Technical Manual for Air Concentration Monitoring in East Asia

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List of contributors

This manual was prepared by the Expert Group on Preparation of Technical Manual for Air Concentration Monitoring under Scientific Advisory Committee of EANET.

Expert Group member:
(Chair) Dr. Duong Hong Son, Vietnam Institute of Meteorology, Hydrology, and Environment, Vietnam
Prof. Min Hu, Peking University, China
Dr. Masahide Aikawa, National Institute for Environmental Studies, Japan
Mr. Hajime Mikasa (Alternatively contributed by Dr. Hu Li), Japan Environmental Technology Associations, Japan
Dr. Akinori Takami, National Institute for Environmental Studies, Japan
Prof. Young Joon Kim, Gwangju Institute of Science and Technology, Republic of Korea
Dr. Kihong Park, Gwangju Institute of Science and Technology, Republic of Korea
Mr. Phunsak Theramongkol, Pollution Control Department, Thailand

Secretariat:
Dr. Keiichi Sato;
Ms. Naoko Take;
Dr. Mingqun Huo;
Dr. Tsuyoshi Ohizumi;
Network Center for EANET
Atmospheric Research Department, Asia Center for Air Pollution Research

Preface

Air concentration monitoring is one of the basic monitoring items in EANET, and the air concentration data are intended to use for dry deposition flux estimation and clarify the state of air pollution in region. EANET previously published several documents regarding for air concentration monitoring. One is QA/QC Program for the Air Concentration Monitoring in East Asia published in 2001, and the other one is Technical Document for Filter Pack Method in East Asia in 2003. Also Technical Manual for Dry Deposition Flux Estimation in East Asia (2010) described brief outline of air concentration monitoring. However, there is no comprehensive manual for air concentration monitoring in EANET countries, which enable to standardize air concentration monitoring and provide comparable data at EANET monitoring sites.

The Expert Group on Preparation of Technical Manual for Air Concentration Monitoring composed of relevant experts is established in November, 2009. The Expert Group reviewed current monitoring methodologies of air concentration monitoring both in EANET participating countries and international networks. Then, the Expert Group prepared the Technical Manual for Air Concentration Monitoring in EANET. Through three meetings of the Expert Group held in August 2011, August 2012 and September 2013, the finalized draft was submitted to the 13th Session of Scientific Advisory Committee of EANET in September, 2013, and the draft was endorsed. Then, the draft was adopted by the 15th Session of Intergovernmental Meeting of EANET in December, 2013.

We hope this Technical Manual will be useful documents for local operators, national QA/QC managers to operate the standardized air concentration monitoring in EANET. Also this manual can be used as the reference describing the monitoring specifications in EANET sites.

December 2013
Dr. Duong Hong Son,
Chair of the Expert Group on Preparation of Technical Manual for Air Concentration Monitoring

1. Introduction

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

Currently, no technical manual for 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 the Expert Group was approved by the Eleventh Session of the Intergovernmental Meeting (IG11) held in November, 2009. The Expert Group had considered current country specific monitoring methodology of air concentration monitoring and necessary calibration procedures for the automatic monitors and prepares a Technical Manual for Air Concentration Monitoring for EANET.

1.2. Objectives

Considering the background described in the Section 1.1, the Expert Group reviewed the previous Technical Document for Filter Pack Method in East Asia and the QA/QC

Program for the Air Concentration Monitoring in East Asia. Then, the Expert Group identified monitoring methods suitable for EANET air concentration monitoring.

The objective to prepare this manual is 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 and mandatory metrological parameters

The Strategy Paper for Future Direction of Dry Deposition Monitoring of EANET (Second Edition) (EANET, 2005) 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. This technical manual intended to describe monitoring methodologies for chemical species shown here.

First priority: SO_2, O_3, NO, NO_2 (urban), HNO_3, HCl, NH_3, Particulate component (SO_4^{2-}, NO_3^{-}, Cl^-, NH_4^+, Na^+, Mg^{2+}, K^+ and Ca^{2+}), PM_{10}
Second priority: NO_2 (rural and remote), $PM_{2.5}$

Also this manual includes monitoring methodology of the mandatory metrological parameters shown below. These parameters are used for evaluation of wet and dry deposition and also providing local meteorological information.

Metrological parameters: Wind Speed, Wind direction, Temperature, Relative Humidity, Solar radiation, Precipitation

1.4. Outline of the manual

This technical manual provides 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. First, feasible automatic monitoring of gaseous species and aerosol mass concentration was described. Since aerosol composition monitoring is feasible only by manual monitoring, its specifications were described. Furthermore, other necessary requirement was described in the latter part. Table 1.1 shows the relationship of monitoring items and described chapter.

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 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 4 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, which enables to avoid artifact of gas and particle interactions, is also described.

Chapter 5 describes a guideline for preparation of standard operating procedures, maintenance of air concentration monitors, recording 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 (Quality Control and Quality Assurance) of air concentration monitoring. This chapter covers overall procedures such as monitoring site, field and laboratory operations, data management, and determination of accuracy and precision. Furthermore, DQOs (Data Quality Objectives) of Fundamental parameters, QA/QC implemented by NC and training programs are 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.

Because air concentration monitoring is closely related to wet deposition monitoring, some common conditions such as location of monitoring site, data reporting procedure, QA/QC, etc., were cited from Technical Manual for Wet Deposition Monitoring in East Asia - 2010 (EANET, 2010). Also general monitoring requirement is followed by Guidelines for Acid Deposition Monitoring in East Asia (EANET, 2000).

The specifications of monitoring air concentrations and meteorological parameter described in this manual can be applied in the fundamental items for dry deposition flux estimation described in Technical Manual on Dry Deposition Flux Estimation in East Asia (EANET 2010).

Table 1.1 Relationship of monitoring items and described chapter

Species/Items	Described Chapter
SO_2	Chapter 3, Chapter4
HNO_3	Chapter 4
HCl	Chapter 4
NH_3	Chapter 4
NO, NO_2, NO_x	Chapter 3, Chapter4
O_3	Chapter 3, Chapter4
PM	Chapter 3
Particulate matter components	Chapter 4
Meteorological parameters	Chapter 3

References

Acid Deposition Monitoring Network in East Asia (2000) Guidelines for Acid Deposition Monitoring in East Asia, Network Center of EANET, 25p.

Acid Deposition Monitoring Network in East Asia (2005) Strategy Paper for Future Direction of Dry Deposition Monitoring of EANET Second Edition, Network Center of EANET, 13p.

Acid Deposition Monitoring Network in East Asia (2010) Technical Manual for Wet Deposition Monitoring in East Asia - 2010, Network Center of EANET, 111p.

Acid Deposition Monitoring Network in East Asia (2010) Technical Manual on Dry Deposition Flux Estimation in East Asia, Network Center of EANET, 61p.

2. Monitoring design

The purpose of this chapter is to describe the general concepts for establishing the ambient air quality monitoring network. The network may be consisted of fixed station over the EANET region. The station is expected to monitor the parameters of sulfur and nitrogen compounds associated with acid deposition problems, PM and O_3 associated with air quality issues, meteorological parameters associated with local meteorology and estimation of dry deposition flux.

The station is generally 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 also be located in urban or other area where assessment of ambient air quality is needed.

Each monitoring station nominated in the EANET should be described in term of physical dimension of representativeness (EANET, 2000). It is 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 categories; remote, rural, and urban.

Multiple factors are considered when deciding the location of air monitoring station. Sites are selected based on the 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 (more than 10 years) site availability. Unfortunately the ideal monitoring site is virtually impossible to acquire, especially in urban areas.

2.1. Siting criteria

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 air quality in background areas. The monitoring data can be used to evaluate long-range transport and transmission models of air pollutants 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. Remote sites should be at least 50 km from those large emission sources and 500 m from main road (more than 500 vehicles per day). 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 air quality in rural areas or hinterlands. The monitoring data can be used, for instance, to evaluate the effects of air pollution 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. Rural sites should be at least 20 km from those large emission sources and 500 m from main road (more than 500 vehicles per day).

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

(c) Urban sites

Urban sites are to be established for the assessment of the state of air quality 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 air pollution on health impacts, buildings, and historical monuments. Monitoring data at these sites may also be useful for the assessment of air pollution and its trends in urban areas.

2.2.Site facilities and Instrumentation (Electricity, Housing, Air conditioning, Inlet, Data communication, monitor arrangement etc.)

2.2.1. Design of monitoring station

The design of a monitoring station depends on the type of housing such as using a part of an existing building or construction of single house.

In addition, the station is expected to be designed considering with the harmonization to the surrounding scenery.

A PM mass concentration monitor should be installed outside of the station fundamentally due to the difficulty and the disadvantage to make a hole which penetrates the station roof for a passage of a sampling tube.

(1) Case of using a part of an existing building

When a part of an existing building is used as the station, it is necessary to ensure an area isolated with a partition and to display all equipment in the area. The sampling inlet should be placed at the position minimizing the contamination from the building and minimizing the distance from the inlet to the automatic monitor.

(2) Case of construction of single house

1) Fixed type

Generally, there are some possible structures of a fixed station made of wooden, prefab, concrete block, etc., with some advantages and disadvantages. A prefabricated structure is cost-effective and also excellent in terms of ease of installation and removal. On the other hand, a concrete block structure is superior in durability, fire protection, and room management aspects.

Recently, some prefab and lightweight aggregate panel structures which have high fire protection function comparable with the concrete block structure have developed. However, the station requires sufficient durability which can support the heavy automatic monitors with the weight of 100 kg or more.

2) Container type

Ordinarily, the container type station is made by aluminum or iron, and the available space is less than that of the fixed type. This type has some problems of fire prevention, but it is easy to install it in the park etc., where construction of the fixed building is restricted. Moreover, it is not difficult to move it when a problem on the representativeness of monitored values will be found. However, the container should be fixed firmly with a concrete foundation by using a anchor bolt in order to prevent damages, such as inclination by earthquake, typhoon etc. It is also desirable to cover the outside of the container with the thermal insulation to enhance the air-conditioning effect.

2.2.2. Facilities

Station is required to have the facilities as the following.

(1) Electric facilities

1) Electric capacity

The electric facility is indispensable to operate the equipment. To prevent the electrical overload, the electric capacity of the station should be ensured with enough margins.

2) Outlet for instruments

The power distribution to each instrument should be supplied by a three line grounding type outlet effectively controlled by a switchboard. A preliminary outlet utilized for inspection and a waterproofed type outlet for outdoor measurements connected to the short circuit breaker, etc., are also recommended to be equipped.

3) Outlet for an air conditioner

When the instruments are connected to the power supply system with large load variation such as that for an air conditioner, the instruments will receive a noise from the system. Therefore, the electric power for the air conditioner should be supplied from the other system than that for the instruments.

(2) Equipment against thunderbolt

The station in which the panzer mast for meteorological instruments is installed has the higher risk of thunderbolt. To prevent the damage of thunderbolt to the electric facility, comprehensive measures are necessary including the installation of a thunder-proof transformer, a surge arrester, a lightning rod, and grounding.

1) Thunder-proof transformer, surge arrester

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

2) Grounding

When the grounding electric outlet is not installed, installation of grounding with the resistance value less than 100 ohm is recommended for keeping safety and preventing thunderbolt influence to the instruments and the data collection device, etc.

(3) Room light

The lighting of brightness enough for the work of check and adjustment of the monitors, etc. is required, and it is desirable to secure more than 120 W per 10 m^2 by using fluorescent light.

In addition, it is desirable to prepare a flashlight for checking inside the monitor or preventing hand darkness.

(4) Ventilation fan

It is necessary to install a ventilation fan for gas leak measures. Especially, when the station is established in the inside of the building, installation of a gas detector, an automatic alarm sensor, and a power supply breaker is desirable because of safety measures. Moreover, placing a ventilator is also desirable. In this case, it is necessary to attach a filter to the ventilator to avoid the inflow of ambient particles and dusts.

(5) Air conditioner

The temperature inside the station may sometimes exceed the allowable range of automatic monitors working in the station due to heat sources such as a sample air exhaust pump and a heater for temperature adjustment, especially during high temperatures in summer. Therefore, installation of an air conditioner is required to operate the instruments correctly. Although the cooling capacity to be installed into the station depends on the size of the internal space, structures, etc., it may be necessary to be in the range of 1500 to 6000 Kcal/h.

(6) Inlet of cable for meteorological monitor and electric power supply

It is necessary to equip intakes for a cable that connects meteorological sensors and recorders, a cable of a power supply, and a cable for data extraction system.

(7) Safety facility for compressed gases

Storage and consumption of compressed gases should be carried out as follows.

i. Do not use the fire within 2 m from the storage of compressed gas cylinders, when the effective shielding measures such as concrete barriers are not taken.
ii. To inform the location of the storage, attach a sticker indicating compressed gases at the entrance of the storage.
iii. Fix the compressed gas cylinder (except less than 5 L) with a stand to prevent shock and damage to a gas regulator by overturning of the cylinder.
iv. Always keep the compressed gas cylinder at temperature less than 40 ^{o}C.
v. Installation of fire extinguisher is desirable. Carbon dioxide fire extinguisher is recommended.
vi. Although the compressed gas cylinder of nonflammable gases can be placed in a main room of the station, it is desirable to construct the cylinder storage looker at the outside of the station for facilitating the cylinder exchange and safety measures in the station. A locker is recommended to maintain ventilation with the open air for safety, and combustible gas must keep away from oxygen and the other reactive gases. Cylinders should be fixed by a belt in order to prevent the fall by earthquake etc.

2.2.3. Air conditioning

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

Therefore, it is desirable to install an air conditioner in the station in order to keep small difference with the temperature at the time of calibration, or to calibrate a monitor at the temperature which the station can adjust.

Furthermore, when the room temperature is set very low compared to the outside air in summer season to keep small the difference with calibration temperature, moisture condensation will occur in a sampling tube and it may cause measurement errors and apparatus trouble. To prevent those problems, heat of the sampling tube is effective. It is also desirable to set the room temperature taking into account the difference with the ambient air and to carry out the calibration in this temperature especially in summer time.

Generally, temperature is set up at 28 °C or more in summer to avoid the water condensation of a sample air and around 18 °C in winter in many cases.

Figure 2.1 shows the relationship between condensation, sample temperature, humidity and room temperature.

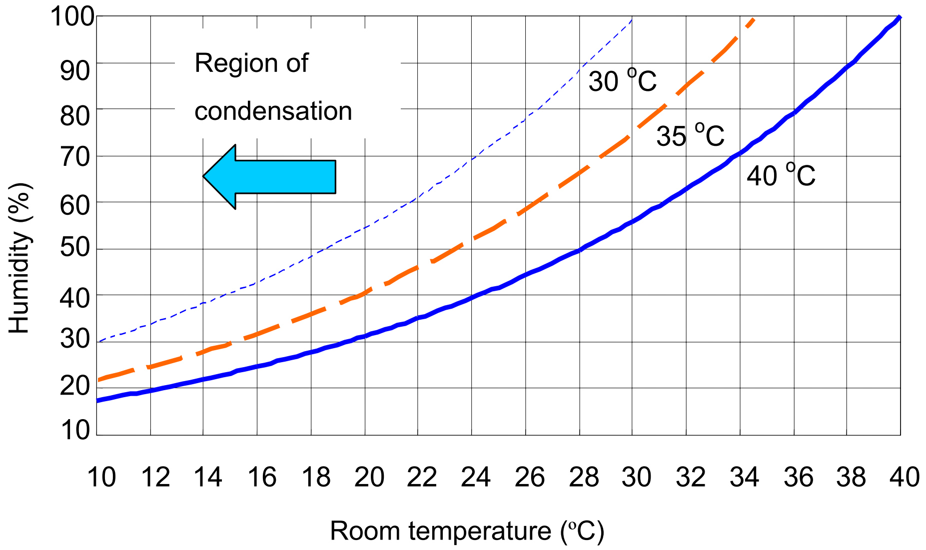

Figure 2.1 Relationship between condensations, sample temperature, humidity, and room temperature. Curved lines show the border of condensation at each sample (ambient air) temperature.

2.2.4. Height of sample inlet

Air concentration monitoring to provide air pollution data to the general public in a timely manner and to support compliance with ambient air quality standards is generally carried out at the height of usual living and breathing of person. The sampling height, however, is also decided in consideration with the regional representativeness, the vertical profile of air pollutants, the practical matters in the monitoring, etc.

US Environmental Protection Agency (USEPA) prescribes the height of sampling inlet of automatic monitor for SO_2, O_3, NO_2, and PM shall be in the range from 2.0 m to 15 m above ground (U.S. Environmental Protection Agency, 2013). EMEP recommends to monitor ambient ozone concentration at least at the height of 2.0 m above ground (Norwegian Institute for Air Research, 2001). On the other hands, Japanese ambient air continuous surveillance manual (Ministry of the Environment Japan, 2010) regulates the height of sampling for SO_2, NO_2, and O_3 is $1.5 \text{ m} \leq h \leq 10 \text{ m}$ above the ground, and the height for PM_{10} 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 monitor or the sampling inlet of PM is installed on the roof of the 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.

Taking into account the above information as well as to decrease the contamination from the ground and to increase the regional representativeness of the site, this manual recommends to monitor SO_2, NO_2 (NO), O_3 and PM at the height of 3.0 – 10 m above ground. Additionally, it is also recommended the sampling inlet should be located at the position higher than the roof of the station building. If it is impossible, the inlet should be located at the position keeping distance 2.0 – 3.0 m or more from the wall of the station building. In the same meaning, when the monitoring is implemented in a forest area, the sampling inlet should be set at the position higher than the top of canopy or keeping enough horizontal distance from the trees.

If it is impossible to install the sampling inlet based on the manner described above or it is not appropriate to follow the manner described above by unavoidable reasons such as difficulty of ensuring land for the station etc., it is required to install the sampling inlet as follows.

i. The height of sampling inlet shall not exceed 30 m above ground.
ii. Parallel measurement shall be done with the neighborhood site which follows the manner described above. It is necessary that the difference between them in daily mean basis is less than 1/10 of the ambient air quality standard in each country. Furthermore, this parallel measurement shall be performed

more than four times a year for grasping the seasonal variations.

2.2.5. Air sampling method

The sampled air flows as follows generally in the air concentration measurement system.

Sampling tube → Filter → Detector → Flow controller → Pump

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

(1) Note of sampling tube

The international standards such as ISO (International Organization for Standardization) or CEN (European Committee for Standardization), of the measurement of NO_2 and O_3 in the ambient air, are defined "Increase of NO_2 concentration due to residence time in the analyzer" or "Calculation of residence times for a maximum allowable NO_2 increase in the sampling line" as the items for checking the performances (The standard value is 2% or less and 4 ppb or less). Detailed explanations are as follows.

As O_3 is generally present in the sampled air, a change in concentrations of NO and NO_2 can occur due to the reaction of NO with O_3 in the sampling line. In order to avoid a significant change in the concentrations of NO and NO_2, the residence time in the sampling system from the sampling inlet to the monitor shall be less than 2 seconds.

The increase in NO_2 can be calculated by the formula given in Annex A of ISO 13964 (International Organization for Standardization, 1998). Calculation of residence times for a maximum allowable NO_2 increase in the sampling line.

The increase of the sampled nitrogen dioxide (NO_2) is due to the effect of the reaction of ambient ozone (O_3) with nitric oxide (NO) in the sampling line. By means of the following formulas, the influence of the residence time on the increase of NO_2 in the sampling line can be estimated:

$$[O_3]_0 = \frac{b \times [O_3]_t}{[O_3]_t - [NO]_t \times e^{(bkt)}} \qquad (2.1)$$

where

$[O_3]_0$ is the ozone concentration at the sampling inlet;

$[O_3]_t$ 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 $[O_3]_t$ and $[NO]_t$: $b = [O_3]_t - [NO]_t$ with $b \neq 0$;

k is the rate constant for the reaction of O_3 with NO : $k = 4.43 \times 10^{-4}$ nmol/mol $^{-1}$ s^{-1} at 25 ºC; and

t is the residence time in seconds.

The increase of NO_2 from the reaction of ozone and nitric oxide is calculated from the loss of ozone:

$$NO_2 = [O_3]_0 - [O_3]_t \qquad (2.2)$$

By assuming certain concentrations for $[O_3]_t$ and $[NO]_t$ and a certain residence time the increase of NO_2 can be calculated and compared to the NO_2 level already present.

Example

Taking the following values:

$[O_3]_t$ – 22 nmol/mol
$[NO]_t$ – 100 nmol/mol
b – 78 nmol/mol ($b = [O_3]_t - [NO]_t$)
k – 4.43×10^{-4} nmol/mol $^{-1}$ s^{-1} at 25 °C
t – 2 seconds

result in the ozone concentration at the sampling inlet $[O_3]_0$ of 24.1 nmol/mol. The increase in NO_2 is 24.1 – 22 =2.1 nmol/mol.

Assuming that the level of NO at the sampling inlet equals to the level of NO_2 at the sampling inlet, the increase of NO_2 equals 2.1/(100 + 2.1) ×100 % = 2 %.

(2) Structure of sampling tube

There are two methods for sampling air, individual sampling method and the manifold method. The structures and usage notes are indicated as follows.

1) Individual sampling method

This is the method that each monitor has a sampling tube individually. The method is generally applied when the sampling inlet to the monitor is less than 5 m in length since adsorption on the surface of the sampling tube induces a problem in the case of a gaseous pollutant. The tip of the sampling tube is attached with a funnel and bent below for preventing rainfall etc. In addition, the extreme bending of the tube should be avoided.

In the case of PM, the individual sampling method is recommended to prevent the absorption to the tube. A net may be installed to prevent penetration of small insects to the sampling inlet. As for PM sampling, it is desired to be small the loss of particle in the sample air which is introduced to a particle size classifier. Moreover, it is also desired to have the structure avoiding rainstorm and foreign substances like insect. To attach raindrop collector which can intercept the penetrated raindrop before reaching to the particle size classifier is recommended.

Furthermore, the maximum length between the particle collector (detecting element) and the sampling inlet shall be 5 m or less and the maximum length between the particle collector (detecting element) and the exit of particle size classifier shall be less than 1.5 m. The sampling inlet and the particle collector (detecting element) shall be present on the vertical line and the sampling tube must not have a bend section. For this reason, when the PM monitor is installed inside the station, the sampling tube shall be placed through the ceiling of the station.

2) Manifold method

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

This method is used for the gaseous pollutants when the distance between the sampling inlet and the monitor is more than 5 m, because this method can reduce the residence time of the gaseous pollutants in the sampling tube due to forcible suction by the blower. However, this method is not used for PM monitoring in which the sampling inlet and the particle collector shall be present on the vertical line as shown in the previous section.

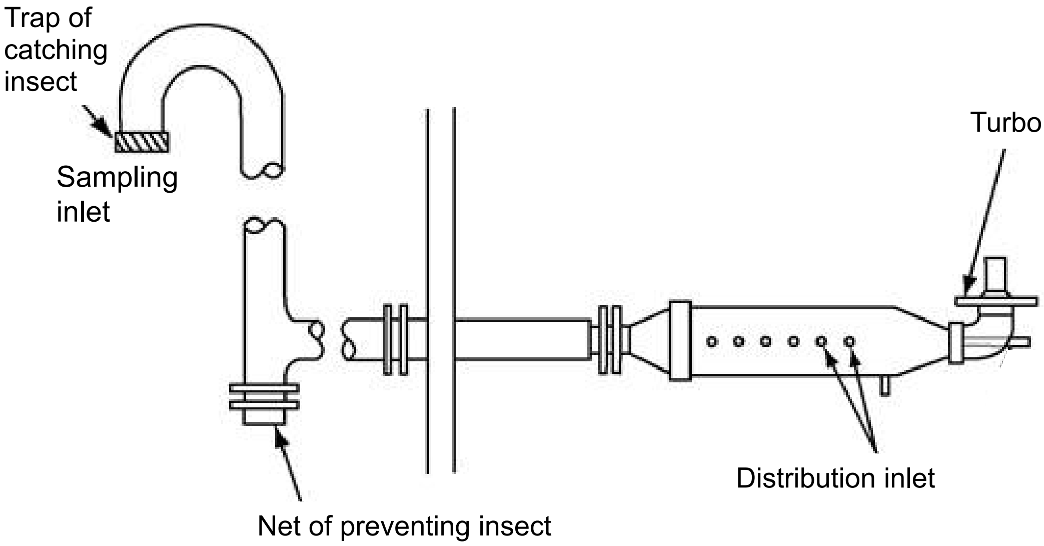

Figure 2.2 Example for a manifold

Fig. 2.2 shows the structure of the manifold used generally. If the manifold inlet is narrow, the monitor inlet may become negative pressure. Therefore, it is desired that the inner pressure is measured at the time of installing the manifold or extending the monitor.

(3) Material of sampling tube

The materials of the sampling tube for the individual sampling method or the tube connecting between the manifold and the monitor should be selected taking the property of measurement species into account. Table 2.1 shows the property of measurement species and the material of sampling tube.

Table 2.1 Property of measurement species and recommended material for sampling tube

Property to be a problem in collection process	Measurement species	Recommended materials for sampling tube
Large adsorption	SO_2, NOx	Polytetrafluoroethylene, Hard glass
Easily decomposition	O_3	
Large adhesion loss	PM_{10}	Vinyl chloride
	$PM_{2.5}$	Stainless steel, Aluminum alloy, etc.

(4) Frequency of cleaning or replacement of sampling tube

The dirt on the inner surface of the sampling tube by adhering of particles will cause the reduction of measurement accuracy because the adsorption or decomposition of the species to be measured will occur on the inner surface. For this reason, the sampling tube should be washed or replaced periodically.

Although the frequency depends on the condition of the sampling tube, it is required to carry out the wash or replacement once or more per year at least. Also the inner surface of the manifold shall be washed (cleaning) once a year or more.

2.2.6. Note on monitor installation

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

i. Vibration

Since a monitor has a vibratory source such as a suction pump the vibration will be transmitted to the other monitors especially on a wooden floor, it is expected to take measures for the floor vibration, if possible.

ii. Corrosive gases and particulates

Corrosive gas and particulates may cause the loose connection of the electric part of the instruments. For this reason, it is necessary to prevent invasion of these substances into the station, and to avoid use and preservation of the reagents, which generate the corrosive gas, in the station.

iii. Low humidity and comparable temperature at the calibration

High humidity in the station causes loose connection such like the item ii. The temperature in the station should be comparable to that at the calibration.

iv. Little fluctuation of power supply voltage and frequency.

It is expected that there is no big electromagnetic induction equipment or the generating equipment of spark discharge near the station. Take measures against thunderbolt, if required.

v. A monitor shall be installed horizontally against the floor.

vi. Maintenance work for safely and easiness

Maintenance and repairs of the monitors may be usually performed from the back side of the monitor. For this reason, it is desirable to keep the space between the monitor and the wall for making maintenance and repair easily.

vii. Shortening of the sampling tube

When the possibility is raised on the adsorption and decomposition of measurement species in the sampling tube, the sampling tube should be as short as possible.

2.2.7. Safety requirement

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

(1) Safe considerations to the surrounding residents

1) At establishing station

i. Entry restrictions into the construction zone

ii. Electric shock preventive measures during the construction

iii. Traffic safety guidance to the construction vehicles

2) At working

Electric shock preventive measures to the surrounding residents after starting the operation

(2) Prevention measure to the toxic substance leakage

Toxic absorption solution and spare parts should be stored with carefully arrangement for avoiding leakage to the outside of the station.

(3) Handling of compressed gas

A gas cylinder shall be kept safely. Detailed information is available in the

Section 2.2.2 (4) and (7) in this manual.

(4) Safe consideration at routine check and maintenance

The measure against handling of toxic substances such as cleaning fluid should be considered at routine check and maintenance.

(5) Measures for natural disaster

1) Against earthquake

To set the caster of the monitor always in the free position, to lay a earthquake-proof mat on the floor, and to fix the instruments by an anchor bolt should be considered as the countermeasure for preventing the fall of heavy loads such as monitor.

2) Against fire

It is cautious of the electric leakage due to leaky ceiling, etc. in usual management. Moreover, when high pressure gas is used, the indicator showing "Compressed gases" is displayed on the door of the station. Other requirements are shown as follows.

i. Preparation of initial fire extinguishing (standing of fire extinguisher)
ii. Fire-resistance of building
iii. Subscription to fire insurance for the instruments or the station

2.3. Monitoring frequency

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 manual samplers (filter packs, denuders, or passive samplers, as may be determined appropriate). For SO_2, 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 or bi-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 SO_2 (fluorescence method), O_3 (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.

References

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3. Automatic monitoring

3.1. Point measurement

3.1.1. SO_2 monitor

3.1.1.1. Principle of the method

Automatic analyzers employing the pulsed fluorescence method are used for SO_2 measurements. Inside the analyzer, pulsating ultraviolet light is band pass filtered and focused into a fluorescence chamber. There it excites SO_2 molecules contained in the air sample into high energy states. As these excited SO_2 molecules go back to their initial states, a characteristic radiation is emitted. The concentration of SO_2 in the air samples is then determined by measuring the intensity of the characteristic radiation (Fig. 3.1).

