}} = \frac{\sum_{i=1}^{m} F_{ij} \cdot S_i \cdot K_{OH_{ii}}}{\sum_{j=1}^{n} L_{OH_j}} \quad (4\text{-}18)$$

Where m is the number of VOCs species, n is the number of source categories, F_{ij} is the fractional contribution of source category j to VOCs species i (%), S_i is the ambient concentration of species i. OFP_j represents the OFP of source j, η_{OFPj} denotes the percentage contribution of source j to the total OFP, L_{OH_j} represents the L_{OH} of source j, and $\eta_{L_{OH}j}$ denotes the percentage contribution of source j to the total L_{OH}.

4.5.3 Assessment of VOCs Contribution to Ozone Formation Based on Observation-Based Modeling

Utilizing the 0-D photochemical box model based on the MCMv3.3.1 mechanism (The Framework for 0-D Atmospheric Modeling, FOAM), relative incremental reactivity (RIR) can be calculated to analyze the sensitivity of O_3 formation to VOCs, and the characteristics of O_3 concentration variations under VOC changes can be further determined via EKMA curves. Additionally, OBM can quantify contributions of various VOC types and pollution sources to O_3 concentrations through scenario assumptions.

The detailed chemical mechanism of MCMv3.3.1 includes 17,224 reactions and 5,832 substances, containing more species and chemical reactions compared to other reaction mechanisms. Detailed kinetic and photochemical data applications in the model are available on the MCM website (http://mcm.leeds.ac.uk/MCM/).

Sensitivity of Ozone Formation to VOCs Species, Groups, and Sectors

Relative Incremental Reactivity (RIR)

Relative Incremental Reactivity (RIR) is defined as the ratio of the percentage change in the net formation rate (or generation amount) of secondary pollutants to the percentage change in the concentration (emission) of a specific species, and can be used to evaluate the contribution degree of specific VOC reductions to O_3 concentrations. When RIR values are positive, it indicates that reducing the concentration of that pollutant is beneficial to lowering O_3 concentrations; higher RIR values signify higher sensitivity and greater benefit for reducing O_3 concentrations. When RIR values are negative, reducing that pollutant is unfavorable for lowering O_3 concentrations.

RIR is obtained by running sensitivity experiments via OBM models. Model recommendations suggest setting precursor reduction proportions at 20%. Precursors typically must include NO_x, anthropogenic VOCs ($AVOCs$, abbreviated as AHC in models), and biogenic VOCs ($BVOCs$, abbreviated as BHC in models). To more accurately judge the sensitivity of O_3 formation to anthropogenic VOCs, AHC can be further subdivided into alkanes ($ALKA$), alkenes ($ALKE$), alkynes ($ALKY$), aromatics ($AROM$), and carbonyl compounds ($OVOCs$), allowing single VOC species simulations. The calculation formula is:

$$RIR(X) = \frac{\Delta PO_X(X)/PO_X(X)}{\Delta S(X)/S(X)} \quad (4\text{-}19)$$

Where X denotes a specific precursor. *P*Ox(X) represents the simulated net Ox formation rate. Δ*P*Ox(X) represents the change in net Ox formation rate after reducing precursor X. S(X) is the measured concentration of precursor X. ΔS(X) is the hypothetical change in X. Obviously, a higher positive value of RIR(X) indicates that reducing X can be more effective at reducing ambient O_3

pollution.

The VOCs sectors determined by the PMF were constrained into the 0-D box model to derive the RIR values of an individual sector, and these average RIR values were calculated as below:

$$\underline{RIR(X)} = \frac{\sum_{S}^{NS} [RIR(X) \cdot PO_X(X)]}{PO_X(X)} \quad (4\text{-}20)$$

Where X represents the VOC sector, and NS is the total number of RIR values of the sector.

Empirical Kinetic Modeling Approach (EKMA)

Empirical Kinetic Modeling Approach (EKMA) curves are widely applied to quantify non-linear response relationships of O_3 reduction to VOC and NO_x cuts. By establishing differing reduction scenarios for VOCs and NO_x in OBM models, running models to acquire O_3 concentrations or rates corresponding to each reduction scenario, O_3 formation iso-concentration/iso-rate curves are plotted against VOC and NO_x reduction percentages.

The connecting line of curve inflection points forms the ridge line.

- *Left of the Ridge Line:* Keeping NO_x concentrations constant while reducing VOC concentrations significantly lowers O_3 concentrations (O_3 formation is in the VOC-limited regime). Here, keeping VOC concentrations constant while reducing NO_x produces the adverse effect of increasing O_3 concentrations.
- *Right of the Ridge Line:* Keeping NO_x concentrations constant results in minor impacts on O_3 concentrations from changing VOC concentrations, whereas keeping VOC concentrations constant while decreasing NO_x concentrations leads to lower O_3 concentrations (O_3 formation is in the NO_x-limited regime).
- *Near the Ridge Line:* Reducing both VOC and NO_x concentrations effectively reduces O_3 concentrations (O_3 formation is in the collaborative VOC- and NO_x-controlled regime), making collaborative reductions at a certain proportion the most effective control strategy.

Contribution of VOCs Species and Sectors to Ozone Formation Concentrations

Input hourly observation data of O_3, NO_x, CO, PAMs, halocarbons, OVOCs, PAN, $HONO$, alongside meteorological variables (including NO_2 photolysis rate coefficients J_{NO_2}, temperature, atmospheric pressure, and humidity) into the model to calculate generated O_3 concentrations and define the baseline scenario.

Reduction scenario simulations are performed by eliminating specific VOC type concentrations. Simulated O_3 concentrations generated under these scenarios minus baseline scenario O_3 concentrations equal the contributions of those VOC types to O_3 formation.

According to PMF source apportionment results, reduction scenario simulations are conducted by eliminating single primary source VOC concentrations. Because certain VOCs are not captured by PMF, these excluded VOCs are reduced according to their concentration proportions within each source's respective components. CO and NO_x concentrations are reduced in combination with local emission inventories or in accordance with anthropogenic VOC concentration proportions across sources. O_3, PAN, and $HONO$ concentrations are scaled according to VOC reactivities (OFP and L_{OH}) apportioned across sources. These reduction measures aim to allocate each input parameter across diverse emission sources within OBM. Simulated O_3 concentrations under these scenarios minus baseline scenario O_3 concentrations represent the contributions of those pollution sources to O_3 formation.

4.5.4 Assessment of VOCs Contribution to Ozone Formation Based on 3D Air Quality Modeling

Sensitivity of Ozone Formation to VOCs Regions and Sectors Emissions

Sensitivity analysis techniques can be employed to investigate how ozone concentrations respond to changes in VOCs. By calculating sensitivity factors, the effectiveness of reducing VOCs emission sources on ozone abatement can be directly assessed, thereby establishing a quantitative relationship between ambient ozone concentrations and VOCs source emissions:

$$S_j = \frac{\partial C_{O_3}}{\partial p_j} \quad (4\text{-}21)$$

Where C_{O_3} represents the ambient ozone concentration, and p_j denotes different emission sources (which may originate from different regions or sectors).

The Decoupled Direct Method is a commonly used forward sensitivity analysis approach in air quality models. It computes semi-normalized sensitivity factors that intuitively indicate the effectiveness of ozone concentration reduction in response to emission source reductions. For instance, if $S_{O3j^*}>0$, it indicates that reducing emission source$_j$ effectively lowers ambient ozone concentrations; conversely, if $S_{O3j^*}<0$, it suggests that reducing source$_j$ is not only ineffective but may actually exacerbate ozone pollution.

$$S_{ij}^* = \tilde{p}_j \frac{\partial C_i}{\partial p_j} = \tilde{p}_j \frac{\partial C_i}{\partial (\epsilon_j \tilde{p}_j)} = \frac{\partial C_i}{\partial \epsilon_j} \quad (4\text{-}22)$$

where $\tilde{p}_j$ represents the baseline (original) emission rate of source j, and ϵ_j denotes the emission reduction fraction (with values ranging from 0 to 1).

The Brute-Force Method is another sensitivity analysis approach. It directly reduces ozone precursor emissions and compares the re-simulated ozone concentrations with those from the base-case simulation, thereby quantifying the sensitivity of ozone to precursor emissions. This method is widely used for evaluating emission reduction effectiveness under ozone control scenarios:

$$S = \frac{(O_3)_{reduction} - (O_3)_{base}}{E_{reduction} - E_{base}} \quad (4\text{-}23)$$

Contribution of VOCs Regions and Sectors Emissions to Ozone Formation

The Ozone Source Apportionment Technology employs a source-tagging approach to statistically attribute the contribution of VOCs from different regions and source categories to ozone formation. In ozone source apportionment, the model first determines whether ozone formation is NOx-limited or VOC-limited. If it is NOx-limited, the model traces the contribution of NOx emissions from different source regions or sectors to ozone formation at the receptor site (denoted as O_3 N), where $P(O_3)$ represents the tagged ozone production. If it is VOC-limited, the model traces the contribution of VOCs emissions from different source regions or sectors to ozone formation (denoted as O_3 V), while simultaneously incorporating the Mximum Incremental Reactivity (MIR) factors for different VOCs tracers to distinguish the reactivity of various VOC-tagged species.

$$O_3N_i^{new} = O_3N_i^{old} + PO_3 \times \frac{N_i^{old}}{\sum N_i^{old}} \quad (4\text{-}24)$$

$$O_3V_i^{new} = O_3V_i^{old} + PO_3 \times \frac{V_i^{old} \times MIR_i}{\sum V_i^{old} \times MIR_i} \quad (4\text{-}25)$$

4.6 Contribution Assessment Methods of Ambient Air VOCs to Secondary Organic Aerosol Formation

The assessment of the contribution of VOCs to SOA formation encompasses three components:

technical data acquisition, determination of key parameters, and comprehensive quantitative modeling. Through online observations or the development of emission inventories, ambient concentrations of VOCs and organic aerosol concentrations in particulate matter are obtained. Meanwhile, source profiles, emission amounts, and major emission sources of VOCs are characterized. On this basis, controlled smog chamber simulation experiments are conducted on these key VOCs, during which the SOA yield curves and formation coefficients of characteristic tracers over the oxidation processes are precisely determined to obtain critical parameters such as SOA yields. Ultimately, multiple assessment methods and models are employed to quantitatively apportion the contributions of different precursor species and even various emission sources to SOA, thereby identifying the VOC species and their sources that contribute most significantly to SOA formation.

4.6.1 Workflow

The assessment method system for the contribution of atmospheric VOCs to SOA formation comprises four parts:

- Environmental concentration/emission inventory analysis of SOA and its precursors;
- SOA formation potential calculation;
- SOA formation concentration calculation;
- Identification of key VOC species and sources.

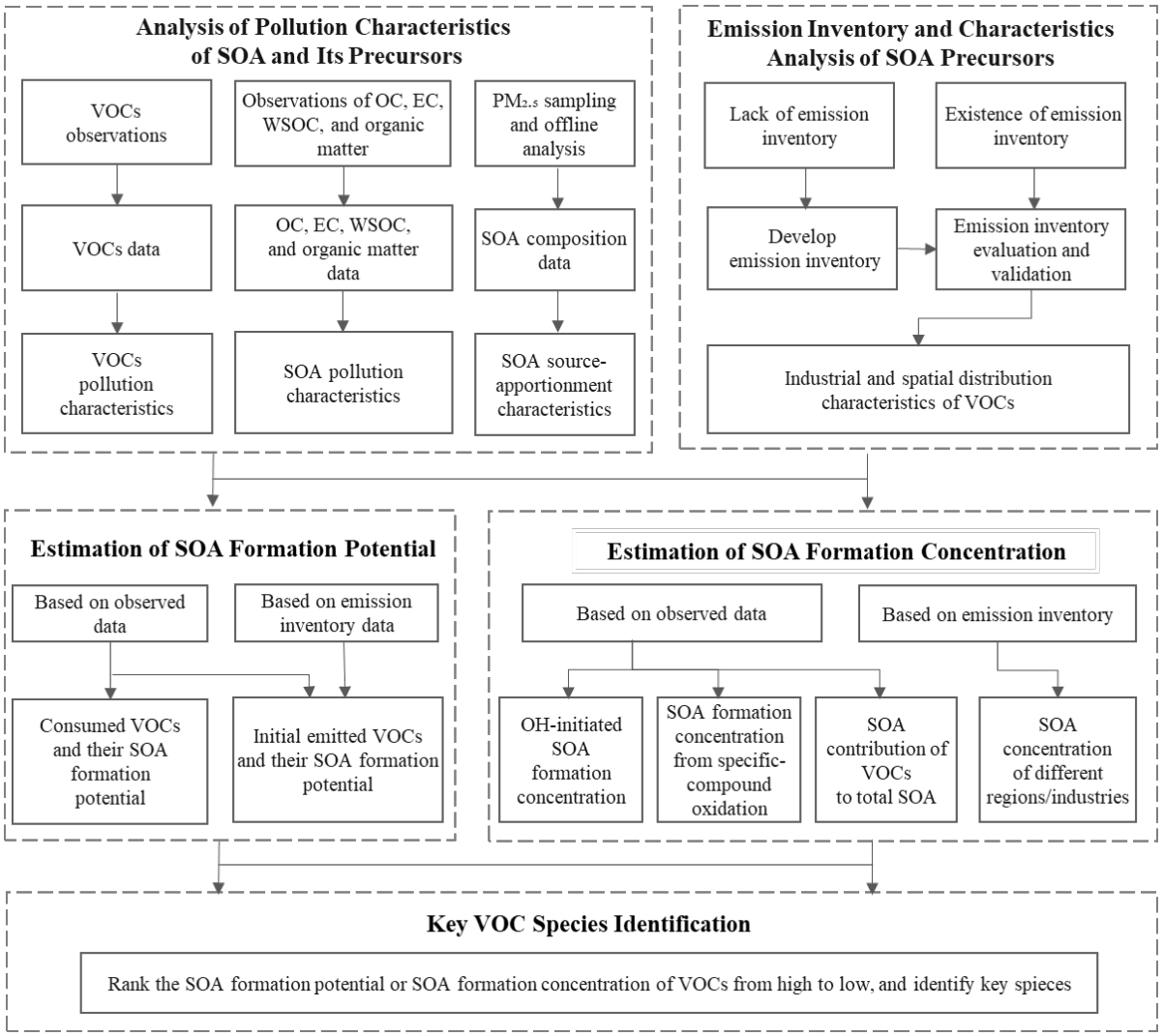


Fig. 4.6 Workflow for Assessing the Contribution of Ambient VOCs to Secondary Organic Aerosol Formation

