

Quality Assurance/Quality Control (QA/QC) Program

for

the Air Concentration Monitoring in East Asia

November 2001

“Quality Assurance/Quality Control (QA/QC) Program for the Air Concentration Monitoring in East Asia” was endorsed at the First Session of the Scientific Advisory Committee held in November 2001 in Chiang Mai, Thailand.

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The draft quality assurance/quality control (QA/QC) program was developed by the Task Force on Dry Deposition Monitoring (hereinafter referred to as the “Task Force”), based on the guidance of the Interim Scientific Advisory Group (ISAG) of the Acid Deposition Monitoring Network in East Asia (EANET) at its First Meeting in October 1998. It was distributed among ISAG members as well as the national focal points and the heads of the national centers in September 1999 for their comments. Based on the comments and discussions with the new Task Force on Dry deposition Monitoring that had been established at the Third ISAG Meeting and the Fourth Working Group Meeting in March 2000 and experts in the participating countries, this final draft was prepared. The program was finally endorsed with some modifications by the Science Advisory Committee (SAC) at its First Session held on 14-16 November 2001 in Chiang Mai, Thailand.

The present program focuses on the QA/QC activities for automatic instruments for the first priority chemicals and particulate mass concentration. Since more discussions are needed at the Task Force concerning QA/QC activities for other air concentration monitoring, such as filter packs, denuders, and passive samplers for the second priority chemicals, the QA/QC activities for these methods will be integrated in this program in the future, taking account of the progress of the discussions at the Task Force. Since no manual has been developed specifically for air concentration monitoring by automatic instruments in East Asia, this program is prepared in reference to the methods described in the Continuous Air Concentration Monitoring Manual (4th Edition) in Japan, the Japan Industrial Standards (JIS) and the US/EPA methodologies.

The participating countries are expected to make efforts for implementing QA/QC activities in accordance with this QA/QC program, taking into account the situation in respective countries. Based on the experiences of the participating countries, and taking into account the progress of discussions at the Task Force, this QA/QC program will be reviewed and revised where necessary.

1. Objective

1.1 Objective of QA/QC programs

Considering the significance of possible future problems regarding acid deposition, it becomes increasingly important to obtain accurate and precise data on acid deposition. With this recognition, many countries of the world have already initiated their acid deposition monitoring programs. However, informed decisions cannot be made on the basis of unreliable data, and therefore certain levels of data quality should be assured. A monitoring system without adequate QA/QC runs the risk of not being able to control the quality of data, and not being able to assure accuracy and precision. QA/QC has thus become essential part of all measurement systems in general, and acid deposition

monitoring in particular, because it requires especially high international comparability of data.

For uses of acid deposition data in recent years, such as assessment of spatial distributions and temporal trends, research on acid deposition related processes and impacts on aquatic and terrestrial ecosystems, and the development and evaluation of long-range transport and transmission models, it is especially important that measured data satisfy specified levels of reliability with necessary information on measurement methods.

The objective of this QA/QC program is to obtain reliable data that can be comparable among the countries of the East Asian region, as well as with other networks.

1.2 Definitions

Quality control is defined as "the routine use of procedures designed to achieve and maintain a specified level of quality for a measurement system". Quality Assurance is defined as "a set of coordinated actions such as plans, specifications, and policies used to assure that a measurement program can be quantifiable and produce data of known quality".

According to the United States Environmental Protection Agency, the difference between quality control and quality assurance is the following: quality control is a "system of activities to provide a quality product" and quality assurance is a "system of activities to provide assurance that the quality control system is performing adequately. In other words, quality assurance is quality control for quality control".

To assure specific data quality, QC activities should be implemented for all the steps of the measurement activities, from sample collection to data reporting. The QA/QC programs should include QA/QC activities for all the components of the measurement/analysis systems, i.e. the field (sampling sites), laboratory, data management and data reporting processes. All QA/QC activities should be documented.

2. Roles of relevant entities

The roles of relevant entities of QA/QC activities are shown in Figure 1.

3. Fundamental matters regarding the QA/QC programs

The QA/QC programs should cover all QA/QC activities, 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.

