

CHAPTER 4

METHODS OF QUANTITATIVE ANALYSIS AND SAMPLING PROCEDURE.

4.1 Introduction

The quantitative analysis by x-ray spectrometer is that an algorithm must be constructed to convert spectral intensity data into elemental concentration. This can be done by absolute x-ray spectrometric analysis as well as comparative methods. For absolute method, calculations require knowledge of (1) spectral distribution of primary x-ray beam; (2) conversion efficiency of each primary wavelength to the analyte-line; (3) absorption coefficient of specimen for each primary wavelength and for the analyte-line; (4) conversion efficiency of each primary wavelength to each matrix element line that can excite the analyte-line; (5) absorption coefficient of specimen for each of these lines; (6) conversion efficiency of each of these lines to the analyte-line, and (7) efficiency of the spectrometer. Obviously, the calculations are extremely complicated, Monte Carlo simulation should be constructed to describe the interaction processes of x-ray photons with matter. The absolute method has only limited success, even only with simple systems having relatively few components. The comparative methods were proved to be better suited to partial analyses, in which interelemental effects are compensated or taken into account indirectly. They are divided into three main groups as follow:

1. Compensation methods

a1. The comparison-standard methods: The analyte concentration in the samples is determined by comparison of the analyte-line intensities from the samples and standards having as nearly as possible the same analyte concentration and matrix.

a2. The internal standard method: It is applicable to variable matrices. The specimens are mixed with a fixed amount of a selected element, called the internal standard, with properties similar to those of the analyte. Then the intensity ratio of the analyte to the internal standard is independent on matrix and is proportional to the concentration of analyte.

a3. The addition (or spiking) method: In which a known amount of the analyte are added to the specimens. The comparison of the line intensities before and after each addition allows, within limits, compensation for the matrix effects.

a4. The double dilution method: It is applicable to the specimens prepared as solid or liquid solutions. Using two ratios of specimen and diluent and comparing the two line intensities of the analyte, the matrix effect can be exactly compensated.

2. Attenuation methods

a1. The dilution method: In which the specimens are diluted in an excess of diluent (as solid or liquid solution); This minimizes the variations in matrix composition and tends to make the line intensities nearly proportional to the concentrations.

a2. The thin-film method: In which the specimens are made so thin (of the order of a few hundreds or thousands of \AA) that absorption-enhancement effect substantially disappears.

3. Absorption correction methods

a1. The scattered intensity method: In which the intensity of the primary x-rays scattered by the specimen is used to correct the absorption-enhancement effect.

a2. The emission-transmission method: It is applicable to specimens of finite thickness; The absorption of the analyte-line and primary radiation by the specimen are determined by a transmission measurement, after which a correction for absorption is applied to the analyte-line intensity.

4.2. Relationship between intensity and concentration of element

In quantitative analysis the measured fluorescent x-ray intensity of a given element is converted into its weight concentration in the sample. As the sample is exposed by an x-ray photon beam, each atom of the analyte element i has the same probability to be excited by the primary beam and to emit its characteristic line λ_i . Indeed, if we deal with separate atoms or ions as in a gas or in a very dilute solution, a linear relationship between intensity and concentration may be expected as a first approximation:

$$I_i = MW_i \quad (4-1),$$

where W_i is the weight fraction of i .

The constant M consists of many physical and instrumental factors as follow:

- Shape and intensity of the primary beam,
- Probability that an atom i emits its characteristic radiation λ_i ,
- Probability that these photons λ_i can escape from the sample surface and reach the detector window.
- Probability that these photons are being detected and registered.

However, if we deal with compact specimens in which the atoms are bound into chemical compound, i.e. both the primary rays and the fluorescent x-rays will be also absorbed by the different atoms in the sample, then the formula (4-1) become more complicated. Let us consider the physical processes that occurs in the sample as it is exposed by a monochromatic radiation beam or a continuous x-ray spectrum.

