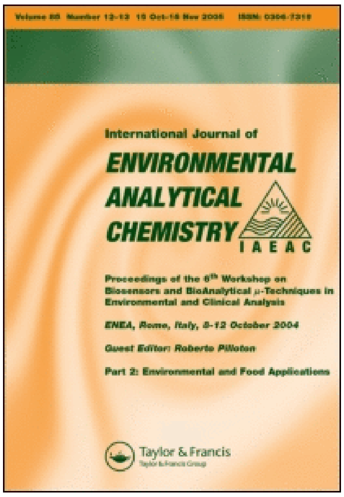

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Determination of Trace Elements in Aerosol Samples Collected on Polycarbonate Filters by Atomic Absorption Spectrometry

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DETERMINATION OF TRACE ELEMENTS IN AEROSOL SAMPLES COLLECTED ON POLYCARBONATE FILTERS BY ATOMIC ABSORPTION SPECTROMETRY

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The multi-element analysis of aerosol samples collected on polycarbonate filters and the wet digestion procedure in open vessel were investigated. The concentrations of Na, K, Ca, Mg and Zn were determined by flame atomic absorption spectrometry with a micro injection system while Cd, Pb, Cu, Ni and V were determined by graphite furnace atomic absorption spectrometry (AAS).

NIES N° 8 "Vehicle Exhaust Particulate" Certified Reference Material from the Japan Environment Agency was used to study the decomposition of the samples. Different treatments were applied in order to completely dissolve the aerosol samples. It was found that, from all the methods tested, attack with micro-quantities of HNO_3 and $HClO_4$ in an air pressure digestion system was the best procedure for the determination of the elements by AAS.

The recommended method was appropriate for all elements and it was applied to real samples. Two non-destructive analytical techniques for the determination of Na, K, Ca, Mg, Zn and Pb have been compared with the proposed method: proton induced X-ray emission (PIXE) and neutron activation analysis (NAA). Results obtained by the application of these three techniques were similar.

KEY WORDS: Airborne particulate matter, decomposition procedure, multielemental analysis, metallic element, atomic absorption spectrometry.

INTRODUCTION

Highly toxic materials from industrial and other urban sources are constantly being released into the environment, as a consequence of the antropogenic activity[1,2]. These toxic materials have surpassed the natural process emissions, producing in some cases remarkable modification in the composition of the atmosphere[3,4]. In order to understand their danger to man's health it is necessary to develop comprehensive analytical methods to detect these materials.

The interest in the multielement analysis of air pollutants collected by means of cellulose filters, glass fiber filters, membrane filters, PTFE filters has constantly increasing[5]. Moreover, as the majority of these contaminants occur in trace and sub trace concentrations, several non destructive instrumental techniques such as X ray fluorescence spectrometry (FRX)[6], neutron activation analysis (NAA)[7,8], proton induced

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X ray emission (PIXE)[9], have been employed. But, these techniques need comparison spectra, longer times and more care. Others, such as inductively coupled plasma atomic emission spectrometry (ICP-AES)[10], anodic stripping voltametry (ASV)[10], and atomic absorption spectrometry (AAS)[11,12] are reliable and more economical methods, but they need to have the elements in solution prior to analysis. This requires an extremely careful handling of conventional laboratory glassware, and a good selection of the chemicals[13]. Comparatively, graphite furnace atomic absorption spectrometry and anodic stripping voltametry have similar sensitivities in trace analysis[11]. For the multi-element analysis of airborne particulate matter several acid digestion procedures in all types of filters have been studied[14–16]. However, few papers describe the analysis of airborne particulate matter collected on polycarbonate membrane filters with complete matrix digestion.

The purpose of this work was to study an AAS method for the multi-element analysis of airbone particulate matter collected on polycarbonate filters. Standard reference materials were used to confirm the accuracy of the analitycal results[10,15]. In order to select the method, various acid mixtures in open vessels were studied using "Vehicle Exhaust Particulates" Certified Reference Material from the Japan Environment Agency (NIES #8). The selection of this Reference Material was done taking into account the high content of carbon (80%) and the quantity of the elements that come from urban sources[17].

In order to evaluate the analytical performance of the proposed method, the results of the analysis of atmospheric aerosol samples collected in Santiago de Chile were compared with two non-destructive analytical techniques (PIXE and NAA).