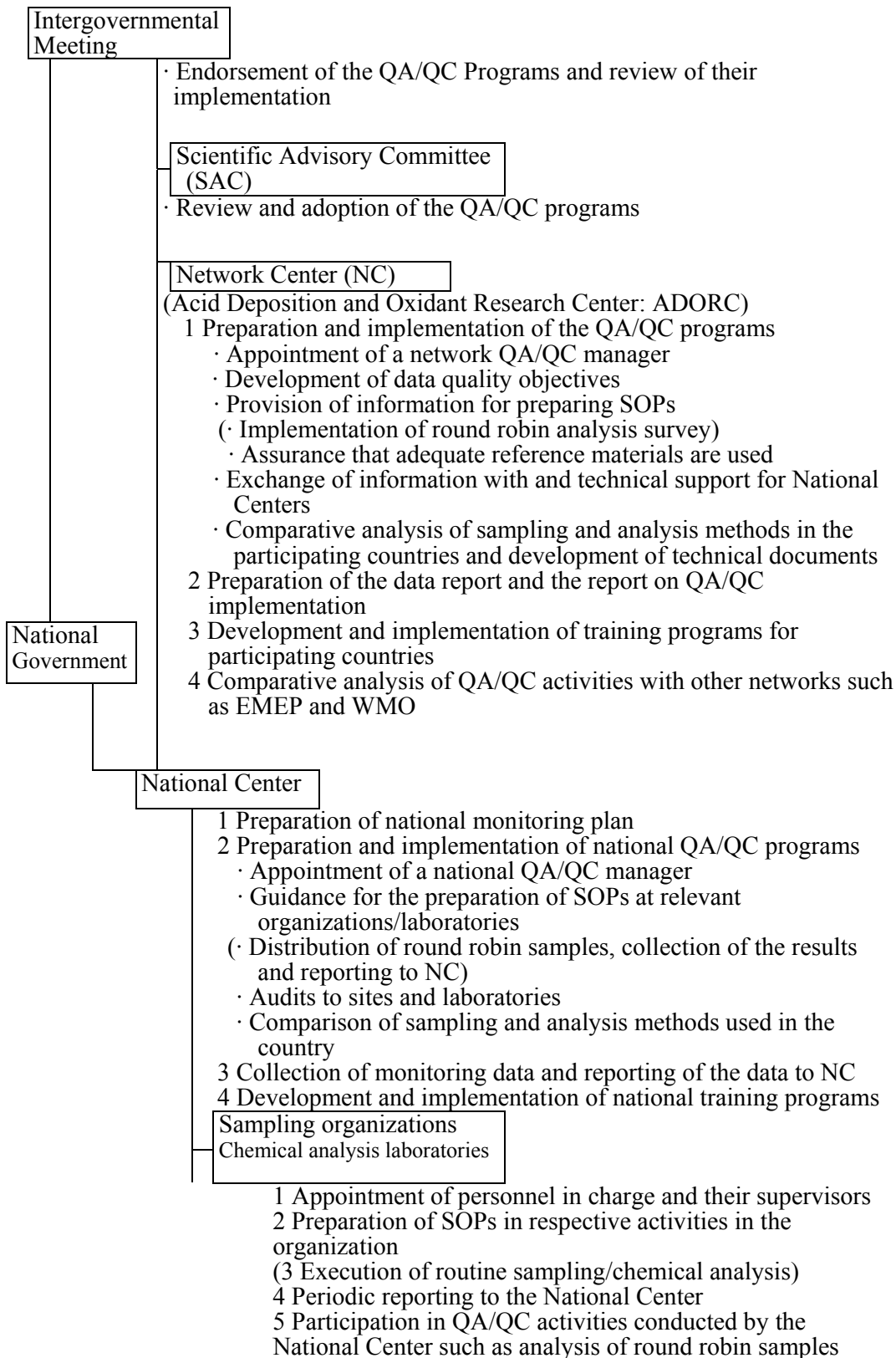


Figure 1 Roles of Relevant Entities

3.1 Development of national QA/QC programs

Each participating country should develop its own QA/QC programs, taking into consideration national conditions.

3.2 Clear assignment of responsibility

In the National Center, a national QA/QC manager should be appointed. In the sampling and/or chemical analysis organizations, personnel in charge of data management and reporting and their supervisors should be appointed; their names should be reported to the National Center.

3.3 Standard operating procedures (SOPs)

SOPs are the procedures used in all the processes of the monitoring system, i.e. in the field, laboratory, and data management areas. SOPs provide a method to ensure that all personnel follow the same procedures to avoid variance of data quality between personnel in charge, and that they conduct their works with good understanding of QA/QC. Each sampling and chemical analysis organization (laboratory) should make effort to prepare SOPs that meet the actual conditions of respective organizations. In preparing SOPs, it is important that they are sufficiently specific and easy to understand, and that they should be reviewed and updated on the basis of latest information and circumstances.

3.4 Required levels of specifications for automatic instruments

Considering the present specifications of automatic instruments for SO₂, NO/NO₂, and O₃, the following requirements for specifications of automatic instruments are proposed in Table 1.

Table 1 Required levels of specifications in air concentration monitoring for automatic instruments

Repeatability*¹	within ±2% of full scale (FS)
Drift*²	within ±2% of FS
Linearity*³	within ±4% of FS
Influence by deviation of electric voltage	within ±1% of FS
Lower detection limit	minimum pollutant concentration which produces a signal of twice the noise level (determined as the standard deviation about the mean output, to express spontaneous, short duration deviations in output which are not caused by input concentration changes.)

*1: Deviation of each indicated value from the mean value based on alternate measurement between zero and span gas more than 3 times

- *2: Zero drift -Maximum deviation of indicated value from set value based on zero gas measurement during 24 hours; Span drift -Maximum deviation of indicated value from set value based on span gas measurement more than 3 times during 24-hour zero drift measurement
- *3: Linearity: Deviation of indicated value from the concentration of standard gas set up middle between zero and span gases

3.5 Data quality objectives (DQOs)

The required data quality objectives (DQOs) can be different, depending on the objectives of different programs. DQOs may also differ if the concentration 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 2 Data quality objective values in air concentration monitoring for automatic instruments

Precision	Fundamentally within $\pm 15\%$ of the measured value
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4 Sampling sites

4.1 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.

4.2 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.

4.3 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.

5 Measurement and analysis

5.1 Measurement parameters

The first priority parameters for air concentration monitoring are NO₂ (urban), SO₂, O₃, and NO, and particle mass concentration. For particle mass concentration, it is recommended to start with a 10 μm cut-off.