4.6.2 Formation Potential Assessment

Aerosol Yield Coefficient Method

The fractional aerosol coefficient (FAC) method utilizes observed concentrations of precursors like VOCs to estimate secondary organic aerosol formation potential (SOAFP):

$$SOAFP = VOCs_0 \times FAC \quad (4\text{-}26)$$

$$VOCs_t = VOCs_0 \times \left(1 - F_{VOC,r}\right) \quad (4\text{-}27)$$

where $SOAFP$ is the SOA formation potential of a given species ($\mu g/m^3$); $VOCs_0$ and $VOCs_t$ are initial precursor concentrations emitted from pollution sources and residual measured concentrations of VOCs oxidized and consumed at receptor points ($\mu g/m^3$), respectively; FAC is the aerosol generation coefficient; $F_{VOC,r}$ is the percentage of VOC species participating in reactions. The FAC method offers simple calculations and wide application.

Yield Method

Based on monitored concentrations of VOCs, the yield method simultaneously achieves estimation of SOA formation potentials and formation concentrations. Estimating SOA formation potential requires first converting observed concentrations of VOCs into photochemical initial concentrations:

$$SOAP_i = HC_{i,0} \times Y_i \quad (4\text{-}28)$$

where $SOAP_i$ is the SOA formation potential of species i, $HC_{i,0}$ and Y_i are the photochemical initial concentration and SOA yield of species i, respectively.

Photochemical initial concentrations of VOCs can be calculated via formulas:

$$HC_{i,t} = HC_{i,0} \times exp\ exp\left(-k_i^{OH}\Delta t\right) \quad (4\text{-}29)$$

$$\Delta t = \frac{1}{[OH](k_C - k_B)} \times ln\ ln\left(\frac{[C]/[B]_{t=t_0}}{[C]/[B]_{t=t}}\right) \quad (4\text{-}30)$$

where $HC_{i,t}$ is the measured concentration of species i; k_i is the reaction rate constant of species i with OH radicals; $[OH]$ is the OH radical concentration; Δt is the photochemical reaction time of species i; k_B and k_C are reaction rate constants of species B and C with OH radicals, respectively; B and C form a pair of VOCs with similar sources yet significant discrepancies in OH reactivities; $([C]/[B])_{t=t_0}$ and $([C]/[B])_{t=t}$ are initial emission concentration ratios and observed concentration ratios at time t for B and C, respectively.

Calculated photochemical initial concentrations are significantly influenced by initial emission ratios of the aforementioned two species. Generally, concentration ratios of B and C within fresh plumes (NO_x/NO_y values $> 80\%$) can serve as initial emission ratios.

Estimation Methods Based on Emission Inventory Data

Utilizing emission inventory data of VOCs, SOA formation potentials for a precursor emitted by a pollution source can be calculated via formula:

$$SOAP_{i,j} = E_{i,j} \times Y_{SOA,j} \quad (4\text{-}31)$$

where $SOAP_{i,j}$ and $E_{i,j}$ are SOA formation potential and emission volume of species j from source i, respectively; $Y_{SOA,j}$ is the SOA yield of that species.

4.6.3 Formation Concentration Estimation

Yield Method

When the yield method estimates SOA concentrations generated by VOCs, observed VOC concentrations must first be converted into photochemically consumed concentrations, calculated via formulas:

$$SOA_i = HC_{i,consumed} \times Y_i \quad (4\text{-}32)$$

$$HC_{i,consumed} = HC_{i,t} \times exp\ exp\left(k_i^{OH}\Delta t - 1\right) \quad (4\text{-}33)$$

$$\Delta t = \frac{1}{[OH](k_C - k_B)} \times ln\ ln\ \left(\frac{[C]/[B]_{t=t_0}}{[C]/[B]_{t=t}}\right) \quad (4\text{-}34)$$

where SOA_i and $HC_{i,consumed}$ are generated SOA concentrations and photochemically consumed concentrations of species i, respectively.

Tracer-Yield Method

SOA species generated from specific VOC precursors can serve as SOA tracers for those precursors. The tracer-yield method calculates SOA concentrations based on smog chamber-derived SOA yields of specific VOCs and corresponding SOA tracer concentrations.

Current applications of this method primarily estimate SOA concentrations generated by aromatics, isoprene, monoterpenes, and sesquiterpenes. The calculation formula for the tracer-yield method is formula:

$$[SOA] = \sum_i \quad \frac{[tr_i]}{f_{soa,\,hc}} \quad (4\text{-}35)$$

where $[SOA]$ and $[tr_i]$ refer to generated SOA concentrations from a specific VOC precursor and concentrations of tracer i related to that precursor ($\mu g/m^3$), respectively; $f_{soa,\,hc}$ is the SOA mass fraction of that VOC precursor.

Organic Carbon to Elemental Carbon Ratio Method (OC/EC Ratio Method)

The OC/EC ratio method utilizes OC and EC concentrations in particulate matter to estimate secondary organic carbon (SOC) concentrations, subsequently yielding SOA concentrations. Based on the premise that "EC possesses solely primary sources and primary organic carbon shares sources similar to EC, calculations proceed via formulas:

$$SOC = TOC - OC_{pri} \quad (4\text{-}36)$$

$$OC_{pri} = EC \times \left(\frac{OC}{EC}\right)_{pri} \quad (4\text{-}37)$$

$$SOA = Coef_{SOA/SOC} \times SOC \quad (4\text{-}38)$$

where SOC, TOC, and EC are concentrations of secondary organic carbon, total organic carbon, and elemental carbon ($\mu g/m^3$), respectively; $(OC/EC)_{pri}$ is the primary pollution source OC/EC ratio; $Coef_{SOA/SOC}$ is the conversion coefficient from SOA to SOC, typically taking $1.4 - -1.6$ in urban anthropogenic pollution zones, and $1.8 - -2.2$ in biogenic and highly oxidized zones.

Non-Biomass Burning Water-Soluble Organic Carbon Method

Atmospheric WSOC divides into primary biomass burning emissions and secondary transformation generation; thus, measured total WSOC concentrations minus OC contributions from biomass burning can estimate SOC. Calculation formulas are:

$$SOC = WSOC - OC_{BB,w/o} \quad (4\text{-}39)$$

where $WSOC$ represents water-soluble organic carbon concentration in particulate matter ($\mu g/m^3$); OC_{BB} is OC concentration emitted from biomass burning, acquirable via chemical mass balance model simulations; $R_{w/o}$ represents the proportion of water-soluble components to total OC in biomass burning particles.

Aerosol Mass Spectrometer-Positive Matrix Factorization Method (AMS/ACSM-PMF Method)

Aerosol Mass Spectrometers (AMS) and Aerosol Chemical Speciation Monitors (ACSM) measure chemical composition and mass concentrations of non-refractory components in $PM_{2.5}$ online in real time—including organics, sulfates, nitrates, ammonium, and chlorides—with time resolutions reaching minutes. Based on high-time-resolution organic mass spectral matrices acquired via AMS or ACSM, combined with Positive Matrix Factorization (PMF) models (AMS/ACSM-PMF method), organic aerosol (OA) sources are quantitatively resolved.

Model Simulation Methods Based on Emission Inventory Data

Numerical simulation represents a core means to quantify VOC contributions to SOA on regional or global scales. Based on emission inventory data, this method quantifies SOA generation contributions from differing types and sources of VOCs. Common models include WRF-Chem, CMAQ, CAMx, and NAQPMS.

4.6.4 Combination of Multiple Methods

Current studies often combine multiple methods to comprehensively evaluate the contribution of VOCs to SOA formation, including the yield method, the tracer-yield method, and the OC/EC ratio method. These approaches, each offering a distinct perspective, are complementary. By comparing results obtained from different methods, researchers can identify key SOA precursor species and verify the consistency of their conclusions.

Although the key precursor species identified by these methods are generally consistent, the estimated total contributions often differ considerably. This is primarily attributable to the inherent limitations and uncertainties of each method: (1) The yield method only accounts for SOA formation from the reactions of VOCs with the OH radical, without considering reactions with other oxidants such as the NO_3 radical. In addition, it does not include SOA formation from VOCs via heterogeneous reactions. (2) The range of measurable VOCs is currently limited, and some precursors that can form SOA are not included in the yield calculation. Moreover, the yields used in the calculation are derived from smog chamber experiments, which may not fully represent the actual reaction conditions in the real atmosphere. (3) There are certain uncertainties in the calculation of photochemical consumption concentrations. (4) SOA can be generated not only from the oxidation of VOCs but also from the aging of primary organic aerosol (POA). (5) The OC/EC ratio method is based on the assumption that EC has only primary sources and shares similar sources with primary OC, and the associated uncertainty in the calculated results is approximately 10%–40%.

4.6.5 Comparative Analysis of Assessment Methods

Comparison of Methods for Estimating SOA Formation Potentials

Methods for assessing contributions of VOCs to SOA formation exhibit differing focuses owing to variations in principles and application scenarios. The FAC method and yield method represent two approaches for estimating SOA formation potential, both quantifying SOA contributions by simulating oxidation processes of single VOC species under controlled conditions; results are heavily influenced by experimental conditions, and extrapolations to real, complex atmospheric environments carry uncertainties.

Comparison of Methods for Estimating SOA Formation Concentrations

Methods for estimating SOA formation concentrations include observation-based estimation methods (yield method, tracer-yield method, OC/EC ratio method, WSOC method, and AMS/ACSM-PMF method) and emission inventory-based model simulation methods (air quality model method). While observation-based methods offer high temporal resolution, they are constrained by available measurement species and assumptions regarding background ratios. Numerical simulation methods provide spatial-temporal continuous distributions on regional scales yet remain sensitive to emission inventory accuracy and chemical mechanism completeness. Combining multiple methods represents the current mainstream approach to improve evaluation reliability.

Table 4.2 Advantages, Disadvantages, and Applicability of methods for estimating SOA formation potential

Method	Category	Output	Required conditions	Advantages	Disadvantages	Applicability
SOA formation yield method	Observation-based estimation method	SOA formation potential from VOCs ($\mu g/m^3$)	Ambient VOC concentrations and SOA yields of individual VOC species	Conceptually straightforward and physically meaningful; easy to calculate and widely applied	FAC values are derived from specific chamber experiments and may have uncertainties when extrapolated to real atmospheric conditions	Suitable for quantifying the SOA formation potential of specific VOCs under controlled conditions
Yield-based method	Observation-based estimation method	SOA formation potential from ambient VOCs ($\mu g/m^3$)	Initial concentrations of VOCs and SOA yields of different species	Quantify the SOA formation potential of various compounds	Experimentally measured yield parameters remain uncertain; initial calculations are based on assumptions of OH-initiated reactions and may neglect the contributions of NO_3 radicals and O_3	
	Emission inventory-based estimation method	SOA formation potential from emitted VOCs (Gg/yr)	Emission quantities of VOCs from pollution sources, and SOA yields of individual species			

3921
3922 **Table 4.3 Advantages, Disadvantages, and Applicability of methods for estimating SOA concentration**

Method	Category	Output	Required conditions	Advantages	Disadvantages	Applicability
Yield-based method	Observation-based estimation method	SOA concentration generated from specific VOC precursors (μg/m^3)	Ambient VOC concentrations and SOA yields of individual species	Quantifies SOA formation from different compounds	Uncertainties remain in experimentally determined yield parameters; assumptions based on OH radical reactions may neglect contributions from NO_3 radicals and O_3, resulting in potential underestimation	Suitable for quantifying SOA contributions from specific VOCs under atmospheric conditions
Molecular tracer-based method	Observation-based estimation method	SOA concentration derived from specific VOC precursors (e.g., isoprene, monoterpenes) (μg/m^3)	Specific SOA tracers and corresponding tracer-to-precursor conversion factors (derived from chamber experiments)	Directly based on environmental measurements; reflects atmospheric oxidation processes; enables quantitative assessment of contributions from different precursor sources	Depends on accurate identification of tracers; tracer-to-precursor conversion factors may vary with environmental conditions; only a limited number of precursor species can be quantified	Suitable for evaluating SOA contributions from specific VOC precursors

