

The Twelfth Session of the Scientific Advisory Committee
on the Acid Deposition Monitoring Network in East Asia
22-24 November 2012, Yangon, Myanmar

Progress Report on the Activities of the Expert Group on Preparation of Technical Manual for Air Concentration Monitoring

Chair of the Expert Group on the preparation of the Technical Manual for Air Concentration Monitoring

I. Background

1. At the First meeting of the Task Force on Dry Deposition Monitoring held at Hanoi in October, 2008, reconsideration of the Terms of Reference, membership and name of the Task Force were discussed. On the recommendation of the Eighth Session of Scientific Advisory Committee of the EANET (SAC8), and the Tenth Session of the Intergovernmental Meeting (IG10) in November 2008 agreed to change the name of the Task Force to “Task Force on Monitoring for Dry Deposition” and agreed to the following new Terms of Reference (TOR) for the Task Force:
 - i) To further develop and elaborate the strategy for dry deposition evaluation in the region
 - ii) To discuss on future direction of dry deposition evaluation and provide guidance on relevant activities based on the strategy
 - iii) To develop the Technical Manuals for Air Concentration Monitoring and Dry Deposition Flux Estimation
 - iv) [To review substances to be monitored]
2. In order to accomplish the TOR of the Task Force, the Task Force proposed to establish the Expert Group on Preparation of the Technical Manual for Air Concentration Monitoring. The Ninth Session of the SAC (SAC9) held in October 2009 agreed to submit the proposal on the establishment of the new Expert Group to the Eleventh Session of the IG (IG11) held in November 2009 and IG11 endorsed the establishment of the Expert Group. SAC9 also appointed Dr. Duong Hong Son as the chairperson of the expert group and the Network Center (NC) was designated as the secretariat. After the establishment of the Expert Group, the Chair nominated 7 members from the EANET participating countries of the Expert Group with help of the NC.
3. The First Meeting of the Expert Group was held at Niigata, Japan from 11 to 12 August 2011. The main discussions of the First Meeting are as follows:
 - i) Review on the current EANET documents regarding air concentration monitoring
 - ii) Review on the existing national air concentration monitoring manuals of EANET participating countries
 - iii) Review on the existing air concentration monitoring manuals of the other international monitoring networks
 - iv) Identification of suitable monitoring methods for EANET air concentration monitoring

v) Table of Contents of the Technical Manual for Air Concentration Monitoring
Then, lead authors for each chapter of the Technical Manual were determined, and the respective authors agreed to prepare the 1st draft of the Technical Manual until the Second Meeting of the Expert Group.

II. Activities

II-1. Second meeting of the Expert Group

4. The draft table of contents of the Technical Manual was reported to the Eleventh Session of the Scientific Advisory Committee (SAC11) held in October 2011, and then each authors started to prepare the draft Technical Manual. Until the end of July 2011, the respective authors sent the 1st draft of the Technical Manual to the secretariat of the Expert Group.
5. The Second Meeting of the Expert Group was held at Niigata, Japan from 23 to 24 August 2012. In the Second Meeting, the draft contents of each chapter of the Technical Manual were reviewed based on the submitted 1st draft by the respective authors. Then, the future revision schedule was determined. The meeting minutes is attached as **EANET/SAC 12/8/2 Annex 1**, and the draft Technical Manual is attached as **EANET/SAC 12/8/2 Annex 2**.

II-2. Members

6. The members of the Expert Group are shown below. Because Prof. Young Joon Kim was appointed as the President of his institute, it has been hard to involve the Expert Group activity for him. Then, Prof. Kihong Park was recommended as the alternative expert of Prof. Kim, and the expert group agreed to join him as an additional member of the expert group.

Dr. Duong Hong Son (Chairperson)	Director, Center for Environmental Research, Vietnam Institute of Meteorology, Hydrology, and Environment, Vietnam
Prof. Min Hu	Professor, College of Environmental Sciences, Peking University, China
Dr. Masahide Aikawa	Deputy Department Chief, Atmospheric Department, Hyogo Prefectural Government, Japan
Mr. Hajime Mikasa	Managing Director, Japan Environmental Technology Associations, Japan
Dr. Akinori Takami	Chief, Asian Environment Research Group, National Institute for Environmental Studies, Japan

Prof. Young Joon Kim	Professor, School of Environmental Science and Engineering, Gwangju Institute of Science and Technology, Republic of Korea
Prof. Kihong Park*	Associate Professor, School of Environmental Science and Engineering, Gwangju Institute of Science and Technology, Republic of Korea
Mr. Phunsak Theramongkol	Director, Ambient Air Quality Section, Pollution Control Department, Thailand

* As the alternative member of Prof. Young Joon Kim, Prof. Kihong Park (GIST, Korea) was appointed as a member of the Expert Group.

II-3. Discussions on the contents of the Technical Manual

7. Discussions on the contents of the 1st draft Technical Manual were summarized as the meeting minutes (EANET/SAC 12/8/2 Annex 1). The major discussions in the Second Meeting are as follows:

(Chapter 1 Introduction)

- Relationship among different chapters should be introduced in Chapter 1 using a schematic figure.
- Background of this manual such as renewed national monitoring standards in some countries may also be introduced.
- In the introduction, two documents related with EANET dry deposition monitoring were cited and the relationship between them should be explained clearly.

(Chapter 2 Monitoring design)

- The location and design of a monitoring site should be determined by critical features such as surroundings, the representation of ecosystem, population density, character of ground surface, relative location of vegetation, distance from emission sources and representative scale, and so on.
- The monitoring site design should be determined by the EANET objectives.
- An urban site should not be close to emission sources, and a remote site should be related to representative ecosystem. It should basically follow EANET guidelines.

(Chapter 3 Manual monitoring)

- The Expert Group agreed to select feasible manual monitoring methods for continuous air concentration monitoring
- How to estimate and control the uncertainty of filter pack method has to be explained in this chapter. The comparison between automatic and manual methods should be also included.
- Automatic methods are primarily recommended for air concentration monitoring. The

advantage and disadvantage of different methods should be also explained.

- One of the EANET objectives is to implement long time monitoring, and thus monitoring cost is also important factor.
- Pros and cons of passive sampler monitoring should be described in this chapter. One of the benefits is that artifact caused by evaporation of particles can be avoided.
- Annular denuder can measure HONO, SO₂, HNO₃ and NH₃. Denuder is useful to monitor NH₃, because there is no automatic instrument for NH₃ measurement.

(Chapter 4 Automatic monitoring)

- An ozone standard which is traceable to a standard reference photometer (SRP) will be provided by the network center to participant countries. Specification of an ozone standard should be introduced in more detail.
- NO_x and SO₂ monitors are usually calibrated by NO and SO₂ standard gas, respectively. How each country can obtain a standard gas should be introduced.
- It was pointed that short time resolution measurement for particulate matter components is necessary for evaluation of deposition flux.
- NO₂ monitors used for routine sampling in other network should be investigated, and it was recommended that NO₂ monitor to detect only NO₂ is adopted for EANET air concentration monitoring.
- DOAS can measure SO₂, NO₂ and O₃ at same time. Because DOAS can measure multiple gases simultaneously, the arrangement of DOAS description in this chapter should be reconsidered.
- Both of TEOM (Tapered Element Oscillating Microbalance) and β-ray absorption methods for PM monitoring should be described, and advantage and disadvantage of these two methods should be introduced.
- There is no traceable method for PM calibration. Comparison between TEOM, other PM monitors and filter based measurement can be considered.
- Meteorological instruments are recommended to be installed at EANET sites. If the monitoring sites have their own meteorological instruments, the description of corresponding parts in the manual are useful.
- This manual is mainly used by local operators and also can be used as a reference for EANET activity.

(Chapter 5 Maintenance)

- The corresponding contents can be cited from previous EANET QA/QC document.
- Basically safety management should comply with the regulations of each country.
- How to prepare a maintenance record sheet should also be explained and maintenance records should be basically kept in stations and laboratories.
- Standard Operating Procedure (SOP) is one of important parts of QA/QC. SOP should be prepared by each lab. This manual will only include necessary items.
- QA/QC of official compendium methods in each country can be referred.

(Chapter 6 Data reporting and validation)

- The unit of data should be different for different data quality objectives (DQOs).
- Time resolution for data submission of different methods should be required.
- Monitoring sites should store raw data for at least 3 years.
- Monitoring should be implemented continuously considering EANET objectives. Intensive and discontinuous monitoring data are not accepted.
- The method to calculate data completeness on monthly and yearly bases should be described in this chapter.
- Guideline for the average data calculation should be described.

(Chapter 7 Quality Control and Quality Assurance)

- It was suggested that comparison of PM monitoring between automatic and filter based method is carried out. Outcomes of parallel PM monitoring can be shown as references.
- DQOs and detection limits will be different between urban and remote sites. The detection limit is dependent on the integration time. Definition of detection limits of air concentrations should be described at first such as two or three times of standard deviations from blank sample analysis for manual monitoring.
- It was recommended to prepare a checklist for confirmation by operation staffs.

(Chapter 8 Future issues)

- New monitoring methods of NO₂ such as PLD, CRDS, LIF, online aerosol composition monitoring, intercomparison of different monitoring methods, etc. will be added in Chapter 8.
- The draft of this chapter will be prepared by Dr. Son and NC after the drafts of other chapters are completed.

8. Based on the discussion on the first draft in the Second Meeting, the secretariat revised critical points in the draft Technical Manual and attached as (EANET/SAC 12/8/2 Annex 2).

II-4. Schedule

9. The Expert Group agreed to follow the following time schedule for its activities:

<u>23 – 24 August,</u> <u>2012</u>	Second Meeting of the Expert Group, Review of the 1st draft of the Technical Manual [Finished]
<u>30 – 31 August,</u> <u>2012</u>	Report activity of the Expert Group and present the draft contents of the Technical Manual at STM12 for comments [Finished]
<u>September – November,</u> <u>2012</u>	Revision of the Technical Manual to prepare the 2nd draft of the Technical Manual
<u>22 – 24 November,</u>	Report activity of the Expert Group and submit the draft

<u>2012</u>	Technical Manual at SAC12 for comments
<u>November, 2012 – May 2013</u>	Revision of the Technical Manual to prepare the 3rd draft of the Technical Manual
<u>June, 2013</u>	Third meeting of the Expert Group to finalize the Technical Manual
<u>Autumn, 2013</u>	Submission of the final draft of the Technical Manual to SAC13 for adoption

II-5. Follow-up actions after the Second meeting

10. The draft Technical Manual should be revised for 2 times by the Expert Group members and the NC before June, 2013. The 3rd draft of the Technical Manual should be circulated and reviewed among members of the Task Force on Monitoring for Dry Deposition and the Scientific Advisory Committee and other relevant people. According to the comments made by them, the Technical Manual will be further elaborated. Then, the Third meeting will be held in June, 2013, and the draft Technical Manual will be finalized.

III. Recommendations to SAC12

11. The Twelfth Session of the Scientific Advisory Committee (SAC12) is invited to consider the progress report on the preparation of the Technical Manual for Air Concentration Monitoring by the Chair of the Expert Group and approve the following:
 - i) One of the Expert Group member, Prof. Young Joon Kim, could not take part in the Expert Group because of his position change. Therefore, Prof. Kihong Park at Gwangju Institute of Science and Technology, Republic of Korea will be nominated as a new member of the Expert Group instead of Prof. Kim.

ACID DEPOSITION MONITORING NETWORK IN EAST ASIA (EANET)

**SECOND MEETING OF THE EXPERT GROUP ON PREPARATION
OF TECHNICAL MANUAL FOR AIR CONCENTRATION MONITORING
UNDER THE TASK FORCE MONITORING FOR DRY DEPOSITION
SCIENTIFIC ADVISORY COMMITTEE (SAC) OF EANET**

(Niigata, 23-24 August 2012)

PROVISIONAL AGENDA

August 23

09:00-09:10

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|--------------------|---------------------|
| 1. Welcome remarks | Dr. Akimoto
(NC) |
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09:10-09:20

- | | |
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| 2. Introduction and Adoption of the Agenda | Chair |
|--|-------|

09:20-09:30

- | | |
|---|-------------------|
| 3. Review of the 1st draft of Chapter 1 | Dr. Son and
NC |
|---|-------------------|

09:30-10:30

- | | |
|---|-------------------------------------|
| 4. Review of the 1st draft of Chapter 2 | Mr. Mikasa
Mr. Phunsak
and NC |
|---|-------------------------------------|

10:30-11:00 Coffee break

11:00-12:30

- | | |
|---|----------------------|
| 5. Review of the 1st draft of Chapter 3 | Dr. Aikawa
and NC |
|---|----------------------|

12:30-14:00 Lunch and Group Photo

14:00-15:00

- | | |
|---|-------------------------------------|
| 6. Review of the 1st draft of Chapter 5 | Mr. Mikasa
Mr. Phunsak
and NC |
|---|-------------------------------------|

15:00-16:00

7. Review of the 1st draft of Chapter 6 NC

16:00-16:30 Coffee break

16:30-17:30

8. Review of the 1st draft of Chapter 7 EG
Members
and NC

17:30 Departure to the hotel

August 24

09:00-10:30

9. Review of the 1st draft of Chapter 4 Prof. Hu
Prof. Park
Dr. Takami
Mr. Mikasa

10:30-11:00 Coffee break

11:00-12:30

9. Review of the 1st draft of Chapter 4 (Continued) Prof. Hu
Prof. Park
Dr. Takami
Mr. Mikasa

12:30-14:00 Lunch

14:00-14:20

10. Review of the 1st draft of Chapter 8 Dr. Son and
NC

14:20-15:00

11. Next steps and schedule Discussion

15:00 Close

MEETING MINUTES

I. Welcome Remarks

Dr. Hajime Akimoto, Director General of ACAP welcomed the members of the Expert Group on Preparation of Technical Manual for Air Concentration Monitoring of the EANET Scientific Advisory Committee to ACAP, Niigata, Japan.

He mentioned that the air quality especially PM and O₃ has become much more concerned for EANET countries and EANET has already identified PM and O₃ as monitoring species as well as the other gases such as SO₂, NO_x, HNO₃ and NH₃. However, EANET still doesn't have a technical manual for air concentration monitoring. At this time the most proper scientists have agreed to join the expert group to prepare the manual. We are very looking forward to this very useful manual for EANET air concentration monitoring.

II. Adoption of the Agenda and membership of the Expert Group

Dr. Duong Hong Son, the chairperson of the Expert Group, made introductory remarks. The other members of the Expert Group also introduced themselves.

III. Terms of reference and membership of the Expert Group, Adoption of the Agenda

Dr. Duong Hong Son, the chairperson of the Expert Group, introduced the terms of reference and the membership of the Expert Group. Prof. Kihong Park was introduced as the alternative expert of Prof. Young Joon Kim, and the expert group agreed to join him as an additional member of the expert group (see Annex 1).

The secretary introduced the provisional agenda, and the expert group adopted it. The meeting will discuss the first draft of the technical manual for air concentration monitoring (TMACM), and comments, suggestions and necessary revisions will be given afterward. The outline of the TMACM and authors for each chapter were decided in the 1st meeting. The participants confirmed that the detailed contents of each chapter will be discussed at the 2nd meeting.

IV. Review of the 1st draft of the Technical Manual for Air Concentration Monitoring (see Annex 2)

In the first meeting, the draft Table of Contents and responsible authors for each chapter were adopted. Each authors submitted the 1st draft before 2nd meeting, and the contents of the 1st draft was reviewed chapter-by-chapter. Discussions on the 1st draft are summarized below.

Chapter 1 Introduction (written by Dr. Son and NC)

The Secretariat presented the outline of Introduction. Major comments were as follows:

- i) Relationship among different chapters should be introduced in Chapter 1 using a schematic figure. Abbreviations should be explained at first.
- ii) Background of this manual such as renewed national monitoring standards in some countries may also be introduced.
- iii) The document number can be used to identify different technical manuals of EANET;
- iv) In the introduction, two documents related with EANET dry deposition monitoring were cited and the relationship between them should be explained clearly.

Chapter 2 Monitoring design (written by Mr. Phunsak, Mr. Mikasa and NC)

Mr. Phunsak, Mr. Mikasa and NC introduced the draft of Chapter 2. Major comments were as follows:

- i) The name of site category should be consistent in this manual. For example, the “Rural background” and “Urban background” should be replaced by “Rural site” and “Urban site”, respectively.
- ii) The location and design of a monitoring site should be determined by critical features such as surroundings, the representation of ecosystem, population density, characteristics of ground surface, relative location of vegetation, distance from emission sources, representative scale, and so on. The manual should be easy to be referred by technical staff to design or select location for a monitoring site. The sampling flow rate will also be different among urban, rural and remote sites.
- iii) The monitoring site design should be determined by the EANET objectives.
- iv) An urban site should not be close to emission sources, and a remote site should be related to the representative ecosystem.
- v) The different monitoring methods and sampling frequency for corresponding monitoring species should be summarized in a table.
- vi) The relationship of EANET manuals with the other international networks’ manual should be explained, and the determinations described in this manual should be consistent with the other manuals.
- vii) General concept of data transport system from monitoring sites to network center can also be introduced.
- viii) Some technologies to ensure the monitoring quality such as noise removal can be introduced, and PM should be collected through dry inlet air to avoid the influence of humidity.

Chapter 3 Manual monitoring (written by Dr. Aikawa and NC)

Dr. Aikawa explained the outline of Chapter 3. This chapter includes the adopted methods such as filter pack and passive sampler but also advanced techniques such as annular denuder and other gas scrubbers. The expert group agreed to select feasible monitoring methods for continuous air concentration monitoring. Major comments were as follows:

- i) Filter pack method has been used for a long time, and thus, for trend analysis, it is better to use the same method to compare with old data.

- ii) The artifacts of filter pack method mainly exist in measurement of particulate NH_4^+ and NO_3^- . How to estimate and control the uncertainty of filter pack method has to be explained in this chapter. The uncertainty of this method is also different among urban or remote site. The artifacts mainly are dependent on ambient temperature. The comparison between automatic and manual methods should be included. Only monitoring of SO_2 can be compared between automatic and filter pack methods.
- iii) Filter pack method has already been used at many monitoring sites. It is better to cite useful research papers describing filter pack data and method in the manual.
- iv) It was recommended that more than two technical staffs work for manual monitoring at one monitoring site in order to share skill. Training program for operation of filter pack should be described in the manual.
- v) The procedure of leak check should be described in a figure.
- vi) It was suggested that the chapter of automatic monitoring should be described before the chapter of manual monitoring.
- vii) Particulate organic acid is also important, and thus could be considered for monitoring in future.
- viii) It was mentioned that the advantage of filter pack method is simultaneous monitoring of gas and particle components.
- ix) The filter pack method is mainly useful for total (gaseous and particulate) NH_4^+ and NO_3^- monitoring.
- x) It was suggested that other filter samplers such as low or high volume samplers can be also introduced in the manual.
- xi) Automatic methods are primarily recommended for air concentration monitoring. The advantage and disadvantage of different methods should be also explained. Practical and reliable methods should be described in manual. In future, the advanced monitoring techniques can be included.
- xii) One of the EANET objectives is to implement long time monitoring, and thus monitoring cost is also important factor. Low cost is one of the advantages of manual monitoring.
- xiii) Pros and cons of passive sampler monitoring should be described in this chapter. One of the benefits is that artifact caused by evaporation of particles can be avoided. Gas collection efficiency of a passive sampler is dependent on the shape of shelter, and time resolution of passive sampler is not good.
- xiv) Wet annular denuder can measure HONO , SO_2 , HNO_3 and NH_3 . Denuder is useful to monitor NH_3 , and there is no automatic instrument for NH_3 measurement. The methodology for NH_3 monitoring should be included in this manual. Denuder method is mainly used for researches and difficult for routine sampling because it requires skillfulness and high cost. Consumable denuder has been used in EMEP.

Chapter 4 Automatic monitoring (written by Prof. Hu, Dr. Takami, Prof. Kim, Prof. Park and Mr. Mikasa)

The secretariat and authors of each section introduced their responsible parts of Chapter 4. Major comments were as follows:

- i) This chapter is related to maintenance and sampling frequency which are shown in other chapters. The relationship of this chapter with the other chapters should be explained in the manual.
- ii) An ozone standard which is traceable to a standard reference photometer (SRP) will be provided by the network center to participant countries. Specification of an ozone standard should be introduced in more detail. A systematic chart to demonstrate how to distribute the primary, secondary and transfer standards should be provided.
- iii) A NO_x monitor is usually calibrated by a NO standard gas. Now only SO₂ and NO standard gases are provided for calibration. The calibration gases have not been distributed among all participating countries. How each country can obtain a standard gas should be introduced. There is no mixture standard gas in China. Thailand imports the standard gas from other countries. The dilution system for standard calibration gas should also be described in the manual. The dilution ratio is dependent on the concentration of standard gas, and typical concentration level is ppm.
- iv) General description of SO₂ and NO_x monitors should be introduced at first. Ground measurement should be modified to point measurement.
- v) It was pointed that short time resolution measurement for particulate matter components is necessary for evaluation of deposition flux.
- vi) NO₂ monitors used for routine sampling in other network should be investigated, and it was recommended that NO₂ monitor to detect only NO₂ is adopted for EANET air concentration monitoring.
- vii) DOAS can measure SO₂, NO₂ and O₃ at same time. Because DOAS can measure multiple gases simultaneously, the arrangement of DOAS description in this chapter should be reconsidered. At first, point measurement methods should be introduced, and afterward DOAS method should be described separately.
- viii) There are two types of DOAS, namely passive and active systems. Passive one can be suitable for long time observation because no light source is required. On the other hand, active DOAS can measure both day and night time. Typical path length and integration time of DOAS are 1 km and 2 minutes, respectively. The benefits of DOAS operating in EANET countries are that maintenance for DOAS is quite easy and calibration system isn't needed. Currently DOAS is mainly used for research projects in Korea and other countries, and China and Philippines use DOAS for routine monitoring. The most common types of commercial instruments can also be introduced. Retail price and maintenance cost of DOAS can be compared with point measurement instruments. For example, active DOAS is sold by a company in Sweden and its price is about 10,000,000 Japanese yen.
- ix) At the beginning of PM introduction, some basic information such as atmospheric particle size should be described.
- x) Both of TEOM (Tapered Element Oscillating Microbalance) and β -ray absorption methods for PM monitoring should be described, and advantage and disadvantage of these two methods should be introduced. Because PM concentration of TEOM is determined a filter based weight standard, TEOM should be better, but replacement of a TEOM filter is very difficult to handle and the filter is easily affected by humidity. Frequency of minus data by TEOM is much fewer than those by β -Ray. Only β -ray is used in Korea, whereas both

methods are adopted in China, Japan and Thailand. It was mentioned that β -ray is more common in air quality monitoring of Thailand.

- xi) The dehumidifier system such as heating and moisture condensation has to be described in the manual.
- xii) There is no traceable method for PM calibration. Comparison between TEOM, other PM monitors and filter based measurement can be considered, and this comparison has to be carried out under dry condition to avoid the influence of humidity. A PM collection filter should be weighed under the designated temperature and humidity. Standard meteorological condition of PM monitors including temperature, humidity and pressure should be identified in the manual. It was recommended that the PM monitors can control humidity and temperature or has sensors for monitoring meteorological parameters and convert to the stand condition. The PM cutting size should be also identified in the manual.
- xiii) Meteorological instruments are recommended to be installed at EANET sites. If the monitoring sites have their own meteorological instruments, the description of corresponding parts in the manual are useful.
- xiv) Current knowledge of intercomparison among different methods is also included.
- xv) This manual is mainly used by local operators and also can be used as a reference for EANET activity.
- xvi) A video to show how to operate the instruments can be considered.

Chapter 5 Maintenance (written by Mr. Phunsak, Mr. Mikasa and Network Center)

The secretariat and authors of each section introduced the outline of Chapter 5. Major comments were as follows:

- i) The corresponding contents can be cited from previous EANET QA/QC documents.
- ii) Basically safety management should comply with the regulations of each country.
- iii) Inspection of sampling inlets for all instruments should be described.
- iv) The figures should be revised to be easily understood for technical staffs.
- v) How to prepare a maintenance record sheet should also be explained and maintenance records should be basically kept in stations and laboratories.
- vi) Standard Operating Procedure (SOP) is one of important parts of QA/QC. SOP should be prepared by each lab. This manual will only include necessary items. The NC will ask each laboratory to prepare SOP. It is not easy to prepare SOP, and operation staffs must refer the manual carefully. The guideline to prepare SOP should be described in this chapter. It is better that a SOP shown in this chapter as one of examples. A site audit should involve the confirmation of SOP.
- vii) SOP will be different among different countries. The validity of SOP can be estimated through inter-laboratory comparison. So far only the inter-lab comparison of filter pack has been conducted for air concentration monitoring.
- viii) The QA/QC of official compendium methods in each country can be referred.

Chapter 6 Data reporting and validation (written by NC)

The secretariat introduced the outline of Chapter 6. Major comments were as follows:

- i) The unit of data should be different for different data quality objectives (DQOs).
- ii) Integration time for each instrument should be different, and thus the integration time for different data should be described. Time resolution for data submission of different methods should be required.
- iii) The determination of invalid data for different methods should be described.
- iv) A flowchart for data storage and transport should be illustrated in this chapter.
- v) Data reporting format should be designed and shown in the appendix.
- vi) Monitoring sites should store raw data for at least 3 years.
- vii) It was recommended to provide data for users via Web site conveniently.
- viii) Monitoring should be implemented continuously considering EANET objectives. Intensive and discontinuous monitoring data are not accepted.
- ix) The method to calculate data completeness on monthly and yearly bases should be described in this chapter. The data completeness is based on integrated time and thus the definition should be different between automatic and manual methods. The abnormal data and instrumental errors should be shown as reference data with flag.
- x) Guideline for the average data calculation should be described.

Chapter 7 Quality Control and Quality Assurance (written by All EG members and NC)

The secretariat, Prof. Park, Prof. Hu, Dr. Takami and Dr. Aikawa introduced the outline of Chapter 7. Discussion was focused on determination of accuracy and detection limit. Major comments were as follows:

- i) It was recommended that different methods for PM monitoring are introduced. There is no reference standard for comparison of PM monitoring. It was suggested that comparison of PM monitoring between automatic and filter based method is carried out. Outcomes of parallel PM monitoring can be shown as references.
- ii) Names of instrument manufacturing companies can be listed in the same manner of EMEP and CASTINET manuals.
- iii) DQOs and detection limits will be different between urban and remote sites. The detection limit is dependent on the integration time. Definition of detection limits of air concentrations should be described at first such as two or three times of standard deviations from blank sample analysis for manual monitoring. Basically, the detection limit is different for each laboratory. The reporting limit should be same for all EANET sites and shown in this manual.
- iv) It was recommended to prepare a checklist for confirmation by operation staffs.

Chapter 8 Future issues (written by Dr. Son and NC)

New monitoring methods of NO₂ such as PLD, CRDS, LIF, online aerosol composition monitoring, intercomparison of different monitoring methods, etc. will be added in Chapter 8. The draft of this chapter will be prepared by Dr. Son and NC after the drafts of other chapters are completed.

Based on the discussion at the 2nd meeting, the secretariat revised the 1st draft of Technical Manual and attached as Annex 2.

X. Next Steps and Schedule

The expert group adopted the Future plan of activity during 2012-2013 (Annex 3). The Meeting also agreed that:

- i) The first draft of manual will be revised according to suggestions in this meeting, and then the revised sent to participants by the end of September with this minute.
- ii) The revised first draft will be submitted to SAC and IG meetings in 2012. Before submission each authors and the NC should modify this draft.
- iii) According to the comments by SAC and IG meetings in 2012, the revised 1st draft will be elaborated again and the 2nd draft will be circulated among participant countries.

LIST OF PARTICIPANTS

Members of the Expert Group

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(EGACM 2/minutes Annex 1)

**SECOND MEETING OF THE EXPERT GROUP ON PREPARATION
OF TECHNICAL MANUAL FOR AIR CONCENTRATION MONITORING
(Niigata, 23-24 August 2012)**

Terms of Reference of the Expert Group

- i) Review the current Technical Document for Filter Pack Method in East Asia and the QA/QC Program for the Air Concentration Monitoring in East Asia
- ii) Identification of monitoring methods suitable for EANET air concentration monitoring
- iii) Preparation of the Technical Manual for Air Concentration Monitoring based on identified monitoring methods

Membership of the Expert Group

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Technical Manual
on
Air Concentration Monitoring
(Draft)

**Prepared by the Expert Group on Preparation of the
Technical Manual for Air Concentration Monitoring,
Scientific Advisory Committee of Acid Deposition Monitoring
Network in East Asia (EANET)**

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Preface

1. Introduction [Dr. Son and Network Center]

1.1 Background

On the recommendation of SAC, the Tenth Session of the Intergovernmental Meeting (IG10) held in November 2008 agreed to change the name of the “Task Force on Dry Deposition Monitoring” to “Task Force on Monitoring for Dry Deposition” and agreed to the following new terms of reference for the Task Force:

- To further develop and elaborate the strategy for dry deposition evaluation in the region
- To discuss on future direction of dry deposition evaluation and provide guidance on relevant activities based on the strategy
- To develop the Technical Manuals for Air Concentration Monitoring and Dry Deposition Flux Estimation
- [To review substances to be monitored]

Currently, no technical manual on air concentration monitoring has been produced by EANET although the NC has produced the Technical Document for Filter Pack Method in East Asia which was adopted by SAC in November 2003 and QA/QC Program for the Air Concentration Monitoring in East Asia published in 2001. In order to obtain comparable and reliable dataset, the standardization of air concentration monitoring methodology and development of technical manual should be promoted. The standardization should agree with those in other monitoring networks in US and Europe. Current specific monitoring methodologies adopted by participating countries should be taken into consideration for the standardization of air concentration monitoring.

The Task Force on Monitoring for Dry Deposition proposed to establish an Expert Group on Preparation of the Technical Manual for Air Concentration Monitoring composed of relevant experts in this field. The establishment of Expert Group was approved by the Eleventh Session of the Intergovernmental Meeting (IG11) held in November, 2009. The Expert Group will consider current country specific monitoring methodology of air concentration monitoring and necessary calibration procedures for the automatic monitors and prepare a Technical Manual for Air Concentration Monitoring for EANET.

1.2 Objectives

- 1) Review the previous Technical Document for Filter Pack Method in East Asia and the QA/QC Program for the Air Concentration Monitoring in East Asia
- 2) To identify monitoring methods suitable for EANET air concentration monitoring
- 3) To provide guideline of air concentration monitoring based on identified monitoring methods and to standardize air concentration monitoring methodology

1.3 Priority chemical species in EANET

The *Strategy Paper for Future Direction of Dry Deposition Monitoring of EANET (Second Edition)* had highly recommended the following priority chemical species for EANET dry deposition monitoring in view of their serious impacts on the ecosystem and human health:

First priority: SO₂, O₃, NO, NO₂ (urban), HNO₃, HCl, NH₃, Particulate component (SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, Na⁺, Mg²⁺, K⁺ and Ca²⁺), PM₁₀

Second priority: NO₂ (rural and remote), PM_{2.5}

1.4 Outline of the manual

This technical manual will provide a comprehensive guideline for air concentration monitoring in EANET countries in order to standardize air concentration monitoring and provide comparable data at EANET monitoring sites. The manual composed of 8 chapters.

Chapter 1 provides general background and the objective of the preparation of this technical manual.

Chapter 2 describes monitoring design such as siting criteria, site facilities and instrumentation at a monitoring station and monitoring frequency for each monitoring item.

Chapter 3 describes a guideline for manual monitoring of filterpack and passive sampler which are widely used for EANET monitoring. Furthermore, a monitoring guideline of annular denuder and other gas scrubbers, which are enable to avoid artifact of gas and

particle interactions, is also described.

Chapter 4 describes a guideline for automatic monitoring of gaseous species, particulate matter and meteorological parameter. This chapter covers specification of automatic monitors and calibration procedures. Specifications of air concentration monitors cover both point measurements and long path measurements.

Chapter 5 describes a guideline for preparation of standard operating procedures, maintenance of air concentrations monitors, records field conditions and instrument maintenance and safety management.

Chapter 6 describes a guideline for data reporting and validation. This chapter covers specification of a monitoring site, how to compile raw monitoring data, how to validate monitoring data, submission of finalized data and data storage for future analysis.

Chapter 7 describes QA/QC of air concentration monitoring. This chapter covers overall procedures such as monitoring site, field and laboratory operations, data management, determination of accuracy and detection limit. Furthermore, DQOs of Fundamental parameters, QA/QC implemented by NC and training programs will be described.

Finally, Chapter 8 introduces future issues to develop air concentration monitoring in EANET. This chapter covers new monitoring methods of NO_2 , online aerosol composition monitoring, intercomparison of different monitoring methods, and so on.

2. Monitoring design [Network Center, Mr. Mikasa and Mr. Phunsak]

The purpose of this section is to describe the general concepts for establishing the ambient air quality monitoring network. The network may consist of fixed station or mobile station. The station may include parameters which much be associated with acid deposition problem: PM₁₀, SO₂, NO_x, O₃ and meteorological instrument.

The station will generally be required to locate in background areas that have minimal influence from manmade point or area source. As well as, the station will provide representative measurement of air quality entering the air shed with point or area source or climate change. However, the station may be located in urban or other area where assessment of ambient air quality is needed.

Each monitoring station in the EANET network should be described in term of physical dimension of representativeness. Closely associated with the area around the station where the pollutant concentrations are seasonably similar. The network design intent in sitting the station is to correctly match the representativeness with the basic monitoring object of the station. Station site are classified into three basic site category:

- a) Remote : site located to measures air pollution impact on vegetation or ecology damage.
- b) Rural background: site located to determine the extent of regional pollutant transport.
- c) Urban background: site located to determine general black ground concentration of the city.

Multiple factors are considered when deciding the location of air monitoring station. Sites are selected based on the pollutant or pollutants to be monitored, the monitoring objectives, proximity to other monitoring stations and operational efficiency. The EANET has developed siting requirements for wet deposition monitoring in east asia. These requirements include distance from trees, buildings and roadways, distance from major point sources. Other factors should be included: site security and access, availability of electricity and telephone service, aesthetics and local zoning issues, and long term (+10 years) site availability. Unfortunately the ideal monitoring site is virtually impossible to acquire, especially in urban areas.

2.1 Siting criteria [Mr. Phunsak and NC]

Air concentration (dry deposition) monitoring sites are classified into three

categories: remote sites, rural sites and urban sites according to the objectives of the monitoring.

(a) Remote sites

Remote sites are to be established for the assessment of the state of acid deposition in background areas. The monitoring data can be used to evaluate long-range transport and transmission models of acidic substances in East Asia.

The location of these sites should be selected in areas with no or least influence from local emission and contamination sources. Therefore, remote sites should be located with sufficient distance from significant stationary sources such as urban areas, thermal power plants, large factories and significant mobile sources such as major highways, ports and railways to minimize these influences. It is desirable for remote sites to be located at existing meteorological stations, in particular, upper wind monitoring stations or in their vicinity

(b) Rural sites

Rural sites are to be established for the assessment of the state of acidic deposition in rural areas or hinterlands. The monitoring data can be used, for instance, to evaluate the effects of acid deposition on agricultural crops and forests.

The location of these sites should be selected in areas with minor influence from local emission and contamination sources. Therefore, rural sites should be sited away from significant stationary and mobile sources and should be free from these influences to the extent possible.

Some rural sites which generally satisfy the criteria for remote sites may also be used to evaluate long-range transport and deposition models of acidic substances.

(c) Urban sites

Urban sites are to be established for the assessment of the state of acidic deposition in urban areas. Urban and industrialized areas, and the areas immediately outside such areas, can be included. The monitoring data can be used, for instance, to evaluate the effects of acid deposition on buildings and historical monuments. Monitoring data at these sites may also be useful for the assessment of acidity of precipitation and the trends in urban areas.

Sampling manifold setting

- When Station is mounted on rooftop, the separation distance to walls, parapets, or building on roof, should be > 20 meters from obstruction.

- Distance from sampler, probe, or 90% of monitoring path to obstacle, such as a building, must be at least twice the height the obstacle
- For collocated an PM₁₀ samplers, a 2-4 meter separation distance between collocated samplers must be met.
- For collocated PM-2.5 samplers, a 1-4 meter separation distance between collocated samplers must be met.

2.2 Site facilities and Instrumentation (Electricity, Housing, Air conditioning, Inlet, Data communication, monitor arrangement etc.) [Mr. Mikasa and NC]

The structure of a monitoring station changes with installation requirements, such as using a part of an existing building and building a new single house.

In addition, it is desirable to design a station to be suitable with ambient environment.

A PM_{2.5} monitor is installed outside of a station fundamentally. If a PM_{2.5} sampler is installed inside of a station, the sampling inlet has to be installed to pass along the roof of a station.

(1) Case of using a part of existing building

If a part of an existing building is used as a station, monitors are arranged according to the actual condition, and it may be necessary to separate a room or construct installation because of physical constraint. The sampling inlet is installed on the place of no influence of the station and the sampling tube is installed to not too long.

(2) Case of building new single house

1) Fixed type

There are wooden, prefab structure, concrete block structure, etc., in general, and if economical efficiency, an assembly, and the ease of demolition is taken into consideration, prefab structure is suitable, but concrete block structure is the most desirable, judging from durability, fire prevention, and an indoor managerial side.

Recently, some prefab and lightweight aggregate panel construction also have refractoriness and firesafety, same as concrete block structure has, and agreed on construction standards and a fire prevention standard.

However, it is needed sufficient durability of the material and structure which are used for a floor because some monitors have about 100kg weight per one set.

2) Container type

Since measurement monitors are installed in the containers of the product made from aluminum, or iron and it is considered as a monitoring station, the area becomes a little narrow from a fixed type. This method has few problems of fire prevention, and it is easy to install it in the park etc. where installation of a building is restricted. Moreover, when it becomes a situation which has a problem of the representation of measured value, or a problem of land use, etc., to make it move after installation is easy. However, to fix firmly by an anchor bolt is required for concrete foundation in order to avoid damage, such as an inclination of a container by the earthquake. Moreover, as for the outer wall of a container, in order to heighten the indoor air-conditioning effect, covering with thermal insulation etc. is desirable.

2.3.2 Equipment

It is necessary to install the equipments in a station as follows.

(1) Power requirement

1) Power volume

An electric facility is equipment indispensable to operation of a monitor, and needs to set up the power supply capacity which had a margin enough from the beginning so that it might not become electrical overload electricity use.

2) Wall socket for monitor

The power distribution to each monitor is taken from 3 line grounding type electric socket (a hooked type electric socket and an electric socket with a surge arrester are desirable) separated effectively with the switchboard.

The reserve electric sockets for check, the waterproofed type electric socket for outdoor measurement from the short circuit breaker of another system, etc., are installed except The sockets for installation monitors.

3) Wall socket for air conditioner

Connecting a monitor with the large power supply system of load changes, such as an air-conditioner, causes a noise to measured value. Therefore, power distribution to large equipment of these load changes is made another system from a monitor.

(2) Equipment against thunderbolt

The measurement office in which the panzer mast for a meteorological instrument was installed has the high danger of a thunderbolt.

Preventing the damage of an electric facility is expected general measures not only

including a thunder-proof transformer and an arrester (surge arrester) but a lightning rod and grounding.

The station in which the panzer mast for a meteorological instrument is installed has the high danger of a thunderbolt. Preventing the damage of an electric facility is expected total measures not only including a thunder-proof transformer and an arrester (surge arrester) but a lightning rod and grounding.

1) Thunder-proof transformer, arrester

It is desirable to install a thunder-proof transformer or arrester at high-risk areas for thunderbolt.

2) A ground (an earth)

When the grounding electric socket is not installed, installation construction of a ground of 100ohms or less is given for the prevention from thunderbolt influence and safety to a monitor, a data collection device, etc.

(3) Room light

The light enough for the work of check and adjustment, etc. is required, and it is desirable to secure more than 120W per 10m². (fluorescent light).

In addition, it is desirable to reserve move light as the check inside a monitor opportunity or a measure against hand darkness.

(4) Ventilation fan

Since it is the measure against exhaust and indoor ventilation when a gas leak occurs, it is necessary to install a ventilation fan. When a station is installed in the inside of a building especially, installation of a gas detector, an automatic alarm receiver, and a power supply interrupting device is desirable because of safety measures. Moreover, although installing also about a ventilation opening is desirable, attach a filter in this case and be careful for neither particulates nor garbage to come in unexpectedly.

(5) Air conditioner

Although a monitor can be used in the fixed ambient air temperature generally, since there are heat sources, such as a sample air extraction pump and a heater for temperature adjustment, at the time of the high temperature of a summer, since exceeding the maximum of this measurement temperature is also considered, installation of an air conditioner is needed. As an air conditioner of a station, although it changes with the area of a measurement office, structures, etc., it is thought that the air conditioning capability about 1500 to 6000 Kcal/h needs to be furnished.

(6) Inlet of cable for meteorological monitor and power

It is necessary to make intakes, such as a cable from an Inlet of cable for meteorological monitor and power meteorological instrument to a recorder, an indoor tie cable of a power supply, and a cable to data extraction equipment.

(7) Safety facility for storing and consuming compressed gas

Storage and consumption of high pressure gas are carried out as follows.

- A Fire etc. are not placed less than 2 m of container place.
- B However, it is not this limitation when the measure which interrupts fire and a container effectively is taken.
- C Since a container place is specified, it is desirable to stick a sticker etc. on an entrance.
- D Fix filling container (except for the net volume 5L) with a cylinder mount etc. in order to prevent the shock and the damage to a valve by a fall and turn.
- E Always keep filling container at 40 °C or less.
- F Installation of fire extinguisher is desirable. Carbon dioxide fire extinguisher is good to fire extinguisher.
- G Although the high-pressure container (cylinder) of nonflammable gas can be placed in a station, it is desirable to install a cylinder hangar on the simplicity of the clearing work of a cylinder or safety measures at outside of a station. It is necessary to make the cylinder hangar into the structure which maintains aeration with the open air from a point of safety measures, and it needs to classify combustible gas, and oxygen and other gas.
- F Cylinder takes the safety measures of fixing in a band in order to prevent the fall by an earthquake etc.

