CHARACTERIZATION OF BANGKOK AIRBORNE PARTICULATES USING THE X-RAY FLUORESCENCE TECHNIQUE

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ABSTRACT

Characterization of airborne particulates in Bangkok urban area has been performed using the X-ray Fluorescence Technique. The average concentrations of major elements in suspended particulates, i.e., Al, Si, K, Ca, Fe and S were 6.32, 22.04, 1.80, 10.36, 1.82 and 4.17 percent by weight respectively. The technique could also detect some trace elements in particulates such as Pb, Br, Mn, Ni, Zn, Ti and Cu. Concentrations of these elements were found to be 2.084, 0.512, 0.272, 0.443, 3.635, 1.775 and 2.066 mg/g respectively. The detection limit of these elements on a 9.621 sq. cm. cellulose filter were found to be 0.22, 0.14, 0.15, 0.09, 0.10, 0.21 and 0.09 micrograms respectively. Wavelength Dispersive X-ray Fluorescence system (WDX) was used to analyse trace elements. For major elements, an Energy Dispersive X-ray Fluorescence system (EDX) was used. The peak-to-background ratio method was used to correct the matrix effects of varied chemical composition. The results compared favorably with analyses obtained by standard instruments such as ICP-AES and AAS.

1. BACKGROUND

Air pollution has become one of the most serious problems in densely populated urban areas in many cities around the world. In Southeast Asia, the economic growth has brought a higher standard of living in materialistic terms. Development of the countries in this area has been very fast, this includes building up of infrastructures, setting up new industries and businesses. Most of these developments would normally concentrate around large cities because of the supporting facilities usually available there. As a consequence, emissions from industrial activities and transportation are usually high and concentrated in these areas. Laws and regulations are lagging behind, so is the enforcement. To protect the environment, several monitoring programs are being done by different organization. Major air pollutants are being measured according to the applicable standards. For example, samplings of total suspended particulate matter are being done using high volume air samplers and gravimetric methods of measurement. Standards concerning very fine particles, less than 10 microns, have recently been adopted. Up till now, characterizations of particulates are not required at the moment and are not being done locally. However, characterizations of particulates into major elements and minor elements may be very useful for the study of source-receptor relationships as well as for the effects on human health. This study concerns the characterization of airborne particulates in the urban areas of Bangkok. The X-ray fluorescence methods have been used throughout the work in order to develop an alternative analytical method that is reliable and of non-destructive nature. Comparisons are being made with some conventional methods such as the Inductively Coupled Plasma Emission Spectrometry (ICP-AES) and the Atomic Absorbtion Spectrometry (AAS)., etc. The results compared favorably with analyses obtained by standard instruments.

2. METHODOLOGY

Airborne particulates in urban areas of Bangkok, about 100m from a busy intersection, were collected on

8”x10” Whatman No. 41 cellulose filter papers by using high volume air samplers. Each sample was collected for 24-hour periods and then was divided into four parts and analyzed by different methods, i.e., the X-ray Fluorescence Spectrometry (XRF), ICP-AES and AAS.

For the XRF, the filters were cut into disc shape of 4.5 cm in diameter. An XR-200 LINK EDXRF spectrometer was used to analyse all the major elements on the filters while a JSX-60PA JEOL WDXRF spectrometer was used to analyse trace elements. The peak-to-background ratio method was used to correct the matrix effects of varied chemical composition of the samples. Standard curves were prepared by spiking atomic absorption grade solutions of the element of interest onto the filters. The analytical results were first checked by using simulated particulate samples prepared from the NIST coal fly ash and coal standard reference materials, i.e., NIST 1633a, NIST 2682a, NIST 2684a,NIST 2685 and NIST 2692.

Additionally, a scanning Electron Microscope with energy dispersive X-ray Analyzer (EDSEM) was also used to analyse the size, shape and chemical composition of micro particles.