Method	Category	Output	Required conditions	Advantages	Disadvantages	Applicability
Organic carbon/elemental carbon ratio method	Observation-based estimation method	SOC and SOA concentrations (μg/m^3)	Particle-phase OC and EC concentrations; reliable primary OC/EC ratio; applicable SOA/OC conversion factor	Easy to apply with simple calculations; requires only observational data	Assumes EC originates exclusively from primary combustion sources and that primary OC/EC ratios remain constant; cannot distinguish SOA contributions from different precursors	Suitable for preliminary estimation of SOA concentrations and long-term observations
Non-biomass-burning water-soluble organic carbon method	Observation-based estimation method	SOC concentration (μg/m^3)	Particle-phase WSOC concentration; proportion of WSOC produced by secondary formation; contribution of biomass-burning water-soluble organic carbon (BB-WSOC)	Relatively simple method; reduces uncertainty caused by primary WSOC; suitable for long-term observations and regional analysis	Key assumptions may introduce large uncertainties; cannot fully separate SOA from primary sources and cannot identify specific precursors	Suitable for regional studies and monitoring of SOA levels
Aerosol mass spectrometer positive matrix factorization method	Observation-based estimation method	SOA concentration and contributions of different SOA components (e.g., SV-OOA/LV-OOA) (μg/m^3)	High-resolution ACSM or AMS mass spectra; PMF analysis model	Directly based on ambient observations without requiring experimental parameters; provides detailed	Requires specialized instruments and complex data analysis; PMF factor interpretation involves uncertainties; OA	Suitable for high-time-resolution characterization and source apportionment of SOA

Method	Category	Output	Required conditions	Advantages	Disadvantages	Applicability
				information on SOA composition and aging processes	sources may not be completely separated	
Air quality model simulation method	Emission inventory-based model method	Regional/global SOA concentration and contributions of different precursor species	Accurate emission inventories; high-resolution meteorological fields; chemical mechanisms describing SOA formation processes	Integrates emissions, transport, chemistry, and deposition processes; provides spatial and temporal distributions of SOA and evaluates precursor contributions	Simulation results strongly depend on emission inventories and chemical mechanisms; uncertainties exist in model parameterizations; different models may produce inconsistent results	Suitable for regional- and global-scale simulations of SOA concentrations and contributions from VOCs

3923

4.7 Sources Apportionment Methods for Ambient Air VOCs

Ambient volatile organic compound (VOC) source analysis aims to identify major VOC sources and qualitatively or quantitatively assess the contributions of different sectors and regions using ambient observations, chemical composition data, and atmospheric chemical transport modeling.

VOC source analysis mainly includes two approaches: observation-based source apportionment and three-dimensional air quality model-based analysis. These approaches can identify major sectoral and regional VOC sources, providing a scientific basis for targeted emission reductions in key sectors and regions and for air pollution control policies.

4.7.1 Workflow

Ambient VOC source analysis mainly includes the following two approaches:

- **Observation-Based Source Analysis Methods.** Based on observational data, qualitative source analysis, industrial source apportionment, regional source apportionment, and secondary source analysis of specific VOC species can be conducted.
- **Three-Dimensional Model-Based Source Analysis Methods.** Three-dimensional models can be used for industrial and regional source apportionment of VOCs.

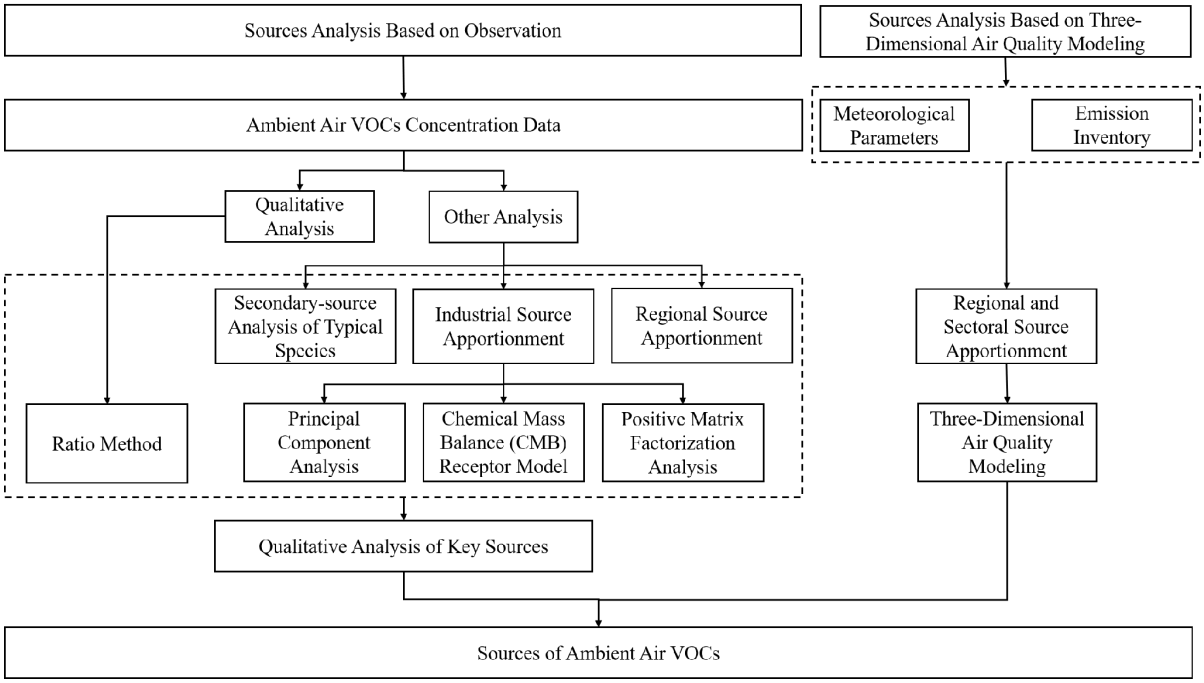


Figure 4.7 Workflow for Ambient Air VOCs Source Apportionment

4.7.2 Sources Analysis Methods for Ambient Air VOCs Based on Observation-Diagnostic ratios

Ratio methods

Different VOC emission sources are characterized by distinct VOC species or species profiles (ratios), which can be used for VOC source identification.

Table 4.4. Examples of Common VOCs Ratios and Their Indicated Sources

Ratio	Ratio Range	Indicated Sources/Significance
i-Pentane/n-Pentane	0.56–0.80	Coal combustion and biomass burning sources
	2.2–3.8	Vehicle exhaust emissions
	1.5–4.6	Fuel evaporation (gasoline/diesel evaporation)
	0.8–1.2	Oil and gas operations, natural gas, and ships
i-Butane/n-Butane	0.2–0.3	Vehicle exhaust
	≈0.46	Liquefied petroleum gas (LPG) evaporation
	0.6–1.0	Natural gas evaporation
Toluene/Benzene	<1	Diesel vehicle exhaust
	1–10	Other vehicle exhaust emissions
	>10	Solvent use and industrial emissions
m,p-Xylene/Ethylbenzene	<3	Aged air masses (long-range transport)
	>3	Fresh air masses (local emissions)
	2.5–2.9	Relatively fresh air masses (typical urban areas)

Observation-based source apportionment methods are currently the most widely used approaches for ambient VOC source analysis. They mainly include diagnostic ratio methods, Positive Matrix Factorization (PMF), and Chemical Mass Balance (CMB), which can be used for qualitative identification or quantitative apportionment of sectoral VOC sources. In addition, observational data can be used to quantitatively assess the secondary formation of representative VOC species and to qualitatively identify regional source contributions, thereby providing further insights into VOC chemical transformation and regional transport.

4.7.3 Sources Analysis Methods for Ambient Air VOCs Based on Observation-E**xploratory methods**+ Quantitative source apportionment **Industrial Source Apportionment**

Principal Component Analysis (PCA) methods

Principal component analysis (PCA) is a statistical receptor-based method that identifies major VOC sources through factor extraction, factor loading analysis, and variance contribution evaluation. Linking extracted factors with emission sources is a key step, relying on distinct VOC chemical profiles from different sources. VOC species are typically analyzed using SPSS, and a Kaiser–Meyer–Olkin (KMO) value above 0.6 indicates the reliability of PCA results.

Chemical Mass Balance (CMB) Model

- Basic Principle: The CMB model is a receptor model with known source profiles. Based on the principle of mass conservation, it utilizes the observed pollutant concentrations at the receptor and the source profile matrices of various pollution sources to calculate the contribution shares of each pollution source to the receptor point concentrations through the least squares method.
- Applicable Conditions: The prerequisite for applying the CMB model is that the representative source profiles (source profile library) of major pollution sources in the study area must be obtained in advance. Furthermore, the number of sources must be less than or equal to the number of measured species, and the sources must be independent of one another.

Positive Matrix Factorization (PMF) Model

The PMF model is a multivariate factor analysis method that does not require pre-determined source profiles, and it is widely applied in ambient air VOCs source apportionment.

- Basic Principle: The PMF model decomposes the source matrix X into a contribution matrix G, a source profile matrix F, and a residual matrix E. Its mathematical expression is:

$$X_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \quad \text{(4-40)}$$

Where X_{ij} is the concentration of the j-th species in the i-th sample; g_{ik} is the contribution of the k-th source to the i-th sample; f_{kj} is the content of the j-th species in the k-th source; and e_{ij} is the residual.

- Data Input and Preprocessing: The input data include the concentration matrix of each VOC species and its corresponding uncertainty. The calculation of uncertainty must consider the Method Detection Limit (MDL) and measurement errors. For missing data or values below the detection limit, $1/2 \times MDL$ is typically used as a replacement, assigned with a larger uncertainty.
- Model Execution and Factor Number Determination: By adjusting the number of factors p (usually trying values step-by-step from 3 to 8), the objective function Q values (including Q_{true} and Q_{robust}) and residual distributions under different factor numbers are examined. Combined with physical meanings and chemical characteristics (such as characteristic species of known sources), the optimal factor number and resolution results are selected.

Regional Source Apportionment

The HYSPLIT model is commonly applied to analyze air mass transport pathways and identify potential VOC source regions. Backward trajectory clustering reveals dominant transport directions, while PSCF and CWT analyses identify and quantify potential source areas. Higher WPSCF values indicate a higher probability of contributing to elevated VOC concentrations, whereas higher WCWT values represent stronger source contributions.

Secondary Source Analysis of Typical Species

A 0-D photochemical box model (FOAM) based on the MCM v3.3.1 mechanism can be used to perform scenario simulations. It can quantify the contributions of different precursor groups and primary emission sources to the secondary formation of representative carbonyl compounds.

The contribution of individual emission sources can be quantified as follows:

- Observational data, including VOCs, OVOCs, conventional air pollutants, J_{NO_2}, and meteorological parameters, are first introduced into the model. Model performance is evaluated by comparing simulated and observed O_3, and relevant model parameters are adjusted accordingly. The target carbonyl species are then sequentially excluded, and the model is run to estimate their secondary formation concentrations, denoted as $Base_i$.
- Source-removal scenarios are then constructed based on the PMF results. The contribution of each primary source to individual VOC species is sequentially removed. Concentrations of conventional pollutants and other VOC species are adjusted according to the PMF-derived source contribution fractions of total VOCs or source-profile information. The model is rerun to obtain the secondary formation concentration of each target species, denoted as $Source_i$. The difference between $Base_i$and $Source_i$ represents the contribution of the corresponding primary source to secondary formation.
- Finally, model performance for $Base_i$ and $Source_i$ is evaluated using statistical metrics such as the index of agreement (IOA), slope, and coefficient of determination (R^2).

The contributions of different VOC groups can be quantified using a similar approach. Specific VOC categories are sequentially excluded under hypothetical scenarios. The model is then run to obtain the secondary formation concentration of each target species, denoted as $VOCs_i$. The difference between

$Base_i$ and $VOCs_i$ represents the contribution of the corresponding VOC category to secondary formation. Model performance is subsequently evaluated for each species in different seasons.

Qualitative Analysis of Key Sources

Qualitative Analysis of Key Sources is a complementary approach that further identifies specific enterprises, key process stages, or critical material sources beyond conventional sector- or category-based source apportionment. It generally includes pollution-characteristic identification, potential-source screening, intensive monitoring and sampling, source–receptor relationship establishment, model-based source apportionment or emission-strength inversion, result validation, and identification of priority control targets. The objective is to establish quantitative relationships between ambient concentrations and specific emission sources, thereby providing a scientific basis for precise VOC control. According to the analytical target, refined source analysis can be divided into two technical pathways: enterprise-level source identification and process/material-level source identification.

4.7.4 Sources Analysis Methods for Ambient Air VOCs Based on Three-Dimensional Air Quality Modeling-Quantitative source apportionment

Three-dimensional air quality models (e.g., CMAQ and CAMx), combined with source apportionment techniques (e.g., OSAT), can quantitatively assess the contributions of different geographic regions, anthropogenic emissions from various sectors, and natural sources to VOC concentrations in a target area based on regional atmospheric transport processes and emission inventories.