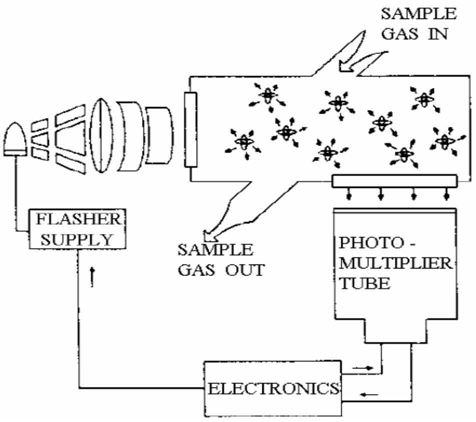


Figure 3.1 Schematic of Operation Principle

Pulsating ultraviolet light with wavelength at 190–230 nm is bandpass filtered and focused into a fluorescence reaction chamber. SO_2 molecules in the reaction chamber are excited into higher energy states and emit radiation as these states decay. A 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

In normal operation, air is drawn into the analyzer through a 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. A hydrocarbon kicker removes hydrocarbon molecules which interfere with the fluorescence activity. Excitation of the SO_2 molecules takes place in the fluorescence reaction chamber (Fig. 3.2). The flowmeter indicates the flow rate in liter per minute (LPM). The nominal flow rate is 0.5 LPM. A 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 254 mmHg is required to remove all interfering hydrocarbons. A vacuum gauge shows the differential pressure within the instrument. An internal sample pump provides the driving force to draw in ambient air or calibration gases.

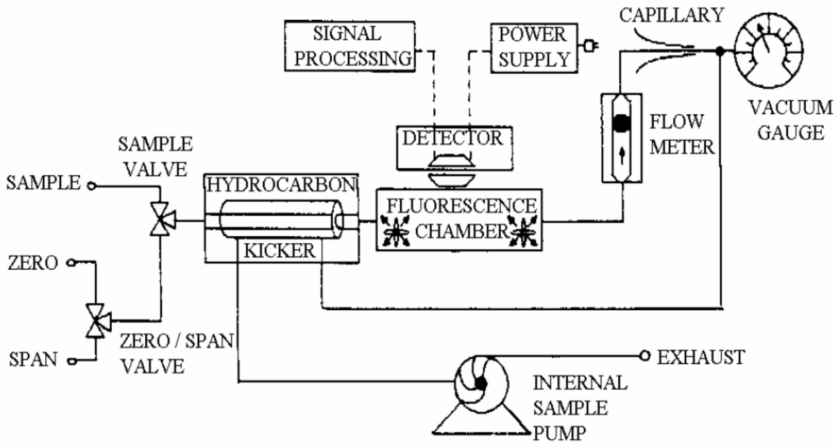


Figure 3.2 Gas Flow Schematic

Optical path

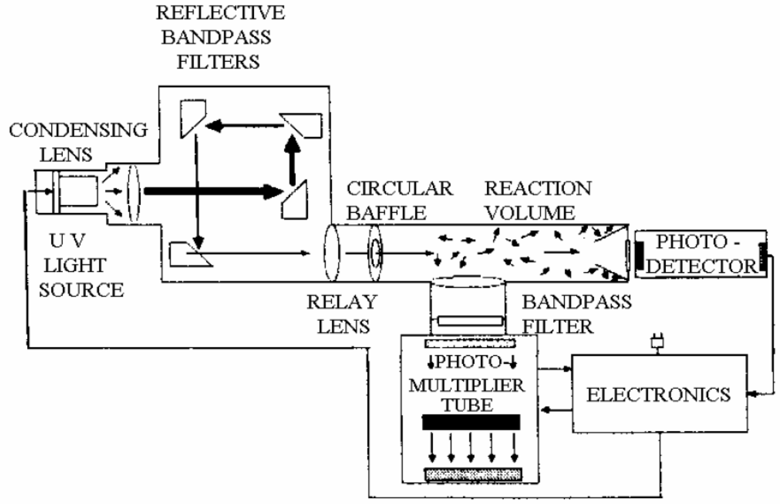


Figure 3.3 Optics System Schematic

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 (Fig. 3.3). 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.

Electronics

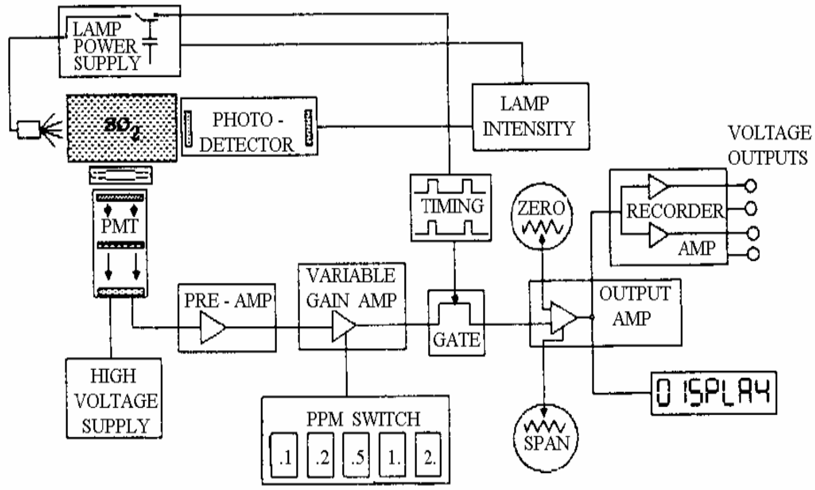


Figure 3.4 Electronics Block Diagram

The photomultiplier tube (PMT) transforms the light intensity into current. The pre-amplifier (PRE-AMP) converts the current into voltage (Fig. 3.4). 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 the 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 ºC. 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.

3.1.1.2. SO_2 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 (e.g. TECO 146; Thermo Fisher Scientific Inc.) have been calibrated by a traceable primary flow standard with a flow calibration curve in the form of linear regression show below:

$$y = mx + b \tag{3.1}$$

   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 in the order of the manifold controller, the manifold block, the manifold controller then the SO_2 analyzer's sample inlet. If trouble shooting required, the connection can make directly from calibrator to analyzer.
5) Ensure the gas cylinder securely to the dynamic calibrator. If connections are re-established, activate the control valve of the calibrator to allow SO_2 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% and more than the normal working flow rate of the analyzer.
7) Activate calibration at ZERO mode by the data logger. Or activate the calibrator in local mode, the "Zero" button.
8) Introduce 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 data logger or analyzer at "SPAN" mode. Then introduce span gas into the calibrator. Select the correct concentration to the normal mid-night zero/span check position to apply span gas (about 70 – 90% of full scale) 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 the steps 7) – 10).

11) Select a concentration of about 50% of the span value (about 40–50% of full scale) 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:

    (i) 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.

    (ii) 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 service 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 the normal operation modes.
18) Reset the data logger 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 the previous results. Check whether precision check result is within ± 20%.
21) Plot the precision check result on a control chart. Complete the precision check data sheet.

This procedure describes the typical calibration operation. If the instrument manual describes specific procedure, one must refer and follow the instruction.

3.1.2. NO, NO_2 monitor

3.1.2.1. Principle of the method

Oxides of nitrogen, NOx, 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 (O_3) produces a characteristic luminescence with an intensity proportional to the concentration of nitric oxide, as follows:

$$NO + O_3 \Rightarrow NO_2 + O_2 + h\nu \qquad (3.2)$$

This reaction only takes place between NO and O_3, and not NO_2 and O_3. 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 NO_2. 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, NO_2 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 NO_2.

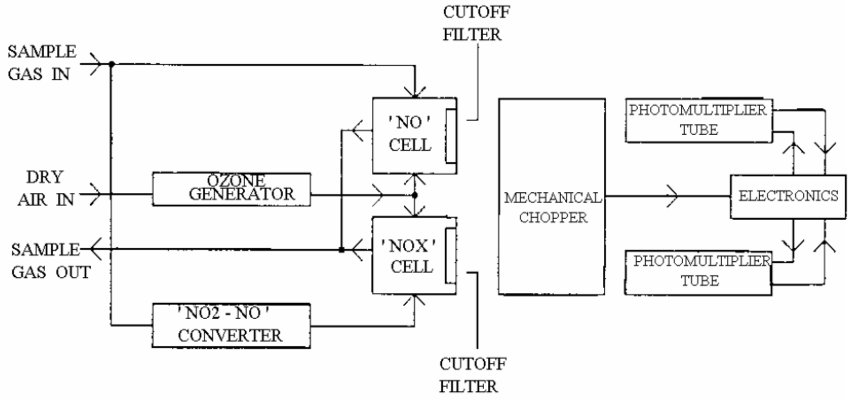


Figure 3.5 Schematic of Operation Principle (Model 8840; Monitor Labs Inc.)

As shown in Fig. 3.5. the NOx analyzer has two reaction cells, namely the "NO" and the "NOx" cell. In the "NO" cell, nitric oxide (NO) in the air sample reacts with ozone (O_3) from the ozone generator to form excited nitrogen dioxide (NO_2*) molecules. Light emission, with a maximum intensity at approximately 1100 nm, results when the excited NO_2* molecules decay to lower energy states. This phenomenon is known as chemiluminescence and the chemical equation is shown as follows.

$$NO + O_3 \Rightarrow NO_2^* + O_2 + h\nu \qquad (3.3)$$

Since one NO molecule is required to form one NO_2* molecule, the chemiluminescent emission 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 (7500 V rms) electrode:

$$3O_2 \Rightarrow 2O_3 \qquad (3.4)$$

Dry air is needed to avoid acid formation and thus contamination of the pneumatic path and ozone generation shown as the equation 3.4. The nitrogen dioxide (NO_2) in the air sample is converted to nitric oxide (NO) by a molybdenum converter (MOLYCON) before it enters the "NOx" reaction cell. This MOLYCON is heated to approximately 315 ºC for the following reaction to take place:

$$3NO_2 + Mo \Rightarrow 3NO + MoO_3 \qquad (3.5)$$

Chemiluminescence reaction also takes place in the "NOx" cell, and the intensity of radiation is then directly proportional to the total nitrogen oxides (NOx) concentration (i.e. NO + 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 analyzer through the sample port of the controller. Calibration gases (zero air, "NO" and "NO_2" 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 (Fig. 3.6). The other air stream enters the "NOx" cell through the MOLYCON and a flow meter. A small (7 mm) 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 small (4 mm) 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 small (3 mm) 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 558.8–660.4 mmHg. A charcoal scrubber is present to remove any ozone (O_3) and nitrogen dioxide (NO_2) from the exhaust of the reaction cells.

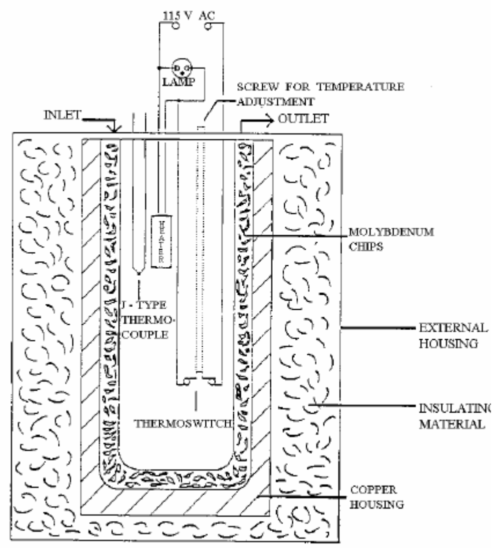


Figure 3.6 Schematic diagram of the MOLYCON version 1

In order to measure the concentration of nitrogen dioxide (NO_2) in the air sample, a molybdenum converter (MOLYCON) is used to convert nitrogen dioxide (NO_2) to nitric oxide (NO). The MOLYCON is kept at 315 ºC to maintain the following conversion process.

$$3NO_2 + Mo \Rightarrow 3NO + MoO_3 \qquad (3.6)$$

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

$$3O_2 + 2Mo \Rightarrow 2MoO_3 \qquad (3.7)$$

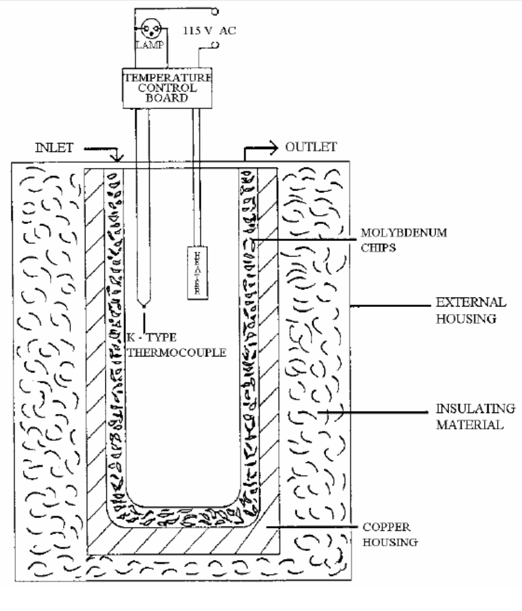


Figure 3.7 Schematic diagram of the MOLYCON Version 2

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 NO/NO_2 monitor (Model 8840; Monitor Labs Inc.). Their difference lies in the design of temperature control and the type of thermocouple used for temperature sensing. In the version 1 MOLYCON, a thermo switch is used to control the ON/OFF state of the heater, as indicated by the neon lamp on the front panel of the analyzer. The operating temperature can be set by turning the temperature adjusting screw. The temperature of the MOLYCON is monitored by the J-type thermocouple.

In the version 2 MOLYCON, temperature is controlled by the temperature control board (Fig. 3.7). The neon lamp is lit when the MOLYCON is being heated up and flashes when the preset temperature (315 ºC) is reached. The thermocouple used is the K-type.

Electronics

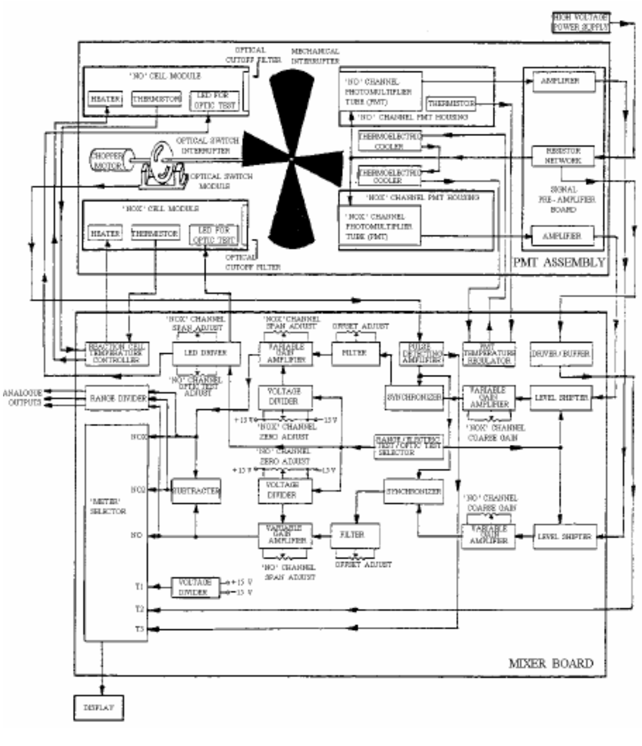


Figure 3.8 Electronics Block Diagram (Model 8840; Monitor Labs Inc.)

One heater and thermistor are mounted on each reaction cell (Fig. 3.8). The reaction cells temperature controller on the mixer board keeps the temperature of the reaction cells at about 50 ºC. 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 ºC to minimize the dark current effect. The high voltage power supply board provides power (around 900 V 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 analyzer 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 (NOx) can be displayed by proper setting of the "METER" selector on the analyzer front panel. The range divider converts the signals to 0-1 V DC analogue outputs for recording purpose. The mixer board power supply (T1), the 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.

3.1.2.2 NOx multi-point calibration procedures

The calibration of the NOx analyzer consists of two parts: (1) evaluation of the characteristics of the NO and NOx channels by dynamic dilution of a standard gas, and (2) evaluation of the characteristics of the NO_2 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, NO_2 is produced according to the following equation:

$$NO + O_3 \Rightarrow NO_2 + O_2 \qquad (3.8)$$

The quantitative nature of this reaction is such that when the NO concentration is known, the concentration of NO_2 can be determined. Ozone is added to excess NO in a dynamic calibration system (e.g. Model 146; Thermo Fisher Scientific Inc.), and the NO channel of the analyzer is used as an indicator of changes in NO concentration. Upon the addition of O_3, the decrease in NO concentration observed on the calibrated NO channel is equivalent to the concentration of NO_2 produced. The amount of NO_2 generated may be varied by adding variable amounts of O_3 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 NO_2, and back-diffusion of O_2 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 linear 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. e.g. 1.0 LPM for a Model 8840 (Monitor Labs Inc.), and 1.7 LPM for a Model 42 (Thermo Fisher Scientific Inc.).
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 the equation 3.9:

$$[\mathrm{NO}]_{out} = [\mathrm{NO}]_{std} \times \frac{F_{NO}}{F_{NO} + F_z} = [\mathrm{NO}]_{std} \times DF \qquad (3.9)$$

Where,

DF = dilution factor = $F_{NO} / (F_{NO} + F_z)$

$[\mathrm{NO}]_{std}$ = certified concentration of the undiluted NO standard

F_{NO} = 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 the equation 3.10.

$$[\mathrm{NOx}]_{out} = [\mathrm{NOx}]_{std} \times DF = ([\mathrm{NO}]_{std} + [\mathrm{NO}_2]_{imp} \times DF \qquad (3.10)$$

Where,

$[NO_2]_{imp}$ = certified concentration of NO_2 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 the equation 3.9 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 the equations 3.9 and 3.10.
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 is about 500 ppb.).
12) Usually the standard gas concentration of NO gas is 50 ppm, the ranges of zero and gas MFCs are respectively 10 LPM and 100 cc/min.

3.1.3. O_3 monitor

3.1.3.1. 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 (Fig. 3.9). The difference between the two values is proportional to the ozone concentration according to Beer-Lambert equation.

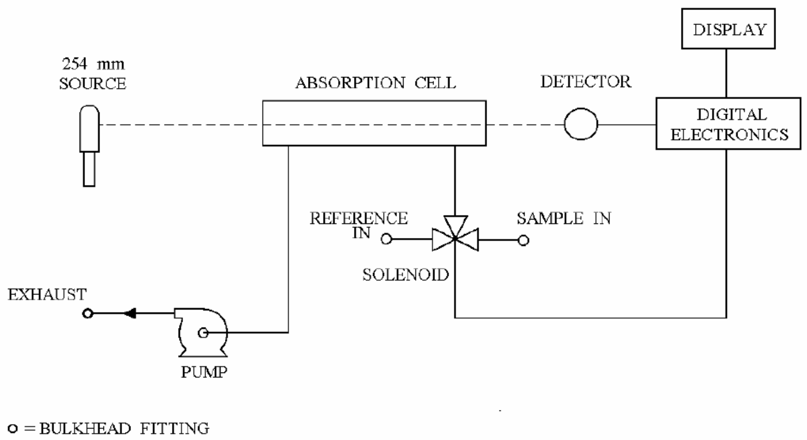


Figure 3.9 Schematic of operation principle

The UV photometric ozone analyzer/calibrator (e.g. Model 49/49PS; Thermo Fisher Scientific Inc.) 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 an 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:

$$I / I_0 = \mathrm{e}^{-KLC} \tag{3.11}$$

where,

K = Absorption coefficient = 308 cm^{-1} at 0 ºC, 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/I_0" of 0.002%. The source must be stable to better than 0.002% in the time frame it takes to measure "I" and "I_0", 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. 3.10 and 3.11.

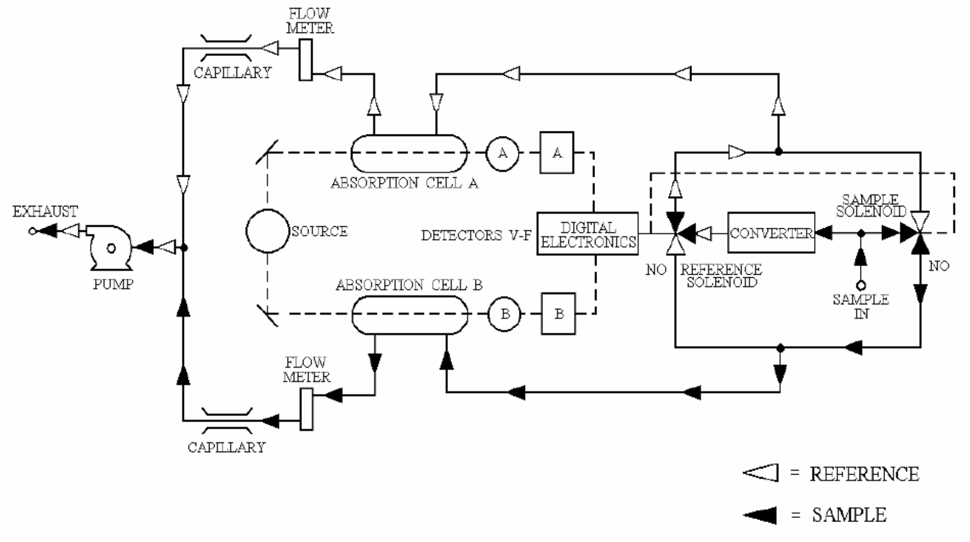


Figure 3.10 The first sampling cycle of ozone monitor

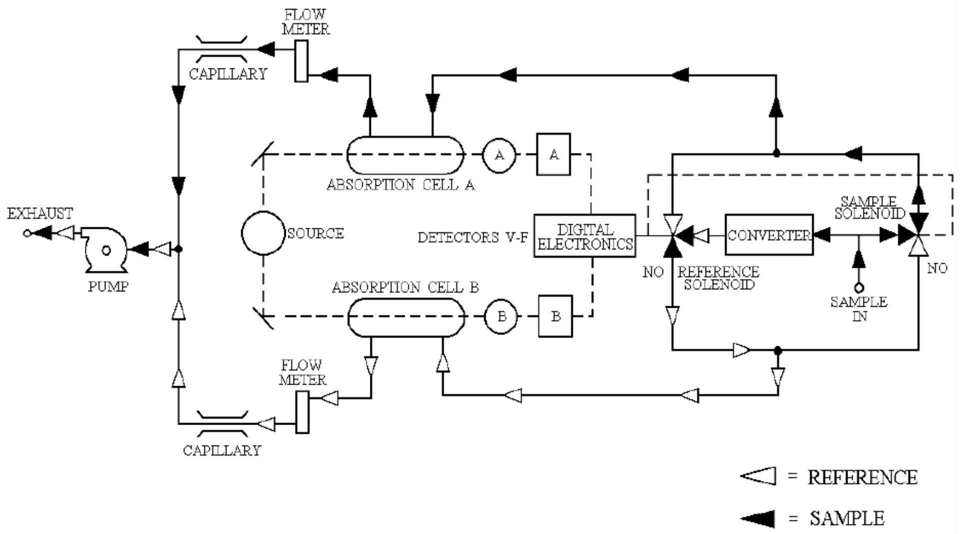


Figure 3.11 The second sampling cycle of ozone monitor

The period of the 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, the 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 ºC and 760 mmHg, is used to represent the ambient ozone concentration. The measurement continues by repeating the two sampling cycles, the temperature/pressure correction and the averaging process.

Pneumatic path

The pneumatic path is explained by the model 49 ozone analyzer and the model 49PS calibrator (Thermo Fisher Scientific Inc.).

Model 49

1) In sampling mode, the zero/span solenoid is de-engerized and so the ambient air sample is directed into the photometers (Fig. 3.12). 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 catalyst to convert the

ozone in the sample to oxygen and so provides the ozone free reference gas.

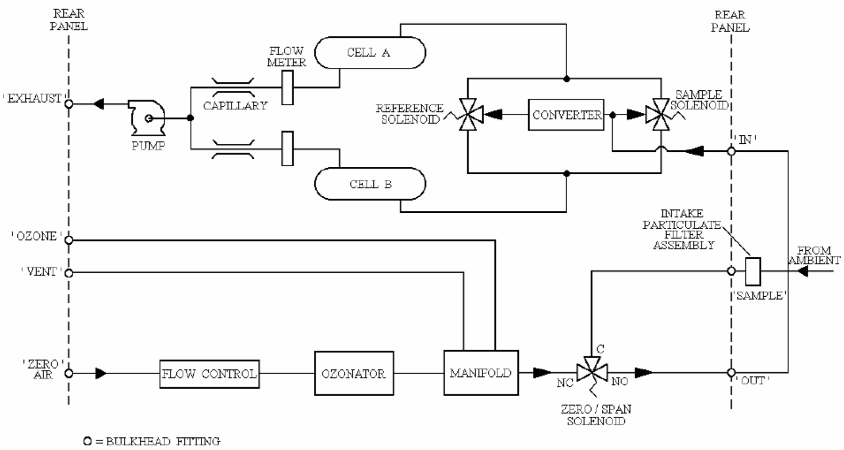


Figure 3.12 Pneumatic path for the model 49 (Thermo Fisher Scientific Inc.)

3) The internal surface of the two absorption cells have been coated with polyvinylidine 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 analyzer being calibrated and one for the atmospheric dump.
10) When the 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 the model 49 could also be used to calibrate other ozone

analyzer.

Model 49PS

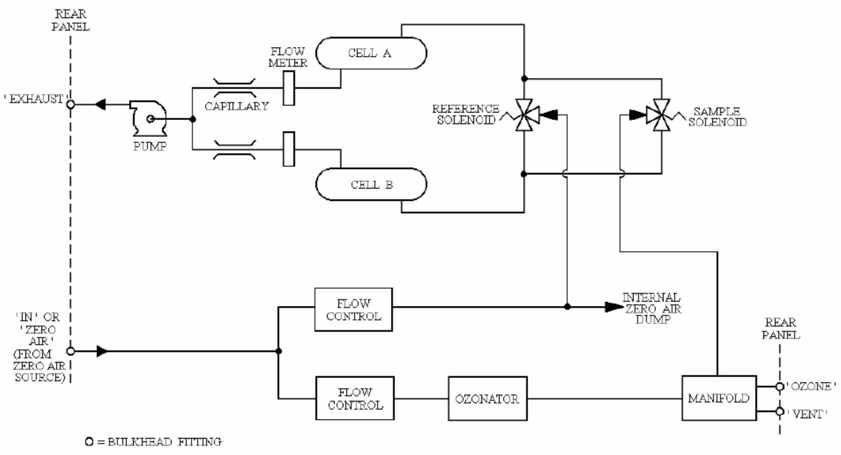


Figure 3.13 Pneumatic path of the model 49PS (Thermo Fisher Scientific Inc.)

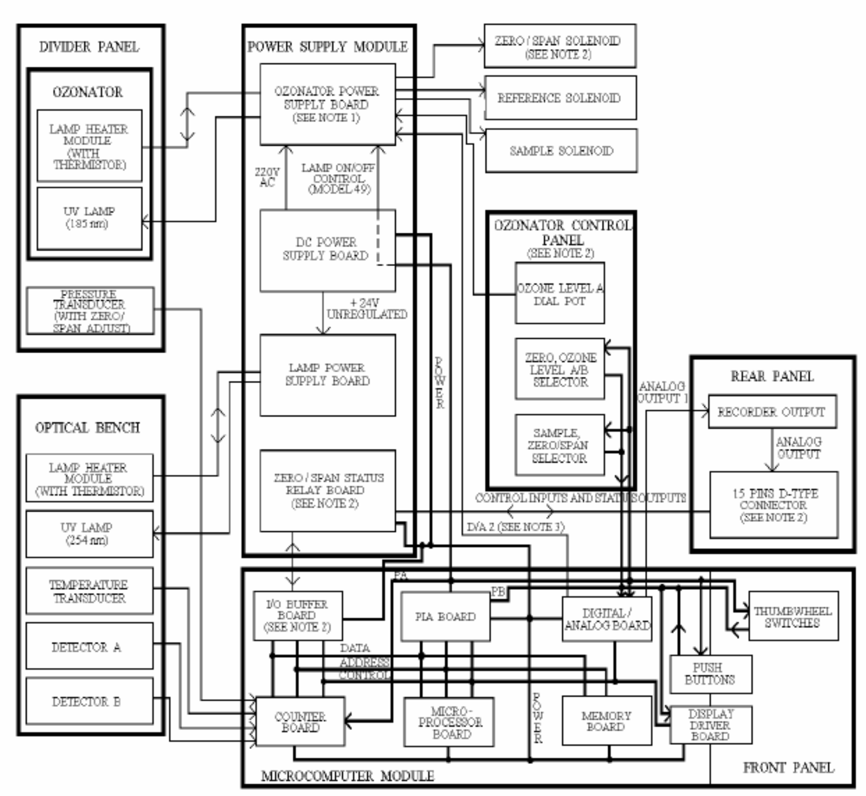
As shown in Fig. 3.13, the pneumatic path of Model 49PS is similar to that of the model 49 excepts for the following:

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 psi.

Electronics

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 vapor lamp with an expected lifetime in excess of one year (Fig. 3.14). 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 aluminum block that provides the necessary thermal stability. The UV lamp will be ignited only if the temperature is above 50 ºC.

The detectors and associated pre-amplifiers are mounted together in a small, well-shielded can to ensure the highest levels of detector stability and the 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.