(Note) Measurement methods for NO₂ concentrations, particularly for remote and rural areas, to avoid influence of NH₃ and HNO₃, need further elaboration

5.2 Measurement instruments and monitoring interval

For routine monitoring of the air concentration, automatic instruments are commercially or conventionally available for SO₂ (such as ultraviolet fluorescent (UVF) method), NO (such as chemiluminescence detection (CLD) method), O₃ (such as ultraviolet photometric method and CLD method) and PM₁₀ (such as β-ray absorption method and TEOM method) to obtain one-hour averaged values. Since these one-hour averaged values can be used for the purpose of the evaluation of air concentration after averaging for one-week, one-hour average values should be used for data reporting. It is desirable that the air concentration monitoring by automatic instruments is carried out throughout a year. If it is difficult, adequate measurement duration should be determined, taking account of the situation in respective countries.

5.3 Registration of persons in charge of measurement and their supervisors

In each monitoring site, personnel in charge of the operation, maintenance and data reporting of respective automatic instruments and their supervisors should be appointed. Their names should be reported to the National Center.

5.4 Automatic instruments for gas concentration monitoring

5.4.1 Measurement theories and compositions

Measurement theories and compositions of the automatic instruments for SO₂, NO/NO₂, and O₃ are presented in Appendix 1 through 4 respectively.

5.4.2 Calibration

Certified standard gases of the concerned chemical species should be used for calibration to check the performance of the instruments. Normally, the calibration curves are considered linear in the case of automatic instruments. Calibration is therefore done at around zero point and the span (the concentration around 80-90 % of the full scale), and a few (desirably three) points between the two. In general, the calibration should be carried out by the following steps:

- Preparation of adequate standard gases (zero gas, span gas) for calibration;
- Calibration of zero point value;
- Calibration of the span value;
- Check of the calibrated values with previous values;
- Check of traceability;
- Check of linearity;
- Check of converter efficiency (for NO/NO₂)

Calibration for SO₂ should be carried out with the dynamic calibration method by using standard SO₂ gases (air-based).

Calibration for NO/NO₂ should be carried out with the dynamic calibration method by using standard NO gases (air-based). Traceability and converter efficiency should be checked in an adequate manner. Standard NO₂ gases are usually used to check converter efficiency.

Calibration for O₃ should be carried out by dynamic calibration method. On site, calibration may be carried out by using calibrated ozone generator and ozone analyzer calibrated by certified methods such as manual analysis of 1 % NBKI solution.

Flow meter should be periodically checked and calibrated as appropriate.

5.4.3 Routine and periodic check and maintenance

It is important for the routine monitoring to operate the instruments for a long time in a stable manner for maintaining high-level of performance and data quality. To this end, check and maintenance are classified into three: routine check and maintenance, periodic check and maintenance, and check and maintenance after a trouble occurred (emergency check).

Routine check and maintenance should be carried out at least once in 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 individuals.

Periodic check and maintenance have more detailed procedures than routine ones, such as the calibration for assuring the data quality and replacement of exhausted parts. The frequency and interval of periodic check and maintenance are different from instrument to instrument (generally between 3 months to one year, depending on the items to be checked and/or maintained). Appropriate frequency and interval should be determined for respective instruments.

5.4.4 Trouble shooting

Emergency checks should be carried out when the concerned instruments are out of order, or when abnormal data are measured. Detailed knowledge is needed for this type of checks.

5.5 Automatic instruments for particle mass concentration (PM10) monitoring

Measurement theories and compositions of the automatic instruments for PM10 are presented in Appendix 4.

Calibration should be carried out by simultaneous measurement with the standard measurement method. The standard measurement method should be the reference method for the determination of particle matter as PM10 in the atmosphere (USEPA: Federal Register/Vol.62, No 138 38753). Each filter should be weighted before and after use to determine the net weight gain due to collected PM10, after moisture equilibration. For daily calibration, however, static calibration such as equivalent input method for β -ray absorption method can also be used, because dynamic calibration is difficult to apply for frequent operation. It is also recommended to carry out simultaneous measurement with the standard measurement method at the monitoring site to check the calibration.

Check and maintenance of the instruments are similar to those mentioned in 5.4.3 and 5.4.4 above.

5.6 Meteorological Measurement

Wind direction/speed, temperature, humidity, precipitation amount and solar radiation should be measured on site. Meteorological measurement should be carried out in accordance with the measurement frequencies and methods of the meteorological monitoring system in each country. If it is impossible, then such meteorological conditions can be measured at the nearest meteorological observatory.

6 Data check and data quality control

6.1 Introduction

There are three purposes concerning quality assurance of data quality control.

- 1) assure that all data will be stored in databases in an adequate manner.
- 2) identify and treat adequately the data whose quality is doubted.
- 3) recognize and describe data that were measured with abnormal conditions, such as instrument trouble.

QA/QC should be carried out in measurement organizations, National Centers, and INC/NC, respectively.

Errors of measured data

Errors of measured data by automatic instruments are caused by bias from the true values and variability. Some errors depend on the concentrations of measured substances, and others are not. Individual errors may be small, but may become significant in total. Data quality control, therefore, should be carefully carried out, and the overall errors should be estimated.