EXPERIMENTAL

Instrumentation

The analysis of NIES materials was performed using a Hitachi Polarized Zeeman Atomic Absorption Spectrometer. The elements Na and K were analysed by flame-AES, Ca, Mg and Zn by flame-AAS and Pb, Cd, Cu, Ni and V by graphite furnace-AAS.

The analysis of the aerosol samples were performed using a Perkin-Elmer 2380 atomic absorption spectrometer equipped with a HGA 400 graphite furnace, a deuterium background corrector unit and a 10 cm slot burner for an air-acetylene flame.

Injection device

A PTFE funnel with an i.d of 0.7 mm and a depth of 18 mm was connected directly to the nebulizer of the instrument.

Reagents

All chemicals were of analytical-reagent grade or higher purity. Deionised water was provided by a Milli-Q system. Stock standard solutions (1000 mg/l^{-1}) of all elements were prepared by diluting titrisol Merck. Working solutions were freshly prepared every day by diluting appropriate aliquots of the stock solution.

Glassware cleaning

Prior to digestion, all glassware and quartz material was cleaned with boiling HNO_3 vapor during 3 hours in a closed system, then washed successively with high purity de-ionised water, and finaly dried at 110°C.

PROCEDURES

Digestion methods

Diferent mixtures of HNO_3-$HClO_4$, and HNO_3-$HClO_4$/HF at ambient pressure were used, for the complete digestion of the samples.

(a) HNO_3-$HClO_4$

100 mg of the NIES N°8 was introduced inside the quartz tube and 9 ml of concentrated HNO_3 and 0.6 ml of concentrated $HClO_4$ were added. The tube was placed in an aluminium block. The block was heated on a hot plate from 20 to 140°C during 70 min and then from 140 to 210°C over 90 min. The solution was reduced to approximately 50 µl and was removed from the hot plate. The resulting clear, colourless sample solution was left to cool completely and then was diluted to 10 ml with 1M HCl.

(b) HNO_3-$HClO_4$/HF

The method used was similar to that in (a) except that the sample was digested with 6 ml of concentrated HNO_3 and 0.4 ml concentrated $HClO_4$. After digestion, the sample solution was transferred into a PTFE beaker and 2 ml of concentrated HF were added. The beaker was heated gently at about 100°C to allow the HF to evaporate. The residue was then diluted to 10 ml with 1M HCl.

(c) HNO_3-$HClO_4$

The reference material was first digested with the mixture of 400 µl concentrated HNO_3 and 40 µl of concentrated $HClO_4$ and heated to 140°C. Then, the sample solution was cooled to room temperature and 500 µl HNO_3 and 100 µl $HClO_4$ were added again, heating from 140 to 210°C during 90 min. If the HNO_3 is evaporated, further HNO_3 should be added to the sample in 500 µl aliquots. The resulting solution was then diluted to 10 ml with de-ionised water.

Atomic absorption spectrometry determination

Na and K were measured by flame AES, Ca, Mg, Zn by flame AAS and Cd, Pb, Cu, Ni, V by GFAAS. The instrumental parameters and reading conditions are summarised in Tables 1 and 2. The furnace the temperature program is presented in Table 3.

Table 1 Hitachi polarized zeeman atomic absorption spectrophotometer instrumental conditions for the determination of Na, Ca, K, Mg, and Zn.

	Na	*K*	*Ca*	*Mg*	*Zn*
Lamp int (mA)	–	–	10	15	10
Wavelength (nm)	589.0	766.5	422.7	285.2	213.8
Slit (nm)	1.3	1.3	0.4	1.3	1.3
Sample aliquot (μl)	50	50	50	50	50
Oxidant	Air	Air	Air	Air	Air
Oxid pressure kg/cm^2	1.60	1.60	1.60	1.60	1.60
Fuel	C2H2	C2H2	C2H2	C2H2	C2H2
Fuel pressure kg/cm^2	0.25	0.30	0.35	0.20	0.20
Measurement mode	Emission	Emission	Absorption	Absorption	Absorption
Calulation	P/H only	P/H only	P/H only	P/H only	P/H only

Table 2 Graphite-furnace hitachi polarized zeeman atomic absorption spectrophotometer. Instrumental parameters and reading conditions for the determination of Cd, Cu, Ni, V, Cd and Pb. Sample volume 20 μl, carrier gas 200 ml/min, interrupted gas 30 ml/min and measurement mode AAS.