4.2.1 Excitation by monochromatic radiation

First we assume that the number of primary photons of wavelength λ_p striking the sample surface at an angle ψ_1 is $I_{p,0}$ per unit time (Figure 4.1). These photons are absorbed by the various atoms in the sample. The remaining intensity $I_{p,x}$ at a layer Δx at a distance x within the sample is:

$$I_{p,x} = I_{p,0} \exp[-\mu_a(\lambda_p)\rho_x \csc(\psi_1)x] \quad (4-2),$$

where $\mu_a(\lambda_p)$ is the mass attenuation coefficient of the sample for λ_p and ρ_x its density.

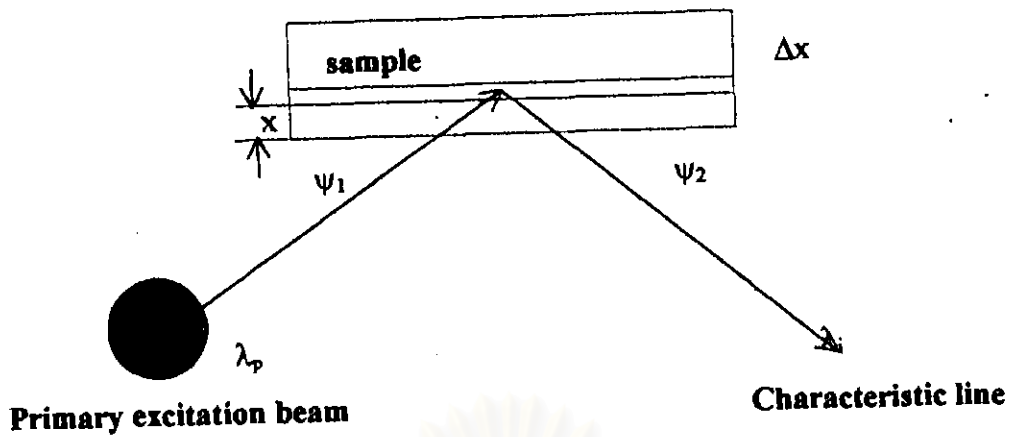


Figure 4.1 The sample is excited by primary photon λ_p

$\mu_a(\lambda_p)$ can be calculated from the weight fractions of the elements present in the sample and their mass attenuation coefficients:

$$\mu_a(\lambda_p) = \sum_{i=1}^n \mu_{a_i}(\lambda_p) W_i \quad (4-3),$$

where n is the total number of elements in the sample.

Fraction of the primary photons that is absorbed in the layer Δx is:

$$1 - \exp[-\mu_a(\lambda_p) \rho_s \csc(\psi_1) \Delta x] \approx \mu_a(\lambda_p) \rho_s \csc(\psi_1) \Delta x \quad (4-4),$$

(because $1 - e^{-a} \approx a$ if a is very small);

In the layer Δx , a certain fraction of the primary photons is absorbed by element i :

$$W_i \mu_{a_i}(\lambda_p) / \mu_a(\lambda_p) \quad (4-5),$$

To yield characteristic radiation, the photon must be absorbed by electrons in the appropriate shell. For example, if K_α is considered, only the fraction of primary photons absorbed by K electrons can yield the desired radiation. Absorption in the K shell is:

$$(r_i - 1) / r_i \quad (4-6),$$

where r_i is the absorption jump ratio. However, only a fraction of the excited atoms i in the K shell give rise to fluorescent x-rays λ_i ; this fraction is called the fluorescence yield ω_i . Furthermore, only a fraction g_i emits K_α rays; other possibilities are K_β photons. Only a certain fraction of these fluorescent rays emitted in the direction of the detector, $d\Omega / 4\pi$ ($d\Omega / 4\pi$ is the solid angle intercepted by the detector system), can pass through the collimator at an angle ψ_2 with respect to the sample surface. These secondary rays are absorbed from the layer Δx to the sample surface according to:

$$\exp[-\mu_a(\lambda_i)\rho_s \csc(\psi_2)x] \quad (4-7),$$

thus, in total the contribution to the total emitted fluorescent radiation λ_i from the layer Δx is:

$$I_i = I_{p,0}(\lambda_p) \exp[-\mu_a(\lambda_p)\rho_s \csc(\psi_1)x] \exp[-\mu_a(\lambda_i)\rho_s \csc(\psi_2)x] W_i \mu_i(\lambda_p) / \mu_a(\lambda_p) [(r_1 - 1) / r_1] \omega_i g_i \mu_a(\lambda_p) \rho_s \csc(\psi_1) \Delta x d\Omega / 4\pi \quad (4-8),$$

