Chapter 9   Air pollution measuring methods (atmosphere)

9.1   Basis of air pollution measurement

9.1.1 Introduction

The first step in air pollutant concentration is to define clearly the objectives of measuring concentrations of air pollutants, and to determine the target substances for measurement.   The objectives that are usually intended are as follows.   ① To thoroughly understand the pollution levels and concentration fluctuations when the sources and pollutants are clearly known;   ② When neither the source nor the pollutants are clearly known, to examine the causes of the pollution;   ③ When the source is identified, to thoroughly understand the levels of pollution and the types of pollutants emitted;   ④ When the pollutant has been identified, to specify the source and to determine the level of its contribution,   ⑤ To easily understand border area concentrations and exposure sites for voluntary periods of time;   ⑥ To thoroughly understand the broad range pollution level and its fluctuations.

Measurements are taken using collection-analysis (manual analysis), concentration meters, continuous (automatic) analyzers, and the other simple measuring equipment.   Manual analysis is applicable to most of compounds that can be used with ordinary equipment such as spectrophotometers and gas chromatographs, because once has been collected at fields, it has to be carried back to the laboratory for analysis.   The concentration meter obtains on-site values in a portable form for the target gas.   The simple measuring equipment is inexpensive and easy to operate, and aims to be able to take measurements on-site.   The continuous analyzer is used for fixed point observations, and records both the time course and the mean concentrations.   In recent years, on-site analytical values have been obtained, and portable continuous analyzers have also been on the market, but the basic patterns of air pollution measurement are these four.

Of the above objectives, ② and ③ require accurate analysis manually, while ① and ⑥ require continuous analysis, and ⑤ uses simple measuring equipment.   For the ④ objectives, both manual and continuous analysis are used contiguously.   Even with expensive measuring equipment, if the selection of the equipment and the operation employed are wrong, accurate environmental information will not be obtained, whereas even with inexpensive equipment, the above objectives can be attained, depending on the approach.   If a specific measuring pattern is selected appropriately, rational measurements are entirely possible.

9.1.2 Measurement methods classification and sampling

There are many different analysis and detection principles that can be used in the above four measuring patterns [1][2]. Fig.9.1.1 shows them ranged in order.   These selections are made while considering the sensitivity of the target substance, the selectivity (interference), accuracy, economic viability, ease of use, and so forth.   Each measurement pattern is explained with reference to the next paragraph.   In addition, there is the laser remote sensing method, which can measure both airborne aerosols and gas across a wide area directly, without the need for sampling.
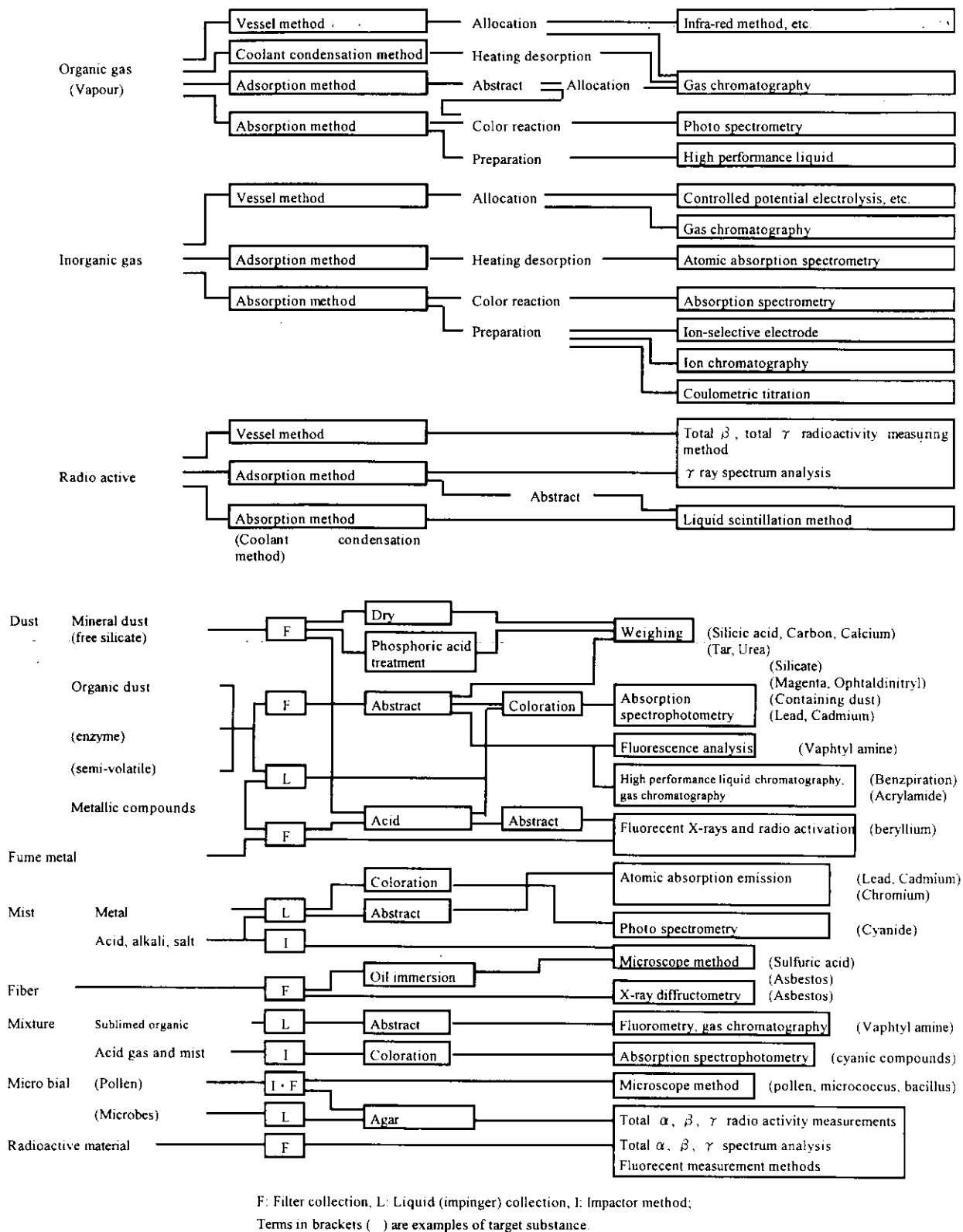
Organic gas
(Vapour)

