CHAPTER 5

EXPERIMENTAL RESULTS

5.1 Measuring Instrument

All elements in particulate were analyzed on PHILIPS 2400 sequential X-ray spectrometer with X-ray tube, Rh-target, Beryllium window thickness 75μm, capacity 3kW, maximum excitation high voltage 60kV, maximum current 125mA. The equipment belonged to the Scientific and Technological Research Equipment Center; Chulalongkorn University. All elements from Beryllium to Uranium can be detected by selecting suitable analyzing crystals such as LiF200, LiF220, PE220, Ge111, PX-1, LiF420, and some multi-layer crystals (PX-3, PX-4) and detectors such as Flow, Scintillation and Proportional Gas (Ar, Xe).

5.2 Analytical method

1. The wavelength dispersive spectra of the samples and blank filter were analyzed qualitatively on WDX-Ray Spectrometer PHILIPS 2400. Based on the spectral peaks obtained for the samples and blank filter, the elements such as Al, Si, Ca, K, S, Fe, Mg, Mn, Ti, Pb, Cu and Ni were found for TSP in ambient air of plant A, and elements such as Al, Si, Ca, K, S, Fe, Mg, Mn and Ti were found for both TSP and PM-10 in ambient air of plant B.

2. The analytical samples are air particulate matters that are collected and pressed on the cellulose filters during operation period of air samplers. Whatman No.41 cellulose filter is very thin (the thickness is 220 μm). For these reasons, In order to determine concentrations of all elements in particulate, the incremental addition (spiking) method. i.e. self-standardization, is proved to be the most suitable. The main advantages of the method are that it usually requires no standards and can be used for samples for which there is inadequate knowledge about the matrix.

3. In sample preparation, the filters were cut into disk shape of 4.5 cm in diameter. As mentioned in 4.3 (Chapter 4), the filter added with a small amount of atomic absorption grade solution of element of interest (analyte) gives an incremental change in concentration of element. This is accompanied with a proportional change in measured characteristic line intensity (countrate). The concentration of the element in original filter could be then given by formula (4-16) as follow:

$$C_X = C_{\Delta X} / ((I_{X+\Delta X} / I_X) - D) \quad\quad (5\text{-}1);$$

$C_{\Delta X}$ is given by (4-13):

$$C_{\Delta X} = C_S / (m_S + M_X) \quad\quad (5\text{-}2);$$

m_S and M_X are weights of the atomic absorption grade solution added and sample, respectively

D is dilution factor determined by (4-15).

I_X and $I_{X+\Delta X}$ are the analyte line intensity from the untreated sample (original filter) and the sample added, respectively.

4. To check the linearity of calibration between incremental changes in concentration and corresponding proportional changes in intensity and to analyze the concentration more accurately, the process can be repeated by adding different amounts of the solution to the filter and plotting the intensities measured versus the concentrations added, then the intercept of the straight line fitted best on the concentration axes gives concentration value of analyte in the original filter.
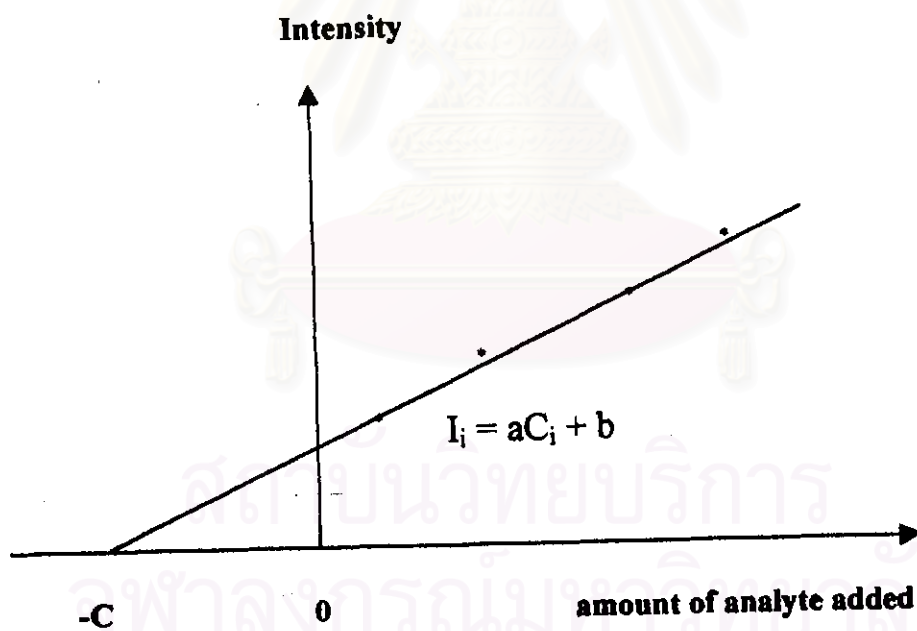
Intensity

$$I_i = aC_i + b$$

-C   0   amount of analyte added

Figure 5.2   Net intensities versus concentrations of analyte added

The concentration of element that is determined by the fitting method has negative value. The physical meaning of the method is that if concentration of element could be separated from the original filter, its net intensity must be equal to zero.

