9.2 Continuous analysis methods

9.2.1 Introduction

Because there are many occasions when measurement results obtained from continuous analyzers are used by government, it is essential to organize the data in a form that can be evaluated. Using measurement methods compatible with environmental standards, it is essential to establish a system that makes possible suitable data management such as data processing, evaluation methods, and so forth. In the case of analyzers, if the equipment in question conforms to both domestic and international standards, there will be no disparity between function and capability, and it is more important to implement appropriate installation of measuring stations and their systematic support management, rather than selecting that particular type of equipment.

Measuring method of monitoring the ambient air comprises the domestic laws and/or standards of each country and also international standards. At present, the bringing into line of standards internationally is being promoted. When building an atmospheric monitoring system, the typical standards that become both the basis and the standard reference are as follows:

ISO: International Organization for Standardization (international standards)

CFR: Cord of Federal registration (US standards)

ASTM: American Society for Testing and Materials (US standards)

JIS: Japan Industrial Standards (Japanese standards), Ambient Air Continuous Monitoring Manual (Environment Agency)

9.2.2 Continuous analyzer

Table 9.2.1 shows data concerning the continuous atmospheric analyzers that are used as standards.

Table 9.2.1 (1) Standard continuous analyzers

Measurement targets		
SO_2 Sulfur dioxide	Principle specifications	Ultraviolet fluorescent method, standard measuring range 0 to 0.05/ 0.1/0.2 /0.5/ 1.0ppm.
	Points to note	Sufficient precautions are required for the following: When the indicated values have incurred direct influence from aromatic hydrocarbons such as toluene and xylene, when a scrubber is needed to remove hydrocarbons, sites where motor vehicle exhaust gas levels are high, when the amount of scrubbing has reached high levels for hydrocarbons generated on building sites, etc., and when replacement frequency has risen.
NOx Oxides of nitrogen	Principle specifications	Chemiluminescence method, standard measuring range 0 to 0.1/ 0.2/ 0.5/ 1.0ppm.
	Points to note	With the switch method, the NO_2 can be scattered if the NO concentration is high, or fluctuates severely. Check dehumidifying measures, because the indicated values are interfered with moisture. High concentrations of NH_4 in the air cause dirtying within the reacting cell due to O_3 from the gas reactions, for which a scrubber is effective in removing the hydrocarbons. Further, there are also occasions when organic nitrogen compounds are measured as NO by the converter.
O_3	Principle specifications	Ultraviolet absorption method, standard measuring range 0 to 0.1/ 0.2/ 0.5/ 1.0ppm.

Table 9.2.1 (2) Standard continuous analyzers

Measurement targets		
Ozone	Points to note	Because this is the switch method, support and management of the ozone decomposer is important. Because the chemiluminescence method requires a supply of ethylene as a reactant gas, the ultraviolet absorption method is most widely used.
CO Carbon monoxide	Principle specifications	Infrared absorption method, standard measuring range 0 to 5/10/20/50/100ppm.
	Points to note	There are two methods, the switch NDIR method and the gas correlation NDIR method. The switch method is a measuring method unique to Japan.
NMHC Non-methane hydrocarbons	Principle specifications	Gas chromatograph method, standard measuring range 0 to 5/10/50ppm.
	Points to note	There are many cases of the measuring equipment being damaged by inadvertently sucking in dirty air when starting Regular maintenance work such as cleaning the switching valves, columns, and pipes is needed. The measured values apply CH_4 conversion and sensitivity checks are done by C_3H_8 is needed. 〈Water supplied to the hydrogen generator〉 pure water that has been specially refined.
THC Total hydrocarbons	Principle specifications	Hydrogen flame ionization method, standard measurement range 0 to 5/ 10 /20 /50 /100ppm.
	Points to note	In the various countries of South east Asia, THC are often measured. This is a continuous measuring method, which is different from the gas chromatograph method.
SPM Suspended particulate matter	Principle specifications	β ray absorption method, standard measurement range 0 to 1/5/10mg/m^3
	Points to note	It is important to ensure that a hood or screen is attached to the tip of the sampling tube to prevent rainwater, insects, or the like from being sucked in. Because measurements in places with high concentrations of automobile exhaust gas (in particular, diesel exhaust gas) suffers from the filter paper becoming clogged, a very powerful suction pump is used. Be careful when handling β ray-emitting isotopes.
CO_2 Carbon dioxides	Principle specifications	Infra red absorption method, standard measurement range 0 to 500ppm, 350 to 450ppm
	Points to note	Highly sensitive measuring equipment in the range of 350 to 450ppm, responsive to global warming, requires various important maintenance measures against ambient temperatures and dehumidification of sample air around -80℃ dew point.