Integrating equation (3-8) for x from zero to infinity gives:

$$I_i = I_{p,0}(\lambda_p) P_i \mu_i(\lambda_p) W_i / [\mu_a(\lambda_p) + G\mu_a(\lambda_i)] \quad (4-9),$$

where P_i is a constant for a given element and a given spectrometer and

$G = \sin\psi_1 / \sin\psi_2$. In this derivation we assumed that:

- . The sample is completely homogeneous,
- . The primary rays are not scattered on their way to the layer Δx ,
- . No enhancement effects occur,
- . The characteristic radiation is not scattered on its way to the sample surface.

4.2.2 Excitation by continuous spectra

When continuous radiation is used to excite the analyte for emitting the characteristic photons λ_i , all the primary wavelengths λ between the minimum wavelength λ_{\min} and the absorption edge wavelength λ_{edge} of the analyte i can contribute to the excitation of i . Thus,

$$I(\lambda) = \int_{\lambda_{\min}}^{\lambda_{\text{edge}}} J(\lambda) d\lambda \quad (4-10),$$

$J(\lambda)$ is the x-ray spectrum. By substituting this expression into equation (4-10) and considering that absorption of the primary and secondary rays by all elements must be taken into account, one obtains

$$I_i = P_i W_i \int_{\lambda_{\min}}^{\lambda_{\text{edge}}} J(\lambda) \mu_i(\lambda) d\lambda / [\sum_j \mu_j(\lambda) W_j + G \sum_j \mu_j(\lambda_i) W_j] \quad (4-11),$$

The constant P contains the fluorescent yield and the weight of the series.

$\mu_j(\lambda)$ is the absorption coefficient for element j for the primary photons and $\mu_j(\lambda_i)$ absorption coefficient for element j for the characteristic wavelength λ_i of the analyte i .

Some conclusions derived from the equation between intensity and concentration are as follows :

- The integration over x for equation (4-8) is taken from 0 to infinity. It is obvious that the first layers contribute more to the intensity of λ_i than the layers more inward. Often infinite depth is defined arbitrarily as that thickness x of which the contribution of the layer Δx is 0.01% of the surface layer. The infinite thickness depends on the value of the absorption coefficients and the density of the sample. It may vary from a few micrometers for heavy matrices and long wavelengths to even centimeters for light matrices and short wavelengths.
- It was assumed that the primary rays follow a linear path to the layer Δx at height x . In practice, the primary rays may also be scattered and, therefore, lost in intensity. The scattering effects become more important the more energetic the primary rays and the lighter the matrix. This scatter may give a higher background in the secondary spectrum, thus leading to poorer precision of the analysis.
- It was assumed that the sample is completely homogeneous. In practice, we deal with discrete atoms in chemical compounds. In powders, the different compounds may have a tendency to cluster. In general, the particles have different sizes and shapes. Placing the sample into solution, either aqueous or solid (melt), may overcome this problem.
- All atoms in the sample may be excited, thus emitting their characteristic radiation in all directions. These characteristic rays are absorbed by other atoms of the analyte. If these x-rays are energetic enough, they may excite the analyte i . Thus, the intensity I_i measured is higher than expected from equation (4-11). The intensity I_i is enhanced by the contribution of heavier elements in the sample. The enhancement may contribute up to 40-50% of the total fluorescent radiation I_i , especially, when the concentration of enhancing elements is much greater than that of the analyte.