3. RESULTS

Blank filters have been analyzed by AAS and ICP-AES to find the trace elements in the filters themselves and the results found were summarized in Table 1. It could be seen that the cellulose filters contain very little trace elements and should be suitable for this kind of investigation where trace elements on filters are of interest. The glass fiber filters, though very strong in mechanical properties, have some drawbacks since they contain a lot more elements such as Si, Al, Na, Ba, Zn, K, Ca, S, Fe, Cu, Sr and Rb.

Table 1 Trace elements in blank filters by AAS and ICP-AES

Element	Conc. in ng/cm^3	Element	Conc. in 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

NB. All elements except Pb, As and Cd were analyzed by ICP-AES. The latter were analyzed by AAS.

For minor elements, such as Pb, Mn, Br, Ni, Zn, Fe, Ti, Cr, Cu, S, etc., the method adopted was the WDX. The most appropriate conditions and parameters for the determination of various elements were determined. These included analysing crystal, angles of diffraction for peak and background, voltage and current of X-ray tubes, detector, counting time, etc. A calibration curve was prepared for each element. The lower limit of detection (LLD) was determined for each element, the results of which are summarized in Table 2.

Table 2 Lower limit of detection for elements determined by WDX method (in microgram/9.621cm^2)

Element	LLD	Element	LLD
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

NB. The excitation area of the filter is 3.5 cm in diameter or 9.621cm^2 in area.

Standard reference materials from NIST were analyzed with the results summarized in Table 3. In general, good agreement between the reference values and the values measured in this study has been consistent. For smaller values, some discrepancies may be noticed.

Table 3 Analysis of standard reference materials in micrograms

Element	NIST1633 a	NIST1633 a	NIST 2684	NIST2684	NIST2682	NIST2682
	Ref. value	Mea.value	Ref.value	Mea.value	Ref. value	Mea.value
Pb	1.54	1.8	N.A.	N.M.	N.A.	N.M.
Mn	3.81	2.9	0.4	small	0.45	small
Br	N.A.	small	0.12	small	0.06	small
Ni	2.71	3.0	N.A.	1.2	N.A.	1.4
Zn	4.69	4.1	1.23	0.9	0.15	1.1
Fe	2,002.2	1789.7	26.76	30.7	41.8	31.8
Ti	170.4	183.2	6.69	8.6	8.7	6.9
Cr	4.17	4.1	0.19	small	0.26	small
Cu	2.51	2.6	N.A.	small	N.A.	small
S	38.3	40.1	334.5	330.7	81.78	111.9

NB. (1) N.A. = not available.

(2) N.M. = not measured.

(3) small = lower than detection limit.

(4) Matrix correction was applied to all measured values.

Thirteen (13) air samples were collected near a busy intersection in a commercial center of Bangkok. Major elements were analysed by the EDX method, the results of which are summarized in Table 4. The concentrations were found to be from 1.46% for potassium to about 24.14% for silicon which forms the major part of the soil.

For minor elements in particulates the WDX method has been used and the results are summarized in Table 5.

Other two standard methods, i.e., ICP-AES and AAS, were used to determine the quantities of elements in the particulates. The results of this study is summarized in Table 6.

Table 4 Major elements in particulates, in percent, as analysed by EDX and WDX methods.

Sample No.	Al	Si	K	Ca	Fe	S
1	6.26	22.64	2.08	9.97	1.66	3.09
2	7.17	24.14	1.97	8.43	2.02	2.31
3	6.78	22.40	1.67	8.16	1.90	3.62
4	6.25	24.03	1.75	10.37	2.05	1.99
5	5.71	21.80	1.77	13.12	1.98	2.59
6	6.62	22.96	1.68	10.01	1.80	2.73
7	6.50	21.43	1.87	10.27	1.77	3.36
8	6.12	22.12	1.94	10.92	1.89	3.26
9	5.91	20.59	1.90	8.97	1.51	5.38
10	5.89	21.81	1.46	10.17	2.25	4.16
11	7.36	20.64	1.62	10.40	1.53	3.64
12	5.66	20.65	1.78	11.76	1.58	4.22
13	5.97	21.38	1.86	11.73	1.77	4.11
Average	6.32	22.05	1.80	10.33	1.82	4.17

NB. Fe and S were analysed by WDX, all other were analysed by EDX.