	Instrumental parameters				
Element	*Lamp (mA) current*	*Wavelength nm*	*Slit nm*	*Read sec*	*Graph. tube*
Cadmium	7.5	228.8	1.3	7	Pirocoated
Copper	7.5	324.5	1.3	6	Pirocoated
Nickel	7.5	232.0	1.3	5	Pirocoated
Lead	7.5	283.3	1.3	6	Pirocoated
Vanadium	12.5	318.4	0.4	10	Pirocoated

Table 3 Graphite-furnace temperature program.

		Cd			*Pb*			*Cu*		
No	*Stage*	*Temperature (°C) start*	*end*	*Time sec*	*Temperature (°C) start*	*end*	*Time sec*	*Temperature (°C) start*	*end*	*Time sec*
1	Dry	60	120	45	60	120	45	80	120	45
2	Ash	300	300	23	400	400	27	700	700	27
3	Ash	300	300	7	400	400	3	700	700	3
4	Atom	2000	2000	7	2200	2200	6	2800	2800	6
5	Clean	2200	2200	3	2400	2400	3	2800	2800	3
Analog monitor:			4–0		3–4				3–4	
Carrier gas:			Interrup		Interrup				Interrup	

		V					*Ni*		
No	*Stage*	*Temperature (°C) Start*	*End*	*Time sec*	*No*	*Stage*	*Temperature (°C) Start*	*End*	*Time sec*
1	Dry	60	120	50	1	Dry	80	120	45
2	Dry	120	120	10	2	Ash	700	700	27
3	Ash	120	900	15	3	Ash	700	700	3
4	Ash	900	900	10	4	Atom	2700	2700	6
5	Atom	3000	3000	10	5	Clean	2800	2800	3
6	Clean	3000	3000	3					
Analog monitor:			4–5					3–4	
Carrier gas:			Interrup					Interrup	

RESULTS AND DISCUSSION

Airborne particulate matter presents a very complex matrix for analysis. It may contain a large number of elements in widely different concentrations and variable amounts of organic material and silicate dust. The composition is subject to significant variations depending on the site location, daytime, season and meteorological conditions.

In order to choose the most adequate decomposition method to determine the various elements in atmospheric particulate matter (a), (b) and (c) methods, were examined using NIES N° 8 "Vehicle Exhaust Particulates" Certified Reference Material. The results are given in Table 4.

Precision and accuracy

Table 4 shows good recovery for all elements. Recovery values over 100% were found for those elements which are easily contaminated (Na, K). Other elements presented recovery values within the expected range.

Full digestion of the samples was obtained for the three digestion procedures. The digestion time for each treatment was similar. The analytical results are in agreement with the certified values, although the Ca values for all digestion procedures showed major differences. One of the possible explanations is that the conditions were not appropriate to dissolve all forms of Ca present in the sample. This may also explain the low value of Zn in the (b) procedure.

Nevertheless, the sensitivity and the reproducibility of the continuous analysis by flame AAS is better than the discrete form, the micro-injection was employed taking into account the small volume of the samples. Table 4 shows that 50 µl injection volumes with flame AAS and 20 µl with GFAAS offered sufficcient sensitivity and reproducibility (RSD < 10%) for the majority of the elements.

Of the three sample digestion procedures method (c) was selected taking into account:

a) the good recovery of the analytes,

b) the low quantities of chemicals used, which gave clear and colourless solutions,

Table 4 Concentrations of elements obtained for the vehicle exhaust particulate reference sample.

Elements	*Methods*						
	(a) *n* = 6	*Recovery* %	*(b)* *n* = 6	*Recovery* %	*(c)* *n* = 9	*Recovery* %	*Certified value*
Na (%)	0.220±0.010	115	0.220± 0.010	115	0.210± 0.004	109	0.192 ± 0.008
K (%)	0.129±0.010	112	0.129± 0.110	112	0.129± 0.004	112	0.115 ± 0.008
Ca (%)	0.440±0.020	83	0.343± 0.035	65	0.301 ± 0.008	57	0.53 ± 0.02
Mg (%)	0.099±0.003	98	0.121 ± 0.016	120	0.096± 0.004	95	0.101 ± 0.005
Zn (%)	0.110±0.005	106	0.076± 0.012	73	0.111 ± 0.006	107	0.104 ± 0.005
Cd (μgg^{-1})	1.15 ±0.01	105	1.41 ± 0.40	128	1.07 ± 0.008	97	1.1 ± 0.1
Pb (μgg^{-1})	237 ± 17	108	237 ± 17	108	228 ± 4.7	104	219 ± 9
Cu (μgg^{-1})	–	–	–	–	67.9 ± 1.8	101	67 ± 3
Ni (μgg^{-1})	–	–	–	–	17.5 ± 1.7	95	18.5 ± 1.5
V (μgg^{-1})	17.6 ± 0.6	104	16.7 ± 4	98	17.0 ± 2.2	98	17 ± 2