4.3 Standard addition method

4.3.1 Principle

If the calibration function, i.e. analyte-line intensity I_A vs analyte concentration C_A , is linear in the region of analytical interest. I_A is proportional to C_A and an incremental or decremental change in C_A gives a proportional change in I_A . Standard addition ('spiking') method usually requires no standards and can be used for samples for which there is inadequate knowledge about the matrix. However, the method is applicable only to trace and minor analytes (less than 5-10%) where the I_A - C_A calibration curve is likely to remain linear for suitable incremental additions. Moreover, an addition must be made for each analyte appropriate for its estimated concentration and the actual weight of substance added should be small compared with the total sample weight. In other words, the analyte concentration in the additive should be high, and the pure analyte itself is preferable whenever its use is feasible. The above-mentioned standard addition method may be regarded as self-standardization method in that the incrementally concentrated sample actually constitutes its own standard.

4.3.2 Method

Essentially, the sample X is added with a small amount of analyte to increase the analyte concentration by ΔX , from C_X to $C_{X+\Delta X}$. Then the analyte-line intensities measured from untreated and treated samples are proportional to the corresponding concentrations, that is:

$$I_X/I_{X+\Delta X} = (C_X/C_{X+\Delta X})[(\mu/\rho)_{X+\Delta X}/(\mu/\rho)_X] \quad (4-12);$$

In practice, the sample X is usually treated with a standard material S having known analyte concentration C_S to form a mixture containing an increase in the analyte concentration $C_{\Delta X}$ given by:

$$C_{\Delta X} = C_S/(m_S + M_X) \quad (4-13),$$

$$\text{And approximately } C_{X+\Delta X} = DC_X + C_{\Delta X} \quad (4-14),$$

$$\text{Where } D = M_X / (m_S + M_X) \text{ is called dilution factor,} \quad (4-15),$$

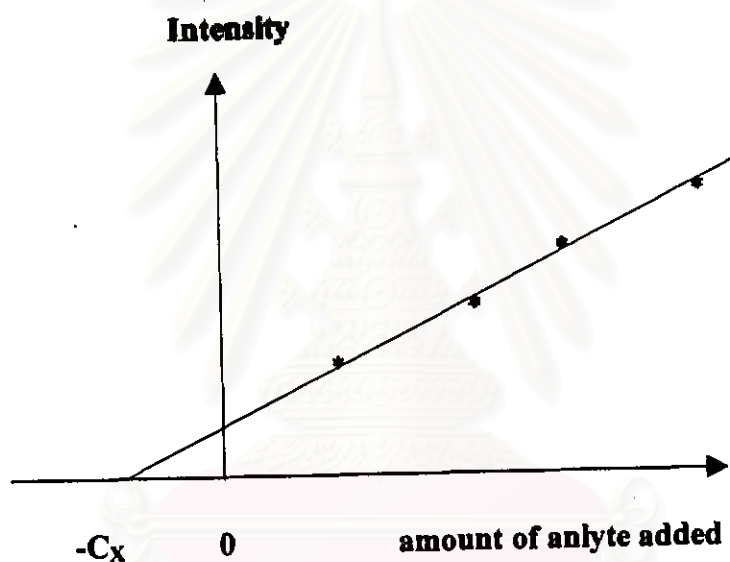
m_S and M_X are weights of the standard material and sample, respectively

Substitute (4-14) into (4-12), concentration of element in the original filter is determined as follow:

$$C_X = C_{\Delta X} / ((I_{X+\Delta X} / I_X) - D) \quad (4-16),$$

the standard material may have a matrix different from that of the sample. Compound and solutions can be used for the standard addition. If the analyte in the original sample is in a different phase than in the additive, care must be taken in the calculation of the concentration. The relevant stoichiometric or gravimetric factors must be included.

In practice, to check the linearity of calibration and to analyze the concentration more accurately, the process can be repeated by adding different amounts of the analyte to the sample and plotting the intensities measured versus the concentrations added. The intercept of the line fitted best on the concentration axes equals concentration of analyte C_X in the untreated sample.