5. It has been proved (9) that background intensity at any wavelength is inversely related to mass absorption coefficient and the peak-to-background ratio (net peak / background) could be used to correct for variations of chemical composition caused by the spiking. From formula (4-12):

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

It can be rewritten as follow:

$$I_X/I_{X+\Delta X} = (C_X/C_{X+\Delta X})[(\text{net peak/background})_{X+\Delta X} / (\text{net peak/background})_X] \quad (5\text{-}3),$$

where (net peak/background)$_{X+\Delta X}$ and (peak/background)$_X$ are taken for a testing element that is close to analyte. The symbols x and x+Δx are signed before and after adding the grade solution of analyte onto the filter. In this case, the concentration of element is determined as follow:

$$C_X = C_{\Delta X}/\{[(I_{X+\Delta X}/I_X)(\text{net peak/background})_{X+\Delta X} / (\text{net peak/background})_X] - D\}$$
$$(5\text{-}4),$$

5.3 Statistical errors of concentration

5.3.1 One addition

In this case, concentration of element is given by (5-1), its error can be determine as follow:

$$\sigma_C^2 = (\partial_C/\partial_{I_X})^2 \sigma^2_{I_X} + (\partial_C/\partial_{I_{X+\Delta X}})^2 \sigma^2_{I_{X+\Delta X}} \qquad (5\text{-}5),$$

$$\sigma_C = C_{\Delta X} \sqrt{\sigma^2_{I_{X+\Delta X}} + \sigma^2_{I_X} I^2_{X+\Delta X}/I^2_X} / (I(I_S/I - D)^2) \qquad (5\text{-}6),$$

where σ_{I_X} and $\sigma_{I_{X+\Delta X}}$ are, respectively, statistical errors of count rates for original and added samples that are given by formula (3-8),

thus, concentration $= C \pm \sigma_C$ $\qquad\qquad (5\text{-}7),$

5.3.2 Several additions

As above mentioned, concentration of element can be determined more accurately by fitting a straight line through the experimental points between concentrations added versus corresponding count rates . If it is supposed that the fitted line has general equation:

$$I_I = aC_i + b \qquad\qquad (5\text{-}8),$$

where C_i are incremental changes in concentration, I_i are corresponding changes in count rate.

The fitting coefficients a, b are given by:

$$a = (n\Sigma I_i C_i - \Sigma I_i \Sigma C_i) / (n\Sigma C_i^2 - (\Sigma C_i)^2) \tag{5-9},$$

$$b = (\Sigma I_i C_i \Sigma C_i - \Sigma I_i \Sigma C_i^2) / ((\Sigma C_i)^2 - n\Sigma C_i^2) \tag{5-10},$$

with n is number of additions,

then, concentration of analyte in original filter is determined at intercept $I_i=0$, i.e.

$$C = |b/a| \tag{5-11},$$

substitution of (5-9) and (5-10) into (5-11) gives a relationship between concentration of element, concentrations added and count rates as follow:

$$C = (\Sigma I_i C_i \Sigma C_i - \Sigma I_i \Sigma C_i^2) / (n\Sigma I_i C_i - \Sigma I_i \Sigma C_i) \tag{5-12},$$

thus, error of concentration, in this case, can be computed directly from (5-12) as follow:

$$\sigma_C^2 = (\partial_C/\partial_{I1})^2 \sigma_{I1}^2 + (\partial_C/\partial_{I2})^2 \sigma_{I2}^2 + \ldots (\partial_C/\partial_{C1})^2 \sigma_{C1}^2 + (\partial_C/\partial_{C2})^2 \sigma_{C2}^2 + \ldots \tag{5-13},$$

$$\sigma_C^2 = \Sigma(\partial_C/\partial_{Ii})^2 \sigma_{Ii}^2 + \Sigma(\partial_C/\partial_{Ci})^2 \sigma_{Ci}^2 \tag{5-14},$$

Where σ_{Ci} is errors of concentrations added, for which it is normally supposed that $\sigma_{Ci} = 0$. thus, σ_C^2 is found as:

$$\sigma_C^2 = \Sigma \sigma_{Ii}^2 \{[(C_i \Sigma C_i - \Sigma C_i^2)(n\Sigma I_i C_i - \Sigma I_i \Sigma C_i) - (\Sigma I_i C_i \Sigma C_i - \Sigma C_i^2 \Sigma I_i)$$
$$(nC_i - \Sigma C_i)]/(n\Sigma I_i C_i - \Sigma I_i \Sigma C_i)^2\}^2 \tag{5-15},$$

and concentration $= C \pm \sigma_C$ as (5-7);

5.4 Experimental Results

In normal practice, mass concentration of particulate matter in air is measured in weight per volume of air. Tables 5.1, 5.2a and 5.2b summarized the average mass concentrations of TSP and PM-10 matters collected.