c) the time employed (three hours/block of 12 test tubes) after the full digestion of the sample,
d) the high concentration of the analytes in the small volume (2 ml) of the final solution.

Limits of detection (LOD)

The detection limits of the method in terms of analyte concentration in the standard solution were calculated according to the IUPAC recomendations, using the equation:

$$\mathrm{LOD} = \frac{3\,\sigma_{n-1}\,C_S}{\mathrm{Abs}}$$

where, Cs = standard concentration near the blank value
Abs. = absorbance of standard

The experimental results for all elements are given in table 5

Blank matrices

Due to the low concentration of the elements in the samples, very low blank values were required. In order to know the content of Na, K, Ca, Mg, Zn, Cd and Pb in the matrices, the blank of polycarbonate membrane filters were studied. The results obtained, together with data from aerosol filter samples collected in Santiago de Chile were compared.

The blanks analysis indicated no contamination during the digestion procedure. These results are summarised in Table 6.

Most of the data are the averages of at least three runs and in all instances the corresponding results are not significant with respect to the aerosol contents.

Table 5 Experimentally obtained limits of detection (LOD).

Analyte	*Method*	*Sample volume (μl)*	*LOD [μg/l]*
Na	AAS	50	24.0
K	AAS	50	53.0
Ca	AAS	50	15.0
Mg	AAS	50	3.5
Zn	AAS	50	39.0
Cd	GF-AAS	20	0.04
Pb	GF-AAS	20	0.4
Cu	GF-AAS	20	0.2
Ni	GF-AAS	20	2.0
V	Gf-AAS	20	1.6

Table 6 Elements concentration (μg/g) in blank filter matrices and aerosol samples collected in Santiago de Chile.

Elements *Samples*	*Na*	*K*	*Ca*	*Mg*	*Zn*
Blank	17.50 ± 1.30	10.10 ± 1.40	26.20± 3.70	7.50 ± 0.70	1.20 ± 0.70
Z-55	7211 ± 53	8677 ± 52	7472 ± 3789	2645± 66	7661 ± 210
Z-109	7028 ± 1086	6929 ± 0	2628 ± 792	948 ± 181	2776 ± 45
Z-127	5635 ± 152	5089 ± 217	2527 ± 65	896 ± 283	2839 ± 240
Z-181	7035 ± 197	8950 ± 498	1231 ± 243	603 ± 162	5805 ± 0
Z-46	10675± 1414	11136 ± 768	1965 ± 40	1447± 60	6768 ± 808
Z-145	2315 ± 303	7361 ± 206	874 ± 248	510 ± 55	2476 ± 0
Z-163	2591 ± 884	5132 ± 18	3257 ± 477	991 ± 159	5922 ± 353
Z-201	3826 ± 188	6926 ± 252	1119 ± 125	937 ± 21	10278± 0

Elements *Samples*	*Cd*	*Pb*	*Cu*	*Ni*
Blank	0.05 ± 0.03	0.71 ± 0.17	0.29 ± 0.05	0.58 ± 0.15
Z-55	133 ± 14	10784 ± 46	707 ± 30	1570± 59
Z-109	291 ± 6	6308 ± 260	746 ± 41	1946± 82
Z-127	139 ± 13	3012 ± 152	399 ± 14	1581± 22
Z-181	239 ± 4	9993 ± 424	490 ± 33	498 ± 17

REAL SAMPLE ANALYSIS

AAS has been applied to several real aerosol samples, collected on polycarbonate membranes after the digestion procedure described above.

NAA and PIXE were used for comparison studies. The results for Na, Ca, Zn in airborne particulate matter using both AAS and NAA are shown in Figures 1–3. A good correlation was found between these techniques. The same was obtained for K when AAS and PIXE were compared (Figure 4).

