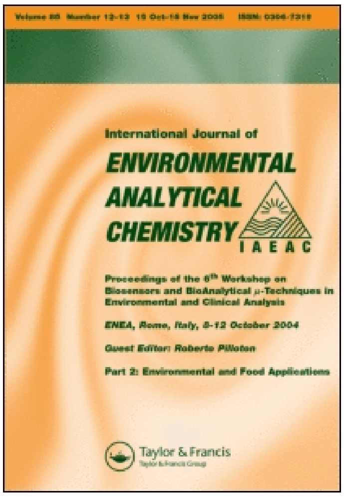

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Trace Elements in Wet Atmospheric Deposition: Application and Comparison of PIXE, INAA, and Graphite-Furnace AAS Techniques

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Trace Elements in Wet Atmospheric Deposition: Application and Comparison of PIXE, INAA, and Graphite-Furnace AAS Techniques†

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The concentrations of 21 soluble trace elements deposited in urban snow collected during 1979 on the island of Montréal have been measured using three different methods: proton-induced X-ray emission (PIXE), graphite-furnace atomic absorption

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Footnote on Page 90.

spectroscopy (AAS) and instrumental neutron activation analysis (INAA). A comparison of the results obtained with these three techniques used for both independent and comparative measurements, clearly show the reliability of PIXE in multi-elemental analyses of aqueous environmental samples. The results reported here constitute a more comprehensive analytical study of atmospheric deposition through snow than has been previously reported.

1. INTRODUCTION

Large amounts of pollutants are dissipated into the air or deposited on soil and water bodies by industrial plants, incinerators, refineries, tanneries, smelters and domestic heating devices. Knowledge of the identities, ambient concentrations and fate of these pollutants is of prime concern to the environmental scientist since it is well known that high pollution levels in air, as well as in water and soil, may cause many biological stresses in the exposed population.

Analysis of wet precipitation (rainfall or snow) is an important indicator of atmospheric pollution and much effort has been devoted recently to detecting the presence of heavy metals and sulphur in rain or snow.[1-8] Several analytical procedures are presently used for assessment of such aqueous samples and probably the techniques best known to the environmental scientist are AAS and INAA. In the last decade X-ray emission methods have also been used with varying degrees of success, in the detection and measurement of trace element concentrations in both liquid and solid samples. In particular the proton-induced X-ray emission (PIXE) is very useful for this purpose because it is a non-destructive procedure and it can attain very low sensitivity limits.[9-12]

We wish to report here a comparison of these three analytical methods (AAS, INAA and PIXE) in the quantitative determination of elemental concentrations in precipitation environmental samples. The advantages and deficiencies of each technique is critically evaluated in terms of their optimal use in environmental pollution investigations.

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2. EXPERIMENTAL PROCEDURES

2.1. Sample collection

Snow samples were gathered over a single 24 hour period at four different locations representing the north (N), northwest (NW), southwest (SW) and southeast (SE) parts of the island of Montréal. The snow collection was carried out late in February to obtain the maximum amount of undisturbed snow before any appreciable meltdown could occur. Approximately 10 litres of snow were collected at each site with a 95 cm × 11 cm pre-cleaned plastic cylinder, which was inserted into the snow always at the same approximate depth and then removed. The sampling sites were chosen sufficiently far from roadways to minimize possible contamination from salt sprinkled on them. The snow samples were placed in polyethylene bags and kept in cold storage to minimize any adsorption on the sides of the bags and to prevent algae growth.

At the time of analysis, approximately 150 g of frozen snow were removed from the centre of each polyethylene bag and allowed to melt in a Millipore Swinex water filtration apparatus. The melted snow sample was filtered through a 0.45 μm HA type Millipore filter which was pre-rinsed several times with distilled and deionized water. The filtered snow was collected in a pre-weighed 250 mL Pyrex flask. To avoid any possible contaminations from the Swinex apparatus and to quickly recover all the snow-water the system was partially modified as follows: first, the standard viton o-ring was replaced by a Teflon o-ring,[13] second, the bottom of the Swinex apparatus was connected to the Pyrex flask by a Teflon tube. In this way a low pressure vacuum could be applied to the flask to speed up the filtration process. All containers and parts which were used in contact with the melted snow had been left at least 24 hours in a 20% solution of nitric acid and then rinsed seven times with distilled and de-ionized water.