9.2.3 Objectives and types of ambient air measurements

There are different types of measuring stations depending on the atmospheric measurement objectives, as shown in Table 9.2.2.

Table 9.2.2 Measuring station objectives and types

General ambient air measuring stations	These are standard atmospheric measuring stations that generally monitor the state of air pollution in cities, residential areas, and industrial zones. They use standard analyzers.
Automobile exhaust gas measuring stations	These are the measuring stations that, continuously monitor the pollution state in the area around junctions and at roadsides where the air pollution is particularly severe due to automobile exhaust gas. They use analyzers that possess highly concentrated measuring ranges. It is important to ensure that dirt and particles do not interfere with the analyzers.
Ambient air measuring stations	These stations were established with the objective of obtaining basic samples from monitoring a wide range of ambient environment (background) conditions in unpolluted areas such as mountains, fields, and beaches, and because they measure low concentrations, the analyzers need to be highly sensitive with few fluctuations from zero. Further, there are occasions when analyzers are also installed to measure H_2S, O_3, CO_2, and acid rain as well.

9.2.4 Construction and facilities of measuring stations

The measuring stations must be constructed so that the analyzers that have been installed can be protected easily

and they are easy to be maintained and managed. The points to note as for the measuring station facilities are shown in Table 9.2.3.

Table 9.2.3 Measuring station facilities

Power source Equipment	There must be sufficient surplus power, so that even when large pumps or the like are being powered, there are no fluctuations in the voltage, and this must also be the same as when an automatic voltage regulator is used. If the voltage fluctuations are severe, ideally an uninterruptable power source such as UPS should be used.
Air conditioner	The air conditioning should ideally maintain the air temperature at about -5℃, and never exceed 30℃, so that the air does not become too cold and have dew form. Also, ensure that the sampling tubes are not exposed to the chill from the air conditioner directly.

Further, the air sampling tubes should be as shown in Table 9.2.4.

Table 9.2.4 Sampling tube laying at measuring stations.

Collective sampling	The air is collected as one large flow in a manifold inside the measuring station building, where the air specimens are distributed through Teflon tubes into the various different measuring equipments. Metal tubes with Teflon lining, or reinforced glass are used. The PVC use materials which are noto charged with electricity such as PVC tubes or stainless tubes,etc..
Individual sampling	The air is absorbed by individual Teflon sampling tubes of 6 to 8mm internal diameter from the outside of the measuring station building, and the SPM uses a PVC tube with an internal diameter of approximately 20mm.

9.2.5 State of international standards

(1) Introduction

Measurement and analysis technology for the ambient air is applied to a wide range of actions, centering on continuous ambient air monitoring, and the target fields are also enormously diverse. It is essential to improve the quality of measuring technology in order to more accurately measure concentrations of hazardous substances in the air than at present. Further, there is much interest in the measure and analysis of greenhouse gasses, which is in itself a problem on a global scale and new air pollutants such as hazardous chemical products, also called HAP, which have recently become as major a topic. The important point in regard to such measurement and analysis is the consistency of their results, and they should have the recreatability and reliability in a broad sense. Recently, overseas technical support has also become very active, and the international consistency on measurement results is being greatly needed. There is a necessity for standardization of the methods of measurement and analysis, and it is necessary to review them constantly to keep them up-to-date.. In Japan, the measurement and analysis of the ambient air is carried out either in accordance basically with JIS, or using methods, directions and manuals in accordance with regulations, notifications, and notices based on the Air Pollution Control Law.

Other countries also have many regulations, and the basic ideas on the ambient air are contained in "Selected Methods for the Measurement of Air Pollutants," which were determined by the U.S. Department of Health, Education, and Welfare in 1965, and it is no exaggeration to say that it forms the basis for the various standards explained below.

In the U.S., the establishment and management of environmental quality standards are laid out by the Cord of Federal Regulation, which are continually revised year after year, and which are also often quoted in other standards. In the U.S., besides the CFR there are various well-known standards, such as ASTM, NIST, IEC, and ANSI. In Europe, there is the DIN in Germany and the BS in Britain and, moreover, internationally, there used to be the renowned WHO Selected Methods, all these standards have been unified internationally as the International Standard, ISO, by the International Organization for Standardization.