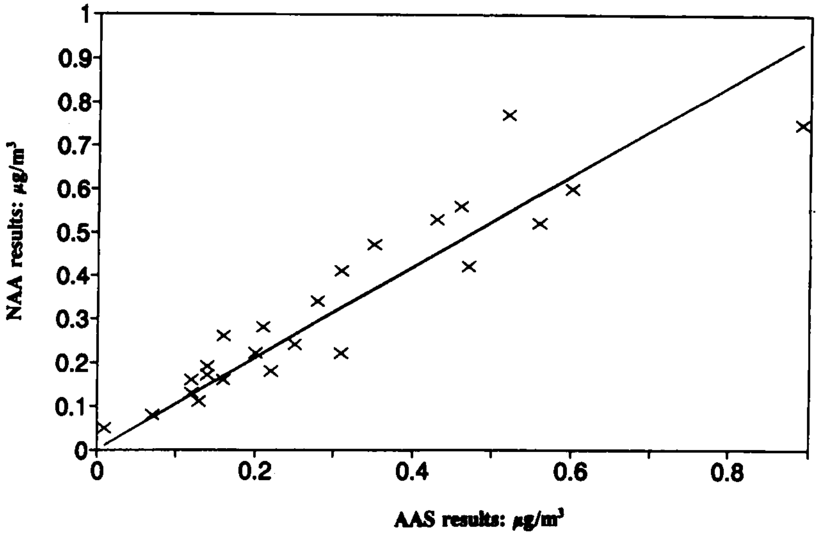

Figure 1 Determination of Na in an aerosol sample. Comparison between NAA and AAS. R = 0.846.

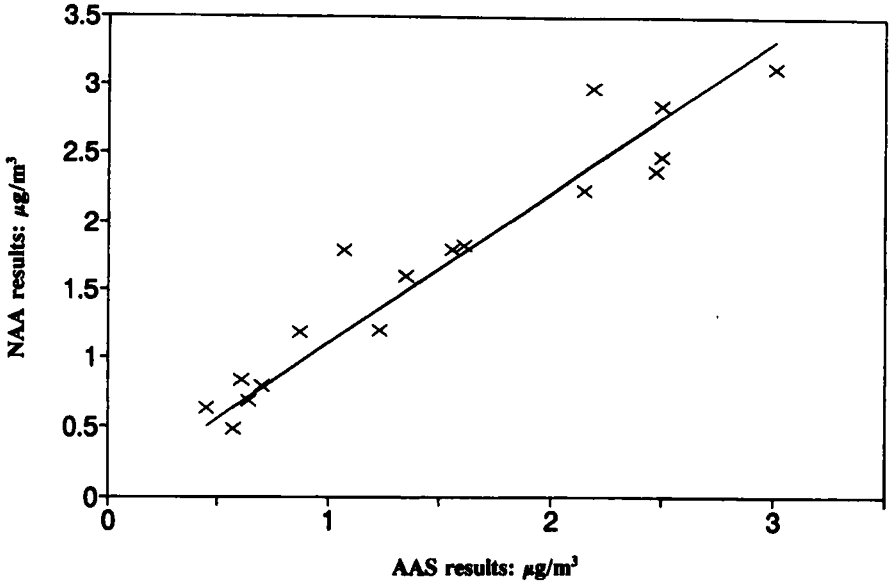

Figure 2 Determination of Ca in an aerosol sample. Comparison between NAA and AAS. R = 0.908.