At the end of each filtration, the flask was weighed to determine the exact amount of melted snow and was then acidified to a content of 1% using a high purity nitric acid (Ultrex HNO_3). This solution was divided into two parts, one to be used for AAS and INAA (about 50 g) and the second part (about 100 g) to be preconcentrated and be used to prepare the samples for INAA and PIXE measurements.

2.2. Experimental techniques

For the AAS measurements a Perkin-Elmer Model 603 absorption spectrophotometer equipped with a Perkin-Elmer HGA-500 graphite furnace assembly, a deuterium background corrector and an AS-1 auto sampler, was used to determine all elements except lead which was measured using a Perkin-Elmer 703 model and HGA-500 graphite furnace. Standard graphite tubes were employed for elements exhibiting atomizing temperatures lower than 2500°C. For elements having atomizing temperatures above this value, pyrolytic tubes were used to improve sensitivity. For the analysis of aluminium, the graphite tubes were modified according to a molybdenum-treating procedure to improve precision.[14] The charring and atomizing temperatures suggested by the Perkin and Elmer manual were found to give maximum sensitivities for the elements in question. The deuterium background corrector was found not to be necessary.

All standard solutions, acidified to a 1% concentration (high purity nitric acid, Ultrex HNO_3), were made up immediately before analysis using distilled and de-ionized water and certified atomic absorption reference solution (1,000 ppm) from Harleco Company. Blank solutions of 1% acidified, distilled and de-ionized water were also analyzed and the working standard curves were accordingly corrected. A $20\,\mu L$ portion of each sample were used. The overall systematic errors from the AAS analysis were estimated to be $\pm 10\%$ including pipetting errors and deviations from the standard working curves.

Preliminary PIXE measurements using unconcentrated filtered snow gave very poor sensitivities, particularly for the heavier elements. On the other hand good results for Na, Al, Cl, V, Mn and Br were achieved with INAA. The melted snow was therefore preconcentrated in order to improve detection limits. This procedure, however, was not necessary for AAS.

After filtration, the filtrates were pre-frozen in a mixture of acetone and dry ice and then quickly placed in a freeze-drier at a reduced pressure of 200 micrometers of Hg for 36 hours. At the end of this period, the residual material was found to be entirely water-free and the flasks were then subjected to ultrasonic treatment for 15 minutes to minimize any adsorption onto the walls of the vessels. Subsequently the residues were redissolved in 2 mL of high purity nitric acid (Ultrex HNO_3) and swirled about. The ultrasonic and swirling operations were then repeated. For the PIXE measurements, 200 μL from each preconcentrated sample were placed in a Falcon plastic test tube and doped with 200 μL of a cobalt solution (300 ppm). Cobalt was chosen as the internal standard for 1.6 MeV protons since this element was not present in the samples and its line did not interfere with those from the other elements in the PIXE spectra. For 3.0 MeV protons the spectra were normalized to calcium which was detected at 1.6 and 3.0 MeV protons. Twenty μL of the well-mixed solutions were deposited on 0.1 μm Nuclepore filters and placed in a vacuum chamber to be freeze-dried for about two hours. The targets thus obtained were then bombarded with 1.6 and 3.0 MeV protons obtained from the Université of Montréal Tandem Van de Graaff accelerator. The targets were placed at 45° to the beam axis and were facing both an X-ray detector, placed at 90° to the beam axis and the proton beam. An Ortec Si(Li) detector, which had a 160 eV (FWHM) resolution at 5.9 keV, was used to measure the X-ray yields. The spectra were recorded using a 1024-channel ADC interfaced to a CDC 3100 computer which was also used for on-line analysis of the data. More details on the experimental PIXE set-up and the automated PIXE data processing can be found elsewhere .[15–17]

For the INAA measurements all preconcentrated liquid (about 1 mL) samples were placed in acid-cleaned plastic vials which were heat-sealed and then thermal neutron-activated in the SLOWPOKE-2 Reactor at the University of Toronto. Depending on the half-lives of the decaying nuclei different neutron fluxes, irradiation, decay and counting times were used as shown in Table I. The list of the γ-rays used for the data analysis is also shown.

The gamma-ray spectra were obtained using a 24% efficiency Ge(Li) detector having a resolution of 1.9 (FWHM) for the 1332 keV cobalt-60 peak. This was used in conjunction with a Canberra Series 80 4096 channel analyser.