Lower detection limit

Any instrument has the limit below which it cannot detect concentrations (lower detection limit). This value is usually defined by using the ratio of signals (S) and noise (N). In both U.S. Federal Regulation and in Japanese "Continuous Atmospheric Concentration Monitoring Manual", lower detection limit is defined as twice the standard deviation of noise. Automatic instruments show expected performance just after the procurement, but in the long run, initial performance cannot be guaranteed. To minimize the lowering of performance, adequate maintenance is inevitable. It is necessary to regularly check the lower detection limit, carry out appropriate maintenance and evaluate that the objective is achieved in order to obtain reliable data.

6.2 Completeness of data

Hourly and daily data should be considered effective when more than 75 % of data are obtained.

6.3 Data check procedures

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.

6.3.1 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.

6.3.2 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.

6.3.3 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.

6.4 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;
 problems of reset signals;
 on-line errors
- data treatment system abnormal initial data
 problems of data treatment equipment;
- others influence of temporary local emissions etc.

Certain criteria should be established to decide whether the data can be used as they are or after adjustment, or cannot be used.

The criteria for non-usable data is established to judge whether some abnormal hourly data are within the allowable range of data reliability, or could be adjusted in principle. This criteria should be established, taking into account the present state-of-arts technologies, and the objectives of the measurements. For instance, the criteria for non-usable data in Japan are presented below:

Criteria for non-usable data in Japan

SO₂

Span of the instrument

Lower limit: within $\pm 4\%$ of the pre-determined value

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

NO_x

Span of the instrument

Lower limit: within $\pm 4\%$ of the pre-determined value

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

O₃

Span of the instrument

Lower limit: within $\pm 4\%$ of the pre-determined value

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 Data reporting

Each organization responsible for air concentration monitoring should record, control and store the following information.

7.1 Measured data

All the measured data should be reported to NC through the National Center, following the protocols in Annex 1 and the Data Reporting Procedures and Formats, adopted at the Third ISAG Meeting in March 2000. Flag should be put on the non-usable data and/or data that are adjusted.

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).

7.2 Information on sites

Effort should be made to obtain the following information.

- (1) Sampling sites (location, site classification, measurement items, etc.)
- (2) A situation around the site at the on-site scale (buildings, trees, parking lots, roads, circumstance and land use around the sampling site, etc.)
- (3) A situation around the site on local scale (major roads, traffic, aviation, navigation, farming, major stationary emission sources, surrounding cities, population, etc.)
- (4) A situation around the site on regional scale (large stationary emission sources, main roads, cities, population, etc.)

7.3 Matters related to measurement

- (1) Measurement instruments (pictures of instrument and design diagrams, model name, manufacturer, manufactured date, etc.)
- (2) Conditions of measurement (detailed information on measurement site, measurement dates and interval, temperature, wind direction, wind speed, etc.)

7.4 Matters related to data quality control

- (1) Calibration and measurement procedures for air concentration monitoring instruments, including the information on the standard substance used for calibration
- (2) Miscellaneous other values required for measurements
- (3) Performance of all procedures prescribed in SOPs, including noises and lower detection limits
- (4) Routine instrument check and maintenance, record of instrument adjustment (calibration of instruments)
- (5) Sensitive variability of analytical instruments
- (6) Results of site performance audit

8 QA/QC implemented by NC

8.1 Management of overall network QA/QC activities and preparation of reports on the network QA/QC activities

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.

8.2 Technical support for National Centers

NC should provide technical support, as appropriate, to each National Center in order to attain such objectives as follows:

- (1) NC should review QA/QC activities carried out by each National Center, that the measurements are carried out and reported adequately, and that all measurements activities are accurately documented and stored.
- (2) NC should, where appropriate, recommend changes that would improve the quality control of the measurements.
- (3) NC should provide useful information in order that the organizations responsible for the field sampling and analytical laboratories in each country can prepare SOPs.

8.3 Comparative analysis of measurement methods among the participating countries and with other networks

NC should compare the quality control level of the air concentration monitoring among the participating countries, and with other networks.

9 Training programs

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:

9.1 Training by NC

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.

9.2 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.

Data Treatment Protocols

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.

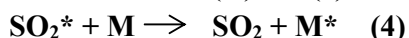
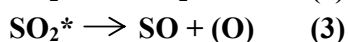
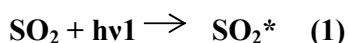
Ultraviolet fluorescent method for SO₂

1. Measurement theory

To measure SO₂, the ultraviolet fluorescent (UVF) method is most popular because it assures higher selectivity of SO₂, requires no auxiliary gas such as H₂, and provides output of higher linearity.

The UVF method consists of (A) measuring the fluorescence generated from SO₂ in the excited state resulting from the absorption of ultraviolet rays by sulfur dioxide (SO₂) in the sample gas, and (B) obtaining the concentration of SO₂ from the changes in the intensity of the fluorescence.

The reaction mechanism is shown in the following equations:



where (1) shows the excited state that occurs when SO₂ has absorbed energy $h\nu_1$ by ultraviolet rays; (2) shows that light energy $h\nu_2$ is emitted when the excited molecules shift to the ground state; (3) shows that the excited molecules are decomposed with the fluorescence emitted; and (4) shows that the excited molecules lose energy by impinging on other molecules, i.e., quenching. The spectral characteristics of the fluorescence of the excited SO₂ and the detector are shown in Fig. A-1-1.