Regional and Local Source Apportionment

Three-dimensional air quality models can integrate emission inventories, meteorological fields, and atmospheric chemical transport processes, and apply source tagging, source tracking, or sensitivity analysis to distinguish emissions from different regions and local sources and quantify their contributions to VOC concentrations in the receptor area. By defining source groups according to geographic region, emission sector, or source category, the relative contributions of regional transport and local emissions to VOCs can be quantitatively determined, thereby identifying the major regional and local sources of VOCs.

Local Industrial Source Apportionment

Three-dimensional air quality models can classify VOC emissions by sector or source category based on local emission inventories. Source tagging, source tracking, or sensitivity analysis can then be applied to separately characterize and simulate emissions from individual sectors and quantify their contributions to VOC concentrations in the receptor area. By comparing the modeled contributions of different source groups, the major local sectors contributing to ambient VOCs and their relative contributions can be identified.

4.8 Insights on Formulating Control Strategies Based on VOCs Data Findings

Based on the VOCs data analysis described above, the following insights can be obtained:

(1) The concentration levels, compositional characteristics, and spatiotemporal variations of VOCs, as well as their influencing meteorological factors.

(2) The atmospheric photochemical reactivity of VOCs and a list of VOC species with relatively high photochemical reactivity.

(3) The contribution of VOCs to ozone formation, including the ozone formation potential (OFP) of VOCs and the sensitivity of ozone formation (from the perspectives of both VOC species and their contributing industrial sectors).

(4) The contribution of VOCs to secondary organic aerosol (SOA) formation, including the SOA

formation potential of VOCs, the quantification of SOA concentrations derived from these precursors and their contributions to total SOA, and the identification of key VOCs species that significantly contribute to SOA formation.

(5) Source information of VOCs, including qualitative source identification, sectoral and regional source apportionment, secondary formation sources of typical VOC species, and refined source attribution of key VOC species (e.g., from specific industrial enterprises or production processes).

Based on the above insights, control strategy recommendations for VOCs can be proposed from the following aspects:

(1) Develop a priority VOCs control list by integrating the species with high concentration proportions and those with relatively high atmospheric photochemical reactivity. Combined with source apportionment results, recommendations can be made regarding the key VOC species, industrial sectors, and enterprises that require priority control from the perspective of VOCs reduction, as well as the regions with which joint prevention and control measures should be coordinated.

(2) Based on the diagnosis of ozone formation sensitivity and VOCs source apportionment results, propose recommendations for ozone pollution control—specifically, identifying the priority VOCs species, sectors, and enterprises to be regulated from the ozone control perspective, along with the regions requiring joint prevention and control.

(3) Based on the assessment of VOCs contributions to SOA formation and VOCs source apportionment results, propose recommendations for SOA pollution control—specifically, identifying the priority VOCs species, sectors, and enterprises to be regulated from the SOA control perspective, along with the regions requiring joint prevention and control.

5. Conclusion

VOCs play essential roles in atmospheric chemistry, serving as important precursors of ground-level ozone and secondary organic aerosols while also representing significant air pollutants in their own right. Reliable VOCs measurements are therefore indispensable for understanding atmospheric processes, identifying emission sources, evaluating emission control strategies, and supporting evidence-based air quality management.

This Technical Training Guidance has introduced several practical monitoring approaches that are suitable for different monitoring objectives and technical capacities within EANET participating countries. Off-line sampling techniques, including canister sampling, sorbent tube sampling, charcoal tube sampling, and passive sampling, provide flexible options ranging from detailed chemical speciation to cost-effective long-term monitoring. Online techniques such as photoionization detectors (PID) and differential optical absorption spectroscopy (DOAS) complement these methods by providing rapid screening or continuous observations under specific applications (Fig. 5.1 and Table 5.1). The guidance has also highlighted the importance of appropriate data evaluation, quality assurance, and quality control in ensuring reliable and comparable monitoring results.

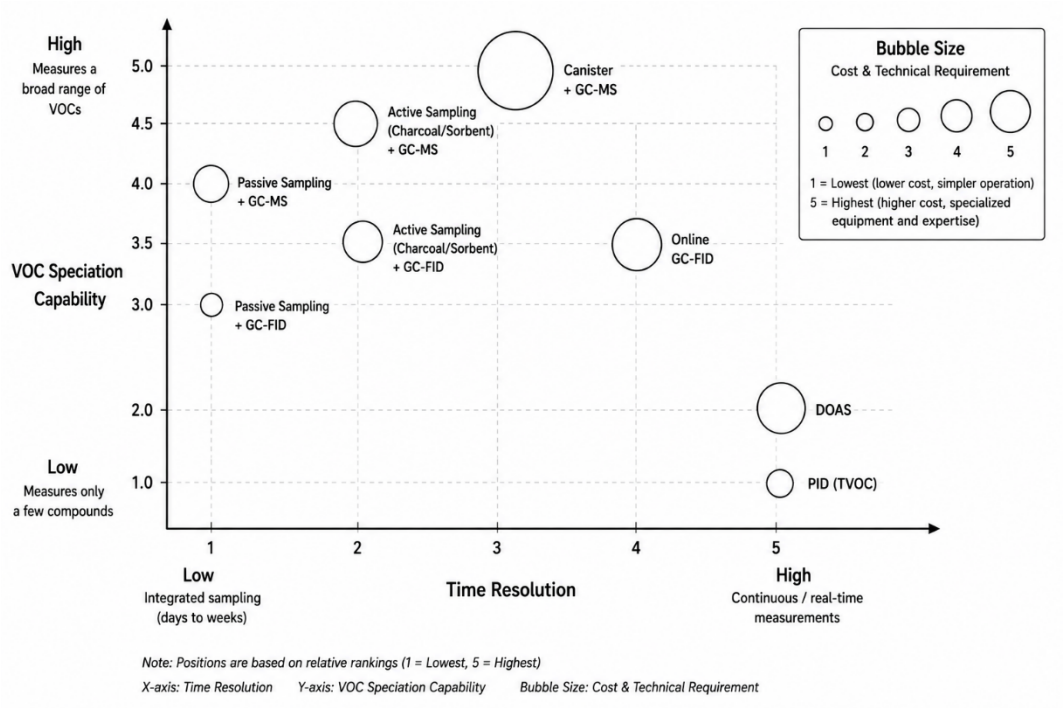


Figure 5.1 Comparison of VOC Monitoring Methods

Multiple VOCs sampling and measurement methods are available, each with different analytical capabilities, resource requirements, strengths, and limitations. Table 5.1 summarizes the principal methods covered in this guidance and their typical applications.

4116 **Table 5.1. Summary of VOCs Monitoring Methods, Analytical Performance, and Recommended Applications**

Method	Recommended Application	Target VOCs	Time Resolution	Typical LOD (pptv)	Strength	Limitation
Canister Sampling + GC-MS	Regulatory monitoring, source apportionment, ozone precursor studies, emission inventory validation	Broad range of VOCs	Minutes to 24 h	10-100	Comprehensive VOC speciation; high sensitivity; suitable for source apportionment and photochemical studies	High cost; requires specialized equipment and laboratory analysis
Sorbent Tube + TD-GC-MS	Routine ambient monitoring, source characterization, exposure assessment, industrial surveys	Wide range of VOCs depending on sorbent type	Hours to days	1-100	Good analytical performance; flexible sampling duration; lower cost than canisters	Potential breakthrough and sorbent limitations; requires thermal desorption and laboratory analysis
Charcoal Tube + Solvent Extraction (GC-FID or GC-MS)	Routine/Occupational monitoring, workplace exposure assessment, targeted VOC investigations	Selected VOCs	Hours	100-1000	Simple, established method; relatively low cost	Limited compound range; possible solvent-related uncertainties
Passive Sampler (Charcoal or Sorbent-Based)	Regional background monitoring, urban exposure assessment, health-risk studies, large-scale monitoring networks	Selected VOCs	Days to weeks	10-1000	Low cost; no power requirement; suitable for large monitoring networks	Low temporal resolution; limited species coverage
PID	Rapid screening, leak detection, emergency	Total VOCs (TVOCs)	Seconds	1000-10000	Rapid response; portable; useful for field	Cannot identify individual

Method	Recommended Application	Target VOCs	Time Resolution	Typical LOD (pptv)	Strength	Limitation
	response, site reconnaissance				screening	compounds; susceptible to interference
Online GC-FID	Ozone precursor monitoring, hydrocarbon trend analysis, continuous regulatory monitoring	Hydrocarbons and selected NMVOCs	Minutes to hourly	50-500	Continuous measurements; good quantification of hydrocarbon species; widely used in O_3 precursor monitoring	Limited compound identification capability compared with GC/MS
Online GC-MS	Advanced research, source apportionment, continuous VOC speciation	Broad range of VOCs	Minutes to hourly	1-50	Continuous speciation data; high analytical capability	High cost and maintenance requirements
PTR-MS	Real-time monitoring of reactive VOCs, atmospheric chemistry research, industrial process monitoring	Many oxygenated and reactive VOCs	Seconds to minutes	<1-100	Very high time resolution; highly sensitive	Expensive; limited compound separation and structural identification
DOAS	Fence-line monitoring, industrial emission studies, open-path monitoring	Selected gases (e.g., formaldehyde, benzene, toluene)	Minutes	100-1000	Open-path monitoring; no sample collection required	Limited target compounds; complex operation and data interpretation

4117

Because no single monitoring method is suitable for every application, the selection of monitoring techniques should be based on clearly defined monitoring objectives, target VOC species, required temporal resolution, available laboratory facilities, financial resources, and technical expertise. Countries initiating VOCs monitoring programs may begin with relatively simple and cost-effective approaches, such as passive sampling or sorbent tube sampling, and progressively expand their monitoring capabilities as technical capacity and analytical infrastructure develop. More advanced methods, including canister sampling combined with GC-MS analysis or continuous online monitoring systems, may be adopted when detailed source apportionment, photochemical studies, or high-temporal-resolution observations are required.

It should also be recognized that VOCs monitoring technologies continue to evolve rapidly. Emerging techniques, including online gas chromatography (GC) systems, proton-transfer-reaction mass spectrometry (PTR-MS), selected ion flow tube mass spectrometry (SIFT-MS), chemical ionization mass spectrometry (CIMS), and other real-time analytical methods, offer significant advantages in temporal resolution and measurement capability. Although these advanced technologies are beyond the scope of this guidance, they are expected to play increasingly important roles in atmospheric research, process studies, and comprehensive air quality monitoring in the future.

Finally, successful VOCs monitoring requires not only appropriate instrumentation but also well-defined monitoring objectives, standardized methodologies, robust quality assurance and quality control (QA/QC), regular technical training, and sustained international cooperation. Considering the diverse technical capacities and available resources among EANET participating countries, a tiered monitoring strategy may provide a practical approach for progressively strengthening regional VOCs observations. Countries may begin with cost-effective passive monitoring for establishing basic monitoring networks, expand to active sampling for routine monitoring and source characterization, and further develop comprehensive monitoring capabilities at selected sites as technical capacity increases. Through continued collaboration, capacity building, and experience sharing, EANET participating countries can progressively improve the quality and coverage of VOCs observations while selecting monitoring methods that best meet their national objectives and circumstances.

References

Ahmed, W., Wilkinson, M., & Fowler, S. J. (2024). Generating pooled quality control samples of volatile organic compounds. *Journal of Breath Research*, 18(4).

Acid Deposition Monitoring Network in East Asia (EANET). (2022). *Technical Manual for Air Concentration Monitoring in East Asia (Second Edition)*. Niigata, Japan: Network Center for EANET, Asia Center for Air Pollution Research (ACAP).

Atkinson, R., & Arey, J. (2003). Atmospheric degradation of volatile organic compounds. *Chemical Reviews*, 103(12), 4605–4638. https://doi.org/10.1021/cr0206420

Bachelier, F., Mascles, M., McGillen, M. R., Amiet, J.-P., Grosselin, B., Bazin, D., & Daële, V. (2024). Development, optimization and validation of automated volatile organic compound data analysis using an on-line thermal desorption gas chromatograph with dual detection and application to measurements in ambient air. *Journal of Chromatography A*, 1735.

Blackline Safety. (2025). *Photoionization Detector (PID) Sensor: Technical Notes*. Manufacturer technical documentation.

Buzcu-Guven, B., & Fraser, M. P. (2008). Comparison of VOC emissions inventory data with source apportionment results for Houston, TX. *Atmospheric Environment*, 42(20), 5032–5043.

Carter, W. P. L. (1994). Development of ozone reactivity scales for volatile organic compounds. *Journal of the Air & Waste Management Association*, 44(7), 881–899. https://doi.org/10.1080/1073161X.1994.10467290

Carter, W. P. L. (2010). *Updated Maximum Incremental Reactivity Scale and Hydrocarbon Bin Reactivities for Regulatory Applications*. Final Report to the California Air Resources Board, Contract No. 07-339. University of California, Riverside.