After neutron bombardment, the liquids were transferred to pre-weighed unirradiated vials to avoid possible contribution from impurities contained in the original vials. The concentrations of the elements were determined using a semi-absolute method reported previously.[18] Two blanks of distilled and de-ionized water were also measured with PIXE and INAA. Contributions from the blanks

TABLE I

Elements determined by thermal neutron activation.

Element	Nuclide formed (n,γ)	Half-life	Gamma-ray (Kev)
	(10 min irradiation – 1.5 min decay – 10 min counting)		
Al	^{28}Al	2.24 min	1779
Ca	^{49}Ca	8.72 min	3084
Cl	^{38}Cl	37.2 min	1642
Cu	^{66}Cu	5.10 min	1039
Mg	^{27}Mg	9.45 min	844, 1014
Mn	^{56}Mn	2.58 h	846
Na	^{24}Na	15.02 h	1368
Ni	^{65}Ni	2.52 h	1481
Sr	^{87}Sr	2.83 h	388
Ti	^{51}Ti	5.75 min	320
V	^{52}V	3.76 min	1434
	(16 h irradiation – 3 d decay – 1 h counting)		
Br	^{82}Br	35.3 h	554
K	^{42}K	12.36 h	1525
	(16 h irradiation – 18–21 d decay – 4 h counting)		
Cr	^{51}Cr	27.71 d	320
Fe	^{59}Fe	45.1 d	1098
Co	^{60}Co	5.27 y	1173
Zn	^{65}Zn	243.8 d	1115

were found to be negligible in the determination of elemental concentrations by INAA. However, corrections for Cr, Fe, Ni, Cu, Br and Zn detected by PIXE were necessary. These elements originated from the Nuclepore filters used as target backings. It was found that these contributions remained fairly constant and could be subtracted from the final results without appreciable loss of precision or accuracy.

For comparison purposes the concentrations of Mg and P were also detected employing an induced coupled plasma (ICP) Spectrometer. The ICP used was an ARL 34000 with no background corrector.

2.3. Sensitivity and accuracy

There are several formulae defining sensitivity or detection limits. For AAS it is the slope of the analytical curve. In γ-ray or X-ray studies a conventional criterion of statistical detectability is defined as three times the standard deviation of the background under a photon peak in an interval of one time or two times the full peak width half maximum. However, a more realistic definition, particularly in environmental monitoring, is one adopted by Currie.[19] For this study the determinable limit 'm_q' or the level at which the precision of the measurement was judged to be satisfactory for quantitative determination (i.e., relative standard deviation of ±10%) was calculated from

$$m_q = 50\left\{1 + \left(\frac{1+\mu_B}{12.5}\right)^{1/2}\right\}$$

where μ_B is the background to be subtracted. The detection limits for the ICP were calculated from the program itself used in the system as 2 times the standard deviation of the signal in a blank.

To confirm the accuracy of our experimental procedures, National Bureau of Standards (NBS) of trace elements in water (SRM 1643a) were measured with AAS and INAA. PIXE analysis of the NBS water reference material was not carried out. For trace elements in water whose concentrations were not certified or reported by the NBS, data was obtained from a NBS coal reference standard (SRM 1632a) for INAA. A minimum of five determinations were made for all samples using AAS and INAA. The error quoted is the statistical standard deviation. Tables II and III give the results of these measurements for NBS and others.[20,21] In virtually all cases, the results are well within the limits of acceptability.

3. RESULTS

The final trace element concentrations of the snow samples, their average overall errors and sensitivities obtained by PIXE, INAA and AAS of four filtered melted-snow samples are shown in Table IV.

One of the common limitations to sensitive measurements in INAA is the presence of large amounts of chlorine, sodium and

TABLE II

Concentrations of elements in NBS-SRM 1643a trace elements in water as determined by INAA and AAS.

Element	Measured value[a] (ng/g) INAA	Measured value[a] (ng/g) AAS	NBS value[b] (ng/g)
V	53±1	NA	53±3
Mn	24±2.5	32.5±3.3	31±2
Fe	ND	80±8	88±4
Ni	ND	54±5	55±3
Cu	ND	17±2	18±2
Zn	ND	70±7	72±4
As	80±1	NA	76±7
Cd	ND	12.5±1.3	10±1
Pb	ND	28±3	27±1

NA—not attempted.