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 3.14 Electronics block diagram of ozone monitor

The ozonator consists of a UV lamp and a lamp heater module (with a thermistor). The light intensity is varied by changing the current into the lamp, which generates various ozone levels. As in the optical bench, the ozonator is maintained at constant temperature to ensure the thermal stability. The power supply module typically houses the ozonator power supply board, the DC power supply board, the lamp power supply board and the zero/span status relay board. 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 the board. It also typically houses circuitry to control the zero/span solenoid and switches the analyzer in the sampling or the 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 ºC. The zero/span status relay board 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, the ozone level A or B calibration/check. The microcomputer module houses the microprocessor board, the memory board, the counter board, the peripheral interface (PIA) board, the display driver board, the digital/analogue board, I/O buffer board and the front panel pushbuttons. The microprocessor board controls the operation of the analyzer/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 the model 49 (Thermo Fisher Scientific Inc.), only segment 7 and 8 of the DIP switch should be turned ON (all others OFF). All segments should be turned OFF in the model 49PS (Thermo Fisher Scientific Inc.).

The display driver board contains circuitry to drive the 6 digits display on the front panel. The digital/analogue 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.

3.1.3.2. O_3 calibration procedures

(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 standard monitor calibrated by a secondary standard monitor is prepared, and the ozone monitor installed in each monitoring station is calibrated using the transfer monitor. The transfer monitor enables the display of minus and 0.1 ppb. It also needs to have a temperature and pressure compensation function. Moreover, it is desirable that zero point measurement by supply of the zero gas from outside instead of a zero point measurement mechanism with the ozone degradation machine to build in can be performed.

(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 Fig. 3.15 and consists of an ozone generator and an ozone monitor.

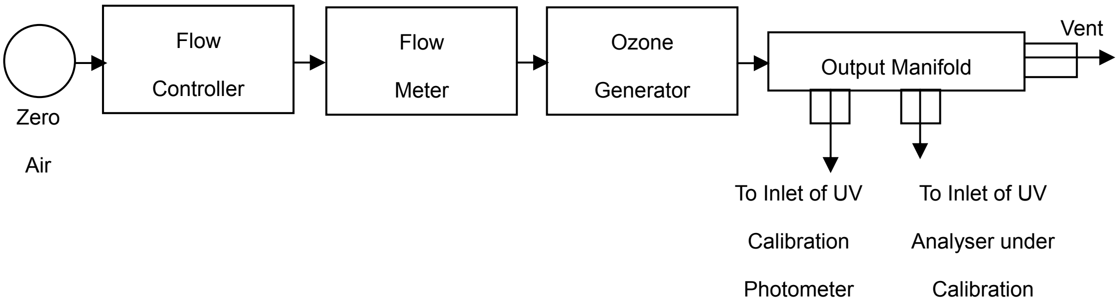


Figure 3.15 Primary ozone calibration systems (Norwegian Institute for Air Research (2001))

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.3.16 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) SRP. One way of obtaining this is to buy from NIST a NIST SRP which periodically will be checked by NIST. Another way is to have the laboratory or national primary calibrator traceable to NIST SRP in another country e.g. once per year. The Network Center (NC) may provide the transfer standard by the request of the country which does not have the primary standard.

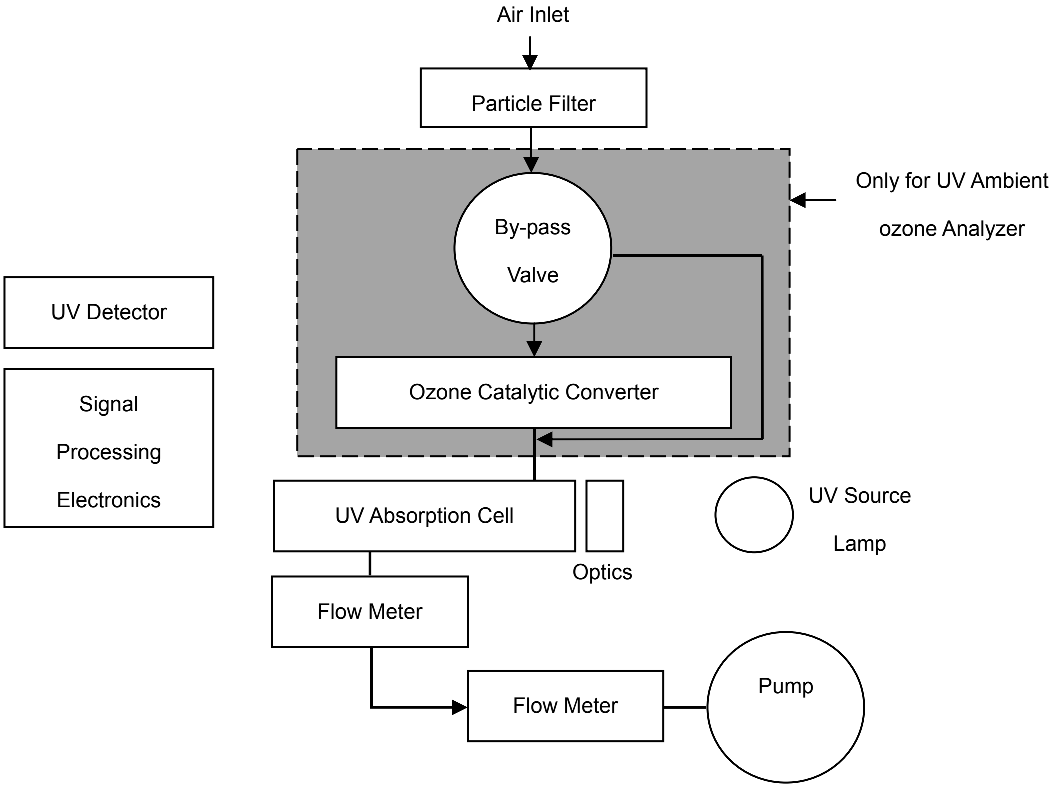


Figure 3.16 UV photometric ozone measurement system (Norwegian Institute for Air Research (2001))

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

It is desired that the primary monitor calibrates every monitor located in monitoring stations. But when the primary monitor cannot be used easily, the 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 200 ppb between successive primary calibrations. And a transfer standard shall be calibrated against the secondary standard every six month and its accuracy shall be maintained within ± 2ppb at level of 200 ppb 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 the relevant references (U.S. Environmental Protection Agency, 2013).

(4) Calibration method of an 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 standard operating procedure (SOP). For this purpose, the ozone generator should be available at the site that has been compared with the transfer standard traceable to the NIST SRP. Before and after a change or the Teflon tubes and filters, the 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 ±5% at level of 200 ppb between successive primary calibrations.

Other notices

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 cylinder. This is especially important for NO gas cylinder, as back-diffused O_2 will oxidize NO to NO_2.

3.1.4. PM$_{10}$ and PM$_{2.5}$ monitors

3.1.4.1. β-ray absorption method

(1) Principle

The β-ray absorption method is most popular for the particulate matter (PM) mass concentration monitoring, recently. An indicated value as a mass concentration is obtained from an increase of absorption amount of β-ray due to the particles collected on a filter paper. The β-ray analyzer is an instrument based on the principle that the absorption rate of β-ray irradiation by the particulate matter collected on the filter paper gives information about its quantity.

The relationship between the intensity of β-ray transmitted and the dust quantity is expressed by the following equation.

$$I = I_0 \exp(-um / xm) \qquad (3.12)$$

I: β-ray intensity transmitted through filter and particulate

I_0: β-ray intensity transmitted only through filter

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

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

Since it can be considered that the mass absorption coefficient, um, is constant without basing on the composition of particles, the mass of PM (xm) can be calculated from the ratio of I to I_0.

$$xm = 1 / um\ (I_0/I) \qquad (3.13)$$

(2) Instrumental setup

The setup of a typical PM monitor by the β-ray absorption method is shown in Fig. 3.17.

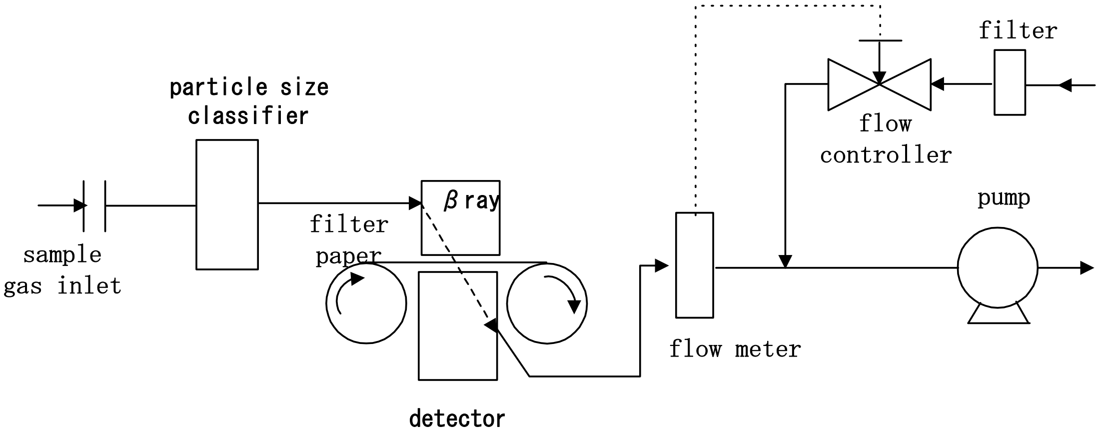


Figure 3.17 PM monitor by β-ray absorption method

(3) Filter

A collection filter that the collection efficiency is 99.7% or more for the particles with the diameter of 0.3μm is used. Moreover, it is desirable to use the filter of manufacturer recommendation. The tape-type glass fiber filter with the length which can be continuously monitored for 1 to 3 months is generally used.

In addition, since the moisture influence to the filter paper causes the measurement error, it is needed to pay attention to the dew condensation in high humidity period.

(4) Notes for measurements

1) Sampling air system

i. Sampling inlet

The individual sampling inlet shall be used for PM sample collection instead of the manifold method fundamentally. The measures to prevent the penetration of rainwater, insect, etc,, into the sampling inlet are recommended.

ii. Materials of sampling tube

The sampling tube which has smooth and clean inner and does not generate any gases disturbing measurement shall be used. When the sampling tube made by the plasticized-polyvinyl-chloride or the copolymer of ethylene and VCM/PVC is used at the temperature of 40 ^{o}C or more, it is reported that the particulate matter is discharged from the tube and it causes a positive error.

iii. Length of sampling tube

The sampling tube should be installed in a vertical direction from the monitor. The tube is also recommended to be a straight and its length should be as short as possible.

iv. Frequency of changing sampling tube

The proceeding dirt induces the adhesion of particulates on the inner wall of the tube and causes the reduction of measurement accuracy. For this reason, a sampling tube should be washed or replaced periodically.

Although the frequency of washing or replacement depends on the situations of the measurement site, it is required to carry out once or twice a year at least.

v. Particle size classifier

The PM_{10} and $PM_{2.5}$ monitors are recommended to have particle size classifiers whose 50% cutpoints are 10±0.5μm and 2.5±0.2μm aerodynamic diameter, respectively. The classifier is also expected to have the character which the ratio of 80% cutoff particle size to 20% cutoff particle size is equal to or less than 1.5 for $PM_{2.5}$ and is about 2.2 for PM_{10}, respectively (Ministry of the Environment Japan, 2010, and U.S. Environmental Protection Agency, 2014).

Since the cyclone type particle size classifier changes its separation characteristics with the dirt on the surface of the inner wall, the big and rough particle receptacle part as well as the inner wall of the classifier should be periodically cleaned by using alcohol, neutral detergent, etc. The cascade impactor should be disassembled and cleaned at least once a year. Wipe the dust residue on the impactor plate and nozzle. Then, compressed air can be used to blow it off. Isopropanol or soap and water can be used for cleaning the parts, but make sure that they are dried before reassemble.

Moreover, at the opportunity of the classifier cleaning, it is better to be cleaned and replaced whole parts between the sampling inlet and the detector.

2) Exchange of collection filter

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

However, since many repetition measurements in a high concentration period and high frequency calibration by using the equivalent film cause faster filter consumption in comparison with usual measurement, the operator should be paid enough attention for the residue of the filter paper not to produce missing period.

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

When the measurement error is out of allowable range as the result of the check by the equivalent film, it is needed to confirm the contribution of filter paper to the measurement error by setting the filter paper with a different lot.

3) Cleaning of flow meter

It is necessary to pay much attention to the dirt of a float and a tapered vessel inner wall of a flow meter of an equipment in which the flow meter is used to monitor the gas exhaust from a pump. Since the inside of a flow meter becomes dirty easily, it should be cleaned by alcohol, neutral detergent, etc. periodically.

Because the dirt of the inner wall, the jam of a small tube, and the dirt of a float may cause the measurement error of the flow rate in the model equipped with a mass flow meter or the model using a constant differential pressure gauge valve, the operator should pay much attention to those situations.

4) Flow stabilizer and pump volume

Since the β-ray absorption method is a filtration method, the air-flow resistance of the filter paper might increase by the collected particles and the flow rate might decrease at a high concentration period. Therefore, the flow stabilizer is usually equipped to measure against the pressure increase in a certain range.

In addition, there are three types of equipment having different function for the situation in which the pressure reaches the control limit (marginal pressure); a model will move the filter paper automatically and start measurement again; a model will continue sampling in spite of the flow rate decreases; and the others will stop the sample collection. However, when the repetition measurement is performed, sampling time for a sample will decrease and an error will increase. Especially, for the monitoring station which is easy to be influenced by the gas exhaust from the vehicles, it is recommended to select the pump which can respond to increase of the air-flow resistance by the exhaust particles prone to clogging.

5) Confirming actual flow rate and adjustment of flow rate stabilizer

The actual flow rate of the sampling air is determined by the standard flow meter connected to the sampling inlet and its value will be compared with a setting flow rate.

A flow stabilizer or the sensor position of a float type variable area flow meter is adjusted so that an actual flow may turn into a setting flow. In addition, when the actual flow rate varies exceeding ±7% of the setting value, it is necessary to check the air leakage from the stabilizer, the suction pump, and the filter paper holder, etc. and perform adjustment or exchange some parts.

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

i. The standard flow meter equipped a valve at the exit side is connected to the sampling inlet.
ii. A differential pressure gauge is built into the pipe which connects a pump with a filter collection part. However, this step is not necessary for the model which can display the indicated value of the pressure sensor and to the model in which the differential pressure gauge is built in.
iii. A new filter paper side is sent out, a valve is opened fully, and then the equipment is operated. After the operation of the flow stabilizer is completed, the indicated value and the difference pressure (initial pressure loss) of a floated type variable area flow meter should be recorded.
iv. When the valve is shut gradually, and the operation of the flow stabilizer is completed, the indicated value and the difference pressure of the floated type variable area flow meter should be recorded.
v. It is confirmed that the setting flow is maintained just before the marginal difference pressure (repetition measurement or difference pressure just before stopping).
vi. It is confirmed that a repetition measurement will begin when the marginal difference pressure is exceeded.

Since the indicated value of the floated type variable area flow meter will vary with atmospheric pressure, temperature, and density of the sample air, the value needs to be converted when the flow meter is used on the condition different from the normal condition (usually 20 ºC, 101.3 kPa) in which the scale calibration is carried out. 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 opening and closing of a valve should be performed slowly and the valve should not be fully opened by any means.

6) Indicated value of air free from particles (blank test)

The filter paper which has little air-flow resistance and can fully remove a particulate matter is set in the filter paper holder. Then the holder is connected to the sampling inlet and the sample air free from particulate matter is measured for 24 hours. It is called the indicated-value examination (blank test) to the air free from particulate matter.

It shall be checked that the arithmetic mean of the hourly value does not exceed ±10 μg/m^3 or ±1% of the maximum scale.

The β-ray absorption method theoretically accompanies the probable error of nuclide collapse, therefore, the production of the counting error about ±10μg/m^3 is not avoided. In this reason, an examination value and a measurement value turn sometime into a minus value.

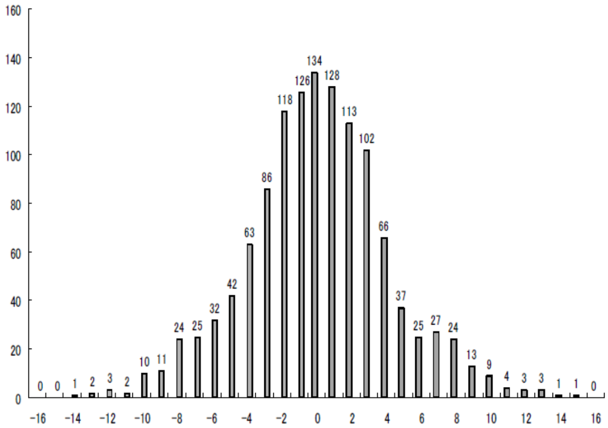


Figure 3.18 Example for indicated value of air free from particles (blank test)

Although some models may process the measured value below zero and display it as zero, the function should be cancelled to prevent the positive error bias. An example of a histogram of this examination values is shown in Fig. 3.18.

7) Replacement of pump and its related parts

Although the frequency of the replacement for the pump and some parts around the pump depends on the model, the pump is recommended to be replaced once in 1 to 3 years. A diaphragm and a packing of the collection part should be exchanged once or twice a year.

8) Handling of radiation source and detector

The source of β-ray is a sealed radiation source, and the low energy model using the radio isotopic sources such as ^{147}Pm and ^{14}C is usually used. Handling must follow the law of each country. Since a protective film of the radiation source is thin and it is easy to damage, sufficient cautions are required for handling. Not to damage an emulsion side at the opportunity of cleaning of the radiation source. The cleaning should be performed using an airbrush, a swab, etc., with careful attention.

In addition, it is desirable to wear protective glasses and latex gloves for operation, since the maximum distance of the source of β-ray in the air is about 20 cm for ^{14}C and is about 30cm for ^{147}Pm.

When abnormalities, such as a hole and dirt, are appeared at the protective film of the radiation source which is directly exposed to the sample air, the film should be exchanged. As for the model that the aluminum evaporated film is used, it needs to be cautious of the corrosion by acidic gas or particle especially.

In addition, the radiation source itself should be exchanged for the model in which there is no radiation source protective film other than the protective film equipped at the radiation source. Moreover, since the counting rate decreases rapidly by the moisture absorption in the air when the ^{147}Pm radiation source is damaged or a pinhole forms the measure for preventing radiation pollution expansion should be taken immediately, and then the radiation sources should be exchanged carefully by asking a manufacturer or a specialized agency. Exchange and abandonment of the radiation source must follow the law of each country.

Pay attention not to touch at the specular surface portion of a semiconductor detector. Moreover, the plastic scintillation counter should be handled paying attention whether the pinhole is made in the surface of aluminum evaporated film, and whether the counter has been corroded by the alkaline water droplet fell from the filter paper of the collection part in high humidity condition.

9) Measure against magnetic field

Since the β-ray is an electron flow with the minus charge and tends to be influenced by a magnetic field, it should be avoided to use the magnet which produces the magnetic field around the radiation source and the primary detecting element.

3.1.4.2. Tapered Element Oscillating Microbalance (TEOM) method

(1) Principle

TEOM is 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, when additional mass is added, the frequency of the vibration decreases. An electronic control circuit senses this vibration and through positive feedback, adding sufficient energy to the system to overcome losses. An automatic gain control circuit maintains the vibration at constant amplitude.

(2) Instrumental setup

Through the PM_{10} or $PM_{2.5}$ inlet, the principle size separation at 10 or 2.5 μm takes place as the sample proceeds. The flow splitter separates the total flow into two parts; a main flow of 1.5-3.0 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 an 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 setup of a typical PM monitor by TEOM method is shown in Fig. 3.19.

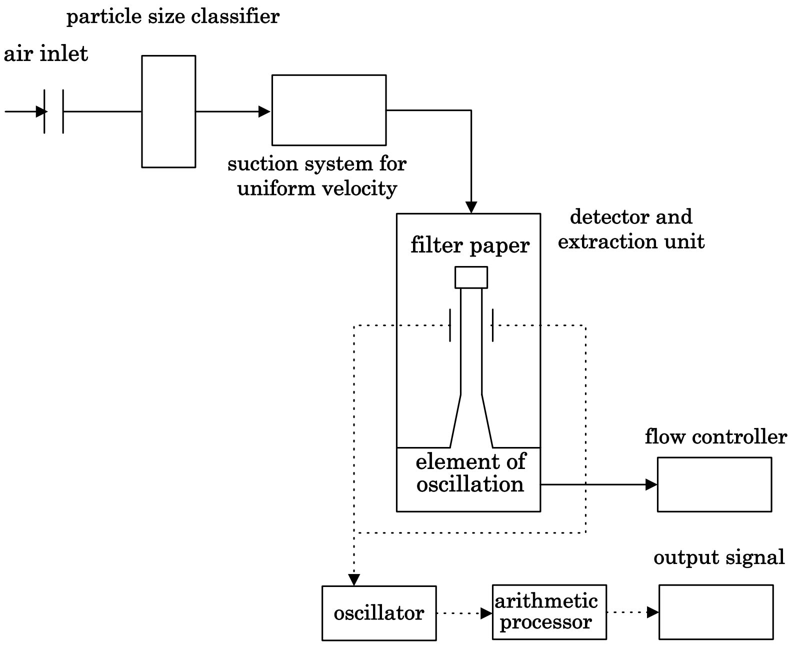


Figure 3.19 Schematic diagram of PM monitor by TEOM method

(3) Filter

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

(4) Notes for measurements

1) Sampling air system

It follows the description in the section of the β-ray absorption method automatic monitor (Section 3.1.4.1).

2) Exchange of filter

The mass flow rate is always displayed in the TEOM method. The filter should be exchanged before it becomes impossible to maintain the setting flow rate. At the site which tends to be influenced by the automobile exhaust particles, the frequency of the filter exchange should be increased because it quickly impossible to maintain the setting flow rate even if the total collection amount is small. When the filter is exchanged, the display of the frequency value should be carefully checked. When the fluctuation is not stable after 10 minutes or more, the attachment of the filter should be confirmed.

3) Flow stabilizer

In the filter oscillation method, the sample air is introduced with the flow rate of 16.7 L/min in order to prevent particles depositing on the surface of the sampling tube, 1.5–3.0 L/min of the total flow is separated by the isokinetic flow splitter tube and then led into the detector. The mass flow controller is used for controlling the flow rate.

4) Confirming actual flow

The actual flow rate of the sample air is determined by the standard flow meter connected to the sampling inlet. The operator should confirm that the flow rate is maintained in the setting value (1.5–3.0 L/min). In addition, when the actual flow rate varies exceeding ±7% of the setting value it is necessary to investigate the capability of the flow stabilizer and the suction pump, air leak, etc., and then to perform adjustment or exchange of parts. Regarding the sample air leakage, it should be confirmed that the displayed flow rate is less than 0.15 L /min when the sampling inlet is sealed.

As for the isokinetic suction pump, its performance should be confirmed by the checking whether the actual flow rate varies within the allowable range from the setting value.

5) Blank test

It follows to the description in the section of the β-ray absorption method automatic monitor (Section 3.1.4.1).

6) Others

Since the filter oscillation method is a measurement method using the oscillating element, when the equipment is installed, the location with flat and minimal environmental vibration should be chosen.

3.1.4.3. Dehumidifier system

For PM automatic monitor, it is required to have a function which controls change in the measured value due to the variation of relative humidity, in order to obtain the measured value equivalent to the filter collection-weighing method. The increase in the mass concentration measured value due to moisture absorption of the ingredient in particles is pointed out on the PM measurement. The mass of PM is easily overestimated when the substance, which has deliquescence property such as ammonium sulfate inorganic salts and secondary organic aerosol, is exposed in moisture.

A dehumidifier system is attached to the sample air inlet for reducing the influence of humidity in many cases. There are three major methods for dehumidifier, a heating method, a diffusion pipe method and a dilution method. Although the condition of operating the dehumidifier system depends on the model of a PM automatic monitor, temperature and humidity are important parameters for controlling the system of many dehumidifiers. It is also important to carry out a routine or periodical check and maintenance for the systems.

Some thermometers and hygrometers for PM monitors are beforehand calibrated at the shipment and cannot be adjusted at the site (when the fixed range is exceeded the sensors should be newly replaced). The others can be adjusted on software by using a correction coefficient obtained in comparison with the calibrated equipment at the site.

In the routine maintenance, the followings should be performed; 1) the check of indicated values on the monitor, 2) the check of heating, and 3) the comparison of temperature and relative humidity measured by the monitor with those parameters which are previously measured in the same monitoring station. Moreover, the indicated values of those parameters should be confirmed by using the official approved values or by periodically calibrated thermometer and hygrometer (once in 6–12 months).

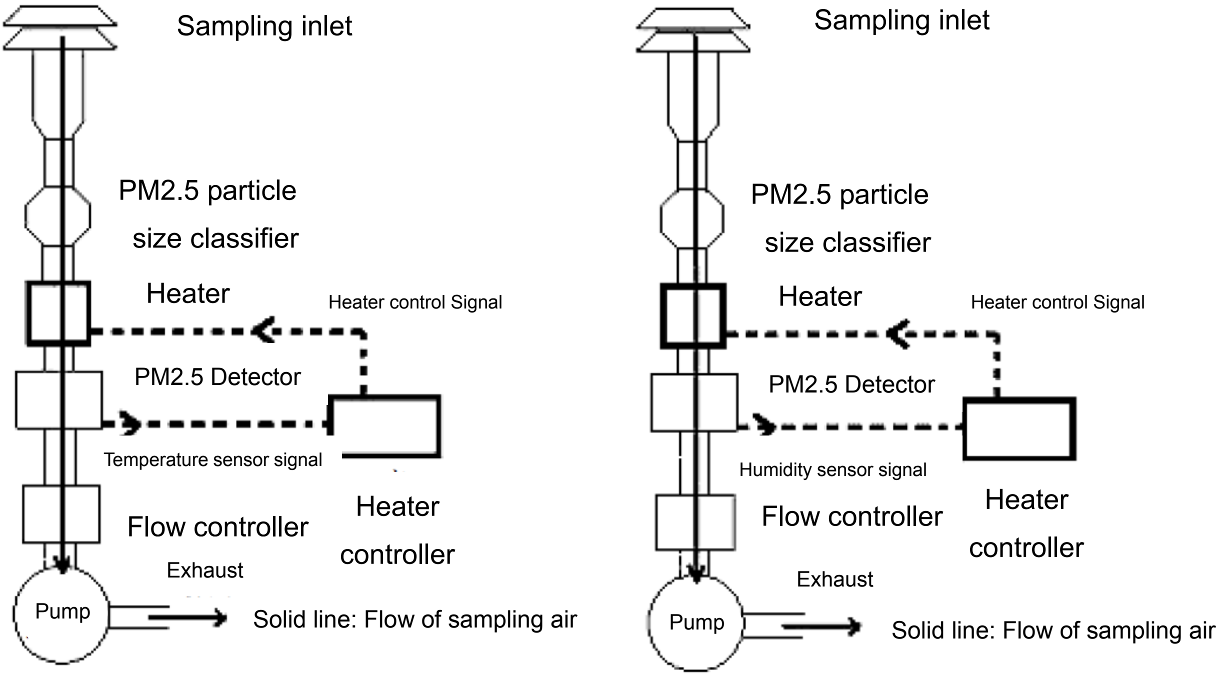
The data of the thermometer and the hygrometer are recorded on the internal memory of the PM automatic monitor in many cases. The recorded data are useful to check whether the dehumidifier system has worked exceeding the usual range, and to judge the reliability of measured values. The detailed specifications of each dehumidify method is described as follows.

(1) Heating method

It is the method for decreasing the relative humidity by heating of the sampling tube from the inlet to the detector with a heater. The following three methods are adopted depending on the model.

A The relative humidity inside of the sampling inlet or near the filter is measured by the sensor, and then the humidity is controlled to achieve the value less than or equal to the predetermined (35%, 40%, 50%, etc.) by heating.
B The sampling tube is always heated at the fixed temperature (35 °C or 45 °C).
C The sampling tube is heated when the humidity exceeds the certain value.

Since the mass loss is possibly caused not only by the evaporation of the moisture but also by the volatilization of the semi-volatile compounds depending on heating temperature necessary to control temperature sufficiently. The schematic diagram of the dehumidifier system by the heating method is shown in Fig.3.20.



Temperature control type

Humidity control type

Figure 3.20 Dehumidifier system by the heating method

It is necessary to confirm the operation condition of the thermometer attached, near the filter for the type A, near the PM detector for the type B, at the sampling tube for the type C. In the case of the monitor which the sensor record of each part remains in its memory, it is possible to check the record in the comparison with the record of temperature and humidity monitored by meteorological observation instruments.

The content of the routine maintenance depends on the types. As for the type A, the preset value of the humidity for starting heat is confirmed to be almost same as the humidity displayed on the monitor. The setting temperature of the heating part is confirmed to be almost same as the temperature displayed on the monitor for the type B.

As for the type C, when the humidity exceeds the setting value, the implementation of the predetermined heating schedule should be confirmed by the humidity displayed on the monitor, the ambient temperature, and the temperature displayed on the monitor. Moreover, it should also be kept in mind for the operator that temperature around the unheated sampling tube is almost the same level as the ambient temperature.

In the periodic maintenance, the displayed values of the thermometer and the hygrometer of the dehumidifier system should be confirmed by the comparison with the thermometer and the hygrometer which are officially approved or calibrated.

As for the type A and B, by the parallel measurement with the reference thermometer or the hydrometer whose sensor is set near the detector, it is recommended to confirm that temperature and humidity around the detector is almost same as the setting value.