Figur 4.2 Net intensity is plotted versus concentrations added

4.4 Internal standardization method

4.4.1 Principle

If an element has a spectral line having excitation, absorption and enhancement properties identical with those of the analyte line in a particular matrix, then that element would be an ideal internal standard (IS) for the analyte X in that matrix, and

$$I_X / I_{IS} = C_X / C_{IS} \quad (4-17),$$

where C and I are concentration and intensity, respectively. In practice, absorption-enhancement effects may be compensated by the addition to all the samples and standards of a constant concentration of an internal standard element IS that fills these

requirements as closely as possible, that is, the relationship between C and I should be:

$$I_X / I_{IS} = kC_X / C_{IS} \quad (4-18)$$

the constant k may be derived from a standard having known concentrations of analyte C_A and internal standard C_{IS} :

$$I_A / I_{IS} = kC_A / C_{IS} \quad I_X / I_{IS} = kC_X / C_{IS} \quad (4-19)$$

thereafter, k can be used to calculate analyte concentration from the intensity ratio measured from the samples.

4.4.2 Selection of internal standard element

The basic requirements that the internal standard must fill have already been mentioned above. In practice, the selection criterion for an internal standard is that it has the characteristic lines and absorption edges as close as possible to those of analyte.

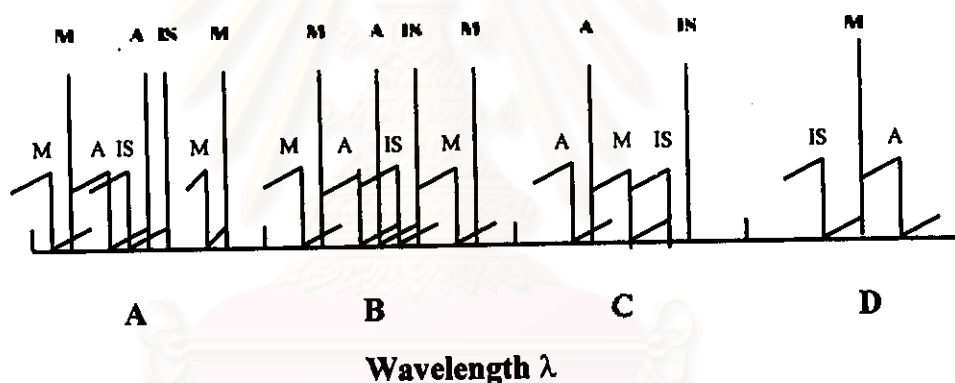


Figure 4.3 Specific absorption-enhancement effects and selection of IS, A is the ideal case, B is acceptable, C and D are unacceptable

Fig. 4.3 shows four cases for the relative wavelengths of the spectral lines, absorption edges of the analyte A and the prospective internal standard IS.

4.5 Dilution method

Dilution method can also eliminate or reduce the variation of the matrix effect, rather than compensating for such variation. The method can be explained from equation (4-9) as follow:

$$\text{set for: } C(\lambda_p, \lambda_i) = \mu_i(\lambda_p) / [\mu_s(\lambda_p) + (\sin \psi_1 / \sin \psi_2) \mu_s(\lambda_i)] \quad (4-20)$$

that is called efficiency factor,

where $\mu_s(\lambda_p)$ and $\mu_s(\lambda_i)$ are the mass attenuation coefficients of the sample for the primary wavelength, λ_p , and analyte wavelength, λ_i , respectively.

$\mu_i(\lambda_p)$ is the absorption coefficient of analyte for λ_p . Apparently, deviations from linearity in the I-C curve are due to variations in $\mu_s(\lambda_p)$ and/or $\mu_s(\lambda_i)$, ignoring enhancement. If D grams of a diluent d for each gram of sample is added to the sample, the denominator of equation (4-18) become:

$$1/(1+D)[\mu_s(\lambda_p)+G\mu_s(\lambda_i)]+D/(1+D)[\mu_d(\lambda_p) + G\mu_d(\lambda_i)] \quad (4-21);$$

where $G = \sin\psi_1 / \sin\psi_2$

if the term $D/(1+D)[\mu_d(\lambda_p)+G\mu_d(\lambda_i)]$ is much larger than

$1/(1+D)[\mu_s(\lambda_p)+G\mu_s(\lambda_i)]$, the factor $C(\lambda_p, \lambda_i)$ becomes essentially a constant and variations due to varying matrix effects between samples become negligible. This can be done in two different ways:

1. Making $D/(1+D)$ large: diluting each sample by adding a large, known amount of a diluent.
2. Adding a smaller quantity of diluent than in the previous case, but with a much larger value for $[\mu_d(\lambda_p)+G\mu_d(\lambda_i)]$. This is called the technique of the heavy absorber. However, both these procedures require addition of reagents to the sample. This can easily be done for dissolved samples in either liquids or fused samples, but is more difficult for powdered samples (homogeneity!).

This method do not eliminate the matrix effects completely, but reduce their influence. On the other hand, they reduce the line intensity of the analyte, and thus a compromise must be sought. Normally, the diluent that is selected is a nonfluorescing (for example H_2O or $Li_2B_4O_7$) to reduce the enhancement effect.

4.6 Correction for matrix absorption effects

4.6.1 Correction for effects of absorption coefficients of matrix

Absorption-enhancement effects often consist simply of absorption effects, that is, the effects of the absorption coefficients of the matrix elements. Let us consider the $Sn K_{\alpha}$ intensity data from tin-lead alloys as an example for illustrating the absorption correction.

At the primary wavelengths that excite $Sn K_{\alpha}$ most efficiently - those near the $Sn K_{\alpha}$ (0.425 A), the mass absorption coefficients of tin and lead are 40 and 25 cm^2/g , respectively. At $Sn K_{\alpha}$, they are 12 and 52 cm^2/g . Then the total mass absorption

coefficients for both primary and Sn K_{α} radiation are, for Sn and Pb, 52 and 77 cm^2/g , respectively. If it is assumed that only absorption effects are present, then:

$$(I_x)_{\text{cor.}} = (I_x)_{\text{meas.}} (\mu/\rho)_x / (\mu/\rho)_{100\text{Sn}} \quad (4-22),$$

where $(I_x)_{\text{cor.}}$ and $(I_x)_{\text{meas.}}$ are corrected and measured Sn K_{α} net intensities from the sample, respectively.

$(\mu/\rho)_x$ and $(\mu/\rho)_{100\text{Sn}}$ are total mass-absorption coefficients of the sample and pure tin, respectively, for both primary and Sn K_{α} radiation.

$(\mu/\rho)_x$ for a sample can not be calculated before the sample composition is known. However, it may be estimated in several ways as follow:

1. If some accuracy may be sacrificed, an approximate analytical concentration may be derived from the uncorrected intensity data, and this value is used to calculate $(\mu/\rho)_x$ as a first approximation.
2. Analytical line intensity may be measured from pure analyte placed behind a sample disk of known mass and thickness. Since both primary and analyte line radiation must pass through the sample disk, total μ/ρ for the matrix may be calculated.
3. If primary absorption can be neglected, the sample disk may be used to attenuate the analyte-line radiation from a sample of pure analyte.

4.6.2 Matrix correction using incoherent scattered radiation

It has been shown first in 1958 that accuracy and reproducibility in x-ray fluorescence analysis can be improved by using scattered radiation as an internal standard. In this way, the influences resulting from variations of tube tension, tube current, sample position and grain sizes are considerably reduced. But more important is the fact, that quite apart from this reduction of outer sample influences, scattered radiation allows to correct measured results for matrix absorption effects without detailed knowledge about sample composition.