2.3.3 Air conditioning

Even if a monitor is in a suitable temperature, when ambient temperature differs from the temperature at the calibration, some monitors may induce a measurement difference.

Therefore, it is desirable to install an air conditioner in a station, and to keep small a difference with the temperature at the time of calibration, or to calibrate at the room temperature in which temperature adjustment of a station is possible.

Furthermore, if room temperature is set up too low at the high temperature in summer in order to keep calibration temperature, the necessity of taking measures may come out, for example, sampling tube is kept warm, because a condensation of a

moisture is produced within a sampling tube, and possibilities of an error of measurement and an apparatus trouble are produced. It is desirable to set a room temperature in consideration of a difference in a temperature with the ambient air of summer, and to carry out the calibration according to this temperature.

Generally, a summer is more highly set up 28 °C order in order to avoid the water condensation of a sample, and winter is set up before and after 18 °C in many cases.

Figure 2.3.1 shows relationship between condensations, sample temperature, humidity and room temperature.

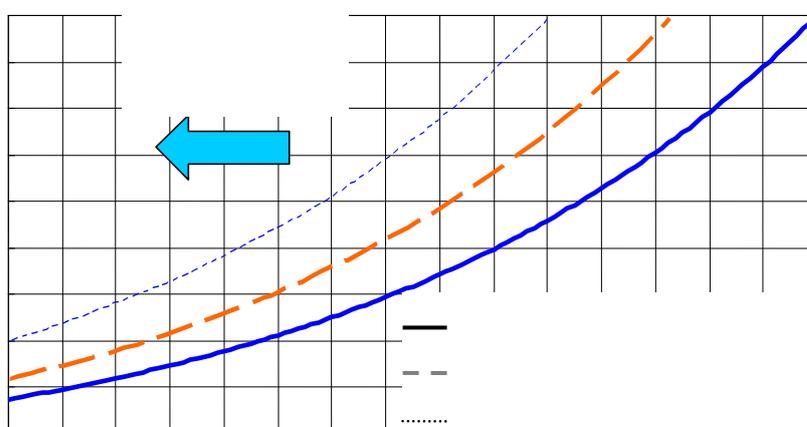


Figure 2.3.1 Relationship between condensations, sample temperature, humidity and room temperature

2.3.4 Height of sample inlet

(1) Fundamental definition

An air sampling is carried out the height of usual living and breathing of person.

- (2) According to the fundamental definition, the height of sampling for sulfur dioxide (SO₂), nitrogen dioxide (NO₂), ozone (O₃), and carbon monoxide (CO) is $1.5\text{m} \leq h \leq 10\text{m}$ above the ground, and the height for suspended particulate matter (SPM) and PM_{2.5} is $3 \text{ m} \leq h \leq 10\text{m}$ above the ground because of preventing influence of the ground, such as winding up the sand, etc. When the PM_{2.5} monitor or the sampling inlet of PM_{2.5} is installed on the roof of a station, it is necessary to decide the height of sampling inlet in order to prevent the influence on the roof, or winding up the sand on the roof.

- (3) When it cannot be based on (2) or when it is not appropriate to be based on (2) by unavoidable reasons that a reservation of a building lot is difficult etc, it is required to install the sampling inlet as follows.
- i. The height of sampling inlet is below 30m.
 - ii. It is measured at same time for more than a month continuously at neighborhood by the sampling inlet whose height is based on (2), and it is compared to the both results of daily mean. It is necessary that the difference is below 1/10 of determination limit of air quality criteria. Furthermore, this parallel measurement is desired to carry out more than four times a year for grasping the seasonal variations.

2.3.5 Air sampling method

The structure of the flow channel by which the sampling air is taken into a monitor and the objective substance in the air is measured is as follows generally.

Sampling tube—Filter—Detector—Flow controller —Pump

It is necessary to handle the channels carefully because many factors which influence the precision of measurement are in them. Notes about the sampling tube are indicated generally as follows.

A sampling tube is to take into the monitor. The material of a tube should be inert to measurement objectives and should not generate any gases disturbing measurement. Furthermore, a shorter length of sampling tube and faster rate of sampling flow are good because adsorption and reaction of an objective are proportional to the residence time from the sampling inlet to the detector.

(1) Note of sampling tube

The international standards, example for ISO (International Organization for Standardization) or CEN (European Committee for Standardization), of the measurement of NO₂ and O₃ in the ambient air, are defined “Increase of NO₂-concentration due to residence time in the analyzer” or “Calculation of residence times for a maximum allowable NO₂ increase in the sampling line” as the items for checking the performances. Those contents are as follows. (In addition, the standard value is 2% or less and 4 ppb or less.)

As O₃ is generally present in the sampled air, a change in concentrations of NO and NO₂ can occur due to the reaction of NO with O₃ in the sampling line. In order to avoid a significant change in the concentrations of NO and NO₂ the residence time in

the sampling system from the sampling inlet to the inlet of the analyzer shall be < 2 s.

The increase in the nitrogen dioxide can be calculated by the formula given in Annex A. Calculation of residence times for a maximum allowable NO₂ increase in the sampling line [ISO 13964]

The increase of the sampled nitrogen dioxide (NO₂) is due to the effect of the reaction of ambient ozone (O₃) with nitric oxide (NO) in the sampling line.

By means of the following formulas the influence of the residence time on the increase of NO₂ in the sampling line can be estimated:

$$[O_3]_0 = \frac{b \times [O_3]_t}{[O_3]_t - [NO]_t \times e^{(b \times k \times t)}}$$

where

[O₃]₀ is the ozone concentration at the sampling inlet;

[O₃]_t is the ozone concentration after t seconds of residence time in the sampling line;

[NO]_t is the nitric oxide concentration after t seconds of residence time in the sampling line;

b is the concentration difference between [O₃]_t and [NO]_t : b = [O₃]_t – [NO]_t with b ≠ 0;

k is the rate constant for the reaction of O₃ with NO : k = 4.43 × 10⁻⁴ nmol/mol⁻¹ s⁻¹ at 25 °C;

t is the residence time in seconds.

The increase of NO₂ from the reaction of ozone and nitric oxide is calculated from the loss of ozone:

$$NO_2 = [O_3]_0 - [O_3]_t$$

By assuming certain concentrations for [O₃]_t and [NO]_t and a certain residence time the increase of NO₂ can be calculated and compared to the NO₂ level already present.

Example

Taking the following values:

[O₃]_t - 22 nmol/mol

[NO]_t - 100 nmol/mol

B - 78 nmol/mol (b = [O₃]_t – [NO]_t)

K - 4.43 × 10⁻⁴ nmol/mol⁻¹ s⁻¹ at 25 °C

t - 2 seconds

results in a ozone concentration at the sampling inlet [O₃]₀ of 24.1 nmol/mol . The increase in NO₂ is 24.1 – 22 = 2.1 nmol/mol .

Assuming that the level of NO at the sampling inlet equals the level of NO₂ at the sampling inlet then the increase of NO₂ equals 2.1/(100 + 2.1) × 100 % = 2 %.

(2) Structure of sampling tube

The method of sampling air is the individual sampling method or the manifold method. The structures and notes during working are indicated as follows.

1) Individual sampling method

This method is that each monitor has each sampling tube. An individual sampling method is applied when the sampling inlet to a monitor is less than 5 m in length in general, since adsorption in a sampling tube induces a problem in the case of a gaseous pollutant. The tip of a sampling tube is attached with a funnel and bent below for preventing rainfall etc. In addition, a tube warns against becoming extreme crookedness.

In the case of SPM, it is desired the individual sampling method with short length at horizontal direction in order to prevent the absorption to the tube.

A net of preventing insect may be installed in order to prevent penetration of small insects to a sampling inlet.

It is desired for a particle loss to be small when the particulate matter in the air is introduced to separating equipment. Structure of such PM_{2.5} is desired.

Moreover, it is desired to the structure that it is no influence of a rainstorm, and foreign substances, such as an insect, and it is desirable to attach raindrop collector so that the raindrop etc. which invaded may not reach separating equipment.

Furthermore, the maximum length to a particle collector (primary detecting element) shall be 5 m or less from a sampling inlet and the maximum length to a particle collector (primary detecting element) shall be less than 1.5 m from an exit of separating equipment. From a sampling inlet, a particle collector (primary detecting element) shall be constituted by the perpendicular line, and a sampling tube must not have a bend section. For this reason, in installing a sampler in a monitoring station, it is necessary for a sampling tube to make the ceiling of a station penetrate.

2) Manifold method

This is the method that makes the air flow into the station from the sampling inlet by Blois (turbofan etc.) collectively and distributes to each monitor.

This method, which is carrying out forcible suction by Blois, is attended when the sampling tube is 5m or more in length because absorption or reaction in a sampling tube induces a problem in the case of a gaseous pollutant. However, this method is not used to PM_{2.5} because it is required to be from a sampling inlet on a plumb line to a particle collector as shown in the preceding clause.

Figure 2.3.2 shows the structure of a manifold in general using.

If the inlet of a manifold is thin, the inlet of a monitor may become negative pressure. Therefore, it is desired that the pressure is measured when installing the manifold or when extending a monitor.

The tube from a manifold to a SPM monitor is connected with the distribution inlet which is carrying out co-current to the atmospheric stream in a manifold.

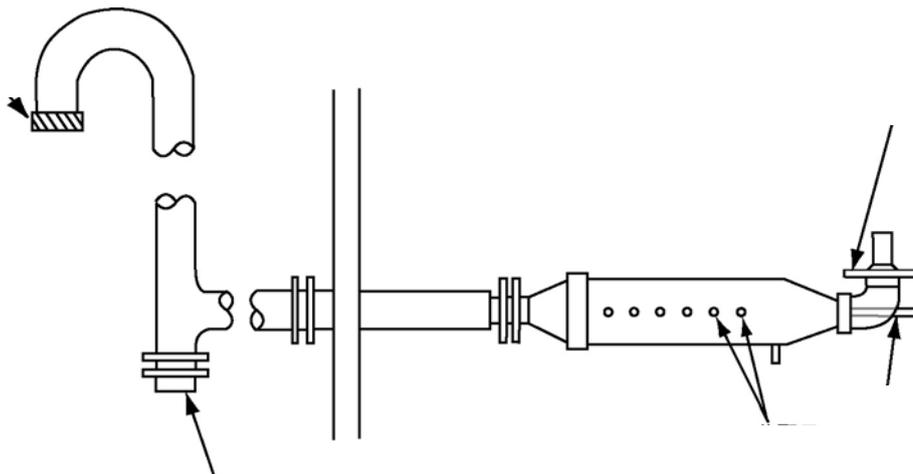


Figure 2.3.2 Example for a manifold

(3) Material of Sampling tube

It is selected the materials of a sampling tube to a monitor using for an individual sampling method or manifold method as considering the character of a measurement objective. Table 2.3.1 shows the character of objective and the material of sampling tube.

Table 2.3.1 Character of objective and material of sampling tube

Character	Objective	Material of sampling tube
Big absorption	SO ₂ , NO _x , NMHC	Polytetrafluoroethylene, Hard glass
Big resolution	O ₃	
Big adhesion loss	SPM	Vinyl chloride
	PM _{2.5}	Stainless steel, Aluminium alloy, etc

(4) Frequency of cleaning or replacement of sampling tube

The dirt, which is the particulates adhering to a tube inner wall, etc., in a sampling tube becomes a cause which raises the error by adsorption or decomposition of a

measuring object substance, and reduces measurement accuracy. For this reason, a sampling tube should wash or exchange periodically.

Although the frequency of washing or exchange changes with situations of contamination of a measurement point, it is required to carry out once or more per year at least.

Also a manifold needs internal washing (cleaning) once a year or more.

2.3.6 Note of monitor installation

It is desired to have the following condition as for the location of a monitor.

i. Little vibration

Since a monitor has a vibratory source of a suction pump etc., and there is a possibility of giving vibration to other monitors, especially when it is a wooden floor, it is necessary to take the measures against a seismic isolation against a floor depending on the case.

ii. Few corrosive gases and particulates

Corrosive gas and particulates have a possibility of waking up the loose connection of the electric part of a measurement machine. For this reason, it is necessary to prevent invasion into the station of these substances, and to avoid use of the reagents which generate the corrosive gas in the interior of a room, and preservation.

iii. Low humidity, moreover, temperature should be near the temperature of the calibration

When the humidity in a station is high, it becomes loose connection's cause like item ii.

iv. Little change of power supply voltage and frequency, moreover, neither big electromagnetic induction equipment nor the generating equipment of spark discharge should be close, measure against thunderbolt depending on the area.

A monitor may be horizontal and not incline

v. Maintenance work can be done safely easily

Maintenance and repairs of a monitor may be performed from the back side of the monitor. For this reason, it is desirable to take and install an interval with a wall so that work on the back side can be carried out.

vi. Short sampling tube, Moreover, don't attract rain water, an exhaust gas, etc. directly.

As for a monitor which has adsorption of a measurement objective, or fear of decomposition with a sampling tube, as the length of a sampling tube shows according to each item, it is desirable to arrange a monitor to a station so that it

may become as short as possible.

2.3.7 Safety requirement

It is necessary to take proper safety measures against installation of a station with careful attention to the following matters.

(1) Safe consideration of peripheral people

1) At establishing station

- A Entry restrictions into A construction zone
- B Electric shock preventive measures under a station installation
- C Traffic safety to construction vehicles

2) At working

Electric shock preventive measures to the peripheral people after a station operation.

(2) Prevention of toxic substance leakage

It is arranged and kept so that a harmful thing may not leak out outside an office with replacement parts etc.

(3) Handling of compressed gas

A gas cylinder is kept safely.

In addition, about details, it is 2.3.2 of this manual. Refer to installation of the safety facilities in storage and consumption of installation of (4) ventilation fans of equipment, and (7) high pressure gas.

(4) Safe consideration at routine check and maintenance

The measure against handling of toxic substances, such as safe consideration at routine check and maintenance cleaning fluid.

(5) Prevention of natural disaster

1) Against earth shake

The methods of always making the caster of the monitor the freelancer as prevention from a fall of heavy loads, such as a measurement machine, such as an earthquake-proof mat and anchor fixation, can be considered.

2) Against fire

It is cautious of the short circuit by leak in the roof, etc. in usual management. Moreover, when high pressure gas is being used, "Compressed gases" is displayed on the door of a station.

- A Preparation of initial fire extinguishing (permanent installation of a fire extinguisher)
- B Fire-resistance of building

C Subscription of fire insurance

There is also an example which has purchased the fire insurance policy etc. about a monitor or a station.

2.3 Monitoring frequency [Network Center]

For evaluation of dry deposition, the sampling period of air concentrations could be longer than one day to one or two week. Hourly data are required where diurnal cycles in deposition velocity are to be explicitly monitored. The actual measurement items can be decided by taking account of the presently available air quality monitoring and feasibility of additional monitoring activities as well. This monitoring might employ either of real-time monitors or integrating samplers (filter packs, denuders, or passive samplers, as may be determined appropriate). For SO₂, for example, use of a real-time monitor is preferred, with data reported so that averages over hourly concentrations can be archived. For all chemicals measured specifically for dry deposition applications, longer time averages (e.g. weekly) would be adequate. These can be derived from daily averages if appropriate, or from any other sampling protocol that might be desired.

For the purpose of air quality monitoring, one-hour averaged values are principally preferred, and the availability of commercial or conventional instruments has to be also considered. For example, automatic instruments for SO₂ (fluorescence method), O₃ (UV absorption method) and NO (ozone chemiluminescence method) are suitable to obtain one-hour averaged values of these species for air quality monitoring. These one-hour averaged values can of course be used for the purpose of the evaluation of dry deposition after averaging over longer periods -- e.g. for one week.

3. Manual monitoring

In order to evaluate the extent of air concentrations in East Asia spatially and temporally, a sufficiently long record of data from a dense network of sites distributed over the region is usually required. The data should also be acquired using reliable methods and practices. Presently, the number of EANET monitoring sites is limited and not well distributed. One of the reasons for the lack of air quality monitoring sites in some countries is the high cost of automatic instruments and recurrent costs of operating the instruments.

One of the possible ways to overcome this problem is to adopt the simpler, low cost methodologies such as filter packs, passive samplers and denuders in less accessible sites. These methodologies are used widely in monitoring networks and for field campaigns in the world.

3.1 Filter pack

A multiple filter-pack method can provide significant information, such as the concentration of chemical species in particulate matter and gaseous compounds including ammonia and nitric acid (Karakas and Tuncel, 1997; Sickles et al., 1999). The monitoring using filter-pack method has been widely conducted all over the world (Aikawa et al., 2005, 2006, 2008, 2010; Endo et al., 2011; Mehlmann and Warneck, 1995; Tørseth et al., 1999; Kim et al., 2001; Matsuda et al., 2001; Viet et al., 2001).

Among the air concentration monitoring methods, filter packs have been adopted for the dry deposition monitoring programs in CASTNet (US), CAPMoN (Canada) and EMEP (Europe). EANET also has experiences to carry out monitoring using the filter pack methods for longtime.

3.1.1 Principle of using filter pack

The four-stage filter pack is composed of four filters in line with the air stream as shown in Fig.3.1. Aerosols are collected on the first filter (F0: made of PTFE), while the gaseous substances such as SO₂, HNO₃, HCl, NH₃ will pass through this filter. The second filter (F1: made of polyamide) collects all HNO₃ and partial SO₂, HCl and NH₃ from the sampling air. The remaining SO₂ and HCl react with alkali substance on the third filter (F2: made of cellulose). Nitric acid and sulphur dioxide will react with potassium hydroxide on this impregnated filter to give potassium nitrate and potassium sulphite. Oxidizing species in air e.g. ozone are believed to convert most of the sulphite

to sulphate during the sampling. The remaining NH_3 reacts with acid substance on the fourth filter (F3: made of cellulose) after passing through the first, second and third filters. Ammonia is effectively retained on a filter impregnated with citric or oxalic acid. The filter pack method is useful for total (gaseous and particulate) NH_4^+ and NO_3^- monitoring.

Aerosols are collected on the aerosol filter (F0) mounted in front of the other filters (F1, F2 and F3) collecting gases. The material of the aerosol filter should not absorb acid and alkali gases and should have acceptable efficiency to collect sub-micron particle because sulfate aerosols are mostly of the fraction below $1 \mu\text{m}$. For this purpose, Teflon (PTFE; polytetrafluoro-ethylene) filters are preferred.

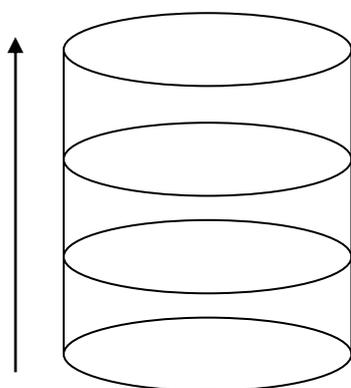


Fig. 3.1 Schematic diagram of the four-stage filter pack (EANET, 2003)

3.1.2 Artifacts of filter pack

The filter pack method has an advantage that it enables one to collect particles and gases simultaneously. However, one has to be aware of the fact that it is subject to artifacts in the measurement of HNO_3 , NH_3 and HCl at high ambient temperatures.

It should be emphasized that filter pack method does not ensure completely precise measurement due to possibility of artifact problems. For example, volatilization of particulate NH_4NO_3 and NH_4Cl after collected on a filter, caused by increase of temperature during sampling period, could occur. The volatilized compounds are collected as gases such as NH_3 , HNO_3 and HCl on following filters. In addition, high humidity might cause a reduction of gas concentration measured by filter pack method due to trapping of gases by condensed water in the filter pack. Previous studies, however, provided some evidences that the artifacts are not so significant (EANET, 2003). The uncertainty of this method is also different among urban or remote site.

A bias may be introduced if the aerosol filter becomes wet during sampling since it

is possible to have absorption of sulphur dioxide on cellulose based filters. This gives an overestimation of the sulphate concentrations in aerosols and a corresponding underestimation of the sulphur dioxide. Another source of error could be that the absorption of sulphur dioxide on the impregnated filter is not 100 per cent effective. Experiments with a second KOH-impregnated filter behind the first have, however, not given measurable amount of sulphur dioxide.

It may be possible to lose components before the analysis due to incomplete extraction from the filter.

Since the filter pack method cannot separate gaseous nitrogen compounds from aerosols only the sum can be given. In other words, the concentration of nitrates in air equals the sum of the nitrate found on the aerosol filter and nitrate found on the alkaline impregnated filter. The same for ammonium where the sum of ammonium concentration equals the sum of ammonium collected on the aerosol front filter and ammonia collected on the acid impregnated filter.

Nitric acid in the gaseous state readily reacts with other atmospheric constituents to form nitrates in the form of atmospheric particles. If ammonium nitrate is formed, the reaction is reversible, and its presence requires a dissociation product of gaseous nitric acid and ammonia, which in turn depends on temperature and relative humidity.

The mechanisms of artifacts are based on the reactions as follows:

(1) Artifacts of HNO_3 ,

- I. $\text{NH}_4\text{NO}_3 (\text{P}) \rightarrow \text{NH}_3 (\text{G}) + \underline{\text{HNO}_3 (\text{G})}$,
- II. $\text{NH}_4\text{NO}_3 (\text{P}) + \text{H}_2\text{SO}_4 (\text{P}) \rightarrow \text{NH}_4\text{SO}_4 (\text{P}) + \underline{\text{HNO}_3 (\text{G})}$,
- III. $\text{NaNO}_3 (\text{P}) + \text{H}_2\text{SO}_4 (\text{P}) \rightarrow \text{NaHSO}_4 (\text{P}) + \underline{\text{HNO}_3 (\text{G})}$,
- IV. $\text{NaCl} (\text{P}) + \underline{\text{HNO}_3 (\text{G})} \rightarrow \text{NaNO}_3 (\text{P}) + \text{HCl} (\text{G})$;

(2) Artifacts of NH_3 ,

- I. $\text{NH}_4\text{NO}_3 (\text{P}) \rightarrow \underline{\text{NH}_3 (\text{G})} + \text{HNO}_3 (\text{G})$,
- II. $\text{NH}_4\text{Cl} (\text{P}) \rightarrow \underline{\text{NH}_3 (\text{G})} + \text{HCl} (\text{G})$,
- III. $\text{H}_2\text{SO}_4 (\text{P}) + \underline{\text{NH}_3 (\text{G})} \rightarrow \text{NH}_4\text{HSO}_4 (\text{P})$,
- IV. $\text{NH}_4\text{HSO}_4 (\text{P}) + \underline{\text{NH}_3 (\text{G})} \rightarrow (\text{NH}_4)_2\text{SO}_4 (\text{P})$;

(3) Artifacts of HCl ,

- I. $\text{NaCl} (\text{P}) + \text{HNO}_3 (\text{G}) \rightarrow \underline{\text{HCl} (\text{G})} + \text{NaNO}_3 (\text{P})$,
- II. $2\text{NaCl} (\text{P}) + \text{H}_2\text{SO}_4 (\text{P}) \rightarrow \underline{2\text{HCl} (\text{G})} + \text{Na}_2\text{SO}_4 (\text{P})$,
- III. $\text{NH}_4\text{Cl} (\text{P}) \rightarrow \underline{\text{HCl} (\text{G})} + \text{NH}_3 (\text{G})$.

(P) and (G) mean "particle" and "gas", respectively.

3.1.3 Specifications of filters

The filter material should not absorb SO₂ and should have acceptable collection efficiency for submicron particles. Cellulose filters are acceptable for this purpose, but membrane filters, e.g. Teflon, are preferred.

1) Filters for aerosol sampling

Aerosols are collected at the first stage. The first stage filter is mounted in front of the other filters collecting gases. The material of the aerosol filter should not absorb acid and alkali gases and should have acceptable efficiency to collect sub-micron particles. For this purpose, Teflon (PTFE; polytetrafluoro-ethylene) filters are preferred. It was evaluated that the differences in the use of a quartz filter and a PTFE filter as a first (F0)-stage filter and the total material to be collected by the four stage filter-pack method was almost the same irrespectively of the first-stage filter used (Aikawa et al., 2010).

2) Filters for nitric acid sampling

The second stage filter is designated to collect nitric acid. Nitric acid passes through the first stage and is caught on the second filter in principle. In order to collect nitric acid separately from other nitrogen oxides, Nylon (polyamide) filters are preferred.

It has to be taken notice that the second polyamide filter collects partial sulfur dioxide, hydrochloric acid and ammonia as along with nitric acid from the sampling air.

3) Filters for sulfur dioxide and hydrochloric acid samplings

The remaining sulfur dioxide and hydrochloric acid that pass through the second stage will be collected on the third stage. The remaining sulfur dioxide and hydrochloric acid react with alkali substance on the filter mounted on the third stage. For this purpose, cellulose filters impregnated by potassium carbonate are preferred.

For the calculations of ambient concentrations, the amounts of sulfur dioxide, hydrochloric acid, and ammonia collected by the second filter have to be added to those collected by the alkali-impregnated filters.

4) Filters for ammonia sampling

The remaining ammonia that passes through the second and third stages will be collected on the fourth stage. The remaining ammonia reacts with acid substance on the filter mounted on the stage (third or fourth). The filters are preferable to be impregnated by phosphoric acid. The cellulose filters, which are same as the third stage filter, could be utilized. For the calculation of ambient concentration, the amount of ammonia collected by the second filter has to be added to that collected by the acid-impregnated filters.

The specifications are summarized in Table 3.1.

Table 3.1 Specifications of filters (EANET, 2003)

Stage	Specifications of filters	Reaction	Collected species
First	Teflon (PTFE) filter	Filtration	Aerosol
Second	Nylon (Polyamide) filter	Adsorption	HNO ₃ Partial SO ₂ , HCl
		Neutralization by collected acid gases	Partial NH ₃
Third	Case 1: Cellulose filter impregnated by K ₂ CO ₃	Neutralization by alkali impregnated on the filter	SO ₂ , HCl
Fourth	Filter impregnated by phosphoric acid	Neutralization by acid impregnated on the filter	NH ₃

3.1.4 Sampling

1) Sampling system

A diagram showing the sampling system is given in Figure 3.2. The air intake should have a cylindrical, vertical section 15 cm wide and at least 25 cm high. This air intake reduces the sampling efficiency for particles which aerodynamic diameter is larger than 10µm, such as soil dust particles, large sea spray droplets, large pollen, and fog droplets. The filter pack is placed directly in the air intake, and it should have separate supports for the aerosol and the impregnated filters in order to avoid contamination from one filter to the next.

In the case of any close obstacles in the surround of the monitoring site such as forest trees, the inlet should be set up higher than 3 meters above the ground, if possible over the top of the obstacles (above tree canopies).

Since the absorption of sulphur dioxide is only quantitative at relative humidities above 30, sampling with a filter pack should take place outdoor, only sheltered from the ambient air by the air inlet. Additions of glycerol may improve the absorption efficiency of the impregnated filter at low humidities.

Maintenance of equipment should be performed in accordance with their instructions for operation of field instruments such as pumps, flow meters and gas volume meters. Calibration of the flow meters and the gas volume meters should be done at least once every year using the national standard method.

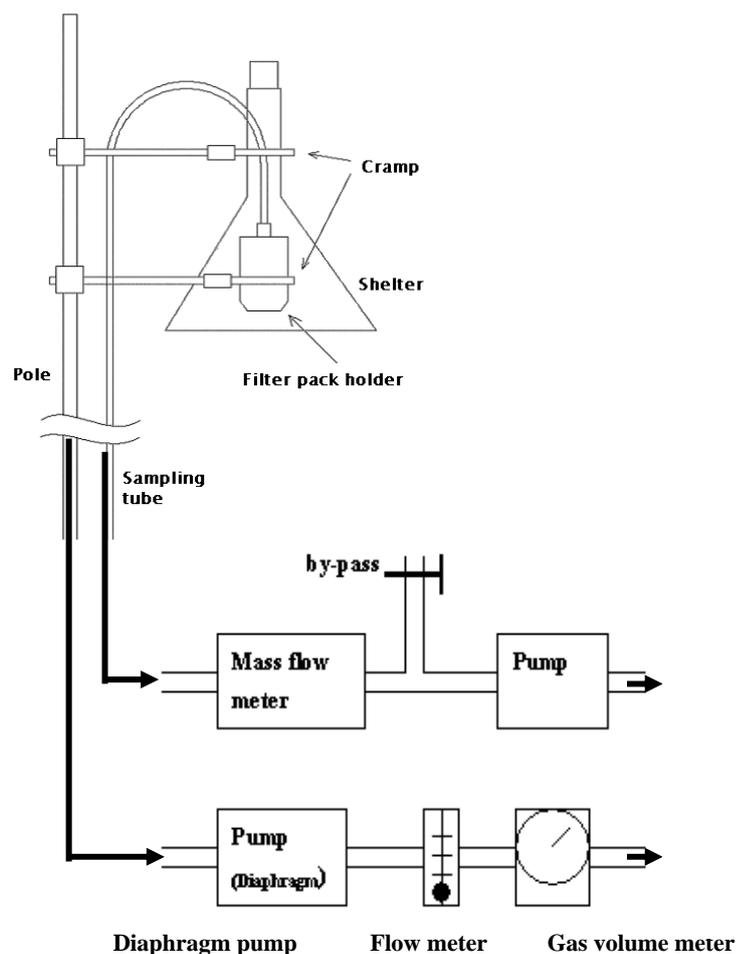


Fig. 3.2 Schematic diagram of filter pack sampling system (EANET, 2003)

2) Flow rate

The flow rate of 1 liter/min is recommended for weekly or biweekly sampling. If it would be difficult to detect concentrations in remote sites, flow rates could be increased up to 2 liter/min. Typical flow rate for daily sampling is around 15 liter/min. Open-face inlet should be recommended in the case of weekly or biweekly sampling. If specific devices are utilized for removing large particles in the inlets such as impactor, the exact flow rates depend on the devices.

Diaphragm pump is recommended for stable flow rates during the sampling. It is recommended to use mass flow controllers to control the sampling rate. Especially at the sites located in high altitude mountain, the mass flow meters should be adopted to avoid the effect of the lower atmospheric pressure. The mass flow meter should be installed between filter holder and pump. Gas volume meters with flow rate meters (of float type) could be also acceptable. In this case, the flow rate meters and gas volume meters should be set up consequently after the pump to measure flow rates and volumes

under the condition of atmospheric pressure.

Air volumes counted by mass flow meters or gas volume meters are used for calculation of ambient air concentration. Accurate volume readings are important for the resulting measurement's accuracy, and the volume meters may need frequent calibrations. Calibrations should under no circumstances be less frequent than once or twice every year. The accuracy must be better than 5%. If the pump and gas meter is kept at room temperature, no corrections are usually required, and the air volume is then assumed to be the sample air volume at 20°C. If deviations of more than $\pm 5^\circ\text{C}$ are expected, the temperature in the gas meter surroundings has to be recorded and the air volume corrected accordingly.

3) Sampling procedure

At the site, and before the filter pack is mounted in the sampling line, the site operator has to write the start date on the filter pack, and likewise the end date of the sampling after exposure. Further details are to be written into the site journal and copied into site reporting forms, worked out for this purpose.

Recommended sampling procedure at monitoring site is described as follows:

[Start]

- 1) Read the registered value of the volume meter counter and record it in the sampling notebook;
- 2) Remove the exclusive cap from the new unexposed filter pack and mount the holder in the sampling system;
- 3) Switch the pump on and record the time and the flow rate in the sampling notebook;

[Stop]

- 4) Record the flow rate in the sampling notebook;
- 5) Switch the pump off and record the time in the sampling notebook;
- 6) Dismount the filter pack holder from the sampling system, put the exclusive cap on and then seal it into a polyethylene bag and an aluminum-coated bag;
- 7) Keep the sealed holder in the transportation box;
- 8) Read the value of volume meter counter and record it in the sampling notebook.

3.1.5. Operation in laboratory

1) Mounting and Transportation of filter packs

It is recommended that the filter pack is assembled and dismounted in the laboratory only. The filters are mounted on the filter holder using clean plastic tweezers. When assembling the filter pack, the parts should be tightened to the torque specified by the

manufacturer to prevent leaks. The leak of air through stage connections should be checked using a flow meter with a pump every time (Fig.3.3). And then the mounted filter holder should be capped by an exclusive cap. Air tight protection covers need to be mounted in both ends of the filter pack. Each filter pack should be tagged with the site code in the laboratory before it is sent to the site.

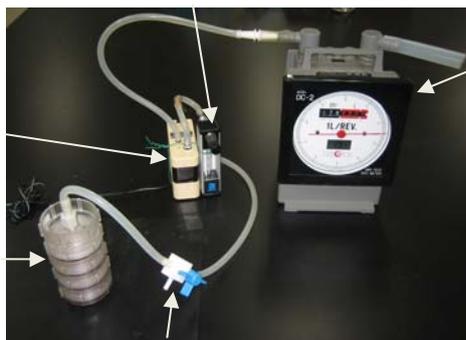


Fig.3.3 Operation of leak check for filter pack

Care should be taken to avoid materials in the filter pack which may be a source of contamination or absorb sulphur dioxide or other air components which are to be determined such as that Nylon will absorb nitric acid. Teflon, polyethylene, polypropylene, PVC, and polycarbonate are recommended materials. Ordinary rubber and nylon contains sulphur and should be avoided.

After leak checking, the mounted filter holder should be sealed into a polyethylene bag. And an aluminum-coated bag should be used to seal it up further. The sealed mounted holder should be kept in a transportation box during their deliverance to a monitoring site. It is recommended to ship filter packs from the laboratory to the site weekly or biweekly, and vice versa. One extra filter pack, complete with filters, should be added as a field blank (i.e. one field blank every week). This filter pack should be handled in every way as the ones to be exposed, returned with the other filter packs from the batch, dismantled, and the filters are given the same chemical treatment and analysis as the exposed filters.

Sample filters are recommended to be dismantled from the holder in the laboratory and be kept separately in clean plastic filter cases with description of sample number. Exposed filter packs should be opened in the laboratory and the filters put into plastic bags, which in advance, have been tagged with site code, start and stop of sampling, and filter type. The filters are now ready for a chemical treatment and the analysis. Normally there is a delay between this step and the time when actual chemical treatment and the analysis takes place. During this period the samples are to be kept in a refrigerator. It is

important to wear a pair of disposable plastic gloves when working with the filters and the filter packs.

2) Preparation of filter pack

PTFE filter (pore size: $0.8\mu\text{m}$, diameter: 47mm) is recommended as the first filter (F0). Polyamide filter (pore size: $0.45\mu\text{m}$, diameter: 47mm) is recommended as the second filter (F1). The third filter (F2) is recommended to be cellulose filter (diameter: 47mm) impregnated with a solution prepared by mixing 6% K_2CO_3 + 2% glycerin in pure water. The fourth filter (F3) is made of cellulose filter (diameter: 47mm) impregnated with a solution of mixed 5% phosphoric acid + 2% glycerin in pure water. A solution to be used for impregnation should be prepared the same day the impregnation of a new series of filters will take place.

Filters and extraction solutions should be handled in the laboratory only under the clean conditions. Moreover they should not be exposed to air longer than necessary due to a possible uptake of gases by filters or solutions. Disposable plastic gloves and tweezers should always be used when handling filters. Only a clean filter holder should be used to prevent excess contamination. Filters, especially impregnated one, should be always sealed up to avoid the contamination by unexpected ambient pollutants before or after the sampling time.

The following procedure may be used. The filters are placed on plastic stoppers after which the impregnation solution is dripped on the filter. The filters may be dried in air, usually is half an hour sufficient. When the filters are dried they must be placed in plastic bags and the zippers closed. The bags should be labeled with type of filters and date.

Recommended preparation procedure of alkali impregnated filter (F2) is described as following steps:

- 1) Prepare the mix solution (6% K_2CO_3 + 2% glycerin);
 - Prepare three 500mL beakers;
 - Weight 30g of K_2CO_3 and 10g of glycerin in each 500mL beaker;
 - Pour deionized water (less than 0.15mS/m) into each beaker and adjust to 500g;
 - Mark the numbers (No.1, No.2 and No.3) of the beakers for distinction;
- 2) Dunk cellulose filters into No.1 beaker and stir them with a glass stick;
- 3) Pull up a filter from the No.1 beaker using plastic tweezers; dunk it in the No.2 beaker for the rinse;
- 4) Pull up the filter from the No.2 beaker using plastic tweezers; dunk it in the No.3 beaker for the rinse;
- 5) Pull up the filter from the No.3 beaker using plastic tweezers, and put the filter

between two sheets of large cellulose sheet (ADVANTEC No.590) to absorb extra water from the impregnated filter;

- 6) Keep the impregnated filter into a clean plastic filter case and seal it in a polyethylene bag with marking “ K_2CO_3 ”;
- 7) Back to step 2) for next filter. But maximum 20 sheets could be prepared by one solution.

Recommended procedure of preparation of acid impregnated filter (F3) is described as following steps:

- 1) Prepare the mix solution (5% H_3PO_4 + 2% glycerin);
 - Prepare three 500mL beakers;
 - Weight 29.4g of H_3PO_4 and 10g of glycerin in each 500ml beaker;
 - Pour deionized water (less than 0.15mS/m) into each beaker and adjust to 500g;
 - Mark the numbers (No.1, No.2 and No.3) of the beakers for distinction;
- 2) Dunk cellulose filters into No.1 beaker and stir them with a glass stick;
- 3) Pull up a filter from the No.1 beaker using plastic tweezers; dunk it in the No.2 beaker for the rinse;
- 4) Pull up the filter from the No.2 beaker using plastic tweezers; dunk it in the No.3 beaker for the rinse;
- 5) Pull up the filter from the No.3 beaker using plastic tweezers, and put the filter between two sheets of large cellulose sheet (ADVANTEC No.590) to absorb extra water from the impregnated filter;
- 6) Keep the impregnated filter into a clean plastic filter case and seal it in a polyethylene bag with marking “ H_3PO_4 ”;
- 7) Back to step 2) for next filter. But maximum 20 sheets could be prepared by one solution.

Filters, especially impregnated one, should be always sealed up to avoid the contamination by unexpected ambient pollutants before or after the sampling time. Disposable gloves and tweezers should be used when handling the filters. Cellulose filters should be cleaned if necessary before use.

Impregnation solution should be used the day it is prepared. After each cleaning and drying process 5 filters should be analyzed for major ions and all concentrations meet strict requirements. If the requirements are not met, all filters from the impregnation batch should be thrown and a new batch made. If the requirements are met the bags should be signed and dated.

Impregnated filters should be kept inside dated and signed plastic bags. Each of the filter cases should be sealed one by one into a polyethylene bag. Furthermore, they should be placed into aluminum-coated bag. After the sealing they should be kept in the

refrigerator. The bags filled with impregnated filters should be stored in desiccators; alkaline impregnated filters in one desiccator and acid impregnated ones in a different one. The desiccator for KOH impregnated filter should have KOH at the bottom, and the one for acid impregnated filter should have citric acid at the bottom. Impregnated filters should not be stored more than 3 months before use. All quality assurance steps and results should be recorded in the laboratory journal.

3) Extraction and chemical analysis

Extractions and chemical analysis of blank filters stored in a laboratory should be carried out at the same time. For the extractions, the sample shakings should be done by using a shaker or an ultrasonic bath during 20 minutes. Chemical analysis should be carried out each month in a lump but as soon as possible after the extractions. Analyzed species and solvent for each stage are shown in Table 3.2.

Table 3.2 Analyzed species and solvent for each stage filter (EANET, 2003)

Stage	Species	Solvent
First	SO ₄ ²⁻ , NO ₃ ⁻ , Cl ⁻ , NH ₄ ⁺ , Na ⁺ , K ⁺ , Ca ²⁺ , Mg ²⁺	Deionized water
Second	SO ₄ ²⁻ , NO ₃ ⁻ , Cl ⁻ , NH ₄ ⁺	Deionized water
Third	Case1: SO ₄ ²⁻ , Cl ⁻	0.05% H ₂ O ₂
Fourth	NH ₄ ⁺	Deionized water

Recommended extraction procedure is described as follows:

- 1) Prepare polypropylene test tubes (50ml) with caps;
- 2) Dunk polypropylene test tubes into the diluted laboratory detergent for overnight and then wash them by water (at the first) and deionized water (at the second), and dry them in clean air;
- 3) Mark the sample identification on each test tube such as F0 filter with sample number, F0 filter blank, F1 filter with sample number, F1 filter blank and so on;
- 4) Put the sample filters into correspondent test tube;
- 5) In the case of F0, F1, F3 stage samples, pour 20mL deionized water into the tubes; in the case of F2 stage sample (alkali impregnated stage) pour 20mL H₂O₂ solution (0.05%-v/v) into the tubes;
- 6) Shake the sample tubes during 20 minutes for their extractions using a shaker or an ultrasonic bath;

- 7) Pick up the filters from the extracted solutions in the tubes and cover the tubes using exclusive caps;
- 8) Filter the insoluble matters out of the extracted solutions using a membrane filter (pore size 0.45µm) previously well washed by deionized water;
- 9) Keep the sample tubes in the refrigerator.

Ion chromatography (IC) is recommended for analysis of the above-mentioned chemical components. The analytical method should follow the procedures described by “Technical Documents for Wet Deposition Monitoring in East Asia”.

If the detection would be still difficult in spite of increasing the air flow rate, the solvent volume might be set less than 20mL but to be enough for analyzing.

It is recommended that 10 samples from each new batch of filters are analyzed as laboratory filter blanks. The purpose of the filter blanks is to control the quality of the filters rather than to estimate the laboratory detection limit. Normally, the blank values should be sufficiently low that their values can be ignored. If high blank values are found a problem has occurred which has to be identified and solved, e.g. by using filters or chemicals from another batch, and by inspection of the routines in the laboratory.

3.1.6 Determinations of concentrations and data reporting

The concentrations of a compound in air are basically determined as follows:

$$C_{\text{Air}} = \alpha \times \text{net } C_{\text{Sol}} \times V_{\text{Sol}} / V_{\text{Air}} \quad (\alpha = 10^3 / M);$$

C_{Air} : concentration in the air (nmol/m³),
 net C_{Sol} : net concentration in the solution (mg/l),
 V_{Sol} : volume of the solution (ml),
 V_{Air} : volume of the sampled air corrected at 20 °C, 1 atm (m³),
 M : molecular weight.