In the case of the type C, the outputs of the thermometer or the hygrometer for ambient air are confirmed to be almost same as the values of the official approval or calibrated thermometer or hygrometer.

When the data confirmation results in re-adjustment, the monitored values after the last maintenance should be verified and judged their adoption. If those values are adopted as the reference value or accepted after correction by using any correction equation, it is always necessary to put the note which explains the reliability of those values.

(2) Diffusion tube method

This is the dehumidifier system using a tube made of hygroscopic polymer membrane (sulfone compounds with fluorinated polyolefin). The sample air and the dry air are circulated to the inside and the outside of the tube, respectively, and moisture in sample gas is absorbed alternatively and discharged. Since it is necessary to take the long passage time through the diffusion tube in principle, this method is used for the monitor which has adopted the low flow rate (3.0 L/min or 1.2 L/min) and the high sensitivity detection principle. Some models are always operating the diffusion dehumidification tube, and the others control the system circulating the dry air when the relative humidity exceeds the setting value. This system has some advantages; no power supply required; high dehumidification capability; and small loss of semi-volatile compound, however, it is cautious to have a possibility declining the dehumidification capability if high relative humidity has continued for a long time. Moreover, it is necessary to exchange parts in a certain fixed period. The schematic diagram of the dehumidifier system with the diffusion tube method is shown in Fig. 3.21.

In the maintenance of the diffusion tube method, the tubes should be replaced within one to three years in general. However, when the dehumidification capacity drops down during the operation, it should be exchanged even for less than a year. For example, a lot of water droplets on the purge filter portion without leakage is caused by the reduction of the dehumidification effect due to the moisture invasion. Moreover, the acidic circumstance tends to proceed the degradation of the equipment.

When the diffusion tube is exchanged, the monitored values after the last maintenance should be verified and judged their adoption. If those values are adopted as the reference value or accepted after the correction by using any correction equation, it is always necessary to put the note which explains the reliability of those values.

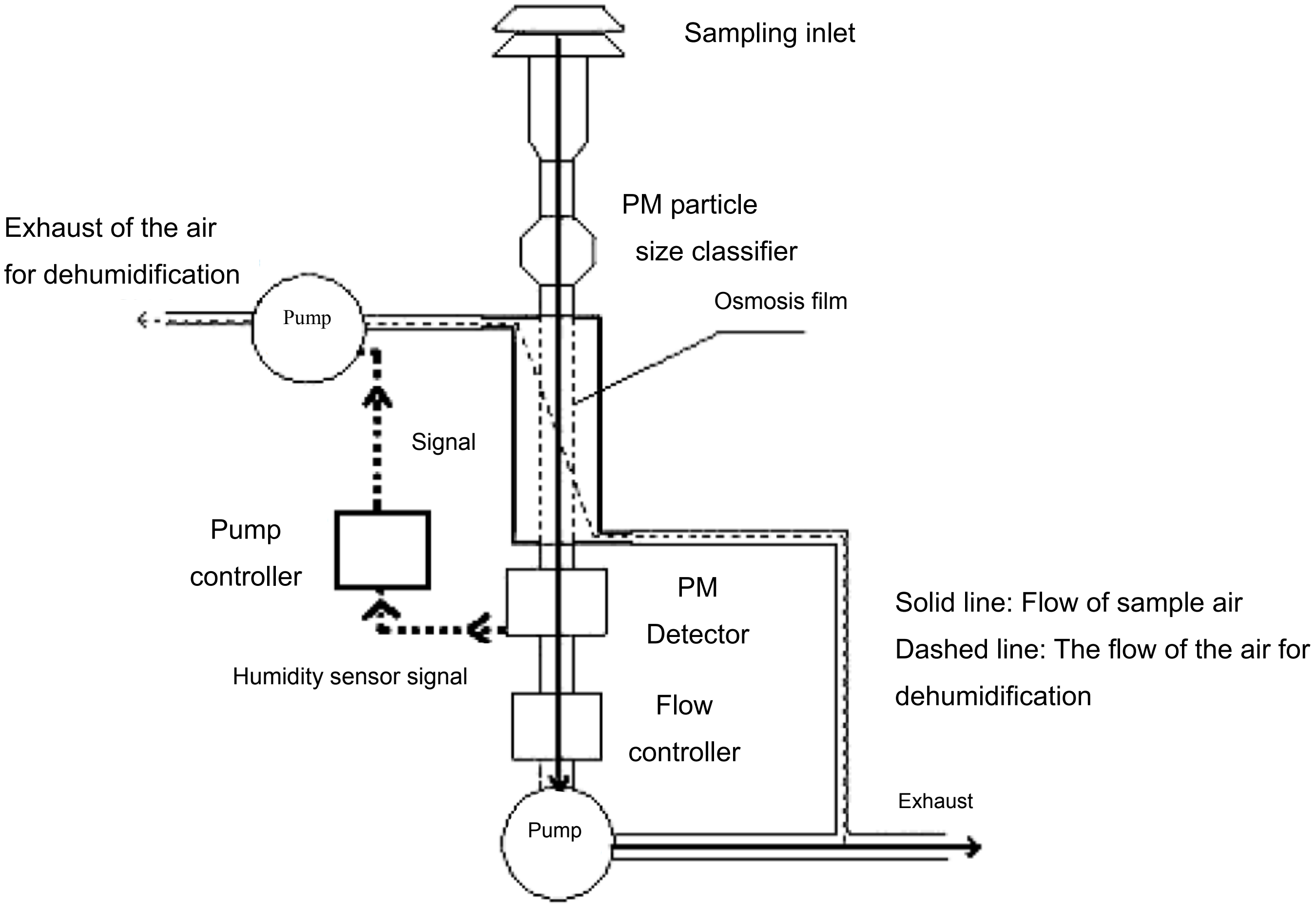


Figure 3.21 Dehumidifier system by the diffusion tube method

(3) Dilution method

This is the method to reduce the relative humidity by inflow of the particle free pure dry air into the sampling tube. The model adopted this system presently has been operated in the two steps dilution procedure. This system has the structure in which a part of sample air passed through the PM collection filter is dehumidified to produce pure dry air. After that, the air is mixed with the sample air and introduced to the detector. Accordingly, the air volume of filter passage is increased by the mixed pure dry air. As the results, it is necessary to pay attention that the PM and/or the semi-volatile compounds contained in the PM may be removed from the filter. The schematic diagram of the dehumidifier system by the dilution method is shown in Fig. 3.22.

A dilution method may use the dehumidifier system using the tube made of hygroscopic polymer membrane (sulfone compounds with fluorinated polyolefin) in the preparation of the pure dry air by the dehumidification. In this case, they should be exchanged in the same manner as the diffusion tube method after a fixed period passes.

Moreover, since it is considered that the change in the dilution rate by pure dry air has a possibility to affect the concentration, the dilution rate consistent with the setting value should be checked periodically.

When the data confirmation results in re-adjustment, the monitored values after the last maintenance should be verified and judged their adoption. When those values are adopted as the reference value or accepted after the correction by using any correction equation, it is always necessary to take note which explains the reliability of those values.

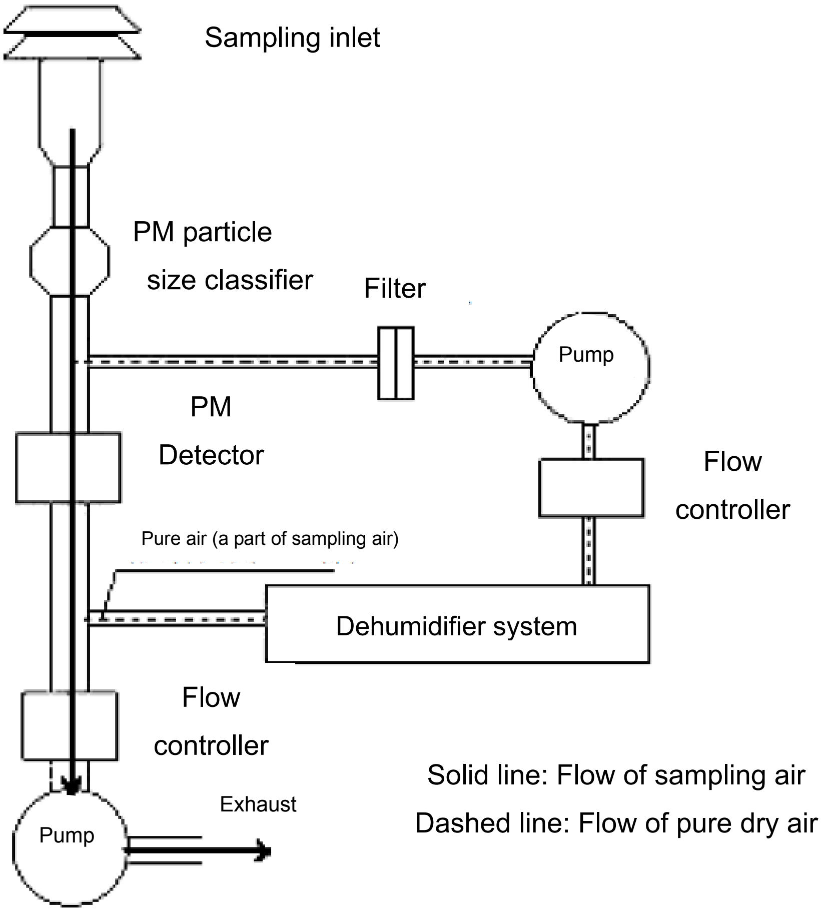


Figure 3.22 Dehumidifier system by the dilution method

3.1.4.4. Calibration of PM monitor

The calibration of the PM monitor should be carried out by the parallel measurement (dynamic calibration) with the standard method using the particle for calibration in principle. All $PM_{2.5}$ monitors should be comparable with the $PM_{2.5}$ Federal Reference Method (FRM) (U.S. Environmental Protection Agency, 1997), and the on-site parallel measurements between $PM_{2.5}$ monitors and the FRM sampler should be conducted.

However, the calibration using the equivalent input material is acceptable although it doesn't follow the dynamic calibration. It is difficult for the installation administrators and local operators to calibrate the monitor by the dynamic calibration in the periodical check and maintenance. Therefore, the static calibration using the equivalent input material is enough as the routine calibration for keeping their performance well.

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

In the case of the β-ray absorption method, as equivalent input material corresponding to the collected particle mass, an equivalent film tool which is consisted of the Maira or polyimide thin film in a cartridge is used for the static sensitivity check.

However, since the static sensitivity check is no more than the method to confirm the detector sensitivity and the operating status of the arithmetic control part, the confirmation by the parallel measurement with the standard method (FRM) under the sample air is needed to check the whole system from the sampling to the exhaust. Such confirmation by the parallel measurement with the standard method is considered as the dynamic sensitivity check. The dynamic sensitivity check should be performed by the installation administrator at the beginning of the monitoring in the monitoring station. And it should also be carried out at the opportunity of the change of the sampling air system, etc.

1) Static sensitivity check

The static sensitivity check is the method of checking whether an indicated value changes more than ±4% compared with the predetermined value by installing the equivalent film used as the equivalent input material on the filter paper, and measuring the change of the amount of the β-ray attenuation.

Since the equivalent film is very thin film of 10 μm or less, handling must be prudent so that surface dirt or crack may not be attached. Moreover, if the filter paper is damaged at insertion or extraction of the film, it would cause a filter paper crushing, so careful cautions are required. Some models have the function which the static sensitivity check is performed automatically and periodically, and the results are recorded.

Although it is usually confirmed that a measured value of the equivalent film is within the fixed range, when the span coefficient is changed, the average value of the repetition measurement of the equivalent film should be used taking the probable error of the β-ray radiation measurement into account.

In addition, as the large systematic error might be produced if the span coefficient is changed without noticing dirt and crack of an equivalent film, and thus one must take extra care for the equivalent film. It is also effective to check by using two or more equivalent films.

Moreover, some cracks and dirt are attached on the film in many cases during repeating use, so the film is recommended to be renewed at that time.

2) Dynamic sensitivity check

The PM monitor is operated for sample air simultaneously with the low volume air sampler method which is the standard method (FRM) and three or more data sets should be obtained in the period of 2 or 3 days. For those data sets, it is confirmed that the differences between the measured value and the value of standard method are within ±10 $\mu g/m^3$ or ±10%.

When the difference does not exceed the criteria but the monitored value shows systematically low in comparison with the value of the standard method, any loss due to the sampling tube should be checked and improved if needed.

The following points should be cared in the implementation of the dynamic sensitivity check.

i. When selecting a position in which the low volume air sampler is set, the position of the sampling inlet should be determined carefully to minimize the difference of concentrations between the PM monitor and the sampler.

ii. Regarding the sample collection filter paper of the low volume air sampler, it is recommended to use tetrafluoroethylene resin (Teflon) filter, quartz fiber filter, or glass fiber filter with surface treatment processing. And those filters are required to fulfill the following condition; initial collection efficiency of 99.7% or more for 0.3 μm particle; low initial pressure loss; little pressure loss in particle collection; little hygroscopicity; little absorption of acidic gas; sufficient strength on handling. Size classifier should be used in the clean condition to prevent the change in the size classification characteristics.

iii The low volume air sampler used for the check should be beforehand calibrated with the standard flow monitor.

iv In addition, as for the model which uses a finite difference pressure valve, it should be used after the adjustment and the confirmation that the actual flow rate is maintained in 20L/min until the marginal difference pressure.

v For the model required the correction of the indicated value according to the increase in difference pressure and the sample air temperature, the sample collection shall be done in the manner that the actual flow rate is always adjusted in 20L/min after correction.

3) Dynamic calibration

The mass concentration of the calibration air including the particle for calibration discharged from the particle generator is beforehand measured by the low volume air sampler, and the relationship between the setting value of the calibration air and the measured mass concentration should be grasped.

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

In the dynamic calibration, the linearity is also checked with the several points of mass concentration including zero and some other concentrations in the measurement range.

The indicated value of the calibration air is evaluated as the following. After zero and span check, the calibration air with the concentration of around 200 $\mu g/m^3$ is put into the monitor and the indicated values are recorded. Then the percentage of the difference between the indicated value and the setting value of the calibration air to the full scale is calculated.

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

1) Dynamic sensitivity check

Since the filter oscillation method theoretically has detected mass directly the dynamic sensitivity check is performed by the check of the filter or element oscillating coefficient calculated by the method shown in the equation 3.14. The variation of the calculated coefficient is required within 5%.

$$K_0 = \Delta m \,/\, (1/f_1^2 - 1/f_0^2) \qquad (3.14)$$

K_0 : 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 dynamic check of the automatic monitor using the ambient air is performed by the comparison with the standard filter method. The remaining sample passed through the isokinetic distributor equipped in the automatic monitor is collected by the filter. The filter is treated according to the standard method in which the filter is weighed by using the precision balance under the prescribed conditions of temperature and relative humidity. The differences between the automatic and standard method is required within 10 μg/m^3 or 10%.

3) Dynamic calibration

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

3.2. DOAS measurement

3.2.1. Principle of DOAS

(1) 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 as well as under simulated atmospheric conditions. Several important atmospheric trace gases such as OH, HONO, NO_3, BrO, IO were measured for the first time using DOAS. Then, a large number of other molecules absorbing the light in the UV and the visible wavelength region, e.g. NO_2, NO, NH_3, ClO, O_3, SO_2, CS_2, 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, NO_3, 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. Several types of DOAS are shown in Fig. 3.23. The LP-DOAS is the most popular one by using the artificial light source and is able to measure concentrations of gases at one dimensional scale (up to several km). The passive DOAS (e.g. MAX-DOAS) uses natural light source without artificial light source and is able to measure concentrations of gases over two dimensional scales.

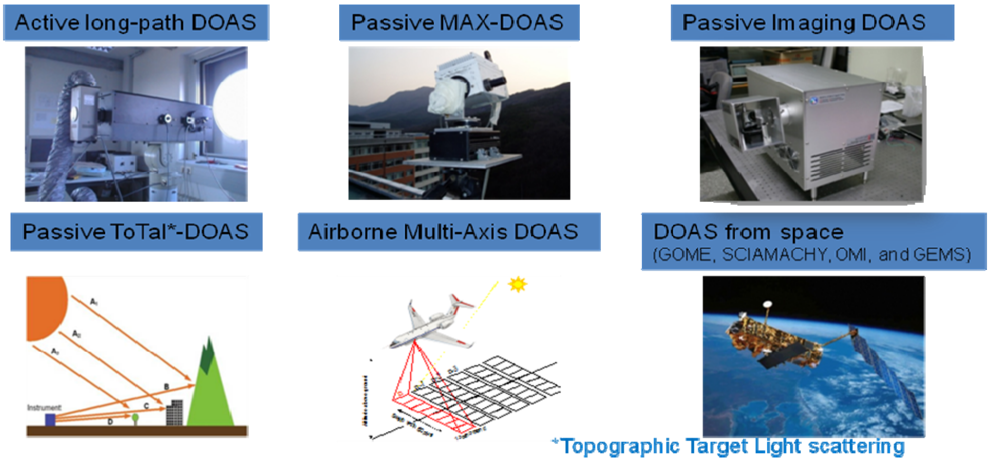


Figure 3.23 Types of DOAS instruments

(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 exited and therefore absorb radiation energy (Fig. 3.24). This process is described by the Lambert – Beer law as shown in the equation 3.15.

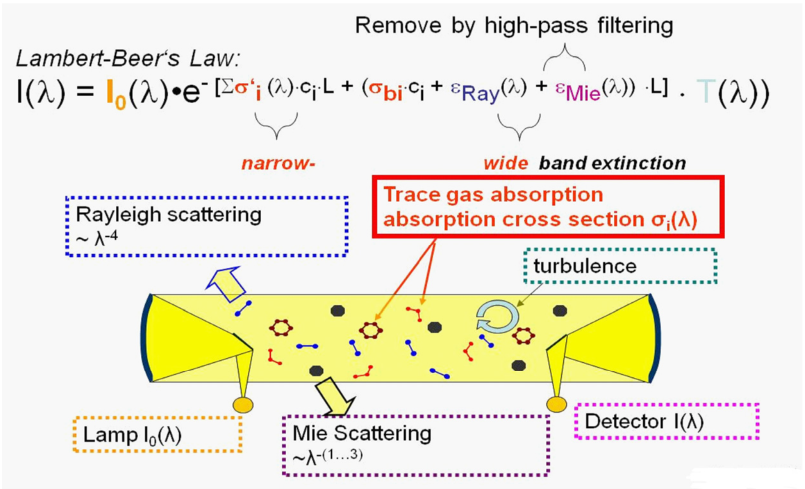


Figure 3.24 Differential Optical Absorption Spectroscopy (DOAS) principle

$$I(\lambda)=I_0(\lambda)\exp\left(-\int_0^L\left(\varepsilon_R(\lambda,l)+\varepsilon_M(\lambda,l)+\sum_i\sigma_i(\lambda,P,T)\,c_i(l)\right)dl\right) \qquad (3.15)$$

where $I(\lambda)$: light intensity after passing through the atmosphere, $I_0(\lambda)$: intensity of the light source, λ: wavelength, ε_R (λ,l): Rayleigh-scattering coefficient, ε_M (λ,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) 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:

$$\sigma(\lambda) = \sigma_{broad}(\lambda) + \sigma'(\lambda) \qquad (3.16)$$

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 Fig. 3.25), 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.

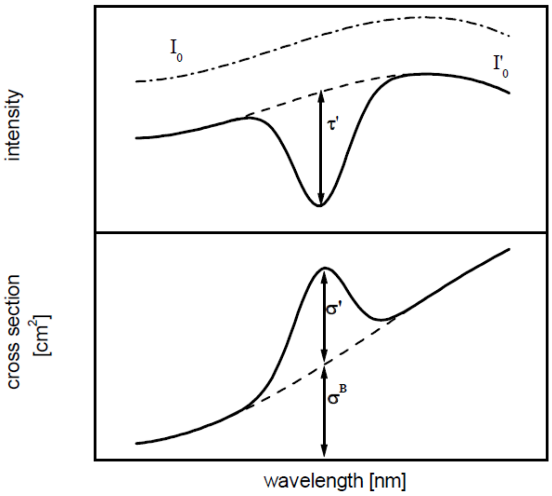


Figure 3.25 Principle of DOAS The absorption is broken down into two contributions. One is slowly varying in wavelength, while the other shows rapid variations in λ (Platt, 1994). The differential absorption τ' corresponds with the differential optical density σ'.

"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 NO_3 radical 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.

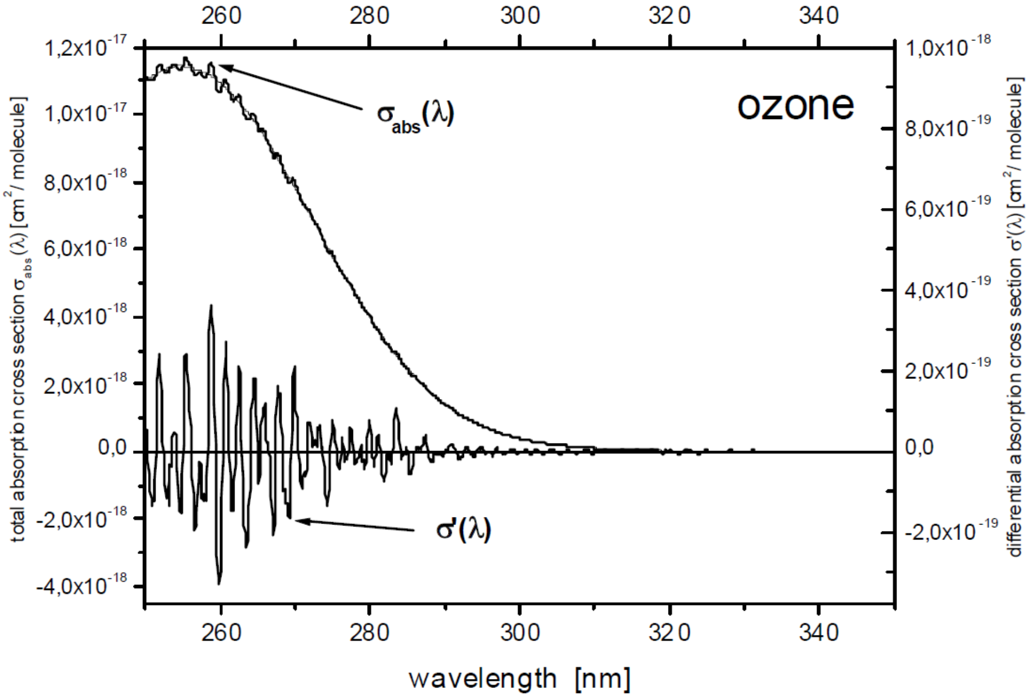


Figure 3.26 Absolute (σ) versus differential (σ') absorption cross section of ozone Note the different scales on the left hand (σ) and on the right hand side (σ').

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. Fig. 3.26 shows the absolute and differential absorption cross section of ozone.

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 3.1 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 3.1 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}
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. Fig. 3.27 clarifies this process by the example of the NO_2 cross section in the wavelength range of roughly 334–375 nm used for the evaluation of the long-term measurements.

A variety of differential cross sections used for LP-DOAS measurements is shown in Fig. 3.28. Of special interest for this study are the cross sections of NO_2, HONO, HCHO, O_3 and O_4. These cross sections are already convoluted to the typical resolution of the LP-DOAS instrument and high-pass filtered by the algorithm specified above.

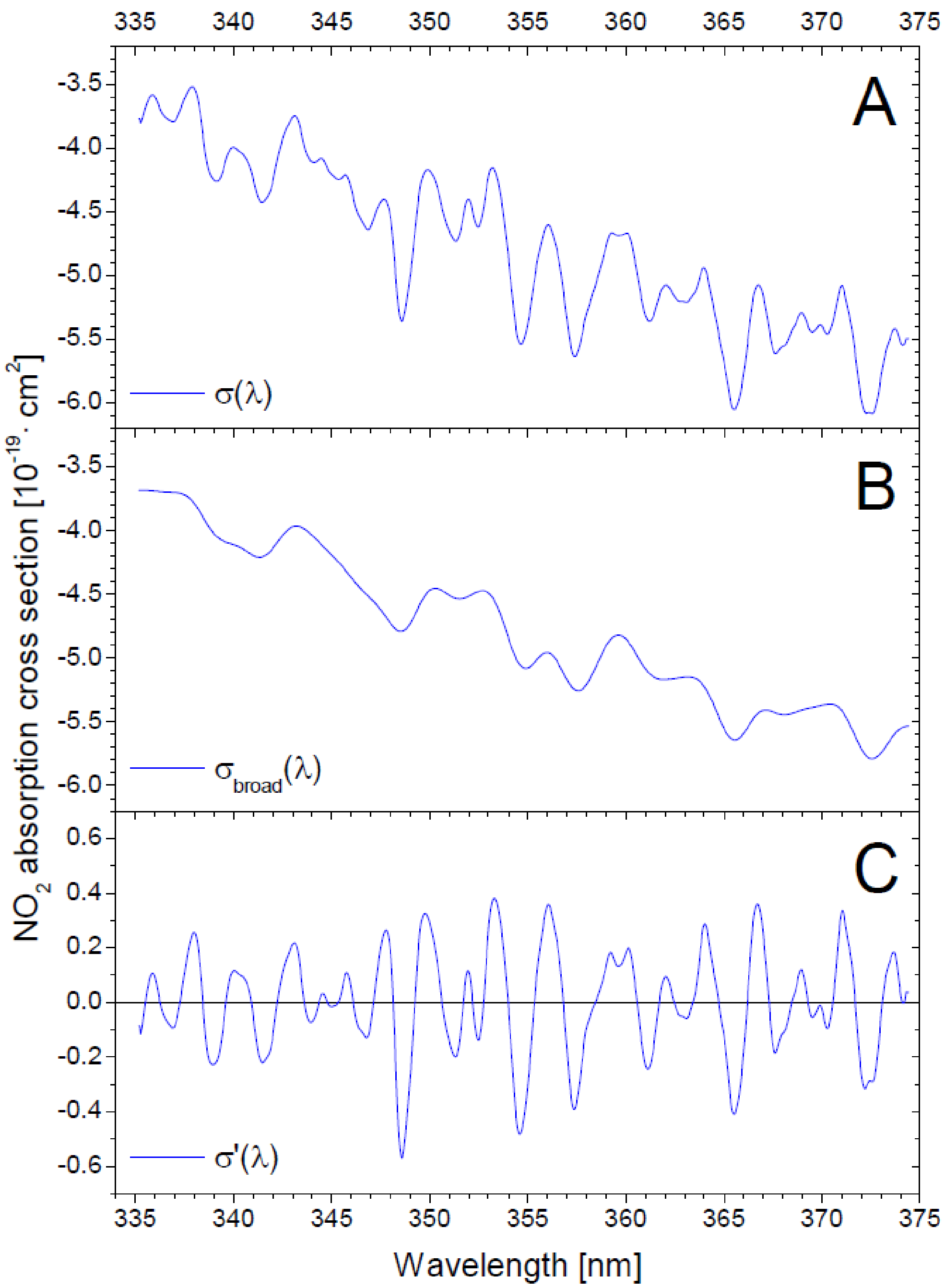


Figure 3.27 Effect of the high-pass algorithm on the total absorption cross section (panel A), exemplified by the NO_2 cross section

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).

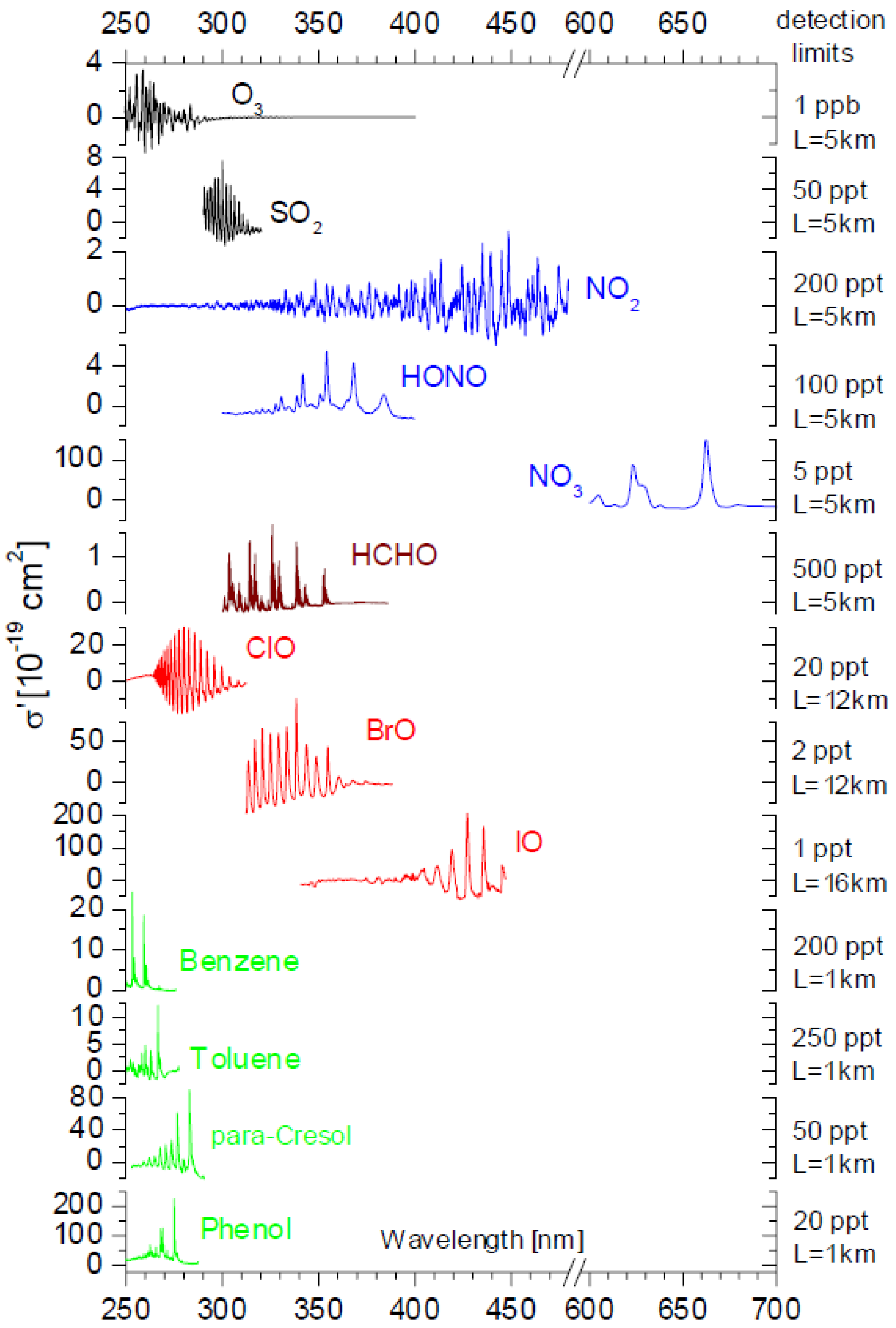


Figure 3.28 Differential absorption cross sections $\sigma'(\lambda)$ of selected atmospheric trace gases measurable by the DOAS technique

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) Gas measurement by LP-DOAS

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 (Fig.3.29).