Carter, W. P. L., & Atkinson, R. (1987). An experimental study of incremental hydrocarbon reactivity. *Environmental Science & Technology*, 21(7), 670–679. https://doi.org/10.1021/es00161a008

Carslaw, D. C., & Ropkins, K. (2012). openair—An R package for air quality data analysis. *Environmental Modelling & Software*, 27–28, 52–61. https://doi.org/10.1016/j.envsoft.2011.09.008

Chameides, W. L., Fehsenfeld, F., Rodgers, M. O., Cardelino, C., Martinez, J., Parrish, D., Lonneman, W., Lawson, D. R., Rasmussen, R. A., Zimmerman, P., Greenberg, J., Middleton, P., & Wang, T. (1992). Ozone precursor relationships in the ambient atmosphere. *Journal of Geophysical Research: Atmospheres*, 97(D5), 6037–6055. https://doi.org/10.1029/91JD03014

Chen, T., Zheng, P., Zhang, Y., Dong, C., Han, G., Li, H., Yang, X., Liu, Y., Sun, J., Li, H., Zhang, X., Li, Y., Wang, W., & Xue, L. (2022). Characteristics and formation mechanisms of atmospheric carbonyls in an oilfield region of northern China. *Atmospheric Environment*, 274, 118958.

European Commission. (2026). *Spatial Representativeness of Air Quality Sampling Points*. Brussels, Belgium: Directorate-General for Environment, European Commission.

European Environment Agency (EEA). (2024). *Monitoring Station Classifications and Criteria for Including Them in the EEA's Assessment Products*. Copenhagen, Denmark: European Environment Agency.

Gao, J., Zhang, J., Li, H., Li, L., Xu, L. H., Zhang, Y. J., & Chen, Y. Z. (2018). Comparative study of volatile organic compounds in ambient air using observed mixing ratios and initial mixing ratios taking chemical loss into account—A case study in a typical urban area in Beijing. *Science of the Total Environment*, 628–629, 791.

Gilman, J. B., Lerner, B. M., Kuster, W. C., & de Gouw, J. A. (2013). Source signature of volatile organic compounds from oil and natural gas operations in northeastern Colorado. *Environmental Science & Technology*, 47(3), 1297–1305.

Goldan, P. D., Kuster, W. C., Williams, E., Murphy, P. C., Fehsenfeld, F. C., & Meagher, J. (2004). Nonmethane hydrocarbon and oxy hydrocarbon measurements during the 2002 New England Air Quality Study. *Journal of Geophysical Research: Atmospheres*, 109(D21). https://doi.org/10.1029/2003JD004455

Grange, S. K., Carslaw, D. C., Lewis, A. C., Boleti, E., & Hueglin, C. (2018). Random forest meteorological normalisation models for Swiss PM10 trend analysis. *Atmospheric Chemistry and Physics*, 18, 6223–6239. https://doi.org/10.5194/acp-18-6223-2018

Grange, S. K., Lewis, A. C., & Carslaw, D. C. (2016). Source apportionment advances using polar plots of bivariate correlation and regression statistics. *Atmospheric Environment*, 145, 128–134. https://doi.org/10.1016/j.atmosenv.2016.09.016

Grosjean, D. (1992). In situ organic aerosol formation during a smog episode: Estimated production and chemical functionality. *Atmospheric Environment*, 26(6), 953–963.

Grosjean, D., & Seinfeld, J. H. (1989). Parameterization of the formation potential of secondary organic aerosols. *Atmospheric Environment*, 23(8), 1733–1747.

Gu, Y., Liu, B., Dai, Q., Zhang, Y., Zhou, M., Feng, Y., & Hopke, P. K. (2022). Multiply improved positive matrix factorization for source apportionment of volatile organic compounds during the COVID-19 shutdown in Tianjin, China. *Environment International*, 158, 106979.

Guo, H., Wang, T., & Louie, P. K. K. (2004). Source apportionment of ambient non-methane hydrocarbons in Hong Kong: Application of a principal component analysis/absolute principal component scores (PCA/APCS) receptor model. *Environmental Pollution*, 129(3), 489–498. https://doi.org/10.1016/j.envpol.2003.11.006

Harper, M. (2000). Sorbent trapping of volatile organic compounds from air. *Journal of Chromatography A*, 885, 129–151.

Health and Safety Executive (HSE). (2004). *MDHS 104: Sampling of Volatile Organic Compounds Using Diffusive Samplers*. Methods for the Determination of Hazardous Substances. Bootle, UK: HSE.

International Council for Harmonisation (ICH). (2005). *Q2(R1): Validation of Analytical Procedures: Text and Methodology*.

International Organization for Standardization (ISO). (2000). *ISO 16017-1:2000, Indoor, Ambient and Workplace Air—Sampling and Analysis of Volatile Organic Compounds by Sorbent Tube/Thermal Desorption/Capillary Gas Chromatography—Part 1: Pumped Sampling*. Geneva, Switzerland: ISO.

International Organization for Standardization (ISO). (2000). *ISO 16200-2:2000, Workplace Air Quality: Sampling and Analysis of Volatile Organic Compounds by Solvent Desorption/Gas Chromatography, Part 2: Diffusive Sampling Method*. Geneva, Switzerland: ISO.

International Organization for Standardization (ISO). (2001). *ISO 16200-1:2001, Workplace Air Quality: Sampling and Analysis of Volatile Organic Compounds by Solvent Desorption/Gas Chromatography, Part 1: Pumped Sampling Method*. Geneva, Switzerland: ISO.

International Organization for Standardization (ISO). (2003). *ISO 16017-2:2003, Indoor, Ambient and Workplace Air: Sampling and Analysis of Volatile Organic Compounds by Sorbent Tube/Thermal Desorption/Capillary Gas Chromatography, Part 2: Diffusive Sampling*. Geneva, Switzerland: ISO.

Ion Science. (2021). *Technical Article TA-01: What Is a PID?* and *Technical Article TA-02: PID Response Factors*. Manufacturer technical documentation.

IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation. *Evaluated Kinetic Data for Atmospheric Chemistry*. https://iupac-aeris.ipsl.fr/

Jacobs, M. I., Burke, W. J., & Elrod, M. J. (2014). Kinetics of the reactions of isoprene-derived hydroxynitrates: Gas phase epoxide formation and solution phase hydrolysis. *Atmospheric Chemistry and Physics*, 14(17), 8933–8946. https://doi.org/10.5194/acp-14-8933-2014

Kleindienst, T. E., Jaoui, M., Lewandowski, M., Offenberg, J. H., Lewis, C. W., Bhave, P. V., & Edney, E. O. (2007). Estimates of the contributions of biogenic and anthropogenic hydrocarbons to secondary organic aerosol at a southeastern US location. *Atmospheric Environment*, 41(37), 8288–8300.

Kumar, A., Sinha, V., Shabin, M., Hakkim, H., Bonsang, B., & Gros, V. (2020). Non-methane hydrocarbon (NMHC) fingerprints of major urban and agricultural emission sources for use in source apportionment studies. *Atmospheric Chemistry and Physics*, 20, 12133–12152.

Kwok, R. H. F., Baker, K. R., Napelenok, S. L., & Tonnesen, G. S. (2015). Photochemical grid model implementation and application of VOC, NOx, and O3 source apportionment. *Geoscientific Model Development*, 8, 99–114.

Lee, J., Lee, M., Chang, L., Shin, S.-A., Kim, K., Choi, Y., Lim, H., Choi, S.-D., & Lee, G. (2024). Assessment of VOC emission inventories in Seoul through spatiotemporal observations using passive and online PAMS measurements. *Atmospheric Environment*, 338, 120857.

Lei, L., Zhou, W., Chen, C., He, Y., Li, Z., Sun, J., . . . Sun, Y. (2021). Long-term characterization of aerosol chemistry in cold season from 2013 to 2020 in Beijing, China. *Environmental Pollution*, 268, 115952. https://doi.org/10.1016/j.envpol.2020.115952

Ling, Z. H., Zhao, J., Fan, S. J., & Wang, X. M. (2017). Sources of formaldehyde and their contributions to photochemical O3 formation at an urban site in the Pearl River Delta, southern China. *Chemosphere*, 168, 1293–1301. https://doi.org/10.1016/j.chemosphere.2016.11.140

Liu, X., Lyu, X., Wang, Y., Jiang, F., & Guo, H. (2019). Intercomparison of O3 formation and radical chemistry in the past decade at a suburban site in Hong Kong. *Atmospheric Chemistry and Physics*, 19(7), 5127–5145.

Liu, Y., Shao, M., Fu, L., Lu, S., Zeng, L., & Tang, D. (2008). Source profiles of volatile organic compounds (VOCs) measured in China: Part I. *Atmospheric Environment*, 42(25), 6247–6260.

Mann, H. B. (1945). Nonparametric tests against trend. *Econometrica*, 13(3), 245–259. https://doi.org/10.2307/1907187

McKeen, S. A., Liu, S. C., Hsie, E.-Y., Lin, X., Bradshaw, J. D., Smyth, S., & Blake, D. R. (1996). Hydrocarbon ratios during PEM-WEST A: A model perspective. *Journal of Geophysical Research: Atmospheres*, 101(D1), 2087–2109. https://doi.org/10.1029/95JD02733

Ministry of Ecology and Environment of the People's Republic of China. (2012). *GB 3095-2012 Ambient Air Quality Standards*. Beijing: China Environmental Press.

Ministry of Ecology and Environment of the People's Republic of China. (2018). *Technical Guideline for Source Apportionment of Ambient Ozone Pollution (Trial)* (Draft for Comments). Beijing: Ministry of Ecology and Environment.

Ministry of Ecology and Environment of the People's Republic of China. (2020). *HJ 1012-2020 Technical Guidelines for Monitoring Volatile Organic Compounds in Ambient Air*. Beijing: China Environmental Press.

Ministry of the Environment, Japan (MOEJ). (2019). *Manual for the Measurement of Hazardous Air Pollutants*. Tokyo, Japan: Ministry of the Environment, Japan.

Morino, Y., Ohara, T., Yokouchi, Y., & Ooki, A. (2011). Comprehensive source apportionment of volatile organic compounds using observational data, two receptor models, and an emission inventory in Tokyo metropolitan area. *Journal of Geophysical Research: Atmospheres*, 116, D02302.

Na, K., & Kim, Y. P. (2007). Chemical mass balance receptor model applied to ambient C2–C9 VOC concentration in Seoul, Korea: Effect of chemical reaction losses. *Atmospheric Environment*, 41(32), 6715–6728.

NASA Panel for Data Evaluation. *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 19*. JPL Publication 19-5. Jet Propulsion Laboratory, Pasadena, California.

National Institute for Occupational Safety and Health (NIOSH). (2003). *Method 1501: Hydrocarbons, Aromatic (Issue 3)*. In *NIOSH Manual of Analytical Methods (NMAM)* (4th ed.). Cincinnati, OH: NIOSH.

National Standard of the People's Republic of China for Ecological Environment. *HJ 759-202□ (Replacing HJ 759-2015). Ambient Air—Determination of Volatile Organic Compounds—Specially Prepared Canisters/Gas Chromatography-Mass Spectrometry (Draft for Comments).*

National Standard of the People's Republic of China for Ecological Environment. *HJ□□□—202□. Technical Specifications for Continuous Automated Monitoring of Volatile Organic Compounds in Ambient Air by Gas Chromatography (Draft for Comments).*

Ou, J., Huang, Z., Klimont, Z., Jia, G., Zhang, S., Li, C., Meng, J., Mi, Z., Zheng, H., Shan, Y., Louie, P. K. K., Zheng, J., & Guan, D. (2020). Role of export industries on ozone pollution and its precursors in China. *Nature Communications*, 11, 5492.

Parrish, D., Stohl, A., Forster, C., Atlas, E., Blake, D., Goldan, P., . . . de Gouw, J. (2007). Effects of mixing on evolution of hydrocarbon ratios in the troposphere. *Journal of Geophysical Research: Atmospheres*, 112, D10S34. https://doi.org/10.1029/2006JD007583

Platt, U., & Stutz, J. (2008). *Differential Optical Absorption Spectroscopy: Principles and Applications*. Heidelberg, Germany: Springer-Verlag.

RAE Systems / Honeywell. (2013). *Technical Note TN-106: Correction Factors, Ionization Energies, and Calibration Characteristics*. Manufacturer technical documentation.

RAE Systems, Inc. (2013). *ToxiRAE Pro PID User's Guide*. P/N G02-4008-000, Rev. C. Manufacturer technical documentation.

Ram, K., & Sarin, M. M. (2011). Day–night variability of EC, OC, WSOC and inorganic ions in urban environment of Indo-Gangetic Plain: Implications to secondary aerosol formation. *Atmospheric Environment*, 45(2), 460–468.

Robards, K., & Ryan, D. (2022). *Principles and Practice of Modern Chromatographic Methods* (2nd ed.). Amsterdam, Netherlands: Elsevier.

Sen, P. K. (1968). Estimates of the regression coefficient based on Kendall's tau. *Journal of the American Statistical Association*, 63(324), 1379–1389. https://doi.org/10.1080/01621459.1968.10480934

Song, S. K., Shon, Z. H., Kang, Y. H., Kim, K. H., Han, S. B., Kang, M., Bang, J. H., & Oh, I. (2019). Source apportionment of VOCs and their impact on air quality and health in the megacity of Seoul. *Environmental Pollution*, 247, 763–774.

Standardization Administration of China. (2019). *GB/T 37822-2019 Ambient Air Quality Monitoring Standard*. Beijing: China Standards Press.

Stein, A. F., Draxler, R. R., Rolph, G. D., Stunder, B. J. B., Cohen, M. D., & Ngan, F. (2015). NOAA's HYSPLIT atmospheric transport and dispersion modeling system. *Bulletin of the American Meteorological Society*, 96(12), 2059–2077. https://doi.org/10.1175/BAMS-D-14-00110.1

Tang, X. Y., Zhang, Y. H., & Shao, M. (2006). *Atmospheric Environmental Chemistry* (2nd ed.). Beijing: Higher Education Press.