Table 5.1 Average mass concentration of TSP matter

in ambient air at Plant A

concentration and air volume	sample 1	sample 2	sample 3	average
Dust concentration (mg)	24	24.2	24.3	
Air volume (m^3)	1597.9	1697.1	1609	
Average dust concentration in air (mg/m^3)	0.01509	0.01426	0.01510	**0.01482**

Table 5.2a   Average mass concentrations of TSP matter in

ambient air at Plant B

concentration and air volume	sample 1	sample 2	average
Dust concentration (mg)	65.1	64.8	
Air volume (m^3)	1920.4	1993.8	
Average dust concentration in air (mg/m^3)	0.0339	0.0325	**0.0332**

Table 5.2b Average mass concentrations of PM-10 matter in ambient air at Plant B

concentration and air volume	sample 1	sample 2	sample 3	sample 4	average
Dust concentration (mg)	36.9	40.6	35.7	42.3	
Air volume (m^3)	813.6	813.6	813.6	813.6	
Average dust concentration in air (mg/m^3)	0.04535	0.0499	0.0438	0.05199	**0.04776**

Blank cellulose filters have been analyzed by the Atomic Absorption Spectrometry (AAS) [8] to find the trace elements in the filter themselves. The Analytical results were summarized in Table 5.3, from which it could be seen that the cellulose filters contain very small amounts of trace elements and would be suitable for analysis of air particulate matters where trace elements in the filter are of interest.

Table 5.3 Trace elements in the blank filters analyzes by AAS [8]

Element	Concentration (ng/cm^3)	Element	Concentration (ng/cm^3)
Cr	1.4	Cu	3.2
Zn	6.0	Ti	1.3
Mn	0.7	Pb	0.1
Fe	32.8	As	0.08
Ca	101.4	Cd	0.4

As mentioned above, all elements in particulate were analyzed on WDX-ray Spectrometer PHILIPS-2400 at the Scientific and Technological Research Equipment Center, Chulalongkorn University, the most appropriate conditions and parameters for the determination of various elements were set up. These included type of analyzing crystals, angles of diffraction for peak and background, targets, voltage and current of X-ray tubes, detectors, counting time, etc. The lower limit of detection (LLD) was determined for each element of interest, the results of which are given in table 5. 4.

Table 5.4 Lower limit of detection for elements (LLD), in $\mu g/9.621 cm^2$

Element	LLD($\mu g/9.621 cm^2$)	Element	LLD($\mu g/9.621 cm^2$)
Pb	0.22	Mn	0.15
Br	0.14	Ni	0.09
Zn	0.10	Fe	0.20
Ti	0.21	Cr	0.18
Cu	0.09	S	2.10

Remark: 9.621 cm^2 (or 3.5 cm in diameter) is excitation area of the filter by
X- ray beam.

In order to prepare the calibration curve, the filter was dropped by an atomic absorption grade solution amount with a known concentration of element of interest. Depending on preliminary estimation for concentration of element and its lower limit of detection, the added solution amount could be varied from 5 to 20 μl per each time of drop. It should be noted that in order to reduce the effects of the matrix changes induced by adding the solutions in the filters, each filter disk of 4.5 cm in diameter was used to analyze only once element. In this analysis, the following solutions were prepared for determination of concentrations of elements in the filters:

Element of interest	Atomic absorption grade solution
Al	$Al(NO_3)_3$ in HNO_3 (5%)
Ca	$Ca(NO_3)_2$ in HNO_3 (5%)
Si	$Na_2O.SiO_2.nH_2O$ in H_2O
Mg	$Mg(NO_3)_2.6H_2O$ in HNO_3 (10%)

S	$(NH_4)_2SO_4$ in HNO_3 (2%)
K	$K NO_3$ in HNO_3 (5%)
Fe	$Fe(NO_3)_2.9H_2O$ in HNO_3 (10%)
Mn	$MnCl_2.4H_2O$ in HCl (10%)
Zn	$Zn(NO_3)_2.6H_2O$ in HNO_3 (10%)
Pb	$Pb(NO_3)_2$ in HNO_3 (10%)
Cu	$Cu(NO_3)_2$ in HNO_3 (10%)
Ti	15% $TiCl_3$ in HCl(10%)

The concentrations of the elements in the above solutions are 1mg/ml, except for Ti. After each drop of the solution, the filter was warmed up for 2 hours before putting in and measuring line intensity on WDX-ray Spectrometer. The measuring time for each spectrum is 100 seconds. The concentration of elements determined in both TSP and PM-10 are given in tables 5.5 to 5.10.