A summary of the contents of the CFR, ASTM, and ISO, which may also be called the typical standards, is given below. Because each standard is continually revised every year, there is a great need for research into accordance with the various Japanese standards. Further, the statements from the international standards cited below are highly detailed, and they are the refer to a lot of literature. They are also highly reliable as standards because their contents are revised, and they have greater value as literature than they do as standards.

(2) Japanese standards

The measuring methods for environmental quality standards in Japan are shown in notices and notifications based on the Air Pollution Control Law, the guideline on support and management of ambient air measuring equipment, and the Ambient Air continuous monitoring manual. The main points of which are as follows:

Sulfur dioxide	Solution electrical conductivity method	JISB7952 solution electrical conductivity method
Sulfur dioxide	Ultraviolet fluorescent method	JISB 79520 ultraviolet fluorescent method
Carbon monoxide	Methods using non-diffuse infrared analyzers	JISB 7951 infrared absorption methods
Suspended particulate matter	light diffusion method, piezo-balance method, β ray absorption method	JISB 7954 light diffusion method, piezo-balance method, β ray absorption method
Photochemical oxidant	absorption spectrophotometry, coulometric method	JSB 7957 absorption spectrophotometry, coulometric method
Nitrogen dioxide	absorption spectrophotometry using Saltzman agent	JISB 7953 absorption spectrophotometry
Nitrogen dioxide	Chemiluminescence method	JISB 7953 chemiluminescence method
Hydrocarbons	Direct measuring method	JISB 7956 hydrogen flame ionization detection method

(3) Cord of Federal Resister (CFR)

This law, which falls under the jurisdiction of the United States government's EPA, is the most influential law for environmental measuring. The 40CFR 50 National Primary and Secondary Ambient Air Quality Standard not only indicates the national standards for air quality, but also regulates the measuring methods in detail for individual substances, as shown in Appendix A to K.

The 40 CFR 53 Ambient Air Monitoring Reference and Equivalent Methods regulates the definitions and methods of experiment for each measurement method. There are two types of measurement methods, manual and automated, and it is extremely interesting that SO_2 is defined to be measured by manual method.

Manual Reference Method

TSP High Volume Sampler

LED High Volume Sampler with Atomic Absorption Analysis

SO_2 Pararosaniline Method

Automated Reference Method

O_3 MP Chemiluminescnce with Ethylene. CP Ultraviolet Photometry

NMHC MP Gas Chromatography with Flame Ionization Detector CP Calibration Gases

NO_2 MP Chemiluminescnce with Ozone. CP Gas Phase Titration of on NO Standard with Ozone or NO_2 Permeation

CO MP Nondisparsive Infrared Spectrometry Device. CP Calibration Gases

Titles for APPENDIX A~K are introduced below.

APPENDIX A - Reference Method for the Determination of Sulfur Dioxide in the Atmosphere (Pararosaniline Method)

APPENDIX B - Reference Method for the Determination of Suspended Particulate Matter in the Atmosphere (High Volume Method)

APPENDIX C - Measurement Principle and Calibration Procedure for the Carbon Monoxide in the Atmosphere (Non-Dispersive Infrared Photometry)

APPENDIX D - Measurement Principle and Calibration Procedure for the Measurement of Ozone in the Atmosphere

APPENDIX E - Reference Method for the Determination of Hydrocarbons Corrected for Methane

APPENDIX F - Measurement Principle and Calibration Procedure for the Measurement of Nitrogen Dioxide in the Atmosphere (Gas Phase Chemiluminescnce)

APPENDIX G - Reference Method for the Determination of Lead in Suspended Particulate Matter Collected from Ambient Air

APPENDIX H - Interpretation of the National Ambient Air Quality Standards for Ozone

APPENDIX I - Reserved

APPENDIX J - Reference Method for the Determination of Particulate Matter as PM_{10} in the Atmosphere

APPENDIX K - Interpretation of the National Ambient Air Quality Standards for Particulate Matter

(4) American Society for Testing and Materials (ASTM)

This is a broad range of standards equivalent to Japanese Industrial Standards (JIS), and it divided into 15 sections, which regulate a vast number of standards concerning all manner of materials, experiments, analyses, measurements, electricity, medical treatment, and so forth. Many standards are quoted by JIS.