ND—not detected.

[a] Errors based upon the average of five determinations and their respective standard deviations.

[b] All NBS value certified.

bromine so prevalent in environmental samples. These three elements produce the nuclides of ^{38}Cl ($t_{1/2}=37.2$ min), ^{24}Na ($t_{1/2}=15.02$ h), ^{80}Br ($t_{1/2}=17.7$ min) and ^{82}Br ($t_{1/2}=35.3$ h). The presence of these nuclides for short and long-lived irradiations made achievement of high sensitivities for the other elements of interest difficult. Preconcentration of the snow samples gave high deadtimes attributed mainly to Cl and Na. This necessitated the use of longer decay times at the expense of achieving better detection limits for elements such as copper and magnesium. Furthermore, Na and the many Br gamma peaks significantly added to the background for the longer-lived irradiations. In many instances the preconcentrated samples exposed to more prolonged irradiations of 16 hours at 2.5×10^{11} n/cm^{2}sec were too active to count until three days later. This made the detection of elements such as K ($t_{1/2}=12.36$ h) and As ($t_{1/2}=26.3$ h) hard to achieve or impossible. The elements S, Ti, Fe, Ni, Sr and Cd were not detected at all in soluble atmospheric precipitation matter. Zinc was detected by means of INAA but only after a decay time of three weeks. In fact the high detection limit of

TABLE III

Concentrations of elements in NBS-SRM 1632a; trace elements in bituminous coal as determined by INAA.

Element	Measured value[a] (ppm)	NBS value[b] (ppm)	Others[c,d] (ppm)
Na (ppm)	787±40	840±40	850±40, 799±15
Al (%)	2.82±0.13	(3.07)	2.9±0.3, 2.9±0.1
Cl (ppm)	776±20	NR	800±70, 770±24
K (%)	0.34±0.01	0.42±0.02	0.42±0.02
Sc (ppm)	6.4±0.2	6.3	6.8±0.6, 5.9±0.2
Ti (ppm)	1560±70	(1750)	1630±70, 1580±80
V (ppm)	39±2	44±3	44±3, 43±1
Cr (ppm)	33.8±2	34.4±1.5	34±2, 34±3.6
Mn (ppm)	27±2	28±2	32±3, 27.3±1.4
Fe (%)	1.08±0.02	1.11±0.02	1.16±0.03, 1.10±0.3
Co (ppm)	8.5±1	(6.8)	6.5±0.2
Zn (ppm)	28±2	28±2	31±6
As (ppm)	8.3±1	9.3±1	11±2, 8.7±0.2
Br (ppm)	38±2	NR	41±4, 40±2.3
Sb (ppm)	0.62±0.02	(0.58)	0.60±0.09, 0.52±0.03
La (ppm)	19±2	NR	18±2, 21±1
Sm (ppm)	2.7±2	NR	2.8±0.3
U (ppm)	1.22±0.1	1.28±0.02	1.21±0.10, 1.31±0.09

[a] Errors based upon the average of five determinations and their respective standard deviations.
[b] NBS certified values except those in parentheses.
[c] Germani *et al.*, 1980.
[d] Ho, 1981.
NR—not reported by NBS.

Zn negates any use of INAA below 100 ng/g. On the other hand PIXE offered good sensitivity for determination of the above mentioned elements. Figure 1 and Figure 2 show typical X-ray spectra for snow samples bombarded at 1.6 and 3.0 MeV while Figure 3 shows a typical INAA spectrum.

To strengthen the confidence in the PIXE techniques elements Ma, Fe, Ni, Cu, Zn, Cd and Pb were also analyzed by AAS while ICP was used for P, Mg and Mn. Figure 4 shows a correlation between PIXE and AAS obtained on sets of the same samples. A correlation factor of $r=0.96$ was calculated at a confidence limit of $P \leqq 0.005$. The following is a list of more specific comments on the concentration measurements of specific elements by a choice of the four methods used.

TABLE IV

Results of the intercomparison of methods of PIXE, INAA and AAS for the snow soluble portion of snow.