Table 5.5   Concentrations of major elements for TSP matter

(in weight percent)   in ambient air at Plant A

Major elements (in weight percent)	Sample 1	Sample 2	Sample 3	Average
Ca	3.82 ± 0.02	5.37 ± 0.03	4.93 ± 0.03	**4.71**
Si	17.1 ± 0.2	14.5 ± 0.2	20.4 ± 0.2	**17.3**
Al	13.77 ± 0.18	12.17 ± 0.15	13.85 ± 0.18	**13.26**
S	8.85 ± 0.08	4.89 ± 0.04	2.79 ± 0.02	**5.51**
Mg	3.56 ± 0.02	2.63 ± 0.02	3.65 ± 0.02	**3.28**
Fe	1.97 ± 0.01	1.03 ± 0.01	1.33 ± 0.01	**1.44**
K	1.06 ± 0.01	1.34 ± 0.01	1.35 ± 0.01	**1.25**

**Table 5.6 Concentrations of trace elements for TSP matter (in mg/g)
in ambient air at Plant A**

Trace elements (mg/g)	Sample 1	Sample 2	Sample 3	Average
Pb	2.08 ± 0.01	5.39 ± 0.03	3.71 ± 0.02	**3.72**
Cu	0.454 ± 0.003	0.332 ± 0.002	0.457 ± 0.003	**0.414**
Zn	3.73 ± 0.02	2.34 ± 0.02	3.16 ± 0.02	**3.08**
Mn	0.512 ± 0.003	0.456 ± 0.003	0.532 ± 0.003	**0.5**
Ti	0.651 ± 0.004	0.616 ± 0.004	0.662 ± 0.004	**0.643**
Ni	0.053 ± 0.003	small	small	

Table 5.7 Concentrations of major elements (in weight percent)

for TSP matter in ambient air at Plant B

Element (in %)	TSP1	TSP2	Average
Ca	0.912 ± 0.003	0.664 ± 0.003	**0.788**
Al	4.06 ± 0.02	3.88 ± 0.02	**3.97**
Si	2.73 ± 0.01	3.44 ± 0.01	**3.085**
Mg	0.710 ± 0.004	1.126 ± 0.006	**0.918**
Na	1.88 ± 0.03	1.31 ± 0.02	**1.595**
S	1.86 ± 0.03	1.46 ± 0.02	**1.66**

**Table 5.8   Concentrations of major elements (in weight percent)
for PM-10 in ambient air at Plant B**

Element (in %)	No1. PM-10	No2. PM-10	No3. PM-10	No4. PM-10	Average
Ca	0.171±0.002	0.133±0.002	0.124±0.002	0.157±0.002	**0.145**
Al	0.610±0.003	0.680±0.003	0.385±0.002	0.732±0.003	**0.601**
Si	0.513±0.003	0.651±0.003	0.383±0.002	0.742±0.003	**0.572**
Mg	0.297±0.002	0.273±0.002	0.403±0.002	0.242± 0.002	**0.303**
Na	0.621±0.006	0.644±0.006	0.442±0.005	0.541±0.005	**0.562**
S	0.781±0.007	0.667±0.006	0.732±0.006	0.434±0.005	**0.654**

Table 5.9 Concentrations of minor and trace elements (in mg/g) for

TSP in ambient air at Plant B

Element (In mg/g)	Sample 1	Sample 2	Average
Mn	0.058 ± 0.004	0.054 ± 0.004	**0.056**
Fe	3.18 ± 0.03	3.05 ± 0.03	**3.115**
K	4.24 ± 0.02	2.68 ± 0.02	**3.46**
Ti	0.377 ± 0.003	0.413 ± 0.003	**0.395**

Table 5.10 Concentrations of minor and trace elements (in mg/g) for
PM-10 in ambient air at Plant B

Element (In mg/g)	No1.PM-10	No2.PM-10	No3.PM-10	No4.PM-10	Average
Mn	0.025±0.002	0.021±0.002	0.0033±0.003	0.019±0.002	**0.0245**
Fe	0.699±0.008	0.656±0.008	0.228±0.003	0.872±0.009	**0.614**
K	Small	0.96±0.01	0.344±0.006	Small	**0.652**
Ti	0.064±0.006	0.045±0.004	0.028±0.003	0.032±0.003	**0.042**