The relative intensities I_1 and I_2 measured under identical conditions from two samples having concentrations C_1 and C_2 of the same analyte are given by:

$$I_1 / I_2 = (C_1/C_2) [(\mu/\rho)_2 / (\mu/\rho)_1] \quad (4-23),$$

where μ/ρ is the mass absorption coefficient for the target line.

$$\Rightarrow C_1/C_2 = (I_1/I_2) [(\mu/\rho)_1 / (\mu/\rho)_2] \quad (4-24),$$

As dealt with in chapter 2, the proportion of incoherent scattered radiation increases as the binding of the orbital electrons decreases, that is, as atomic number of the scatterer decreases. Therefore, within the energy range between some tens and hundred KeV, it is approximated that:

$$(\mu/\rho)_1/(\mu/\rho)_2 \propto (I_2)_{inc}/(I_1)_{inc}$$

where I_{inc} is the intensity of incoherent scattered radiation, hence:

$$C_1/C_2 = (I_1/I_2)[(I_2)_{inc}/(I_1)_{inc}] \quad (4-25);$$

$$\Rightarrow C_x = C_s (I_x/I_s)[(I_s)_{inc}/(I_x)_{inc}] \quad (4-26);$$

x - sample

s - standard.

Up to now, this method has been utilized to analyze various substances such as aqueous and organic solutions, coal, silicate rocks, ores and alloys. Registration of radiation has been made both in wavelength and energy dispersive modes and satisfying results have been achieved in most cases, especially for low concentration range of heavy elements in light matrix.

Another modified correction method is to use the ratio of coherent to incoherent (Rayleigh to Compton) scattered intensities. It was shown that for light matrixes, μ/ρ is a linear function of the ratio of the intensities of the coherent (Rayleigh) I_R and incoherent (Compton) I_C scattered target lines. That is,

$$\mu/\rho \propto I_R/I_C = R$$

Then, the analyte concentration C_x in the sample is given by:

$$C_x = C_s (I_x/I_s)(R_x/R_s) \quad (4-27);$$

The analyte line intensities are measured from the sample I_x and from a single standard I_s , having known analyte concentration C_s in a matrix similar to that of the sample. Rayleigh and Compton scattered target line intensities are measured from both the sample and standard.

4.7 Sampling procedure

4.7.1 Principle and applicability

Sampling of total suspended air particulate (TSP) matter and 10 μ m air particulate matter (PM-10) is made using standard high volume air sampler and standard PM-10 air sampler, respectively. The procedure for TSP and PM-10 samples can be summarized as follow:

1. Air is drawn into covered housing and through a filter by a high flow rate blower at a flow rate of 1.13 to $1.7 \text{ m}^3 / \text{min}$ (40 to $60 \text{ ft.}^3 / \text{min}$) that allows suspended particles having diameters less than $100\mu\text{m}$ to pass to the filter surface. A TSP high volume air sampler is shown schematically in figure 4.4. The mass concentration of suspended particulate in the ambient air (mg / m^3) is computed by measuring the mass of collected particulate and the volume of air sampled.
2. This method is applicable to measurement of the mass concentration of suspended particulate in ambient air. The size of the sample collected is usually adequate for other analyses.
3. When the sampler is operated at an average flow rate of $1.7 \text{ m}^3 / \text{min}$ ($60 \text{ ft.}^3 / \text{min}$) for 24 hours, an adequate sample will be obtained even in an atmosphere having concentrations of suspended particulate as low as $1\mu\text{g} / \text{m}^3$. If particulate level are unusually high, a satisfactory sample may be obtained in 6 to 8 hours or less. For determination of average concentrations of suspended particulate in ambient air, a standard sampling period of 24 hours is recommended.
4. For ten-micron air particulate, the high flow rate blower must be operated at the flow rate of $1.13 \text{ m}^3 / \text{min}$ ($40 \text{ ft.}^3 / \text{min}$).

4.7.2 Interference

Some particulate matter such as photochemical smog or wood smoke may blocks the filter and cause a rapid drop in air flow at a non-uniform rate. Dense fog or high humidity can cause the filter to become too wet and severely reduce the air flow through the filter.