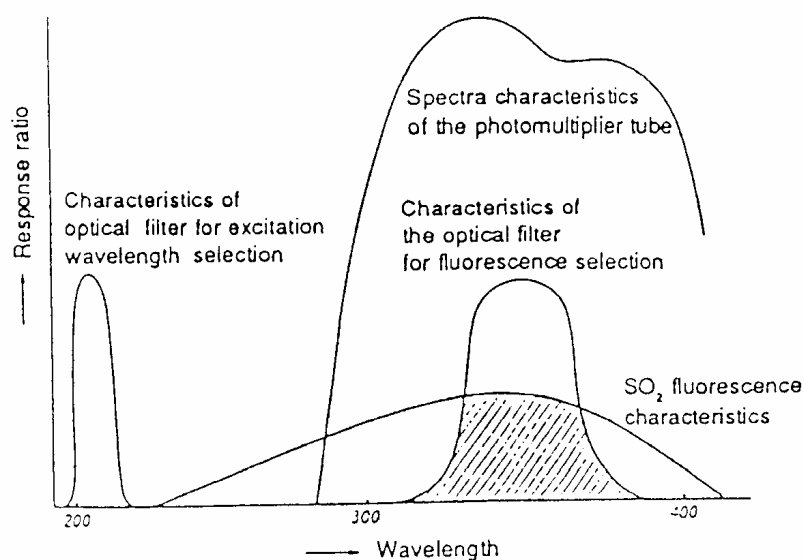


Fig. A-1-1 Spectral characteristics of fluorescence of excited SO₂ and detector

2. Composition of the instruments

A typical example of the basic configuration is shown in Fig. A-1-2.

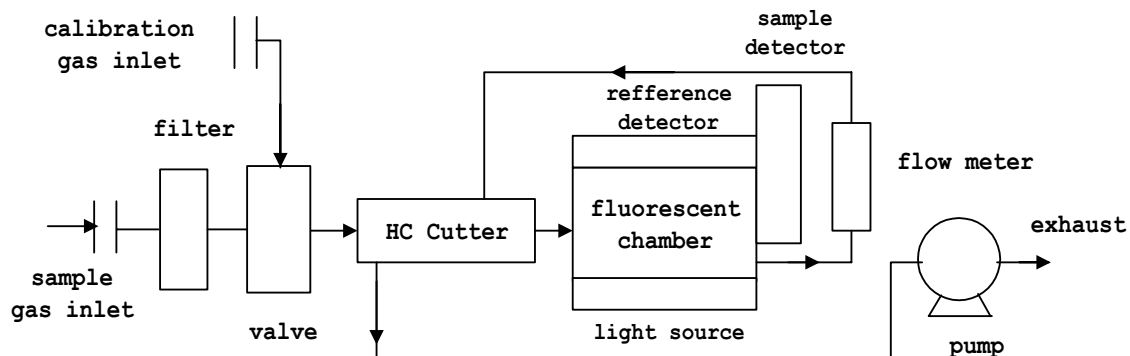


Fig. A-1-2 An example of UVF configuration

For the excitation light source, a xenon or zinc lamp is used. In order to stabilize the changes in dark current of the detector and process the signals, pulse switching and an optical chopper are used.

The lateral light measuring method is used to detect the fluorescent light. The fluorescent chamber is geometrically designed to minimize diffused light (strayed light) because diffused light affects the stability of the zero point and S/N. Added is a detector which is used to compensate for changes in light quantity of the light source. The interference elements of UVF include aromatic hydrocarbons (such as m-xylene), which are eliminated by using a dual-tube selective permeable membrane. If nitrogen is used as the base gas for calibration, a large error occurs. This phenomenon suddenly takes place when the oxygen concentration is 1.5% maximum. Its cause is presumed to be the changes in the intensity of the excited ultraviolet rays or the background difference due to the difference between the quenching of O₂ and N₂.

Chemiluminescence detection method for NO₂ (urban) and NO

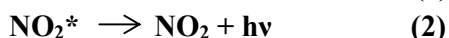
1. Measurement theory

The air pollutants to be measured as nitrogen oxide (NO_x) include nitrogen dioxide (NO₂) and nitrogen monoxide (NO).

To measure NO_x, the chemiluminescence detection (CLD) method is most popular.

The CLD method ensures high selectability by its own light emission reaction using vapor phases and by the selection of the wavelength of its emission light. For the measurement of NO_x, the reaction between NO and ozone (O₃) is used.

When nitrogen monoxide in an air sample reacts with ozone, nitrogen dioxide is generated in its excited state. When the generated nitrogen dioxide returns to the ground state, it emits light (chemiluminescence). The concentration of nitrogen monoxide can be determined by measuring the intensity of this chemiluminescence.



If the sample air is passed through a converter to convert nitrogen dioxide into nitrogen monoxide, the concentration of nitrogen oxides (nitrogen monoxide and nitrogen dioxide) can be obtained by measuring the intensity of the chemiluminescence. The concentration of nitrogen dioxide in the sample air can be obtained by calculating the difference between the two measured values.

The emission spectrum obtained from the reaction between nitrogen monoxide and ozone is found within the wavelength zone between 600 and 3,000 nm. Its maximum wavelength is around 1,200 nm. In order to eliminate the effects of other chemiluminescence, an optical filter is used in the photoelectric sensor. The photoelectric sensor also uses a photomultiplier tube (PMT), but because of the characteristics of its photoelectric surface, the wavelength range available for detection is narrower (from 600 to 900 nm). Recently, therefore, some monitoring systems have begun to use photoelectric elements which are more sensitive to wide wavelengths (e.g., silicon photodiode).