The net C_{Sol} should be calculated by:

$$\text{net } C_{\text{Sol}} = C_{\text{Sol, Sample}} - C_{\text{Sol, Blank}} ;$$

$C_{\text{Sol, Sample}}$: concentration in the solution from the

sample filter,

$C_{\text{Sol, Blank}}$: median concentration in the solutions from the blank filters.

A blank value should be determined as median of 5 analytical results of blank filters. One median value is available as the blank value for sample sets obtained for one month. Chemical analysis of samples and blanks should be done each month in a lump. When a

blank value is detected as higher than the sample value, the corresponded data should be regarded as non-detected data (N.D.). If samples seem to be obviously contaminated, the data should be treated as unrecorded data. If sampling processes are stopped by any accident during sampling periods (for example; shutdown of electricity), the samples obtained in these periods should be rejected, because filter packs absorb gases like passive samplers when they are in the breaks.

Regarding the determinations of concentrations, the equations are summarized in Table 3.3.

Table 3.3 Equations for determinations of concentrations (EANET, 2003)

Specie	M	Equation
SO ₄ ²⁻	96.06	$C_{Air} = \alpha \times \text{net } C_{Sol, F0} \times V_{Sol} / V_{Air}$
NO ₃ ⁻	62.01	
Cl ⁻	35.45	
Na ⁺	22.99	
K ⁺	39.10	
NH ₄ ⁺	18.04	
Ca ²⁺	40.08	
Mg ²⁺	24.31	
SO ₂	96.06 (SO ₄ ²⁻)	$C_{Air} = \alpha \times (\text{net } C_{Sol, F1} + \text{net } C_{Sol, F2}) \times V_{Sol} / V_{Air}$
HNO ₃	62.01 (NO ₃ ⁻)	$C_{Air} = \alpha \times \text{net } C_{Sol, F1} \times V_{Sol} / V_{Air}$
HCl	35.45 (Cl ⁻)	$C_{Air} = \alpha \times (\text{net } C_{Sol, F1} + \text{net } C_{Sol, F2}) \times V_{Sol} / V_{Air}$
NH ₃	18.04 (NH ₄ ⁺)	$C_{Air} = \alpha \times (\text{net } C_{Sol, F1} + \text{net } C_{Sol, F3}) \times V_{Sol} / V_{Air}$

#1 $\alpha = 10^3 / M$

#2 net C_{Sol, F1} means the net C_{Sol} of the F1 sample filter

It was recommended that more than two technical staffs work for manual monitoring at one monitoring site in order to share skill. The technical staffs that are in charge of filter pack operation can be trained by Network Center of EANET.

3.2 Passive sampler

Passive samplers provide a simple and cost effective way of monitoring specific species at urban, regional and global scales, and offer broad capacity building opportunities. While the appropriateness of the use of passive samplers has been questioned in the past due to concerns related to reliability and accuracy, current developments and studies indicate that passive samplers are now a viable option for

many species and many applications.

Passive samplers offer a wide variety of advantages for use in the field. There is no need for calibration and electricity, and thus are easy to be fixed in the field. The passive samplers are simply fastened inside shelter to avoid splashing from precipitation attached to a pole which is typically 1 meter high. They are small inexpensive, and provide time-integrated, and continuous samples. One of the benefits is that artifact caused by evaporation of particles can be avoided. The time-resolution of passive sampler is very low, so the passive sampler can only monitor the weekly average concentrations.

They can be used to check spatial variability in pollution fields and the representativeness of locations of advanced sampling stations, used to measure background concentrations at places where other measurements are difficult, and can be used in urban environments.

3.2.1 Basic principles

A passive sampler is a very simple device consisting of an impregnated filter or molecular sieve which preferentially sorbs the gas to be analyzed, and a diffusion barrier (usually an entrapped air volume) that keeps the sampling rate constant. If the sampling efficiency is sufficiently high, then the sampling rate can be calculated using Fick's first law of diffusion from the cross sectional area perpendicular to the transport direction and the distance that the gas has to diffuse.

The sampling technique is based on the property of molecular diffusion of gases, hence the term passive (also referred to as diffusive) sampling. The gas molecules diffuse into the sampler where they are quantitatively collected on an impregnated filter or an absorbent material. Thus they achieve a time-integrated (or average) concentration. No electricity, pumps or other supporting equipment are needed.

Inorganic gases are absorbed by chemical reaction on a filter, impregnated with a solution specific to each pollutant measured. The reaction product, which is washed out of the filter prior to analysis, is specific to the particular gas in question. When species do not react sufficiently fast with other chemicals (e.g., organics) they are instead trapped on an absorbent material. Such gases are then desorbed from the adsorbent during analysis.

To work properly (and quantitatively) it is essential that the transport occurs solely by molecular diffusion and that no gas is lost to the walls of the sampler. Under these conditions then the sampling rate, and thus the concentration range of the sampler, is directly proportional to its cross sectional area and inversely proportional to its length. Furthermore, since the rate of molecular diffusion depends on temperature (through the

temperature dependency of the molecular diffusivity), the average sampling rate (sorbed amount per unit time divided by the ambient concentration) is a temperature dependent constant for a given species and sampler.

Care must be taken to ensure that the gas is transported to the filter by molecular diffusion. If the inlet end of the tube is left open then convective transport can occur, resulting in a higher sampling rate and thereby an overestimation of the concentrations (EANET, 2008). It was showed that covering the inlet region of the sampler with a fine mesh (stainless steel mesh with a thread diameter of 0.08mm and mesh aperture of 0.125 mm) can minimize these errors for high-dose samplers (EANET, 2008). Low-dose samplers are more sensitive to wind effects, and porous membranes supported by steel mesh are commonly used to cover the sample inlet (EANET, 2008).

The success of a diffusion sampler rests critically on the collection efficiency of the impregnated filter. A solid and stable reagent which selectively and quantitatively chemisorbs the targeted species and transforms it into another stable form in which other pollutants do not interfere is needed for passive samplers. This is the key factor which determines which species are suitable for passive sampling. The average concentration at the measurement site over the time period that the sampler is exposed to ambient conditions is determined by chemical analysis of the filter. Analysis consists of removing the impregnated filter and leaching the reaction product, typically using de-ionized water.

The leachate is then analyzed using an appropriate analytical technique. The highest concentration that can be measured depends on the amount of sorbent on the impregnated filter. This is typically estimated by the stoichiometric amount of the impregnate reduced by a safety factor (typically a factor of 2).

The lower detection limit of the samplers is determined by the use of blanks. As soon as a filter is impregnated it will begin to measure ambient levels. A filter kept in the laboratory will measure laboratory levels, while field blanks will measure the integrated exposure during the transport and storage periods. Just before the samplers are sent to the field, the filters are impregnated, samplers labeled for batch number, a few filters checked immediately, and then filters identified for lab and field blanks. The laboratory blanks are stored in the lab and periodically tested. The field blanks are kept in their containers and accompany the samplers to the field and are returned after the filters are exposed, and are analyzed along with the exposed samples. The concentrations determined from the exposed filters are then corrected using the blanks. The lower detection limit is commonly defined as 2 to 3 times the standard deviation of the blanks. Thus, procedures/improvements which reduce the standard deviation of the blanks result in significant improvements in the lower detection limits of the samplers. The repeatability of the results is quantified and checked by use of duplicate samples.

Blank filters will be analyzed at same time for each compound.

The samplers are very easy to manufacture. They are also very cheap to manufacture and all components, except the impregnated filter can be reused. They have many other advantages as well for use in the field. For example they are small, light, and require no electricity.

It should be emphasized that they provide time integrated concentrations with continuous time coverage, with the averaging time determined by the period they are exposed to ambient air (which can be daily, weekly, monthly, etc.). They are obviously not well suited for monitoring temporal variations over short time intervals, or for detection of individual peak values, or when real-time measurements are needed.

3.2.2 Species specific information

Passive samplers are being used for a variety of applications and for a variety of species. The specific information for the measurement of ambient SO₂, NO₂, and NH₃ concentrations is described as follows.

1) SO₂

The measurement of SO₂ using passive samplers utilizes a NaOH impregnated cellulose filter. On the filter sulphite is oxidized to sulphate during sampling and the sulphate amount is analyzed using suppressed ion chromatography. The cellulose filters also were found to have a sulphate blank that could not be completely reduced. It was discovered that the use of a very fine stainless steel net in parallel with the impregnated cellulose filters, eliminated this extra peak. Thus a steel net placed in the outer cap is recommended both to insure molecular diffusion, and to reduce chemical interferences. The short samplers have a measurement range of ~0.05 to 40 ppb for a sampling time of 2 months (or 0.1 to 80 ppb for monthly sampling).

2) NO₂

The most commonly used sorbent for NO₂ sampling is triethanolamine, but stability problems have been encountered with its use. The arsenite and ethylene glycol has been reported to perform the best and is the one recommended for use ^[3]. It also has the added benefit of being insensitive to light and thus the impregnated filters can be stored for several months before as well as after sampling. On the filters NO₂ is converted to nitrite and then analyzed spectrophotometrically using FIA (Flow Injection Analysis). NO₂ measurements using this impregnation method in an active-filter mode have been compared to those using a standard chemiluminescent technique.

3) NH₃

Citric acid is used to impregnate the NH₃ samplers. The NH₄⁺ in the exposed filters is analyzed after separation through a gas diffusion membrane using FIA. The concentration range of a short passive sampler is 0.1~ 15 ppb (0.2~30 ppb for monthly

sampling). The performance of the passive samplers for ammonia was found not to be as good as that for SO₂ and NO₂ (WMO). The repeatability was improved after replacing the inlet screen with a solid cap after sampling to minimize volatilization (equilibrium) with a solid phase which deposits on the inlet screen (WMO).

Based on the above discussion of the state-of-the-science it is concluded that there are a number of species for which passive samplers offer a viable method for ambient measurements, and several species for which the success of passive sampling is highly probable, but require further testing.

3.2.3 Procedures of the Passive sampling

Passive samplers take a variety of forms. The procedure is explained for the sampling and analysis of Ogawa Passive method as follows. Figure 3.4 and Table 3.4 show the construction and principles of Ogawa Passive sampler.

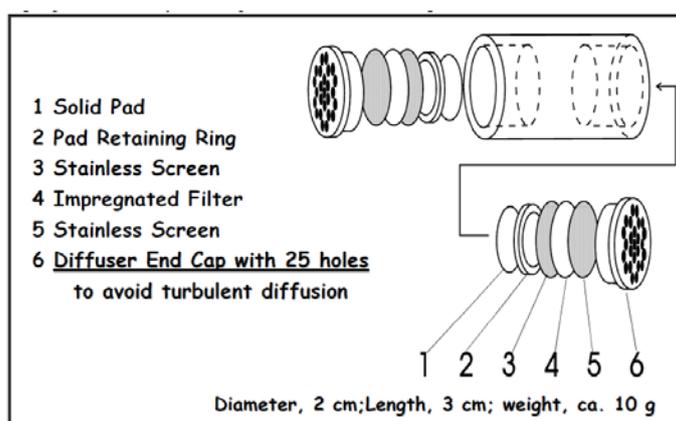


Figure 3.4 Construction of Ogawa Passive sampler (EANET, 2008)

Table 3.4 Principles of the Passive samplers (EANET, 2008)

Compound	Reagent for filters	Analytical methods
SO ₂	10% TEA	SO ₄ ²⁻ by IC
O ₃	NaNO ₂ +K ₂ CO ₃	NO ₃ ⁻ by IC
NH ₃	Citric Acid	NH ₄ ⁺ by IC
NO ₂	10% TEA	NO ₂ ⁻ by Spectrophotometer NO ₂ ⁻ by IC
NO _x	10% TEA+PTIO	NO ₂ ⁻ by Spectrophotometer NO ₂ ⁻ by IC

TEA: Tri-ethanol-amine,

PTIO: 2-Phenyl 1-4,4,5,5-tetramethylimidazoline 3-oxide 1-oxyl

IC: Ion Chromatograph

Table 3.5 Apparatuses are used on station and in laboratory (EANET, 2008)

Station	Laboratory	
Plastic glove	Tweeze	
Plastic bag	Plastic glove	
Plastic box	Deionized water	
Field note	Test tube	NO _x
Shelter	Plastic tube	SO ₂ , O ₃ , NO ₂
Cooler box	Ultrasonic cleaner	

It is shown in Table 3.5 that the apparatuses used on station and in laboratory.

1) Set up of samplers

<In laboratory>

Pack of impregnated filters should be used to store in polyethylene bag further. And the polyethylene bag should be stored in freezer. There are 20 impregnated filters in a pack. 2 impregnated filters will be set to a sample holder of the respective pollutants for each sampling period by using clean tweezers and plastic gloves. Four samplers should be prepared for each sampling period. The samplers should be stored in plastic bag/box. The samplers should be shipped to the station by using cooler bag/box.

<On Station>

Take out new samplers from plastic bag/box by using plastic glove. And install it in the shelter. Write following information on the Field note. The sampling period is 1 week to 1 month.

Start date of the measurement period: dd/mm/yyyy (e.g. 29/11/2006)

Start time of the sampling: hh:mm (e.g. 10:10 AM)

Name of reporter

Notes (e.g. Strong wind)

2) Recovery of samplers

<On Station>

Remove the samplers from the shelter and pack them in plastic bags/box. Ship the samplers to the laboratory by using cooler box. Write following information on the Field note.

End date of the measurement period: dd/mm/yyyy (e.g. 29/11/2006)

End time of the sampling: hh:mm (e.g. 10:10 AM)

Name of reporter

Notes (e.g. Strong wind)

<In laboratory>

[Extraction of filter]

Remove exposed filters from samplers and put them into test tubes (12-20mL) by using clean tweezers and plastic glove. Pour 10mL deionized water into test tubes for SO₂ and O₃ analysis. If using the IC for NO₂ and NO_x analysis, pour 10mL deionized

water into test tubes. If using the Spectrophotometer for NO₂ and NO_x analysis, pour 8mL deionized water into test tubes. Stop up test tubes with cap. Store test tubes in refrigerator until chemical analysis.

[Clean of sampler]

Store passive sampler into wire netting bag. Soak wire netting bag into Ultrasonic cleaner for 10 minutes. Wash wire netting bag with deionized water. Dry wire netting bag in laboratory.

3.2.4 Procedures of the chemical analysis

Plastic Glove, test tube or Plastic tube, water bus, vial and micro pipetter should be prepared for pretreatment of samples. Chemical analysis can be done using Ion Chromatography (IC) or Spectrophotometer. Before IC or Spectrophotometer analysis sample temperature should be returned to room temperature. Store samples in refrigerator after chemical analysis. Keep it until the data are informed. Number of standards should be more than 5. Types of standards, and some special apparatus and analytical operation are shown as follows.

- 1) Analytical method for SO₂
Standard solution 1000mg/L (SO₄²⁻)
Range: 0.01-5.0mg/L

[Apparatus]

Hydrogen Peroxide
Platinum fiber (φ0.1mm, 2cm)

[Analytical operation]

Add 0.2ml of Hydrogen Peroxide solution (1.75% solution) and then shake gently. Hold it for 10 minutes.

Add Platinum fiber (φ0.1mm, 2cm) and soak it into water bath(50°C) for 10 minutes.

Platinum fiber can be reused. Wash platinum fiber by deionized water after chemical analysis.

- 2) Analytical method for O₃
Standard solution 1000mg L⁻¹ (NO₃⁻)
Range: 0.01-5.0mg/L
- 3) Analytical method for NH₃
Standard solution 1000mg L⁻¹ (NH₄⁺)
Range: 0.01-5.0mg/L
- 4) Analytical method for NO₂, NO_x (using IC)

Standard solution 1000mg L⁻¹ (NO₂⁻)

Range: 0.01-5.0mg/L

5) Analytical method for NO₂, NO_x (using Spectrophotometer)

Standard solution 1000mg/L (NO₂⁻)

Range: 0.01-1.0mg/L

[Apparatus]

Test tube (NO_x)

Plastic tube (NO₂)

Diethyl ether (Ethyl ether)

Pipet Glass

<For Color producing reagent>

Sulfanilamide

Phosphoric acid

N- (1-Naphthyl)-ethylenediamine dihydrochloride (NEDA)

[Preparation of Color-producing reagent]

Prepare color-producing reagent immediately before use.

<For Sulfanilamide solution >

Dissolve 8g of reagent grade sulfanilamide in a mixture of 20ml concentrated phosphoric acid and 70ml water.

Dilute with water to make a total of 100ml.

Change amount according the number of samples.

<For NEDA solution >

Dissolve 0.056g N-(1-Naphthyl)-ethylenediamine dihydrochloride into 10ml water.

Store in a refrigerator.

Change amount according the number of samples.

<For Color-producing reagent>

Mix the Sulfanilamide solution and the NEDA solution in a 10:1 ratio. (10 parts Sulfanilamide solution to 1 part NEDA solution)

<For NO₂ >

Pour 8ml standard solution (including blank solution) into test tubes.

Add 2ml Color-producing reagent and shake gently.

Store it for 30 minutes in refrigerator.

Send them to colorimetric analysis at a wavelength of 545nm.

Wastewater should be treated.

<For NO_x >

Pour 8ml standard solution (including blank solution) into test tubes.

Add 4ml Diethyl ether to remove PTIO. Do it two times.

Add 2ml Color-producing reagent and shake gently.
Store it for 30 minutes in refrigerator.
Send them to colorimetric analysis at a wavelength of 545nm.
Wastewater should be treated.

[Analytical method for NO₂]

Return sample temperature to room temperature.
Add 2ml Color-producing reagent and shake gently.
Store it for 30 minutes in refrigerator.
Send them to colorimetric analysis at a wavelength of 545nm.
Wastewater should be treated.

[Analytical method for NO_x]

Return sample temperature to room temperature.
Add 4ml Diethyl ether to remove PTIO. Do it two times.
Add 2ml Color-producing reagent and shake gently.
Store it for 30 minutes in refrigerator.
Send them to colorimetric analysis at a wavelength of 545nm.
Wastewater should be treated.

3.2.5 Calculation of concentration from collected amount

Fick's Law (the first law)

$$J = -D (\Delta c / \Delta x)$$

$$\Delta c = C_A - C_0$$

$$\Delta x = L - L_0$$

Where,

J, transport amount

D, diffusion coefficient

Practical use of the Fick's Law

$$J = D (C/L) \quad \text{--- (1)}$$

Where,

J, transport amount (ng/cm²/sec)

D, molecular diffusion coefficient (cm²/sec)

C, concentration (ng/cm³)

L, diffusion length (cm)

$$JA = DA (C/L) = \text{ng/sec} = W/t \quad \text{--- (2)}$$

Where,

A, area (cm²); W, weight; t, time

In the active sampling, collection rate (ng/min) can be expressed by the formula of concentration (C, ng/L) and sampling rate (SR, L/min).

$$W/t = SR \cdot C \text{ --- (3)}$$

$$W/t = DA (C/L) = (DA/L) \cdot C \text{ --- (4)}$$

D of NO₂ = 0.1567 cm²/sec at 20°C

$$A = 0.785 \text{ cm}^2$$

$$L = 0.6 \text{ cm}$$

$$SR = DA/L$$

$$= 0.205 \text{ cm}^3/\text{sec} = 12.3 \text{ cm}^3/\text{min}$$

$$C = (L/DA)(W/t) \text{ --- (5)}$$

Concentration can be expressed by the formula of collection rate (W/t).

$$C_v = \alpha (W/t) \text{ --- (6)}$$

Where,

C, concentration (ppbv)

t, collection time (min)

W, collected weight (ng)

α , coefficient (ppbv·min/ng)

$$\alpha = (1/60)(1/f)(1/D)(L/A)(V/M) \cdot 10^3 \text{ --- (7)}$$

Where,

α , coefficient (ppbv·min/ng)

f, coefficient for calculation from gas phase to ion phase

D, molecular diffusion coefficient (cm²/sec)

L, diffusion length (cm)

A, area (cm²)

V, volume of 1 molar gas (L)

M, weight of 1 molar gas (g)

The concentrations of ambient pollutants are calculated as follows:

$$SO_2 \text{ (ppbv)} = \alpha_{SO_2} \cdot W_{SO_2}/t$$

$$NO \text{ (ppbv)} = \alpha_{NO} \cdot (W_{NOX} - W_{NO_2})/t$$

$$NO_2 \text{ (ppbv)} = \alpha_{NO_2} \cdot W_{NO_2}/t$$

$$NH_3 \text{ (ppbv)} = \alpha_{NH_3} \cdot W_{NH_3}/t$$

$$O_3 \text{ (ppbv)} = \alpha_{O_3} \cdot W_{O_3}/t$$

where,

W, collection volume of each gas [ng]

α , conversion coefficients of each gas (ppbv·min/ng)

t, exposed time (min)

The following coefficients were reported at 20 °C, 70% relative humidity, and 1 atm.:

$$\alpha_{\text{SO}_2} = 39.4$$

$$\alpha_{\text{NO}} = 56$$

$$\alpha_{\text{NO}_2} = 57$$

$$\alpha_{\text{NH}_3} = 43.8$$

$$\alpha_{\text{O}_3} = 46.2 \times 10^2 / (9.94 \times \ln(t) - 6.53)$$

Coefficients in different conditions can be calculated by the following formula. Coefficients were updated several times.

$$\alpha_{\text{SO}_2} = 39.4 \times (293 / (273 + T))^{1.83}$$

$$\alpha_{\text{NO}} = 45.3 \times (-0.046 \times T + 219.94) / (-0.439 \times P \times \text{RH} + 208.16)$$

$$\alpha_{\text{NO}_2} = 77.2 \times (2.003 \times T + 89.41) / (0.637 \times P \times \text{RH} + 131.47)$$

$$\alpha_{\text{NH}_3} = 43.8 \times (293 / (273 + T))^{1.83}$$

$$\alpha_{\text{O}_3} = 46.2 \times 10^2 \times (293 / (273 + T))^{1.83} / (9.94 \times \ln(t) - 6.53)$$

where,

T = average temperature during the measurement period (°C),

$$P = (2 \times P_N / (P_T + P_N))^{2/3}$$

P_N = water-vapor pressure at 20 °C (17.535 mmHg)

P_T = water-vapor pressure at the average temperature (mmHg)

3.3 Annular denuder

The sampling by a diffusion denuder and subsequent chemical analysis by ion chromatography are recommendable methods.

3.3.1 Annular denuder

1) Introduction

Two different denuder systems are available for sampling and determination of gaseous nitric acid and ammonia. The first procedure uses simple cylindrical tubes and the second procedure uses so-called annular denuders, where the air is passed through the annular space between two concentric cylinders. The annular denuder arrangement allows the airflow rate to be increased, and makes the subsequent chemical analyses somewhat less demanding. It was reported that the precision estimates of simultaneous samples for most of the measured species are similar for weekly annular denuder systems and composited filter packs (Sickle et al., 1999).

Sampling artifacts due to the volatile nature of ammonium nitrate, and possibly due to interaction with other atmospheric constituents make separation of these gases and particles by a simple aerosol filter unreliable. This can be achieved using denuders where one takes advantage of the different diffusion velocities of gas and aerosol particles in a sampling device, which is simply a tube coated on the inside by an absorbing reagent, usually sodium chloride or sodium carbonate. The same sampling principle may also be used for sampling of ammonia, using citric, oxalic, or phosphoric acid as the absorbent. Particulate organic acid is also important, and thus could be considered for monitoring in future. Because the diffusion speed of ammonia in air is about twice that of nitric acid, a shorter diffusion tube will achieve >95% absorption. If the flow is laminar, minimal deposition of particles occur, and if the tube has proper dimensions in relation to the flow rate and the diffusion speed of gaseous nitric acid in air, nitric acid is efficiently deposited to the walls of the tube. Since the denuders give a possibility to determine the individual concentrations of HNO_3 (g) and NO_3^- (particle); and NH_3 (g) and NH_4^+ (particle) it is a recommended method to use in the EMEP network.

Denuders can be rather impractical and are relatively expensive, and as filter packs are mostly more reliable and less demanding in terms of sampling and sample preparation, this procedure is often chosen. However, since the filter pack technique is poorer when it comes to separate gas and particle phase, only the sum of nitric acid and nitrate and for the sum of ammonium and ammonia are obtained. Information on the partition between the gaseous and the particle formed may sometimes be inferred also from filter pack data. Denuder is useful to monitor NH_3 , and there is no automatic instrument for NH_3 measurement. This may be meaningful for the areas where the concentration of gaseous ammonia is usually high, or where the concentrations of both nitric acid and ammonia gas concentrations are so low that the partial pressure product necessary for ammonium nitrate to be present is not reached. The separation of $\text{SO}_2/\text{SO}_4^{2-}$ is good in both techniques. Consumable denuder has been used in EMEP.

2) Principle of annular denuder

The air is drawn through a series of annular denuders, and filters. The two first denuders are internally coated with sodium carbonate (Na_2CO_3) and glycerol for the collection of nitric acid and sulphur dioxide, the third is coated with citric acid, oxalic acid or phosphorous acid for the collection of ammonia. Evaporation of the coating layer can be a problem.

The coated denuders are then followed by a three-filter pack system. The first filter is a membrane filter with high collection efficiency for submicron particles, followed by a filter impregnated with potassium hydroxide for collection of nitric acid which may have evaporated from the particle filter, and a filter impregnated with oxalic acid for the collection of ammonia which may also have evaporated.

Nitrous acid (HNO_2) is also absorbed in the alkaline denuders, but will normally not cause a significant interference as it is usually detected as nitrite in the sample extracts. Glycerol prevents oxidation of nitrite to nitrate by ozone. Nitrogen dioxide and PAN is partially absorbed as nitrite, this interference in the eventual determination of nitrous acid may be corrected for from the distribution of nitrite between the first and the second denuder.

A schematic description of the sampling equipment used in EMEP is given in Figure 3.5. It consists of a small insulated box, with a fan for internal air circulation and provisions for heating to a temperature $\sim 2^\circ\text{C}$ above the ambient temperature, and with a rack for mounting the denuder sampling trains and filter packs, electromagnetic valves connecting the sampling trains to a manifold, a leak-proof membrane pump which gives a sampling rate of 15 l/min, and a gas meter for recording of the sample volume. The electromagnetic valves activating each of the sampling trains are operated by means of an electronic timer. Denuder and filter pack sampling trains can also be activated and changed manually. The number of sampling lines may be extended up to eight.

The sampling train consists of an air intake, 2 annular denuders of length 242 mm, and one denuder of length 120 mm. The denuders are connected by special threaded connectors, and capped with threaded caps when not in use. A special connect is used to connect the denuder train to a 3-stage filter pack containing an aerosol filter, a KOH-impregnated filter and a citric- or oxalic acid-impregnated filter.

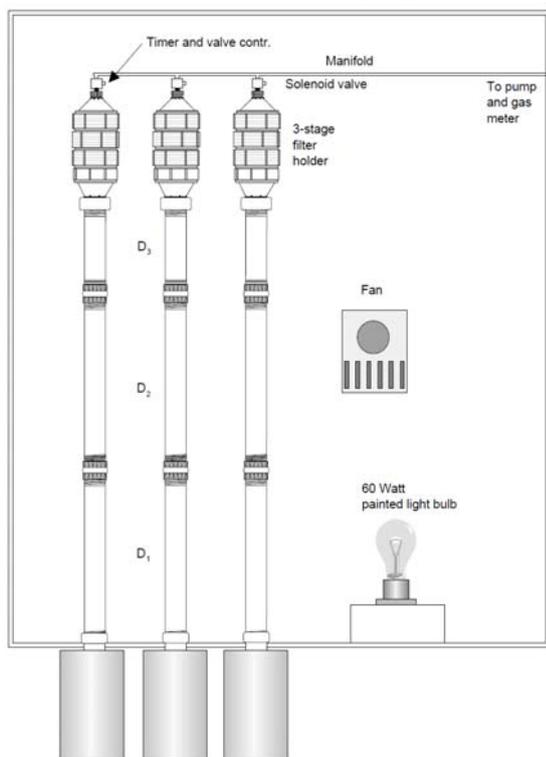


Figure 3.5 Sampling arrangements for denuder sampling (EMEP)

Annular denuder technique is technically demanding and requires good control of chemical analyses and particularly of blank values. The sampling set-up is relatively simple, but needs to be defined in relation to the sampling site and practical arrangements in connection with transport of unexposed denuder sampling trains and filter packs. The recommended denuder tubes are both expensive and brittle. The simple tubular denuder systems require much less expensive equipment. If blank values (including field blanks) and chemical analyses can be controlled, this system is an alternative to the system described above.

3) Sampling procedure

The preparation and coating of the denuders should take place in the laboratory that will carry out the chemical analyses of the collected samples. The denuders have to be thoroughly cleaned, preferably by immersion in strong detergent for several hours, and then rinsed in deionized water. A solution of 1% Na_2CO_3 and 1% glycerol is prepared by dissolving 1 g of the analytical grade reagents in 50 ml of deionized water, and diluting to 100 ml with methanol. Similarly, 1 g of citric acid (or oxalic- or phosphorous acid) is dissolved in a few drops of deionized water and diluted to 100 ml with ethanol.

For the coating procedure, a source of clean, dry air is needed. Compressed air must be filtered, and may have to be scrubbed. Passing the air through 2 tubes filled with cotton or filter paper impregnated with, respectively, sodium carbonate and citric acid will be safeguards against contamination. It is also possible to use clean and dry nitrogen from a steel cylinder.

Put on a screw-thread cap on one end of the denuder, add 2–3 ml of the coating solution, and rotate the denuder so that all internal surfaces are wetted. Pour off excess liquid, take off the screw-cap and put on another cap with connection to the dry air source. Pass dry air through the denuder, while rotating the denuder slowly. Observe the evaporation of the liquid film, and continue for a few seconds more to make sure that the evaporation is complete. Close the denuder with screw-caps.

At least 3 of the denuders should be set aside for the determination of blank values for each batch of denuders, which is being prepared in this way. (Alternatively, sodium chloride may be used as an internal coating for the absorption of nitric acid in D1 and D2. This absorbent may partly absorb SO_2 and will not absorb nitrous acid or PAN). One set of denuders and one filter pack should be reserved for use as field blanks every week. These are to be sent to the field sampling site, and returned to the laboratory without being exposed at the site.

Denuders and filter holders will have been prepared and should be transported to the sampling site in special transport containers. They are to be connected to the sampling equipment according to specific instructions, and should be marked with sampling date and time period (from-to) and denuder number (D1, D2, D3) in the laboratory before

transport to the site. Make sure that connections are leak proof. A sampling form should be filled in, with date and identification of denuders and filterpacks, gas meter readings, and notes of observations, which may be of interest in connection with the evaluation of the results. The denuders and filter packs should be capped after exposure, and put in the container used for transport to the chemical laboratory (together with the field blanks).

It is suitable for the determination of nitric acid and ammonia in the concentration ranges 0–50 $\mu\text{g}/\text{m}^3$ $\text{HNO}_3\text{-N}$ and 0–5 $\mu\text{g}/\text{m}^3$ $\text{NH}_3\text{-N}$, respectively. If higher ammonia concentration levels are expected, the sampling procedure must be modified.

4) Chemical analyses

The preparation of samples for chemical analyses is shown as follows:

D1 ($\text{Na}_2\text{CO}_3\text{-imp}$) 10 ml deionized water with H_2O_2 (0.3%)

D2 ($\text{Na}_2\text{CO}_3\text{-imp}$) 10 ml deionized water with H_2O_2 (0.3%)

D3 (Citric acid) 10 ml 0.01M HNO_3

F1 (aerosol filter) 10 ml deionized water

F2 (alkaline imp. filter) 10 ml deionized water with H_2O_2 (3%)

F3 (oxalic acid filter) 10 ml 0.01 M HNO_3

Unscrew the cap at one end of the denuder to be extracted, add exactly 10 ml of the extraction solution with a pipette, put on the cap and shake the denuder, then transfer the extract to a stoppered test tube for subsequent analysis. It is essential to work quickly in order to minimize contamination hazards! The filters may be folded and transferred to the same kind of stoppered test tubes to which 5 ml of extraction solution is added. Stopper and agitate shortly. If a hydrophobic (e.g. fluoropore) membrane filter is used as the first filter in the filter pack, immersion in an ultrasonic bath may be useful. Chemical analyses of the extracts are to be made as follows:

Table3.6 Chemical analysis of the extracts from denuder and filter pack (EMEP)

Sample	Ions to be determined	Analysis methods	Reference
D1	$\text{NO}_3^- \text{-N}$, $\text{SO}_4^{2-} \text{-S}$ (Cl^- , $\text{NO}_2^- \text{-N}$)	Ion chromatography	Section 4
D2	$\text{NO}_3^- \text{-N}$, $\text{SO}_4^{2-} \text{-S}$ (Cl^- , $\text{NO}_2^- \text{-N}$)	Ion chromatography	Section 4
D3	$\text{NH}_4^+ \text{-N}$	Spectrophotometry or ion chromatography	Section 4
F1	$\text{NO}_3^- \text{-N}$, $\text{SO}_4^{2-} \text{-S}$, $\text{NH}_4^+ \text{-N}$ (Cl^- , $\text{NO}_2^- \text{-N}$)	Ion chromatography and spectrophotometry	Section 4
F2	$\text{NO}_3^- \text{-N}$, $\text{SO}_4^{2-} \text{-S}$ (Cl^- , $\text{NO}_2^- \text{-N}$)	Ion chromatography	Section 4
F3	$\text{NH}_4^+ \text{-N}$	Spectrophotometry or ion chromatography	Section 4

5) Calculation of results

The results from the chemical analyses will be given in $\mu\text{g}/\text{ml}$ of the respective ions. After subtraction of blank values, the following formulas are used for the subsequent calculation of the concentrations of $\text{HNO}_3\text{-N}$, $\text{SO}_2\text{-S}$ and $\text{NH}_3\text{-N}$ in air ^[1]:

$$\text{HNO}_3 \text{-N } (\mu\text{g}/\text{m}^3) = [(D1-D2)/0.94] \times (10/V),$$

$$\text{SO}_2\text{-S } (\mu\text{g}/\text{m}^3) = [(D1-D2)/0.96] \times 10/V,$$

$$\text{NH}_3\text{-N } (\mu\text{g}/\text{m}^3) = D3 \times 10/V,$$

Where D1, D2, and D3 stand for the concentrations of the relevant components in the respective denuder extracts and V is the sample air volume in m³. The correction factors are based on theoretically calculated absorption efficiencies and it is assumed that interfering particles and other substances (e.g. PAN) are collected with the same efficiencies in D1 and D2.

Correspondingly:

$$\text{NO}_3\text{-N}(\text{particles}) = (F1+F2+2.5 \times D2) \times 10/V,$$

$$\text{NH}_4\text{-N}(\text{particles}) = (F1+F3),$$

$$\text{SO}_4\text{-S}(\text{particles}) = (F1+2.5 \times D2).$$

Note that if the absorption capacity of denuder D3 for ammonia is exceeded, F3 will retain gaseous ammonia, which has passed through the denuder system. Therefore, if this amount of ammonium-N collected on F1 and F3 is significantly larger than the equivalent amount needed to balance the nitrate and sulphate on F1 and F2, the calculated excess should be added to the NH₃-N concentration determined from D3.

There are also other manual monitoring methods, such as low or high volume samplers for particle monitoring and gas scrubbers (USEPA).

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4. Automatic monitoring

4.1 Calibration (including standard gases, O₃ SRP, zero gas) [Prof. Hu for SO₂ and NO_x, Dr. Takami for O₃ and PM]

4.1.1 SO₂ MULTI-POINT CALIBRATION PROCEDURES

Dynamic Calibration by Dilution

- 1) Record the analyzer, site and transfer standard parameters on the calibration data sheet. Check and record the ID number and calibration expiry date of the gas cylinder.
- 2) Carry out a visual check of the analyzer prior to calibration.
- 3) Ensure that the mass flow controllers of the dynamic calibrator (TECO 146) have been calibrated by a traceable primary flow standard with a flow calibration curve in form of

$$y = mx + b \text{ by regression,}$$

Where,

y = true flow in standard condition,

x = flow reading of the calibrator,

m = slope,

b = intercept

- 4) Ensure the connection of the pneumatic path is from the output of the multigas dynamic calibrator to the Manifold Controller, Manifold Block, Manifold Controller then SO₂ analyzer's sample inlet. If trouble shooting required, the connection can make directly from Calibrator to Analyzer.
- 5) Ensure the bottle gas securely to the dynamic calibrator. If connections are re-established, activate the control valve of the calibrator to allow SO₂ gas to pass through the calibrator. Purge the regulator and delivery system for calibration gas properly prior to calibration to avoid any undesirable back-diffusion of air into the gas bottle.
- 6) Adjust the diluent air flow to be not less than 100% more than the normal working flow rate of the analyzer.
- 7) Activate calibration at ZERO mode by the datalogger. Or activate the calibrator in local mode, the 'zero' button.
- 8) Input zero air to the analyzer for 15-20 minutes. Record the stable response as unadjusted zero response. Adjust the analyzer zero pot to read this as zero plus a little offset (1-3 ppb).
- 9) Activate the datalogger or analyzer at SPAN mode. Then push 'gas A' button on the calibrator. Select the correct concentration to the normal mid-night zero/span

check position to apply span gas (about 70 - 90% URL) to the analyzer. Wait for about 25 - 30 minutes and record the stable reading as 'unadjusted' span reading on the data sheet.

- 10) Adjust the analyzer's 'SPAN' pot to read the span gas concentration. Wait for the analyzer's reading to stabilize and then record the reading as adjusted span reading.

Due to interaction between zero and span pots, if substantial adjustments of the span pot are necessary, recheck the zero and span adjustments by repeating steps 7) – 10).

- 11) Select a concentration of about 50% of the span value (about 40 - 50% URL) by the 'ZERO' gas thumbwheel switches of the calibrator. Record the analyzer's stable readings and the actual concentration.
- 12) Select the concentration at the normal precision check level (90 ppb ± 10 ppb) by the 'ZERO' gas thumbwheel switches of the calibrator. Record the analyzer's stable reading and the actual concentration.
- 13) Apply zero air to the analyzer and then record the stable zero response as zero response.
- 14) Apply span gas to the analyzer and then record the stable span response as span response.
- 15) Plot the analyzer's response versus the input concentration by linear regression.

For an acceptable linearity check, the following two criteria should be met:

- (1) Plot the analyzer responses during calibration with respect to the input testing concentration by linear regression in the form of $y = mx + b$, where y represents the analyzer response and x represents the pollutant concentration. The correlation coefficient, r , should be greater than 0.9975.

- (2) The deviation of the analyzer response at low level (precision check level) should be less than 10%:

If any of the above criteria are failed, investigation should be initiated. Repeat all the points or the point with the greatest deviation. Check the flow of the calibrator if required.

If the linearity check still fails after repeating the points, the analyzer needs trouble-shooting. Refer to relevant appendix and equipment instruction manual. Consult the Maintenance Laboratory if necessary.

- 16) Restore the sample connection of the analyzer and the calibrator in the remote mode. Reset thumbwheel settings of the calibrator to meet other automatic calibration conditions.
- 17) Recheck that the controls of the analyzer are at normal operation modes.
- 18) Reset the datalogger to normal operation modes if it has been altered.

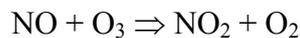
- 19) Complete the dynamic calibration data sheet.
- 20) Complete the precision check data sheet and record the percentage difference to PC1. Check whether precision check result exceeds $\pm 20\%$.
- 21) Plot the precision check result on a control chart. Complete the precision check data sheet.

4.1.2 NO_x MULTI-POINT CALIBRATION PROCEDURES

The calibration of the NO_x analyzer consists of two parts : (1) evaluation of the characteristics of the NO and NO_x channels by dynamic dilution of a standard gas, and (2) evaluation of the characteristics of the NO₂ channel by gas phase titration (GPT), by which the converter efficiency of the Molycon can be estimated also.

Gas Phase Titration

When the standard NO gas reacts with ozone, NO₂ is produced according to the following equation:



The quantitative nature of this reaction is such that when the NO concentration is known, the concentration of NO₂ can be determined. Ozone is added to excess NO in a dynamic calibration system (such as TECO 146), and the NO channel of the analyzer is used as an indicator of changes in NO concentration. Upon the addition of O₃, the decrease in NO concentration observed on the calibrated NO channel is equivalent to the concentration of NO₂ produced. The amount of NO₂ generated may be varied by adding variable amounts of O₃ from a stable ozone generator.

Set-up of Calibration System

- 1) The regulator and delivery system for calibration gas must be purged prior to the start of calibration to avoid any undesirable conversion of the standard NO to NO₂, and back-diffusion of O₂ into the gas bottle.
- 2) Connect the calibration set-up.
- 3) Ensure that the mass flow controllers (MFC) of the dynamic calibrator have been calibrated with a flow calibration curve in form of $y = mx + b$ by regression, where:

y = true flow in std. condition,

x = reading

b = intercept

m = slope

The relationship between the actual flow rate and the display is:

$$\text{Actual flow rate} = m * \text{Display} + b$$

- 4) By the flow equation of the MFCs, choose settings to produce span NO gas of

concentration about 900 ppb, precision NO gas of concentration about 200 ppb, and in addition, NO gas of mid-point concentration about 500 ppb. The guidelines for settings are as follows:

Selection of Settings

- 5) The diluent air flow should be at least 100% more the normal working flowrate of the analyzer. i.e. 1.0 lpm for a ML8840, and 1.7 lpm for a TECO 42.
- 6) The flow settings depend on the concentration of gas standard and the ranges of the MFCs. Besides, MFCs should work on >20% of URL to minimize error.
- 7) The NO concentration input to the analyzer can be calculated by equation (1):

$$[NO]_{out} = [NO]_{std} \cdot \frac{F_{no}}{F_{no} + F_z} = [NO]_{std} \cdot DF \quad (1)$$

Where,

DF = dilution factor = Fno/(Fno + Fz)

[NO]std = certified concentration of the undiluted NO standard

Fno = actual flow rate of NO standard (gas flow rate), corrected by MFC flow equation

Fz = actual flow rate of zero air, corrected by MFC flow equation

Similarly the NOx concentration input to the analyzer can be calculated by equation (2)

$$[NO_x]_{out} = [NO_x]_{std} \cdot DF = ([NO]_{std} + [NO_2]_{imp}) \cdot DF \quad (2)$$

Where,

[NO2]imp = certified concentration of NO₂ impurity in the standard NO cylinder.

