

9.6 Methods of analyzing airborne particulate matter

9.6.1 Introduction

The measuring of airborne particulate matter determines the concentration of the particles by collecting them on a filter using either a high volume sampler (hereinafter called an HV) or a low volume sampler (hereinafter called an LV), to provide an analysis of the metal content of the sample, and so forth ^{1) 2) 3)}. In addition, an Anderson Sampler ⁴⁾ or similar may be used as a means of collecting particles with different diameters.

If the metals are analyzed using either atomic absorption photometry or ICP (Inductivity Coupled Prazuma) luminescent analysis, it is first necessary to acid decompose the sample beforehand and liquefy the target substance, and then non-destructive analysis is possible through both radio activation analysis and X-ray fluorescence analysis.

Here, this article is concerned with atomic absorption photometry, which is the most widely used means of analyzing the metal content of particles, and explains in outline radio activation analysis, with which non-destructive analysis is possible.

9.6.2 Atomic absorption photometry

(1) Sample collection and measuring mass concentration

A high volume (HV) sampler is shown in Fig.9.6.1, and a low volume (LV) sampler is shown in Fig.9.6.2. The filter requires a collection rate of at least 99% for particulate matter with a diameter of $0.3 \mu\text{m}$, low pressure loss, low reactivity to adhesion of gas particles and humidification, and must not include particles that may interfere with analysis. Normally, in the HV, a quartz fiber filter, fluorine resin filter, and a nitrocellulose filter are used, and in the LV, in addition to the above filters, a membrane filter is also used. The collection period for the HV is normally 24 hours, and for the LV is between four days to one week.

The filter is weighed following measurement of the stable temperature (normally 20°C) for a minimum period of 24 hours both before and after the sample collection, and after the constant room humidity (50%) has been measured, and the particle density ($\mu\text{g}/\text{m}^3$) is determined.

(2) Adjusting the sample solution (fluoric acid, nitric acid, perchloric acid method)

- a) The sample collection filter has an appropriate volume removed, is placed in a 100 ml tetrafluoride ethylene beaker, 20 ml nitric acid and 5 ml chloric acid are added, and the beaker covered by a tetrachloride ethylene clock dish, and heated gently on a hotplate at 130°C for approximately one hour. The clock dish is removed, and if the solution volume is about 5 ml, 5 ml of nitric acid, and the whole is reheated.
- b) After cooling, 10 ml nitric acid, 3 ml perchloric acid, and 3 ml hydrofluoric acid are all added, the clock dish is removed, the solution covered, and heated gently on a hotplate at approximately 200°C .
- c) When the perchloric acid begins to generate white smoke again, the solution is cooled, 5 ml nitric acid is added, and the whole heated. When the perchloric acid begins to generate white smoke again, the beaker is completely covered with the clock dish and continually heated, and the clock dish is removed once the contents

are no longer white, or pale yellow in color, whereupon they are dried and solidified, and once a thin white smoke begins to appear, the heating is stopped and the product cooled.

- d) 50 ml hot water and 10 ml nitric acid (1⇒10) are added, and heated for approximately a further 10 minutes either over boiling water or on a hotplate, and the solid matter is dissolved.
- e) After leaving to cool, the contents are filtered through a No.5C filter paper. The beaker and the filter paper are both washed in warm nitric acid (1⇒10), and filtered in the same way. All of the filtered solution is transferred to a 100 ml tetrafluoride ethylene beaker, gently heated either over boiling water or on a hotplate, and evaporated to a solid.
- f) After cooling, 10 ml hydrochloric acid (1⇒10) is added to the first beaker, which is then heated and dissolved over water. After cooling, the full volume is transferred to a flask (25 ml), water is added to a fixed volume, and the sample solution is thereby obtained.
- g) A blank specimen solution is prepared separately using a blank specimen filter by following the same steps a) to f) above.

In addition, the filter on which the specimen was collected is subjected to heat analysis in both a pressure analyzer and by aqua regia as a way of adjusting the sample solution, of which there are several ³⁾.

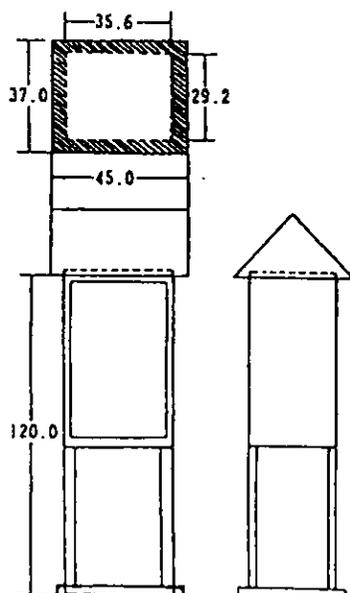
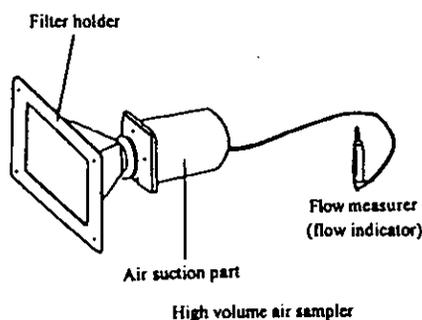
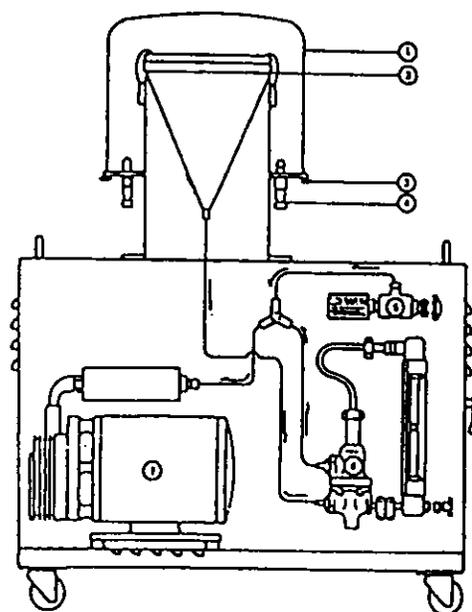