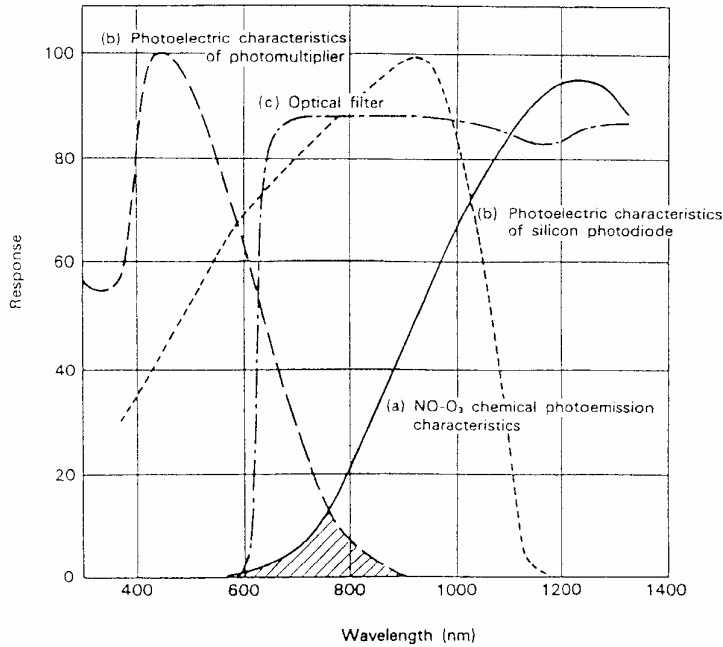


Fig. A-2-1 Spectral characteristics of chemiluminescence and detector

2. Composition of the instruments

A typical example of the basic configuration is shown in Fig. A-2-2.

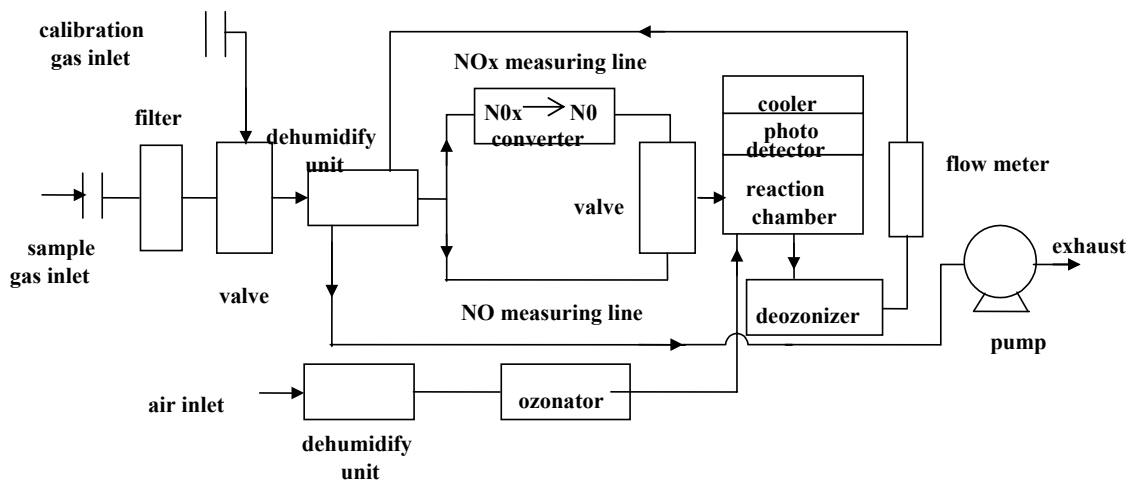


Fig. A-2-2 An example of CLD configuration

Because nitrogen monoxide and nitrogen oxides must be measured individually, different measuring methods are employed including the flow path switching method, the optical path switching method and the two-flow path/two-optical path method. Each of these methods has a problem with the stability of the passage selection valve or of the optical path switching chopper, and requires that the performance (such as

responsiveness and time-course changes) be matched between two detectors.

In principle, calibration is performed using nitrogen monoxide as the standard gas. Therefore, if the efficiency of converting nitrogen dioxide into nitrogen monoxide is below 100%, the measured concentration of nitrogen dioxide decreases by the same rate.

There are two types of converters available: a thermal reaction converter that decomposes nitrogen dioxide at 600-800°C and a chemical reaction converter that uses graphite carbon, molybdenum, tungsten, metal-impregnated carbon or some other similar carbon to reduce nitrogen dioxide at 100-400°C. When the temperature rises to 400°C or more, ammonia is oxidized. This generates nitrogen monoxide, which causes an interference effect. For this reason, the chemical reaction converters, which use a carbonaceous substance at 300°C or less, are used predominantly. The chemical reaction converter itself is oxidized in the process of deoxidizing the nitrogen dioxide, so it must be replaced, in principle, every 12 months. However, this replacement frequency increases when the converter is used in places where the concentration of nitrogen dioxide is high. The definite frequency should be determined by checking the conversion efficiency of the suitable converter. Care must be given to the fact that nitrogen oxides other than nitrogen compounds (e.g., PAN) are converted together with nitrogen dioxide into nitrogen monoxide and cause an interference effect.