Vessel method	— Allocation	Infra-red method, etc
Coolant condensation method	— Heating desorption	
Adsorption method	Abstract — Allocation	Gas chromatography
Absorption method	Color reaction	Photo spectrometry
	Preparation	High performance liquid

Inorganic gas

Vessel method	Allocation	Controlled potential electrolysis, etc.
		Gas chromatography
Adsorption method	— Heating desorption	Atomic absorption spectrometry
Absorption method	Color reaction	Absorption spectrometry
	Preparation	Ion-selective electrode
		Ion chromatography
		Coulometric titration

Radio active

Vessel method		Total β, total γ radioactivity measuring method
Adsorption method	Abstract	γ ray spectrum analysis
Absorption method		Liquid scintillation method

(Coolant   condensation
method)

Dust   Mineral dust
       (free silicate)   — F — Dry / Phosphoric acid treatment — Weighing   (Silicic acid, Carbon, Calcium)
                                                                              (Tar, Urea)

Organic dust   (Silicate)
                                                                              (Magenta, Ophtaldinitryl)
                        — F — Abstract — Coloration — Absorption spectrophotometry   (Containing dust)
(enzyme)   (Lead, Cadmium)

(semi-volatile)   Fluorescence analysis   (Vaphtyl amine)

                        — L —   High performance liquid chromatography,   (Benzpiration)
Metallic compounds   gas chromatography   (Acrylamide)

                        — F — Acid — Abstract — Fluorecent X-rays and radio activation   (beryllium)

Fume metal

Mist   Metal   — L — Coloration / Abstract — Atomic absorption emission   (Lead, Cadmium)
                                                                                   (Chromium)
       Acid, alkali, salt — I —   Photo spectrometry   (Cyanide)

Fiber   — F — Oil immersion — Microscope method   (Sulfuric acid)
                                                                  (Asbestos)
                                              X-ray diffructometry   (Asbestos)

Mixture Sublimed organic — L — Abstract — Fluorometry, gas chromatography   (Vaphtyl amine)

         Acid gas and mist — I — Coloration — Absorption spectrophotometry   (cyanic compounds)

Micro bial (Pollen)   — I·F — Microscope method   (pollen, micrococcus, bacillus)

            (Microbes)   — L — Agar — Total α, β, γ radio activity measurements

Radioactive material   — F — Total α, β, γ spectrum analysis
                              Fluorecent measurement methods

F: Filter collection, L: Liquid (impinger) collection, I: Impactor method;

Terms in brackets ( ) are examples of target substance.