- 8) In calculating the MFC settings for span check, it is desirable to select the gas MFC to be 100%. By equation (1) and assuming that [NO]out = 900 ppb , the zero flow can be estimated and a suitable setting can be selected.
- 9) From the selected settings, the SGC (standard gas concentration) for NO and NOx in span check can be calculated by flow equations, and equations (1) and (2).
- 10) The settings for a precision check can be determined by setting the zero flow MFC to be 100%.
- 11) Likewise, settings for the mid-point concentration can be determined (NO concentration about 500 ppb)
- 12) Usually the standard gas concentration of NO gas is 50 ppm, ranges of zero and gas MFCs are respectively 10 lpm and 100 cc/min.
- 13)

4.1.3 O₃

(1) Traceability organization

"The standard reference photometer (SRP)" made by "National Research Institute of a standard and technology (NIST)" performs international comparison periodically and is internationally made into the standard. Ozone concentration at a monitoring station is determined based on the traceability organization by the SRP.

However, it is physically difficult to calibrate all the ozone monitors with the primary standard ozone monitor. So, the secondary standard monitor calibrated by the primary standard monitor is prepared, and also the transfer monitor calibrated by a secondary standard monitor is prepared, and the ozone monitor installed in each monitoring station is calibrated using the transfer monitor.

2) Calibration method by ozone gas (dynamic calibration)

1) Gases for calibration

1. Zero air
2. Span gas

2) Calibration method with primary ozone monitor

A simplified scheme of a primary ozone calibration system is shown in Figure 4.1.x and consists of an ozone generator and an ozone monitor.

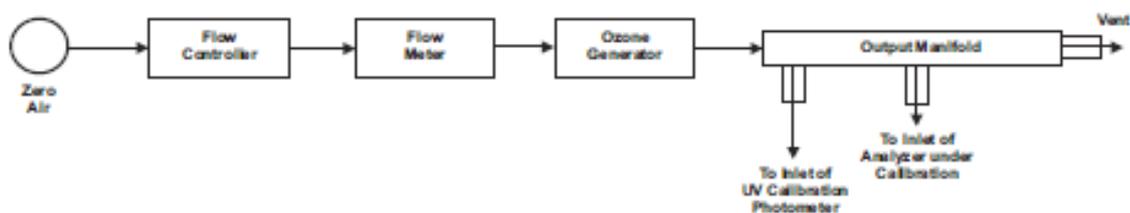


Figure 4.1 Primary ozone calibration system (by EMEP manual)

The primary ozone monitor shall be used for only that purpose and shall be carefully maintained under stable laboratory conditions. The different parts of the monitor are the same as shown in Fig.4.1.x+1 but without the catalytic ozone scrubber. Every part shall be manufactured optimum care.

When using the expression primary monitor in this section, it will normally mean a laboratory or e.g. a country's primary monitor. It is desired that each country has each primary monitor. Such primary monitor should preferably be traceable to the NIST (US National Institute of Standard and Technology) UV-photometer. One way of obtaining this is to buy from NIST a NIST-UV photometer which periodically will be checked by NIST. Another way is to have the laboratory or national primary calibrator calibrated against a NIST-UV photometer in another country e.g. once per year. To the

CCC's knowledge there are at least three NIST-UV photometers in Europe:

3) Calibration method with a secondary standard and a transfer standard

It is desired that a primary monitor calibrates every monitor located in monitoring stations. But when a primary monitor cannot be used easily, a secondary standard and a transfer standard can be prepared.

A secondary standard shall be calibrated against the primary monitor at least once per year and its accuracy shall be maintained within ± 2 ppb at level of 200ppb between successive primary calibrations. And a transfer standard shall be calibrated against the secondary standard every six months and its accuracy shall be maintained within ± 2 ppb at level of 200ppb between successive secondary calibrations.

The recommended (portable) transfer standard calibration method is a secondary standard with its own zero air and ozone supply. The other acceptable transfer standard calibration methods are the gas-phase titration of excess nitric oxide by ozone (or vice versa). For details see EPA (1979b).

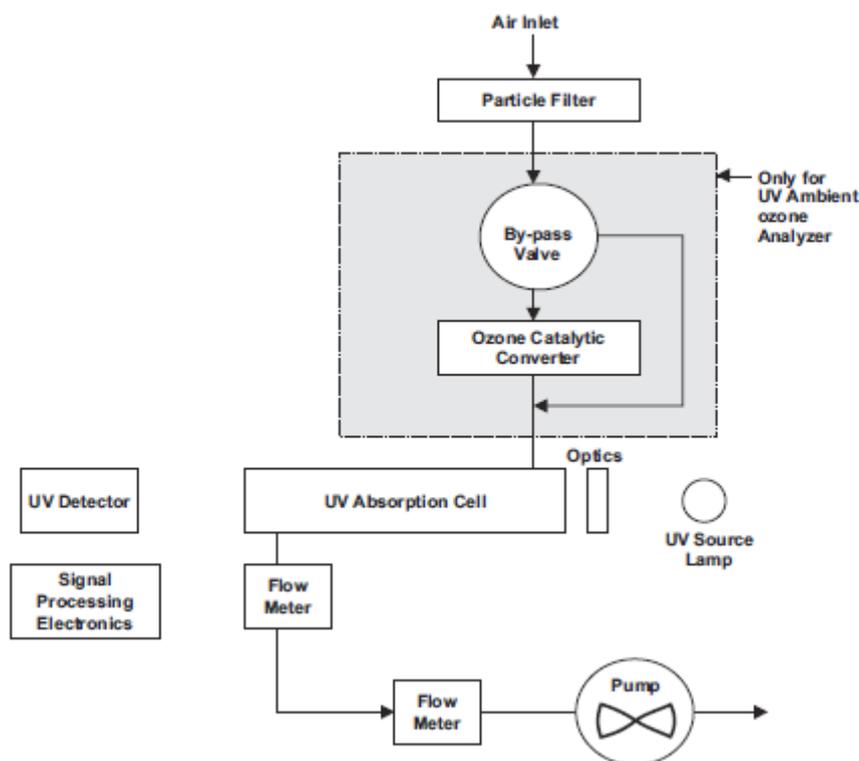


Figure 4.2 UV photometric ozone measurement system (by EMEP manual)

4) Calibration method of a ozone monitor located in a monitoring station

The ozone monitor should be thoroughly checked by the site technician on a regular basis every six months but additional internal calibrations are required after any

monitor malfunction/repair (before and after any change or manipulation in the instrument such as UV lamp replacement, mirrors and absorption cell cleaning, etc) as specified by the ozone SOP. For this purpose an ozone generator should be available at the site that has been compared with a transfer standard traceable to the NIST UV-photometer. Before and after a change or the teflon tubes and filters, a zero check with a carbon active charcoal, manganese dioxide or equivalent filter should be performed. The scrubber efficiency may vary with the level of ozone concentration and the site technician should be aware of this possibility.

The accuracy of a ozone monitor located in a station shall be maintained within $\pm 5\%$ at level of 200ppb between successive primary calibrations.

Others

A calibration log will be maintained for each site containing dates and times of calibration, name of person making entry, calibrations values and sensor responses (before and after adjustments). A zero, span, precision, and shelter temperature record will be kept and control charts will be maintained.

Gas cylinders with standard gas must be handled with great care. Never move or transport a gas cylinder with regulator installed or valve exposed. Moreover, regulator should be stored in sealed plastic bag for storage or during transportation in order to avoid contamination.

When a gas cylinder and/or regulator is replaced or reused after exposure to air, great care must be taken to avoid any back-diffusion of air into the gas bottle. This is especially important for NO gas cylinder, as back-diffused O₂ will oxidize NO to NO₂.

4.1.4 PM

It is carried out a calibration of a PM monitor by coincidence measurement (dynamic calibration) with a standard measuring method using a calibration particle in principle.

However, it is good for a periodic calibration for keeping their performance well by using an equivalent input because it is difficult for an installation administrator to calibrate by a dynamic calibration as a periodic check and maintenance, and it is able to calibrate by using an equivalent input even if not based on a dynamic calibration in principle.

(1) Scale calibration for β ray absorption method automatic monitor

In the case of the beta ray absorbing method, the method of performing a static sensitivity check is substituted by an equivalent input as a collection particle

mass, using the equivalent film which made thin films, such as maira and polyimide, the shape of a cassette.

However, since a static sensitivity check is only the method for confirming with a sensitivity of a detector and performance of operating state of an arithmetic control part, it is needed to confirm by parallel measurement with a standard measurement method using the sample atmosphere for keeping performance well of the whole measurement monitor included from the sampling system to the exhaust system.

The check by parallel measurement with such a standard measuring method is positioned as a dynamic sensitivity check. It is desired that an installation administrator carries out a dynamic sensitivity check in a setting place at the beginning of using, and at change of a sampling air system etc.

1) Static sensitivity check

A static sensitivity check is the method of checking whether indicated value changed more than $\pm 4\%$ compared with a predetermined value by sticking the equivalent film used as an equivalent input in filter paper, and measuring change of the amount of attenuation of a beta ray.

Since an equivalent film is a 10 micrometers or less-thick very thin film, handling must be prudent so that surface dirt or crack may not be attached. Moreover, if filter paper is damaged at insertion or extraction, it would become a cause of a filter paper piece, so careful cautions are required. Some models have which perform a static sensitivity check automatically and periodically and record it.

Although it is usually confirmed that the measured value of an equivalent film is within fixed limits, it should be used the average value of the repetition measurement of an equivalent film at changing the span coefficient in consideration of the probable error of radiation measurement.

In addition, a systematic big error of measurement might be produced if the span coefficient is changed without noticing dirt and the crack of an equivalent film, so cautions are required, and it is also effective to check by the equivalent film of two or more sheets.

Moreover, while repeating use, since some cracks and dirt are attached in many cases, updating periodically is desirable.

2) Dynamic sensitivity check

It measures 3 times or more in the period of 2 or 3 days simultaneously with the low volume air sampler which is a standard measuring method using the sample atmosphere, and it is confirmed that the difference of measured value with a standard measuring method is $\pm 10 \mu\text{g}/\text{m}^3$ or in $\pm 10\%$ of the limits.

In addition, even if it is this within the limits, when it is accepted that a low value comes out systematically as compared with a standard measuring method, it is necessary to examine whether there is any loss with a sampling tube, and to aim at an improvement if needed.

The following points are cared about in implementation of a dynamic sensitivity check.

- ① When selecting the position which low volume air sampler sets, it is cautious of the sampling inlet position so that both of sampling air concentration may not differ.
- ② As sampling collection filter paper of a low volume air sampler, it is used the filter made of 4 fluoridation ethylene resin, quartz fiber filter paper, or glass fiber paper with surface treatment processing, which fulfills the following condition, to have initial collection rate of 95% or more to a 0.3-micrometer particle, to have low initial pressure loss, to have little increase pressure loss with a particle collection, to have little hygroscopicity, to have little absorption of acidic gas and to have sufficient intensity on handling.
- ③ Sizing equipment is used in the pure state so that the sizing characteristic may not change.

A low volume air sampler uses the apparatus beforehand calibrated with the standard flow monitor. In addition, it is adjusted, checked and used so that an actual flow may be maintained with 20 L/min to marginal difference pressure in the model which uses a finite difference pressure valve.

It samples in rectifying that an actual flow may always be 20 L/min on flow instrument indicated value about a model to be rectified according to increase of difference pressure and sample atmospheric temperature.

3) Dynamic calibration

The mass concentration of the air for calibrating which made it generate from the particle genesis equipment using a calibration particle is beforehand measured by the low volume air sampler, and the relationship between a setup of the air for calibrating and mass concentration are grasped.

The air for calibrating is introduced into the measurement monitor for calibrating, and the monitor for calibrating is adjusted to show right indicated value.

The linearity is checked with the several points of mass concentration which are different in the domain of zero check and measured concentration within the limits in this case by a dynamic calibration.

It is supposed to ask for the percentage of the indicated value to the mass concentration of the air for calibrating in the maximum scale value by

introducing the air for calibrating near concentration $200\mu\text{g}/\text{m}^3$ after performing the zero check and the span check by an equivalent input.

(2) Scale calibration for Tapered Element Oscillating Microbalance (TEOM) method automatic monitor

1) Dynamic sensitivity check

Since the filter oscillation method has detected mass directly theoretically, the oscillating coefficient of a filter or an element is calculated by the method shown in formula (1) as a dynamic sensitivity check, and it is investigated the change of whether it is over $\pm 5\%$.

$$K_0 = \Delta m / (1/f_1^2 - 1/f_0^2) \quad \dots\dots(1)$$

K_0 : the oscillating coefficient (g/sec^2)

Δm : Mass of the particles on the filter weighed with the electronic balance (g)

f_1 : Frequency before the increase in mass (Hz)

f_0 : Frequency after the increase in mass (Hz)

2) Dynamic check

The sampling air remaining isolated preparatively with the uniform suction distributor, is collected on a filter and it is confirmed that the difference of measurement value by the precision balance at 20°C of the temperature and 50% of relative humidity according to the standard measuring method it is $\pm 10 \mu\text{g}/\text{m}^3$ or in $\pm 10\%$ of within the limits.

3) Dynamic calibration

It applies to the β -ray absorption method automatic measurement monitor.

4.2 Point measurement

4.2.1 SO_2 monitor [Prof. Hu]

Principle of the Method

Automatic analyzers employing the pulsed fluorescence method are used for sulphur dioxide measurements. Inside the analyzer, pulsating ultraviolet light is band pass filtered and focused into a fluorescence chamber. There it excites sulphur dioxide molecules contained in the air sample into high energy states. As these excited sulphur dioxide molecules go back to their initial states, a characteristic radiation is emitted. The concentration of sulphur dioxide in the air samples is then determined by measuring the

intensity of the characteristic radiation.

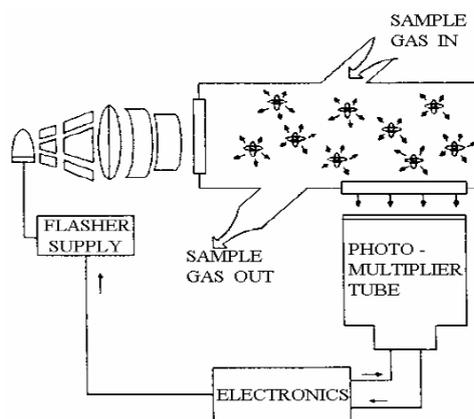


Figure 4.3 Schematic of Operation Principle

Pulsating ultraviolet light with wavelength at 190-230 nm is bandpass filtered and focused into the fluorescence reaction chamber. SO₂ molecules in the reaction chamber are excited into higher energy states and emit radiation as these states decay. The photomultiplier tube converts this radiation into an electrical signal, which is then filtered and amplified by the electronics to levels appropriate for display.

Pneumatic Path

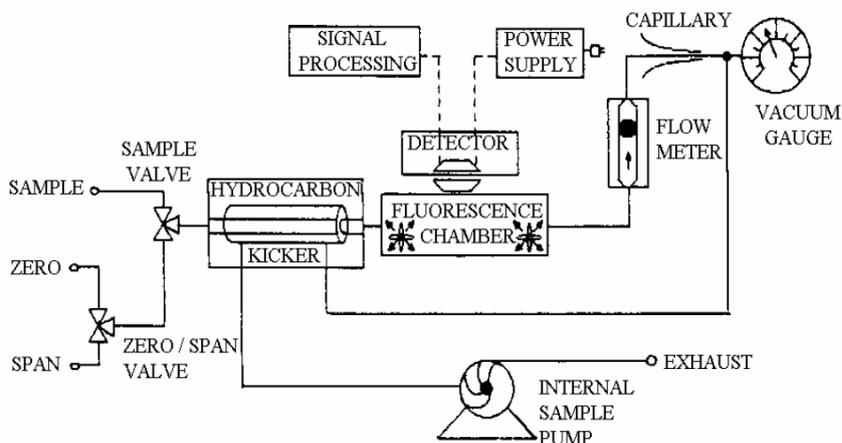


Figure 4.4 Gas Flow Schematic

In normal operation, air is drawn into the analyser through the sample valve. Calibration gases (zero air and span gas) are only fed in during calibration by proper control on the sample and zero/span valves. The hydrocarbon kicker removes hydrocarbon molecules which interfere with the fluorescence activity. Excitation of the SO₂ molecules takes place in the fluorescence reaction chamber. The flowmeter indicates the flow rate in litre per minute (LPM). The nominal flow rate is 0.5 LPM. The capillary tube restricts the gas flow and creates a differential partial pressure across the

wall of the kicker for the hydrocarbons removal. A differential pressure of at least 10" Hg is required to remove all interfering hydrocarbons. Vacuum gauge shows the differential pressure within the instrument. The internal sample pump provides the driving force to draw in ambient air or calibration gases.

Optical Path

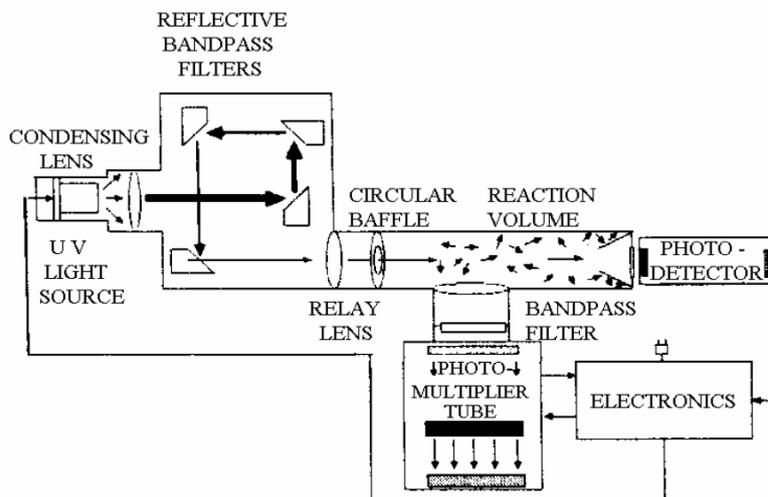


Figure 4.5 Optics System Schematic

A hermetically sealed UV lamp is pulsed at a rate of 10 times per second. The UV light is focused with a condensing lens onto the mirror assembly. The mirror module acts as a reflective bandpass filter which selectively reflects only those wavelengths used in excitation of SO_2 molecules. It also intensifies and stabilizes the radiation reaching the reaction chamber. The UV light passes through a relay lens into the reaction chamber. A circular baffle helps to keep stray light from entering the actual detection volume. Another condenser lens collects and focuses light from the reaction chamber. The light collected is further bandpass filtered before reaching the photomultiplier tube. The photodetector facing the UV light source continuously monitors the incident light and helps to automatically compensate for the fluctuation in the UV lamp output.

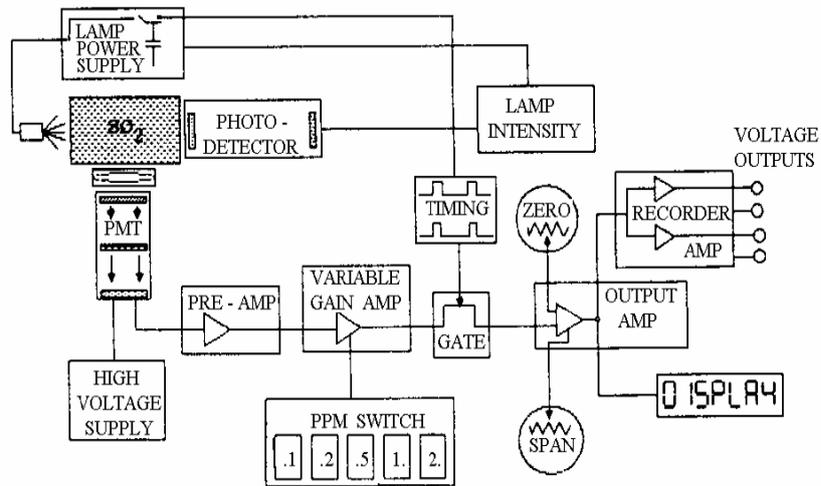


Figure 4.6 Electronics Block Diagram

The photomultiplier tube (PMT) transforms the light intensity into current. The pre-amplifier (PRE-AMP) converts the current into voltage. The signal voltage is amplified by variable gain amplifier according to the range setting. An electronic gate functions to synchronize the signal with the flash lamp pulse. The timing circuitry generates the signals used to initiate both the flash trigger and the sampling of signal. The voltage is further amplified and level shifted based on the setting of "zero" and "span" pots. The conditioned signal is then sent to a digital display and a recorder amplifier. The recording amplifier converts the conditioned signal to 0-1 V DC analogue output for recording purpose. The output from the photodetector is compared to a reference signal, and the difference is used to control the lamp voltage. Any fluctuation in the UV lamp output is therefore compensated. The temperature effects in the electrical and optical component are eliminated by a temperature control circuitry which maintains the reaction chamber at a stable temperature of about 40° C. The lamp power supply provides a pulsating voltage of 800-1200 V for the generation of pulsating ultraviolet light. The high voltage supply generates a stable DC voltage of around -700 to -2000 V for the PMT operation.

4.2.2 NO₂ monitor [Prof. Hu]

Principle of the Method

Oxides of nitrogen, NO_x, and nitric oxide, NO, are measured either by dual-channel or single-channel analyzers using the gas-phase chemiluminescence method. The gas-phase reaction of nitric oxide (NO) and ozone (O₃) produces a characteristic luminescence with an intensity proportional to the concentration of nitric oxide, as follows:



This reaction only takes place between NO and O₃, and not NO₂ and O₃. Inside a dual-channel analyzer, the air sample is directed into two channels, one to measure NO and the other to measure both NO and NO₂. In the NO channel, the concentration of NO can be determined simply and directly by the intensity of the characteristic light emission. In the second channel, NO₂ is first converted into NO by a molybdenum converter, and then the total NO is determined. The difference between the second channel reading and the NO reading in the first channel gives the concentration of NO₂.

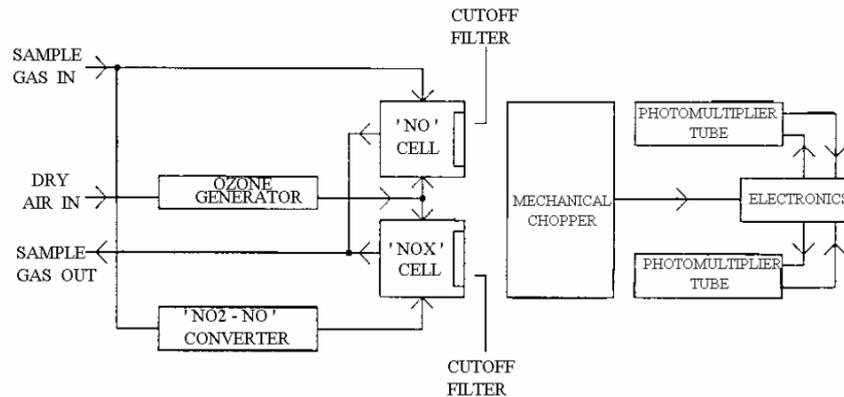
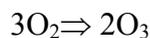


Figure 4.7 Schematic of Operation Principle

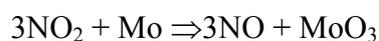
The Model 8840 NO_x analyser has two reaction cells, namely the 'NO' and the 'NO_x' cell. In the 'NO' cell, nitric oxide (NO) in the air sample reacts with ozone (O₃) from the ozone generator to form excited nitrogen dioxide (NO₂^{*}) molecules. Light emission, with a maximum intensity at approximately 1100 nm, results when the excited NO₂^{*} molecules decay to lower energy states. This phenomenon is known as chemiluminescence.



Since one NO molecule is required to form one NO₂^{*} molecule, the chemiluminescence intensity is proportional to the NO concentration in the air sample. The ozone required for the above reaction is generated when a steady stream of dry air is ionized by the discharge of a high voltage (7500V rms) electrode :



Dry air is needed to avoid acid formation and thus contamination of the pneumatic path and ozone generation. The nitrogen dioxide (NO₂) in the air sample is converted to nitric oxide (NO) by a molybdenum converter (MOLYCON) before it enters the 'NO_x' reaction cell. This MOLYCON is heated to approximately 315° C for the following reaction to take place:



Chemiluminescence reaction also takes place in the 'NO_x' cell, and the intensity of radiation is then directly proportional to the total nitrogen oxides (NO_x) concentration

(i.e. $\text{NO} + \text{NO}_2$) in the ambient air sample. A mechanical chopper is used to interrupt the chemiluminescent emission from the reaction cells at about 87 times per second in order to maintain stability. The chemiluminescent energy is emitted in full view of the photomultiplier tubes through the optical cutoff filters in each reaction cell. The outputs of the two photomultiplier tubes, corresponding to the concentration of nitric oxide (NO) and the total concentration of nitric oxide (NO) and nitrogen dioxide (NO_2), are then filtered and amplified by the electronics to levels appropriate for display. Their difference is also electronically calculated so as to obtain the concentration of nitrogen dioxide (NO_2) in the air sample.

Pneumatic Path

In normal operation, air is drawn into the analyser through the sample port of the controller. Calibration gases (zero air, 'NO' and 'NO₂' span gas) are fed in only during calibration. A teflon filter removes particulates from the incoming air stream. The incoming air is split into two streams. One stream passes through a flow meter and enters the 'NO' cell. The other air stream enters the 'NOx' cell through the MOLYCON and a flow meter. A 7 mil orifice is present in each of the reaction cells to restrict the flow rate of each air stream to 200-250 cc/min, as indicated by the corresponding flow meter. The life span of a new MOLYCON is in excess of 6000 ppm- hrs.

The ozone required for the chemiluminescence reaction is provided by the ozone generator. Each reaction cell also houses a 4 mil orifice to limit the total ozone flow rate to around 120-180 cc/min., as indicated by the corresponding flow meter.

The dry air required by the ozone generator is provided by drawing ambient air into a particulate filter where particulates are trapped, and then through a perma pure dryer where water vapor is removed. The 3 mil orifice creates the differential pressure across the wall of the semi-permeable membrane inside the perma pure dryer for the continuous drying process.

The external sampling pump provides the driving force to draw in the sample air as well as the ambient air required for ozone generation. The vacuum gauge at the outlets of the reaction cells should read 22-26 in. Hg. A charcoal scrubber is present to remove any ozone (O_3) and nitrogen dioxide (NO_2) from the exhaust of the reaction cells.

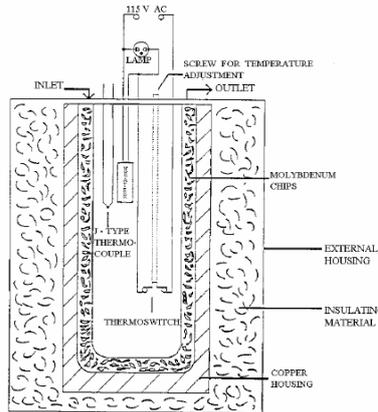
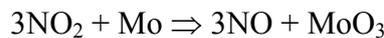
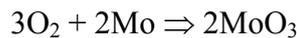


Figure 4.8 Molycon Version 1

In order to measure the concentration of nitrogen dioxide (NO₂) in the air sample, a molybdenum converter (Molycon) is used to convert nitrogen dioxide (NO₂) to nitric oxide (NO). The Molycon is kept at 315° C to maintain the following conversion process.



Oxygen in the air sample will also oxidize the molybdenum chips in the Molycon.



The build-up of molybdenum trioxide will lower the converter efficiency, and the converter must be replaced when its efficiency drops below 96%. Two versions of Molycon are currently installed in the Model 8840 analyser. Their difference lies in the design of temperature control and the type of thermocouple used for temperature sensing. In the version 1 Molycon, a thermoswitch is used to control the ON/OFF state of the heater, as indicated by the neon lamp on the front panel of the analyser. The operating temperature can be set by turning the temperature adjusting screw. The temperature of the Molycon is monitored by the J-type thermocouple.

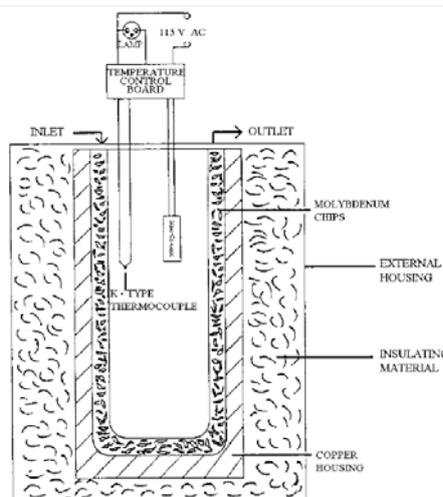


Figure 4.9 Molycon Version 2

In the version 2 Molycon, temperature is controlled by the temperature control

board. The neon lamp is lit when the MOLYCON is being heated up and flashes when the preset temperature (315°C) is reached. The thermocouple used is K-type.

Electronics

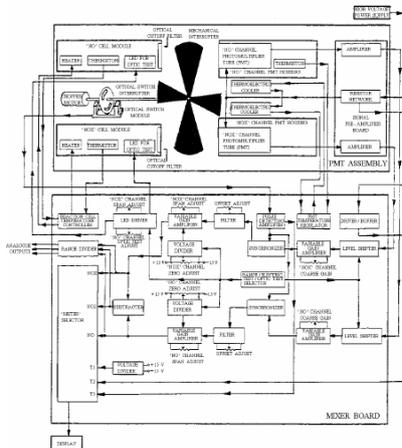


Figure 4.10 Electronics Block Diagram

One heater and thermistor are mounted on each reaction cell. The reaction cells temperature controller on the mixer board keeps the temperature of the reaction cells at about 50°C . The temperature effect is therefore eliminated. Each reaction cell assembly houses a LED which is driven by the LED driver on the mixer board when the optic test is performed. The photomultiplier tubes (PMT) transform the chemiluminescent emission into current. The signal pre-amplifier then converts the current into voltage. The PMT temperature regulator together with the thermoelectric coolers and thermistor maintain the temperature of the PMTs at around 4°C to minimize the dark current effect. The high voltage power supply board provides power (around 900V DC) for the PMT. The resistor network on the signal pre-amplifier board provides a step down voltage for the driver circuitry (on the mixer board), which drives the analogue ammeter display, when the HVPS test is performed. The outputs of the pre-amplifier of the 'NO' and 'NOx' channels are level shifted by the mixer board. The signals are then amplified by a variable gain amplifier.

As the chemiluminescent emission is chopped by a mechanical interrupter, synchronizers are needed to synchronize the processing of signal with the chopped emission. The outputs of the synchronizer are filtered to minimize noise. The filtered signals are further amplified and level shifted by a variable gain amplifier based on the settings of the 'SPAN' and 'ZERO' pots on the analyser front panel. The final output of the 'NO' channel is subtracted from that of the 'NOx' channel to obtain a signal corresponding to the nitrogen dioxide (NO_2) concentration. The concentration of nitric oxide (NO), nitrogen dioxide (NO_2) and their summation (NO_x) can be displayed by proper setting of the 'METER' selector on the analyser front panel. The range divider

converts the signals to 0-1V DC analogue outputs for recording purpose. The mixer board power supply (T1), HVPS output (T2) and the pulse detecting amplifier output (chopper speed T3) can also be displayed on the analogue ammeter by proper setting of the 'METER' selector.

4.2.3 O₃ monitor [Prof. Hu]

Principle of the Method

The 254 nm ultraviolet light absorption method is used for ozone monitoring. The method is based on the direct gas-phase absorption of ultraviolet light over a narrow band. The sample air first passes through a selective removal system for ozone, then enters the absorption cell and absorbs a certain amount of the ultraviolet light, and this is stored as the reference. Then, in the next cycle, sample air enters the cell bypassing the ozone selective scrubber and the ultraviolet absorption is again stored. The difference between the two values is proportional to the ozone concentration according to Beer-Lambert equation.

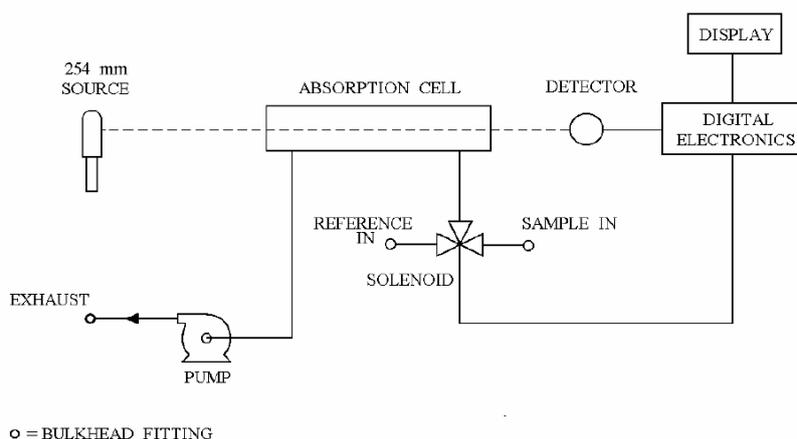


Figure 4.11 Schematic of Operation Principle

The U.V. photometric ozone analyser/calibrator (Model 49/49PS) determines the ozone concentration in the ambient air or from the internal ozonator by measuring the attenuation of light due to ozone in the absorption cell, at a wavelength of 254 nm. The concentration of ozone is related to the magnitude of the attenuation. The reference gas passes into the absorption cell to establish a 'zero' intensity reading (I_0). The solenoid then switches, and the sample gas passes through the absorption cell to establish a 'sample' light intensity reading (I). The reference gas is generated by passing the sample through the ozone removing catalytic converter (ozone scrubber). The scrubbing element is manganese dioxide and the ozone in the sample is converted into oxygen.

The ratio of these two readings (I/I_0) is a measure of the light absorbed by ozone in the sample at 254 nm. It is directly related to the concentration of ozone in the sample

through the Beer-Lambert law shown below:

$$I / I_0 = e^{-KLC}$$

where K = Absorption coefficient = 308 cm⁻¹ at 0° C, 1 atmosphere and at 254 nm

L = Length of the cell, in cm

C = Concentration in ppm

A change in 'C' of ±1 ppb leads to a change in 'I/I₀' of 0.002%. The source must be stable to better than 0.002% in the time frame it takes to measure 'I' and 'I₀', in order for the photometer to have a sensitivity of ±1 ppb. Model 49/49PS meets this criterion by using two photometers. The determination of the ozone concentration is composed of two sampling cycles shown in Figs. 2a and 2b.

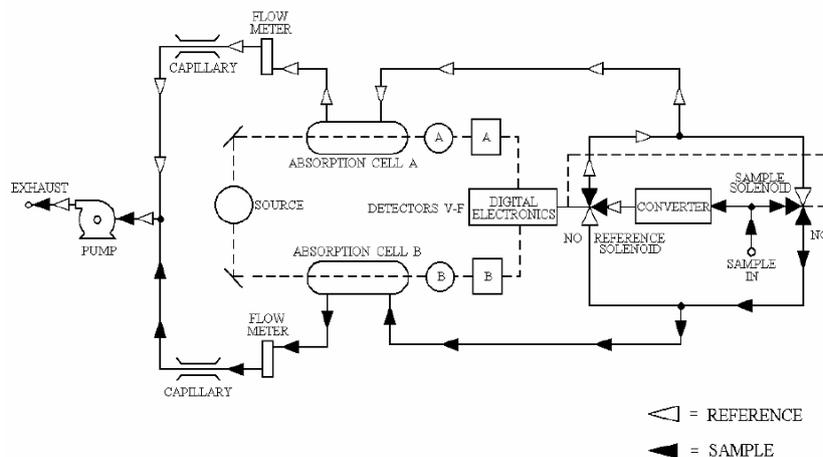


Figure 2a - The First Sampling Cycle

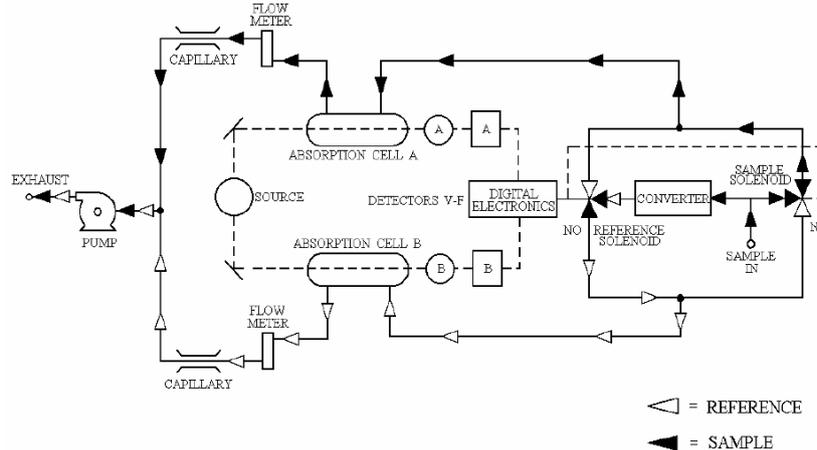


Figure 4.12 The Second Sampling Cycle

The period of a sampling cycle is 10 seconds. The first 7 seconds is for flushing and signal integration takes place in the last 3 seconds. The photometers are two separate but similar absorption cells and detector systems, sharing the same UV source. In the first sampling cycle, ambient air sample enters the absorption cell B while the reference

gas goes to the absorption cell A. $I(B)$ and $I_0(A)$ are therefore determined. In the second sampling cycle, ambient air sample and reference gas goes to the absorption cell A and B respectively. $I(A)$ and $I_0(B)$ are measured in this cycle. The ozone concentration measured by absorption cells A and B is calculated based on ' $I(A)/I_0(A)$ ' and ' $I(B)/I_0(B)$ ' respectively. The fluctuation in lamp intensity is factored out by averaging these two readings. The average value, which is corrected to 0° C and 760 mm Hg, is used to represent the ambient ozone concentration. The measurement continues by repeating the two sampling cycles, temperature/pressure correction and averaging process.

Pneumatic Path

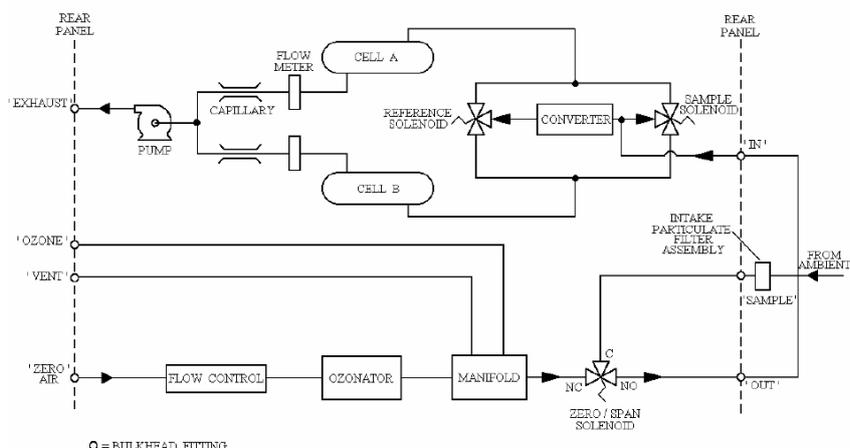


Figure 4.13 Pneumatic Path for Model 49

Model 49

(1) In sampling mode, the zero/span solenoid is de-energized and so the ambient air sample is directed into the photometers. The reference and sample solenoids are energized alternatively in the sampling cycles to synchronize (but 180° out of phase) the operation of the two photometers.

(2) The manganese dioxide inside the converter acts as the catalyse to convert the ozone in the sample to oxygen and so provides the ozone free reference gas.

(3) The internal surface of the two absorption cells have been coated with polyvinylidene fluoride to ensure that ozone undergoes no decomposition upon exposure to the internal surface of the cells.

(4) Two 0.018" capillary tubes restrict the sample flow passing through each absorption cell at 1 LPM. The two flowmeters provide the corresponding flow indication.

(5) The internal pump provides the driving force to draw air into the photometers.

(6) The pneumatic path of the internal ozonator is comprised of three parts, namely the flow control (pressure regulator followed by a capillary tube), ozonator and

distribution manifold.

(7) The zero air flow entering the ozonator is held constant by the flow control regulator followed by the capillary tube. It is normally set between 8-10 psig with at least 3 LPM of zero air passing through the ozonator. The external zero air supply should be able to supply 3-5 LPM of zero air at 20 psig.

(8) The ozonator operates on the photolytic principle. The ozone level produced is a function of light intensity at 185 nm and zero air flow. Since the zero air flow is held constant, so the ozone concentration could be varied by changing the current into the UV lamp.

(9) The distribution manifold is all teflon with three outputs, one to supply the photometers, one to supply the other ozone analyser being calibrated and one for the atmospheric dump.

(10) When Model 49 is in calibration mode, the zero/span solenoid is energized, which directs the ozone from the internal ozonator to the photometers.

(11) The internal ozonator of Model 49 could also be used to calibrate other ozone analyser.