Element	Method	Site				Error[a,b,c,d]	Average Sensitivity[e,f,g]
		5 (ng/g)	15 (ng/g)	24 (ng/g)	31 (ng/g)	(%)	(ng/g)
Na	PIXE	6,406	13,845	3,084	13,788	±17%	660
	INAA[h]	4,469	1,583	1,944	4,567	±6%	32
	AAS[i]	—	—	—	—	—	—
Mg	PIXE	324	429	403	192	±39%	234
	INAA	<293	<177	<225	<321	—	<254
	AAS	—	—	—	—	—	—
	ICP	265	373	334	227	±6%	20
Al	PIXE	93	100	<37	77	±42%	197
	INAA	29	32	29	31	±7%	4
	AAS	36	88	103	45	±10%	1
P	PIXE	101	151	27	88	±22%	136
	INAA	—	—	—	—	—	—
	AAS	—	—	—	—	—	—
	ICP	82	60	30	70	±22%	53
S	PIXE	1,310	2,665	1,650	871	±10%	100
	INAA	<15,000	<9,000	<10,000	<16,000	—	<12,500
	AAS	—	—	—	—	—	—
Cl	PIXE	242	455	240	258	±17%	95
	INAA	427	221	254	204	±8%	44
	AAS	—	—	—	—	—	—
K	PIXE	679	1,930	846	746	±13%	65
	INAA	1,167	<780	<867	<1,234	±35%	<1,000
	AAS	—	—	—	—	—	—
Ca	PIXE	1,978	6,486	3,170	1,469	±14%	60
	INAA	3,303	953	1,419	914	±35%	217
	AAS	—	—	—	—	—	—
Ti	PIXE	13	8	13	19	±25%	20
	INAA	<34	<25	<28	<39	—	<38
	AAS	—	—	—	—	—	—
V	PIXE	5	7	4	3	±50%	15
	INAA	4	2	2	1	±6%	0.2
	AAS	—	—	—	—	—	—
Cr	PIXE	<7	<7	<7	<7	—	<35
	INAA	<20	<16	<15	<12	—	<16
	AAS	—	—	—	—	—	—

TABLE IV (continued)

Mn	PIXE	9	8	25	6	±15%	5
	INAA	7	6	15	5	±6%	0.5
	AAS	6	10	16	8	±10%	1
Fe	PIXE	27	2	34	39	±19%	59
	INAA	<1,686	<1,435	<1,500	<1,600	—	<1,550
	AAS	35	22	40	46	±10%	22
Ni	PIXE	63	48	20	48	±12%	51
	INAA	<120	<130	<140	<100	—	<125
	AAS	58	50	45	49	±10%	1
Cu	PIXE	24	35	14	22	±10%	1
	INAA	29	19	12	22	±20%	15
	AAS	21	35	22	23	±10%	1
Zn	PIXE	97	106	84	72	±10%	1
	INAA	128	118	93	74	±15%	115
	AAS	108	115	87	67	±10%	1
As	PIXE	<0.2	<0.2	<0.2	<0.2	—	<1
	INAA	<2	<2	<2	<2	—	<2
	AAS	—	—	—	—	—	—
Br	PIXE	7	9	9	4	±26%	1
	INAA	7	7	3	3	±9%	2
	AAS	—	—	—	—	—	—
Sr	PIXE	5	19	9	4	±26%	1
	INAA	<43	<23	<30	<35	—	<33
	AAS	—	—	—	—	—	
Cd	PIXE	15	3	2	6	±60%	1
	INAA	58	60	65	55	—	60
	AAS	9	3	4	7	±10%	1
Pb	PIXE	12	3	7	9	±21%	3
	INAA	—	—	—	—	—	—
	AAS	12	3	7	9	±10%	1

[a] PIXE error analysis is the sum of the standard deviation of reproducibility of each element, pipetting (2%), relative detection efficiency (3%), and standard deviation of reproducibility of the internal standard: for 1.6 MeV (3.7%), for 3.0 MeV (3.3%).

[b] INAA error analysis is the sum of the standard deviation of the activation constants (5%) and the standard deviation of reproducibility.

[c] AAS error analysis is the sum of standard deviation of the reproducibility (3%–5%), pipetting errors (2%) and deviations from the standard working curves.

[d] ICP error analysis is the standard deviation of the reproducibility.

[e] Sensitivities for PIXE and INAA are the determination limits (±10% at a 95% confidence limits).

[f] Sensitivities for AAS determined by the slope of the standard working curves.