Fig.9.1.1   Measuring pattern of various kinds of pollutants using manual methods [3]

In environmental measuring, except for the aforementioned remote sensing, because only part of the air is taken as a sample, sampling is essential so that both spatial and temporal representative values might be obtained.   In

246

order to learn the pollution level for a given region, samples are taken at points so as to obtain mean concentrations and sites for which the highest concentrations can be expected: ground level of noxious substances emitted from specific chimneys and the side of major roads. On the other hand, because the concentration is governed by wind speed, climate, day of the week, and season, sampling is performed with reference to conditions that indicate both the highest and the lowest concentration in order to obtain an overview of the pollution level with only a small sample, or else measurements are taken continuously throughout the year. Moreover, in order to determine the annual mean concentration, it is necessary to take samples twice a month, each sample being over a 24 hour period.

9.1.3 Manual analysis methods

This pattern is used for nearly all pollutants (Fig.9.1.1), and the state in which they are introduced to the analyzing equipment is nearly always either liquid or gas. At this point, the concentrations of the samples in the air are determined by Eq. (1) (except for vessel collection), so that the quantitative concentration range is determined not only by the sensitivity of the analyzers, but also by the sample air volume.

$$C = \frac{M}{V} \hspace{2em} \dotfill \hspace{1em} (1)$$

Where, C: Concentration, M : Target substance amount (Detection amount $\times$ Collection quantity / Injection quantity), V: Sample air volume (Aeration flow rate $\times$ Time)

Consequently, in order to measure lower concentrations with the same equipment, it is necessary to increase the sample air volume within a range that does not affect accuracy. Measurement accuracy [in addition to operational errors and analytical instrument accuracy] are governed by collection efficiency and the measurement accuracy of sample air flow rate. For this reason, a balance between them is important, and if reasonable collection conditions are unclear, it is necessary to verify the collection efficiency and then, correctly connect a integrated flow meter, and start the collection. The collection efficiency by both the concentration and the flow (or gas meter) rate. This can be verified by connecting up the two collector in series. It is important to be careful here, as the flow meter (including the rota meter and hot wire types) can be easily affected by contamination in the measuring line.

When analyzing air pollutants manually, both spectrometry (absorption spectrophotometry, atomic absorption spectrometry, and ICP emission method), which is widely used, and chromatography (gas chromatography and liquid chromatography) are given in detail as examples as follows.

(1) Spectrometry

The responses (relative values of absorption and emission strength) for the sample solutions and the standard solutions are obtained using a spectrophotometer. The calibration curve is usually prepared for the determination. The responses are plotted as the Y-axis and concentrations of five types or more of the standard solution as X-axis. Which are prepared by diluting the proto standard solution (standard substances dissolved in solvents, and sometimes

247

available on the market). Using the usually linear relationship, the amount of the target substance in the samples determined from the sample solution responses, parallel with which, the blank values (the smaller the better) are determined from responses to the unused absorption solution and the extract from the filter paper, the difference between the being the amount of the target substance. The causes of error of the process are thought to be ① operating error (injection of the sample solution into the analyzer and transfer of the specimen of the collected target substance to the sample solution) and the analytical instrument and ② error due to the reproducibility of the equipment itself and ③ interference from coexisting substances. Against the ③ causes of error, we are to use specific collecting solutions, to select the spectrometer conditions (wave length of the spectrometer and atomization atmosphere, emission temperature, etc.), and to pretreat the sample appropriately, but these are not perfect to avoid the interference. On the other hand, the standard addition method is effective in correcting the negative and systematic error.

(2) Chromatography

Chromatography, representative differential analytical method, is to identify over a retention time of the chromatogram peak, and then determine over the peak area. Both gas chromatograph and liquid (ion) chromatograph analyzers are composed of a separating column, a detector and a carrier introducer, and a thermostat. In order to use one, it is essential to set the temperature, the length of the column, internal diameter, packing, species of stational faces liquid, type of detector, flow rate and species of carrier gas, (composition of carrier solution), sample injection volume, and other analysis conditions. In particular, the column conditions govern the degree of separation, and the detector the sensitivity and selectivity. The standard substance is injected under the set conditions, and the peak retention time is measured. Unknown samples of many kind of volatile organic compound should be identified in parallel with a mass spectrometer because the peak positions may well overlap. The atmospheric concentration is normally low, so that by collecting as shown in Fig. 9.1.1 and infusing either the whole sample collected or part thereof, the response of the volume of the control substance and the sample can be compared and calculated as per Eq. (2).

$$C = \frac{(\frac{\ell}{\ell_0}) \times (\frac{P_0}{P}) \times m}{V} \quad \dotfill \quad (2)$$

Where, C = Concentration; v= Sample volume, v_0 = Injection volume, P = Response for standard substance, P_0= Response for sample; m = Amount of standard substance, V = Volume of air sample.