Fig.9.6.1 HV (top) and its shelter (bottom)



Low volume air sampler

- ① Top cover (stainless steel)
- ② Filter holder, filter clamp (stainless steel)
- ③ Top cover tightening screw (5× plastic screws)
- ④ Cyclone (×3)
- ⑤ Regulation valve and filter (stainless steel)
- ⑥ Differential pressure valve (stainless steel, cover is acrylic)
- ⑦ Rotary pump (200 W)

Fig.9.6.2 LV construction

(3) Flame atomic absorption spectrometer conditions setting and equipment adjustment

The sample solution adjusted in 9.6.2 (2) is atomized by an oxy-acetylene flame, the absorption wavelengths of each target measurement substance is measured, and their volume determined from the calibration curve.

The flame atomic absorption analysis conditions should be set appropriately with reference to the following:

Analysis wavelength: Wavelength of each target substance (e.g., for nickel, 232.0 nm)

Lamp current: Depends on each target substance (e.g., for nickel, 10 mA)

Gas flow: Acetylene (1.7 l/min), air (15 l/min)

(4) Compiling the calibration curve

0.3 to 6.0 of the control solution for each target substance (100 μ g/ml) is transferred in steps into a total volume flask (100 ml), and after heating the acid under the same conditions as for the sample solution, water is added to make up the appropriate volume. A control concentration series with at least five steps, including zero, is then created.

The conditions in (3) are operated for each control concentration series created, and the calibration curve thereby compiled.

(5) The blank sample solution and the sample solution are both subjected to the operations in question, and both the blank value (M_b : μ g/ml) and the volume for each target substance (M_s : μ g/ml) are determined.

(6) Calculating the concentration

The airborne concentration of each target measurement substance is calculated using Eq. (1).

$$C = \frac{(M_s - M_b) \times E \times S}{s \times V_{20}} \dots\dots\dots (1)$$

Here,

C = Airborne concentration of each target measurement substance (μ g/m³)

M_s = Concentration of each target substance in the sample solution (μ g/ml)

M_b = Concentration of each target substance in the blank sample solution (μ g/ml)

E = Volume of sample solution obtained in (2) (ml)

S = Surface area of filter that collected the sample (cm²)

s = Surface area of filter used in the analysis (cm²)

V_{20} = Air collection volume at 20°C (m³)

9.6.3 Activation analysis

(Principles and features)

Activation analysis is the general name given to analytical methods based on nuclear reaction. Of these,

thermal neutron radio activation analysis, which uses a semiconductor detector to measure gamma rays from radio active nuclides created by irradiating the sample with high density thermal neutrons in an atomic reactor can analyze trace amount of multiple chemical elements. As with airborne particulate matter, it is a method highly suited to the analysis of samples containing many trace elements, or where the amount of sample obtained is small, and it possesses the following features:

<Advantages>

- A highly sensitive method for analyzing multiple elements, and can analyze approximately 30 elements in airborne particulate matter.
- Because it can analyze non-destructively without chemical processing, there is little contamination (pollution) of the analysis.

<Disadvantages>

- Needs a semiconductor Ei-ray detector and atomic generator facilities for the experiment.
- Takes approximately one month for all analysis results to be obtained, due to the half-life of radioactive elements.
- Poor sensitivity for elements such as lead and cadmium.

(Analysis example)

Using a low volume air sampler at the Environment Agency's national air surveillance network, airborne particulate matter collected by a nitrocellulose membrane filter was irradiating and measured under the following conditions, and approximately 30 elements were analyzed ⁵⁾.

- Atomic reactor and thermal neutron density: Rikkyo University Atomic Research Institute, thermal neutron density 0.5 to 1.5×10^{12} n/cm²/sec.
- Thermal neutron irradiation: Irradiation for three minutes (short-lived nuclide) and six hours (long-lived nuclide).
- Gamma ray measurement: For five minutes after several minutes (short-lived nuclide), for 20 minutes after several days (medium-lived nuclide), and for one hour after several weeks (long-lived nuclide).
- Elements measured: Ag, Al, As, Ba, Br, Ca, Ce, Cl, Co, Cr, Cs, Cu, Fe, Hf, K, La, Lu, Mn, Na, Sb, Sc, Se, Sm, Th, Ti, V, W and Zn
- Other elements: Cd, Ni, and Pb were analyzed using X-ray fluorescence analysis.

Using radio activation analysis, and by measuring the various constituent elements in the atmosphere, the future of airborne particles could be characterized. Further, using the CEM (Chemical Element Balance) method, the rate of contribution from typical sources such as the soil (Al, Sc, etc.), sea salt (Na, Cl), steelworks (Mn, Fe, etc.), waste substance incinerators (K, Sb, etc.), and petroleum combustion (V, Ni, etc.), could be estimated from the measurement values of indicator elements. In addition, it is also used in earth sciences research to explain the yellow sands phenomenon.