Model 49PS

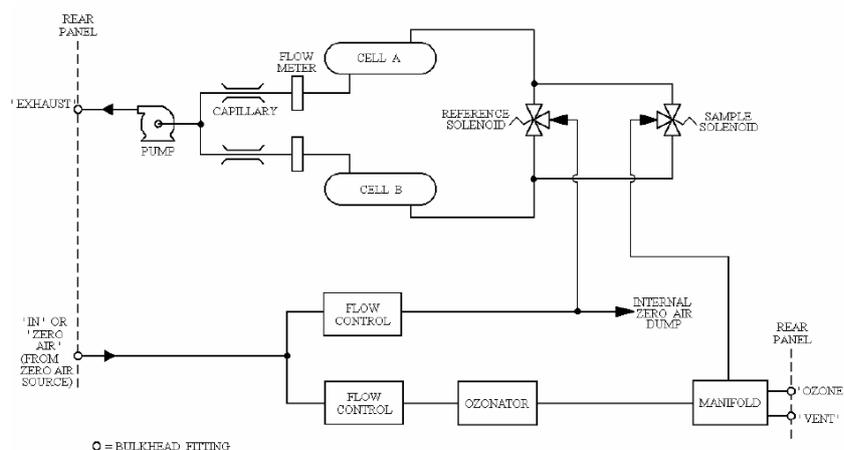


Figure 4.14 Pneumatic Path of Model 49PS

The pneumatic path of Model 49PS is similar to that of Model 49 excepts for the following:

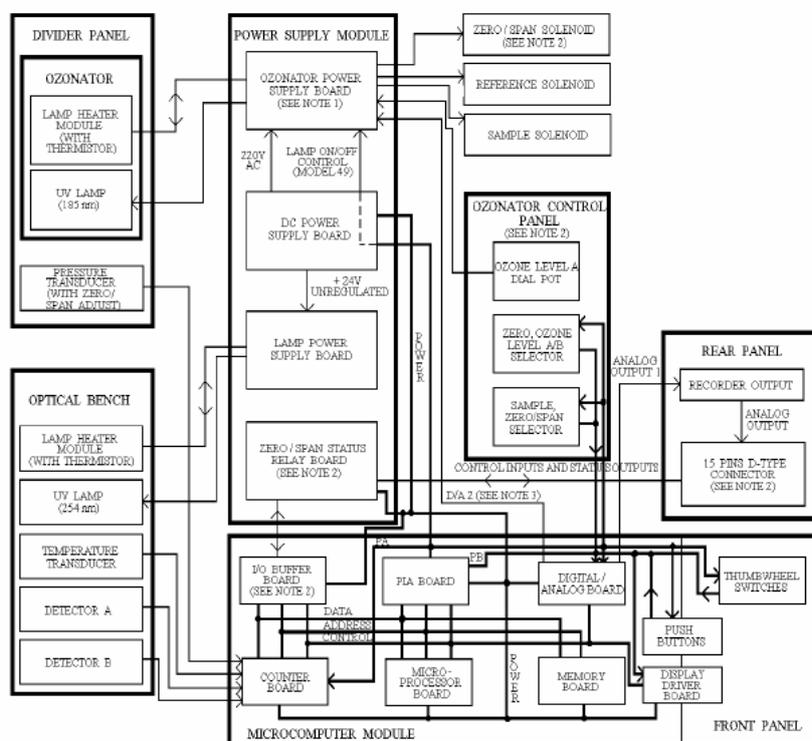
(1) The photometers are used to measure the ozone from the ozonator which provides control feedback to maintain the preset concentration.

(2) Zero/span solenoid valve and converter are absent and the reference gas is the zero air supplied by the external zero air supply. An additional flow control regulator is present to ensure adequate reference gas flow. The pressure regulator is normally set between 8-10 psig with at least 1 LPM from the internal zero air dump.

(3) The external zero air supply should be able to supply at least 6-8 SLPM of zero

air at 20 psig.

Electronics



NOTE 1 : EITHER THE POTENTIOMETER FOR SETTING OZONE LEVEL B IN MODEL 49 OR OZONE LEVEL IN MODEL 49PS IS PRESENT
 NOTE 2 : ABSENT IN MODEL 49PS
 NOTE 3 : IT IS EITHER THE ON/OFF CONTROL FOR ZERO/SPAN SOLENOID IN MODEL 49 OR OZONE LEVEL CONTROL IN MODEL 49PS

Figure 4.15 Electronics Block Diagram

The optical bench houses the lamp heater module (with thermistor), UV lamp (254 nm), temperature transducer and two detector modules. The source is a low pressure mercury vapour lamp with an expected lifetime in excess of one year. The lamp is driven by a precisely regulated power supply with a square wave at about 15 kHz to ensure a high level of stability. In order to achieve the highest level of stability of light output, the lamp itself is mounted in a temperature controlled, insulated aluminium block that provides the necessary thermal stability. The UV lamp will be ignited only if the temperature is above 50° C.

The detectors and associated pre-amplifiers are mounted together in a small, well-shielded can to ensure the highest levels of detector stability and lowest levels of noise. The detectors are small solar blind vacuum photo-diodes and their frequency output is directly proportional to the light intensity. The pressure and temperature transducers sense the pressure and temperature inside the absorption cells for temperature/pressure correction.

The ozonator consists of UV lamp and lamp heater module (with thermistor). The

light intensity is varied by changing the current into the lamp, which generates various ozone level. As in the optical bench, the ozonator is maintained at constant temperature to ensure the thermal stability. The power supply module houses the ozonator power supply board, DC power supply board, lamp power supply board and the zero/span status relay board (absent in Model 49PS). The ozonator power supply board drives the ozonator lamp based on the setting of the ozone level A dial pot on the ozonator control panel or the level B potentiometer on board. It also houses circuitry to control the zero/span solenoid (absent in Model 49PS) and switches the analyser in sampling or calibration mode.

The DC power supply board provides +24 V unregulated, ± 15 V and +5 V regulated power for the operation of various electronics parts. It also contains the driving circuitry necessary to energize the reference and sample solenoids. The lamp power supply board drives the UV lamp in the optical bench. It also includes the lamp block heating circuit to maintain the temperature at above 50° C. The zero/span status relay board (absent in Model 49PS) allows the remote control of the internal ozonator via the 15 pins D-type connector on the rear panel. The zero and span status is output to acknowledge receipt of the remote control command signals.

Two selecting switches are located on the ozonator control panel. One selector is used for selecting the sampling or calibration mode while the other is for activating the zero, ozone level A or B calibration/check. The microcomputer module houses the microprocessor board, memory board, counter board, peripheral interface (PIA) board, display driver board, digital/analog board, I/O buffer board (absent in Model 49PS) and the front panel pushbuttons. The microprocessor board controls the operation of the analyser/calibrator with the aid of other circuit boards in the microcomputer module. It instructs and co-ordinates other circuit boards to ensure normal operation. The memory board houses the program written by the Manufacturer. It contains algorithms for operation control, signals monitoring, calculation, compensation and output communication. The data memory on this board can be thought of as a scratch pad for the microprocessor board and is used to store intermediate values during operation.

The counter board acts as the interface between all the signals monitored by the microprocessor board. The signals monitored include the frequency signal from the detectors A and B, the pressure and temperature in the absorption cells. The peripheral interface (PIA) board acts as the interface between the microprocessor board and the front panel pushbuttons/thumbwheel switches. It also decodes the data from the microprocessor board into the format recognized by the display driver board. An eight segment DIP switch is located on this board for system configuration. For Model 49, only segment 7 and 8 of the DIP switch should be turned ON (all others OFF). All segments should be turned OFF in Model 49PS.

The display driver board contains circuitry to drive the 6 digits display on the front panel. The digital/analog board converts the digital data representing the measured ozone concentration into analog voltage (1 V full scale). I/O buffer board acts as the interface between the zero/span status relay board and the microprocessor board. The remote control signals for the internal ozonator are encoded on this board and passed to the microprocessor for action.

4.2.4 PM₁₀ and PM_{2.5} monitors [Dr. Takami]

β-ray absorption method

(1) Principle

Recently, the β-ray absorption method is most popular. The PM10 monitor requires the installation of a 10 μm-step classifier (50%cut) to measure harmful particles of 10μm maximum in dust. For this classifier, the cyclone or impactor method is generally used.

An indicated value as a mass concentration is obtained from the increase of the absorption amount of β-rays due to particles collection on filter paper. The β-ray analyzer is an instrument based on the principle that absorption rate of β-ray irradiation on the particle matter collection on the filtration paper gives information about its quantity.

The relationship between intensity of β-ray transmitted and dust quantity is expressed by the following equation. Since it can consider that the mass absorption coefficient μ_m is constant without basing on composition of particles, x_m can be calculated from the ratio of I to I_0 .

$$I = I_0 \exp(-\mu_m/x_m)$$

I : β-ray intensity transmitted through filter and particulate

I_0 : β-ray intensity transmitted only through filter

μ_m : Mass absorption coefficient (cm^2/g)

x_m : Mass of particulate matter (g/cm^2)

$$x_m = 1/\mu_m (I_0/I)$$

From this equation, the mass of PM10 is calculated as.

(2) Monitor performance

(3) Composition of the instruments

The components of a typical PM monitor by β-ray absorption method is shown in Figure 4.5.1.

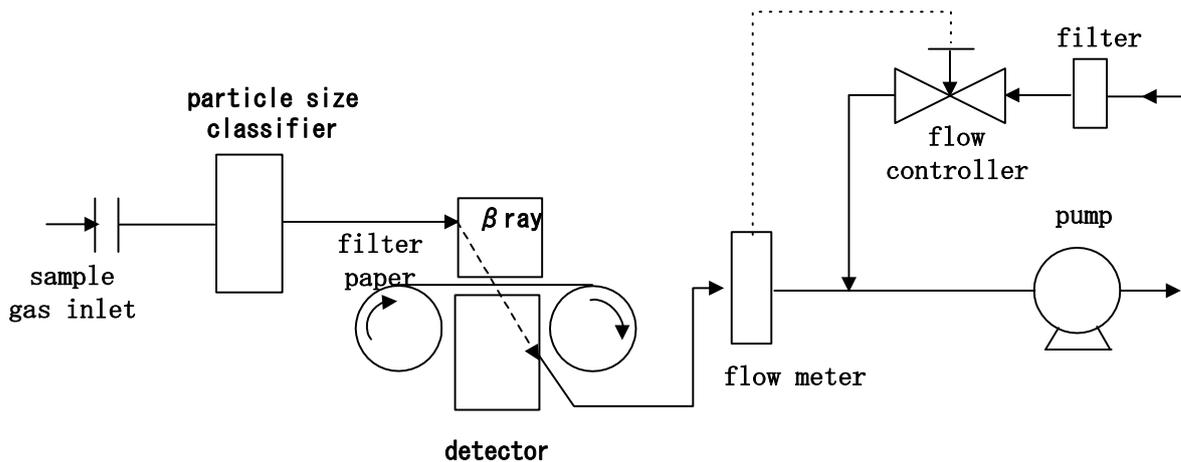


Figure 4.16 PM monitor by β -ray absorption method

(4) Filter

A collection filter is used that the collection efficiency is 95% or more for particles of the diameter $0.3\mu\text{m}$. Moreover, it is desirable to use the filter of maker recommendation. It is used that the tape-like glass fiber filter of the length which can be continuously used for 1~3 months in general.

In addition, since an error of measurement will be produced if filter paper is subject to moisture influence, the dew condensation at humid requires cautions.

(5) Notes for measurements

1) Sampling air system

1. Sampling inlet

In the case of PM, it is used the individual sampling method instead of the manifold method fundamentally. A measure is installed in order to prevent penetration of small insects, rainfall etc. to a sampling inlet. But if it is used a manifold method unavoidably, it is required the flow of sampling air from the distribution inlet is carrying out co-current to the atmospheric stream in a manifold in order to prevent the absorption of particles to the tube.

2. Materials of sampling tube

The sampling tube is used that it has smooth and clean inner and does not generate any gases disturbing measurement. If the temperature of the materials reaches $40\text{ }^{\circ}\text{C}$ or more, it is accepted that the materials discharge the particulate matter that causes to rise measured value in the case of the sampling tube made by the plasticized-polyvinyl-chloride or the copolymer of ethylene and VCM/PVC.

3. Length of sampling tube

A length of sampling tube is as short as it can, it is within 3m at horizontal.

Moreover, it is avoided a bend of a tube if possible and it is made for the radius to be set to 1 m or more if it is bent unavoidably.

4. Frequency of changing sampling tube

The proceeding dirt, which is the particulates adhering to a tube inner wall, etc., in a sampling tube becomes a cause which raises the error by adsorption or decomposition of a measuring object substance, and reduces measurement accuracy. For this reason, a sampling tube should wash or exchange periodically.

Although the frequency of washing or exchange changes with situations of contamination of a measurement point, it is required to carry out once or twice per year at least.

It is cautious of the crushing in the bend part of a tube, disconnection of a terminal area, etc. at changing the tube.

5. Separate equipment

Since the particle size classifier at a cyclone type changes with advance of the dirt of an inner wall, it is carried out to clean periodically not only the cleaning of a big and rough particle receptacle part but also inner wall of the particle size classifier using alcohol, neutral detergent, etc.

Moreover, to compensate for characteristic equipment cleaning, cleaning or exchange of a tube to a detector is performed.

2) Change of collection filter

Although the exchange frequency of collection filter paper differs depending on the model, roll-like collection filter paper needs to be exchanged in 1~3 months once.

However, since consumption of filter paper becomes early from the usual measurement when many cases where the duplicate measurement at high concentration continues for a long time, and equivalent film measurement are performed, it is cautious of filter paper residual quantity enough, and makes it not produce missing values.

In addition, when collection filter paper is exchanged, it is required to perform the static sensitivity check which certainly uses an equivalent film.

When an error of measurement is outside tolerance level as a result of the check by an equivalent film, it is needed that it is set with the filter paper of a different lot and the it is confirmed of whether a cause with error is filter paper.

3) Cleaning of flow meter

It is necessary to pay attention for the tapered vessel inner wall of a flow meter, or the dirt of float especially from the model which is an exhaust gas side of a pump and uses the floated type variable area flow meter. Since the inside of a flow meter becomes dirty easily, it is cleaned by alcohol, neutral detergent, etc. periodically.

From the model equipped with mass flow meter, or the model using a constant differential pressure gauge valve, since the dirt of an inner wall, and a jam of a small tube and the dirt of float cause an error of measurement of a flow, cautions are required.

4) Flow stabilizer, pump volume

Since the beta ray absorbing method is a filtration method, the air-flow resistance of filter paper increases because collection particles adhere and there is a possibility that a flow may fall at the high concentration. Therefore, it has the flow stabilizer and has a mechanism in which it can respond to increase of the difference pressure of the fixed range.

In addition, when the difference pressure (marginal difference pressure) of the limit which can control a flow is reached, some models move filter paper automatically and starts measurement again, some models continue sampling even if it causes flow fall and some models stop suction of the sample atmosphere. However, if repetition measurement is performed, sampling time will decrease and an error will also increase. The pump which can respond to increase of the air-flow resistance by the exhaust particles which are easy to cause a clog enough needs to be selected in the monitoring station which is easy to be subject especially to the influence of motor exhaust.

5) Confirming actual flow and adjustment of flow stabilizer

The actual flow of the sampling air connects and measures a standard flow meter to a sampling inlet, and compares with a setting flow. A flow stabilizer or the sensor position of a floated type variable area flow meter is adjusted so that an actual flow may turn into a setting flow. In addition, when changing the actual flow exceeding $\pm 7\%$ of a setting flow, it is necessary to investigate the air leak from the capability of a flow stabilizer, a suction pump and a filter paper control part, etc., and to perform adjustment or exchange of parts.

The confirming of the control facility of a flow stabilizer is performed by the following method.

- i. The standard flow meter which equipped the exit side with the valve is connected to a sampling inlet.
- ii. A differential pressure gauge is built into piping which connects a pump with a filter collection part. However, the necessity does not exist about the model that can display the indicated value of a pressure sensor or that differential pressure gauge is built in.
- iii. A new filter paper side is sent out, a valve is opened fully, and equipment is operated. After operation of a flow stabilizer is completed, the indicated

value and difference pressure (initial pressure loss) of a floated type variable area flow meter are read.

- iv. When a valve is shut gradually and operation of a flow stabilizer is completed, the indicated value and difference pressure of a floated type variable area flow meter are read.
- v. It is confirmed that the setting flow is maintained just before marginal difference pressure (repetition measurement or difference pressure in front of a stop).
- vi. When marginal difference pressure is exceeded, it is confirmed that repetition measurement begins.
- vii. Directions of a floated type variable area flow meter need to convert indicated value, when using it on different conditions from the normal condition (usually 20 °C, 101.3kPa) which carried out the scale calibration, since it changes with the sample atmosphere, temperature, and density. In addition, since some models have a possibility that the rapid change of pressure may damage the protective film of the radiation source and the protective film of a detector, it is performed opening and closing of a valve slowly and don't make it "full open" by any means.

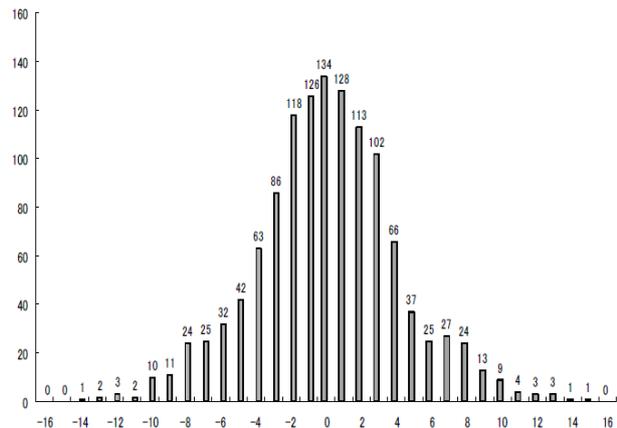
6) Indicated value of air not including particles (blank test)

The filter paper that is little air-flow resistance which fully removes a particulate matter in the filter paper holder is connected the sampling inlet, and carried out 24 time tests using the sample air which removed the particulate matter. It is called indicated-value examination (blank test) to the air which does not contain a particulate matter.

It checks that the arithmetic mean value of an hourly value does not exceed $\pm 10 \mu\text{g} / \text{m}^3$ or $\pm 1\%$ of the maximum scale.

In addition, by the beta ray absorbing method, since it is theoretically accompanied by the probable error of nuclide collapse, producing an about $\pm 10 \mu\text{g} / \text{m}^3$ about counting error is not avoided.

Therefore, it also needs to care that some examination value and a measurement value turn into a minus value.



Since the measured value below zero is processed depending on a model and it is displaying as zero, a check is required at the time of updating.

The example of a histogram of this examination value is shown in Fig. 4.5.2.

7) Equipment concerned with pump

Although it differs depending on the model, the main part of a pump will be exchanged 1~3 times per a year, a diaphragm will be exchanged once or twice per a year, packing of a collection part will be exchanged once or twice per a year.

8) Handling of the radiation source and a detector

The source of a beta ray is the sealed radiation source, and the model of low energies, such as ^{147}Pm and ^{14}C , is used. Handling follows the law of each country. The protective film of the radiation source is thin, and since it is easy to damage, sufficient cautions are required for handling. Not to damage an emulsion side at the time of cleaning of the radiation source, using an airbrush, a swab, etc., pay careful attention and perform it.

In addition, it is desirable to equip and operate protective glasses and latex gloves, since the maximum range in the air of the source of a beta ray is 20 cm grade at ^{14}C and is 30 cm grade at ^{147}Pm . When abnormalities, such as a hole and dirt, are seen by the protective film of the radiation source by which direct exposure is carried out to the sampling air, a radiation source protective film is exchanged for it. About the model that is using the aluminum evaporated film, it needs to be cautious of the corrosion by acidic gas or acid particles especially. In addition, the radiation source itself is exchanged about the model which does not have a radiation source protective film in addition to the protective film.

Moreover, since the rapid decline in a counting rate is accepted by absorption of moisture in the air when the ^{147}Pm radiation source is damaged or a pinhole arises, after taking the measure of the prevention from radiation pollution expansion immediately, a manufacturer or a specialized agency is requested and the radiation sources are exchanged carefully. Exchange and abandonment of the radiation source follow the law of each country.

Pay attention not to touch at the specular surface portion of a semiconductor detector. Moreover, it is careful for the handling of a plastic scintillation counter whether pinhole is in a surface aluminum evaporated film, and whether it has corroded the alkaline water drop fell from the filter paper of the collection part at high humidity.

9) The measure against a magnetic field

Since the beta ray is a flow of an electron with the electric charge of minus, and since

it tends to be subject to the influence of a magnetic field, it is avoided use of a magnet which a magnetic field produces near the radiation source and a primary detecting element.

Tapered Element Oscillating Microbalance (TEOM) method

(1) Principle

This method can be used, a gravimetric instrument that draws ambient air through a filter at a constant flow rate, continuously weighing principle of TEOM is different from most others. The tapered element is in essence a hollow cantilever beam with an associated spring rate and mass, and vibrates precisely at its natural frequency. As in any spring-mass system, if additional mass is added the frequency of the vibration decreases. An electronic control circuit senses this vibration and through positive feedback, adds sufficient energy to the system to overcome losses. An automatic gain control circuit maintains the vibration at constant amplitude.

(2) Composition of the instruments

Through the PM10 inlet, the principle size separation at $10 \mu\text{m}$ takes place as the sample proceeds. The flow splitter separates the total flow into two parts: a main flow of 3 l/min that enters the sensor unit through the sample tube, and the auxiliary (bypass) flow. The main flow passes through the exchangeable filter in the mass transducer, and then proceeds through an air tube and in-line filter before it enters a second mass flow controller. A single pump provides the vacuum necessary to draw the sample stream through the system.

The components of a typical PM monitor by TEOM method is shown in Figure 4.5.2.

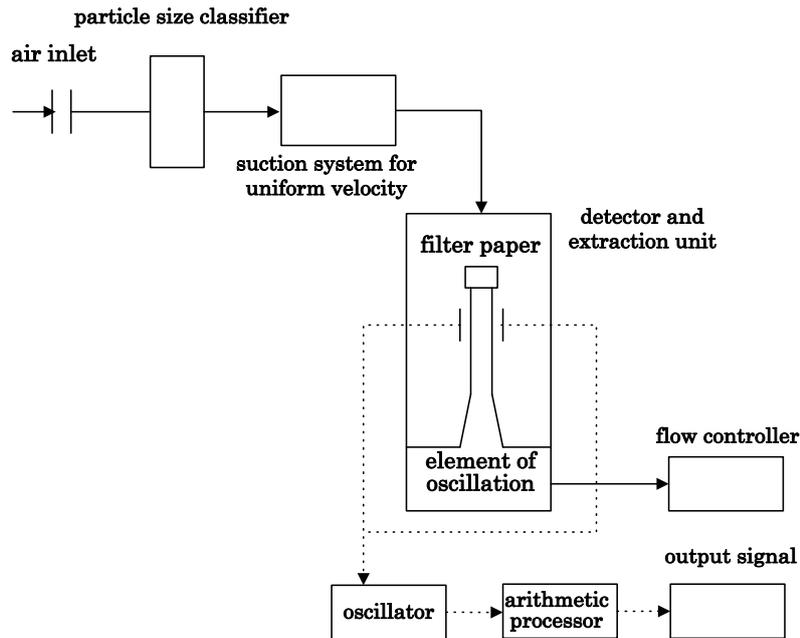


Figure 4.18 PM monitor by TEOM method

(3) Filter

The glass fiber filter with the surface treatment etc. that processed into exclusive cartridge is used for a collection filter.

(4) Notes for measurements

1) Sampling air system

It applies to the beta ray absorption method automatic monitor altogether about sampling inlet, material of sampling tube, length of sampling tube and frequency of sampling tube.

2) Filter

The mass flow rate is always displayed in a filter oscillation method, filters are exchanged before it becomes impossible to maintain a setting flow. At the site which is easy to be subject to the influence of automobile exhaust particles, exchange frequency is increased because there is a case where it becomes impossible to maintain a setting flow even if the total amount of collection is little. It is cautious of the display of a frequency value at exchange of a filter. When Change is large after taking 10 minutes or more, it is needed to confirm attachment condition of a filter.

3) Flow stabilizer

In the filter oscillation method, the sample air was introduced by the flow of 16.7 L/min, 3 L/min of them was shunted with the uniform suction distribution tube and it has led to a detector in order to prevent particles depositing in a sampling tube.

The mass flow controller is used for control of a flow.

4) Confirming actual flow

The actual flow of the sample air is confirmed being maintained to the setting flow (3.0 L/min) with being measured by the standard flow meter connected sampling inlet. In addition, when changing the actual flow exceeding $\pm 7\%$ of a setting flow, it is necessary to investigate the capability of a flow stabilizer and a suction pump, an air leak, etc., and to perform adjustment or exchange of parts. About the sample air leaking, when a sampling inlet is sealed, it is confirmed that a flow display is below 0.15L/min.

An actual flow is also confirmed whether the setting flow is maintained by the pump for uniform suction.

5) Blank test

It applies to the beta ray absorption method automatic monitor.

6) Others

Since a filter oscillation method is measurement by an oscillating element, when selecting the site for installation of a measurement monitor, it should be selected one where is flat and has little environmental vibration.

Dehumidifier system

It is required to have a function which controls change of the measured value by relative humidity to obtain measured value of a PM2.5 automatic monitor equivalent with a filter collection-weighing method. The increase in the mass concentration measured value by moisture absorption of the ingredient in particles is pointed out on PM2.5 measurement. The mass of PM2.5 is easy to be overestimated when the substance which has deliquescence like ammonium sulfate, etc. takes in moisture. The same thing may occur by not only inorganic salts but also secondary organic aerosol.

A dehumidifier system is attached to a sampling air inlet for the purpose of reduction of the influence of humidity in many cases. Three systems for dehumidifier, a heating method, a diffusion pipe method and a dilution method, using for the automatic monitor are in present. Although the conditions of operating a dehumidifier system are different with depending on the model of a PM2.5 automatic monitor, a temperature and a humidity are important parameters for controlling the monitor. It is important to carry out a routine or periodic check and maintenance for many dehumidifier systems.

Some thermometer and hygrometer of a PM2.5 monitor are beforehand calibrated at the shipment and cannot be adjusted at the site (when the fixed range is exceeded,

sensors are exchanged newly). Some are calculated a correction coefficient from comparison with the calibrated equipments at the site and are set on software.

It is carried out the check of indicated values on a monitor, the check of heating, and the comparison with the temperature and relative humidity which are measured in the same monitoring station etc., by a routine check. Moreover, it is confirmed the indicated value using by the official approval or calibrated thermometer and hygrometer by fixed frequency (6 months to 1 year).

The data of a thermometer and a hygrometer is recorded on the internal memory of a PM2.5 automatic monitor etc. in many cases. The recorded data are useful to check whether the dehumidifier system has worked exceeding the usual range, and to judge the reliability of measured value.

(1) Heating method

It is the method of heating the sampling inlet to a detector with a heater, and lowering relative humidity. The following three method are adopted depending on the model.

A What measures the relative humidity the inside of a sampling inlet or near a filter by the sensor, and carries out heating control to below the relative humidity (35%, 40%, 50%, etc.) that is defined beforehand

B What is always heated at a fixed temperature (35 °C or 45 °C)

C What will add fixed warming if a certain humidity is exceeded

Since there is a possibility of causing the mass loss by not only moisture but also volatilization of a semi-volatile compounds depending on heating temperature, it is cautious to control temperature sufficiently. The schematic view of the dehumidifier system by a heating method is shown in Fig. 4.5.3.

It is necessary to confirm an operation condition of a thermometer attached, near a filter at type A, near PM2.5 detector at type B, at sampling tube at type C. It is possible to check the record by comparing the record of the temperature and humidity of weather survey equipment, in the case of the monitor which record of the sensor of each part remains in its memory.

The contents of a routine check differ for every type.

It is confirmed that a humidity preset value for starting heat and a humidity value displayed on a monitor are almost same at type A.

It is confirmed that the temperature setting value of heating and a temperature value displayed on a monitor are almost same at type B.

When the set-up humidity is exceeded, it is confirmed that it is the set-up warmed rise in heat with the humidity value displayed on a monitor, the outside-air-temperature value, and the temperature value of a corresponding section at type C.

Moreover, it also becomes a standard for a check that the temperature near a sampling

tube without warming becomes comparable as outside air temperature in general.

It is confirmed the indicated value of the thermometer and the hygrometer of a dehumidifier system, by comparison with the official approval or calibrated thermometer and hygrometer at a periodic check.

It is good to place the sensor of the thermometer or hygrometer which prepared to compare near a detector and to carry out parallel operation at type B. It is confirmed the temperature or humidity is almost same with the set-up value. the sensor of the thermometer or hygrometer prepared for comparing, is placed near a detector and parallel operation is carried out at Type B. It is suitable for confirming, if temperature or humidity is almost the same as a setup value.

It is confirmed that indicated value of the thermometer and the hygrometer for outside air are almost same with the official approval or calibrated thermometer or hygrometer at type C.

When it adjusts as a result of a check, it verifies about the measured value from the time of checking before it, and judges the propriety of adoption of each measured value. When you use measured value as the correction value by a correction formula, or a reference value, be sure to attach notes and to show clearly about the reliability of measured value.

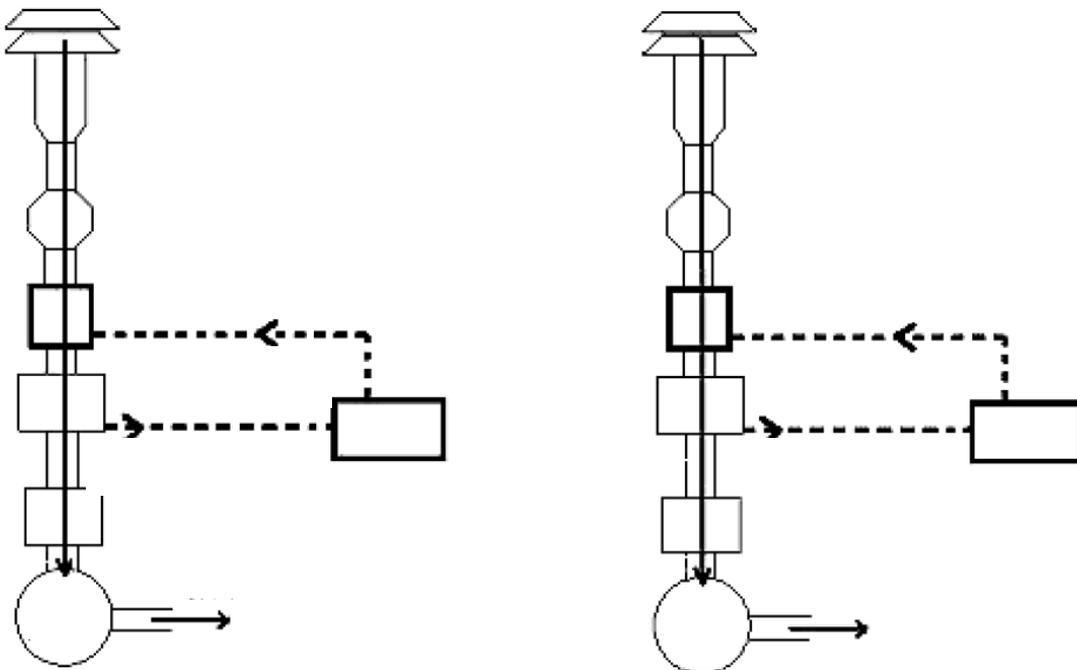


Figure 4.19 Dehumidifier system by heating method

(2) Diffusion pipe method

It is the dehumidifier system using the tube manufactured by the hygroscopic polymer membrane (sulfone compound of fluorination polyolefin). The sample air is circulated in inside a tube, and the dry air is circulated in outside a tube, respectively. Moisture in sample gas is absorbed alternatively and discharged. Since it is necessary to take the long passage time through a diffusion pipe in principle, it is used for the monitor which has adopted the high sensitivity detection principle by the low flow rate (3.0 L/min or 1.2 L/min). Some models are always operating the diffusion dehumidification pipe, and some models currently control to circulate dry air when fixed relative humidity is exceeded. There is no necessity for a power supply, has the high dehumidification capability and has few loss of a semi-volatile compounds. But it is cautious to have a possibility to decline dehumidification capability if high relative humidity continues for a long time. Moreover, it is necessary to exchange parts in a certain fixed period. The schematic view of the dehumidifier system by a diffusion pipe method is shown in Fig. 4.5.4.

Tubes are exchanged within one to three year by the maintenance management on a diffusion pipe method in general. However, when the dehumidification effect falls during using, it is exchanged in less than a year. For example, when a lot of water drop have adhered to the purge filter portion without leak, the dehumidification effect falls and it is judged that moisture has entered. Moreover, there is a tendency for degradation to become early under an acid atmosphere.

When it exchanges as a result of a check, it verifies about the measured value from the time of checking before it, and judges the propriety of adoption of each measured value. When you use measured value as the correction value by a correction formula, or a reference value, be sure to attach notes and to show clearly about the reliability of measured value.

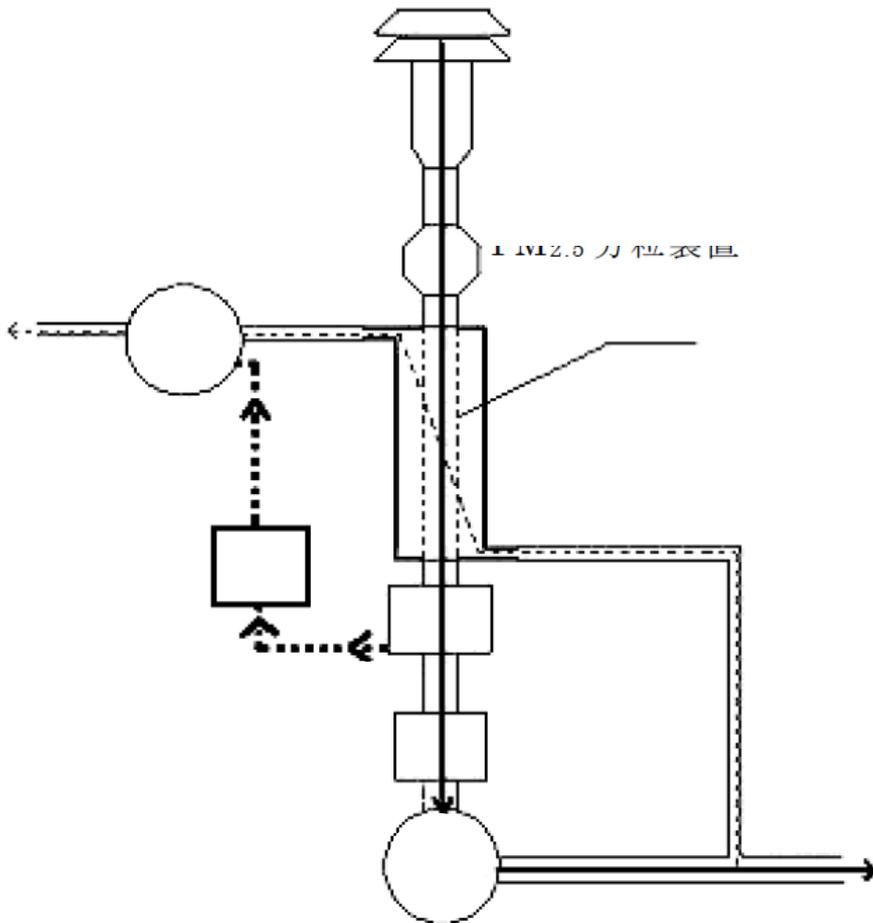


Figure 4.20 Dehumidifier system of TEOM

(3) Dilution method

It is the method to make relative humidity low by making the pure dry air which does not contain particles mix in a sampling tube, the model which has adopted this system presently has twice dilution magnification. It is PM2.5. A part of sample air after collection filter passage is dehumidified to make pure dry air, is mixed with the sample air, and is introduced to a detector structurally, and the volume of filter passage is increasing in a mixed part of pure dry air. It is necessary to care about that there is a possibility that the semi-volatile compounds contained in PM2.5 particles and the collection sample may volatilize as a result. The schematic view of the dehumidifier system by a dilution method is shown in Fig. 4.5.5.

A dilution method may use the dehumidifier system using the tube manufactured by the hygroscopic polymer membrane (sulfone compound of fluorination polyolefin) when it is dehumidified and makes pure dry air. It will need to exchange them like a diffusion pipe method after a fixed period passes. Moreover, a possibility that change of the dilution magnification by pure dry air will affect concentration can be considered, and it is necessary to check periodically that the dilution magnification as a setting is

obtained.

When it adjusts as a result of a check, it verifies about the measured value from the time of checking before it, and judges the propriety of adoption of each measured value. When you use measured value as the correction value by a correction formula, or a reference value, be sure to attach notes and to show clearly about the reliability of measured value.

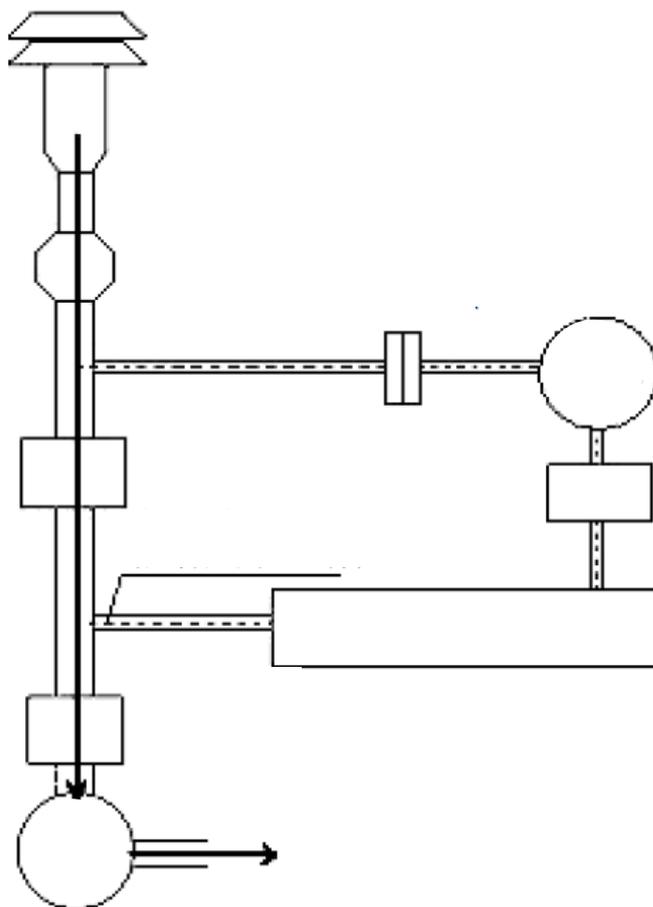


Figure 4.21 Dehumidifier system by dilution method

4.3 DOAS measurement [Prof. Kim]

4.3.1 Principle of DOAS

(1) DOAS introduction

The DOAS technique allows the determination of different trace gas concentrations at the same time without disturbing the chemical behaviors of the substances to be investigated (Platt, 1994). With the DOAS technique the absorption of light, which is unique for different trace gases, is measured. Atoms and molecules absorb specific wavelengths of light, the wavelength determined what electronic transitions are induced. In addition, molecules are excited to higher rotational and vibrational levels. As they

differ in their moments of inertia and their strength of bonding, they show different rotational and vibrational levels. That is the reason that the absorption in dependence of the wavelength is characteristic of each compound like a fingerprint. In 1979, Differential Optical Absorption Spectroscopy (DOAS) was introduced to measure atmospheric trace gas concentrations using an artificial light source (Platt et al., 1979). Since then, DOAS has been applied to measure trace-gas concentrations in the troposphere and stratosphere (Solomon et al., 1987; Platt, 1994) as well as under simulated atmospheric conditions (Etzkorn, 1998). Several important atmospheric trace gases were measured for the first time using DOAS, e.g. OH (Perner et al., 1976), HONO (Perner and Platt, 1979; Platt and Perner, 1980), NO₃ (Platt et al., 1980), BrO (Hausmann and Platt, 1994) and IO (Alicke et al., 1999) in the troposphere, and OClO and BrO (Sanders et al., 1988) in the stratosphere. A large number of other molecules absorbing the light in the UV and the visible wavelength region, e.g. NO₂, NO, NH₃, ClO, O₃, SO₂, CS₂, HCHO, etc, have also been detected (Platt, 1994). DOAS is a very sensitive measurement technique for these trace gases since they exhibit strong and highly structured absorption cross sections in the UV and visible spectral regions. Because DOAS is capable of measuring trace species in the open atmosphere it is especially useful in the detection of highly reactive species, such as the free radicals OH, NO₃, halogen oxides (ClO, BrO, IO, etc.). The simultaneous determination of the concentration of several trace gases, by analyzing the sum of their absorptions in one wavelength interval, reduces measurement time and allows analysis of the average chemical composition of the observed air mass with high temporal resolution.

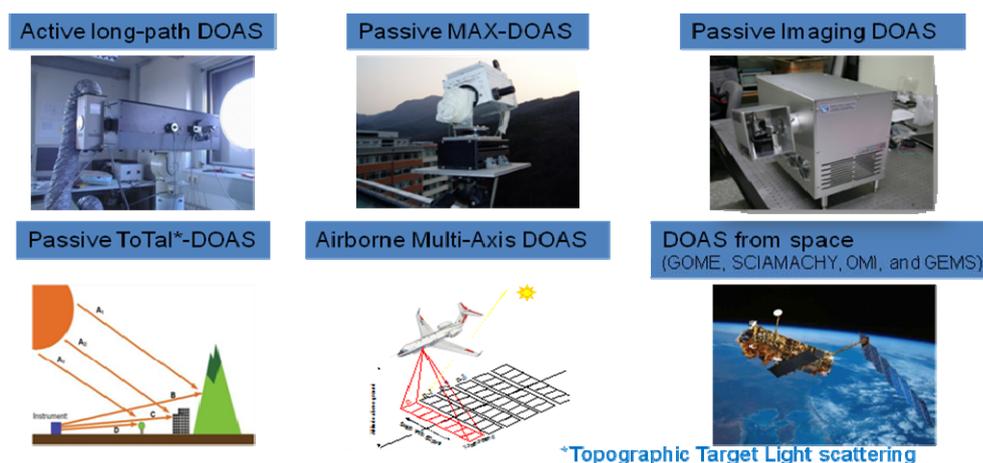


Figure 1. Types of DOAS instruments.