The linearity of the calibration curve must be confirmed once in the concentration range used. Moreover, the blank values are measured in determination with the pretreatment, such as the concentration operation. The error factors, such as collection conditions, including the collection rate, and the injection operation, the reproducibility of the equipment and so forth, are the same as for the spectrometry.

Computer software with data loggar, or built-in computer data processors are usually used for chromatogram data processing, but manual calculation with a pen recorder is essentially the same. Rather, it is essential to

monitor such analogue data as the peak shape and so forth, and never be remiss in checking and evaluating the analytical results.

The reproducibility of the peak position (retention time) is characteristic in the chromatography to effect on errors of the identification. Because the carrier flow rate and the temperature govern the peak position and area, they must be checked after setting a stable condition. Further, over long periods, the column suffers from deterioration due to the flow out of the stationary phase liquid (gas chromatograph) and the contamination (liquid chromatograph), so that the retention time gradually changes. The retention time and area of the standard must be checked once every few days during continuous use, as well as when the equipment is first to be used each time. Moreover, the air sample collected in the vessel can be used to check the preservability, and the active gas should be collected to be changed into stable components.

9.1.4 Concentration meter

Both gas concentration meters and total suspended dust concentration meters are used. Gas concentration meters introduce the air sample to the measuring equipment, and thereby measure the concentration of the target substance directly. For coexisting substances, there is a sufficient selectivity factor (response for the target gas/response for the coexisting gas), and if the detection limit is less than 1/10 of the environmental standard, the detection is very efficient. However, the concentration meter has limits to its selectivity and accuracy, therefore especially in measuring the approximate concentration level of the coexisting gases, which interfere positively with the measurement, so it is essential to check in advance the extent of the interference due to an accumulation in the concentration and reciprocal selection factors.

The meter is set to zero passing zero gas that does not contain the target component, and sets the sensitivity controlling tweezers so that the index value fits in that of a standard gas. The frequency of adjustment depends on the principles involved. For example if the principle is photometric, regular checks by the manufacturer are few and far between, and if the principle is electrochemical, the checks must be carried out each time the equipment is used. The precision is expressed as the coefficient of variation and the zero drift per unit time. Dust concentration meters are also relative concentration meters, which introduce the standard dust flow to the concentration meter, and thereby adjust the sensitivity, and neither principle experiences much in the way of fluctuation in sensitivity during normal operation, so that regular checks by the manufacturer alone are sufficient to used it.

9.1.5 Continuous analyzers

Continuous analyzers are automatic devices that continuously introduce the air sample, and record the output either continuously or with intervals. Such devices have standard gas generators built-in, and introduce the standard gas in place of the air sample on average once a day, check the sensitivity, and adjust it as necessary, so that the equipment involved usually tends to be rather large. The accuracy is expressed in the same way as for the concentration meters.

9.1.6 Measurement accuracy and measurement management

(1) Measurement accuracy [4]

This section recounts detection limits and determination limits which depend upon measurement accuracy. Taking the detection limit (Cd in Fig.9.1.2) to be the threefold value of the standard deviation (S_b) of the response (mean value R_{Bl}) of the blank sample is also recommended in a IUPAC report (Fig.9.1.2.) The R_b and S_b in Fig.9.1.2 are determined by the blank tests of 10 to 20 times. Around the detection limit, the coefficient of variation is extremely huge. Fig.9.1.2 also shows the relation between the "coefficient of variation" and the concentration of Zn in ICP emission analysis [5]. If the "minimum determination limit" (Ct in Fig.9.1.2) is taken as a concentration equivalent to $R_b + 10S_b$, an accuracy of about 10% can be expected. On the other hand, generally, because accuracy is also reduced at high concentrations, is also important to review the fact that there is a maximum determination limit. When only measurement accuracy is researched from literature, the determination limit is viewed as being in the range of 10 to 100 times the measurement accuracy.