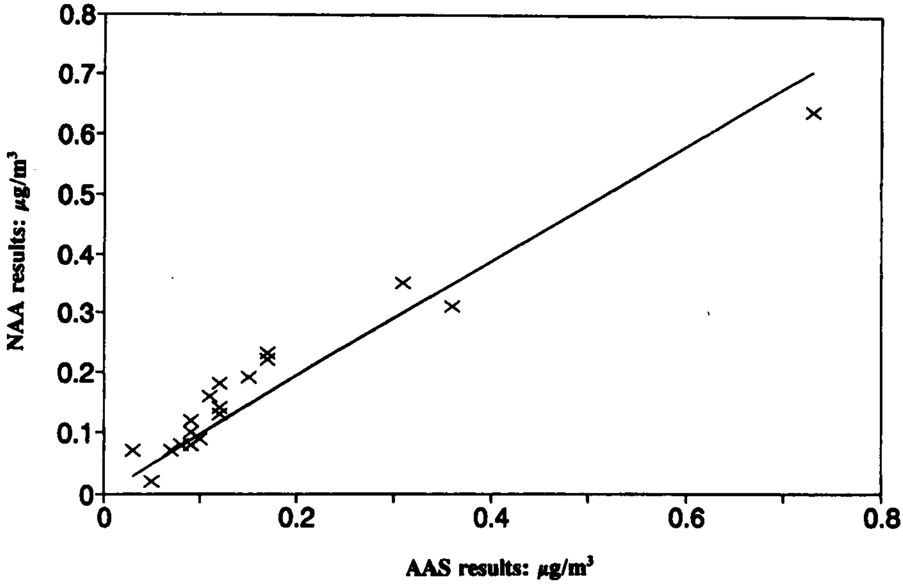

Figure 3 Determination of Zn in an aerosol sample. Comparison between NAA and AAS. R = 0.917

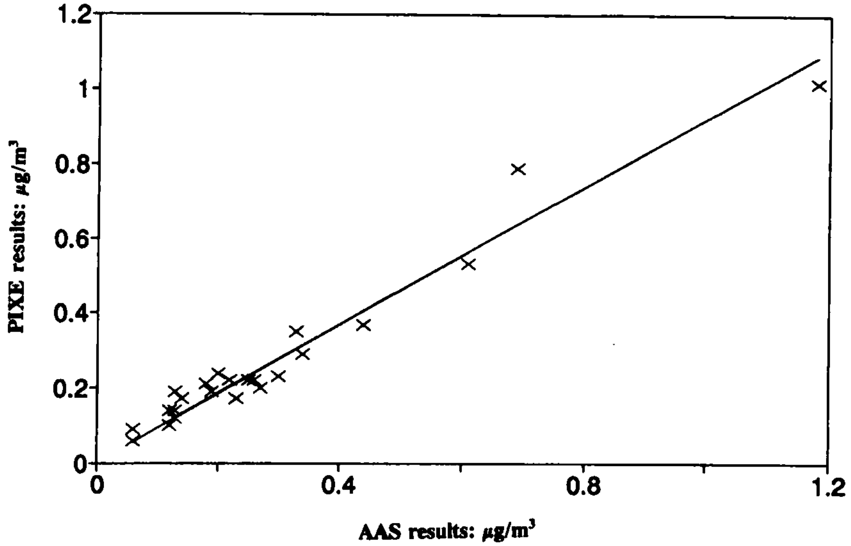

Figure 4 Determination of K in an aerosol sample. Comparison between PIXE and AAS. R = 0.951.

In Figures 5 and 6 it can be seen that the correlation obtained between AAS and PIXE was worse than AAS and NAA for Ca and Zn.

NAA and PIXE did not give results for Mg and Cd owing to the low sensitivity of these techniques for these elements. At the same time, no good correlation between the Pb results by AAS and PIXE was obtained and it was only possible to compare the highest values (Figure 7).

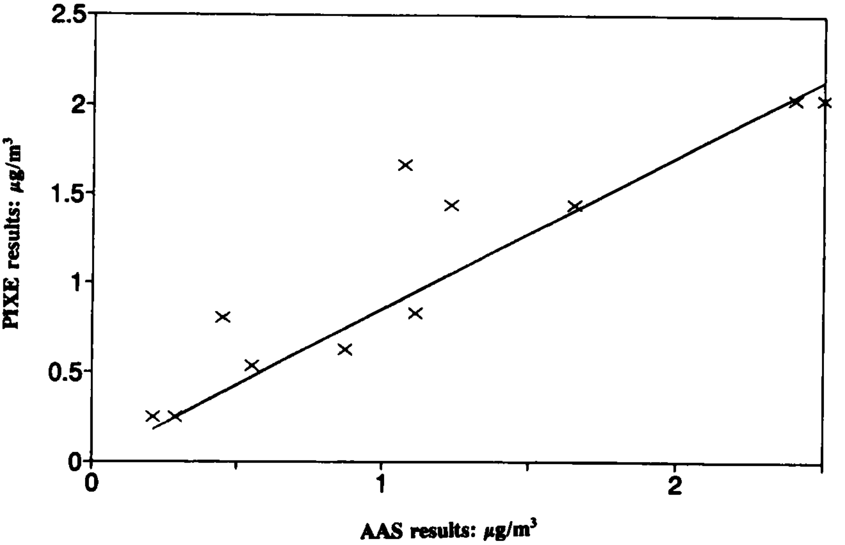

Figure 5 Determination of Ca in an aerosol sample. Comparison between PIXE and AAS. R = 0.802.