(2) Absorption Spectroscopy

Absorption spectroscopy uses the fact that every molecule, when irradiated by electromagnetic radiation, absorbs at distinct wavelengths. These are directly linked to

electronic, vibrational and rotational states of the molecule that can be excited and therefore absorb radiation energy. This process is described by the Lambert – Beer law:

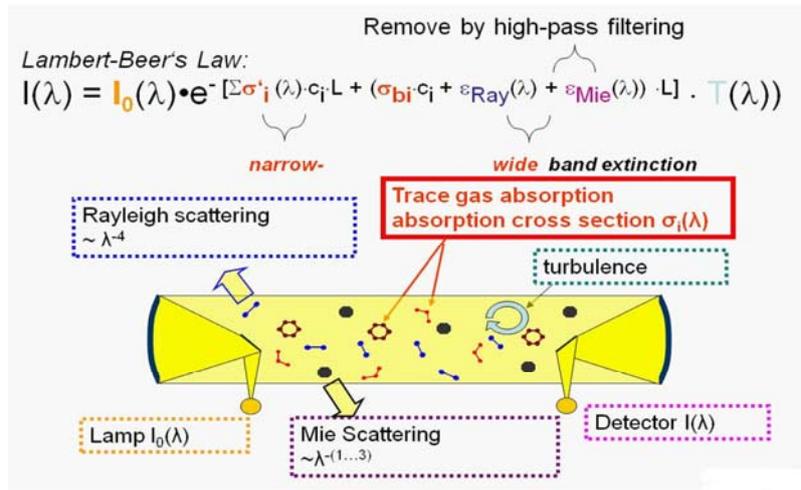


Figure 4.22 Differential Optical Absorption Spectroscopy (DOAS) principle

$$I(\lambda) = I_0(\lambda) \cdot \exp\left(-\int_0^L \left(\epsilon_R(\lambda, l) + \epsilon_M(\lambda, l) + \sum_i \sigma_i(\lambda, P, T) \cdot c_i(l)\right) \cdot dl\right) \quad (\text{Eq. 4.2.1})$$

where $I(\lambda)$: light intensity after passing through the atmosphere, $I_0(\lambda)$: intensity of the light source, λ : wavelength, $\epsilon_R(\lambda, l)$: Rayleigh-scattering coefficient, $\epsilon_M(\lambda, l)$: Mie-scattering coefficient, $\sigma_i(\lambda, P, T)$: absorption cross section of absorber i , $c_i(l)$: concentration of absorber i , L : total light path length. Some characteristics of the contributing processes are of special significance for the analysis of atmospheric absorption spectra: The scattering coefficients ϵ_R and ϵ_M depend mainly on two factors: the location along the light path and the wavelength. Of crucial importance is the fact that both coefficients depend on the wavelength in a monotonous manner: the Mie-scattering coefficient ϵ_M , which describes the scattering on particles larger than the wavelength, shows a dependence on $\approx \lambda^{-1.3}$. The scattering on particles or molecules smaller than the actual wavelength is described by the Rayleigh-coefficient ϵ_R and depends on λ^{-4} .

(3) DOAS basic principle

As every molecule is characterized by the composition and arrangement of the elements it consists of, its electronic and ro-vibronic states also generate a characteristic absorption cross section. The cross sections of all absorbers σ_i therefore form a basis – in the mathematical sense – from which each absorption spectrum can be composed as a unique linear combination. So the concentrations of all compounds that absorb in the observed wavelength range can be measured simultaneously. But the basic Lambert – Beer Law cannot be applied to trace gas concentration measurements in the atmosphere.

It is impossible to quantify all extinction processes from an absorption spectrum measured on a light path in the real atmosphere, even if all instrument-specific spectral structures were known. Additionally, the knowledge of the trace gas concentrations gained from the characteristic absorption structures would still leave the problem of the quantification of extinction by scattering processes.

To overcome the problem that atmospheric scattering by molecules and particles and broadband absorption can hardly be quantified, the DOAS technique divides the absorption cross section of trace gasses in two parts:

$$\sigma(\lambda) = \sigma_{broad}(\lambda) + \sigma'(\lambda) \quad (\text{Eq. 4.2.2})$$

where σ' , which is often referred to as the differential absorption cross section, describes only the characteristic narrow-band absorption structures of the different trace gasses. The broad band structures caused by scattering and broad-band absorption are characterized by σ_{broad} . This is the key principle of DOAS (see Figure 3), as it allows to split the exponent of the Lambert-Beer-Law in two parts: the first varying only “slowly” with the wavelength and containing scattering processes and broad-band absorption. The second part characterizes the variations in transmitted intensity featuring a strong dependency on the wavelength due to narrow-band trace gas absorption.

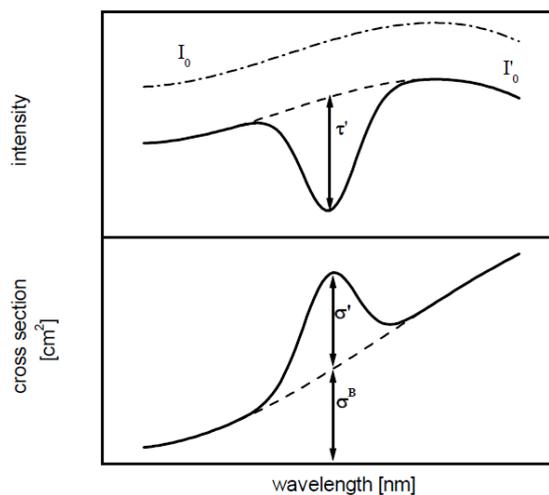


Figure 4.23 Principle of DOAS. The absorption is broken down into two contributions. One is slowly varying in wavelength, while the other shows rapid variations in λ (Platt, 1994). The differential absorption τ' corresponds with the differential optical density σ' .

‘Rapid’ and ‘slow’ variations of the absorption cross sections are in fact a function of both the observed wavelength interval and the width of the absorption bands that needs to be detected. The nitrate radical NO_3 shows relatively slow variations in λ around 640 nm, while the aromatics show very sharp bands in the UV at about 260 nm. Both can be

detected using the DOAS technique. In practice, σ_{abs} is smoothed or a polynomial is adapted to gain a spectrum which represents the part of σ_{abs} slowly varying in wavelength. In the next step σ_{abs} is divided by this spectrum. This leads to the differential absorption cross section σ' , which represents only the part rapidly varying in wavelength. Figure 4 shows the absolute and differential absorption cross section of ozone.

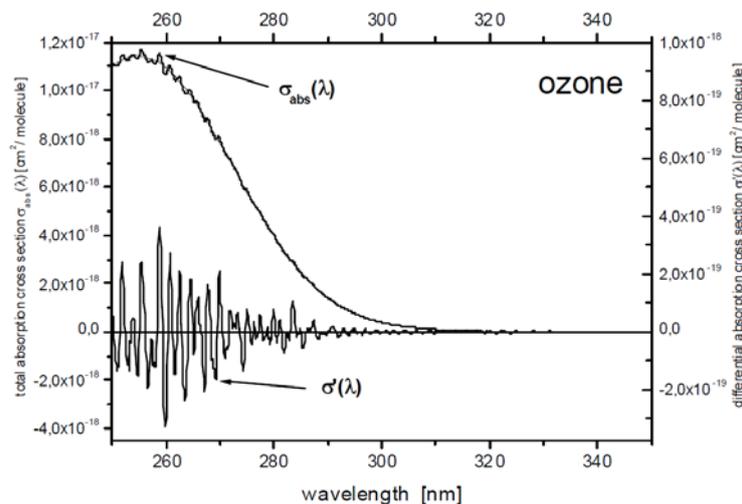


Figure 4.24 Absolute (σ) versus differential (σ') absorption cross section of ozone. Note the different scales on the left hand (σ) and on the right hand side (σ').

An integral part of the spectra evaluation is represented by the trace gas references fitted to the measured spectra. As already discussed above, these references are generated by convolution with the instrument function from high-resolution cross section spectra. Table 1 presents the literature cross sections that were used for the trace gas concentration retrieval. The spectral resolution, both for the literature cross sections and the convolution algorithm, is of crucial importance for the quality of the reference spectra: the highest resolution of the literature spectra and of the wavelength grid used for the convolution guarantee that under-sampling effects are effectively suspended and that the Lambert-Beer-Law is also valid for the lower resolutions. For the convolution, all reference spectra were interpolated to a wavelength grid of 0.001 nm, and subsequently processed using the normalized instrument function. The instrument function was derived by normalizing the area below a measured spectrum of the Mercury emission line at 366.33 nm. This line is well isolated from other lines and therefore ideally suited for the determination of the instrument function.

Table 4.1 Specifications and references for the trace gas absorption cross sections.

Species	Source	Rel. error	Resolution
NO ₂	FTIR	± 3.5%	0.5 – 1 cm ⁻¹
HONO	GRAT	± 5 %	0.1 nm
HONO	GRAT	± 5 %	0.01 nm
O ₃	FTIR	± 3-7 %	5 cm ⁻¹
O ₄	FTIR	n/a	1 cm ⁻¹

FTIR: Fourier transform spectrometer

GRAT: Grating spectrometer

After the convolution, all spectra were high-pass filtered to remove all broad-band spectral structures: a triangular smoothing algorithm provided by the MFC software was applied to a copy of the original spectrum 800 times successively. Subsequently, the retained original spectrum was divided by the smoothed spectrum, yielding a high-pass filtered spectrum. These spectra, which contained only the narrow-band absorption structures, were used for the DOAS evaluation. Figure 5 clarifies this process by the example of the NO₂ cross section in the wavelength range of roughly 334 - 375 nm used for the evaluation of the long-term measurements.

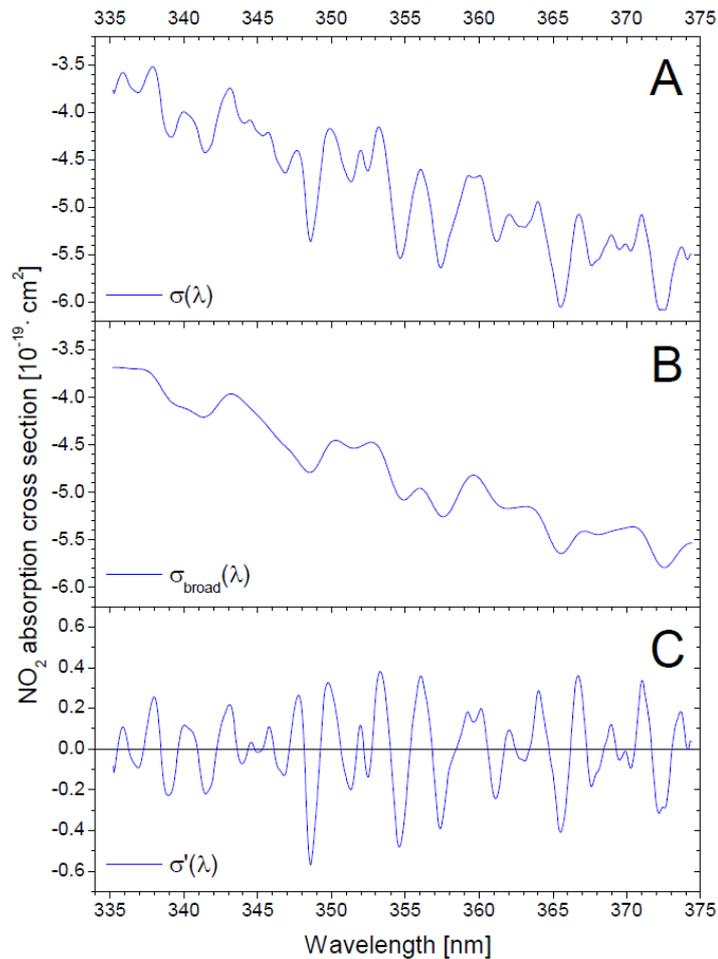


Figure 4.25 Effect of the high-pass algorithm on the total absorption cross section (panel A), exemplified by the NO₂ cross section. The smoothed cross section (panel B) contains only the broad-band structures. The narrow-band differential absorption cross section $\sigma'(\lambda)$ (plotted in row C) is obtained by dividing the original by the smoothed spectrum (i.e. row A / B).

A variety of differential cross sections used for LP-DOAS measurements is shown in Figure 6. Of special interest for this study are the cross sections of NO₂, HONO, HCHO, O₃ and O₄. These cross sections are already convoluted to the typical resolution of a LP-DOAS instrument and high-pass filtered by the algorithm specified above.

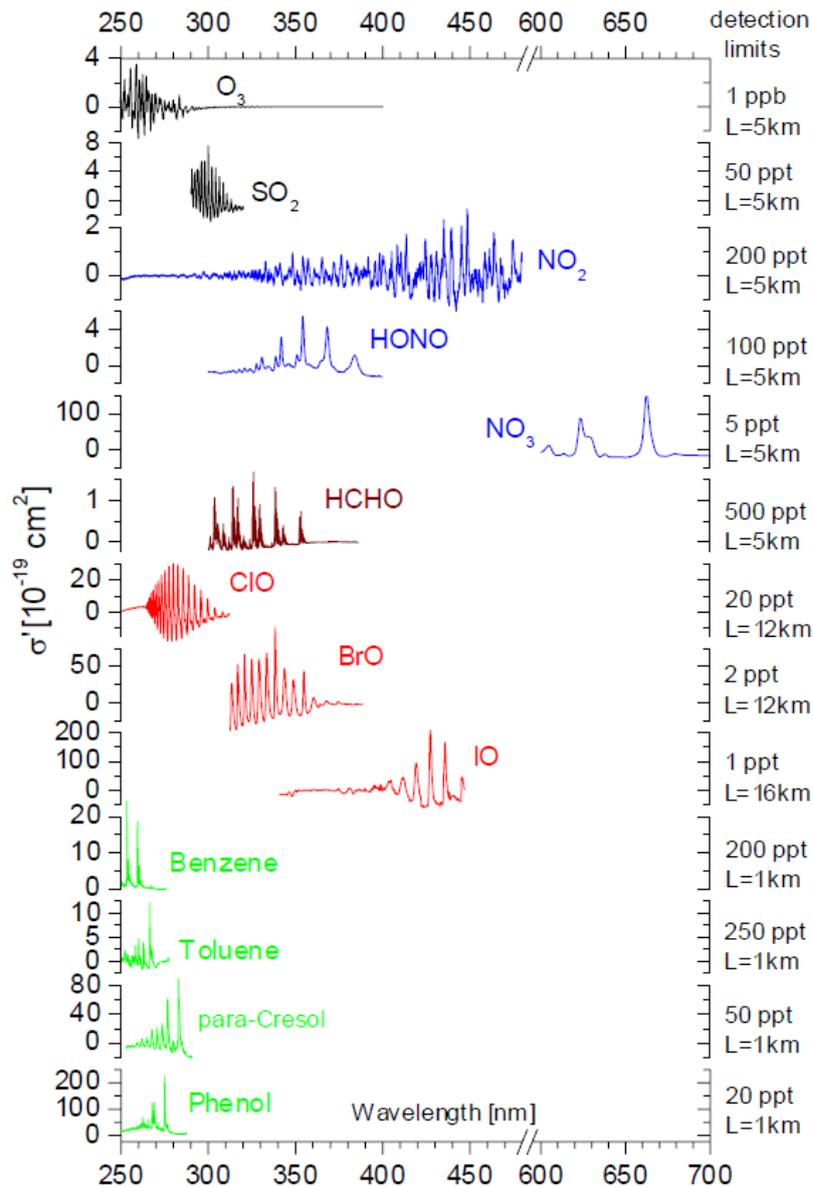


Figure 4.26 Differential absorption cross sections $\sigma'(\lambda)$ of selected atmospheric trace gases measurable by the DOAS technique. For the calculation of the detection limits on the right side a minimum detectable optical density of 10^{-3} and the indicated light path lengths were assumed.

(4) SO₂, NO_x, and O₃ measurement

① LP-DOAS instrument

This presents the characteristics of the instrument, the evaluation algorithm used for the evaluation of the spectra and a detailed estimation of the errors for the measured trace gas concentrations.

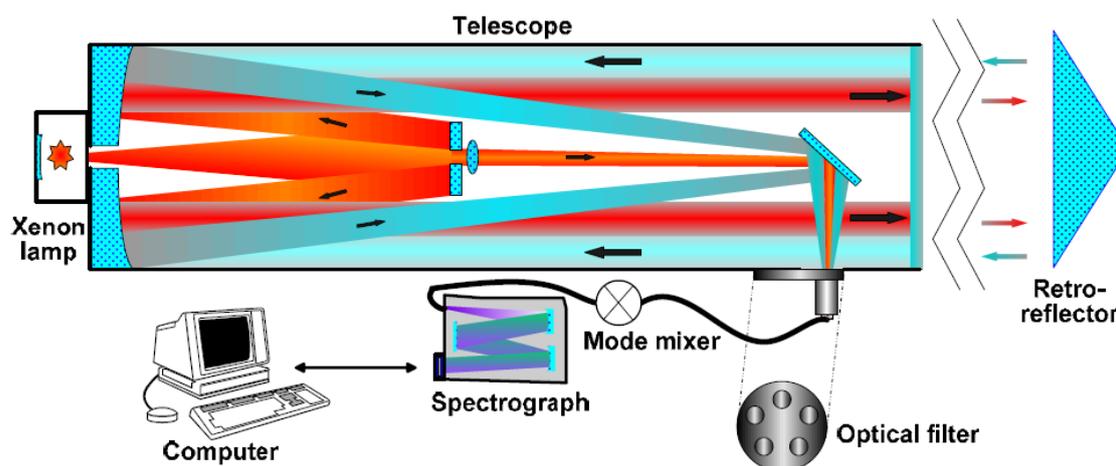


Figure 4.27 Schematic drawing of the LP-DOAS system. The LP-DOAS system is made up of main three parts: the light source, telescope and retro-reflector, and detection unit.

The HMT-DOAS

The DOAS system presented here is developed in close cooperation with Hoffmann Meßtechnik (HMT), Rauenberg / Germany, and will therefore be referred to as HMT-DOAS. In the following, the components of this system will be discussed in detail.

Light source

The light source used for the LP-DOAS system is high-pressure Xenon (Xe) arc lamps, as they are commercially available. Xe short-arc lamps are point light sources providing high luminance and color temperature. They emit a continuous spectrum of light, ranging from UV through visible to infrared. A high-voltage ignition discharge plasmasizes the Xe-gas and produces a light arc of approximately 1 mm diameter between the anode and the cathode. The typical spectrum of a Xe arc lamp is a superposition of the thermal emission according to Max Planck's law and single Xe emission lines. Under operating conditions the Xe gas is under high pressure of up to 100 bar in the lamp body. Therefore the atomic emission lines are broadened by pressure and temperature. The color temperature of the lamps is approximately 6000 K, which is similar to that of the sun. A high local light intensity and a small divergence of the emitted light beam can be attained because the small distance of the electrodes results in a small arc length. As a Xenon lamp bulb consists of a quartz glass which is extremely resistant to pressure and temperature relatively high light intensity in the UV region can be attained. The electrodes are made of tungsten with endowments depending on the lamp type. The cathode has a spiky peak to focus the electron emission, while in contrast to that the anode is made of massive material which is to

absorb the kinetic energy of the incoming electrons. Characteristic parameters of lamps used within this work are described in Table 2.

Table 4.2 Characteristic parameters of the lamp used for the LP-DOAS.

Parameter	Specification
Manufacturer	Hamamatsu, Japan
Type	L2273
Power consumption	150 W
Arc length	2.0 mm
Window material	Fused silica
Spectral distribution	185 – 2000 nm
Voltage	18 V (DC)
Current	8.5±0.5 A (DC)
Typical life time	1800 hr

The telescope

The telescope, a single transmitter and receiver unit, of the LP-DOAS is a coaxial Schumidt-Cassegrain type with a 200 mm parabolic main mirror (focal length of 800 mm). Light from a Xe lamp installed on the back of the telescope is emitted through a hole at the center of the main mirror towards the ambient air (see Figure 7). As can be seen in Figure 7, three aluminum-coated plane mirrors were mounted in the telescope. One circle plane mirror with a hole in the center and one elliptic plane mirror were mounted on the optical axis of the telescope. The third small circle mirror was attached on the side of the telescope. The first reflects the light coming from the lamp to parabolic main mirror. A parallel outgoing light beam is obtained if the light source is placed in the focal point of the main mirror. A retro-reflector array at a distance of several hundreds to kilometers was used to reflect the parallel light beam exactly back into the telescope, where it is focused through the main mirror. The light reflected by the second elliptic plane mirror was focused by the third mirror onto an 8 m long optical quartz fiber with a 200 μm core diameter and a 0.16 numerical aperture. The quartz fiber passes a mode mixer and transmits the light into the spectrograph.

There were two shutters for the lamp and outgoing light in the telescope. The first mounted between the lamp and telescope could block the light from the lamp, allowing obtaining the background signal. The second shutter was located in front of the first plane mirror. If the second shutter was closed, the light from the lamp could not reach the main mirror and directly reflected by the second plane mirror through the hole of the first plane mirror, allowing recording the signals of light without transmission of the atmosphere.

The optical image of the light beam emitted through the telescope is not perfect as the light source is no real point source, but shows an expansion of about one square millimeter. Therefore the light beam slightly diverges along its path through the atmosphere, resulting in a loss of light depending on the distance from the retro--reflectors. Furthermore, caused by the two plane mirrors along the optical axis of the telescope, only a ring of light can be sent out to the atmosphere, leading to a loss of light intensity of ~65 %.

Retro-reflector

The retro-reflectors were corner cubes (quartz triple prisms) of 600 mm diameter, which are mounted in a thin metal or plastic housing. Within a precision of 2 arc sec the incoming light is reflected back to the telescope. Usually a number of retro-reflectors are arranged very close to each other, forming a ‘retro-reflector array’. The retro-reflector array used in this work consisted of 19 corner cubes.

Quartz fiber and mode mixer

The light from the telescope is transmitted to the spectrograph by a quartz fiber to ensure a stable illumination of the grating and the PDA independent from the telescope orientation. The standard quartz fiber installed in the HMT-DOAS is a multi-mode step-index fiber with a numerical aperture of 0.12. A general problem of the use of quartz fibers for light transmission in LP-DOAS instruments are interference fringes produced by the total reflections within the fiber: as the light leaves the fiber, interference patterns in the shape of concentric circles and rings featuring different light intensities can be observed. (Stutz and Platt, 1997) found that heterogeneous illumination of the grating and the PDA leads to a higher residual noise compared to a uniform illumination. To compensate this effect, a quartz fiber mode mixer described is installed to the system.

Spectrograph

The spectrograph used for this dissertation was a Czerny-Turner type instrument (JobinYvon TRIAX320) with a 320 mm focal length has three gratings that are interchangeable and PC-controllable. This study used a holographic diffraction grating (1200 gr/mm) brazed at the wavelength of 300 nm, yielding a spectral coverage of approximately 63 nm. The grating was thermostated to 35°C. The spectrograph slit width was set to 100 μm yielding a spectral resolution of 0.3 nm (FWHM, Full Width at Half Maximum at an atomic emission line). The light coming through entrance slit into the spectrograph was paralleled by the spherical mirror and reflected to a plane diffraction grating. The dispersed light was then focused by a second convex spherical

mirror onto the detector unit.

PDA detector unit

A photodiode array (PDA) detector (dimensions 2.5×25.4 mm: Hamamatsu S3904, 1024 pixels) was used for the signal reading. The PDA detector was cooled to -15°C with a Peltier cooler in order to reduce the effects of thermal noise. The data produced by the PDA detector was recorded on a PC through a 16-bit analogue-digital converter.

Hamamatsu S3904 PDA has 1024 Si photo diodes (CMOS) of a width of 25 μm and a height of 2.5 mm each. The PDA was located in a steel can which was evacuated and filled with argon (Ar) gas of 1.2 bar. Inside the can the Peltier element cascade was used to cool the PDA down to -15 to -35 °C. The capacity of a diode is 10 pF, full charge corresponds to 1.3×10^8 photo electrons. Each photo diode of PDA represents an n-p junction. During operation an inverse voltage of 2.06 V is applied to the diode inducing a depletion layer which is almost as large as the whole diode area. Incoming light excites a number of electrons proportional to the light intensity into the conducting layer of the semiconductor. These mobile charge carriers reduce the applied inverse voltage. The voltage is also reduced by the transition of thermally activated electrons into the conducting layer. This dark-current effect must be considered in the evaluation procedure especially at low light intensities. In order to reduce dark current, which decreases exponentially with decreasing temperature, the PDA was cooled down. As the dark current depends also on the integration time an integration-time-corrected dark-current spectrum is subtracted from every atmospheric spectrum during the evaluation procedure.

After the PDA has been read out, the signals are electronically amplified. To exclude negative signals under low light conditions an offset signal is added to every PDA signal. As the final spectrum can be composed of a number of single scans, it is obvious that the offset-correction of the final spectra must be performed with respect to the number of scans. The signals are then digitized by a 16-bit analogue-to-digital converter (ADC) with full saturation of $2^{16} = 65,536$ counts. Finally the spectra are transmitted to a computer.

The PDA is covered with a thin quartz window, which can lead to Fabry-Perot etalon structures in the spectra. These structures are caused by the interference of multi-reflected light inside this surface layer. Furthermore, even if the detector unit has been evacuated and filled with dry Ar gas as inert gas, residual water vapor could freeze out on the cooled PDA. This may cause etalon or other structures in the spectra as well. Another effect of PDAs is the memory effect. That means that structures of a former spectrum can be seen in the following spectra. However, its origin is unclear to date. Usually the memory effect can be significantly reduced by multiple readouts of the PDA

without light exposure or by an adequate relaxation between the scans.

Operation

Every photo diode consists of a n-p semiconductor junction: prior every measurement, an inverse voltage of 2.06 V is applied to the diode inducing a depletion layer which is almost as large as the whole diode area.

At the beginning of the measurement, the PDA is disconnected from the power supply. Subsequently, the incoming light excites a number of electrons proportional to the light intensity into the conducting layer of the semi-conductor. These mobile charge carriers reduce the applied inverse voltage. However, the same mechanism works also via thermally activated electrons transiting into the conducting layer. This effect is called dark current and must be considered in the evaluation procedure, especially at low light intensities. In order to reduce the dark current, the PDA was cooled down to a temperature of -15 the Peltier cascade. Thereby the dark current decreases exponentially regarding the Stefan-Boltzmann-law. In addition to its temperature dependence, the dark current is known to depend on integration time, and on signal operation of the diode array. As soon as the intended integration time is over, the PDA is read out by reconnecting it to the power supply and measuring the current caused by the rechargement of the PDA. The resulting signal of a scan is amplified electronically within the detector unit. An offset signal is added to every PDA signal to exclude negative signals under low light conditions. This offset signal is proportional to the number of scans added up to a spectrum and must be corrected for in the evaluation process. The signal is digitized by a 16 bit analogue-digital converter (ADC, full saturation corresponds to $2^{16} = 65536$ counts) and then transferred to the computer. A thin protective silicon oxide layer on the diodes leads to a Fabry - Perot etalon structure in the spectra. This structure is caused by the interference of multi reflected light beams inside this surface layer. Additionally, water vapor can freeze on the PDA due to the cooling of the detector unit and can also cause an etalon structure. To minimize this effect, the detector is evacuated and filled with dry argon. Another effect of PDAs is the so-called memory effect: intense spectral structures can appear in the spectra recorded afterwards for some time (some seconds to some minutes, depending on the PDA temperature. Its origin is still unclear. The memory effect can usually be reduced significantly by multiple scans without light (or with very short integration times) or just by waiting for a short while.

Spectral resolution of the instrument

To compute the spectral resolution and the dependency between diode number of the PDA and the wavelengths, emission spectra of Ne and Hg high pressure lamps are

recorded. Fitting a polynomial of second order to the central wavelengths plotted against the corresponding diode numbers of the line centers, yields the dispersion relation

$$\lambda(j) = 374.41 \text{ nm} - (0.0375 \text{ nm} \cdot j) - (8,3 \cdot 10^{-7} \text{ nm} \cdot j^2) \quad (\text{Equ. 4.2.3})$$

which slightly changes with time in shift and squeeze i.e. in the zero and first order constants due to thermal expansion and compression of the spectrograph-detector unit. The width of a single emission line yields the width of the instrument function and therefore the minimal spectral distance between two absorption/emission lines that can be positively distinguished from each other with the instrument. Now, the spectral resolution can be computed using the FWHM of such a line (in nm) as $\Delta\lambda$: the detector – in combination with the holographic grating of 1800 grooves / mm installed in the spectrograph– features a spectral resolution ($\Delta\lambda/\lambda$) of $0,93 \cdot 10^{-3}$ at 362 nm and a spectral window ranging from 336.0 to 374.4 nm.

Offset

The mean offset was determined by adding up 1000 scans taken at the minimum integration time (100 ms) at dark conditions. This spectrum contains the signal of 1000 offsets and a dark current of 100 s. As stated below, the ratio of both signals is larger than 1:104. Thus dark current can be neglected in this spectrum.

The offset signal was measured routinely, at least once in the lifetime of a lamp. Neither a clear trend of the mean offset signal with time nor a dependence of the residuals or detection limits of the evaluation procedure on the offset level or structure could be found.

Dark current

The dark current are determined by the measurement of a spectrum with an integration time of 300 sec with a single scan in dark conditions. Subsequently, the offset signal is corrected for. The resulting dark current spectrum contains only the signal generated by thermal transitions of electrons in the conducting layer. Obviously, several diodes feature a peak dark current signal, which can be attributed most likely to endowment errors of these diodes, because these peaks do not change with time after evacuation and re-filling of the detector. These structures are due to a thin layer of water and dirt that remains after the evacuation or leaks into the detector by leakages and then freezes on the surface of the PDA. Besides their effect on the dark current, structures due to dirt in the PDA have a strong influence on residuals of the fitting algorithm.

The dark current is also found to decrease slightly with increasing saturation of the PDA. But this can be neglected in the evaluation procedure as the resulting error is

generally smaller than the errors of the fit.

Residual Noise

The residual noise of one spectrum consists of two different noise signals:

- Electronic noise due to the resolution of the digitalization, the noise of the ADC, and of other electronic components; the electronic noise level can be determined by subtraction of two offset spectra from each other. Subsequently, the root mean square (RMS) of the difference spectrum is calculated, which corresponds to the 1σ noise. It is remarkable that the peak to peak residual structure is generally found to be 6 - 7 times higher than the RMS of the spectrum. In order to obtain the electronic noise of one scan, the RMS is divided by the square root of the total number of scans. For this instrument, an electronic noise signal of 3.23 counts per scan was detected, which is well in the range measured with other detector and controller systems of the same type.

- Photon noise is another source of noise in a measured spectrum: According to Poisson statistics, the mean photon noise signal equals the square root of the number of photons. Considering the well depth of the single diodes of the PDA (1 count = 1962 photo electrons), the photon noise (1σ) of a spectrum with 10^4 or 10^6 counts would be $2.3 \cdot 10^{-4}$ or $2.3 \cdot 10^{-5}$, respectively.

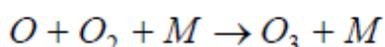
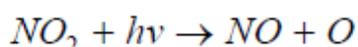
Photon noise and electronic noise must be added up in order to establish the total residual noise, which can be determined experimentally by the division of two (offset-corrected) spectra scanned one after the other with the same integration time. A very stable halogen lamp was used as the light source for these measurements. The lamp light was transmitted into the spectrograph by the standard quartz fiber, including the mode mixer. It should be noted here that the use of a quartz fiber (even if a mode mixer is included) to transmit the light to the spectrograph generally increases the residual noise. This might be caused by the partial illumination of the PDA (200 μm quartz fiber diameter compared to 2.5 mm PDA height). In order to remove broad-band lamp structures from the resulting spectrum a high pass filter (800 times binomial smoothing) was applied. Subsequently, the residual structure (1σ) can be calculated for this spectrum. Figure 8 shows the resulting variation of residual noise with the number of counts for the detector. As expected from the Poisson theory presented above, the noise decreases with the square root of the number of counts.

4.3.2 NO_x monitor

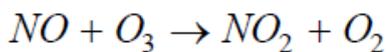
The gas-phase chemistry of the troposphere involves the oxidation of organic molecules in the presence of oxides of nitrogen under the action of sunlight. Like a flame, atmospheric oxidation proceeds via chains of free radical reactions. For organic

molecules these chains can be long and complex. Unlike combustion, however, atmospheric oxidation involves a very dilute fuel, at mixing ratios of parts per million or even parts per billion. Because of these very low concentrations, an external source of energy is required to trigger the reactions, and that energy is provided by solar radiation.

In the urban and continental troposphere a large number of other anthropogenic and biogenic hydrocarbons and organic species are present. As a result of combustion emissions, greatly enhanced levels of NO_x over those in the background troposphere exist in urban and continental areas, and NO_x is a key in the chemistry of the troposphere. When sunlight is introduced in the presence of NO and NO₂, ozone formation occurs as a result of the photolysis of NO₂ at wavelength <424 nm,



Where M represents N₂ or O₂ or another third molecule that absorbs the excess vibrational energy and thereby stabilizes the O₃ molecule formed. There are no other significant chemical production routes of ozone in the atmosphere other than reaction above and stratospheric intrusion. Once formed, O₃ reacts with NO to regenerate NO₂,



Only about 50% of the tropospheric ozone has its origin in the stratosphere and is transported through the tropopause (Fishman and Crutzen, 1978). The production of ozone in the troposphere is driven by NO_x chemistry and reactions involving methane or higher hydrocarbons. A key sequence for the formation and destruction of tropospheric ozone are reactions involving NO_x. with the rate constants given in units of cm³/molec·s.

An LP-DOAS system consists of a photodiode-array detector (PDA, Hamamatsu S3904) coupled with a spectrometer, a coaxial telescope, a set of seven retroreflectors, and an electronic control system, as described in Lee et al. (2002). A spectrometer, a conventional czerney-turner type, with a holographically grooved grating, blazed at 330nm with 1200 grates/mm, was used to measure the trace gas species (NO₂, SO₂, O₃, and HNO₂) in each respective ultraviolet (UV) region. The instrument is periodically calibrated using the Hg emission spectrum. The spectral resolution is ~0.3nm (FWHM) at around 334 nm. To prepare the corresponding reference absorption cross-sections, the literature-based absorption spectra were convoluted and interpolated with this instrumental function.

The concentration data of each gas species in the wavelength range 290–350nm are obtained sequentially by taking logarithms, filtered, and then followed with the

non-linear fitting of the absorption spectra for a set of measurements. From the differential optical depth ($D'_{\text{meas}}(\lambda_k) = \ln(I_0(\lambda)/I(\lambda))'$) determined by two spectra, the respective values (c_i, a_j) of *i*th species' concentration and a coefficient of the polynomial of degree *j* are acquired by the following fitting process (Platt, 1994), which complies with the Beer–Lambert law:

$$\left| \sum_k \left\{ D'_{\text{meas}}(\lambda_k) - L \left(\sum_i c_i \sigma'_i(\lambda_k) - \sum_j \alpha_j \lambda_k^j \right) \right\} \right| = \text{Residual.} \quad (\text{Equ. 4.2.4})$$

Here $\sigma_i(l_k)$ denotes the differential cross-section of the *i*th trace gas at the wavelength of the *k*th pixel of the photodiode. The residual term shown in Equ. 4.2.4 is left after fitting to atmospheric spectra; these residual term values then tend to vary within a few per mil (%). The residuals may stem from the combined effects of the following factors: the atmospheric absorption of unidentified species, the irremovable instrumental spectral patterns, the detector state, the statistical fit errors of the least square (LSQ) function, and the erroneous matches of the measurement and reference spectra. Therefore, its structure has an important role in determining a lower detection limit (DL).

4.3.3 O₃ monitor

O₃ could be evaluated in the measured data by substituting the relative measurement reference with an absolute reference and including O₃ in the fit between 276 and 288 nm. Due to interferences in the DOAS retrieval, it is not possible to obtain dependable O₃ values at SO₂ column densities above 2×10^{18} molecules/cm². Therefore, spectra with these extreme SO₂ absorption values were omitted in the O₃ retrieval. Figure 8 shows the average O₃ mixing ratio along the light path for the time periods in which the night-time measurements took place (April 17 – 20, 2007 and April 23 – 27, 2007). The ambient O₃ mixing ratios varied between 20 and 40 ppb, with the higher values typically occurring during daylight hours.

A comparison of the O₃ and SO₂ column densities revealed no apparent dependency between the two. One might anticipate an anticorrelation of the two measurements, as the volcanic plume is quite likely depleted in O₃ as compared to the background concentration due to autocatalytic O₃ destruction, and the SO₂ column density is a tracer for the amount of plume the light path passes through at a given time. Two reasons are held responsible for the absence of this finding: Firstly, the largest portion of the light path is always outside the plume, and the retrieved O₃ column is therefore mainly representative of the O₃ abundance outside the plume, especially since measurements with high SO₂ column densities could not be evaluated for O₃.

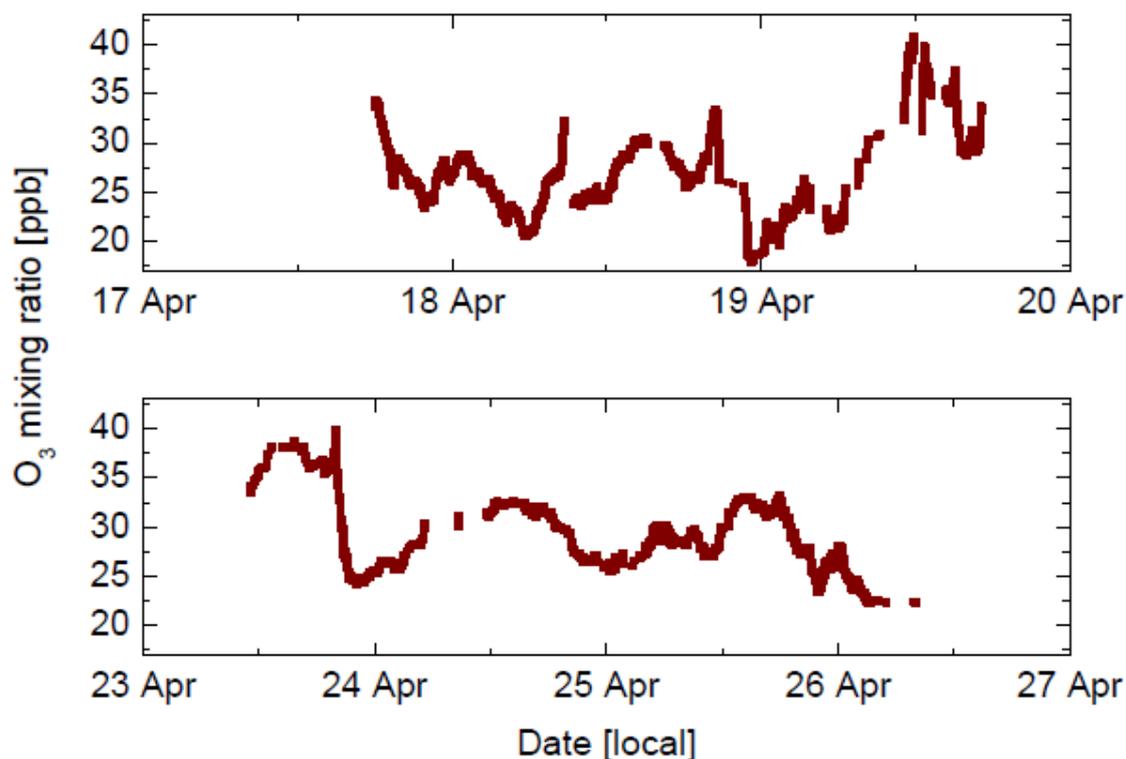


Figure 4.28 Average O₃ mixing ratio along the measurement light path for the two time periods in which the night-time measurements took place (April 17 – 20, 2007 and April 23 – 27, 2007).

① Evaluation procedure

The evaluation is performed with the software MFC (Gomer et al., 1996), which uses the spectra simulation and analysis model. Briefly, the fitting algorithm processed like this:

1. Correction of offset and dark current in the lamp reference spectrum.
2. High pass filtering, application of the logarithm and smoothing of the lamp spectrum.
3. Linear fit of the diode structure reference spectrum and a polynomial of 5th order to the lamp spectrum. Extraction of the residual structure of this fit for use as a lamp reference.
4. Correction of offset and stray light (by offset-corrected atmospheric stray light spectrum) in the atmospheric absorption spectrum.
5. High pass filtering, application of the logarithm and smoothing of the atmospheric absorption spectrum.
6. Non-linear fit of all references and a polynomial of 5th order to the atmospheric

absorption spectrum.

The evaluation algorithm automatically filtered out all measurement spectra that showed over- or under-range signal-to-noise ratios (resulting in errors within the fit) and assured that all spectra were corrected for the lamp structure, even if no lamp spectrum directly associated to the actual measurement spectrum was available (e.g. due to problems with the shortcut system). A detailed description of the single steps can be found below.

Offset and dark current/stray light correction

Prior to evaluation, all spectra were corrected for the offset by subtracting an offset spectrum recorded within one or two weeks prior or after the measurement spectra, weighted by the numbers of scans in the measured and offset spectrum. The dark current was only corrected for in the lamp shortcut spectra and the atmospheric absorption spectra were corrected for dark current and atmospheric stray light within one step by the integration-time weighted subtraction of the atmospheric stray light spectrum.

High-pass filter

To remove the broad-band structures due to scattering processes and broad-band absorption, a low pass filter was applied: the spectra were smoothed by performing a triangular smoothing, for all 1024 channels simultaneously, 800 times. The original spectrum was subsequently divided by its smoothed equivalent, leaving only the narrow-band spectral structures. After applying the logarithm to prepare the spectra for the fit, the corrected and filtered spectra were smoothed by the same triangular smoothing algorithm, but only performed two times to even out noise structures. This mechanism was used for both the corrected atmospheric and the lamp spectra as well as for all reference spectra.

Correction of fixed diode and Xe-Lamp structures

The fixed diode structures that proved to be highly variable were corrected by generating a reference spectrum for these structures: a halogen lamp spectrum recorded together with the other reference spectra was high-pass filtered by the algorithm described above (including the logarithm and smoothing). The resulting spectrum was used as the reference for the fixed diode structures. For the correction of the Xe-lamp spectra, a linear fit of the diode structure reference spectrum and a polynomial of 5th order to the lamp spectrum were performed. The residual of this fit represents a lamp reference spectrum that contains only the Xe-lamp structure and is independent from fixed diode structures.

Correction of Fraunhofer structures

An evaluation of the atmospheric stray light spectra yielded the result, that significant Fraunhofer structures could be identified, especially on the upper light path in broad daylight. These structures are caused by sunlight being scattered in the light path of the LP-DOAS system and collected by the receiving telescope. Under constant atmospheric conditions, these structures are expected to remain constant over integration time: thus, the stray light correction would remove these structures, too. In episodes with changing cloud cover, however, the optical density of these structures might change substantially. Therefore, the division of the atmospheric absorption spectrum by its associated stray light spectrum would leave differential Fraunhofer structures that cause increased residuals of the fit. To overcome this problem, a Fraunhofer reference spectrum was generated and included in every set of references: adding up 10 to 20 stray light spectra measured on the upper light path in broad daylight (if possible within one or two hours), applying the high pass filter, logarithm and smoothing leaves only the narrow-band Fraunhofer structures that would disturb the fit.