Tay, H. C., Miller, A., Moseley, H. N. B., Beckley, L., & Pennell, K. G. (2025). Systematic quality assurance/quality control framework for a volatile organic compound real-time monitoring instrument, autonomous rugged optical multigas analyzer for VOCs. *ACS Omega*, 10(22), 22627–22636.

Tong, M., Zhang, Y., Zhang, H., Chen, D., Pei, C., Guo, H., Song, W., Yang, X., & Wang, X. (2024). Contribution of ship emission to volatile organic compounds based on one-year monitoring at a coastal site in the Pearl River Delta region. *Journal of Geophysical Research: Atmospheres*, 129(2), e2023JD039999.

United States Environmental Protection Agency (U.S. EPA). (1999). *Compendium Method TO-16: Long-Path Open-Path Fourier Transform Infrared Monitoring of Atmospheric Gases*. In *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (Second Edition). Cincinnati, OH: Center for Environmental Research Information, U.S. EPA.

United States Environmental Protection Agency (U.S. EPA). (1999). *Method TO-15: Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)*. In *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (Second Edition). Cincinnati, OH: Center for Environmental Research Information, U.S. EPA.

United States Environmental Protection Agency (U.S. EPA). (1999). *Method TO-17: Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling onto Sorbent Tubes*. In *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (Second Edition). Cincinnati, OH: Center for Environmental Research Information, U.S. EPA.

United States Environmental Protection Agency (U.S. EPA). (2017). *Field Guidance on the Use of Direct-Reading Photoionization Detectors for VOC Screening*. Washington, DC: U.S. EPA.

United States Environmental Protection Agency (U.S. EPA). (2017). *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Ambient Air Quality Monitoring Program* (EPA-454/B-17-001). Research Triangle Park, NC: U.S. EPA, Office of Air Quality Planning and Standards.

United States Environmental Protection Agency (U.S. EPA). (2018). *AERMOD Modeling System User's Guide*. Research Triangle Park, NC: U.S. EPA, Office of Air Quality Planning and Standards.

United States Environmental Protection Agency (U.S. EPA). (2018). *EPA Handbook: Optical and Remote Sensing for Measurement and Monitoring of Emissions Flux of Gases and Particulate Matter* (EPA-454/B-18-008). Research Triangle Park, NC: U.S. EPA.

United States Environmental Protection Agency (U.S. EPA). (2018). *PAMS Data Validation and Analysis Training Material*. Office of Air Quality Planning and Standards, Research Triangle Park, NC.

United States Environmental Protection Agency (U.S. EPA). (2019a). *Method 325A: Volatile Organic Compounds from Fugitive and Area Sources: Sampler Deployment and VOC Sample Collection*. Washington, DC: U.S. EPA.

United States Environmental Protection Agency (U.S. EPA). (2019b). *Method 325B: Volatile Organic Compounds from Fugitive and Area Sources: Sampler Preparation and Analysis*. Washington, DC: U.S. EPA.

United States Environmental Protection Agency (U.S. EPA). (2019c). *Technical Assistance Document for Sampling and Analysis of Ozone Precursors for the Photochemical Assessment Monitoring Stations Program* (Revision 2, EPA-454/B-19-004). Washington, DC: U.S. EPA.

United States Environmental Protection Agency (U.S. EPA). (2023). *Technical Assistance Document for Sampling and Analysis of Ozone Precursors for the Photochemical Assessment Monitoring Stations Program* (Revision 3). Research Triangle Park, NC: U.S. EPA.

United States Environmental Protection Agency (U.S. EPA). *40 CFR Part 53: Ambient Air Monitoring Reference and Equivalent Methods*. Code of Federal Regulations.

United States Environmental Protection Agency (U.S. EPA). *40 CFR Part 58, Appendix E: Probe and Monitoring Path Siting Criteria for Ambient Air Quality Monitoring*. Code of Federal Regulations.

United States Environmental Protection Agency (U.S. EPA). *40 CFR Part 60, Appendix A-7: Method 21: Determination of Volatile Organic Compound Leaks*. Code of Federal Regulations.

United States Environmental Protection Agency (U.S. EPA). *40 CFR Part 136, Appendix B: Definition and Procedure for the Determination of the Method Detection Limit*. Code of Federal Regulations.

Wang, G., Kawamura, K., Lee, S., Ho, K., & Cao, J. (2006). Molecular, seasonal, and spatial distributions of organic aerosols from fourteen Chinese cities. *Environmental Science & Technology*, 40(15), 4619–4625. https://doi.org/10.1021/es060291x

Wang, H., Wang, Q., Gao, Y., Zhou, M., Jing, S., Qiao, L., . . . Li, Y. (2020). Estimation of secondary organic aerosol formation during a photochemical smog episode in Shanghai, China. *Journal of Geophysical Research: Atmospheres*, 125(7), e2019JD032033. https://doi.org/10.1029/2019JD032033

Wang, P., Wang, T., & Ying, Q. (2020). Regional source apportionment of summertime ozone and its precursors in the megacities of Beijing and Shanghai using a source-oriented chemical transport model. *Atmospheric Environment*, 224, 117337.

Wang, Y., Jiang, S., Huang, L., Lu, G., Kasemsan, M., Yaluk, E. A., Liu, H., Liao, J., Bian, J., Zhang, K., Chen, H., & Li, L. (2023). Differences between VOCs and NOx transport contributions, their impacts on O3, and implications for O3 pollution mitigation based on CMAQ simulation over the Yangtze River Delta, China. *Science of the Total Environment*, 872, 162118.

Warneke, C., McKeen, S. A., De Gouw, J. A., Goldan, P. D., Kuster, W. C., Holloway, J. S., & Trainer, M. (2007). Determination of urban volatile organic compound emission ratios and comparison with an emissions database. *Journal of Geophysical Research: Atmospheres*, 112(D10), D10S47.

Woolfenden, E. (2010). Sorbent-based sampling methods for volatile and semi-volatile organic compounds in air. Part 1: Sorbent-based air monitoring options; Part 2: Sorbent selection and other aspects of optimizing air monitoring methods. *Journal of Chromatography A*, 1217, 2674–2684; 2685–2694.

Wu, R., & Xie, S. (2018). Spatial distribution of secondary organic aerosol formation potential in China derived from speciated anthropogenic volatile organic compound emissions. *Environmental Science & Technology*, 52(15), 8146–8156. https://doi.org/10.1021/acs.est.8b01269

Wu, X., Vu, T. V., Shi, Z., Harrison, R. M., Di, L., & Kuang, C. (2018). Characterization and source apportionment of carbonaceous PM2.5 particles in China—A review. *Atmospheric Environment*, 189, 187–212.

Yang, X., Xue, L., Wang, T., Wang, X., Gao, J., Lee, S., Blake, D. R., Chai, F., & Wang, W. (2018). Observations and explicit modeling of summertime carbonyl formation in Beijing: Identification of key precursor species and their impact on atmospheric oxidation chemistry. *Journal of Geophysical Research: Atmospheres*, 123(2), 1426–1440.

Yang, Y., Liu, B., Hua, J., Yang, T., Dai, Q., Wu, J., & Hopke, P. K. (2022). Global review of source apportionment of volatile organic compounds based on highly time-resolved data from 2015 to 2021. *Environment International*, 165.

Yuan, B., Hu, W. W., Shao, M., Wang, M., Chen, W. T., Lu, S. H., & Hu, M. (2013). VOC emissions, evolutions and contributions to SOA formation at a receptor site in eastern China. *Atmospheric Chemistry and Physics*, 13(3), 6631–6679.

Yuan, Q., Lai, S., Song, J., Ding, X., Zheng, L., Wang, X., & Zhong, L. (2018). Seasonal cycles of secondary organic aerosol tracers in rural Guangzhou, Southern China: The importance of atmospheric oxidants. *Environmental Pollution*, 240, 884–893.

Zhang, X., Bi, F., Li, M., Zhao, L., Zhang, H., Li, Y., Xue, L., Gao, R., Zhang, Y., Wang, X., Wu, Z., Wang, Z., Wang, W., & Li, H. (2025). Atmospheric carbonyls in urban Beijing in the summertime under the continuous implementation of clean air actions: Decreasing trends, source

apportionments and new insights for control strategies. *Journal of Cleaner Production*, 501, 145300.

Bao, J., Zhang, X., Wu, Z., Zhou, L., Qian, J., Tan, Q., Yang, F., Chen, J., Li, Y., Liu, H., Deng, L., & Li, H. (2025). Atmospheric carbonyl compounds are crucial in regional ozone heavy pollution: Insights from the Chengdu Plain Urban Agglomeration, China. *Atmospheric Chemistry and Physics*, 25, 1899–1916.

ANNEX A Principle of Photoionization Detection

Ionization by ultraviolet light

A PID draws sample air into an ionization chamber illuminated by an ultraviolet (UV) lamp. When a molecule (R) absorbs a photon (hν) whose energy exceeds the molecule's ionization energy (IE), an electron is ejected:

$$R + h\nu \rightarrow R^{+} + e^{-} \qquad \text{(A-1)}$$

The resulting ions and electrons are collected at a pair of biased electrodes, producing a small current that is proportional to the concentration of ionizable species in the sample; this current is amplified and displayed as a VOC concentration (Ion Science, 2021; Blackline Safety, 2025). The process is non-destructive, so the sample stream can, in principle, be passed to a downstream detector.

The fundamental selection rule is simple: a compound can be detected only if its ionization energy is lower than the photon energy of the lamp (Ion Science, 2021). For example, a 10.6 eV lamp can ionize benzene, toluene and the xylenes, and even hydrogen sulfide (IE ≈ 10.5 eV), but cannot ionize methane (IE ≈ 12.6 eV), ethane, carbon monoxide, carbon dioxide or water, all of which have higher ionization energies. This is why a PID does not respond to the major components of air and is largely insensitive to methane (Ion Science, 2021).

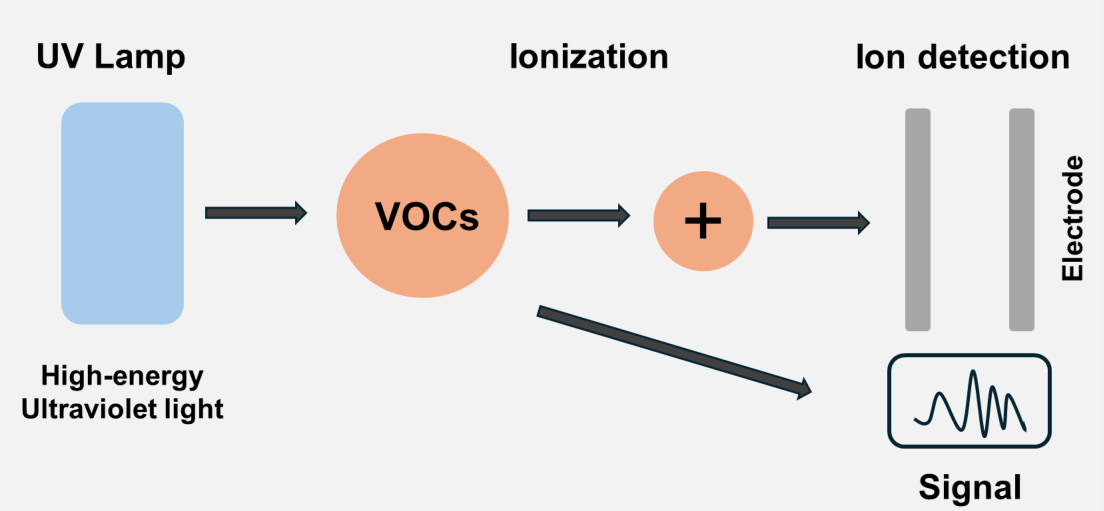


Figure A1 Operating principle of a photoionization detector: a UV lamp ionizes VOC molecules whose ionization energy is below the lamp photon energy; the resulting ions are collected at biased electrodes to give a current proportional to VOC concentration.

Because detectability is governed entirely by the ionization energy, it is useful to compare the ionization energies of typical VOCs and of the major air constituents against the common lamp energies. Table 1 lists representative values; a compound is detectable when its ionization energy lies below the lamp photon energy (Ion Science, 2021). Most target VOCs — aromatics, alkenes and many oxygenates — have ionization energies well below 10.6 eV and are readily detected, whereas

the bulk gases of air (N_2, O_2, CO_2, H_2O) and methane are not, which is what allows the PID to respond selectively to the VOC burden.

Table A1 Ionization energies of representative VOCs and major atmospheric constituents relevant to PID detection.

Species	Ionization energy (eV)
m-Xylene	≈ 8.56
Styrene	≈ 8.46
Toluene	≈ 8.83
Ethylbenzene	≈ 8.77
Benzene	≈ 9.24
1,3-Butadiene	≈ 9.07
Isobutylene (reference)	≈ 9.24
Acetone	≈ 9.70
Ammonia	≈ 10.07
Hydrogen sulfide	≈ 10.46
Ethanol	≈ 10.48
Methanol	≈ 10.85
Formaldehyde	≈ 10.88
Ethane	≈ 11.52
Methane	≈ 12.61
Water	≈ 12.62
Oxygen / Carbon dioxide / Nitrogen	12.1 / 13.8 / 15.6

The measured current is, over the instrument's working range, linearly proportional to the concentration of ionizable species, which is the basis for quantification; at very high concentrations the response saturates and becomes non-linear, and readings should then be treated as indicative only. Because ionization removes only a small fraction of the analyte, the technique is non-destructive (Ion Science, 2021).