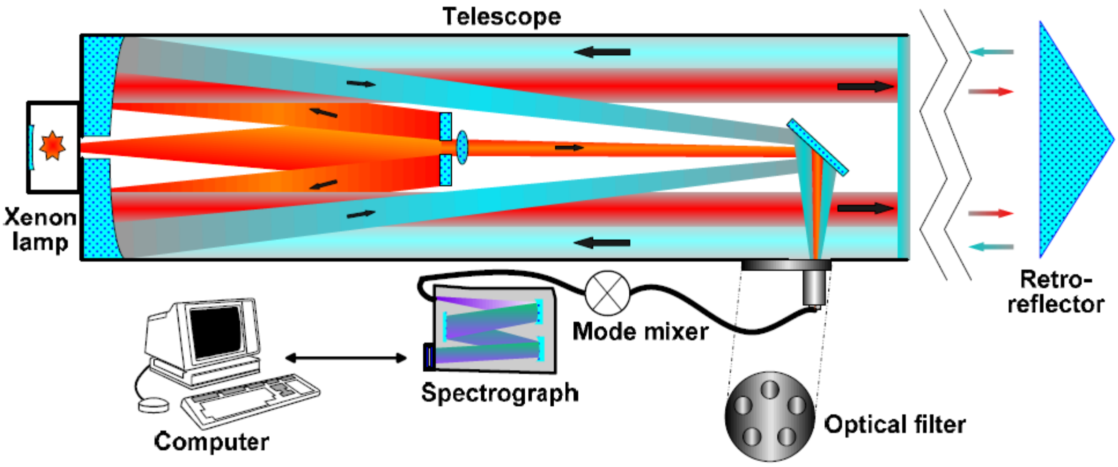


Figure 3.29 Schematic drawing of the LP-DOAS system

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 it 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 the Xe arc lamp is the 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 the Xe 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. Typical characteristic parameters of lamps for the LP-DOAS are described in Table 3.2.

Table 3.2 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 the 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 Fig. 3.29). As can be seen in the Fig. 3.29, 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 up to 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). Due to this heterogeneous illumination of the grating, 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 (e.g. TRIAX320, Jobin Yvon Spex Horiba Inc.) with a 320 mm focal length has three gratings that are interchangeable and PC-controllable. 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 (e.g. model S3904, Hamamatsu Photonics K.K., 2.5×25.4 mm dimensions, 1024 pixels) was used for the signal reading. The PDA detector is usually 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.

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 de-creases 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.

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 as shown in the equation 3.17.

$$\lambda(j) = 374.41\ \mathrm{nm} - (0.0375\ \mathrm{nm} \cdot j) - (8.3 \times 10^{-7}\ \mathrm{nm} \cdot j^2) \qquad (3.17)$$

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.

Offset

The mean offset was determined by adding up 1000 scans taken at the minimum integration time (100 ms) at dark conditions. 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 seconds with a single scan in dark conditions. The resulting dark current spectrum contains only the signal generated by thermal transitions of electrons in the conducting layer. 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.

Residual Noise

The residual noise of one spectrum consists of two different noise signals: (1) 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. (2) 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.

3.2.2. NO_2 monitor

As described above, the LP-DOAS system consists of a photodiode-array detector coupled with a spectrometer, a coaxial telescope, a set of seven retroreflectors, and an electronic control system. A spectrometer, a conventional czerney-turner type, with a holographically grooved grating, blazed at 330 nm with 1200 grates/mm, was used to measure the trace gas species (NO_2, SO_2, O_3, and HONO) in each respective ultraviolet (UV) region. The instrument is periodically calibrated using the Hg emission spectrum. The spectral resolution is less than 0.3 nm (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 NO_2 in the wavelength range 425–450nm 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 determined by two spectra shown in the equation 3.18,

$$D'_{\mathrm{meas}}(\lambda_k) = \ln\left((I_0(\lambda) / I(\lambda)\right)' \qquad (3.18)$$

the respective values (c_i, a_j) of ith 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 as shown below:

$$\left|\sum_k \left\{ D'_{\text{meas}}(\lambda k) - L\left(\sum_i c_i \sigma'_i(\lambda_k) - \sum_j \alpha_j \lambda^i{}_k \right) \right\}\right| = \text{Residual} \qquad (3.19)$$

Here $\sigma_i(\lambda_k)$ denotes the differential cross-section of the ith trace gas at the wavelength of the kth pixel of the photodiode. The residual term shown in the equation 3.19 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).

3.2.3. O_3 monitor

As well as NO_2, O_3 could be evaluated in the measured data by substituting the relative measurement reference with an absolute reference and including O_3 in the fit between 276 and 288 nm. Due to interferences in the DOAS retrieval, it is not possible to obtain dependable O_3 values at SO_2 column densities above 2×10^{18} molecules/cm^2. Therefore, spectra with these extreme SO_2 absorption values were omitted in the O_3 retrieval.

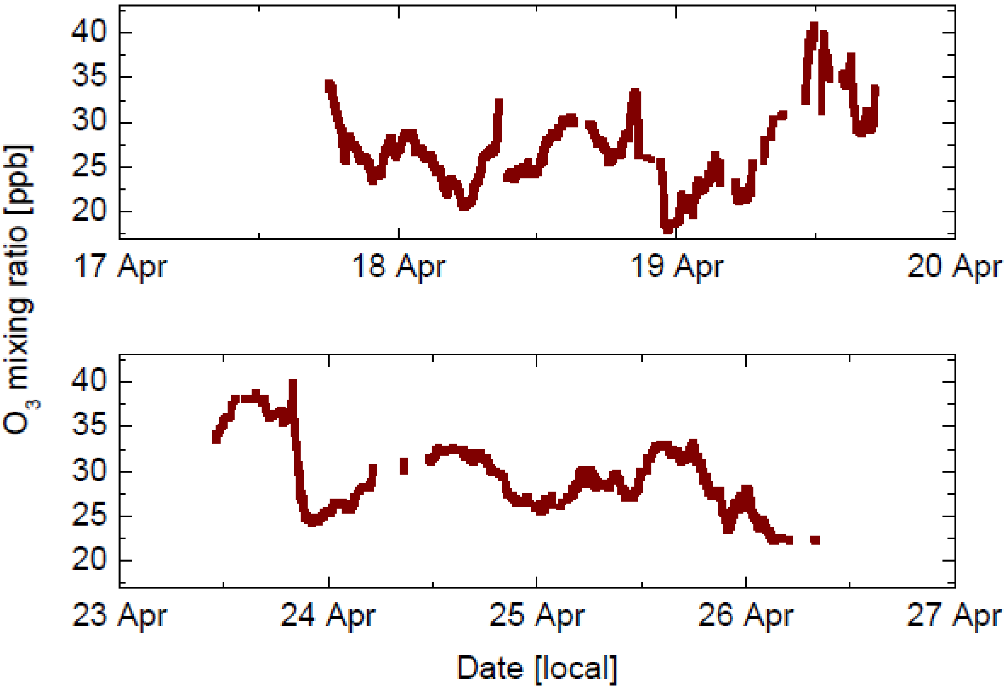


Figure 3.30 Average O_3 mixing ratio along the measurement light path for the two time periods in which the night-time measurements took place (April 17 – 20, 2007 and April 23 – 27, 2007)

Fig. 3.30 shows the average O_3 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 O_3 mixing ratios varied between 20 and 40 ppb, with the higher values typically occurring during daylight hours.

3.2.4. Evaluation procedure

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

i. Correction of offset and dark current in the lamp reference spectrum.
ii. High pass filtering, application of the logarithm and smoothing of the lamp spectrum.
iii. 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.
iv. Correction of offset and stray light (by offset-corrected atmospheric stray light spectrum) in the atmospheric absorption spectrum.
v. High pass filtering, application of the logarithm and smoothing of the atmospheric absorption spectrum.
vi. 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. NO_2 cross section convoluted from (Voigt et al., 2002)
2. HONO cross section convoluted from (Stutz et al., 2000)
3. HCHO cross section convoluted from (Meller and Moortgat, 2000)
4. O_3 cross section convoluted from (Voigt et al., 2001)
5. O_4 cross section interpolated from (Hermans et al., 1999)
6. SO_2 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 NO_2 fit to exclude arbitrary shifting and squeezing due to small absorption structures. For the O_3 reference, permitting a shift or squeeze decreased the quality of the fit and was therefore denied. The correct wavelength scale calibration for the NO_2 and HCHO references was deduced from reference cell measurements. This was not possible for HONO and O_3 due to the lack of suitable reference gas cells, but for both trace gasses no significant shift versus the NO_2 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.

3.3. Meteorology

3.3.1. Objectives

A weather survey is the important item in order to grasp a natural phenomenon, and daily survey is important to understand long-term change of an atmospheric state. Some surveys are aimed for grasping change of natural phenomenon in a relatively wide area, and other surveys for obtaining the data of an air pollution phenomenon elucidation. In the air pollution continuous monitoring, it is required to grasp the weather change at short range near the ground from the toxic substances emitted in the air being spread with various forms according to a climate condition. Moreover, the surveys of variations of local wind direction, wind velocity and temperature are also important for the measure against air pollution in an emergency.

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

3.3.2. Wind direction anemometer

A wind is denoted by vector quantity of wind direction and wind velocity. Because the wind direction and wind velocity in the environment are changed continuously, the hourly value is usually obtained by the average value for the last 10 minutes on the hour. Wind direction shows where the wind blows from, and it is shown by the clockwise rotation angle which makes 16 directions. The north direction denotes 0 degrees. Wind velocity is the distance which the air moves in unit time. It is measured in m/s unit and to be recorded up to 0.1 digits.

Although there are many kinds of the meteorological instruments for monitoring wind direction and wind velocity, the windmill type wind direction anemometer and the ultrasonic type wind direction anemometer are generally 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 including a synchronization, a potentiometer, or a rotary light encoder type directly linked with the axis of the tail, is carried out, and the wind direction is outputted in the range from 0 to 540 degree covering the direction, NESWNES (Fig. 3.31).

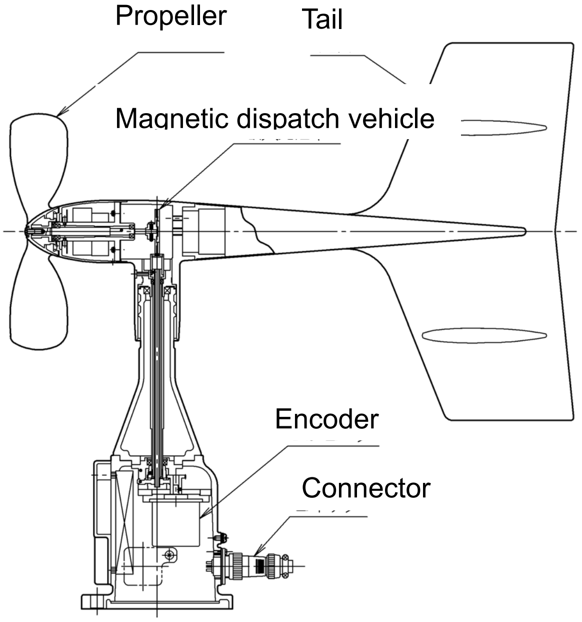


Figure 3.31 Example for Windmill type anemometer

B Wind velocity

The power generation type outputs 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 results of pulse counts proportional to wind velocity during rotation of the propeller by a wind.

The rotary light encoder type (5 bits or 8 bits) and the magnetic system are used for the wind direction, and the pulse type (a magnetic pulse, a lightwave pulse) is used for the wind velocity.

2) Ultrasonic type

The ultrasonic type measures the speed of the sound which spreads in the air changing with wind velocity and temperature. The wind direction and the wind velocity are outputted by the vector composition of each propagation time of the X-axis (horizontal) and the Y-axis (vertical direction), measuring the speed of the ultrasonic wave of the high frequency which is not felt for human and spreads in the air.

Generally, the speed of the sound wave signal which mutually transmitted between the two points on the horizontal surface in the air is determined by the wind velocity component of the direction of the two points and by the speed of sound in the still air.

For example of an typical ultrasonic type wind direction anemometer, the sum and difference of the time, when the 100 kHz ultrasonic wave is mutually transmitted between the transducers which are located at the fixed distance of 20 cm, are measured.

By using the 2 sets of transducers intersected perpendicularly, and installing them in the direction of east and west and in the direction of north and south, the east-west component (X component) and a north-south component (Y component) of the wind are measured simultaneously, and a wind direction and a wind velocity are obtained by the vector composition. Moreover, some anemometers can perform observation of a three-dimensional wind by installing a transducer also in a vertical direction.

(2) Installation criteria

1) Installation place

According to the World Meteorological Organization (WMO) criteria, the wind direction anemometer should be set in the flat and opened place which does not have an obstacle in the surroundings. A panzer mast or a support pole should perpendicularly set at the 10 m height on the ground.

When the height at 10 m is not securable, or when the representative place is not obtained, it is desirable to select a setting place as follows. However, convenience of the maintenance should be considered at the selection of the installation position.

i. The highest place of the roof is ideal, and the influence from the structure of the roof should be considered.

ii. The influence of upward blowing near the outer wall of the roof and its circumference should be avoided.

(A transmitter is installed at the angle of 40 degrees or more against the roof side at which a downward wind produces.)

iii. The standard height 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 as shown below.

A By using a magnet compass

Compass is put on the place which is not close metal and ferroconcrete buildings, and does not have disorder of geomagnetism. The direction of "N" is temporarily appointed at north, and then the gap angle of north and magnetic north should be corrected. In north east Asia, the deflection angle (the west deflection) can be determined by the following empirical formula calculated from the latitude and longitude of an observation place.

$$D = 7°5'45+21'03\mathit{\Delta}\varphi - 5'84\mathit{\Delta}\lambda - 0'360\mathit{\Delta}\varphi^2 + 0'274\mathit{\Delta}\varphi \cdot \mathit{\Delta}\lambda - 0'470\mathit{\Delta}\lambda^2 \qquad (3.20)$$

D : the west deflection angle

$\mathit{\Delta}\varphi$: $\varphi - 37°$N（φ denotes latitude in degree unit）

$\mathit{\Delta}\lambda$: $\lambda - 138°$E（λ denotes longitude in degree unit）

B By using the high resolution map

Prepare the high resolution local map, and the object on the known azimuth line as far as possible from the anemometer is defined on the map. Then, the direction is set according to the object.

C By using the solar position

There are two methods. One is to determine north and south by the shadow made by hanging a weight exactly at noon. Another is to determine the true azimuth by the special measurement equipment on a flat plate and measuring projection, latitude, longitude and time.

(3) Maintenance protocol

Since the sensing part of the wind direction anemometer is installed in the outside, and it always runs continuously, the maintenance of a meteorological instrument is also important for measurement accuracy as well as the maintenance of a monitoring station.

The maintenance consists of the "daily check" for checking normal operation of meteorological instruments and "periodical check" for maintaining measurement accuracy.

1) Daily check
   - i. The existence of abnormalities is visually checked for the appearance of the transmitter.
   - ii. Abnormalities of directions and record are checked.
   - iii. There is no gap between the indicated value of anemometer and a compass.
   - iv. Input signal cable is removed, and the zero signal of wind velocity is checked.

2) Periodical check

Usually periodical check is implemented by the maintenance contractor. It is necessary to conduct not only the comparability test with the standard conversion output but also the performance test of external outputs, such as indicated values, record values, and telemeter output.

3.3.3. Thermometer

Air temperature is greatly changed by time, the place, and the height. In particular, the difference from the state of surface, such as a concrete ground, a bare ground, and a grass ground, and the temperature gradient around the ground may largely affect observation results. Therefore, unless the observed values are obtained under the same conditions, comparison of the data is difficult. In the case of air monitoring stations, there are few cases attain the stable condition, so one must be careful to use the temperature data. The unit of the temperature is ^{o}C and to be recorded up to 0.1 digits. There are a number of types of thermometer, but the electric resistance type thermometer using a platinum thermo sensor is used for the air monitoring station.

(1) Principle of measurement

A platinum resistance temperature sensor is used for the electric resistance type thermometer. This sensor utilizes the principal that metal resistance is changed by temperature. Temperature can be determined by measuring electrical resistance.

The platinum resistance temperature sensor is formed of a coiled platinum wire of diameter approximately 0.1 mm around a thin mica or porcelain board, and the sensor is placed in a protective stainless steel tube, which is completely waterproof. The platinum resistance thermometer has the 3 line type and the 4 line type, which are developed for eliminating interferences of platinum resistivity.

(2) Installation criteria

The thermometer should be installed on the opened lawn ground where there is no shade of buildings and trees. The ground should be treated as good water drainage. A wooden Stevenson screen or a vent sleeve is installed on the observation ground, and the thermometer is contained inside.

1) The case of using vent sleeve

   The thermometer is contained in the vent sleeve with the ventilating device. The height of the air inlet of the vent sleeve is set to 1.5 m above the ground. When it is installed in a building, it should be set at the height which is not subject to the influence of reflection or radiation.

2) The case of using Stevenson screen

   The Stevenson screen is made of wood and can protect the meteorological instrument from solar reflection and radiation. The leg is buried and fixed on the ground so that the height of leg comes out at 1 m above the ground. However, in heavy snow areas, the leg height must be higher according to snow coverage. Moreover, the front door should set at north so that sunshine is not be irradiated the inside. A thermometer should be installed at 1.5 m above the ground.

(3) Maintenance protocol

1) Daily check
   - i. A piece of paper is brought to the inlet of the vent sleeve to confirm the ventilating device properly working. It should be also cautious of the dust and the freeze on the sleeve.
   - ii. The Stevenson screen should be kept clean from dirt by rain and sand and a cobweb, etc.
   - iii. The external output and recording status are checked.
   - iv. Comparison test with the Assmann Type Psychrometer should be performed to confirm that the difference between them is less than ±0.5 ^{o}C. Because the Psychrometer is affected by solar radiation, the comparison test should be conducted on a cloudy day.
   - v. 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) Periodical check
   - i. The signal cable is disconnected from the input terminal of converter, and the resistance of the sensor is measured to confirm the prescribed value.
   - ii. It is necessary to apply the pseudo resistance to thermometer and conduct the performance test for external outputs such as indicated values, record values, and a telemeter outputs. Usually this periodical check is implemented by the maintenance contractor.

3.3.4. Hygrometer

There are some parameters indicating the water vapor contents in the air such as relative humidity, absolute humidity, vapor pressure and dew point, but relative humidity is most widely used. Although a hair hygrometer and a dew point hygrometer was used formerly, but an electrostatic capacity type hygrometer is widely used in the air monitoring because it can be installed together with a thermometer in the same vent sleeve.

1) Relative humidity

Relative humidity is expressed the ratio of vapor pressure (e) and the saturated vapor pressure at the measured temperature (E) with the percentage of $e / E \times 100$. It is represented by an integer with an unit of %.

2) Vapor pressure

The vapor pressure is defined as the partial pressure in the air. The saturated vapor pressure is defined as the pressure in the state of thermodynamic equilibrium between the water or ice phase and the air at a certain temperature. The unit of vapor pressure is hPa and it is recorded up to 0.1 digits.

3) Dew point

If the air is cooled under the constant pressure, the water vapor will be saturated at a certain temperature, and then water condensation and dew formation occur. The temperature is called the dew point temperature with an unit of degree and to be recorded up to 0.1 digits.

(1) Principle of measurement

1) Electrostatic capacity type hygrometer

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

2) Dew point type hygrometer

Due to the hygroscopicity of a lithium chloride (LiCl), there is a relationship between the LiCl solution and vapor pressure. The dew point is measured by the temperature when the ambient vapor pressure is equal to the saturated vapor pressure of LiCl solution. However, there is restriction that the dew point cannot be measured below the ambient pressure.

3) Hair hygrometer

When the humidity in the air changes, a hair stretches depending on humidity. Because the extension rate of hair varies almost logarithmically with the relative humidity between 20 to 100%, the relative humidity can be determined.

(2) Installation criteria

Basically, the hygrometer should be place as the same condition of the thermometer described in of the Section 3.3.3. The installation height is 1.5 above the ground. In general, a hygrometer is placed in a Stevenson screen, whereas it should be placed in a small-type screen equipped with the ventilation device if the space is limited. When an electrostatic capacity type hygrometer is used, it is stored in the vent sleeve by together with the thermometer.

(3) Maintenance protocol

1) Daily check

Daily check should be conducted according to each observation method.

A Electrostatic capacity type hygrometer

The dirt of the membrane filter which protects the sensor is checked. When sea salt particle, dust, or smoke is deposited on the filter, it is removed from the sensor unit and washed by distilled water, then dried in air.

B Dew point type hygrometer

At heavy polluted area and coastal area, the frequency of LiCl replacement would be more. Therefore, it is important to conduct comparison measurement between the Assmann Type Psychrometer and the hygrometer.

C Hair hygrometer

The dirt of hair is checked and it is carefully cleaned with a feather to remove sand and smoke, etc. When the dirt is remarkable or it is used for several months, the hair should be cleaned by using a brush immersed with distilled water, and then dried in air.

2) Periodical check

Because the maintenance requires skillfulness and specific knowledge, the periodical check should be conducted by the maintenance contractor. It is necessary to carry out not only the comparability test for sensor and signal converter, but also the test for external outputs, such as indicated values, record values, and telemeter outputs.

3.3.5. Actinometer

The solar radiation is defined as the quantity of the solar energy irradiated into the plane per unit area near the ground. Because the solar radiation largely affected by water vapor, dust and cloud, it is evaluated as integrated amounts during a certain period. The unit of solar radiation is kW/m^2 for the instantaneous value and MJ/m^2 for integrated value.

1) Direct solar radiation

The direct solar radiation is defined as the amounts of solar radiation directly transmitted from the sun. It can be measured during sunrise and sunset. Supposing the atmosphere does not exist in the earth, the direct radiation from the sun would be almost constant because it is determined only by solar activity and the distance from the sun. This amount, so-called the Solar constant, is 1.38 kW/m^2 for the instantaneous value and 5.0 MJ/m^2 for the integrated value.

2) Global solar radiation

The global solar radiation is defined as total solar radiation irradiated into the plane per unit area. The global solar radiation includes direct solar radiation, the dispersion solar radiation from all sky, and the reflective solar radiation from cloud. It is slightly observed also before sunrise and after sunset.

3) Dispersion solar radiation

The dispersion radiation is defined as total solar energy dispersed by atmospheric molecules, water vapor and aerosol etc irradiated into the plane per unit area. The direct solar radiation is not included.

(1) Principle of measurement

The actinometer uses the characteristics that the temperature of the object rises by the absorption of the heat of the energy when it receives solar radiation. A thermopile is connected between the acceptance surface (warm junction) and the thermal reference point such as an outer shell (cold junction), and the difference of temperature between both junctions are measured, and then it is converted to solar radiation.

(2) Installation criteria

The actinometer should be installed on the rooftop or the plain field where direct solar radiation is not interrupted at any times and where no obstacles such as buildings, trees, antennas, and plume sources exist. If there is no ideal installation place, one must select the place in which the effect from surroundings should be as little as possible. Moreover, it is necessary to consider convenience for a routine check and maintenance.

(3) Maintenance protocol

1) Daily check

  i. Any dirt on the glass dome covering the acceptance surface is checked and the dome should be cleaned, if necessary.
  ii. The moisture absorption condition of the desiccant is checked, and it is replaced, if necessary.

- iii. It should be checked that the signal increases after sunrise and becomes zero after sunset.
- iv. It should be also confirmed that the instantaneous and integrated values are less than 1.4 kW/m^2 and 5.0 MJ/m^2, respectively.

2) Periodical check
   - i. It should be checked whether there are any abnormalities on the glass dome.
   - ii. Substantial change in color and detachment of pigment on the acceptance surface is checked.
   - iii. Disconnection and loose connection in the output connector is checked.
   - iv. Confirm the external outputs, such as indicated values, record values, and telemeter outputs when the pseudo voltage equivalent to 5.0 MJ/m2 is applied.

3.3.6. Rain gauge

Precipitation is defined as the quantity of rainwater which has reached on the ground surface or the monitoring surface during a certain time, and it is expressed as the depth of rain water. The precipitation is represented as a unit of mm and to be recorded up to 0.1 digits. However, when the minimum measurement unit of a rain gauge is 0.5 mm, the amount less than 0.5 mm is round off to be 0.0 mm, and the amount over 0.5 mm and below 1.0 mm is round off to be 0.5 mm.

(1) Principle of measurement

Rainwater is introduced from a funnel through a filtering equipment and into the one side of the reversing measure (Fig. 3.32). When the one side is filled with rainwater, the gravity center moves to the opposite side, and the measure is flipped at the precipitation of 0.5 mm. The signal is counted at every flipping event, and one pulse is transmitted to the connected electric circuit.

(2) Installation criteria

It is necessary to choose the place where an air current becomes horizontal as much as possible, and it should be kept away from a sloping ground, a high ground, a depressed ground, a mountain ridge, an outer wall of a rooftop in which a wind blows up. Furthermore, it is ideal to kept away from buildings and trees at the distance of 4 times or more of those height. If it is impossible, it selects from the place where there is no obstacles at an angle of elevation at more than 30 degrees. Moreover, the rain gauge should be placed horizontally and be avoided from the rebound of rain from the ground.

Because the rain gauge is used for wet deposition monitoring in some stations, the place should be satisfied with the criteria of Technical Manual for Wet Deposition Monitoring in East Asia - 2010 (EANET, 2010).

(3) Maintenance protocol

1) Daily check

Remove garbage such as leaves and insects on the filtering equipment, other inner parts and a water exhaust pipe, and clean the inner surface of the reversing measure.

2) Periodic check and maintenance

Electronic parts such as a reed switch and connector are cleaned. It is carried out not only cleaning of a reed switch and a connector, but also check external outputs, such as indicated values, and telemeter outputs when the pseudo pulse is applied.

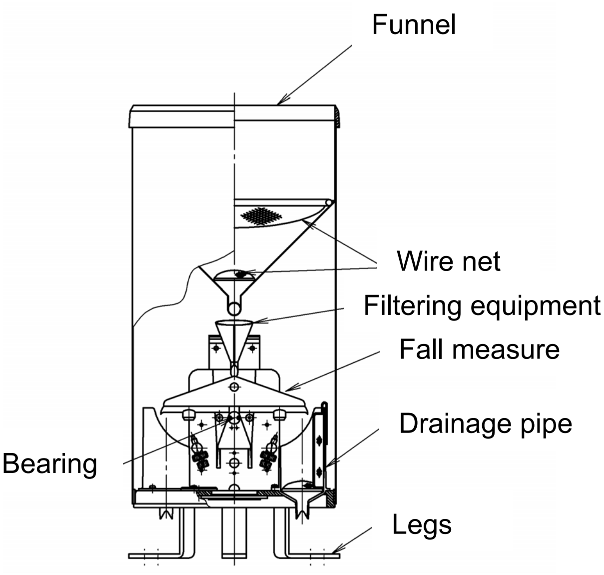


Figure 3.32 Example for fall measure type rain gauge

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4. 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. 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 occasional costs of operating the instruments. One of the possible ways to overcome this problem is to adopt the simpler, low cost methodologies such as passive samplers.

Besides mass of atmospheric particles which is measured using automatic method as described in previous chapter, the particulate components are also very important for air quality evaluation. Filter packs and denuders are the only methods to measure particulate components in this manual. The filter pack method is useful for total (gaseous and particulate) NH_4^+, NO_3^- and Cl^- monitoring, and the denuder can measure gases and particulate components separately. These methodologies are used widely in monitoring networks and for field campaigns in the world.