Fitting procedure

For the determination of the trace gas column densities from the atmospheric absorption spectra, the non-linear fitting algorithm was used. The following references are fitted to the measured spectra:

1. NO₂ cross section convoluted from (Voigt et al., 2001b)
2. HONO cross section convoluted from (Stutz et al., 2000)
3. HCHO cross section convoluted from (Meller and Moortgat, 2000)
4. O₃ cross section convoluted from (Voigt et al., 2001a)
5. O₄ cross section interpolated from (Hermans et al., 1999)
6. SO₂ cross section convoluted from (Vandaele et al. 1994)
7. Fraunhofer spectrum
8. Corrected lamp structure spectrum
9. Fixed diode structure spectrum

The references 2, 3, 5 and 7 were linked to the shift and squeeze parameters obtained from the non-linear NO₂ fit to exclude arbitrary shifting and squeezing due to small absorption structures. For the O₃ reference, permitting a shift or squeeze decreased the quality of the fit and was therefore denied. The correct wavelength scale calibration for the NO₂ and HCHO references was deduced from reference cell measurements. This was not possible for HONO and O₃ due to the lack of suitable reference gas cells, but for both trace gasses no significant shift versus the NO₂ reference could be observed. The diode structures were fitted without permitting a shift or squeeze, because no shift or squeeze is expected due to the nature of these structures.

For each evaluated spectrum, the residual was saved to disk and added to the residuals of the spectra evaluated before. After a first run of the evaluation algorithm, residuals featuring a delta above 5 ‰ (which hints on the occurrence of an error within the fit) were removed from the sum of all residuals. The resulting spectrum is used as an additional ninth reference for a second run of the evaluation. The justification for this process is the fact that atmospheric spectra often feature absorption structures that are not explained by the mathematical description. Such structures might be caused by unknown absorbers or absorption structures in the atmosphere or by structures caused within the instrument due to optical faults (nonhomogeneous illumination of the grating and/or the PDA). All mixing ratios presented in the following are computed from the trace gas column densities obtained in the second evaluation run including the residual reference.

4.4 Meteorology [Mr. Mikasa]

4.4.1 Objectives

A weather survey is an important item in order to grasp a natural phenomenon, and daily survey is important for it in order to understand long-term change of an atmospheric state. Some survey is for grasping change of natural phenomenon in a comparatively wide area and some survey is for obtaining the data of an air pollution phenomenon elucidation. In the air pollution continuous monitoring, it is required to catch the weather change at short range near the ground from the toxic substance discharged in the air being spread with various forms according to a climate condition. Moreover, the survey of variation of local wind direction, wind velocity or temperature is also important for the measure against air pollution in an emergency, and the weather survey for this purpose is performed.

Since the meteorological instrument may be distant from the monitoring station in the case of the weather survey, a periodic check for change in circumference environment, growth of trees, new building, etc. is required.

4.4.2 Wind direction anemometer

A wind is denoted by vector quantity of a wind direction and wind velocity. Since the wind direction and wind velocity in environment are changed continuously, The just time value is usually made by the average value for last 10 minutes of observation. Wind direction shows where the wind blows from, and it is shown by the clockwise rotation angle which makes 16 directions or north 0 degrees. Wind velocity is the distance which the air moves in unit time, and the unit is m/s shown to the 1/10.

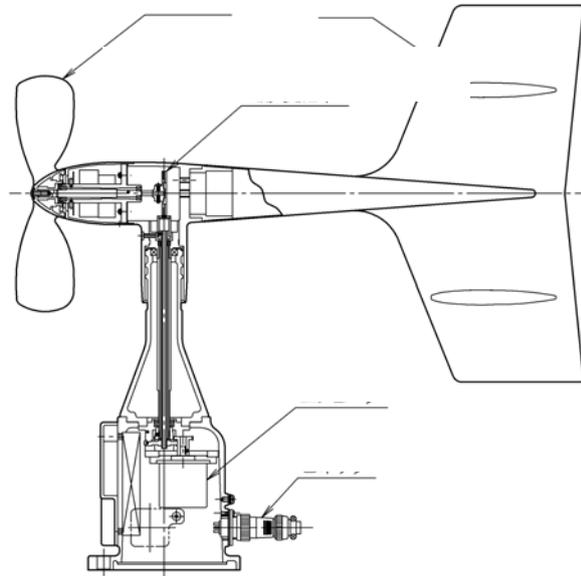
Although there are many kinds of the meteorological instruments of a wind direction and wind velocity, the windmill type wind direction anemometer and the ultrasonic type wind direction anemometer are used for air pollution continuous monitoring measurement.

(1) Principle of measurement

1) Windmill type

A Wind direction

A tail rotates following a wind direction. Arithmetic processing of the signal from transmitters, such as a synchronization, a potentiometer, or a rotary light encoder type directly linked with the axis of the tail, is carried out, and a wind direction is outputted. The wind direction range is 0 to 540 of all the directions NESWNES degrees.



B Wind velocity

The power generation type is outputting the voltage inducing by AC generator attached to the axis of a propeller which is proportional to wind velocity and rotates. The pulse type is outputting the calculation result of pulse amount proportional to wind velocity making rotation of the propeller by a wind.

Since digital processing is easy recently, a rotary light encoder type (5 bits, 8 bits) and a magnetic system is used for the wind direction, and a pulse type (a magnetic pulse, a lightwave pulse) is used for the wind velocity.

2) Ultrasonic type

Principle of measurement is that the speed of the sound which spreads the inside of the air changes with wind velocity and temperature. A wind direction and a wind velocity are outputted by vector composition of each propagation time of the X-axis (horizontal) and the Y-axis (vertical direction), using the speed of the ultrasonic wave of the high frequency which is not felt for human

and spreads the inside of the air.

Generally, the speed of the sound wave signal which gets across mutually for two points on the horizontal surface in the air to an opposite direction is determined by the wind velocity ingredient of the direction to which two points are connected, and the acoustic velocity in the stillness air.

In an ultrasonic type wind direction anemometer, the sum and difference of the time when a 100-kHz ultrasonic wave gets across mutually to an opposite direction between the transducers which fixed the distance of 20 cm, as an example, are measured.

By making 2 sets of transducers intersect perpendicularly mutually, and installing them in the direction of east and west and in the direction of north and south, an east-west ingredient (X ingredient) and a north-south ingredient (Y ingredient) of a wind are called for simultaneously, and a wind direction and a wind velocity are obtained by a vector composition. Moreover, some equipment can perform observation of a three-dimensional wind by a transducer installed also in a vertical direction.

(2) Installation criteria

1) Installation place

By the world weather mechanism (WMO), the standard for a wind direction anemometer is to select the place which does not have an obstacle in the circumference environment and which is flat and opened, to stand a panzer mast or a support perpendicularly, and to install at 10m height on the ground.

Since there are many obstacles in fact, when the height which is 10 m is not securable, or when representation place is not obtained, it is desirable to select a setting place as follows. But it is considered about a check and maintenance at any case to select a installation position.

A The highest place of the roof is ideal and it considers the influence from the structure of the roof.

B The influence of blowing up near the outer wall and its circumference at the roof are avoided.

(A transmitter is installed at 40 degrees or more against the roof side which an exfoliation wind produces.)

C The height standard of the support which attaches a transmitter is 0.35 or more times of the height of the building.

2) Setting of direction

It is necessary to decide the exact direction of south and north in the case of

installation of a wind direction anemometer, there are the following method etc.

A The method by compass (magnet)

Compass is put on the place which has neither metal nor ferroconcrete buildings close, and does not have disorder of geomagnetism, and the direction of "N" is temporarily appointed at north.

Although it is different depending with areas, the gap angle of north and magnetic north is corrected and set up.

It can ask for a deflection angle (the west deflection) by the following empirical formula from the latitude and longitude of an observation place.

$$D = 7^{\circ} 5'45 + 21'03\Delta\varphi - 5'84\Delta\lambda - 0'360\Delta\varphi^2 + 0'274\Delta\varphi \cdot \Delta\lambda - 0'470\Delta\lambda^2$$

D : the west deflection angle

$\Delta\varphi$: $\varphi - 37^{\circ}$ N (φ is latitude)

$\Delta\lambda$: $\lambda - 138^{\circ}$ E (λ is longitude)

※ Unit of latitude and longitude are degree

B The method by map

1/50,000 of the maps of the land are prepared, an object on the azimuth line as distant as possible from the present point on a map is defined. And a direction is set up according to the object.

C The method by a solar position

There are two methods. One of them is how to unite north and south with the shadow which is made by hanging down the weight at noon correctly. It is necessary to ask for the time of noon at the installation place. Another is how to ask for a true azimuth by a projection, latitude, longitude and time set up with the measurement equipments on a level plate.

(3) Check protocol

Since the admiration part of a wind direction anemometer is installed in the outdoors and it always runs continuously, the maintenance of a meteorological instrument is also important for maintaining of measurement accuracy as same with the maintenance of a monitoring station.

Maintenance has a "daily check" for checking normal operation of a meteorological instrument and "periodic check" for maintaining measurement accuracy for them.

1) Routine check and maintenance

A The existence of abnormalities is checked about the form of a transmitter (part), etc. by visual check.

B It is checked that abnormalities will be in directions and a record.

C It is checked that there is no gap in the indicated value of a wind direction

with magnet.

D Input signal cable is removed and the zero point of wind velocity is checked.

2) Periodic check and maintenance

The maintenance management contractor who accepted the trust from the maker or the maker is requested, and it carries out in many cases.

It is necessary to arrange enough about a check item and to carry out not only controlled study with the standard of a dispatch part (conversion output) but also the performance test of external outputs, such as indicated value, a record value, and a telemeter output.

4.4.3 Thermometer

Air temperature is called temperature and the temperature of change by time, the difference from a place, and the difference from height is great. In particular, it has big influence on observations that the difference from the state of earth surface, such as concrete, a bare ground, and a grassy place, and the temperature gradient by the height near the ground is large. Therefore, if the observed value of temperature is not the result of being measured under the same conditions, a mutual comparison is difficult for it, and since there are few examples by which this condition is fulfilled for various restrictions at a monitoring continuous measurement station, you need to keep in mind when using the results. Temperature is expressed per °C and recorded to the 1/10.

Although a thermometer has many kinds by the kind of thermo-sensitive device, or the difference in a spotter plane style, the electrical resistance type thermometer of Class A element which used platinum for the thermo-sensitive device is used for continuous monitoring measurement.

(1) Principle of measurement

Platinum resistance temperature sensor is a method using resistance changing conductors, such as metal, with temperature, it is known about temperature by measuring electrical resistance.

The platinum resistance bulb which coiled the platinum wire of diameter 0.1mm around thin boards, such as mica and porcelain, is paid to the protective tube made from stainless steel, and it is considered as the full waterproofing type. In addition, a platinum resistance thermometer has 3 line type and 4 line type, and it is devised so that all may remove the influence of the lead resistance between converters from a sensor.

(2) Installation place

The installation place is carried out banking around the place which the circumference opened so that it may not become shades, such as a building and trees, and it is improved of drainage. It is desirable to plant a lawn to make an installation place after them.

A wooden instrument screen or vent sleeve is prepared in an observation field, and a thermometer is stored to the inside (central part).

* Although based on attaching a thermometer so that it may generally become a height of around 1.5 m from an earth surface top, when a setting position is limited, the method is needed to remove the influence by the minimum setting position, and to obtain minimum representation.

1) The case of using vent sleeve

A thermometer puts an admiration part in the forced-draft pipe (central part) with the ventilating device .

The height of the fresh air inlet of a vent sleeve is based on 1.5 m above ground. When installing in a building etc., it is made the height which is not subject to the influence of reflection or radiation.

Especially in the case of natural draft, it is desirable to choose a higher position, considering as a wind, solar radiation, and radiation, and to cover a floor with an artificial lawn.

2) The case of using Instrument screen

An instrument screen is wooden and is the structure which can protect the meteorological instrument of temperature or humidity from a rainstorm etc., and can be covered from solar radiation or radiation.

The leg is buried and fixed in the earth so that it may come out 1m on the ground. However, in many snow areas, the leg may be made high according to snow coverage. Moreover, the front is carried out for north so that solar radiation may not hit an admiration part directly, when a door is opened.

A thermometer is attached so that it may become a height of around 1.5 m from an earth surface top.

(3) Check protocol

1) Routine check and maintenance

A In the case of a forced-draft pipe, it has a piece of paper etc. in a suction mouth, and it performs checking of operations. Moreover, it is cautious also of the garbage and the freeze which are attached to a fan.

- B The dirt by rain and sand, a cobweb, etc. in instrument screen, are cleaned.
- C It is checked whether abnormalities will be in external output direction and a record.
- D Aspirated psychrometers, such as an Assmann ventilation dryness-and-moisture degree meter, perform comparison observation, and it checks that both difference is less than ± 0.5 °C. Since an Assmann ventilation dryness-and-moisture degree meter is subject to the influence of solar radiation, comparison is performed at cloudy day. Moreover, it is desirable to check in a time zone with few temperature changes in a day.
- E Since water may go into a vent sleeve and an obstacle may appear in measurement when strong wind and rain occur, it is cautious of data.

2) Periodic check and maintenance

- A The signal cable connected to the input terminal of converter is removed (since it changes with a sensor and cables, specified for every thermometer), and the resistance is measured. The resistance is checked that it is a specified value.
- B It is necessary to give the false resistance by thermometer set tester (standard meter with traceability) etc., and to also carry out the performance test of external outputs, such as indicated value, a record value, and a telemeter output.
 Since a periodic check is requested from the maintenance management contractor entrusted to the maker or the maker and it carries out in many cases. It is needed to arrange enough about a check item.

4.4.4 Hygrometer

Although humidity is an index showing the water vapor content of the air and it is expressed with various indices, such as relative humidity, absolute humidity, steam pressure, and dew point temperature, relative humidity is used most widely.

1) Relative humidity

Relative humidity expresses the ratio of steam pressure (e) and the maximum vapor tension (E) at the temperature with percentage $e/E \times 100$. A unit is % and shown integrally.

2) Absolute humidity

The vapor partial pressure in the air is called water vapor pressure, and it is only called steam pressure in a weather survey. The steam pressure which is in water or ice, and a thermodynamic equilibrium situation at a certain temperature is called maximum vapor tension of the temperature. The unit of steam pressure is hPa

and recorded to the 1/10

3) Dew point temperature

If air is cooled under pressure regularly, the water vapor of the air will reach saturation at a certain temperature, will begin condensation, and will connect dew. The temperature is called dew point temperature, and a unit is degree and recorded to 1/10.

Although the hygrometers used for continuous monitoring measurement of air pollution were a hair type hygrometer and a dew point type hygrometer once, electric capacity type hygrometers incorporable into the same vent sleeve with a thermometer have increased in number.

(1) Principle of measurement

1) Electric capacity type

Change of the dielectric constant by moisture absorption of a macromolecule thin film is regarded as change of frequency in an oscillating circuit, and is outputted as relative humidity.

2) Dew point type

From the hygroscopicity of a lithium chloride (LiCl), a self-equilibrium is between the steam pressure of the air which touches water solution and the solution.

In this equilibrium situation, a fixed relation between the steam pressure of the air which touches a solution and the solution is depending on the concentration in the solution. Depending on this method, a dew point temperature is asked for by measuring temperature (solution dew point temperature) when the steam pressure in the air reaches the maximum vapor tension of solution.

3) Hair type

If the humidity in the air changes, hair expands and contracts according to hygroscopicity of hair. Because the extension rate of hair changes almost in logarithm at 20 to 100% relative humidity, relative humidity can be measured using this character.

However, the use of this type decreased at present because of much degradation of mechanical structure and the hair itself in the area near the seashore with many sea salt particles, or with much ammonia or acid, etc.

(2) Installation place

It is considered as the same conditions as a thermometer of the Chapter 4.7.3 fundamentally. When using a hair type hygrometer, it is stored to the metal instrument screen or small instrument screen of a forced-draft type. When using an

electric capacity type hygrometer, it is stored to an integral-type vent sleeve by combination with a thermometer in many cases.

(3) Check protocol

1) Routine check and maintenance

The check not only according to checking whether abnormalities will be in directions and a record but also each observation method is required.

A Electric capacity type

The dirt of the membrane filter which has protected the sensor is checked, and when a sea salt particle, dust, or smoke adheres and is dirty, a filter is removed from a sensor, and natural seasoning is carried out after distilled water washes.

B Dew point type

Since it is necessary to increase the applies frequency of a lithium chloride, it is important to carry out comparison measurement to an Assmann psychrometer used as a standard meter and to check in the remarkable point of air pollution, and the seashore district which is subject to the influence of a sea salt particle.

C Hair type

The dirt of hair is checked and the dirt, such as sand and smoke, is carefully cleaned with a feather etc. When a dirt is remarkable, or when it is used several months, a brush contained with distilled water is prepared, and is washed by soft touch. Natural seasoning is carried out.

2) Periodic check and maintenance

Since the maintenance management contractor who entrusted the maker or the maker is requested and it carries out in many cases, it is necessary to arrange enough about a check item.

It is necessary to carry out the controlled study not only of a dispatch part (admiration wet part) and a conversion part, but also of external outputs, such as indicated value, a record value, and a telemeter output. It is carried out by giving the false resistance by a set tester etc. to the converter about a dew point thermometer, and by giving humidity change to a sensor with the humidity calibrating meter which used the reagent about the electric capacity type hygrometer.

4.4.5 Actinometer

An amount of insolation is the quantity per unit area of the solar energy which enters into the level plane near the ground. Since change is sharp by being subject to the influence of the water vapor of the air, dust, clouds, etc., not the moment value of a

certain time but the amount of addition in a definite period of time is used for an amount of insolation in many cases. By advice of WMO, an unit is denoted by kilo watt per square meter (kW/m^2) to a moment value and is denoted by mega joule per square meter (MJ/m^2) to an amount of addition from January, 1981.

1) Direct amounts of insolation

The direct amounts of insolation which reach directly from the sun can be observed except for scattering light and catoptric light among the solar radiation which enters into the level surface of a unit area from sunrise to sunset.

Supposing the atmosphere does not exist in the earth, the radiant quantities which the earth receives from the sun would become almost constant because it is decided only by solar activity and distance. This is called solar constant. It is 1.38kW/m^2 at average of moment value, and, is about 5.0MJ/m^2 of integrated value.

2) Amount of global solar radiation

Direct solar radiation, the dispersion solar radiation which enters from the sky all, and the reflective solar radiation from clouds are united to the total amount of the solar radiation which enters into the level surface of a unit area, and it is called global solar radiation. It is slightly observed also in front of sunrise and after sunset.

3) Dispersion amount of insolation

It is observed as an amount of energy of the light scattered about by an air molecule, vapor, aerosol, etc. in the air except for direct solar radiation among the solar radiation which enters into the level surface of a unit area.

(1) Principle of measurement

The object has the character that makes its temperature rise by absorption of the heat of the energy when receiving solar radiation. The character is used. A thermoelectric pile (what connected many thermoelectric piles in series or in parallel) is arranged between the acceptance surface (warm junction) which carried out black paint, and the thermal reference point (cold junction) arranged on the body etc. And the difference in temperature of the warm junction and the cold junction is outputted as thermoelectric power, and is converted into the amount of insolation which entered.

(2) Installation criteria

It is an observation field and the roof, without interrupting direct solar radiation from sunrise to sunset through one year, the influence of strong catoptric light, the building which covers the sky widely, a standing tree, an antenna, and smoke, etc. When ideal conditions are not acquired, a place with as much as possible little these

influence is selected. Moreover, it is necessary to consider about a routine check and maintenance.

(3) Check protocol

1) Routine check and maintenance

- A It checks whether there is any dirt in the glass dome of an admiration part, and cleans up if needed.
- B The moisture absorption condition of a drier is checked and driers are exchanged if needed.
- C It is checked whether indicated record becomes high from sunrise and after sunset has become zero.
- D It is checked whether an abnormal value, such as exceeding 1.4kW/m^2 with a value at the moment and exceeding about 5.0 MJ/m^2 with an integrated value, has appeared.

2) Periodic check and maintenance

- A It is checked whether there are any abnormalities in a glass dome.
- B It is checked whether acceptance surface paint discolors, or has exfoliated remarkably.
- C It is checked whether there are disconnection and loose connection in the feeling part output connector.
- D Directions, record, and the output of a telemeter are checked when false voltage (5.0MJ/m^2) is given.

4.4.6 Net radiometer

The atmosphere of the earth and thermal radiation which is proportional to the temperature also from earth surface are performed at the same time it emits the atmosphere and the earth surface of the earth from the sun, namely, it absorbs solar radiation and it gets warm. The difference of the radiant quantities received from the sun and the radiant quantities emitted from the earth shows the amount of radiation income and outgo.

A unit is denoted by kilo watt per square meter (kW/m^2) to a moment value and is denoted by mega joule per square meter (MJ/m^2) to an amount of addition.

(1) Principle of measurement

The amount of insolation from the whole sky and the radiant quantities from earth surface are observed by the thermoelectric pile of copper/Constantin constructed so that it might be located up and down, and the difference in temperature is outputted as an amount of radiation income and outgo.

(2) Installation criteria

It is desirable to select the place which cannot have the shadow from sunrise to sunset through one year and which it is flat and opened, and to cover earth surface with the grassy place.

The place which has a waterway, a drain pipe, etc. in the earth is avoided, and a net radiometer is attached at 1.5 m height on the ground horizontally. Moreover, the pillar to attach is installed in the north side and solar radiation is made not to be interrupted in the shadow with a pillar.

(3) Check protocol

1) Routine check and maintenance

A Although a polyethylene dome can usually be used for about one month, it will exchange, if there is dirt or breakage.

The bird injury by standing the wire about length 24cm and thickness 2cm is effective, since a polyethylene dome may be damaged with a bird. The product made from stainless steel is desirable to prevent to rusted.

B It is checked whether the polyethylene dome has swollen normally or there is not any jam for a leak nozzle (air bent) simultaneously.

C The state of indicated record is checked, since it can use as a weather meter at night, the weather in the night on several before check is grasped.

2) Periodic check and maintenance

A Check of appearance and form is performed and a polyethylene dome is exchanged.

B The air filter of Blois is cleaned.

C Since the dehumidified water accumulates into dorain, it is drained once a month .

D False voltage is given and indicated record and the output of a telemeter are checked.

4.4.7 Rain gauge

Rain is a phenomenon that the piece of ice or water drop falls. They are the water drop which condensed vapor, and the piece of ice sublimated the water drop in the air. Or they are the piece of ice which freeze water drop, and the water drop dissolved the piece of ice in the air. Precipitation is the quantity of rain which reached the level surface of the earth surface, or the level surface of projection of the earth surface to within a certain time, and it expresses with the depth of rain water. Precipitation is expressed unit of mm and even recorded to 1/10. However, when the minimum measurement of a rain gauge unit is 0.5 mm, 1/10 of an observed value of grades are expressed as follows. “less than 0.5mm is 0.0 mm”, or “0.5 mm or more and less than

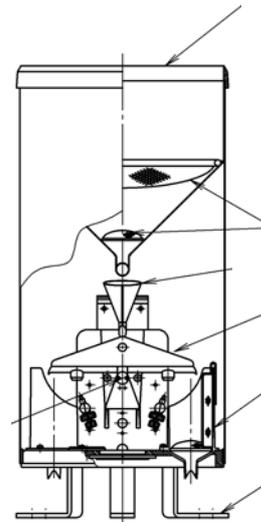
1.0 mm are 0.5 mm”.

(1) Principle of measurement

One side of fall measure is filled with the rain included in a receiver from a funnel through a filtering equipment. The center of gravity of fall measure moves to the counter direction of a fulcrum by collected rain. The measure will fall and drain collected rain, if precipitation reaches 0.5mm. For every time of a fall, a reed switch works and generates one pulse in the connected electric circuit.

(2) Installation criteria

It is necessary to choose the place where an air current becomes level as much as possible, and it is separated from a sloping ground, a high ground, a depressed ground, the outer wall of the roof in which a wind blows up, and the ridgeline of a mountain as much as possible. Furthermore, it is ideal to separate into the distance of 4 times or more of the height from the place which has a tree and a building in the circumference. If it is impossible, it selects from the place so that an ascending vertical angle may be 30 degrees or less at the lowest. Moreover, a receiver is horizontally installed in consideration of the rebound from the ground.



(3) Check protocol

3) Routine check and maintenance

Removal of garbage for, such as water receiving equipment, filtering equipment or a movable part, and an exhaust port, removal of the dirt for inside of a fall measure, etc. are performed.

4) Periodic check and maintenance

5) It is carried out not only cleaning of a reed switch and a connector, but also check indicated record and the output of a telemeter by giving a false pulse.

5. Maintenance [Mr. Mikasa, Mr. Phunsak and Network Center]

5.1 Standard operating procedures [Network Center]

SOPs are written procedures used in all the processes of the monitoring system, i.e. in the field, laboratory and for data management. SOPs provide a method designed to ensure that all personnel follow the same procedures in an identical manner minimizing the variance of data quality between individuals ensuring each person conducts their works with a scientifically sound understanding of QA/QC. Each of the sampling and chemical analysis organizations or laboratories should ensure that SOPs they prepare meet the requirements of their respective organizations and that SOPs comply with the Technical Manuals and the national QA/QC programs. SOPs need to be straight forward and sufficiently clear to ensure that beginners can perform the tasks in an effective manner. SOPs are to be updated in a timely manner and should take into consideration changes in technology and advances in science. Essential components of the SOPs are outlined as shown below.

1. Monitoring

1.1. Appointment of monitoring staff and their supervisors

1.2. Check of possible changes around the monitoring sites

- 1) Local situation (new construction of emission and contamination sources etc.)
- 2) On-site situation

1.3. Check of monitoring instruments

- 1) Appearance of instruments (check for corrosion etc.)
- 2) Operation of instruments
- 3) Cleaning of sampling parts

1.4. Sampling methods

- 1) Sampler and monitors (including documentation of check and maintenance)
- 2) Sampling intervals

2. Sample transportation and storage for manual monitoring

2.1. Transportation of samples

2.2. Sample storage

- 1) On-site storage
- 2) Laboratory storage

3. Chemical analysis

3.1. Appointment of analysis staff and their supervisors for each item

3.2. Training plan

3.3. Pure water

- 1) Daily maintenance
- 2) Documentation of maintenance
- 3.4. Measurement by automatic instruments
 - 1) Measuring conditions of instruments
 - 2) Calibration
 - 3) Performance tests (sensitivity, stability, interference and its removal, documentation of repair)
 - 4) Calculation of lowest detection limits and lowest determination limits
 - 5) Documentation of maintenance
- 3.5. Operating procedures for measurements
 - 1) Preparation of calibration curves
 - 2) Measurement/analysis of samples
 - 3) Repeated measurements/analyses
 - 4) Check of sensitivity fluctuation
- 3.6. Treatment of measurement results
 - 1) Calculation of concentrations
 - 2) Measurement of sensitivity fluctuation
 - 3) Repeat measurements/analyses
 - 4) Calculation of ion balances
 - 5) Comparison of measured and calculated electric conductivity
4. Quality assurance and quality control
 - 4.1. Evaluation of manual sampling
 - 1) Comparison of manual monitoring and a automatic monitor
 - 2) Evaluation of ion balance
 - 4.2. Evaluation of reliability
 - 1) Evaluation of sensitivity fluctuations
 - 2) Evaluation of repeated measurements/analyses
 - 3) Evaluation of field blanks
 - 4) Comparison between measured data and lowest detection and determination limits
 - 4.3. Evaluation of results
 - 1) Representativeness of sampling sites
 - 2) Evaluation of sample validity
 - 3) Evaluation of completeness for the sampling period
 - 4) Determination of total precision
5. Management of sampling instruments, laboratory, measurement/analysis instruments and reagent/glassware
 - 5.1. Management of sampling instruments

- 1) Appointment of management staff and their supervisors
 - 2) Documentation of names of manufacturers, types, manufacture dates and operation methods
 - 3) Daily and regular maintenance and inspection methods (including troubleshooting, parts supply and recording)
- 5.2. Laboratory management
- 1) Appointment of management staff and their supervisors
 - 2) Daily and regular maintenance and inspection methods (including items and recording format)
- 5.3. Management of measurement/analysis instruments
- 1) Appointment of responsible staff for each instrument, and overall measurement
 - 2) Documentation of names of manufacturers, types, manufacture dates and operation methods
 - 3) Daily and regular maintenance and inspection methods (including troubleshooting, parts supply and recording)
- 5.4. Management of reagents, standard materials, etc.
- 1) Appointment of management staff and their supervisors
 - 2) Receiving and disposal of reagents (recording format of dates, manufacturer names, dealers, purity, degree of standard and valid period)
6. External audit
- 1) Check of sampling sites
 - 2) Measurement of field blank values
 - 3) Operation check of samplers
 - 4) Evaluation of the results of quality control
 - 5) Evaluation of the measured results

5.2 Maintenance of manual samplers and analytical instruments [Mr. Phunsak and Network Center]

Station maintenance is a portion of preventive maintenance that does not occur on a routine basis. These tasks usually occur on an “as needed” basis. The station maintenance items are checked monthly or whenever an agency knows that the maintenance needs to be performed. Examples of some station maintenance items include:

- Floor cleaning & vacuuming
- Shelter inspection
- AC filter replacement, replace battery in remote control
- Weed abatement

- Inspect roof mounted equipment
- Inspect Meteorological sensors and cables
- Verify True north orientation for Wind Direction
- Ensure UPS operates in excess of 30 minutes
- Ensure there are operating schedule for each monitor.
- Ensure a copy of the manual for each analyzer is kept in the air monitoring station and at the Instrument Support Electronics Shop.

Routine station operation

Station visits: recommend 15 day, and the new employees much receive on-the job training from experienced site operators. Manual for each analyzer is used as Standard Operating Procedures for continuous measurement.

- Sample filter change, leak check after filter replacement.
- Check auto drain in zero air unit
- Check chemical zero air scrubbers for moisture.
- Clean sample manifold
- Clean Size Selective Inlet for both PM10&2.5 samplers replace sample tape as necessary, perform zero flow check.
- Station temperature $27^{\circ}\text{C} \pm 3^{\circ}\text{C}$
- Check main gas pressure in cal gas cylinder
- Perform zero/ span Check on all analyzers
- Verify Meteorological sensors are operational

5.3 Maintenance of automatic monitors [Mr. Mikasa]

It is important for the routine monitoring to operate an automatic monitor for a long time in a stable manner for maintaining high-level of performance and data quality.

The purposes of the routine monitoring are defined that it was necessary to obtain the effective data above ● % in day, month, and year, such as above ● hours in day, above ● hours in month and above ● hours in year (above ● days in year for PM2.5). It is described in Chapter 7.2 in detail. For the attainment of these purposes, a monitor should be maintained fundamentally according to two methods as follows.

- ① Preventive maintenance : the methods to maintain preventively to the parts of a minotor with possibility to break out and repair, such as routine and periodic checks and maintenance, and overhauls.
- ② Troubleshooting : the methods to deal with the anomalous behaviors and research their causes, after breaking out and repairing, such as emergency check

An automatic monitor has the possibility of failures, for example, early “infant

mortality” failure, random failures during operating the monitors, and wear out failures because of consuming their parts and themselves, although a monitor is assured its fundamental faculties by maker tests before delivering. It is important to plan the maintenance schedule of a monitor from the time when it is delivered because failure rates can be decreasing by accurate maintenance. Figure 5-3-1 shows an overview of the change of failure rates during operating apparatus.

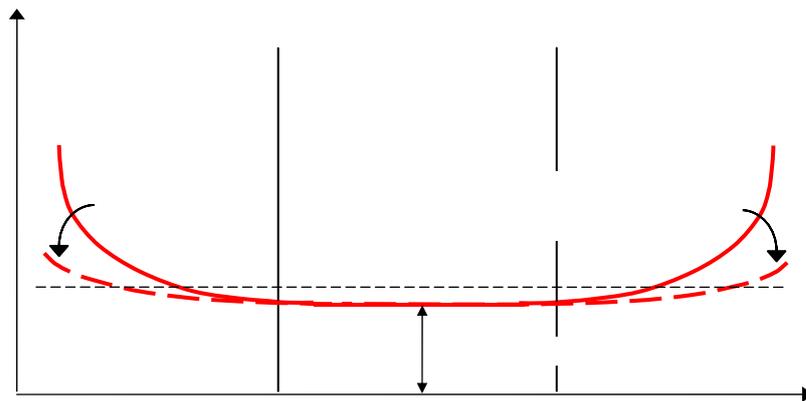


Figure 5-3-1 Changes of failure rates during operating apparatus

REFERENCE

This figure shows the relationship between the operating time of apparatus and the failure rates, and it is called “The Bathtub Curve” because its figure is like bathtub.

The failure rates of almost apparatus show the curve like this “The Bathtub Curve”.

“The Bathtub Curve” is classified into three periods as follows.

(1) Infant Mortality Period

Many failures happen as soon as the apparatus are set because of failures caused during making the apparatus.

This is the period of initial failures.

(2) Constant Failure Period

This is the period of constant failure without initial failure.

(3) Wear Out Failure Period

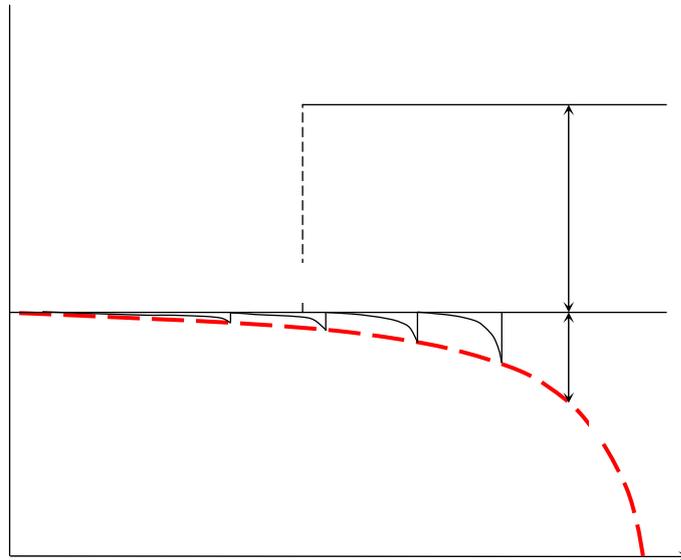
This is the period that many failures happen because of wearing out the apparatus by consuming their parts and themselves.

It is changed by the apparatus durability and the circumference whether this period comes early.

5.3.1 Schedule of maintenance

It is necessary to plan a long term schedule of maintenance, for example frequency of maintenance, calibrations, overhauls, and updating of a monitor, for the routine monitoring to operate a monitor for a long time in a stable manner for maintaining high-level of performance and data quality. And the performance of a monitor is getting deterioration by aged deterioration because of continuous measurements.

Therefore it is necessary to plan a frequency of the periodic maintenance for within the criteria and it is important the judgment of each monitor status exactly. And it is important to grasp the features of the monitors because each monitor condition is different with its situation and its setting place, too.



5.3.2 The kind and contents of maintenance

Table 5-3-1 shows the sections, objectives, frequency, and contents of maintenance.

(1) Visual confirming

The data of each monitoring station (child station) are gathered in the central station (parent station), and they are converted hourly reports, daily reports, etc. Normal operation of an automatic monitor is checked from these reports and when anomalous behaviors appeared, it is coped with suitably in order to recover a normal operation. The condition of automatic monitor should be grasped in the monitoring station using the function on the monitor of the signal with temperature, pressure, or an unusual state.

The monitor which can be transmitted the information on check items, such as a sampling air flow (volume and temperature), with a telemeter is useful without going to check in the monitoring station.

Recording a missing value with its cause is more effective rather than a missing value stored only. It is useful for checking the monitor and deciding of measured value.

Table 5-3-1 The contents of maintenance

Sections	Objectives	Frequency	Contents
Routine check and maintenance	To operate the automatic monitors in a stable manner (to obtain data)	Once/week	<ol style="list-style-type: none"> 1. Confirming the operating of an automatic monitor 2. Replacement or addition of consumables 3. Check and calibrating simple parts 4. Cleaning and replacement the simple parts
Periodic check and maintenance (more detailed procedures than routine check) (Transmission accuracy check)	To keep an automatic monitor in high-level of performance and quality, and to maintain preventively (to assure the precision and accuracy within their criteria)	Once/year	<ol style="list-style-type: none"> 1. Test of flow department 2. Test of detection department 3. Test of control and transmission department 4. Test of amplification and record department
Emergency check	To carry out emergency check against anomalous behaviors or failure (to restore a monitor normally)	When anomalous behaviors appeared	<ol style="list-style-type: none"> 1. Detection of failure and emergency repair 2. researching the causes and repair (by makers)

(2) Routine check and maintenance

Routine check and maintenance is to confirm the monitor operations and conditions, it should be carried out at least once in a week or two weeks to check the operation of the concerned instruments, and change consumables as appropriate.

Routine check and maintenance are mainly carried out by visible check. A check list should be prepared to minimize the difference among individual and results should be recorded without delay. A recording chart of an automatic monitor should be filled in check time, a canvasser, the contents of check, missing data time, and so on because it would become leading data when the question will arise in a monitoring result later. Moreover, if an anomalous behavior appeared and its repair cannot be carried out, the situation should be filled in as finely as possible and it would enable to direct exactly when repairing.

The lack of check items of routine check and maintenance can be prevented by dividing the checking part of each.

(3) Periodic check and maintenance

Periodic check is to concern the precision and characteristic of an automatic monitor, and it needs to have full knowledge of a monitor in order to carry out calibration which assures the measurement accuracy of a monitor, and replace the parts getting deterioration. Periodic check about a monitor which has official approval is carried out by a maker especially.

The frequency of replacement of parts or the frequency of the check of measurement accuracy is different according to the kinds of automatic monitors.

(4) Emergency check

Emergency check is to research the cause of a monitor broken out or an anomalous behavior of a monitor at once, if it is found at visual confirming or routine check and maintenance, and to recover normal operation. Detailed knowledge about the principle and system of measurement methods and the abundant experiences about the trouble restoration are needed for this type of checks.

5.3.3 Useful life of an automatic monitor

Since an automatic monitor works for 24 hours continuously for a long time, it is unavoidable to consuming the component parts by working. A standard of useful life of a monitor would be seven years in general even if a monitor is maintained exactly by routine or periodic check and maintenance, example for replacement parts of a monitor, when a factor like the increase in the failure occurrence frequency by aging is judged synthetically. It is necessary to establish the updating standard of each monitor based on this, and to carry out as planned. The updating standard of a monitor which needs official approval is established in consideration of the term of official approval, the official approval term of a one of meteorological monitors is five years, for example.

The synthetic judgment including an economical standpoint is required for an updating standard in addition to the technical standpoint that assures the accuracy of an automatic monitor. The updating standard is the time when the sum total of a repairing cost and parts replacement cost is the minimum. But generally, the updating standard is set up experientially, because the time of minimum cost is changeable by the setting condition of the monitor.

In addition, a discharge entrepreneur has to process properly an unnecessary monitor as a waste obtained during his business in his responsibility.

5.3.4 Overhaul

An automatic monitor may have to work exceeding the useful life in some cases. Generally, even if sufficient maintenance is carried out to a monitor, the monitor consumes according to progress of working. Therefore, the periodic check which is requested from a monitor maker may be carried out in addition to routine check and maintenance. However, since a periodic check is usually carried out in a monitoring station, the range of an assurance is limited by time restrictions etc.

An overhaul is carried out when it needs to keep the accuracy of a monitor and the period check is insufficient. A monitor maker brings the monitor back to his company, takes it apart, checks the performance of each part, and put them together again after exchanges or repairs parts if needed, and operates in certain fixed period for assuring the function and accuracy of each part. It can be obtained the synthetic assurance in order to carry out overhaul over many hours with the institution to which equipment was well ready. Therefore, when it becomes clear to be difficult to keep the accuracy of a monitor, such as the increase in the missing value by failure of a monitor, only by a periodic check and maintenance, an overhaul should be carried out.

5.4 Field record [Network Center]

All monitoring sites should essentially satisfy the siting criteria. If there are some differences from the criteria, they should be documented and evaluated. Any significant changes around sampling sites and conditions should be properly reported in the record sheet and the report should be submitted to NC through the National Center upon request.

The example of field record sheet is shown in the following table.

(Example of field record sheet)

局番号	所在地																
(測定機外観写真)		大気汚染防止法第15条別表3の地域区分															
		本 地域管理区分 第 地域															
設置年月	年 月	設置形態	独立局舎		方式	消費電力											
局舎構造		局定置面積	mf														
採気口	地上よりの	高さ	m	敷地面積			地・地()										
空気採取装置	設置年月	内径	m	長さ	m	滞留時間	分	力所	所在地								
風向・風速	地上より	温・湿度計	地上より				所有者 氏名										
監視及びデータ取得	予レメータ・その他	年 月	知覚開始					年 月 日 円		年 月 日 円							
高圧ガス	数	使用機器数	空中	m	山岳・高 浜			年 月 日 円		年 月 日 円							
		その他	備品等														
測定機	項目	測定開始年月	型式	測定機製造番号	製造年月	更新年月	型式	測定機製造番号	製造年月	更新年月	型式	測定機製造番号	製造年月	更新年月	付帯設備	TM・冷房・暖房・空気装置・貯蔵・遊置等	
															項目	型式・製造番号	消費電力
															TM		
															冷房		
															暖房		
															空気		
															貯蔵		
															遊置等		
															照明		

5.5 Maintenance record [Network Center]

According to the recent development of monitoring instruments, most of instruments can be used for more than 5 years. It is important to take records of the status of monitoring instrument when one try to analyze long term trends of sir concentrations. The necessary items of maintenance record are shown below.