The base line (zero air) noise band (peak to peak for 100 noise units) can be corresponded to in the recorder charts and concentration meter responses and the detection limits and determination limits defined as previously. Moreover, if the environmental concentration has no specific objectives, an effective figure for the mean value of two digits alone is sufficient.
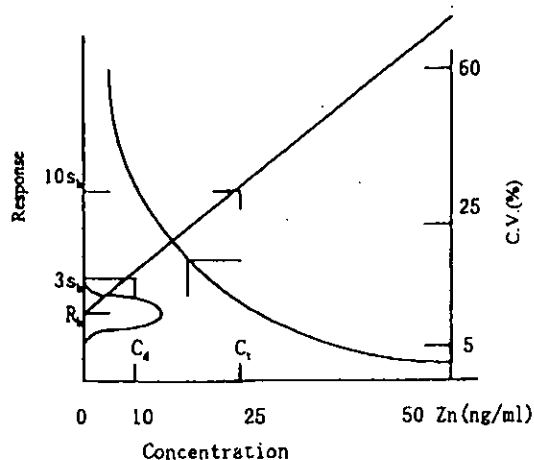

Fig. 9.1.2   Determination limits (Ct), detection limits (Cd) (Y-axis on the left) and standard deviation of blank (Sb) in the calibration curve, and example of the relation between coefficient of variation (C.V.) and concentration of zinc in ICP emission spectrometry.

(2) Accuracy guarantees and management: Tracability

No matter which measurement of the three given above which needs collection of air pollutants requires a standard for guaranteeing the accuracy. With both the liquid and solid standard substances, it is essential to consider purity of the standard substance (minimum 99.9%, though 99% alone is sufficient upon occasion.) and the stability of the prepared standard solution. On the other hand, with the concentration meters or the continuous analyzers, a standard gas cylinder is often used, and the manufacturer is requested to manage the accuracy of the cylinder concentration. Further, there are also concentration meters for which the regular inspection for the management is obligatory, and because for example, a part of the NO can change to NO_2 while it is stored, or substances such as

formaldehyde may be adsorbed on the inside wall of the cylinder, these cylinders must be handled with care in the user's position.

9.1.7 Laboratory management

When using a laboratory to analyze hazardous substances, it is important to consider both the environment and safety. Environment means hygiene in the work environment for the analysts, and countermeasures to contamination of air and water. Basically, it is best to choose processes that use as small amount of hazardous chemicals as possible. It is essential, for example, to use a dry process and to reduce the amount of preparation of standard solutions used to the minimum.

The first and foremost problem in the work environment is exposure of analysts to toxic vapor and suspended particles. Local ventilation must be installed in the rooms and the rooms must be kept well ventilated. Secondly, waste of analytical solution that has been used must be treated. Organic solvents can be burned, and metallic ion waste solution is treated by both adsorption and sedimentation, and if even small amount of the waste is extremely toxic, it must be put in a safe container, and labeled as such, and stored appropriately.

For safety, it is important to manage flammable gas and solvents. Large amount of hydrogen gas may leak or organic solvents could be volatilize, which when mixed with the air in the room, even to a concentration of only a few percent, once they meet a flammable source, detonation may start in the room. Care must be taken so that the storage shelves do not collapse, and that ventilation is good. Moreover, there is no danger in an ordinary room (not tightly closed) when the hydrogen leaks out of an FID gas chromatograph because it is diluted. Secondly is anoxia deficient room environment: This can be caused by major leaks of odorless nitrogen and argon. Thirdly, misoperation of the equipment should be prevented.

When setting out to analyze hazardous chemical substances such as dioxin, which has recently become a serious problem, it is needed to provide the hardware aspect such as buildings and other facilities, high quality analyzers. And so forth, analysis must be carried out in such facility as maintains rigorous safety management, such as control of waste substances, and a security system for people coming and going, and the work state. Also essential are a Quality Assurance/Quality Control (QA/QC) system, the introduction of recording systems, and a thorough comprehension of the history of a sample, from income of sample, up to the final treatment and disposal.

Because dioxin is 5,000 times more toxic than potassium cyanide, it must be kept in a room with reduced pressure to prevent its escape into the surrounding environment. In order to achieve sufficient pressure reduction, a special work box and compartment must be used. Dioxin in emission gasses and waste water from the laboratory must be treated by means of activated carbon, preventing its escape to the outside. Further, laboratory waste materials such as wipe clothes and used activated carbon must be stored in perpetuity, so appropriate facilities are also required.

Dioxin normally has a determination limit of approximately 1pg (pico gram, or 10^{-12} g), so that solvents, reagents, and glass wears must be of the best quality so as to prevent contamination, and used only for dioxide analysis. Further, a blank test is combined, and the blank value from contamination during experiments is checked to be below the determination limit.

251