The advantage of filter pack is to simultaneously determine gases and chemical components in particulate matter although the problem of artifacts mentioned in 4.1.2 is remaining as agenda. Annular denuder can also determine gases and chemical components in particulate matter simultaneously without artifacts; on the other hand, the disadvantage of annular denuder is complication of handling and relatively high cost compared with filter pack.

4.1. 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). 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, the filter pack method has 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.

4.1.1. 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. 4.1. Aerosols are collected on the first filter (F0: made of PTFE), while the gaseous substances such as SO_2, HNO_3, HCl, NH_3 will pass though this filter. The second filter (F1: made of polyamide) collects all HNO_3 and partial SO_2, HCl and NH_3 from the sampling air. The remaining SO_2 and HCl react with alkali substance on the third filter (F2: made of cellulose). Oxidizing species in air such as ozone are believed to convert most of the sulfite to sulfate 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 phosphoric, citric or oxalic acid.

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 μm. For this purpose, Teflon (PTFE; polytetrafluoro-ethylene) filters are preferred.

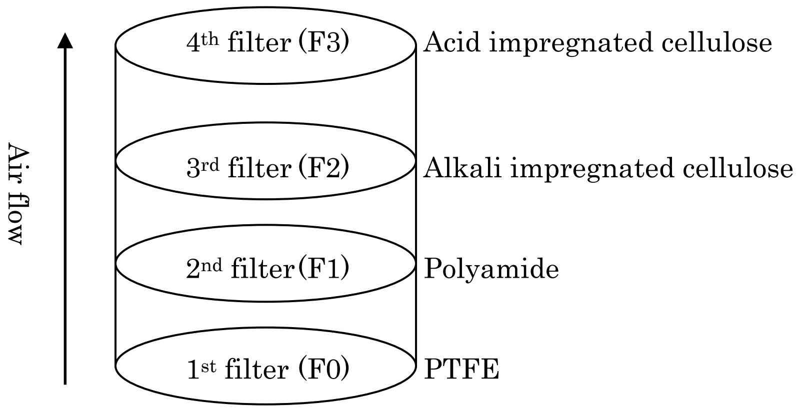


Fig. 4.1 Schematic diagram of the four-stage filter pack

4.1.2. 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. Therefore, the filter pack method is used for total (sum of gaseous and particulate) NH_4^+, total NO_3^- and total Cl^- monitoring.

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 sulfur dioxide on cellulose based filters. This gives an overestimation of the sulfate concentrations in aerosols and a corresponding underestimation of the sulfur dioxide. Another source of error could be that the absorption of sulfur dioxide on the impregnated filter is not 100% effective.

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. $NH_4NO_3\ (P) \rightarrow NH_3\ (G) + \underline{HNO_3\ (G),}$

II. $NH_4NO_3\ (P) + H_2SO_4\ (P) \rightarrow NH_4HSO_4\ (P) + \underline{HNO_3\ (G),}$

III. $NaNO_3\ (P) + H_2SO_4\ (P) \rightarrow NaHSO_4\ (P) + \underline{HNO_3\ (G),}$

IV. $NaCl\ (P) + \underline{HNO_3\ (G)} \rightarrow NaNO_3\ (P) + HCl\ (G);$

(2) Artifacts of NH_3,

I. $NH_4NO_3\ (P) \rightarrow \underline{NH_3\ (G)} + HNO_3\ (G),$

II. $NH_4Cl\ (P) \rightarrow \underline{NH_3\ (G)} + HCl\ (G),$

III. $H_2SO_4\ (P) + \underline{NH_3\ (G)} \rightarrow NH_4HSO_4\ (P),$

IV. $NH_4HSO_4\ (P) + \underline{NH_3\ (G)} \rightarrow (NH_4)_2SO_4\ (P);$

(3) Artifacts of HCl,

I. $NaCl\ (P) + HNO_3\ (G) \rightarrow \underline{HCl\ (G)} + NaNO_3\ (P),$

II. $2NaCl\ (P) + H_2SO_4\ (P) \rightarrow \underline{2HCl\ (G)} + Na_2SO_4\ (P),$

III. $NH_4Cl\ (P) \rightarrow \underline{HCl\ (G)} + NH_3\ (G).$

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

4.1.3. Specifications of filters

The filter material should not absorb SO_2 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 the 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. 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 of filters including as well as reaction and collected species for each filter are summarized in Table 4.1.

Table 4.1 Specifications of filters (EANET, 2003)

Stage	Specifications of filters	Reaction	Collected species
First (F0)	Teflon (PTFE) filter	Filtration	Aerosol
Second (F1)	Nylon (Polyamide) filter	Adsorption	HNO_3 Partial SO_2, HCl
		Neutralization by collected acid gases	Partial NH_3
Third (F2)	Cellulose filter impregnated by K_2CO_3	Neutralization by alkali impregnated on the filter	SO_2, HCl
Fourth (F3)	Filter impregnated by phosphoric acid	Neutralization by acid impregnated on the filter	NH_3

4.1.4. Sampling

1) Sampling system

A diagram showing the sampling system is given in Fig. 4.2. 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 10 μm, 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.

Regarding the sampling height of the FP system, the height should be basically the same level as that of automatic instruments described in Section 2.2.4 because all air concentration monitoring instrument is located in the same stations. Here shows the specific condition for the filter pack instrument to estimate dry deposition flux. In the case of any close obstacles in the surrounding 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 (e.g. above tree canopies).

Since the absorption of sulfur dioxide is only quantitative at relative humidity 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 humidity.

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. The leak check of the sampling system should be done more than twice a year.

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.

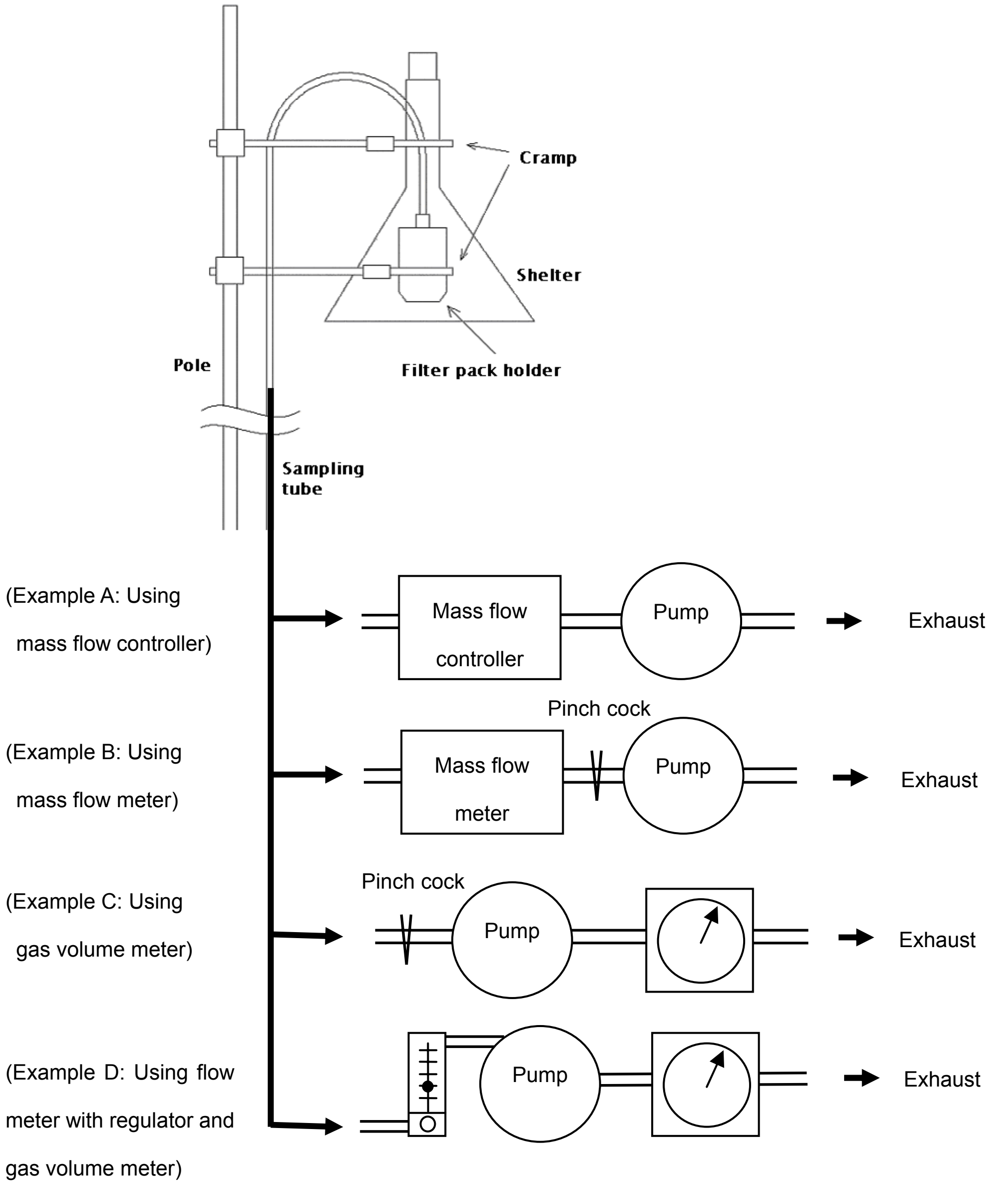


Fig. 4.2 Schematic diagram of filter pack sampling system

A diaphragm pump is recommended for stable flow rates during the sampling. If the pump is so powerful to use at 1 or 2 liter/min, it is better to make a bypass for easier flow control. It is recommended to use a mass flow controller to control the sampling flow rate (Example A in Fig. 4.2). If the mass flow controller cannot be used, it is necessary to control the sampling rate by using a pinch cock or a flow meter with regulator before the pump as well as a gas volume meter (Example C and D in Fig. 4.2).

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 the filter holder and the pump (Example B in Fig. 4.2). A gas volume meter with the flow controlling unit could be also acceptable. In this case, the gas volume meters should be installed consequently after the pump to measure flow rates and volumes under the condition of atmospheric pressure (Example C and D in Fig. 4.2).

Air volume measured by a mass flow meter or a gas volume meter is used for calculation of ambient air concentration. Accurate volume reading is important for the measurement accuracy, and the volume meter may require frequent calibrations. Unless special circumstances, calibration of the gas volume meters should be implemented once a 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 ±5 °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 record the start date and time of the sampling, and likewise the end date of time the sampling after exposure. Further details should be written into the field note if operator find special notes that may affect the monitoring results.

Recommended sampling procedure at the monitoring site is described as follows:

[At start]

1) Read the indicated value of the volume meter before sampling and record it in the field note;
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 starting date and time and the flow rate in the field note;

[At end]

4) Record the flow rate in the field note;
5) Switch the pump off and record the ending date and time in the field note;

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 with coolant;
8) Read the indicated value of the volume meter after sampling and record it in the field note.

4.1.5. Operation in laboratory

1) Mounting and transportation of filter packs

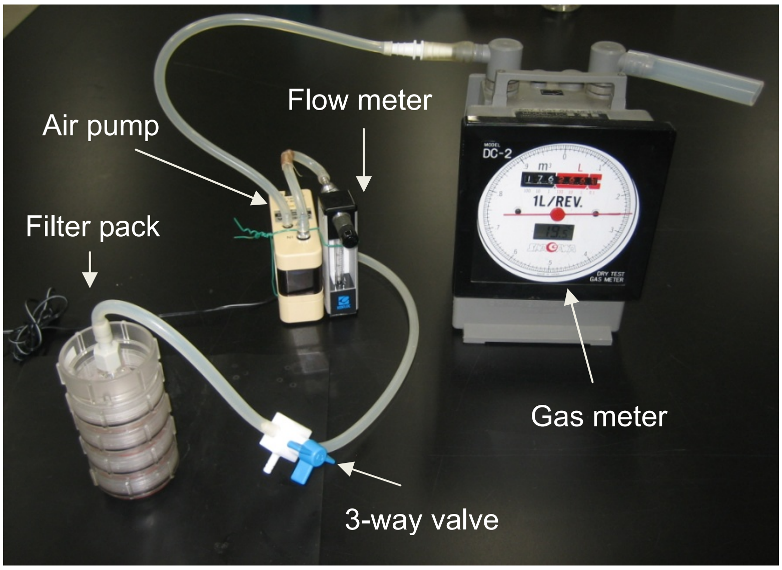
It is recommended that the filter pack is assembled and dismounted only in the laboratory. The filters are mounted on the filter holder using clean plastic tweezers. When assembling the filter pack, the parts should be tightened at the torque specified by the manufacturer to prevent leaks. The leak of air through stage connections should be checked using a flow meter with a pump every time (Fig.4.3). If the rotameter shows 0 liter/min or the needle of the gas volume meter stops moving while the inlet of the filter pack is attached with the rubber sheet, and air is drawn by a pump, it will be confirmed the filter pack has no leak. It is recommended to open a 3-way valve slowly because of preventing breaking filters in the case of example A in Fig.4.3. Then, the mounted filter holder should be capped by an exclusive cap. Airtight protection covers need to be mounted at the both ends of the filter pack. Each filter pack should be tagged with the site code in the laboratory before it is shipped to the site.

Care should be taken to avoid materials in the filter pack which may be a source of contamination or absorb sulfur dioxide or other air components. Teflon, polyethylene, polypropylene, PVC, and polycarbonate are recommended materials. Ordinary rubber and nylon contains sulfur 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 shipping to a monitoring site. It is recommended that a transportation box is kept low temperature about 10 ^{o}C cooling by reusable coolant in order to avoid evaporation of the sampled substances during transportation. Shipping interval of the filter packs from the laboratory to the site is weekly or biweekly, and vice versa depending on the sampling interval. 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, dismounted, and the filters are given the same chemical treatment and analysis as the exposed filters.

Sample filters are recommended to be dismounted 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.

(Example A)



(Example B)

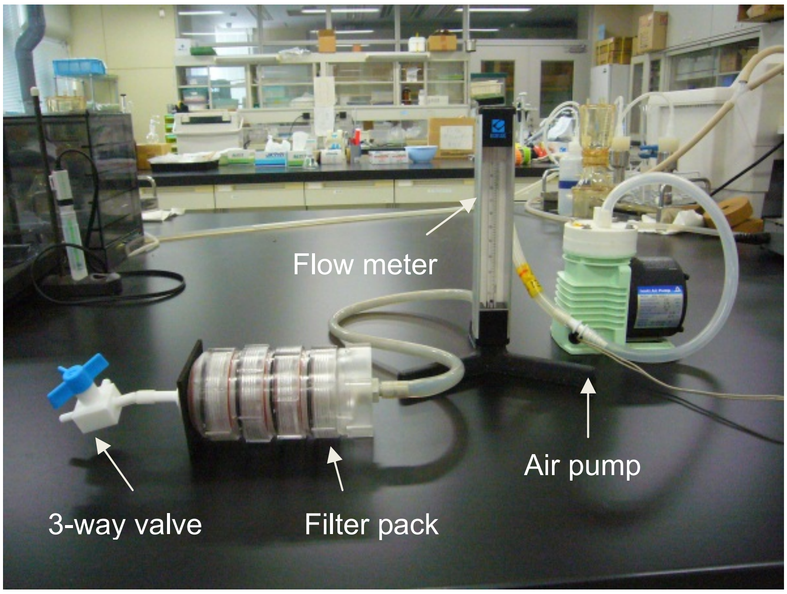


Fig.4.3 Operation of leak check for filter pack

2) Preparation of filter pack

As mentioned in the Section 4.1.3, PTFE filter (pore size: 0.8μm, diameter: 47mm) is recommended as the first filter (F0). Polyamide filter (pore size: 0.45μm, 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 5% phosphoric acid + 2% glycerin in pure water. The solution to be used for impregnation should be prepared on the same day when the impregnation of a new series of filters is conducted.

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 for the filter pre-treatment. The filters should be placed on hygroscopic papers such as chromatography papers after the impregnation solution is dripped on the filter. Then, the moisture should be removed by pressing the hygroscopic papers. When the filters are dried, they must be placed in plastic bags and the zippers closed. The bags should be labeled with the type of filters and the preparation date.

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

1) Prepare the mix solution (6% K_2CO_3 + 2% glycerin);
   - Prepare three 500 ml beakers;
   - Weight 30 g of K_2CO_3 and 10 g of glycerin in each 500 ml beaker;
   - Pour deionized water (less than 0.15 mS/m) into each beaker and adjust to 500 g;
   - 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 the 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 (e.g. ADVANTEC No.590, Toyo Roshi Kaisha, Ltd.) 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 the step 2) for next filter. But maximum 20 sheets could be prepared by one set of 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 500 ml beakers;
    - Weight 29.4 g of H_3PO_4 and 10 g of glycerin in each 500 ml beaker;
    - Pour deionized water (less than 0.15 mS/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 the 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 (e.g. ADVANTEC No.590, Toyo Roshi Kaisha, Ltd.) 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 filters could be prepared by one set of 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 solutions should be used up on the same day of preparation. After each cleaning and drying process, 3 filters should be analyzed for major ions, and blank values should be determined. If the blank level is too high, all filters from the impregnation batch should be thrown, then a new batch should be made. If the blank level is within usual one, the storage bags should be marked and dated.

Impregnated filters should be kept in the marked and dated 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 another one. The desiccator for alkaline impregnated filter should have citric acid at the bottom, and the one for acid impregnated filter should have KOH 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 the sample and 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 4.2.

Table 4.2 Analyzed species and solvent for each stage filter

Stage	Species	Solvent
First (F0)	SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}	Deionized water
Second (F1)	SO_4^{2-}, NO_3^-, Cl^-, NH_4^+	Deionized water
Third (F2)	SO_4^{2-}, Cl^-	0.05% H_2O_2
Fourth (F3)	NH_4^+	Deionized water

Recommended extraction procedure is described as follows:

1) Prepare polypropylene test tubes (50 ml) 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 the correspondent test tube;
5) In the case of F0, F1, F3 stage samples, pour 20 ml deionized water into the tubes; in the case of F2 stage sample (alkali impregnated stage) pour 20 ml H_2O_2 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 Manual for Wet Deposition Monitoring in East Asia - 2010 (EANET, 2010).

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

4.1.6. Determinations of concentrations and data reporting

The concentrations of gas and aerosol components in the air are basically determined as follows:

$$C_{\mathrm{Air}} = \alpha \times \text{net } C_{\mathrm{Sol}} \times V_{\mathrm{Sol}} / V_{\mathrm{Air}} \tag{4.1}$$

C_{Air} : concentration in the air (nmol/m^3),

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 (m^3),

M : molecular weight,

$\alpha = 10^3 / M$.

The net C_{Sol} should be calculated by the equation 4.2:

$$\text{net } C_{\mathrm{Sol}} = C_{\mathrm{Sol,\ Sample}} - C_{\mathrm{Sol,\ Blank}} \tag{4.2}$$

$C_{\mathrm{Sol,\ Sample}}$: concentration in the solution from the sample filter,

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

Regarding the determinations of concentrations, the equations are summarized in Table 4.3.

Table 4.3 Equations for determinations of concentrations

Species	M	Equation
SO_4^{2-}	96.06	$C_{\mathrm{Air}} = \alpha \times \text{net } C_{\mathrm{Sol,\ F0}} \times V_{\mathrm{Sol}} / V_{\mathrm{Air}}$
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-})	$C_{\mathrm{Air}} = \alpha \times (\text{net } C_{\mathrm{Sol,\ F1}} + \text{net } C_{\mathrm{Sol,\ F2}}) \times V_{\mathrm{Sol}} / V_{\mathrm{Air}}$
HNO_3	62.01 (NO_3^-)	$C_{\mathrm{Air}} = \alpha \times \text{net } C_{\mathrm{Sol,\ F1}} \times V_{\mathrm{Sol}} / V_{\mathrm{Air}}$
HCl	35.45 (Cl^-)	$C_{\mathrm{Air}} = \alpha \times (\text{net } C_{\mathrm{Sol,\ F1}} + \text{net } C_{\mathrm{Sol,\ F2}}) \times V_{\mathrm{Sol}} / V_{\mathrm{Air}}$
NH_3	18.04 (NH_4^+)	$C_{\mathrm{Air}} = \alpha \times (\text{net } C_{\mathrm{Sol,\ F1}} + \text{net } C_{\mathrm{Sol,\ F3}}) \times V_{\mathrm{Sol}} / V_{\mathrm{Air}}$

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

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

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 (e.g. shutdown of electricity), the samples obtained in these periods should be rejected, because the filter packs absorb gases like passive samplers when they are in the breaks.

Ions balance (R_1) check can be considered for F0 filter in the same way as described in Technical Manual for Wet Deposition Monitoring in East Asia - 2010 (EANET, 2010), but if the organic acid or carbonate ions significantly exists in particulate matter, the ions balance will be not good.

4.1.7. Blank test and inter-laboratory comparison

It is recommended that 3 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 so low that their values can be ignored. High blank values may identify the laboratory issues to be solved, for example, by using filters or chemicals from another batch, and by inspection of the routines in the laboratory. A blank value should be determined as the median of 3 analytical results of blank filters. One median value is available as the blank value for the sample sets obtained for one month.

The Network Center prepares artificial filter pack samples and distribute to the EANET participant countries to conduct inter-laboratory comparison survey once a year. The results of this survey in respective laboratory can be also used for improvement of data quality.

4.2. Annular denuder

Compared with filter pack method, denuder method can avoid artifact and measure particulate components and gases separately, so the sampling by a diffusion denuder and subsequent chemical analysis by ion chromatography is also recommendable method.

4.2.1. 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 air flow rate to be increased, and makes the subsequent chemical analyzes somewhat less demanding. It was reported that the precision estimates of simultaneous samples for most of the measured species are similar between weekly annular denuder systems and composited filter packs (Sickle et al., 1999).

Sampling artifacts due to the volatility 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 efficiency. 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 (Norwegian Institute for Air Research, 2001).

Denuders can be rather impractical and are relatively expensive, and as filter packs are mostly more operative and less demanding in terms of sampling and sample preparation skillfulness, the latter 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 phases may sometimes be inferred also from filter pack data. Denuder is useful to selectively 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 SO_2/SO_4^{2-} is good in both techniques. Consumable denuder has been used in EMEP (Norwegian Institute for Air Research, 2001).

4.2.2. 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 PTFE membrane filter with high collection efficiency for submicron particles, followed by a filter impregnated with potassium hydroxide for collection of nitric acid which may be evaporated from the particle filter, and a filter impregnated with oxalic acid for the collection of ammonia which may also be evaporated.

Nitrous acid (HNO_2) is also absorbed in the alkaline denuder, 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 by the distribution of nitrite between the first and the second denuder.

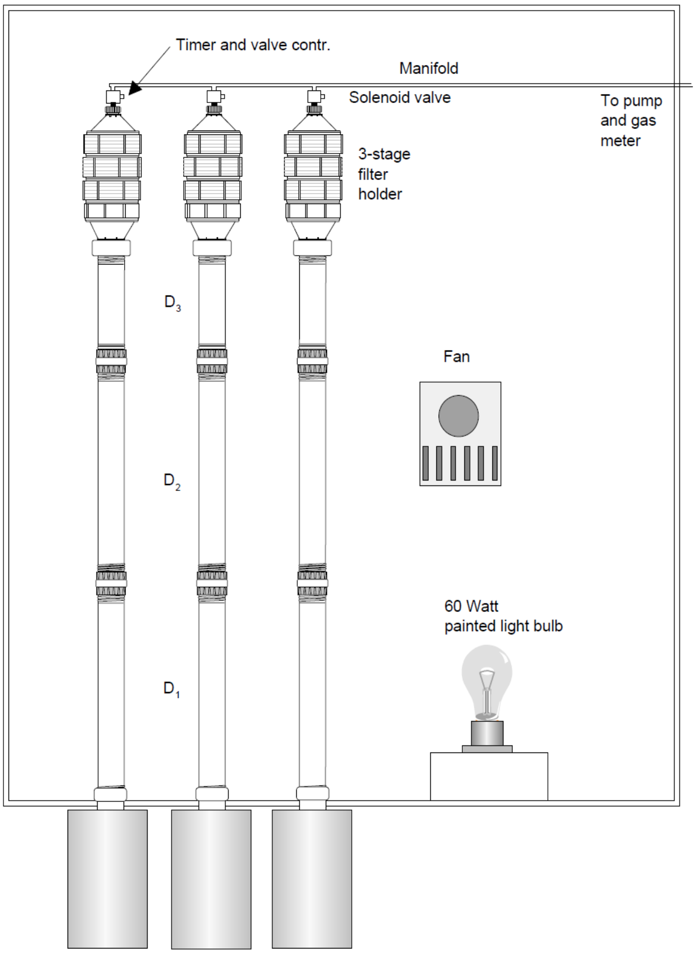


Figure 4.4 Sampling arrangements for denuder sampling
(Norwegian Institute for Air Research, 2001)

A schematic description of the sampling equipment used in EMEP is shown in Fig. 4.4 (Norwegian Institute for Air Research, 2001). It consists of a small insulated box, with a fan for internal air circulation, a heating unit to control a temperature up to 2 °C above the ambient temperature, a rack for mounting the denuder sampling trains and filter packs, electromagnetic valves connecting the sampling trains to a manifold, a leak-proof pump which gives a sampling rate of 15 l/min, and a gas volume 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 the length 242 mm, and one denuder of the 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 a PTFE aerosol filter, a KOH impregnated filter and a citric or oxalic acid-impregnated filter.

Annular denuder technique is technically demanding and requires good control of chemical analyzes and particularly of blank values. The sampling setup 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 analyzes can be controlled, this system can be adopted as the alternative to the above described system.

4.2.3. Sampling procedure

(1) Preparation of the sampling unit

The preparation and coating of the denuders should take place in the laboratory that will carry out the chemical analyzes 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. For collection of HNO_3 (D1), a solution of 9% NaCl and 1% glycerol is prepared by dissolving in 100 ml of 50/50 (v/v) methanol-water solution. For collection of acidic gases (D2), 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 then diluting to 100 ml with methanol. Similarly, for collection of NH_3 (D3), 1 g of citric acid (or oxalic or phosphorous acid) is dissolved in 50 ml of deionized water, and then diluted to 100 ml with methanol.

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 gas 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 for approximately 10 minutes, and then connected with the other end to repeat drying. Observe the evaporation of the liquid film in the denuder, and continue for a few seconds more to make sure that the evaporation is complete. Close the denuder with screw-caps.

(2) Sampling

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. Sodium chloride is used as an internal coating for the absorption of nitric acid in D1. 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 at once for 2 or 3 measurements. 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 the sampling date and time period (start and end) and the type of denuder number (D1, D2, D3) in the laboratory before transport to the site. Make sure that connections are leak proof. The sampling period, identification of denuders and filterpacks, gas volume meter readings, and notes of observations should be recorded in the field note for 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 $\mu g/m^3$ HNO_3-N and 0–5 $\mu g/m^3$ NH_3-N, respectively for weekly monitoring. If the air concentration levels are expected to breakthrough of the denuder, the sampling period must be modified.

(3) Chemical analysis

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

D1 (NaCl-imp) : Extraction with 10 ml deionized water
D2 (Na_2CO_3-imp) : Extraction with 10 ml deionized water with H_2O_2 (0.3%)
D3 (Citric acid) : Extraction with 10 ml deionized water
F1 (aerosol filter) : Extraction with 10 ml deionized water
F2 (alkaline imp. filter) : Extraction with 10 ml deionized water with H_2O_2 (3%)
F3 (oxalic acid filter) : Extraction with 10 ml deionized water

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, and then transfer the extract to a stoppered test tube for subsequent analysis. It is essential to work quickly in order to minimize contamination. The filters may be folded and transferred to the same kind of stoppered test tubes to which 20 ml of extraction solution is added. The tubes are shaken by a shaker or an ultrasonic bath during 20 minutes. Chemical analyzes of the extracts are to be made as follows shown in Table 4.4.

In the same way as filter pack, ion chromatography (IC) is recommended for analysis of the above-mentioned chemical components. The analytical method should follow the procedures described by Technical Manual for Wet Deposition Monitoring in East Asia - 2010 (EANET, 2010).

Table 4.4 Chemical analysis of the extracts from denuder and filter pack

Sample	Ions to be determined	Analysis methods	Reference
D1	NO_3^--N, SO_4^{2-}-S (Cl^-, NO_2^--N)	Ion chromatography	Section 4
D2	NO_3^--N, SO_4^{2-}-S (Cl^-, NO_2^--N)	Ion chromatography	Section 4
D3	NH_4^+-N	Spectrophotometry or ion chromatography	Section 4
F1	NO_3^--N, SO_4^{2-}-S, NH_4^+-N (Cl^-, NO_2^--N)	Ion chromatography and spectrophotometry	Section 4
F2	NO_3^--N, SO_4^{2-}-S (Cl^-, NO_2^--N)	Ion chromatography	Section 4
F3	NH_4^+-N	Spectrophotometry or ion chromatography	Section 4

4.2.4. Calculation of results

The results from the chemical analyzes will be given in μg/ml of the respective ions. After subtraction of blank values, the following equations are used for the subsequent calculation of the concentrations of HNO_3–N, SO_2–S and NH_3–N in air (Norwegian Institute for Air Research, 2001).

$$HNO_3\text{–N}\ (\mu g/m^3) = [(D1-D2)/0.94]\times(10/V) \qquad (4.3)$$

$$SO_2\text{–S}\ (\mu g/m^3) = [(D1-D2)/0.96]\times 10/V \qquad (4.4)$$

$$NH_3\text{–N}\ (\mu g/m^3) = D3\times 10/V \qquad (4.5)$$

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 m^3. 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:

$$NO_3\text{–}N(\text{particles}) = (F1+F2+2.5\times D2)\times 10/V \quad (4.6)$$

$$NH_4\text{–}N(\text{particles}) = (F1+F3)\times 10/V \quad (4.7)$$

$$SO_4\text{–}S(\text{particles}) = (F1+2.5\times D2)\times 10/V \quad (4.8)$$

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 sulfate on F1 and F2, the calculated excess should be added to the NH_3–N concentration determined from D3.