- Name of station
- Name and type of instruments
- Regular inspection of instruments (Date, Contents, Results)
- Calibration records (Date, Species, Method, Range, Spen and Zero factor)
- Instrumental failure and repairs (Date, Contents, Results)

5.6 Safety management [Network Center]

It is important to consider safety management regarding high pressure gas cylinders, disposal of chemicals and parts of monitoring instruments.

5.6.1. Management of high pressure gas cylinders

- Person in charge of safety management
- Storage record sheet
- Consumable equipments
- Ventilation of storage room

5.6.2. Disposal of chemicals, solution waste and monitoring instruments

- Manner of disposal should be followed by local laws
- Neutralization of acid or alkaline solutions
- Treatment of radioactive substances such as β -ray detector
- Disposal of the other consumables as industrial wastes

6. Data reporting and validation [Network Center]

The data are processed by the personnel in charge of the laboratory (PCL), the national QA/QC managers (NAM) in each participating country and the network QA/QC manager (NEM). The PCL has to collect the measurement data of air concentrations and meteorological parameters and input these data to the reporting format. In addition, other relevant information regarding dry deposition should be reported to NAM of each participating country. The National Center and the NAM have to report monitoring data to the Network Center. The Network Center and the NEM has to compile, compute and verify the database of air concentration and provide a copy of the database to the participating countries when requested.

6.1 Site specification

The local circumstances information to be reported by individual country (NAM) are: (1) the information which affects air concentrations such as specific meteorological data, climate, climate vegetation and life style, (2) the information which affects measurement accuracy such as conditions of monitoring instruments, laboratory conditions. These data should be reported when there is a demand.

(1) Information of effects on air concentrations

- Specific meteorological data
- Climate (rainy and dry season, season of sand storm, volcanic condition, etc.)
- Vegetation (the type of tree, season of pollen dispersion, etc.)
- Life style (agricultural operation, biomass burning, etc.)

(2) Information on the precision of monitoring results

- Conditions of monitoring instruments, (calibration methods, failure and incidents on instruments, maintenance conditions, etc.)
- Laboratory condition (maintenance conditions for ion chromatography, instrument list, chemicals, etc.)

6.2 Compilation of raw monitoring data

The data to be reported to NAM are grouped into two types: 1) Information about sites, monitoring condition, shipping of the filter pack samples, laboratory operation, chemical analysis, etc., 2) Measurement results of air concentrations by automatic monitors and the filter pack methods, measurement results of meteorological parameters,

and other parameters required to calculate dry deposition fluxes. Remarks and notes also compose major parts of the measurement results.

(1) Information about sites, sampling, shipping, laboratory operation, chemical analysis

- Name of country and site (Code of country and site)
- Name of NAM
- Name of responsible laboratory and PCL (Code of laboratory)
- Information of site (on -site scale, local scale and regional scale)
- Information of monitoring condition (automatic monitors, a filter pack sampling instrument, meteorological instruments, etc.)
- Information of filter pack samples history (shipping frequency, packing procedure, laboratory operation, etc.)
- Chemical analysis condition by ion chromatography (Control Chart)

(2) Measurement and calculated results

- Name of country and site (Code of country and site)
- Name of NAM
- Name of responsible laboratory and PCL (Code of laboratory)
- Sample number (Code consist of country code, site code, year, month and number)
- Start and end of date and time of monitoring
- Date of chemical analysis for the filter pack samples
- Air concentration measured by automatic monitors (SO₂, NO, NO₂ and O₃)
- Air concentration measured by the filter pack method (SO₂, HNO₃, HCl, NH₃, and Particle matter components)
- Meteorological parameters (Wind Speed, Wind direction, Temperature, Relative humidity and Solar radiation)
- Leaf Area Index (Optional)
- Notes and any other information

All the measured data should be reported to NC through the National Center, following the protocols as shown below.

The units to be used for SO₂, NO/NO₂ and O₃ should be ppb, and that for PM should be ug/m³.

For automatic instruments, SO₂, NO/NO₂ and O₃ should be expressed one digit under decimal, and PM should be expressed by integral numbers (e.g., 15.3 ppb for SO₂ and 52 ug/m³ for PM).

(Data treatment protocol)

1. Hourly data should be effective when more than 3/4 of the data during the measurement period is effective.
2. The ending time should be used for the hourly data (e.g., hourly data for 1 p.m. should be the data between noon and 1 p.m.)
3. Hourly average should be calculated as the arithmetic mean of the sum of the data except non-usable ones divided by the effective duration. Daily average should be the value calculated as the sum of the all hourly data from 1 a.m. to 12 p.m. (excluding the non-usable hourly data) divided by effective hours of the day. Daily average should be used only when 3/4 of the hourly data of the day is effective.
4. Monthly (annual) average should be calculated as the sum of the hourly data of the month (year) divided by the effective hours of the month (year). Therefore, it should not be the average of the daily averages.
5. Non-usable data should be the data that are not considered adequate, due to such reasons as the maintenance, calibration or breakdown of the instruments. Non-usable data should not be used for statistical treatment, but should be reported with flags.
6. Annual average should be calculated by using the data from January through December of the year.

6.3 Data validation

Data checking or validation is based upon:

- Experience with the data from earlier measurements,
- Knowledge about spatial and temporal variation.

Records of old data can be used to create simple statistics including percentiles, mean values and standard deviations. Log-transformed data are sometimes considered. These statistics can be used in connection with control chart or in other comparisons of new data with aggregation of the old ones.

Relations between various chemical components (including ion balance of particulate matter components), relationship between sea salt components, and relationship between air concentrations from neighboring stations and time-series plots are also useful.

6.3.1 Statistical tests

The statistical tests are comparisons between new measurement and calculated results and data already stored in the database. The tests are carried out to identify possible

outliers and results which may be wrong. They can be based upon assumption about the data distributions. In some cases, respective air concentrations and calculated dry deposition fluxes may be compared with earlier data using the lognormal distribution. Data which is not within the four times the standard deviations range, should be checked by comparison with air concentrations and other results obtained on earlier and later days, and results from neighboring sites.

6.3.2 Data completeness

Data completeness should be evaluated in terms of the flagged or invalid data for automatic monitoring and the filter pack method. Data completeness describes the fraction of valid data coverage length in a certain monitoring period. Data completeness also should be described in the report form. The definition of data completeness is expressed as follows;

$$\begin{aligned} & \text{(Data completeness for automatic monitor)} \\ & = (\text{Number of valid hourly data}) / (\text{Number of total measured hourly data}) \quad (3.1) \end{aligned}$$

$$\begin{aligned} & \text{(Data completeness for filter pack method)} \\ & = (\text{Number of valid measurement days}) / (\text{Number of total measurement days}) \quad (3.2) \end{aligned}$$

In order to evaluate monthly and annual dry deposition fluxes, data completeness should be no less than 70%. Otherwise, those data will be flagged in the report.

6.3.3 Analytical precision

The precision of laboratory chemical analyses of blank samples for the filter pack method should be tested and be reported by the method described on “the Technical Document for Filter Pack Method in East Asia”.

6.3.4 Data flags and invalid data

To indicate quality information to data users, data flags and/or data comments are useful; they will indicate whether a data is valid or invalid. The function of the flags and comments is to ensure that the user has full knowledge of the data validity, and of conditions which produce that level of validity. Thereby, the user can select the data most appropriate to his/her application.

(Code number of data flags)

999	Missing measurement
781	Below detection limit
701	Less accurate than usual
699	Mechanical problem
599	Contamination of the samples or the sampling system

6.4 Submission of finalized data

Data reporting forms may be used for the reporting site condition (on site, local scale, regional scale), monitoring condition, sample history, chemical analysis condition and measurement results (air concentrations, meteorological parameters and other necessary results, flags and data completeness). Staffs in the Network Center in charge of dry deposition data will have responsibility for ensuring that all data elements are properly entered into the appropriate databases. Data should be submitted to the Network Center once every year.

The Network Center will provide the formatted data reporting form as a Microsoft Excel file. All data should be input in the distributed data form. The followings should be described on every data form: name of country and site (code of country and site), name of NAM, name of laboratory (code of laboratory) and name of PCL.

6.4.1 Information about sites, sampling, shipping, laboratory operation

(1) Site condition

Any change in the circumstances of the site should be reported every year, even if the site selection criteria remain satisfied. Name and code of each site should be given first. The category of a site should be determined by consideration of the siting criteria. No site is included in more than one class.

The area around the site should be especially described in terms of potential sources of contamination of samples on three different scales. Maps of the site and potential contamination sources should be provided to the Network Center.

- **On-site scale**

Description of the on-site scale is given for the area within a radius of 100m from the site. Locations of automatic monitors, a filter pack instrument, and meteorological instruments should be given. Trees, overhead wires, buildings, and other physical obstacles should be also described. Ground cover and slope, and farmlands etc., are also important factors. Pictures of the monitoring instruments and their surroundings should be attached. Seasonal specific condition such as snowfall, dust storm and seasonal

variation of site conditions should be reported. This information will be used for land use information described in Chapter 2.3.

- Local scale

Surface storage of agricultural products, fuels, vehicles, parking lots, or maintenance yards and feed lots, dairy barns or a large concentration of animals within a radius of 100m-10km should be described. Urban areas will be also described with population.

- Regional scale

Both stationary and mobile emission sources within 50 km should be described with emitted chemical species and emission intensities. Urban areas with population greater than 10,000 should be described. Near meteorological stations should be described on the map with available information.

(2) Sampling condition

- Automatic monitors

The following should be reported: model and manufacturer of the monitors, kind of calibration gas, calibration methods, calibration frequency, shapes of a manifold or a sample inlet, tubing, air condition status in the monitoring station. Start and end times of sample collection in the sampling plan should be reported. Pictures of collector and design diagrams should be attached.

- Filter pack instrument

The following should be reported: model and manufacturer of a filterpack, suction pump, and a flow meter, calibration method of flow rate, arrangement of instrument components, tubing, air condition status in the monitoring station. Start and end times of sample collection in the sampling plan should be reported. Pictures of collector and design diagrams should be attached.

- Meteorological instruments

The following should be reported: model and manufacturer of the instruments, maintenance records, arrangement of the instruments in the site, and monitoring frequency (duration interval). Pictures of collector and design diagrams should be attached.

(3) Sample history

Sample history plays an important role in sample handling from collection to

chemical analysis of the filter pack samples.

- Shipping

Shipping frequency and packing procedure for collected samples should be also reported.

- Laboratory operation

The following should be reported: sample preparation procedure, plan of chemical analysis frequency, range of laboratory room temperature.

6.4.2 Analytical condition for filter pack samples

The chemical analysis of the filter pack samples and control chart should be reported as the laboratory QA/QC data for each sampling station. The following items are included in the form: Method applied, instrument name and type, detection limit, calibration curve (5 points), ion concentrations in the deionized water (when a dilution process is included), data obtained from analysis of standard solution (commercial SRM) of known ion concentrations, data from duplicate or triplicate analysis of samples, data of blank filters.

6.4.3 Measurement results and flags

Air concentrations obtained by automatic monitors and analytical results obtained by the filter pack methods must be accurately input in the proper place in the formatted data report form. Items to be input are listed as follows:

- 1) Gas concentration unit with the unit of ppb (SO₂, NO, NO₂, NO_x* and O₃)
- 2) Analytical results of the filter pack method with the unit of mg L⁻¹ (F0: SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, Na⁺, K⁺, Mg²⁺ and Ca²⁺; F1: SO₄²⁻, NO₃⁻, Cl⁻ and NH₄⁺; F2: SO₄²⁻ and Cl⁻; F3: NH₄⁺). Duration time of the filter pack monitoring.
- 3) Meteorological Parameters (Wind Speed with the unit of m/s, Wind direction, Temperature with the unit of °C, Relative humidity with the unit of %, Sunshine duration with the unit of hours, Solar radiation with the unit of MJ/m²) Duration time of meteorological measurement.
- 4) Class of vegetation.

If data are flagged or failed results, corresponding cells must be kept the blank. The reporting form should also include sampling conditions, date of chemical analysis, and

other remarks. An example of the data report form is shown in Table X. Each national center should keep all the raw measurement data for future reference.

6.5 Data storage

Primary monitoring data such as chart recorder data, digital data with high time resolution, analytical data of manual monitoring should be kept in the responsible organization at least for 3 years. These data should be provided for data validation and further air concentration analysis upon request.

Stational data of monthly and annual mean concentrations will be prepared by the NC and reported in EANET data report after validation and finalization. The NC will produce a data base of air concentrations in EANET sites. Hourly data for automatic monitors and highest time resolution data for manual monitoring will be provided depending on EANET data disclosure policy.

7. Quality Control and Quality Assurance [All EG members and Network Center]

7.1 Fundamental matters [Network Center]

Quality Control and Quality Assurance (QA/QC) should cover all QA/QC matters, including the activities of NC, the National Centers and the sampling/chemical analysis organizations. The National Centers and the sampling/chemical analysis organizations need to execute various QA/QC activities, including development of national QA/QC programs and SOPs, according to the above mentioned roles (2). In these processes, the following fundamental matters should be taken into account.

(National Center)

- ① Preparation of national monitoring plan
- ② Preparation and implementation of national QA/QC programs
 - Appointment of a national QA/QC manager
 - Guidance for the preparation of SOPs at relevant organizations/laboratories
- (• Distribution of round robin samples, collection of the results and reporting to NC)
 - Audits to sites and laboratories
- Comparison of sampling and analysis methods used in the country
- ③ Collection of monitoring data and reporting of the data to NC
- ④ Development and implementation of national training programs

(Sampling/chemical analysis organizations)

- ① Appointment of personnel in charge and their supervisors
- ② Preparation of SOPs in respective activities in th organization
- ③ Execution of routine sampling/chemical analysis)
- ④ Periodic reporting to the National Center
- ⑤ Participation in QA/QC activities conducted by the National Center such as analysis of round robin samples

7.2 Data Quality Objectives (DQOs) [Network Center]

The required data quality objectives (DQOs) can be different, depending on the objectives of different programs. The DQO values define the desirable levels of accuracy, precision and completeness required by the program. DQOs may also differ if the concentrastion levels are significantly different. Considering the present status of the air quality monitoring in East Asia, the following DQOs are considered adequate for

the participating countries.

Table 7.2.1 Data quality objective values for required accuracy, precision, and completeness (unit: %)

Accuracy	Precision	Completeness
	Fundamentally within $\pm 15\%$ of the measured value	

b) Detection limits and determination limits for air concentration data

Detection limits for individual species depend on specification of instrument or procedures of sampling and analysis. NC set up expedient detection limits as shown in Table 7.2.2 taking into account methods adopted by each country. Data under the detection limit were treated as “N.D.” in the tables. Regarding the particulate matter components measured by filter pack method, the detection limits for particulate matter components were determined as $0.01 \mu\text{g}/\text{m}^3$ for sampled air volume of 20.16 m^3 considering the value of 3σ , where σ is the standard deviation of blank values obtained at Japan sites since 2003.

Table 7.2.2 Data quality objective values for required detection limits

Species	Detection limits
SO ₂	0.1 ppb
HNO ₃	0.1 ppb
HCl	0.1 ppb
NH ₃	0.1 ppb
NO, NO ₂ , NO _x	0.1 ppb
O ₃	1 ppb
PM	$1 \mu\text{g}/\text{m}^3$
Particulate matter components	$0.01 \mu\text{g}/\text{m}^3$

7.3 Monitoring site (Site audit) [Network Center]

7.3.1 Site selection

Selection of sampling sites is a critical factor in the monitoring, and the siting criteria are described in the Monitoring Guideelines for Acid Deposition Monitoring in East Asia and the relevant technical manuals. The same sites used for wet deposition monitoring are recommended for air concentration monitoring. When air concentration monitoring is difficult at a wet deposition monitoring site, a new sampling site should be selected by sufficient consideration for uniformity of ground surface, in addition to the criteria for wet deposition monitoring.

Intake points of automatic instruments should be 5 to 10 meters from the ground if no obstructions are located around the sites. They should be around 3 meters higher than the height of the buildings if buildings or other obstructions are located around the sites, or the intake points are on the buildings.

It should also be noted that the environmental conditions such as temperature and humidity in which instruments are located should be carefully assessed. Air conditioning should be provided in a cabin where automatic instruments are located. However, if the temperature in the cabin is significantly lower than outside temperature, it will lead to condensation of water in sample inlet lines, and measurement errors. Such measurement errors may happen, particularly in the case of SO₂ because it is easy to dissolve in water.

7.3.2 Documentation of conditions around sampling sites

All monitoring sites should essentially satisfy the siting criteria. If there are some differences from the criteria, they should be documented and evaluated. Any significant changes around sampling sites should be promptly reported to NC through the National Center.

7.3.3 Site performance audit

A site performance audit should be made at least once a year by the National Center. This audit provides field training and exchange of information. A site performance audit should also include items such as operation checks of instruments, data management, data reporting and so on. The National Center should prepare the SOP for site audits. The results of each audit should be documented and stored at the National Center.

7.4 Field and laboratory operations [Network Center]

Precision and accuracy are an integral part of laboratory quality control. Ensuring that precision and accuracy meet the DQOs is an important step in the validation of chemical analyses of wet deposition samples and ensuring the quality control standards are sufficiently maintained.

(1) Analytical precision

To estimate the analytical variability, duplicate analysis of a sample should be determined a minimum of 1 in every 20 samples. Large volume samples should be divided into two aliquots, one half for immediate routine analysis and the other should be immediately refrigerated and stored at 4°C and analyzed in less than 7 days as part of another analytical run. Analytical precision is defined as the standard deviation between the two analyses:

$$S_i = (\sum d_i^2 / 2N_i)^{1/2}$$

where d_i denotes the difference between the two measurements, and N_i is the number of the sample pairs for the duplicate analysis in the reporting period. The factor, 2, is included in the denominator to account for the random error associated with both measurements.

(2) Accuracy of chemical analysis

The accuracy of analytical measurements is evaluated by analyzing simulated filter samples referred to as inter-laboratory comparison samples. Within EANET the inter-laboratory comparison samples are prepared using reagent grade chemicals supplied to all analytical laboratories by the Network Center on an annual basis. Analytical performance is evaluated using the data from the chemical determination of the inter-laboratory comparison samples. Statistical analysis and control charting of the results is helpful in identifying deficiencies and finding solutions to analytical issues and will result in an improvement of data quality.

(3) Definition of “not detected” and “lowest determination limit”

The measurement is not always addressed by a definite number. For example some analytes may be “not detected” or at the “lowest determination limit”. In order to define these parameters, a standard solution is prepared at concentration levels near the lower determination limit. Analyze the above standard solution five times to determine the standard deviation (s.d.) over the five runs. The “not detected” and “lowest determination limit” are defined as three and ten times of the standard deviation, respectively.

Not detected = 3 (s.d.)

Lowest determination limit = 10 (s.d.)

The numerical figures for these measures may differ considerably depending upon experimental conditions including the types of instruments, the instrumental history, and operator experience. For this reason, the standard deviation should be determined whenever the analytical conditions are changed.

7.5 Data management [Network Center]

There are various data check procedures. Typical data check procedures include routine data check, confirmation of measured data, and data screening. When the sensitivity of instruments is not stable, or when data significantly differ from the range of other measured data, reliability is considered low, and the data may need to be treated as abnormal.

7.5.1 Routine data check

Routine data check is the most fundamental process to identify abnormal data by comparing the transmitted on-line data with the pre-determined standard values when data tables are prepared. Rather simple criteria, such as upper and lower limit could be used for routine data check activities. Check of QA/QC activities, maintenance of the instruments should also be included in this procedure.

7.5.2 Confirmation of measured data

Confirmation of measured data is the procedure for finding missing and abnormal data, and validating the measured data by comparing them with various kinds of information, such as operation and maintenance reports. Generally speaking, confirmation of measured data is carried out when monthly reports are prepared. It starts from comparison of transmitted on-line data with the recorded data at the measurement site. While it is desirable to check all the measured data, it is extremely troublesome, and therefore, in some cases, sample data, such as those in every 5 or 10 days, are checked.

7.5.3 Data screening

Data screening is the process to identify abnormal data, based on the certain criteria. Such criteria may be established, taking into account the hourly, daily, monthly averages of the previous several years, and their statistic characteristics. The methods generally used for screening include:

- Methods using the previous data of the concerned instrument, such as upper and lower limits of measured data, upper or lower limit of difference with the previous data;
- Methods using change of measured data, taking account of differences of daily or other periodic variations;
- Methods using rate of change in measured data with data of the same time on other days; or
- Methods using other parameters of the same monitoring stations and/or same parameters of the neighbouring stations

Such data screening can be conducted manually, if the volume of the data is not significant. However, a part of data screening activities is, in many cases, computerized.

Abnormal values may be caused by measurement, collection/transmission of data, and data processing. Once abnormal values are identified, the cause should be carefully analyzed.

7.5.4 Treatment of abnormal data

To ensure certain level of reliability, abnormal data should be identified, and identified abnormal data should be adequately treated. These activities are called as treatment of abnormal data. Abnormal data can be identified through routine data check, confirmation of data, and/or data screening. Such data can still be used, if it is confirmed that the measurement is appropriately conducted. If it is confirmed that appropriate measurement is not conducted due to some reasons such as inadequate maintenance activities, then the data should not be used.

There are many factors to possibly cause abnormal data. They include:

- Measurement system: problems of intake tube;
 problems of the instrument;
 problems of the recorder;
 problems of CPU;
- data collection system problems of telemeter outputs;

Upper limit: within $\pm 10\%$ of the pre-determined value

Zero value of the instrument

Lower limit: within $\pm 2\%$ of the maximum scale value

Upper limit: within $\pm 4\%$ of the maximum scale value

PM10

Span of the instrument

Lower limit: within $\pm 4\%$ of the pre-determined value

Upper limit: within $\pm 10\%$ of the pre-determined value

(Note) Lower limit means the minimum value that needs adjustment.

Upper limit means the maximum value that can be adjusted.

7.6 Determination of accuracy and detection limit [Prof. Kim for DOAS, Prof. Hu for Point measurement, Dr. Takami for PM, Dr. Aikawa for Manual Monitoring]

(DOAS)

(1) Determination of accuracy

The errors of the DOAS measurements can be split into systematic (instrumental) and statistical errors. The systematic error describes all errors caused by the recording of the spectra, whereas the statistical error results from statistical processes, like photon noise, and the process of evaluation. An overview of systematic errors is given below. Beside absolute systematic errors (concentration offsets) the error is defined by the signal to noise ratio in the retrieved spectra. The total noise consists of photon (“shot”) noise σ_p , the optical noise σ_o (Stutz and Platt, 1997) and the instrumental noise σ_i . For good instruments the photon noise σ_p is the limiting factor in the signal to noise ratio. In comparison to the other noise, it is for sure pure statistical, and can be reduced by accumulating more photons. At a certain number of photons the photon noise will be so small that the other noise sources will dominate and the total noise will not further decrease with increasing number of registered photons (or rather photo-electrons). This is the real limit for the best achievable measurement quality of a DOAS measurement. It is important that this number of photons (or number of photoelectrons / scans) is determined for each instrument. Here a short overview of the different noise sources and their mathematical description is given. It is followed by an estimation of the absolute DOAS error of a measurement and details on averaging of data points to increase the signal to noise ratio.

① Systematic errors

The most important systematic errors are:

- Uncertainties and errors of the literature cross sections. Depending on the trace gas of interest, the error of the literature cross section is between 1 % and 15 %.
- Stray light in the spectrometer gives a negative offset to the determined concentration. The applied Acton spectrometer (300i and 500i) display only very low stray light (~0.1 %) and thus this error is very small (< 1 %). Additional filters may be applied to further reduce the light of the unused spectral range. Reflections can also produce stray light like reflection at the detector window. All these stray light errors are estimated to be smaller than 3 % (Stutz, 1996).
- For the used configuration additional stray light arise due to the simultaneous measurement of absorption spectra from different light paths with one spectrometer detector unit. It could be found that for some extreme configurations with different intensities this can contribute up to 10 % and thus to an error of the same order. For equal light intensities of the different received light paths, this additional stray light is in the order of 1 %.
- The convolution process and differences in the wavelength-pixel mapping can cause errors up to 1-3 %.
- Errors made by the determination of the length of the absorption light path. With the typical applied laser range finders this error is in the order of 0.1 %.
- Errors by the conversion of the concentration to mixing ratios due to errors in the pressure and temperature. If the simultaneous measured pressure and temperature are used, for typical accuracies their influence is less than 1 %.

② Photon Noise (σ_p)

The photon noise (σ_p) is in principle the theoretically achievable accuracy for measurements of electromagnetic radiation. The detected photons (i.e. the photoelectrons) are Poisson distributed. That means there is a randomness of the arrival of each photon and each detection event is independent of each other and independent of the already detected events. The measurement accuracy generally increases with an increased number of detected photons, but is limited by the photon noise (σ_p), which is equal to the square root of the total amount of measured photons (n_p):

$$\sigma_p = \sqrt{n_p} \quad (\text{Eq. 7.6.1})$$

Thus, if many measurements are done with a certain exposure time t_0 there will be a

mean number of photons measured by a single detector element: $n_p(t_0)$. The standard deviation of all single measurements is:

$$\sigma_p(t_0) = \sqrt{n_p(t_0)} \quad (\text{Eq. 7.6.2})$$

The signal to noise ratio therefore is:

$$\left(\frac{S}{N}\right)_{\text{ration}}(t_0) = \frac{n_p(t_0)}{\sigma_p(t_0)} = \frac{n_p(t_0)}{\sqrt{n_p(t_0)}} = \sqrt{n_p(t_0)} \quad (\text{Eq. 7.6.3})$$

Now instead of using a single channel of the detectors chip and performing a large number of measurements, one can also do only two measurements and use a whole bunch of neighboring channels (for which the intensity does not change very much) as statistically independent measurements.

To receive the signal to noise ratio of the two spectra I_1 and I_2 they have to be divided channel-wise. This gives a ratio spectrum with values distributed around unity, where all systematic differences between different channels are eliminated and only statistical variation remaining. The observed standard deviation of I_1/I_2 is:

$$\begin{aligned} \sigma_{p, \frac{I_1}{I_2}}(t_0) &= \sqrt{\left(\frac{\sqrt{n_p(t_0)}}{n_p(t_0)}\right)^2 + \left(\frac{\sqrt{n_p(t_0)}}{n_p(t_0)}\right)^2} \\ \sigma_{p, \frac{I_1}{I_2}}(t_0) &= \sqrt{2 \cdot \left(\frac{\sqrt{n_p(t_0)}}{n_p(t_0)}\right)^2} \\ \sigma_{p, \frac{I_1}{I_2}}(t_0) &= \sqrt{\frac{2}{n_p(t_0)}} = \frac{\sqrt{2}}{\sqrt{n_p(t_0)}} = \sqrt{2} \cdot \sigma_p(t_0) \end{aligned} \quad (\text{Eq. 7.6.4})$$

Thus as a consequence of the channel-wise division of the two spectra, the standard deviation increases by an additional factor of root 2 compared to the original relative standard deviation (the original ‘‘signal to noise ratio’’). Plotting the observed $\sigma_{p, \frac{I_1}{I_2}}(t_0)$ (using the Root Mean Square (RMS) values of the divided spectrum) on a double logarithmic scale, we receive:

$$\log\left(\sigma_{p, \frac{I_1}{I_2}}(t_0)\right) = \log\left(\frac{\sqrt{2}}{\sqrt{n_p(t_0)}}\right) = \frac{1}{2} \cdot \log 2 - \frac{1}{2} \cdot \log n_p \quad (\text{Eq. 7.6.5})$$

Thus the received straight line will have a slope of -1/2. To calculate the correct signal to noise ration from the divided spectrum we have to multiply by the factor of root 2. Thus one obtains:

$$\left(\frac{S}{N}\right)_{\text{ration}}(t_0) = \frac{n(t_0)}{\sigma_p(t_0)} = \frac{\sqrt{2}}{\sigma_{p, \frac{I_1}{I_2}}(t_0)} \quad (\text{Eq. 7.6.6})$$

By increasing scans, and thus observed photons, the photon noise can in principle be reduced unlimited. But in reality from the total noise mainly the photo noise is reduced, and thus at a certain scan number the total noise will not further decrease, as it is then dominated by the instrument noise. It is important to determine at which noise level and after how many scans this level is reached. To perform more scans during a measurement is useless and will only reduce the temporal resolution but not increase the signal quality.

Since for DOAS measurements and data evaluation the noise is displayed in the residuum spectrum, for simplicity, in the noise test we take into account only the standard deviation and not the signal to noise ratio. This makes it easier to compare the achieved values in the noise test with those of measurements. As we are in DOAS observations only interested in narrow-band absorption structures, all broad-band variations will be ignored.

③ Optical Noise (σ_0)

Optical noise can arise from all optical components. First of all, the light source can be unstable in the spectral characteristic or intensity. For example a spectral change of the used xenon arc lamp or even a halogen lamp is not necessarily spectrally stable. For the noise test a stable halogen lamp with a stable power supply should be used to exclude any fluctuations arising from this source.

Other optical noise sources are the fiber, which will change its transmittance with different bending. Also other components like mirrors and lenses can be responsible for optical noise if they change the spectrum with time. The spectrograph with the grating can produce optical noise; especially if the fiber will not homogeneously illuminate the grating and the detector of the spectrometer. In this case changes in the light distribution can lead to spectral structures. To prevent such inhomogeneous distribution a mode mixer is applied. For example a different illumination of the fiber arose in the presented LP-DOAS measurements between shortcut and atmospheric measurement configuration. The shortcut is much closer to the instrument and due to an optimization of the optical adjustment for far retro reflectors, the reflected light of the shortcut is not homogeneously focused into the fiber. The mode mixer should reduce these effects.

As the noise test is performed with a stable light source and optical set up, it will not determine the optical noise of the measurement. The optical noise can only be determined by comparing the residuum of a measurement to the noise determined in a noise test.

④ Instrument Noise (σ_i)

Instrument noise summarizes all noise sources arising associated with the instrument detection and data unit. The main part is electronic noise. In several instruments it is influenced by electromagnetic fields. Thus detector, spectrometer and electronic have to be set on the same ground level. Another noise source is the non-linear sensitivity of the detector with increasing saturation.

(2) Detection limit

The detection limit defines the value above which the concentration of a species is considered to be significantly above the background noise. Thus, the detection is always directly linked to the noise level and no general detection limit exists. It depends on the quality of each measurement if the absorber can be identified. But still a detection limit for a specific noise level can be given. There are two methods to estimate the detection limit of DOAS measurements.

① Detection Limit from Measurement Error

In order to obtain the detection limit for DOAS measurement, statistical considerations are used. Assuming the measurement being subject to Gaussian error statistics, the retrieved measurement error can be used to calculate the detection limit. As the measurement error calculated from the statistical fit error gives the $1 \cdot \sigma$ range of a measurement, the true measurement value is in this range with a probability of 68 %.

If the DOAS measurement also contains beside statistical errors systematic errors which do not follow Gaussian error statistics, this 1σ range can be used if the error is corrected with the factor C. The $2 \cdot \sigma$ confidence interval with a probability to find the measurement true value within 95 %, is obtained by multiplying the error by 2. If the $2 \cdot \sigma$ interval is entirely located above null and thus the determined concentration is larger than the $2 \cdot \sigma$ value than the measurement has a probability of more than 95 % of being above null. Usually, this is considered as significant detection of a certain species. The $3 \cdot \sigma$ confidence interval would give a detection probability of 99.7 %.

② Detection Limit from Fit Residual

If the optical density of the residuum is small compared to the trace gas absorption derived in the fitting procedure, the respective trace gas may certainly be detected. Thus, another method to estimate detection limits of a DOAS instrument is the evaluation of the fit residuum. The assumption is made because a DOAS instrument cannot measure any trace gases whose absorptions structures are smaller than the current fit residual $\Delta\Psi$:

$$(S'_{\max} - S'_{\min}) \cdot \bar{c} \cdot L \geq \Delta\Psi \quad (\text{Eq. 7.6.7})$$

Differences arise in the rating of the absorption structure compared to the residuum. A worst case approximation is using the peak to peak value ($\Psi_{\max}(j) - \Psi_{\min}(j)$) as $\Delta\Psi$. A more realistic approximation uses twice the average deviation from the mean value in the wavelength interval of the considered trace gas absorption band. Since the depth of trace gas absorption structures is a direct function of its differential absorption cross section S' , its average concentration c and the observed path length L are the only parameters theoretically limiting the detection limit, beside from the photon noise. The minimum detectable average concentration is therefore:

$$\bar{c}_{\min} = \frac{\Delta\Psi}{(S'_{\max} - S'_{\min}) \cdot L} \quad (\text{Eq. 7.6.8})$$

(Point measurement)

7.6.1 SO₂ PRECISION CHECK PROCEDURE

A precision check should be performed at least bi-weekly. The result of 0.09 ± 0.01 ppm level in a dynamic calibration can be used as a precision check result.

Moreover steps 6) to 8) below should be followed.

Manual Method on Site

- 1) The test gas for precision check can be generated by bottled gas and dilution by calibrator.

If practicable, the test gas should be fed into the analyzer through the sample intake, manifold and particulate filter of the analyzer.

- 2) The analyzer should remain at normal operation mode.
- 3) Activate the precision sequence from the data logger. Check that the calibrator (TECO 146) delivers a SO₂ test gas concentration, preferably between 0.08 and 0.1 ppm. Allow 20 minutes to stabilize.
- 4) Record the true concentration and analyzer response values into the precision report form and get a data print out for record. Calculate the adjusted analyzer response and record it into the data log sheet.
- 5) Confirm the analyzer and datalogger are back to normal operating conditions. Ensure the first 10 to 15 minutes reading immediately after precision check is invalidated.
- 6) Complete the precision check data sheet and record the percentage difference to PC1.
- 7) Check whether precision check result exceeds $\pm 20\%$.

- 8) Plot the result on a control chart.

Automatic Method

9) Normally, the precision check is being done automatically once every two weeks. Therefore, staff should check the daily calibration summary and complete the above task 4) to 8) at office.

7.6.2 NO_x PRECISION CHECK PROCEDURES

Manual Method

The precision check should be performed at least bi-weekly. The result at the precision check concentration of a dynamic calibration can be used as a precision result to replace a routine precision check, if desired.

- 1) The ozonator and MFCs of a TECO 146 should have been certified and the settings suitable for a precision check selected. The gas produced by such a setting would produce precision check gas of about 110 ppb NO + 90 ppb NO₂. The operator just has to set the TECO 146 according to the certification table provided on the front panel of the TECO 146.
- 2) Disconnect the analyzer from the manifold and then connect to the output port of the TECO 146. (The analyzer must be operated in its normal operation mode, and the precision test gas must pass through all filters, scrubbers, and as much as practicable all other components used during normal ambient sampling.)
- 3) With the MFC settings at precision check and the ozonator off, switch on the gas supply and then supply the test gas into the analyzer, record the stable responses of NO and NO_x into the Worksheet. (Denoted by [NO]_{Resp.} and [NO_x]_{Resp.}, respectively)
- 4) Turn on the ozonator at the setting for precision check. Record the stable responses of NO and NO_x into the Worksheet.

Calculation

- 5) 4.5 Assuming that there is no, or negligible, NO₂ impurity in the bottle gas, the concentration of actual NO₂ concentration can be calculated as follow:

$$[NO_2]_{Act} = Adj. [NO]_{O_3(OFF)} - Adj. [NO]_{O_3(ON)} \quad (3)$$

Where,

Adj.[NO]_{O₃(OFF)} is the adjusted NO response without ozone applied, Eq. (5)

Adj.[NO]_{O₃(ON)} is the adjusted NO response with ozone applied, Eq. (5)

- 6) The adjusted response of the NO₂ channel, Adj.[NO₂] can be calculated by equation (4):

$$Adj. [NO_2] = Adj. [NO_x] - Adj. [NO] \quad (4)$$

$$\text{Adj. [NO]} = ([\text{NO}]_{\text{RESP}} - Z_{\text{NO}}) \cdot \text{SF}(\text{NO}) \quad (5)$$

$$\text{Adj. [NO}_x] = ([\text{NO}_x]_{\text{RESP}} - Z_{\text{NO}_x}) \cdot \text{SF}(\text{NO}_x) \quad (6)$$

Where,

Z_{NO_x} , Z_{NO} = NO_x and NO zero readings, respectively, and

$\text{SF} = \text{SGC} / (\text{span} - \text{zero})$

Zero and span readings can be obtained from the previous night's automatic zero/span check or from a manual zero/span check immediately before the precision check.

- 7) Enter the $[\text{NO}_2]_{\text{Act.}}$ and adjusted NO_2 response $\text{Adj.}[\text{NO}_2]$ of analyzer into the precision check data sheet for NO_2 and then calculate the percentage difference. Check whether the difference exceeds $\pm 20\%$.
- 8) Check the analyzer and calibrator is in normal operating condition.
- 9) Complete the precision check and converter efficiency data sheets.
- 10) Plot the result on the precision check control chart.

Automatic Method

- 11) When the precision check is done by using automatic method, steps 1) to 4) will be performed automatically. Then follow 4.5 to attain the % difference of NO_2 and complete other related tasks until 10).

7.6.3 O₃ PRECISION CHECK

A precision check should be performed at least bi-weekly. The result of 90 ± 10 ppb level in a dynamic calibration can be used as a precision check result.

Automatic Method

- 1) Normally, the precision check is being done automatically once every two weeks. Therefore, staff should check the calibration summary and complete the precision check data sheet and record the percentage difference to PC1.
- 2) Check whether precision check result exceeds $\pm 20\%$.
- 3) Plot the result on a control chart.

Manual Method

Precision Check by TECO 146

(This procedure is normally used in field stations)

(1) Disconnect the sample line of the ozone analyzer from the manifold and then connect to the output of the TECO 146. Plug the ozone outlet of the manifold. Operate the TECO 146 to feed an ozone testing gas at precision level (about 90 ppb) into the ozone analyzer.

(2) Record the certified concentration of the precision check and the stable analyzer

response into the precision check data sheet for ozone. Calculate the adjusted response and then the precision for reporting.

- (3) Restore the connections and settings for normal operation.
- (4) Complete the precision check data sheet and record the percentage difference to PC1.
- (5) Check whether precision check result exceeds $\pm 20\%$.
- (6) Plot the result on a control chart.

By Ozone Calibrator

(1) If a certified ozone calibrator is available in the station, a precision check can easily be done by the ozone calibrator.

(2) Connect a zero air supply to the ozone calibrator. Warm up the calibrator for about 30 minutes.

(3) Disconnect the analyzer from the station manifold. Cap the manifold outlet for ozone, and then connect the ozone calibrator to the analyzer. A vent should be provided at the analyzer input and sufficient vent air should be maintained during the precision check.

(4) If an independent sample inlet is used for ozone, the test gas should be fed in via the sample air intake point.

(5) Adjust the ozone calibrator to generate an ozone gas concentration of 90 ± 10 ppb.

When the analyzer response is stable, record the reading on the precision check report form. Calculate the actual ozone concentration from the calibration line of the calibrator and then record on the form.

(6) Calculate the adjusted analyzer response, and then report the precision by the adjusted response and the actual ozone concentration.

(7) Disconnect the ozone calibrator from the analyzer and then restore normal connection of analyzer. Resume normal analyzer operation.

(8) Complete the precision check data sheet and record the percentage difference to PC1.

(9) Check whether precision check result exceeds $\pm 20\%$.

(10) Plot the result on a control chart.

By Internal Ozonator - TECO 49PS

(1) Connect the zero air supply to the "ZERO AIR" bulkhead.

(2) Operate the ozonator in local mode and at level B (precision level). Allow sufficient time for the ozonator and analyzer to stabilize. (Stabilization can be judged by the variation of analyzer response).

(3) Record the stable response and the certified level B concentration on the precision report form. Calculate the adjusted response and enter into the report form PC1.

(4) Disconnect the zero air supply, resume the normal setting and connection of the analyzer, and report the time period of the precision check to DP for data invalidation.

(5) Complete the precision check data sheet and record the percentage difference to PC1.

(6) Check whether precision check result exceeds $\pm 20\%$.

(7) Plot the result on a control chart. Complete the precision check data sheet

(PM)

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(Manual Monitoring)

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Leave one line between each section.

7.7 QA/QC implemented by NC [Network Center]

NC should appoint a network QA/QC manager, who is responsible for managing overall network QA/QC programs and will provide appropriate guidance and advice to the participating countries based on this QA/QC program. NC should prepare reports on the QA/QC activities implemented by the participating countries, and QA/QC levels with other relevant networks. NC should provide technical support, as appropriate, to each National Center in order to attain such objectives as follows:

- (1) Preparation and implementation of the QA/QC programs
 - Appointment of a network QA/QC manager
 - Development of data quality objectives
 - Provision of information for preparing SOPs
 - (• Implementation of round robin analysis survey)
 - Assurance that adequate reference materials are used
 - Exchange of information with and technical support for National Centers
 - Comparative analysis of sampling and analysis methods in the participating countries and development of technical documents
- (2) Preparation of the data report and the report on QA/QC implementation
- (3) Development and implementation of training programs for participating countries
- (4) Comparative analysis of QA/QC activities with other networks such as EMEP and WMO

7.8 Training programs [Network Center]

It is necessary to improve knowledge and expertise related to air concentration monitoring. Therefore, NC and the others should undertake training for personnel responsible for the implementation of the monitoring activities in each National Center and technical training for leading to technicians in national or local governments in East Asian countries as follows:

(Training by the Network Center)

Based on the results of the First Meeting of the Interim Scientific Advisory Group held in October 1998, INC had carried out the First EANET Training Workshop for senior officials responsible for implementation of the monitoring activities in each National Center, to disseminate the details of the QA/QC programs and the data reporting procedures and formats etc. The JICA Trainig Course on Monitoring and Control Technologies of Acid Deposition has been carried out annually, which includes subjects on air concentration monitoring. NC should continue the training on dry deposition monitoring for experts in the participating countries.

(Training by the National Center in each participating country)

The National Center in each participating country should prepare a national training program, and implement, as appropriate, training on methodologies of air concentration monitoring. The National Center should also provide guidance for the preparation of SOPs to national organizations that carry out air concentration monitoring.

**8. Future issues [Dr. Son and Network Center]
(New monitoring methods of NO₂ (PLD, CRDS, LIF), online aerosol composition monitoring, Intercomparison of different monitoring methods)**

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