[g] Sensitivities for ICP determined as twice the standard deviation of the signal of a blank run.

[h] P, S, and Pb not applicable with INAA.

[i] Na, Mg, P, Cl, K, Ca, Ti, V, Cr, As, Br, and Sr not analyzed with AAS. S and P are not applicable with AAS.

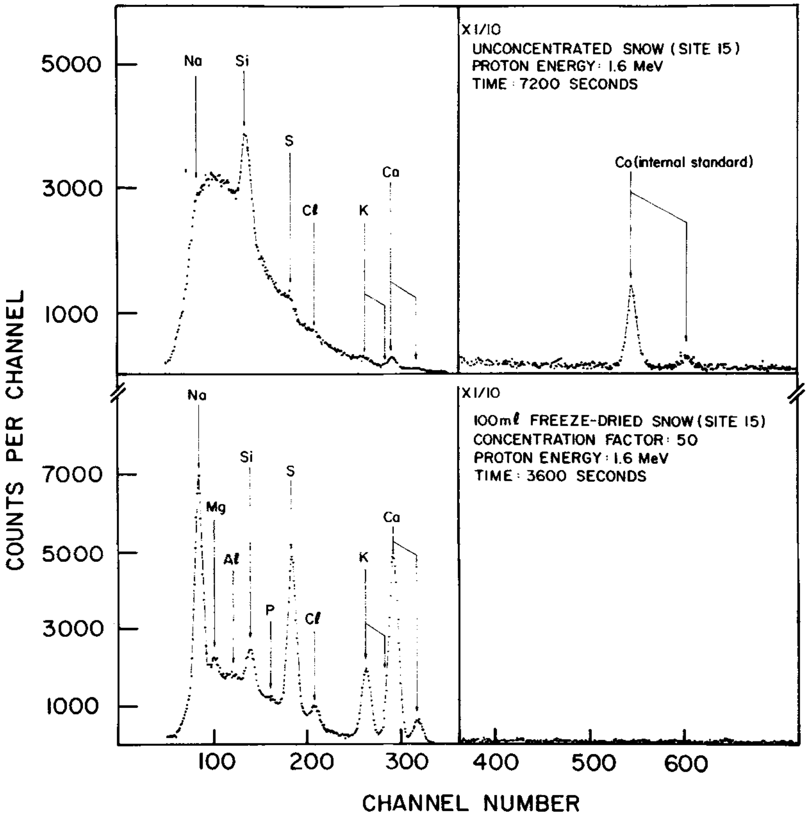

FIGURE 1 Spectrum of snow sample bombarded with 1.6 MeV protons. Top-half unconcentrated sample and bottom-half concentrated sample.

Na. INAA appears to be the most suitable technique to measure traces of Na. PIXE does not give good results since the Na X-ray peak is located on the down-slope of a high background region caused by general Bremsstrahlung radiation which hampers a reliable analysis. Flame atomic absorption spectroscopy can also be used as an alternative.

Mg and Al. The PIXE analysis of these two elements is also difficult since their X-rays also sit on a high background region (Bremsstrahlung). INAA does not yield good results for Mg because the intense 847 keV γ-ray of any Mn, present in the samples,