Lamp energy and selectivity

Commercial PID lamps are available at several discrete photon energies, produced by different fill gases and window materials. The choice of lamp sets the range of compounds that can be seen and provides a degree of selectivity (Ion Science, 2021). Table A2 lists the common lamps.

Table A2 Common PID lamp energies, window materials, and characteristic selectivity.

Nominal lamp energy	Typical window	Notes
9.8 eV	—	Most selective; excludes many higher-IE compounds
10.0 eV	—	Intermediate selectivity
10.6 eV	MgF_2	Most common; long lamp life; broad VOC response
11.7 eV	LiF	Widest range; shorter lamp life; window degrades faster

The 10.6 eV lamp is the standard choice for general VOC monitoring because it combines broad response with long service life. An 11.7 eV lamp extends the range to some higher-IE compounds but has a markedly shorter lifetime and a window that degrades more quickly. A lower-energy lamp (9.8 eV) can be used to gain selectivity by excluding compounds with intermediate ionization energies (Ion Science, 2021).

ANNEX B Comparison of VOC Sampling Methods

1. Introduction

In this guidance, several offline sampling approaches are described, including canister sampling and active sampling using sorbent or charcoal tubes. Although each method has practical advantages, information on the comparability of these methods under actual ambient air conditions is useful for understanding their applicability and potential limitations.

As a preliminary evaluation to support the development of this guidance, parallel 24 h ambient air sampling experiments were conducted at the Center for Environmental Science in Saitama, Japan, during summer and winter. Three sampling approaches were compared during the summer experiment: canister sampling, active sorbent-tube sampling, and active charcoal-tube sampling. During the winter experiment, the same methods were evaluated together with an additional charcoal-tube condition using a higher sampling flow rate.

BTEX compounds were selected as representative VOCs for the comparison. Benzene, toluene, ethylbenzene, m,p-xylene, and o-xylene were evaluated separately.

The purpose of this preliminary experiment was to provide supporting information for the preparation of this guidance by (1) examining the agreement among the canister, sorbent-tube, and charcoal-tube sampling methods under ambient conditions; (2) evaluating whether differences among the methods varied among individual VOC compounds; and (3) examining possible seasonal differences in method performance. Because substantial seasonal differences were observed in the method comparisons, the summer and winter datasets were evaluated separately rather than pooled into a single combined analysis.

It should be noted that these experiments were preliminary and were conducted at a single monitoring site in Saitama, Japan. The degree of agreement among sampling methods may vary depending on local VOC composition and concentrations, meteorological conditions, sampling environment, and other site-specific or operational factors. Therefore, the results presented here should be regarded as reference information rather than as universally applicable performance criteria. Where appropriate, laboratories applying these methods are encouraged to conduct their own comparative evaluations under local conditions to confirm the suitability and comparability of the selected sampling methods.

2. Materials and Methods

2.1 Experimental design

Preliminary parallel ambient-air sampling experiments were conducted at the Center for Environmental Science in Saitama, Japan, to obtain supporting data for the development of this guidance. The experiments were performed during two seasons: summer, from late June to early July 2025, and winter, from mid-February to March 2026.

For each comparison experiment, all sampling methods were operated simultaneously. Sampling was started at the same time, and samples were collected after the same 24 h sampling period. This parallel sampling design minimized the influence of temporal variations in ambient VOC concentrations and allowed direct comparison of concentrations obtained for the same ambient air exposure period.

During the summer experiment, the following three sampling methods were compared:

1) canister sampling

2) active sorbent-tube sampling

3) active charcoal-tube sampling at 50 mL min^{-1}.

During the winter experiment, four sampling conditions were compared:

1) canister sampling;

2) active sorbent-tube sampling;

3) active charcoal-tube sampling at 50 mL min^{-1}

4) active charcoal-tube sampling at 80 mL min^{-1}

All sampling procedures followed the procedures described in this guidance.

2.2 Canister sampling

Ambient air was collected using 6 L canisters over a 24 h period. The nominal sampling flow rate was 3 mL min^{-1}.

The canister measurements were used as a common basis for comparison with the sorbent and charcoal tube measurements. However, the canister method was not assumed to represent an absolute true concentration. The results were therefore interpreted in terms of agreement and systematic differences among the sampling methods rather than in terms of accuracy relative to a certified reference value.

2.3 Active sorbent-tube sampling

Active sorbent sampling was conducted using Air Toxics sorbent tubes compatible with the sampling approach described for U.S. EPA TO-15A-related VOC measurements. Ambient air was actively drawn through each tube for 24 h at a flow rate of 6 mL min^{-1}.

2.4 Active charcoal-tube sampling

Active charcoal-tube sampling was conducted over 24 h at a flow rate of 50 mL min^{-1} in summer and at both 50 and 80 mL min^{-1} in winter. The two flow-rate conditions used in winter were compared to examine the effect of sampling flow rate on the measured VOC concentrations.

2.5 Target VOCs

BTEX compounds were selected as representative VOCs for the comparison. Benzene, toluene, ethylbenzene, m,p-xylene, and o-xylene were evaluated separately. Concentrations were expressed in µg m^{-3}.

2.6 Data pairing and quality control

Only samples collected over corresponding sampling periods were used for pairwise method comparisons. Measurements were matched using the sampling date or sample identifier so that concentrations obtained by two methods represented the same 24 h atmospheric sampling period.

Consequently, the number of paired observations varied among method comparisons depending on the availability of valid measurements. In the summer dataset, 10 paired observations were available for the canister–sorbent comparison, while up to 14 paired observations were available for the canister–charcoal comparison. For the winter experiment, 8–10 paired observations were generally available depending on the comparison.

Summer and winter observations were not pooled for the primary statistical analysis. Each season was evaluated independently because the magnitude and, in some cases, the direction of method-dependent differences varied substantially between seasons.

2.7 Statistical analysis

Method agreement was evaluated separately for each target compound and each season. For each pair of sampling methods, the concentration ratio (R) was calculated as:

$$R = C_B / C_A \quad \text{(B-1)}$$

where C_A and C_B represent the concentrations obtained by the two methods being compared. When the canister method was used as the comparison basis, a ratio of 1.0 indicated identical concentrations between the alternative method and the canister method. Ratios below 1.0 indicated lower concentrations using the alternative method, whereas ratios above 1.0 indicated higher concentrations.

The relative difference was calculated as:

$$\text{Relative difference (\%)} = (C_B - C_A) / C_A \times 100 \quad \text{(B-2)}$$

Because the number of paired observations was relatively small and normality could not be assumed for all compound-specific differences, systematic differences between paired sampling methods were evaluated using the two-sided Wilcoxon signed-rank test. Statistical significance was defined as $p < 0.05$. Associations between concentrations obtained using different methods were evaluated using Spearman's rank correlation coefficient (ρ).

The interpretation of method comparability was not based solely on statistical significance or correlation coefficients. Particular emphasis was placed on the magnitude of the median concentration ratio and relative difference because a strong correlation can occur even when one method shows a consistent positive or negative bias relative to another method.

For comparisons that were available in both seasons, seasonal differences in the distributions of method-to-method concentration ratios were evaluated using the two-sided Mann–Whitney U test. This analysis was used to examine whether the degree of agreement between sampling methods differed between the summer and winter experiments.

For the winter charcoal tube experiment, measurements obtained at 50 and 80 mL min^{-1} were additionally compared directly using paired concentration ratios and the Wilcoxon signed-rank test to evaluate the effect of sampling flow rate.

3. Results

3.1 Summer comparison

During the summer experiment, canister, sorbent-tube, and charcoal-tube sampling at 50 mL min^{-1} were compared using simultaneous 24 h samples. An overview of the concentration ratios relative to the canister method is shown in Fig. 1, and the statistical results are summarized in Table 1.

Figure 1 Summer comparison of VOC concentration ratios for the sorbent tube and charcoal tube (flow rate of 50 mL min^{-1}) methods relative to the canister method. A ratio of 1.0 indicates identical concentrations between the compared methods.

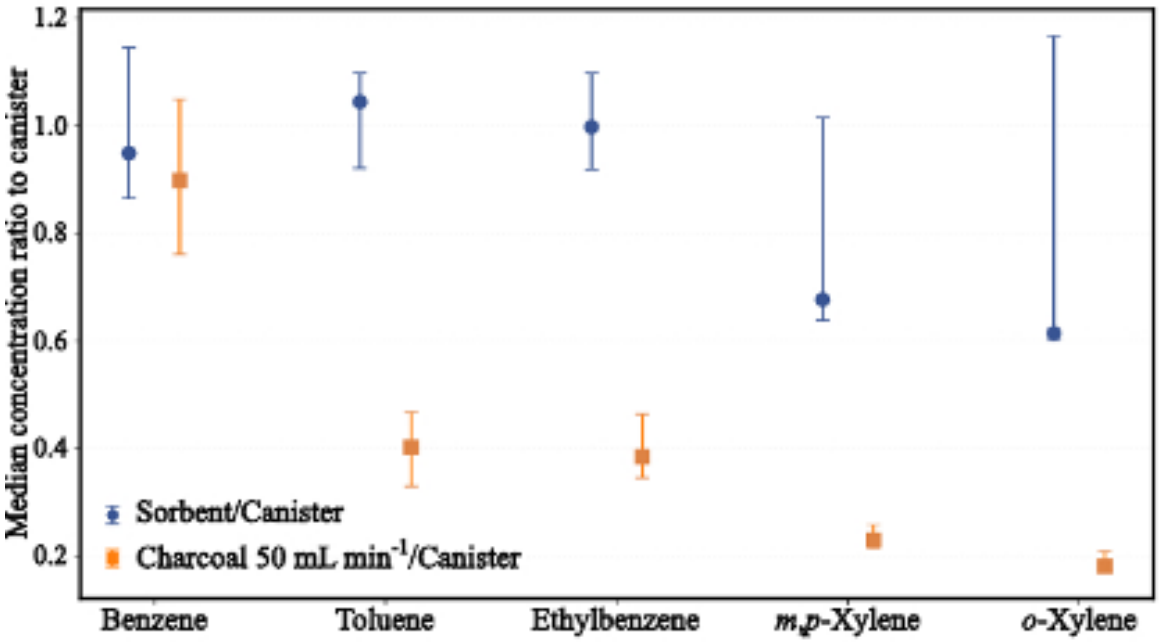


Figure B1 Summer comparison of VOC concentration ratios for the sorbent tube and charcoal tube (flow rate of 50 mL min^{-1}) methods relative to the canister method. A ratio of 1.0 indicates identical concentrations between the compared methods.

Table B1 Summary of comparisons with the canister method in summer.

Comparison[1)]	Compound	*n*	Median ratio	Median relative difference (%)	Spearman *ρ*	Wilcoxon *p*
Sorb/Cani	Benzene	10	0.949	−5.1	0.879	0.625
	Toluene	10	1.044	+4.4	0.964	0.922
	Ethylbenzene	10	0.998	−0.2	0.842	0.922
	m,*p*-Xylene	10	0.677	−32.3	0.818	0.037
	o-Xylene	10	0.614	−38.6	0.879	0.084
Char50/Cani	Benzene	14	0.898	−10.2	0.618	0.153
	Toluene	14	0.402	−59.8	0.789	<0.001
	Ethylbenzene	14	0.385	−61.5	0.886	<0.001
	m,*p*-Xylene	14	0.230	−77.0	0.873	<0.001

o-Xylene	14	0.181	−81.9	0.877	<0.001

1) Sorb/Cani, sorbent tube concentration divided by canister concentration; Char50/Cani, charcoal tube concentration at 50 mL min^{-1} divided by canister concentration.

3.1.1 Canister and sorbent tube methods

The sorbent tube method showed relatively good agreement with the canister method for benzene, toluene, and ethylbenzene (Fig. 1). The median sorbent/canister concentration ratios were close to 1.0 for these compounds, and no statistically significant differences were detected using the Wilcoxon signed-rank test (Table 1).

In contrast, lower concentrations were observed for the xylenes using the sorbent-tube method. The median sorbent/canister ratios were 0.677 for *m*,*p*-xylene and 0.614 for *o*-xylene, corresponding to median relative differences of −32.3% and −38.6%, respectively. The difference was statistically significant for *m*,*p*-xylene ($p = 0.037$), whereas the difference for *o*-xylene was not statistically significant at the 0.05 level ($p = 0.084$). Relatively high Spearman correlation coefficients were observed for all five compounds, ranging from 0.818 to 0.964.

Overall, the canister and sorbent-tube methods showed similar concentrations for benzene, toluene, and ethylbenzene in summer, whereas the sorbent-tube method produced lower concentrations for the xylenes.