Table 5 Concentration of minor elements, in mg/g, in particulates as analysed by WDX method

No.	Pb	Mn	Br	Ni	Zn	Ti	Cu
1	1.959	.202	.731	.081	2.550	1.394	1.813
2	1.756	.276	.665	.162	1.650	1.468	1.286
3	1.369	.254	.528	small	1.627	1.468	1.559
4	1.488	.263	.508	.078	2.448	1.421	.838
5	1.572	.370	.796	small	1.537	1.543	1.423
6	1.946	.178	.688	small	1.690	1.653	1.618
7	2.156	.170	.702	.084	8.466	1.389	1.727
8	1.575	.298	.724	.183	1.977	1.704	3.276
9	3.669	.237	1.274	.112	3.770	1.264	2.724
10	1.894	.576	.593	.160	3.686	1.351	1.106
11	2.850	.286	1.225	small	2.646	2.010	1.673
12	1.493	.154	.666	small	3.345	1.483	1.506
13	1.481	.277	.973	.437	2.889	1.796	1.985
Avg.	2.084	.272	.512	.443	3.635	1.775	2.066

Table 6 Concentrations of elements, in milligrams per gram except for Fe which is in %, in particulates as analysed by ICP-AES and AAS

No.	Pb	Mn	Ni	Zn	Fe(%)	Cu	Cr	As	Cd
1	2.230	.210	.0746	3.451	1.55	2.257	.0628	.0403	.006
2	1.864	.317	.0972	2.164	2.01	1.367	.0472	.026	.003
3	1.445	.288	.0287	2.347	1.91	1.919	.0575	.0354	.007
4	1.707	.241	.0592	2.979	2.09	1.728	.0576	.0347	.003
5	-	-	-	-	-	-	-	-	-
6	2.176	.193	.0725	2.296	1.62	1.555	.0551	.0232	.006
7	2.436	.182	.0811	10.76	1.79	2.257	.0511	.0511	.008
8	1.737	.293	.160	2.481	1.83	3.493	.0607	.0330	.007
9	3.898	.261	.0833	5.188	1.59	2.903	.0682	.0423	.007
10	2.020	.581	.168	4.315	2.38	1.153	.0838	.177	.008
11	3.458	.316	..0588	3.881	2.44	2.791	.143	.0336	.014
12	1.710	.148	.0375	4.412	1.56	1.945	.0541	.0569	.007
13	-	-	-	-	-	-	-	-	-

NB. Samples number 5 and 13 were not analysed.

4. CONCLUSION AND DISCUSSION

It could be concluded that the X-ray Fluorescence method could be used for characterizing particulates in a reliable, convenient and economical way. The EDX method is suitable for analysing major elements such as Al, Si, K, Ca, Fe, S etc. while the WDX method is more suitable for analyzing minor elements such as Pb, Mn, Br, Ni, Zn, Ti, Cu, etc. The EDX method is a quick and easier method which could be used to make a preliminary analysis to determine the major elements in particulates and also to see traces of other elements which may require further analyses.

The values obtained by the XRF method, when analyzing the reference materials from the NIST, were quite close and consistent to the reference values as can be seen in Table 3.

The XRF method yielded results which were comparable with those analyzed by other standard methods, i.e., ICP-AES and AAS as can be seen when comparing Table 4 and Table 5 with Table 6. For example, the t-test for Pb, Zn and Fe indicated that the two methods would yield statistically the same results with a significance level of 0.01. The XRF method has the advantage of being non-destructive and needs no sample preparation. The analyses could be repeated if needed. It is normally cheaper than the conventional methods so it presents a good potential of being an alternative method for the characterization of airborne particulates on a routine basis.

5. REFERENCES

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6. KEY WORDS

XRF, EDX, WDX, X-ray fluorescence, airborne particulates.