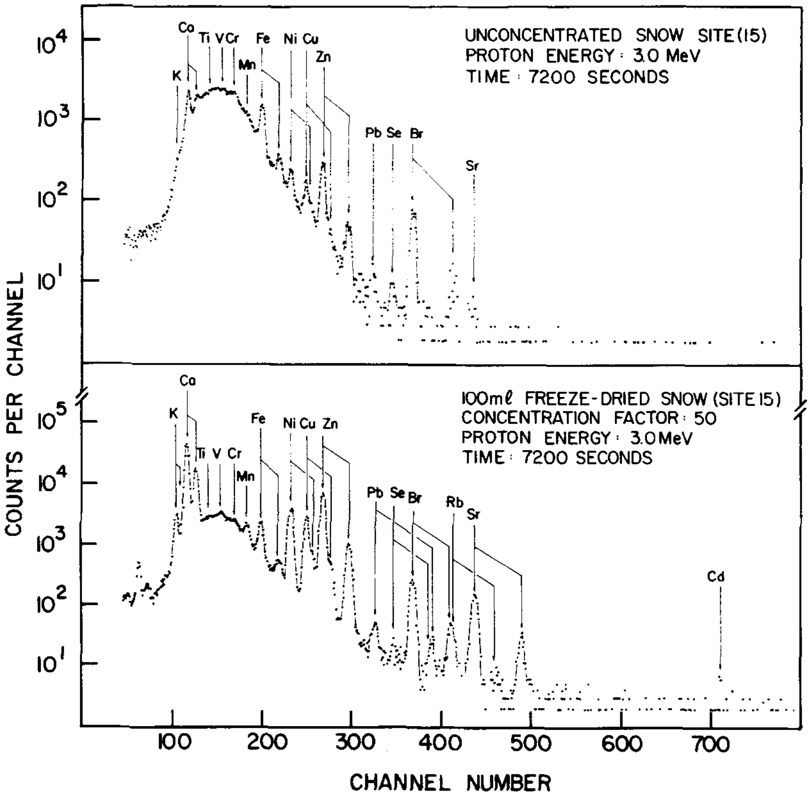

FIGURE 2 Spectrum of snow sample bombarded with 3.0 MeV protons. Top-half unconcentrated sample and bottom-half concentrated sample.

interferes strongly with the 844 keV γ-ray of Mg. Thus the weaker 1014 keV γ-ray of Mg must be used with a resultant decrease in detection efficiency. Furthermore there is the interfering ^{27}Al(n, p)^{27}Mg reaction produced by fast neutrons further impairs even more any reliable measurement of Mg. Flame AAS is reliable for Mg but lanthanum must usually be added to the sample to minimize interferences from other elements. This in turn may add to contamination of the samples.

INAA is certainly the better technique to measure aluminium because AAS is not as precise (see Table IV) even though the

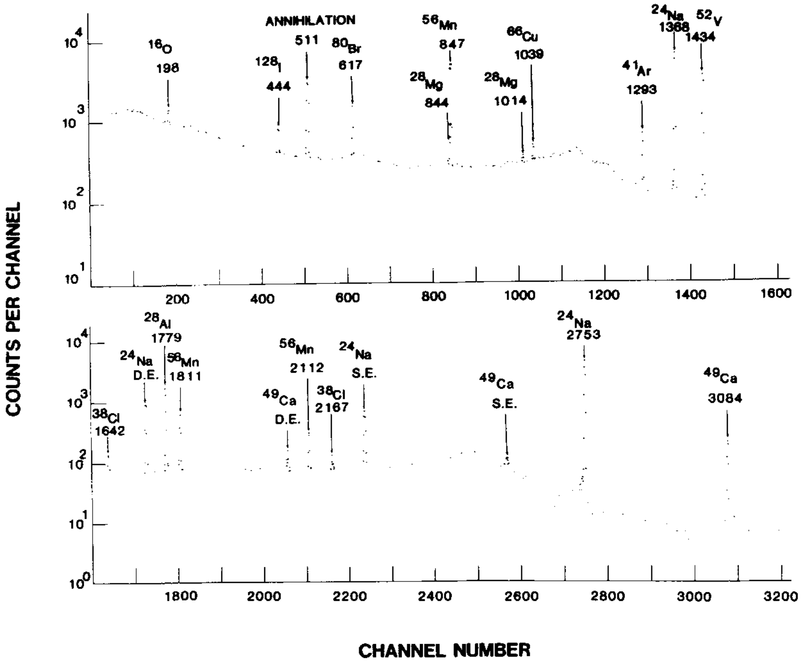

FIGURE 3 Spectrum of preconcentrated snow using INAA: flux $= 1.0 \times 10^{12}$ n.cm^{-2} sec^{-1}; $t_i = 10$ min; $t_d = 90$ sec; $t_c = 10$ min.

attainable detection limit is lower than for INAA. It has been well documented in a recent review article that Al may suffer from a wide variety of interferences in the presence of many different S elements and various halides resulting in the suppression or enhancement of the atomic absorption signal.[22] One can observe that Mg is measured very precisely by the ICP and its agreement with PIXE is very good. Thus, the use of PIXE for Mg is very well justified as shown in previous river-water studies.[21,23]

P and S. PIXE is a very good technique for the detection and measurement of traces of these two elements. The importance of the use of PIXE in the study of sulfur in atmospheric deposition has been already stressed.[1] The agreement between ICP and PIXE results for P is very good and only for one site is it poor. Neither AAS nor INAA are not applicable to P and S at levels found in these samples.