3.1.2 Canister and charcoal tube methods

A different pattern was observed for the charcoal-tube method at 50 mL min^{-1} (Fig. 1). For benzene, the median charcoal/canister ratio was 0.898, corresponding to a median relative difference of −10.2%, and no statistically significant difference was observed. For toluene, ethylbenzene,

m,*p*-xylene, and o-xylene, however, the charcoal-tube concentrations were substantially lower than the canister concentrations. Median charcoal/canister ratios ranged from 0.181 to 0.402, corresponding to median relative differences of approximately −60% to −82% (Table 1). The differences were statistically significant for all four compounds ($p < 0.001$). Despite these large differences in concentration, relatively strong correlations were observed between the charcoal tube and canister measurements, with Spearman correlation coefficients ranging from 0.789 to 0.886 for these four compounds. The direct comparison between the sorbent and charcoal tube methods showed a similar pattern. Median charcoal/sorbent ratios were 0.353 for toluene, 0.391 for ethylbenzene, 0.348 for *m*, *p*-xylene, and 0.293 for *o*-xylene, with statistically significant differences for all four compounds ($p = 0.0039$).

These results indicate that the charcoal tube method produced substantially lower concentrations than the other two methods for toluene, ethylbenzene, and the xylenes under the summer sampling conditions.

3.2 Winter comparison

During the winter experiment, the canister and sorbent tube methods were compared together with charcoal tube sampling at 50 and 80 mL min^{-1}. The concentration ratios relative to the canister

method are shown in Fig. 2, and the statistical results are summarized in Table 2.

Figure B2 Winter comparison of VOC concentration ratios for the sorbent tube and charcoal tube methods relative to the canister method. Charcoal tube measurements at both 50 and 80 mL min^{-1} are shown. A ratio of 1.0 indicates identical concentrations between the compared methods.

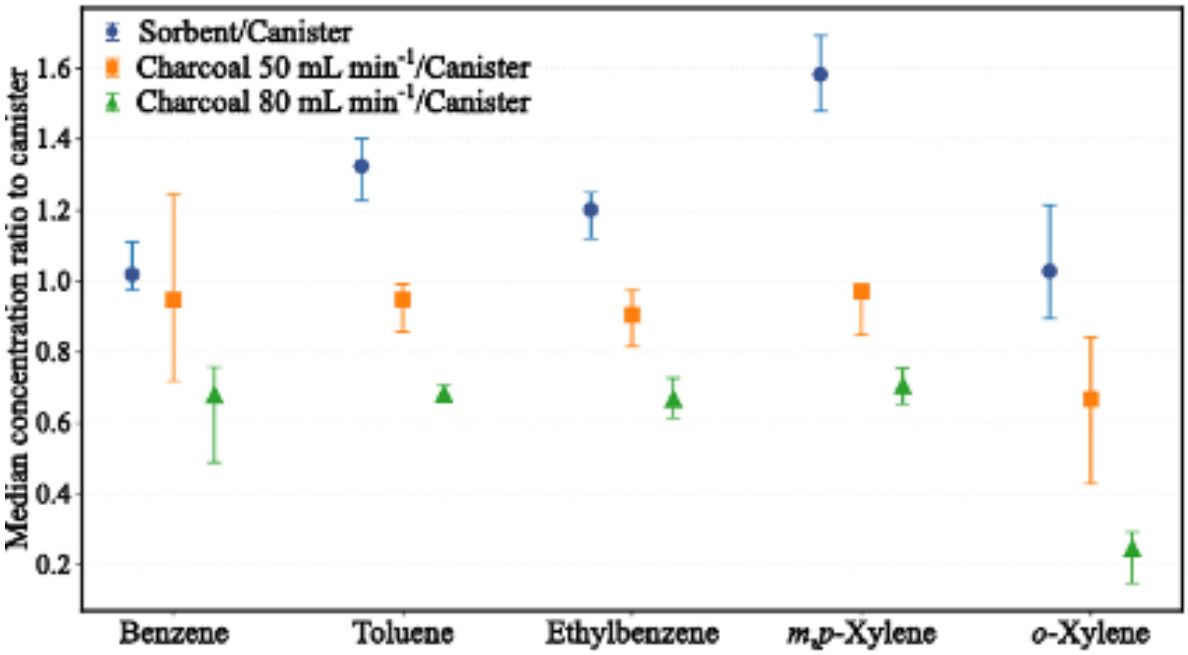


Figure B2 Winter comparison of VOC concentration ratios for the sorbent tube and charcoal tube methods relative to the canister method. Charcoal tube measurements at both 50 and 80 mL min^{-1} are shown. A ratio of 1.0 indicates identical concentrations between the compared methods.

Table B2 Summary of comparisons with the canister method in winter.

Comparison[1)]	Compound	*n*	Median ratio	Median relative difference (%)	Spearman ρ	Wilcoxon *p*
Sorb/Cani	Benzene	10	1.018	+1.8	0.830	0.275
	Toluene	10	1.324	+32.4	0.976	0.002
	Ethylbenzene	10	1.201	+20.1	0.976	0.002
	m,*p*-Xylene	10	1.582	+58.2	0.976	0.002
	o-Xylene	10	1.027	+2.7	0.939	0.432
Char50/Cani	Benzene	8	0.946	−5.4	0.262	0.461
	Toluene	8	0.947	−5.3	0.881	0.039
	Ethylbenzene	8	0.904	−9.6	1.000	0.023
	m,*p*-Xylene	8	0.971	−2.9	1.000	0.195

	o-Xylene	8	0.667	−33.3	0.952	0.0078
Char80/Cani	Benzene	8	0.676	−32.4	0.310	0.0078
	Toluene	8	0.679	−32.1	0.976	0.0078
	Ethylbenzene	8	0.665	−33.5	0.905	0.0078
	m,*p*-Xylene	8	0.702	−29.8	0.905	0.0078
	o-Xylene	8	0.243	−75.7	0.881	0.0078

1) Sorb/Cani, sorbent tube concentration divided by canister concentration; Char50/Cani, charcoal tube concentration at 50 mL min^{-1} divided by canister concentration; Char80/Cani, charcoal tube concentration at 80 mL min^{-1} divided by canister concentration.

3.2.1 Canister and sorbent tube methods

For benzene, the sorbent tube and canister methods showed close agreement, with a median sorbent/canister ratio of 1.018. No statistically significant difference was observed. For toluene, ethylbenzene, and *m*,*p*-xylene, the sorbent tube concentrations were higher than the canister concentrations. The median sorbent/canister ratios were 1.324, 1.201, and 1.582, respectively, corresponding to median relative differences of +32.4%, +20.1%, and +58.2% (Table 2). The differences were statistically significant for all three compounds. Strong correlations were observed between the two methods, with $\rho = 0.976$ for toluene, ethylbenzene, and *m*,*p*-xylene. For *o*-xylene, the median sorbent/canister ratio was 1.027, corresponding to a median relative difference of only +2.7%. No statistically significant difference was observed. Thus, although strong correlations were observed for most compounds, systematic differences in absolute concentrations were evident for toluene, ethylbenzene, and *m*,*p*-xylene.

3.2.2 Canister and charcoal tube methods at 50 mL min^{-1}

At 50 mL min^{-1}, the charcoal tube and canister methods showed relatively close agreement for benzene, toluene, ethylbenzene, and *m*,*p*-xylene during winter (Fig. 2). The median charcoal/canister ratios ranged from 0.904 to 0.971 for these four compounds. Although statistically significant differences were detected for toluene and ethylbenzene, their median relative differences were relatively small, at −5.3% and −9.6%, respectively. For o-xylene, a larger difference remained. The median charcoal/canister ratio was 0.667, corresponding to a median relative difference of −33.3%, and the difference was statistically significant.

3.2.3. Canister and charcoal tube methods at 80 mL min^{-1}

At 80 mL min^{-1}, charcoal tube concentrations were lower than the corresponding canister concentrations for all five compounds (Fig. 2). Median charcoal/canister ratios ranged from 0.665 to 0.702 for benzene, toluene, ethylbenzene, and *m*,*p*-xylene, corresponding to differences of approximately −30% to −34%. A particularly large difference was observed for o-xylene, for which the median ratio was 0.243. Statistically significant differences were observed for all five compounds (Table 2).

3.3 Effect of charcoal tube sampling flow rate in winter

The effect of charcoal tube sampling flow rate was examined by directly comparing simultaneous measurements conducted at 50 and 80 mL min^{-1} during winter (Fig. 3). For all five BTEX compounds,

concentrations obtained at 80 mL min⁻¹ were lower than those obtained at 50 mL min⁻¹. Median 80/50 concentration ratios were approximately 0.69–0.75 for benzene, toluene, ethylbenzene, and *m*,*p*-xylene, indicating reductions of approximately 25–31% (Table 3). A substantially larger difference was observed for *o*-xylene, for which the median 80/50 ratio was 0.329, corresponding to a median decrease of 67.1%. The differences between the two flow-rate conditions were statistically significant for all five compounds. Nevertheless, relatively strong correlations were observed between the two conditions, with Spearman correlation coefficients ranging from 0.817 to 0.950.

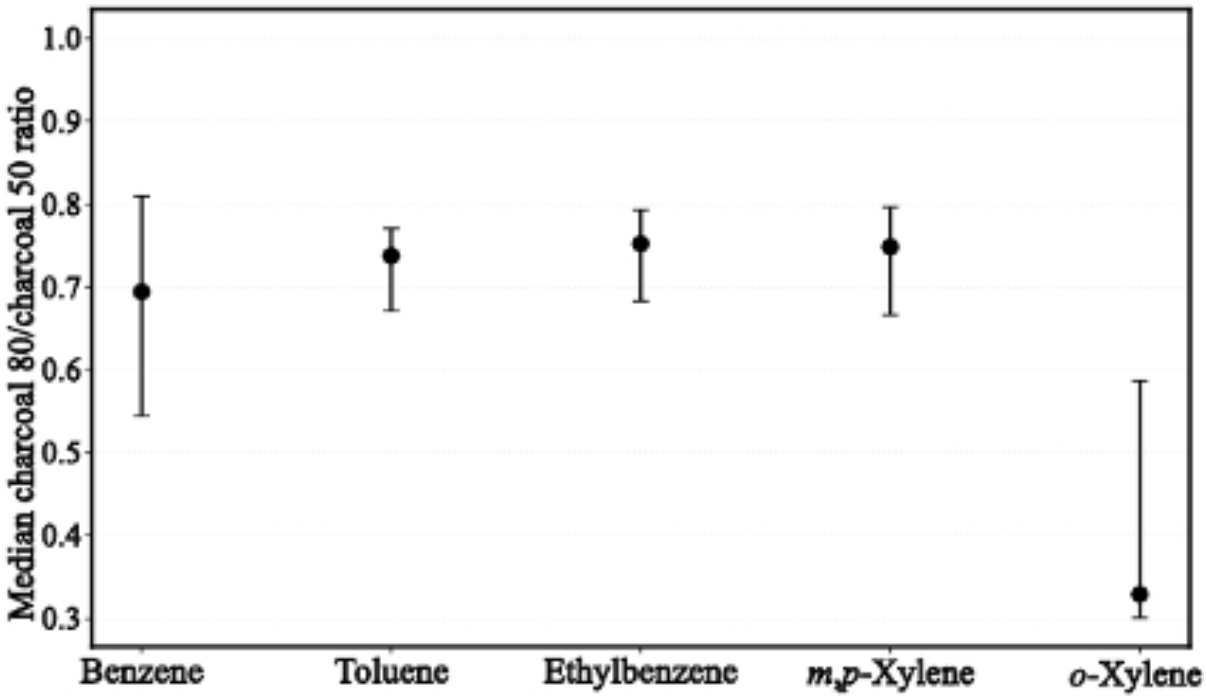


Figure B3 Comparison of charcoal tube measurements obtained at 80 and 50 mL min⁻¹ during winter. Ratios below 1.0 indicate lower concentrations at 80 mL min⁻¹.

Table B3 Summary of comparison of charcoal tube sampling at 50 and 80 mL min⁻¹ in winter.

Compound	*n*	Median 80/50 ratio	Median difference (%)	Spearman *ρ*	Wilcoxon *p*
Benzene	9	0.694	−30.6	0.817	0.0039
Toluene	9	0.738	−26.2	0.950	0.0039
Ethylbenzene	9	0.752	−24.8	0.933	0.0039
m,*p*-Xylene	9	0.748	−25.2	0.933	0.0039
o-Xylene	9	0.329	−67.1	0.933	0.0078

3.4 Seasonal differences in method comparability

Seasonal differences were observed in the comparison between the charcoal tube and canister methods at 50 mL min⁻¹. For toluene, the median charcoal/canister ratio increased from 0.402 in summer to 0.947 in winter. Similar increases were observed for ethylbenzene (0.385 to 0.904), *m*,*p*-xylene (0.230 to 0.971), and *o*-xylene (0.181 to 0.667). The distributions of the charcoal/canister ratios differed significantly between summer and winter for toluene, ethylbenzene, *m*,*p*-xylene, and *o*-

xylene. In contrast, no statistically significant seasonal difference was observed for benzene.

Seasonal differences were also observed in the sorbent/canister comparison. The median ratio increased from 1.044 in summer to 1.324 in winter for toluene, from 0.998 to 1.201 for ethylbenzene, and from 0.677 to 1.582 for *m*,*p*-xylene. Statistically significant seasonal differences were detected for all three compounds.

These results indicate that the degree of agreement among the sampling methods was not constant between the summer and winter experiments. Therefore, results from the two seasons were evaluated separately rather than combined into a single dataset.