Moisture quenches the chemiluminescence resulting from the reaction between nitrogen monoxide and ozone, causing negative interference. The degree of this interference varies depending on the pressure and flow rate in the reaction chamber. If there is a great difference between the water content of the calibration gas and that of the measured air, the measurement is particularly affected. For this reason, the monitoring system is equipped with a semipermeable membrane filter, humidity controller, or the like that is used to maintain a constant water content of the sample air. The decrease in the reading of nitrogen monoxide is specified as 4.0% maximum when the temperature is 25°C and the relative humidity is 80%.

Carbon dioxide, which causes quenching just as moisture does, may be ignored under normal conditions. However, note that carbon dioxide cannot be ignored if its concentration is high (more than several percent).

Ultraviolet photometric and Chemiluminescence method for O₃

1. Measurement theory

(1) Ultraviolet photometric Method

This method is to measure continuously the ozone concentration in the sample ambient air by measuring the variation of absorbing quantity of ultraviolet rays near 254nm by ozone.

The UV photometric method is not subject to interference from any of the common gaseous air pollutants.

The sample ambient is drawn into the absorption cell through a scrubber which removes all ozone and light intensity(I₀) is determined. The valve is then switched to allow ambient air to fill the cell. During this measurement cycle the light intensity(I) is determined.

The Beer-Lambert Law gives the relationship between these measurements and the ozone concentration as follows.

$$O_3(\text{ppm}) = \frac{10^6}{kL} \times \frac{760}{P} \times \frac{T}{273} \times \ln \frac{I_0}{I} \quad (1)$$

K : absorption coefficient = 134cm⁻¹ atm⁻¹

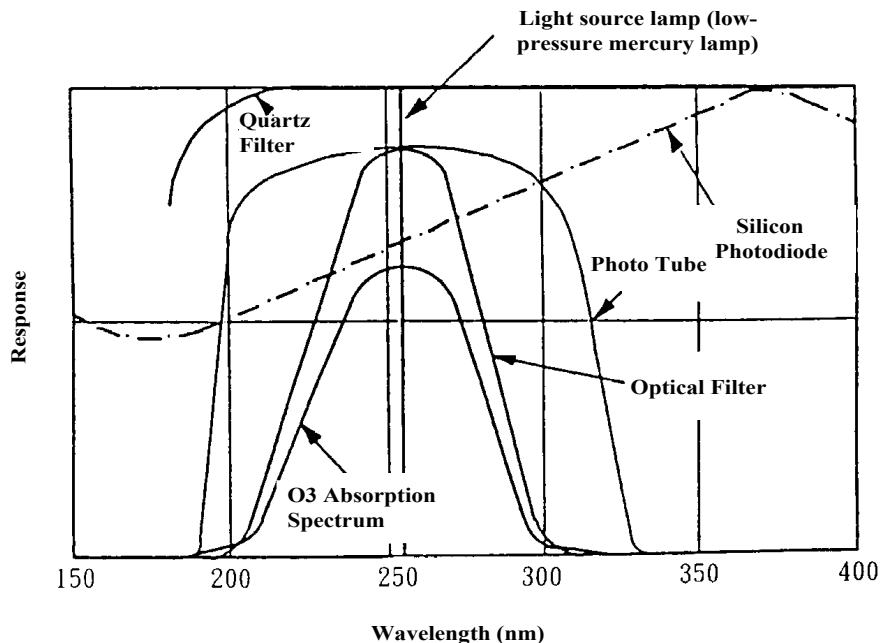
I : Transmitted light quantity

I₀ : Incident light quantity

L : Cell length (cm)

T : Cell outlet temperature

P : Cell outlet pressure (corrected to 760mm Hg)



(2) Chemiluminescence Method

This method is to measure continuously the ozone concentration contained in the sample ambient air by chemiluminescence method, by making reaction between ozone and ethylene. Ozone and ethylene react instantaneously to produce light in the visible region with a maximum at a wavelength of about 450nm. The reaction of ozone in the air sample and is measured by a photomultiplier tube.

2. Composition of the instruments

UV photometric ambient ozone analyzer shall be composed of filter, ozone scrubber, three-way-valve, UV absorption cell, UV source lamp, detector, flowmeter, sample ambient air suction pump and the like as shown in the example of Fig .A-3-1