Measurement and analysis of the ambient air is given in,

Section 11 Water and environmental Technology

Volume 11.03 Atmospheric Analysis

The following titles are cited for items relating to ambient air continuous monitoring in Japan:

D- 1607- 91 Standard Test Method for Nitrogen Dioxide Content of the Atmosphere (Griess-Saltzman Reaction)

D- 1704- 95 Standard Test Method for Determination the Amount of Particulate Matter in the Atmosphere by Measurement of the Light Absorbance of a Filtered Sample

D- 2914- 95 Standard Test Method for Sulfur Dioxide Content of the Atmosphere (West - Gaeke Method)

D- 3249- 95 Standard Practices for General Ambient Air Analyzer Procedures

D- 3608- 91 Standard Test Method for Nitrogen Oxides (Combined) Content in the Atmosphere by the Griess-Saltzman Reaction

D- 3609- 91 Standard Practices for Calibration Techniques Using Permeation Tubes

D- 3824- 95 Standard Test Method for Continuous Measurement of Oxides of Nitrogen in the Ambient or Workplace Atmosphere by the Chemiluminescent Method

D- 4298- 95 Standard Guide for Intercomparing Permeation Tubes to Establish Traceability

D- 4536- 95 Standard Test Method for High- Volume Sampling for Solid Particulate Matter and Determination of Particulate Emissions

D- 5011- 92 Standard Practices for Calibration of Ozone Monitors Using Transfer Standards

D- 5110- 94 Standard Practices for Calibration of Ozone Monitors and Certification of zone Transfer Standards Using Ultraviolet Photometry

D- 5149- 90 Standard Test Method for Ozone in the Atmosphere: Continuous Measurement by Ethylene Chemiluminescent

D- 5015- 95 Standard Test Method for pH of Atmospheric Wet Deposition Samples by Electrometric Determination

D- 5280- 94 Standard Practice for Evaluation of Performance Characteristics of Air Quality Measurement Methods with Linear Calibration Function

(5) International Organization for Standardization (ISO)

The ISO International Standard is the international standard for quality control. The ISO standards are attracting attentions by the debut of the ISO9000 and ISO14000 series. ISO holds an international position as the global standards across a wide range of materials, processing, motor vehicle, plastics, foodstuffs, medical treatments, and measuring and analysis.

Items concerning the measurement and analysis of the ambient air are basically as below, but both CFR and ASTM are often quoted with regard to their content.

13. Environment and Health Protection. Safety

13. 040 Air Quality

13. 040. 10 General Aspects

ISO 4225 : 1994 Air Quality - Vocabulary - Biling Edition

ISO 4226 : 1993 Air Quality - Unit of measurement

ISO 6879 : 1983 Air Quality - Performance characteristics and related concepts for air quality measuring methods

ISO 7708 : 1983 Air Quality - Particle size fraction definition for health - related sampling

ISO 8756 : 1994 Air Quality - Handling of temperature, pressure and humidity data

ISO 9169 : 1994 Air Quality - Determination of performance characteristics of measurement methods

13. 040. 20 Ambient atmospheres

ISO 4219 : 1979 Air quality - Determination of gaseous sulfur compounds in ambient air Sampling equipment

ISO 4220 : 1983 Ambient air - Determination of a gaseous acid pollution index - Titrimetric method with indicator potentiometric end-point detection

ISO 4221 : 1980 Air quality - Determination of mass concentration of sulfur dioxide in ambient air - Thorin spectrophotometric method

ISO 4227 : 1989 Planing of ambient air quality monitoring

ISO 6767 : 1990 Ambient air - Determination of the mass concentration of sulfur dioxide - Tetrachloromercurate (TMC) /Pararosaniline method

ISO 6768 : 1985 Ambient air - Determination of the mass concentration of nitrogen dioxide - Modified Griess-Saltzman method

ISO 7168 : 1985 Air quality - Presentation of ambient air quality data in alphanumerical form

ISO 7996 : 1985 Ambient air - Determination of the mass concentration of nitrogen oxides - Chemiluminescence method

ISO 8186 : 1986 Ambient air - Determination of the mass concentration of carbon monoxide - Gas chromatographic method

ISO 9359 : 1989 Air quality - Stratified sampling method for assessment of ambient air quality

ISO 9835 : 1993 Ambient air - Determination of a black smoke index

ISO 9855 : 1993 Ambient air - Determination of the particulate lead content of aerosols collected on filters - Atomic absorption spectrometric method

ISO 10313 : 1993 Ambient air - Determination of the mass concentration of ozone - Chemiluminescence method