4.3. 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 (Ohizumi, et al., 2013).

Passive samplers offer a wide variety of advantages for use in the field. There is no need for calibration gases and electricity, and thus they are easy to be fixed in the field. The passive samplers are simply fixed inside a shelter to avoid splashing from precipitation and strong wind, which is attached to a pole at typically 1 meter height. They are small inexpensive, and provide time-integrated samples. One of the benefits is that artifact caused by evaporation of particles can be avoided. The time-resolution of passive sampler is relatively low, so the passive sampler can mainly 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 also in urban environment by changing monitoring duration.

4.3.1. 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 the 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. Therefore, they achieve a time-integrated (or averaged) 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 target gas. 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 on the walls of the sampler. Under these conditions then the sampling rate, 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 the given species and the type of 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 (Ohizumi, et al., 2013). It was showed that covering the inlet region of the sampler with a fine mesh (e.g. stainless steel mesh with a thread diameter of 0.08 mm and mesh aperture of 0.125 mm) can minimize these errors for high-dose samplers (Ohizumi, et al., 2013). Low-dose samplers are more sensitive to wind effects, and porous membranes supported by steel mesh are commonly used to cover the sample inlet (Ohizumi, et al., 2013).

The accuracy of a diffusion sampler depends 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 necessary 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 extracting the reaction product, typically using deionized water.

The extract is then analyzed using an appropriate analytical technique. The measurable highest concentration 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 blank, while field blank will measure the integrated exposure during the transport and storage periods. The filters should be impregnated just before the samplers are sent to the field. Some filters are labeled as the field blank and, the others are analyzed immediately, and those filters are identified for laboratory 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 of the standard deviation of the 3 blank values. 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 at daily, weekly, or monthly intervals. 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.

4.3.2. 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 SO_2, NO_2, NH_3, and O_3 concentrations is described as follows.

(1) SO_2

The measurement of SO_2 using passive samplers utilizes a NaOH impregnated cellulose filter. On the filter, sulfite is oxidized to sulfate during sampling and the sulfate amount is analyzed using ion chromatography (IC). The cellulose filters also were found to have a sulfate 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 from 0.05 to 40 ppb for a sampling time of 2 months (or 0.1 to 80 ppb for monthly sampling).

(2) NO_2

The most commonly used sorbent for NO_2 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 (WMO GAW, 1997). 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, NO_2 is converted to nitrite and then analyzed by IC or spectrophotometry. NO_2 measurements using this impregnation method in an active filter mode have been compared to those using a automatic NOx analyzer.

(3) NH_3

Citric acid is used to impregnate the NH_3 samplers. The NH_4^+ in the exposed filters is analyzed by IC. 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 SO_2 and NO_2 (WMO GAW, 1997). The repeatability was improved after replacing the inlet screen with a solid cap after sampling to minimize volatilization with a solid phase which deposits on the inlet screen (WMO GAW, 1997).

(4) O_3

$NaNO_2$ is used to impregnate the O_3 samplers. O_3 oxidizes nitrite to produce nitrate. Because the converted amounts of nitrate is stoichiometrically equal to the sampled O_3, ozone concentration is determined by the nitrate concentration in extract by using IC. This monitoring is widely used in global network such as WMO (WMO GAW, 1997), and it is suitable to monitoring AOT40 in mountainous area where electricity is hard to obtain. However, the previous study showed that, in the case of higher wind speed (> 5 m/s) condition, O_3 concentration measured by a passive sampler is underestimated when it was compared with the automatic monitor results. Therefore, meteorological condition should be considered for O_3 monitoring (Ohizumi, et al., 2013).

4.3.3. 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. Fig. 4.5 and Table 4.5 show the construction and principles of Ogawa Passive sampler. The apparatuses used on station and in laboratory are also shown in Table 4.6.

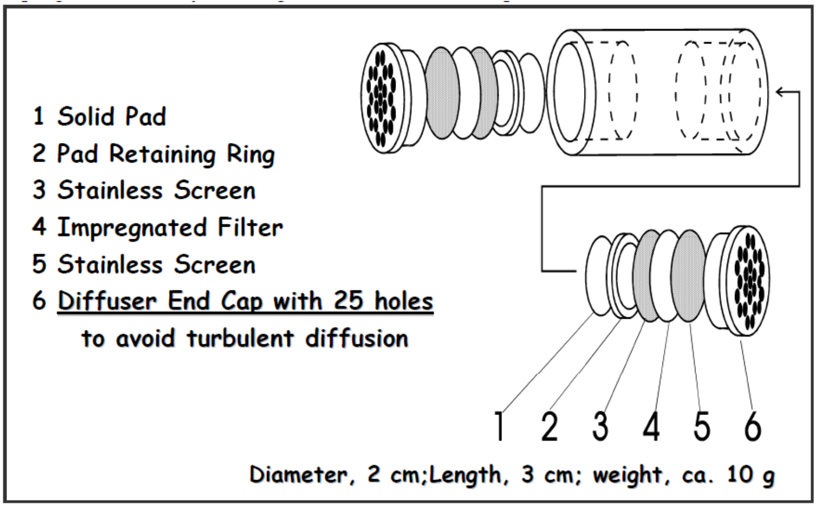


Figure 4.5 Construction of Ogawa Passive sampler

Table 4.5 Principles of the Passive samplers

Compound	Regent for filters	Analytical methods
SO_2	10%TEA	SO_4^{2-} by IC
O_3	$NaNO_2$+K_2CO_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-tetramethlimidazoline 3-oxide 1-oxyl
IC: Ion Chromatograph

Table 4.6 Apparatuses are used on station and in laboratory

Station	Laboratory	
Plastic glove	Tweeze	
Plastic bag	Plastic glove	
Plastic box	Deionized water	
Field note	Test tube	NOx
Shelter	Plastic tube	SO_2,O_3,NO_2
Cooler box	Ultrasonic cleaner	

(1) Set up of samplers

<In laboratory>

The impregnated filters should be packed in a polyethylene bag, and the polyethylene bag should be stored in freezer. In one use commercial filters, there are typically 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 kinds of samplers are prepared for each sampling period. The samplers should be stored in sealed plastic bag/box. The samplers should be shipped to the station by using a cooler bag/box to avoid deposition of the ambient gas.

<On Station>

Take out new samplers from the plastic bag/box by using plastic gloves, and then install it in the shelter. Write following information in the field note. The sampling period is between 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 a cooler bag/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 (12–20 ml) by using clean tweezers and plastic glove. Pour 10 ml deionized water into test tubes for SO_2 and O_3 analysis. If using the IC for NO_2 and NO_X analysis, pour 10 ml deionized water into test tubes. If using the spectrophotometer for NO_2 and NO_X analysis, pour 8 ml deionized water into test tubes. Stop up the test tubes with cap, and then store them in refrigerator until chemical analysis.

[Clean of sampler]

Store passive sampler into a wire netting bag. Soak wire netting bag into an ultrasonic bath for 10 minutes. Rinse the wire netting bag with deionized water, and then dry it in laboratory avoiding ambient air contamination.

4.3.4. Procedures of the chemical analysis

Plastic glove, test tube or plastic tube, water bath, sample vial and micro pipetter should be prepared for pretreatment of samples. Chemical analysis can be done using IC or spectrophotometer. Before analysis, sample temperature should be returned to room temperature when samples are stored in refrigerator. The number of ion standard levels should be more than 5.

In the same way as filter pack, ion chromatography (IC) is recommended for analysis of chemical components. The analytical method should follow the procedures described by Technical Manual for Wet Deposition Monitoring in East Asia - 2010 (EANET, 2010). The following describes the types of standards, and some special apparatus and analytical operation, especially in the case of analysis using spectrophotometer.

1) Analytical method for SO_2
   Standard solution 1000 mg/L (SO_4^{2-})
   Range: 0.01–5.0 mg/L
   [Apparatus for SO_2]
   Hydrogen Peroxide, Platinum fiber (φ0.1 mm, 2 cm)
   [Analytical operation]
   Add 0.2 ml of Hydrogen Peroxide solution (1.75% solution) and then shake gently. Hold it for 10 minutes. Then add Platinum fiber (φ0.1 mm, 2 cm) and soak it into water bath (50 ^{o}C) for 10 minutes. Platinum fiber can be reused. Wash platinum fiber by deionized water after chemical analysis.
2) Analytical method for O_3
   Standard solution 1000 mg L^{-1} (NO_3^-), Range: 0.01–5.0 mg/L
3) Analytical method for NH_3
   Standard solution 1000 mg L^{-1} (NH_4^+), Range: 0.01–5.0 mg/L
4) Analytical method for NO_2, NO_x (in the case of using IC)
   Standard solution 1000 mg L^{-1} (NO_2^-), Range: 0.01–5.0 mg/L
5) Analytical method for NO_2 / NO_x (using spectrophotometer)
   Standard solution 1000 mg/L (NO_2^-), Range: 0.01–1.0 mg/L
   [Apparatus for O_3, NH_3, NO_2 / NOx]
   Test tube (NO_x), Plastic tube (NO_2), Diethyl ether (Ethyl ether), Pipet Glass

<For Color producing reagent>

Sulfanilamide, Phosphoric acid, N- (1-Naphthyl)-ethylenediaminedihydrochloride (NEDA)

[Preparation of color-producing reagent for NO_2 / NOx]

Prepare color-producing reagent immediately before use.

<For Sulfanilamide solution >

Dissolve 8 g of reagent grade sulfanilamide in a mixture of 20 ml concentrated phosphoric acid and 70ml water. Dilute with water to make a total of 100 ml. Change amount according the number of samples.

<For NEDA solution>

Dissolve 0.056 g N-(1-Naphthyl)-ethylenediaminedihydrochloride into 10 ml 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 NO_2>

Pour 8 ml 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 545 nm. Wastewater should be treated.

<For NOx>

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 NO_2 by using spectrophotometer]

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 545 nm. Wastewater should be treated.

[Analytical method for NOx by using spectrophotometer]

Return sample temperature to room temperature. Add 4ml Diethyl ether to remove PTIO. Do it two times. Add 2 ml 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.

4.3.5 Calculation of concentration from collected amount

As mentioned in Section 4.3.1, the sampling rate can be calculated using the 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. However, the sampling rate is affected by the ambient temperature. The empirical equations correct such dependency to the standard condition (Yokohama City Research Institute of Environmental Science, 2010). Here shows the equations to calculate ambient air concentrations.

The Fick's first law of molecular diffusion is shown below.

$$J = - D\,(\Delta c/\Delta x) \qquad (4.9)$$

Where,

$\Delta c = C_A - C_0$, $\Delta x = L - L_0$, J: transport amount, D diffusion coefficient

And the Practical use of the Fick's Law is shown below.

$$J = D\,(C/L) \qquad (4.10)$$

Where,

J: transport amount (ng/cm^2/sec), D: molecular diffusion coefficient (cm^2/sec)

C: concentration (ng/cm^3), L: diffusion length (cm)

Then,

$$JA = DA\,(C/L) = \text{ng/sec} = W/t \qquad (4.11)$$

Where,

A: collection area (cm^2), W: weight of collected substances (ng); t, sampling time (min)

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).

$$W/t = SR\cdot C \qquad (4.12)$$

$$W/t = DA\,(C/L) = (DA/L)\cdot C \qquad (4.13)$$

D of NO_2 = 0.1567 cm^2/sec at 20°C

Where,

$A = 0.785$ cm^2, $L = 0.6$ cm, $SR = DA/L = 0.205$ cm^3/sec = 12.3 cm^3/min

Then,

$$C = (L/DA)(W/t) \qquad (4.14)$$

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

$$C_v = \alpha\,(W/t) \qquad (4.15)$$

Where,

C: concentration (ppbv), t: collection time (min), W: collected weight (ng)

α: coefficient (ppbv·min/ng)

Then,

$\alpha = (1/60)(1/f)(1/D)(L/A)(V/M)\cdot 10^3$ (4.16)

Where,

α: coefficient (ppbv·min/ng), f: coefficient for calculation from gas phase to ion phase, D: molecular diffusion coefficient (cm^2/sec), L: diffusion length (cm), A: area (cm^2), V: volume of 1 molar gas (L), M: weight of 1 molar gas (g)

In consequence, the concentrations of ambient pollutants are calculated as follows.

SO_2 (ppbv) = $\alpha_{SO2}\cdot W_{SO2}/t$ (4.17)

NO (ppbv) = $\alpha_{NO}\cdot(W_{NOX} - W_{NO2})/t$ (4.18)

NO_2 (ppbv) = $\alpha_{NO2}\cdot W_{NO2}/t$ (4.19)

NH_3 (ppbv) = $\alpha_{NH3}\cdot W_{NH3}/t$ (4.20)

O_3 (ppbv) = $\alpha_{O3}\cdot W_{O3}/t$ (4.21)

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 ºC, 70% relative humidity, and 1 atm (Yokohama City Research Institute of Environmental Science, 2010).

$\alpha_{SO2} = 39.4$

$\alpha_{NO} = 57$

$\alpha_{NO2} = 57$

$\alpha_{NH3} = 87.6$

$\alpha_{O3} = 46.2\times10^2/(9.94\times\ln(t)-6.53)$

Coefficients in different conditions can be calculated by the following formula (Yokohama City Research Institute of Environmental Science, 2010). Since the coefficients were updated several times, one must use the most updated coefficients when the coefficients are revised by relevant organizations.

$\alpha_{SO2} = 39.4\times(293/(273+T))^{1.83}$

$\alpha_{NO} = 4.746\times(4781.3-T)/(474.2-P\times RH)$

$\alpha_{NO2} = 1.050\times10^6\times(44.6\times T)/(206.4\times P\times RH)$

$\alpha_{NH3} = 87.6\times(293/(273+T))^{1.83}$

$\alpha_{O3} = 46.2\times10^2\times(293/(273+T))^{1.83}/(9.94\times\ln(t) - 6.53)$

where,

T = average temperature during the measurement period (ºC),

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

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

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

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5. Maintenance

5.1. Standard operating procedures

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 the SOPs meet the requirements of their respective organizations and that the SOPs comply with the Technical Manuals and the national QA/QC programs in EANET. The SOPs need to be straight forward and sufficiently clear to ensure that beginners can perform the tasks in an effective manner. The 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 an 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/analyzes
  4) Check of sensitivity fluctuations
3.6. Treatment of measurement results
  1) Calculation of concentrations
  2) Measurement of sensitivity fluctuations
  3) Repeat measurements/analyzes
  4) Calculation of ion balances
  5) Comparison of measured and calculated electric conductivity (if applicable)
4. Quality assurance and quality control
4.1. Evaluation of manual sampling
  1) Comparison of manual monitoring and an automatic monitor
  2) Evaluation of ion balance
4.2. Evaluation of reliability
  1) Evaluation of sensitivity fluctuations
  2) Evaluation of repeated measurements/analysis
  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 stuff 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 and instruments
4) Evaluation of the results of quality control
5) Evaluation of the measured results

5.2. Maintenance in a monitoring station

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 maintenance contractor.

Routine station operation

The operator is recommended to visit the station no longer than 15 day interval, and the new employees should take on-the job training from experienced site operators. Manual for each analyzer is used as the Standard Operating Procedures (SOPs) for continuous measurement. Here are examples of routine station operation.

- 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 and 2.5 samplers replace sample tape as necessary, perform zero flow check.
- Station temperature 27 °C ± 3 °C
- Check main gas pressure in calibration gas cylinder
- Perform zero/ span levels check on all analyzers
- Verify meteorological sensors are operational

5.3. Maintenance of automatic monitors

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 70 % in day, month, and year, such as above 16 hours in day, above 504 hours in month and above 6132 hours in year. It is described in Section 7.2 in detail. For the attainment of these purposes, a monitor should be maintained fundamentally according to two methods as follows.

i) Preventive maintenance : the methods to maintain preventively to the parts of a monitor with possibility to break out and repair, such as routine and periodic checks and maintenance, and overhauls.

ii) Troubleshooting : the methods to deal with the anomalous behaviors and investigate their causes, after breaking out and repairing, such as emergency check.

An automatic monitor has the possibility of failures, for example, initial 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 specifications by qualification tests before installation. It is important to plan the maintenance schedule of a monitor from the time when it is installing because the failure rate can be decreased by accurate maintenance. Fig. 5.1 shows an overview of the change of failure rate with operating time.

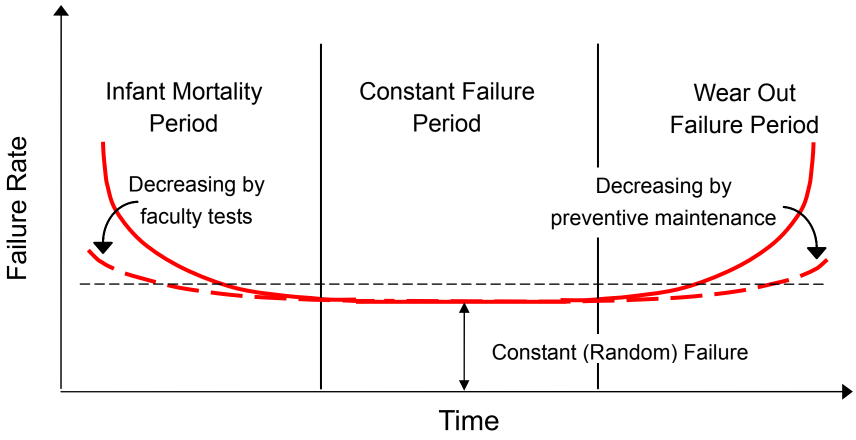


Figure 5.1 Changes of failure rate with operating time
(Ministry of the Environment Japan, 2010)

This figure shows the relationship between the operating time of instruments and the failure rates, and it is called “The Bathtub Curve” because its shape is like bathtub. The failure rates of most instruments show the "The Bathtub Curve". The curve is classified into three periods as follows. (1) Infant Mortality Period: Many failures happen as soon as the apparatus are set because of initial failures during making the instruments. (2) Constant Failure Period: This is the period of constant failure without initial failure, and it could be happen in regular operation. (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 lifetime of the instruments and the surrounding conditions.

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 replacement of the instruments, in order to operate the instruments monitor for a long time in a stable manner by maintaining high-level of performance and data quality. The performance of the instrument is generally getting worse by aged deterioration (Fig. 5.2) because of continuous measurements. Therefore, it is necessary to plan a frequency of the periodical maintenance within appropriate period and to judge each instrument status exactly. It is also important to grasp the features of the instruments because each condition is different with its situation and its setting location.

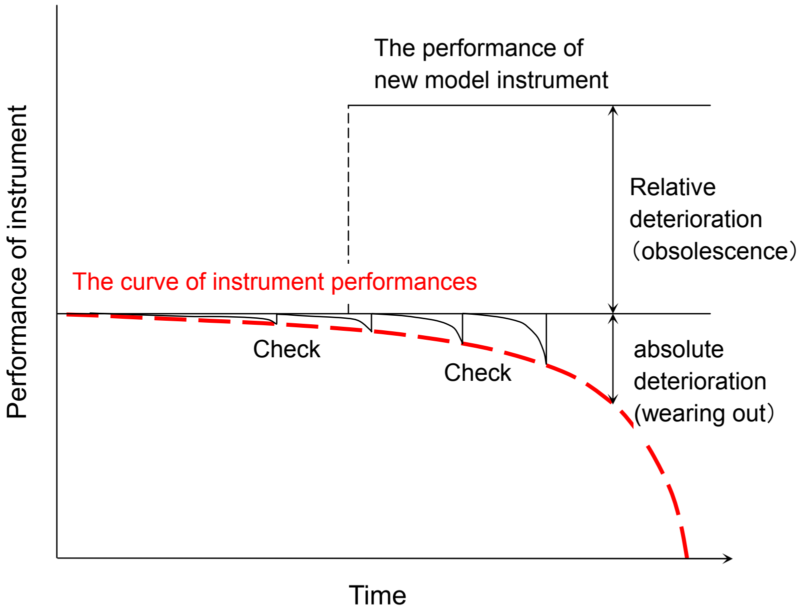


Figure 5.2 Example for changes in instrument performances by aged deterioration (Ministry of the Environment Japan, 2010)

5.3.2. Contents of maintenance

Table 5.1 shows the sections, objectives, frequency, and contents of maintenance. Detailed explanations are shown below.

(1) Visual check

Normal operation of an automatic monitor is checked when the local operator visit the site. If instrumental data (e.g. air concentration, flow rate, instrumental temperature) can be seen through the telemeter system, the responsible person should check such data. When abnormalities occur, the operator or the other responsible person must take efforts to resolve the problems in order to reduce missing data. At the station, instrumental status such as temperature, pressure, flow rate, error codes, should be observed by the local operator.

Missing data should not only be recorded as "no data" but also the reasons of missing data should be recorded in order to use for maintenance and data verification.

(2) Daily check

Daily check is to confirm operating statuses of the instruments, and it should be conducted once or twice a week. At the daily check, the local operator or the maintenance contractor should check the abnormalities of instruments and replace consumable parts according to the necessity.

In order to keep constant condition of the instruments, the responsible person must prepare the check list and the results must be recorded in the daily check reporting form. Because the instruments are different for station by station, this record form should be prepared for each station as appropriate. A recording chart of an automatic monitor should be described the check date and time, the name of operator, the contents of daily check, missing data period, etc. because it would be important record when questions on the monitoring data are raised.

Moreover, if abnormalities are found and the problem cannot be solved, the operator must take the condition as much as possible so that proper repair can be conducted.

Table 5.1 The contents of maintenance

Sections	Objectives	Frequency	Contents
Daily check	To operate the automatic monitors and samplers in a stable condition To retrieve data and collect the samples	Once / week	1. Confirming the operating of the instruments 2. Replacement or addition of consumables 3. Simple calibration and check the results 4. Cleaning and replacement the simple parts
Periodical check	To keep an automatic monitors in good conditions To prevent instrumental failure To check standard instrumental specifications	Once / year	1. Test of flow tubes and a manifold 2. Test of detection parts 3. Test of control and data transmission parts 4. Test of amplification and recording parts
Emergency check	To carry out emergency check against abnormality To recover from missing data period	When serious failure occur	1. Detection of failure and emergency repair 2. Investigation of the causes and repair ask for manufacturers

(3) Periodical check

Periodical check is to check the parameter that affects the precision and condition of the instruments, and it needs full knowledge of the instruments in order to carry out the calibration which assures the measurement precision of the monitor, and replace the deteriorated parts in the instruments. Therefore, the periodical check is usually carried out by the maintenance contractor dispatched from the manufacturers. Because the frequency of replacement of parts and the measurement precision check may be different for station by station, the responsible person should consult with the maintenance contractor about the contents of periodical check.

(4) Emergency check

Emergency check is to investigate the cause of instrumental failure when abnormalities and failures are found in daily or periodical check. Then, the failed instruments are repaired as much as possible by emergency repair. It is also important to reduce mission data period, but the very high skillfulness and knowledge are required because this kind of trouble cannot be easily resolved. Usually, the responsible person will ask the repair service staffs dispatched by the manufacturers.

5.3.3. Lifetime of instruments

Because automatic monitors and the other instruments work for 24 hours per day for a long time, it is unavoidable to consuming the component parts by long use. The standard lifetime of the instruments would be 10 years in general even if each one is maintained properly by daily or periodic check and maintenance inside of the station. If instrument is placed on the outside of the station, general lifetime would be 7 years. It is necessary to replace of each monitor based on these periods. Some instruments must be replaced in the fixed period by laws. For example, in the case of Japan, the official certified meteorological instruments should be replaced in every five years because of expiration of the certificate. In this case, the expiry period would be one of the indication of replacement.

If it is difficult to replace the instruments because of budgetary limitations, the responsible person should ask the manufacturers about longer maintenance so that operating costs should be kept as low as possible. In addition, disposal of the instruments must follow the laws in each country.

5.3.4. Overhaul

Some instruments must be used for longer than their standard lifetimes in some cases. Generally, the precision of the instruments decrease with the operation time even if sufficient maintenance is carried out. Therefore, the frequency of periodical check may increase than usual because many instrumental problems may be raised especially after standard life time. However, the periodical check cannot cover the comprehensive maintenance and repair because of limitation of available instrumental parts, checking times and skilled staffs.

An overhaul is carried out when it needs to keep the good precision of the instruments and the period check is insufficient. In the overhaul, the manufacturers bring their instruments in the factory. The instrument will be disassembled, and the performance of each part is checked. After the replacement of necessary parts, the instruments will be assembled again. Finally, the operation test is performed for a fixed period and the overall performance is checked. Because the comprehensive facilities are required for overhaul and the instruments must be temporally removed from the station, overhaul should be conducted if serious instrumental problems are not resolved and the periodical check cannot improve measurement precisions. Moreover, the alternative instruments should be installed when the overhaul is conducted.

5.4. Field record

All monitoring sites should essentially satisfy the siting criteria. If there are some differences from the criteria, they should be documented and evaluated for integrity and validity of the monitoring data. Any significant changes around sampling sites and conditions should be properly reported in the record sheet and the report should be submitted to the Network Center (NC) through the National Center upon request. The example of field record sheet is shown in the Fig. 5.3.

5.5. Maintenance record

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 air concentrations. The necessary items of the maintenance record are shown below.

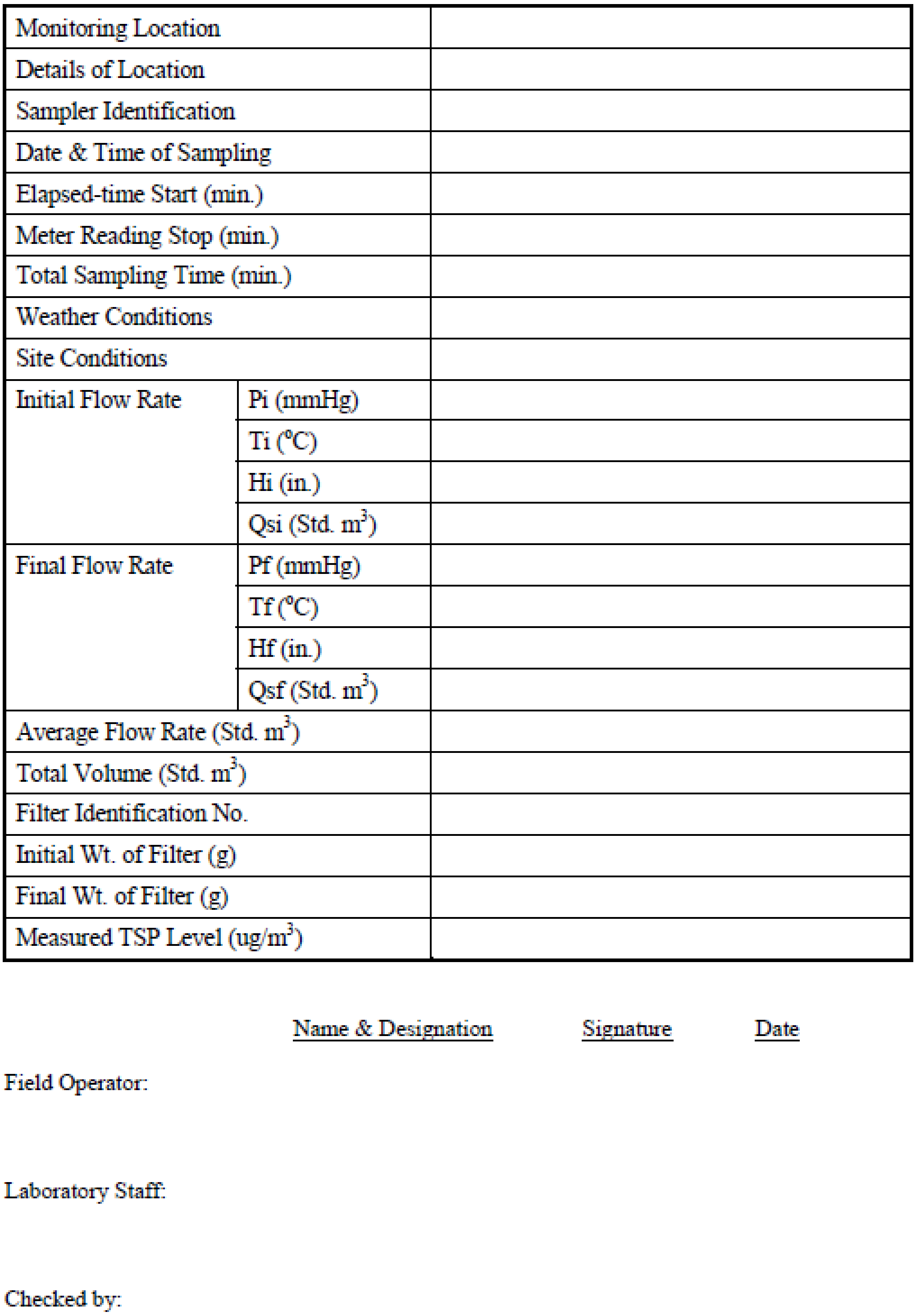
- Name of station
- Name and type of instruments
- Regular inspection of instruments (Date, Contents, Results)
- Calibration records (Date, Species, Method, Range, Spen and Zero factor)
- Instrumental failure and repairs (Date, Contents, Results)

5.6. Safety management

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

The gas cylinder should be fixed by chains and the storage room should have good



Monitoring Location		
Details of Location		
Sampler Identification		
Date & Time of Sampling		
Elapsed-time Start (min.)		
Meter Reading Stop (min.)		
Total Sampling Time (min.)		
Weather Conditions		
Site Conditions		
Initial Flow Rate	Pi (mmHg)	
	Ti (°C)	
	Hi (in.)	
	Qsi (Std. m^3)	
Final Flow Rate	Pf (mmHg)	
	Tf (°C)	
	Hf (in.)	
	Qsf (Std. m^3)	
Average Flow Rate (Std. m^3)		
Total Volume (Std. m^3)		
Filter Identification No.		
Initial Wt. of Filter (g)		
Final Wt. of Filter (g)		
Measured TSP Level (ug/m^3)		

	Name & Designation	Signature	Date
Field Operator:			
Laboratory Staff:			
Checked by:			

Figure 5.3 Example of field record sheet (Environmental Resources Management, 2007)

ventilation condition. The gas cylinder has to be connected to valve and the pressure should meet the requirement of instrument. Leak check should be done every time before open the valve. The staff in charge of safety management should open and close valve slowly and carefully. The pressure of gas cylinder should be recorded every time and if the remaining pressure of gas is lower than 0.5 MPa the cylinder should be replaced. It means that the gas should remain at least 0.5 MPa. Name and valid date and other information should be labeled on the cylinder. The valid date of cylinder and valve should also be recorded and make sure to use both of cylinder and valve within valid date. Some gas cylinders should use special valve, for example, it is better to use red color valve for the Hydrogen cylinder.