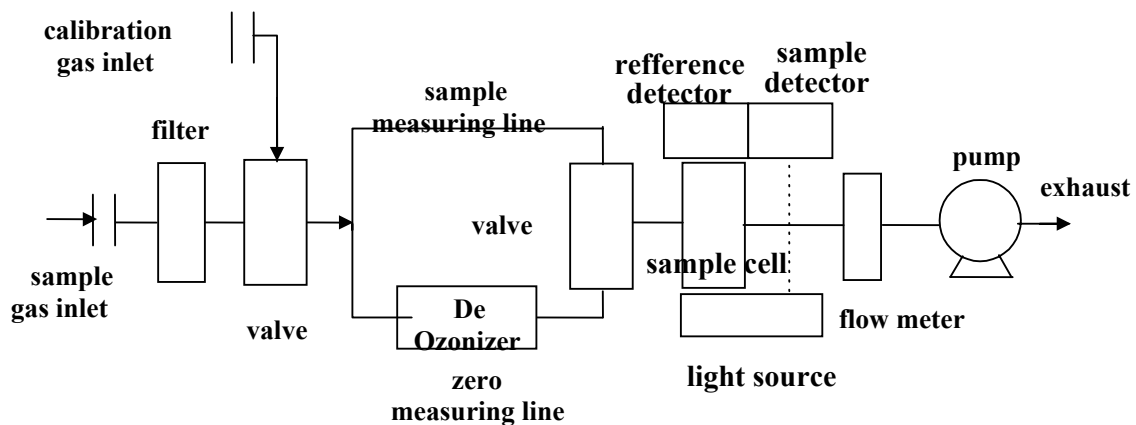


Fig. A-3-1 An example of UV photometric Method configuration

A typical example of CLD configuration is shown in Fig. A-3-2.

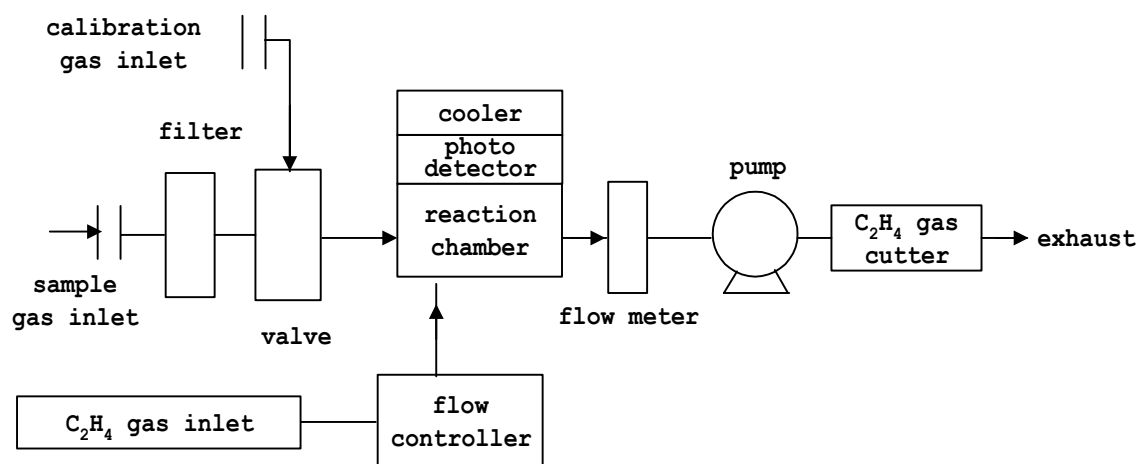


Fig. A-3-2 An example of CLD configuration

β-ray absorption and TEOM methods for PM10

1. Measurement theory

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 10 μm maximum in dust. For this classifier, the cyclone or impacter 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 increases in proportion to the mass of the substance when its quality remains constant and the ray at a low energy level irradiated the substance. Thus the 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

$$I=I_0 \exp(-um/xm)$$

I : β-ray intensity transmitted through filter and particulate

I₀: β-ray intensity transmitted only through filter

um: Mass absorption coefficient(cm²/g)

Xm: Mass of particulate matter(g/cm²)

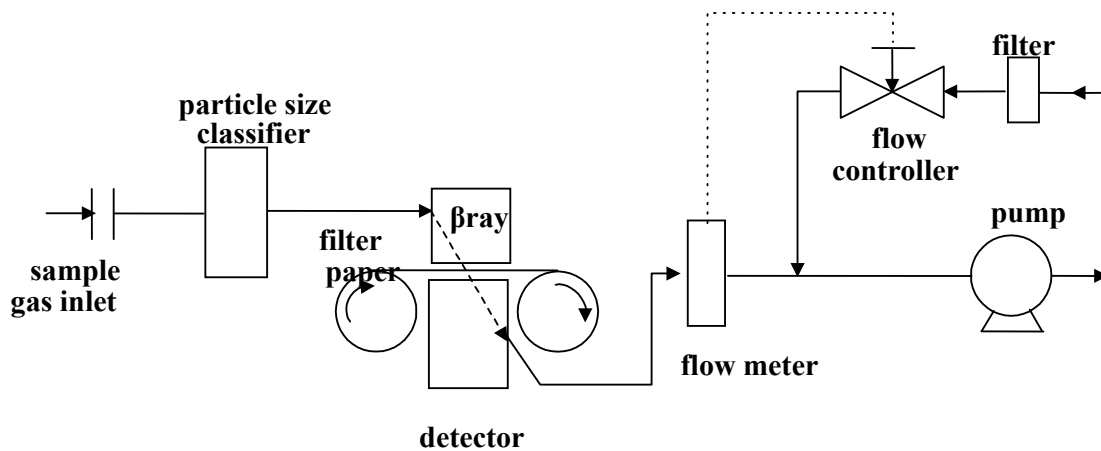
$$Xm=1/um \ln(I_0/I)$$

From this equation, the mass of PM10 is calculated as

Another method which can be used is TEOM (Tapered Element Oscillating Microbalance), a gravimetric instrument that draws ambient air through a filter at a constant flow rate, continuously weighing the filter and calculating mass concentration. The 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 a constant amplitude.

2. Composition of the instruments

(1) β -ray absorption method



(2) TEOM method

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 to a mass flow controller. The bypass flow is filtered in the large bypass 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.