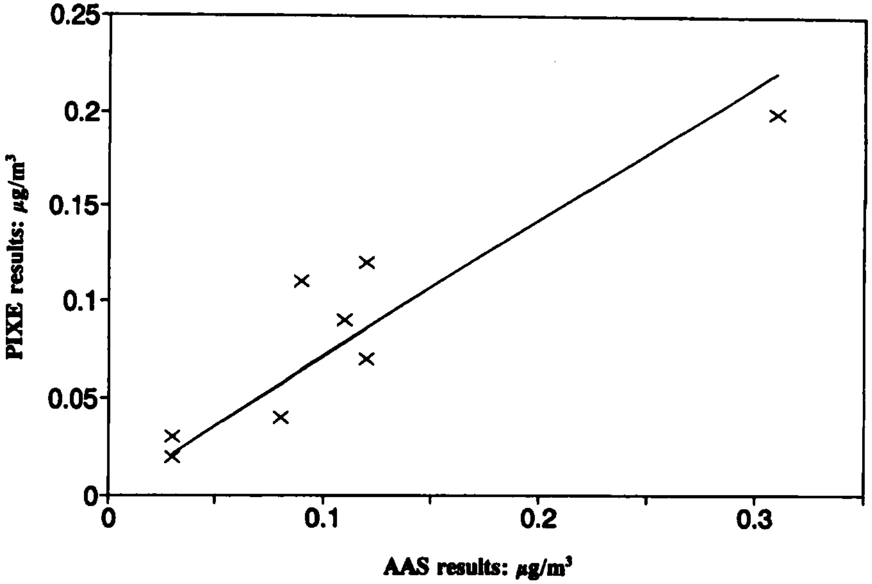

Figure 6 Determination of Zn in an aerosol sample. Comparison between PIXE and AAS. R = 0.818.

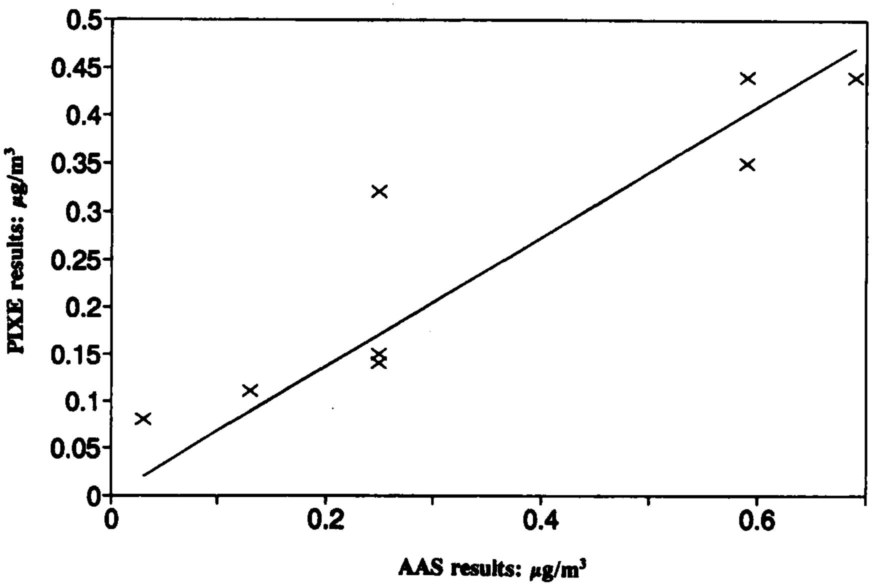

Figure 7 Determination of Pb in an aerosol sample. Comparison between PIXE and AAS. R = 0.792.

CONCLUSION

The generally good agreement between reference values and preliminary results presented here clearly illustrate the viability of the described methods as a means of preparing the aerosol samples for analysis by Flame-AAS and GFAAS.

The analysis of aerosol samples can be readily achieved using the proposed digestion method. This approach has a number of advantages over other reported methods since it not only improve the analysis time but also the detection limits.

In addition, this approach reduces contamination, requires less chemicals and improves safety. Additionaly, the selected microanalysis techniques facilitate the use of much smaller volumes of sample which are often difficult to obtain.

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