5.6.2. Disposal of chemicals, solution waste and monitoring instruments

The acid and alkaline waste solution should be mixed and collected in waste tank and then neutralized by acid or alkaline solution until pH value ranges from 6 to 9 before throwing away. The name of waste solution should be labeled on the tank. Avoid direct sunshine to the waste tank. The common acid and alkaline chemical used for neutralizing are hydrogen chloride (HCl) and carbonate calcium ($CaCO_3$).

The treatment of β-ray detector has already been mentioned in the sector of β-ray monitoring method. The low level of radioactive substance should be stored in special tank with specific label describing the half-life period.

References

Ministry of the Environment Japan (2010) Ambient air continuous surveillance manual (6th Edition), 366p. [in Japanese]

Environmental Resources Management (2007) Environmental monitoring and audit manual, Environmental Protection Department, Hong Kong, 150p.

6. Data reporting and validation

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 (NC). The NC 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 the date and time of monitoring
- Date of chemical analysis for the filter pack samples and other manual samples
- Air concentration measured by automatic monitors (SO_2, NO, NO_2, NOx, O_3, PM_{10}, $PM_{2.5}$)
- Air concentration measured by the filter pack and other manual samples (SO_2, HNO_3, HCl, NH_3, 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 the NC through the National Center, following the protocols as shown below.

The units to be used for SO_2, NO/NO_2 and O_3 should be ppb, and that for PM_{10} and $PM_{2.5}$ should be $\mu g/m^3$.

For automatic instruments, SO_2, NO/NO_2 and O_3 should be expressed one digit under decimal, and PM should be expressed by integral numbers (e.g., 15.3 ppb for SO_2 and 52 $\mu g/m^3$ for PM).

(Data treatment protocol)

i. Hourly data should be effective when more than 3/4 of the data during the measurement period is effective.

ii. 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.) expressed as local time of each country.

iii. Hourly average should be calculated as the arithmetical 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.

iv. 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.

v. 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.

vi. 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 in previous years.

Records of the 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 (R_1) 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;

(Data completeness for automatic monitor)
= (Number of valid hourly data) / (Number of total measured hourly data) (6.1)

(Data completeness for filter pack and other manual methods)
= (Number of valid measurement days) / (Number of total measurement days) (6.2)

In order to evaluate monthly and annual air concentrations and monthly and annual dry deposition fluxes, the 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 analyzes of blank samples for the filter pack method should be tested and be reported by the method described in the Section 4.1.7.

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 data
781	Below detection limit
701	Less accurate than usual
699	Mechanical problem
599	Contamination of the samples or the sampling system
881	Calibration of instrument

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 NC will have responsibility for ensuring that all data elements are properly entered into the appropriate databases. Data should be submitted to the NC once every year.

The NC 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 NC.

· On-site scale

Description of the on-site scale is given for the area within a radius of 100 m 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.

· 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 10000 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 also 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, model and manufacturer of other manual monitoring equipment (if applicable), 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 also 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 monitoring 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. The NC will provide the formatted data reporting form as a Microsoft Excel file. All data should be input in the distributed data form. Items to be input are listed as follows:

1) Gas concentrations (SO_2, NO, NO_2, NOx, O_3) with the unit of ppb
2) Particulate matter mass concentrations (PM_{10}, $PM_{2.5}$) with the unit of $\mu g/m^3$
3) Analytical results of manual monitoring method with the unit of mg L^{-1} (In the case of filter pack, F0: SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Na^+, K^+, Mg^{2+} and Ca^{2+}; F1: SO_4^{2-}, NO_3^-, Cl^- and NH_4^+; F2: SO_4^{2-} and Cl^-; F3: NH_4^+). Duration time of the filter pack and other manual monitoring.
4) Meteorological Parameters (Wind Speed with the unit of m/s, Wind direction, Temperature with the unit of ^oC, Relative Humidity with the unit of %, Solar radiation with the unit of MJ/m^2, Precipitation with the unit of mm), Duration time of meteorological measurement.

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 6.1–6.3. 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.

Statistics 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 of 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.

Table 6.1 Report form of automatic monitors

	Site Name		2012	Raw_Data														
	Month	Day	Hour	SO2	Flag	NO	Flag	NOx*	Flag	O3	Flag	PM10	Flag	PM2.5	Flag	NO2	Flag	Note
1/1	1	1	1	0.1		0.0		0.2		32.4		−90000.0	*	3.4				
	1	1	2	0.1		0.0		0.3		32.4		6.0		4.7				
	1	1	3	0.1		0.0		0.3		33.0		5.7		3.8				
	1	1	4	0.1		−0.1		0.3		33.6		−1.7		3.4				
	1	1	5	0.1		0.0		0.3		33.8		9.2		4.5				
	1	1	6	0.1		0.0		0.3		33.4		2.8		4.9				
	1	1	7	0.1		0.0		0.3		33.2		6.2		4.0				
	1	1	8	0.1		0.0		0.3		33.4		5.8		5.2				
	1	1	9	0.1		0.0		0.3		33.5		6.6		4.8				
	1	1	10	0.1		0.0		0.4		34.2		7.3		3.5				
	1	1	11	0.1		0.0		0.3		33.8		9.1		3.0				
	1	1	12	0.1		0.0		0.5		33.1		−90000.0	*	3.0				
	1	1	13	0.1		0.0		0.3		32.0		14.6		4.8				
	1	1	14	0.1		0.0		0.7		30.2		12.5		1.8				
	1	1	15	0.1		0.0		0.3		32.0		5.3		2.4				
	1	1	16	0.1		0.0		0.3		31.8		7.7		3.6				
	1	1	17	0.1		0.0		0.3		30.6		7.4		3.6				
	1	1	18	0.1		0.0		0.3		29.8		7.8		3.7				
	1	1	19	0.0		0.0		0.3		28.5		3.2		3.0				
	1	1	20	0.1		0.0		0.3		27.8		2.1		2.8				
	1	1	21	0.1		0.0		0.3		28.0		−0.2		3.0				
	1	1	22	0.1		0.0		0.3		26.0		1.0		1.3				
	1	1	23	0.0		−0.1		0.3		25.0		−90000.0	*	1.8				
	1	1	24	0.0		0.0		0.2		23.1		0.0		1.3				
1/2	1	2	1	0.0		0.0		0.2		24.8		−90000.0	*	1.1				
	1	2	2	0.0		0.0		0.2		26.2		−2.6		2.0				
	1	2	3	0.0		−0.1		0.2		29.1		−0.5		3.5				
	1	2	4	0.0		0.0		0.2		28.6		−1.3		2.0				
	1	2	5	0.0		−0.1		0.2		29.5		−1.6		1.6				

Table 6.2 Report form of manual monitoring (In the case of filter pack)

Form (Dry) **Results of air concentration analysis (Filter Pack)**

Site name: **Site Classification:**

Name of Laboratory: **Name of reporter:**

Unit: **nmol/m^3**

Sample No.	Sampling period				Gas				Particle							
	Start		End		SO_2	HNO_3	HCl	NH_3	SO_4^{2-}	NO_3^-	Cl^-	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
	Date	Time	Date	Time												

Table 6.3 Report form of meteorological parameters

	Site Name		2012	Raw_Data									
	Month	Day	Hour	WS	Flag	WD	Flag	Temp	Flag	RH	Flag	SR	Flag
1/1	1	1	1	2.4		WNW	0.0	−0.5		67.0		0.0	
	1	1	2	3.8		W	0.0	−0.1		67.0		0.0	
	1	1	3	3.4		WNW	0.0	−0.4		65.0		0.0	
	1	1	4	3.7		WNW	0.0	0.0		64.0		0.0	
	1	1	5	3.6		WNW	0.0	0.0		67.0		0.0	
	1	1	6	2.8		WNW	0.0	0.2		66.0		0.0	
	1	1	7	3.7		WNW	0.0	0.6		69.0		0.0	
	1	1	8	4.1		WNW	0.0	0.7		67.0		0.0	
	1	1	9	4.0		WNW	0.2	1.2		66.0		0.2	
	1	1	10	4.4		WNW	0.4	1.2		63.0		0.4	
	1	1	11	4.4		W	0.5	1.3		60.0		0.5	
	1	1	12	3.8		WNW	0.5	1.2		72.0		0.5	
	1	1	13	2.7		W	0.7	−0.2		90.0		0.7	
	1	1	14	1.5		W	0.6	0.4		67.0		0.6	
	1	1	15	0.2		W	0.2	−0.3		73.0		0.2	
	1	1	16	0.8		W	0.1	−0.2		73.0		0.1	
	1	1	17	0.7		W	0.0	−1.5		91.0		0.0	
	1	1	18	0.4		W	0.0	−1.8		95.0		0.0	
	1	1	19	1.2		W	0.0	−1.8		96.0		0.0	
	1	1	20	0.6		WNW	0.0	−1.9		96.0		0.0	
	1	1	21	0.6		W	0.0	−1.8		97.0		0.0	
	1	1	22	0.9		W	0.0	−2.0		98.0		0.0	
	1	1	23	1.1		W	0.0	−3.8		97.0		0.0	
	1	1	24	0.3		W	0.0	−3.3		96.0		0.0	
1/2	1	2	1	2.7		W	0.0	−3.7		96.0		0.0	
	1	2	2	2.7		WNW	0.0	−3.6		93.0		0.0	
	1	2	3	0.9		WNW	0.0	−2.3		85.0		0.0	
	1	2	4	1.0		WNW	0.0	−2.3		86.0		0.0	
	1	2	5	0.7		WNW	0.0	−2.0		80.0		0.0	

7. Quality Control and Quality Assurance

7.1. Fundamental matters

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 monitoring/chemical analysis organizations need to execute various QA/QC activities, including development of the national QA/QC programs and the SOPs. The following fundamental items should be taken into account.

(National Center)

i. Preparation of the national monitoring plan
ii. Preparation and implementation of the national QA/QC programs
  ・Appointment of the national QA/QC manager
  ・Guidance for the preparation of SOPs at relevant organizations/laboratories
  ・Distribution of inter-laboratory samples, collection of the results and reporting to the NC
  ・Audits to sites and laboratories
  ・Comparison of sampling and analysis methods used in the country
iii. Collection of monitoring data and reporting of the data to the NC
iv. Development and implementation of the national training programs

(Monitoring/chemical analysis organizations)

i. Appointment of personnel in charge and their supervisors
ii. Preparation of SOPs in respective activities in the organization
iii. Execution of routine monitoring/chemical analysis
iv. Periodic reporting to the National Center
v. Participation in QA/QC activities conducted by the National Center such as analysis of inter-laboratory samples

7.2. Data Quality Objectives (DQOs)

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 concentration levels are significantly different. Considering the present status of the air quality monitoring in East Asia, the following DQOs are considered to adequate for the participating countries.

Table 7.1 Data quality objective values for required accuracy, precision, and completeness (unit: %)

Accuracy	Precision	Completeness
Within ±15% for the certified values of the inter-laboratory samples	Within ±15% determined by duplicate measurements	More than 70% of annual and monthly data.

7.2.1. Detection limits and reporting limits for air concentration data

Detection limits for individual species depend on specification of instrument or procedures of sampling and analysis. The NC set up the reporting limits as shown in Table 7.2 taking into account methods adopted by each country. Data under the detection limit were treated as "N.D." in the tables of the report. Regarding the particulate matter components measured by filter pack method, the detection limits for particulate matter components were determined as 0.01 μg/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 (EANET, 2003).

Table 7.2 Data quality objective values for the reporting limits

Species	Detection limits	Averaging time
SO_2	0.1 ppb	1 hour (Auto)/1 week (Manual)
HNO_3	0.1 ppb	1 week
HCl	0.1 ppb	1 week
NH_3	0.1 ppb	1 week
NO, NO_2, NO_x	0.1 ppb	1 hour (Auto)/1 week (Manual)
O_3	1 ppb	1 hour (Auto)/1 week (Manual)
PM	1 μg/m^3	1 hour (Auto)
Particulate matter components	0.01 μg/m^3	1 week

7.3. Monitoring site (Site audit)

7.3.1. Site selection

Selection of sampling sites is a critical factor in the monitoring, and the siting criteria are described in the Guidelines for Acid Deposition Monitoring in East Asia (EANET,

2000) 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 (EANET, 2010).

As described in Section 2.2.4, intake points of automatic instruments should be the height of sampling for SO_2, NO, NO_2, and O_3 is 1.5 m $\leq$ h $\leq$ 10 m above the ground, and the height for PM_{10} and $PM_{2.5}$ is 3 m $\leq$ h $\leq$ 10 m above the ground.

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 the station where automatic instruments are located. However, if the temperature in the station 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 SO_2 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 for integrity and validity of the monitoring data. 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 also 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

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 analyzes of manual samples and ensuring the quality control standards are sufficiently maintained.

(1) Analytical precision

To estimate the analytical variability of manual monitoring, 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 ^{o}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 analyzes:

$$S_i = (\Sigma d_i 2/2N_i)1/2 \qquad (7.1)$$

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 of dry deposition are prepared using reagent grade chemicals supplied to all analytical laboratories by the NC 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 should be prepared at concentration levels near the lower determination limit. Analyze the above standard solution repeating for 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, as shown below.

$$\text{Not detected} = 3\ (\text{s.d.}) \qquad (7.2)$$

$$\text{Lowest determination limit} = 10\ (\text{s.d.}) \qquad (7.3)$$

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

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 to be 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 the 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 the 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. Confirmation of measured data should be carried out when the monthly reports are prepared. If the data at the monitoring station can be access to the other offices, the preliminary data should be compared to the previous data. Although it is desirable to check all the measured data every day, it is extremely troublesome, and therefore, in some cases, the monitoring data for every 5 or 10 days will be 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 for 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 neighboring 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 as follows

- Measurement system: problems of intake tube, the instrument, the recorder, and CPU
- Data collection system: problems of the telemeter outputs, the reset signals, and the on-line errors
- Data treatment system: abnormal initial data and problems of data treatment equipment
- Others: influence of temporary local emissions etc.

Certain 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 are established to judge whether some abnormal hourly data are within the allowable range of data reliability, or could be adjusted in principle. These 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 (Ministry of the Environment Japan, 2010):

(Criteria for non-usable data in Japan)

SO_2

Span of the instrument

Lower limit: within ± 4% of the pre-determined value

Upper limit: within ±10% of the pre-determined value

Zero value of the instrument

Lower limit: within ± 2% of the maximum scale value

Upper limit: within ± 4% of the maximum scale value

NO, NO_2, NOx

Span of the instrument

Lower limit: within ± 4% of the pre-determined value
Upper limit: within ±10% of the pre-determined value

Zero value of the instrument

Lower limit: within ± 2% of the maximum scale value
Upper limit: within ± 4% of the maximum scale value

O_3

Span of the instrument

Lower limit: within ± 4% of the pre-determined value
Upper limit: within ±10% of the pre-determined value

Zero value of the instrument

Lower limit: within ± 2% of the maximum scale value
Upper limit: within ± 4% of the maximum scale value

SPM (Almost equivalent to PM_7)

Span of the instrument

Lower limit: within ± 4% of the pre-determined value
Upper limit: within ±10% of the pre-determined value

Zero value of the instrument

Lower limit: within ± 5 $\mu g/m^3$
Upper limit: within ± 10 $\mu g/m^3$

(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 precision

7.6.1. Point measurement

7.6.1.1. SO_2 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.

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 (e.g. Model 146; Thermo Fisher Scientific Inc.) delivers a SO_2 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 data logger 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.
7) Check whether precision check result exceeds ±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 according to the above steps 4) to 8) at office.

7.6.1.2. NOx precision check procedures

Manual method on site

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 the MFCs of the calibrator (e.g. Model 146; Thermo Fisher Scientific Inc.) 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 NO_2. The operator just has to set the calibrator.
2) Disconnect the analyzer from the manifold and then connect to the output port of the calibrator. 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 NOx into the worksheet. (Denoted by $[NO]_{Resp.}$ and $[NOx]_{Resp.}$, respectively)

4) Turn on the ozonator at the setting for precision check. Record the stable responses of NO and NOx into the worksheet.

Calculation

5) Assuming that there is no, or negligible, NO_2 impurity in the bottle gas, the concentration of actual NO_2 concentration can be calculated as follow:

$$[NO_2]\,Act = Adj.[NO]\,O_3\,(OFF) - Adj.[NO]\,O_3\,(ON) \qquad (7.4)$$

Where,

$Adj.[NO]O_3(OFF)$ is the adjusted NO response without ozone applied, Eq. (7.6)

$Adj.[NO]O_3(ON)$ is the adjusted NO response with ozone applied, Eq. (7.6)

6) The adjusted response of the NO_2 channel, $Adj.[NO_2]$ can be calculated by the equation (7.5):

$$Adj.\ [NO_2] = Adj.\ [NOx] - Adj.\ [NO] \qquad (7.5)$$

$$Adj.\ [NO] = ([NO]_{RESP.} - Z_{NO}) \cdot SF(NO) \qquad (7.6)$$

$$Adj.\ [NOx] = ([NOx]_{RESP.} - Z_{NOx}) \cdot SF(NOx) \qquad (7.7)$$

Where,

Z_{NO}, Z_{NOx} = NO and NOx zero readings, respectively, and

$SF = SGC / (span - zero)$

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 $[NO_2]Act.$ and adjusted NO_2 response $Adj.[NO_2]$ of analyzer into the precision check data sheet for NO_2 and then calculate the percentage difference. Check whether the difference exceeds ± 20%.
8) Check the analyzer and calibrator is in normal operating condition.
9) Complete the precision check and converter efficiency data sheets.
10) Record the result on the precision check control chart.

Automatic method

11) When the precision check is done by using automatic method, the steps 1) to 4) will be performed automatically. Then it will attain the % difference of NO_2 and complete other related procedures until the step 10).

7.6.1.3. O_3 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.

2) Check whether precision check result exceeds ± 20%.
3) Record the result on the precision check control chart.

Manual Method on site

<u>Precision check by Model 146 calibrator</u>

1) Disconnect the sample line of the ozone analyzer from the manifold and then connect to the output of the Model 146 calibrator (Thermo Fisher Scientific Inc.). Plug the ozone outlet of the manifold. Operate the calibrator 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
5) Check whether precision check result exceeds ± 20%.
6) Record the result on the precision check control chart.

<u>By Other Ozone Calibrators</u>

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.
6) 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.
7) Calculate the adjusted analyzer response, and then report the precision by the adjusted response and the actual ozone concentration.
8) Disconnect the ozone calibrator from the analyzer and then restore normal

connection of analyzer. Resume normal analyzer operation.

9) Complete the precision check data sheet and record the percentage difference.
10) Check whether precision check result exceeds ±20%.
11) Record the result on the precision check control chart.

By Ozone standard with internal ozonator - Model 49PS

1) Connect the zero air supply to the "ZERO AIR" bulkhead of Model 49PS ozone standard (Thermo Fisher Scientific Inc.).
2) Operate the ozone standard in local mode and at the precision level. Allow sufficient time for the ozone standard and analyzer to stabilize. Stabilization can be judged by the variation of analyzer response.
3) Record the stable response and the certified level concentration on the precision report form. Calculate the adjusted response and take record.
4) Disconnect the zero air supply, resume the normal setting and connection of the analyzer, and record the time period of the precision check.
5) Complete the precision check data sheet and record the percentage difference.
6) Check whether precision check result exceeds ± 20%.
7) Record the result on a control chart. Complete the precision check data sheet.

7.6.1.4. Particulate matter

The filter paper that has little air flow resistance and fully removes a particulate matter is put in the filter holder, and then it is connected to the sampling inlet. 24 hour sampling test is carried out by using this blank monitoring system. The precision can be determined as the relative standard deviation of duplicated measurement results using this blank filter or standard filter. For each PM_{10} automatic monitoring instrument, the measurement of precision should be done at least 4 times a year.

As for a PM_{10} monitor, the accuracy can be determined as relative error between monitoring value and setting value of flow rate or measuring results of the standard filter using automatic instrument or gravitational filter weight method. The determination of accuracy should be done once for three months for one PM automatic monitoring instrument. The accuracy test should be done before zero setting and any parameters of the instrument.

7.6.1.5. Manual monitoring

For manual monitoring method the precision test can be determined as relative standard deviation of duplicated measurement using blank filter or standard filter. Blank filters are treated exactly like a sample even to the point of mounting them in the sampling device. The only difference is that air is not drawn through them. The measurement of precision should be done at least 4 times a year. The accuracy can be determined as relative error between measuring results and setting values using standard filter. The value of accuracy values should be checked at least once a year.

7.6.2. 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 the 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 (up to 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 %.
- For the used configuration additional stray light arise due to the simultaneous

measurement of absorption spectra from different light paths with one spectrometer detectotion 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 rations 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):

$$\sigma_p = \sqrt{n_p} \tag{7.8}$$

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:

$$\sigma_p(t_0) = \sqrt{n_p(t_0)} \tag{7.9}$$

The signal to noise ratio therefore is:

$$\left(\frac{S}{N}\right)_{ration}(t_0) = \frac{n_p(t_0)}{\sigma_p(t_0)} = \frac{n_p(t_0)}{\sqrt{n_p(t_0)}} = \sqrt{n_p(t_0)} \tag{7.10}$$

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:

$$\sigma_{p\cdot\frac{I_1}{I_2}}(t_0)=\sqrt{\left(\frac{\sqrt{n_p(t_0)}}{n_p(t_0)}\right)^2+\left(\frac{\sqrt{n_p(t_0)}}{n_p(t_0)}\right)^2}$$

$$\sigma_{p\cdot\frac{I_1}{I_2}}(t_0)=\sqrt{2\cdot\left(\frac{\sqrt{n_p(t_0)}}{n_p(t_0)}\right)^2}$$

$$\sigma_{p\cdot\frac{I_1}{I_2}}(t_0)=\sqrt{\frac{2}{n_p(t_0)}}=\frac{\sqrt{2}}{\sqrt{n_p(t_0)}}=\sqrt{2}\cdot\sigma_p(t_0) \qquad (7.11)$$

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 $\sigma_{p\cdot\frac{I_1}{I_2}}(t_0)$ (using the Root Mean Square (RMS) values of the divided spectrum) on a double logarithmic scale, we receive the following:

$$\log\left(\sigma_{p\cdot\frac{I_1}{I_2}}(t_0)\right)=\log\left(\frac{\sqrt{2}}{\sqrt{n_p(t_0)}}\right)=\frac{1}{2}\cdot\log 2-\frac{1}{2}\cdot\log n_p \qquad (7.12)$$

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:

$$\left(\frac{S}{N}\right)_{ration}(t_0)=\frac{n_p(t_0)}{\sigma_p(t_0)}=\frac{\sqrt{2}}{\sigma_{p\cdot\frac{I_1}{I_2}}(t_0)} \qquad (7.13)$$

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. DOAS monitoring only focuses on 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.

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) Determination of the 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 $1\cdot\sigma$ 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 the DOAS instrument is the evaluation of the fit residuum. The assumption is made because the DOAS instrument cannot measure any trace gases whose absorptions structures are smaller than the current fit residual $\Delta\Psi$:

$$\left(S'_{\max} - S'_{\min}\right)\cdot \bar{c}\cdot L \geq \Delta\Psi \qquad (7.14)$$

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:

$$\overline{c_{\min}} = \frac{\Delta\Psi}{\left(S'_{\max} - S'_{\min}\right)\cdot L} \qquad (7.15)$$

7.7. QA/QC implemented by the NC

The NC should appoint the 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. The NC should prepare reports on the QA/QC activities implemented by the participating countries, and the QA/QC levels with other relevant networks. The 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 the network QA/QC manager
  - Development of data quality objectives (DQOs)
  - Provision of information for preparing SOPs
  - Implementation of inter-laboratory comparison 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

It is necessary to improve knowledge and expertise related to air concentration monitoring. Therefore, the 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, The Interim NC had carried out the 1st 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. Currently the NC provides the EANET individual training course inviting beginner operators in participating countries every years. The JICA Trainig Course on Monitoring and Control Technologies of Acid Deposition has been carried out annually, which includes subjects on air concentration monitoring. The NC should continue the training on air concentration and 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.

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8. Conclusions

This manual shows guideline of air concentration monitoring in EANET in order to standardize air concentration monitoring methodology. In principal, each air concentration monitoring sites EANET should follow satisfy the conditions in this manual. However, some requirements in participating countries will not comply with those in this manual. For such case, the requirements specific in each country can take precedence unless monitoring data are comparable with those in the other countries.

In order to develop air concentration monitoring methodology which will fulfill the scopes of EANET, some issues should be considered.

First, the conventional NOx analyzer cannot selectively detect NO_2. The alternative monitoring methods of NO_2 are recommended to install especially in remote sites.

Photothermal Laser Deflection (PLD) is an analytical technique to measure in real-time the mass concentration of particles and gaseous pollutants. PLD uses a pump laser to locally heat the particle or gaseous species, thus changing the refractive index of the surrounding gas to form a thermal lens.

A probe laser beam travelling through the thermal lens is temporarily deflected, and the amount of deflection is proportional to the species mass concentration. Cavity Ring-Down Spectroscopy (CRDS) contains diode lasers to detect volatile organic compounds (VOCs), NO_2, various radicals, and atmospheric aerosol particles. The typical detection limit of CRDS for VOCs and NO_2 are in the parts per billion (ppb) to parts per trillion (ppt) range (Kebabian et al., 2008).

Laser Induced fluorescence (LIF) equipment for selective NO_2 measurement consists of a tunable broad-band optical parametric oscillator laser pumped by the third harmonic of a Nd:YAG laser is used as a fluorescence excitation source. The difference signal between peak and bottom wavelength is used to determine the NO_2 concentration. The sensitivity of NO_2-LIF is 30 pptv in 10 second integration time.

Second, among the current monitoring methods, only filter pack monitoring is feasible for monitoring of aerosol composition. Because there are usually diurnal variations of dry deposition velocity, hourly measurement of air concentration is preferable. However, time resolution of filter pack is one or two weeks described in this manual. Therefore, adoption of aerosol measurement with shorter time resolution could be desired. A Particle-Into-Liquid Sampler coupled with Ion Chromatograph (PILS-IC), Monitor for AeRosols and GAses (MARGA) a Gas-Particle Ion Chromatograph (GPIC), a Gas and Aerosol Collector-Ion Chromatograph (GAC-IC), Sulfate and Nitrate Monitors (R&P 8400S and R&P 8400N) and a Semi-Continuous OC/EC Analyzer (Sunset Inc.) are automated or semi-continuous instruments capable of acquiring highly temporal resolution measurements of chemical composition of atmospheric PM.

Third, validity of air concentration monitoring methods described in this manual should be checked by the other monitoring methods. Especially, $PM_{2.5}$ is sensitive for relative humidity, and thus it is hard to confirm validity in tropical regions. Some countries established criteria that each $PM_{2.5}$ monitor should verified by equivalence of the standard method of weight measurement (U.S. Environmental Protection Agency, 1997; Ministry of the Environment Japan, 2010). Parallel monitoring of the testing method and standard or verified methods is recommended at the monitoring stations.

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Asia Center for Air Pollution Research
1182 Sowa Nishi-ku, Niigata-shi, 950-2144, Japan
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