4.7.3 Sampling area

In this work, air particulate matter were taken at two industrial plants in Rayong Industrial Centre. The first plant (Plant A) produces polymer and plastic while the second plant (Plant B) is a fertilizer producer. There are about one hundred of medium and large scale plants concentrated in this industrial estate. Most of them are chemical and petro-chemical plants. As a consequence, their emissions including waste water, gas and wastes are serious and must be regularly monitored. Analysis of elemental constituents in air particulate matter provides partly some information about the environmental problem in this area. Both types of dust, i.e. TSP and PM-10, were collected on 8"x10" Whatman No.41 cellulose filter. At the first sampling trip, only the TSP samples were collected in ambient air of plant A for which the purpose is: (1)

to determine the average concentrations of all elements in total suspended particulate, and (2) to characterize particulate. The sampling time was 24 hours per an adequate sample

At the second sampling trip, both types of TSP and PM-10 samples were collected in ambient air of Plant B on 8"x10" Whatman No.41 cellulose filter. Because the cellulose filter is, for PM-10, saturated more rapidly than for TSP matter, so the sampling periods were 12 hours and 24 hours for PM-10 and TSP samples, respectively. The purpose of the work is to compare elemental constituents of TSP matter and PM-10 matter. This work is useful due to the fact that 10 μ m particulate may easily infiltrate into lung by breathing and could cause serious effect on human health. The work done here did not aim at assessing environmental impact of the plants themselves.

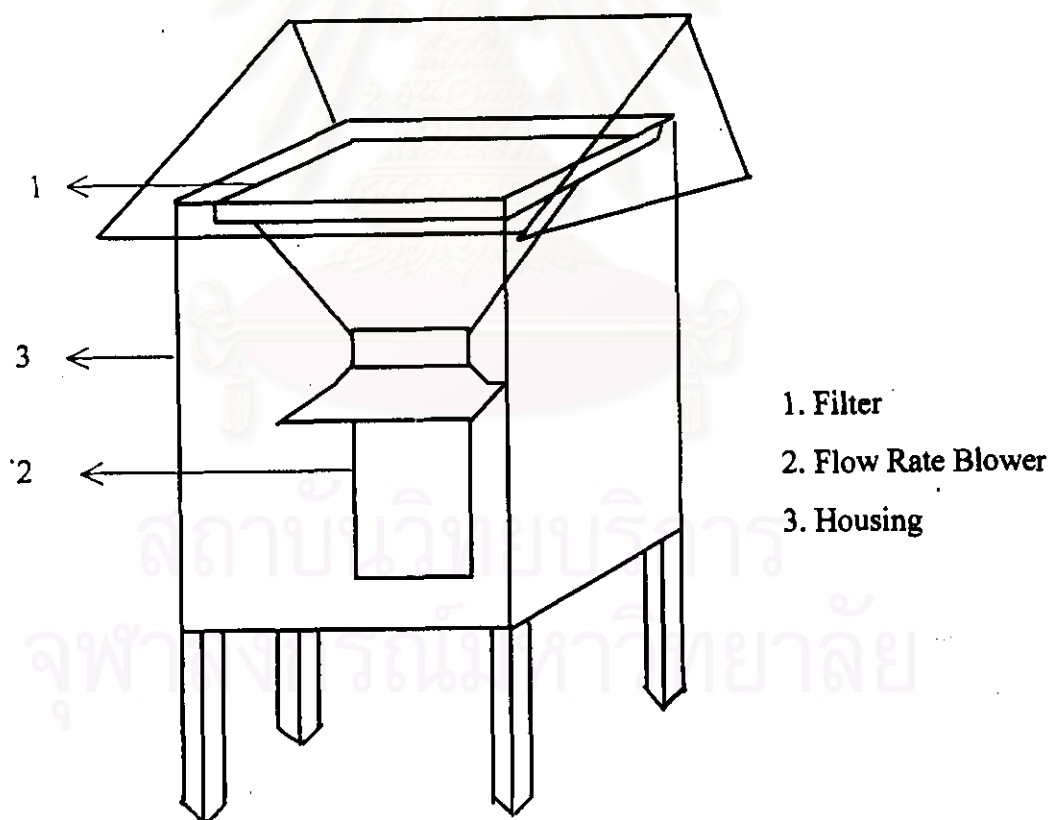


Figure 4.4 Assembled sampler and shelter for TSP