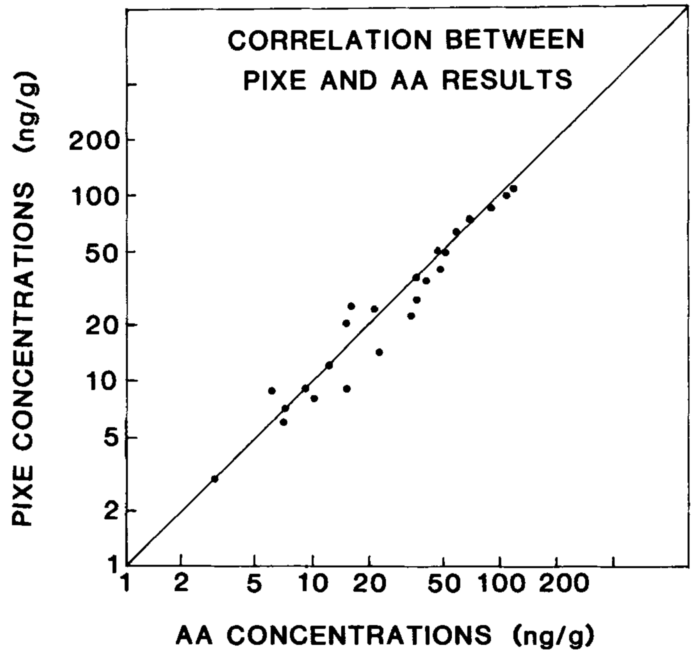

FIGURE 4 Overall correlation between PIXE and AAS for four samples for Mn, Fe, Ni, Cu, Zn, Cd and Pb. Correlation coefficient $r=0.96$ at $P \leq 0.005$.

Cl and K. The agreement between PIXE and INAA for Cl is fair. However, some chlorine may have been lost during the freeze-drying process and may also be expected to evaporate to some extent under a proton beam bombardment. Thus, INAA which yields very good results, (without the need for any preconcentrations) is more preferable than PIXE. The values shown for K in Table IV are already self-explanatory. Potassium may also be analysed by flame AAS.

Ca. There is a large disagreement for this element between PIXE and INAA. However, PIXE is considered more reliable since the Ca cross-section for INAA is low as well as the detection efficiency of the 3084 keV γ-ray even for large Ge(Li) detectors. The two effects together cause the Ca sensitivity or INAA to be much poorer than that achieved with PIXE. Flame AAS may also be used for Ca. An additional three snow samples were analysed for Ca using both

PIXE and flame AAS. The results agreed within ±15% of each other. However, lanthanum was added to the sample.

Ti and V. For a precise Ti measurement INAA is not feasible whereas in the case of V it appears to be a good method. Even if V is present in very low concentrations in snow samples and the V X-ray peak appears to lie on a high background region of the X-ray spectrum, the results obtained with PIXE are good enough to warrant the use of this analytical method. Both Ti and V can also be analysed with AAS.

Cr. Chromium is not detected below 35 ng/g since Cr impurities present in the Nuclepore filters limits PIXE analysis. INAA shows poor sensitivity, therefore no conclusive results can be obtained with both methods for Cr analysis. AAS most probably would offer the best results.

Mn, Fe, Ni, Cu and Zn. PIXE and AAS results are in good agreement for these elements, as are between PIXE and INAA in the case of the Mn, Cu and Zn. However, the INAA method must be used with some caution in the detection of low concentrations of Cu and Zn because of its poorer sensitivity for these two elements. With the exception of Mn, PIXE yields better sensitivities and this may favour more routine use of PIXE in the future analysis of these metals.

As. Very little can be said on this element whose X-ray peak was not even visible in the X-ray spectra and was not detected by INAA. However, these studies have shown that PIXE has a much better sensitivity than INAA. Arsenic may be detected by AAS, requires chemical procedures since this metal should be used in a hydride form, which may add contamination.

Br and Sr. Some bromine impurity is present in the Nuclepore filters and this may limit accurate analysis of this element in the samples with PIXE. However, the results obtained through INAA are very comparable. At present INAA seems to be a better and more reliable technique in the determination of Br which is an important element in environmental studies (e.g. Pb/Br ratios). INAA offers very poor detection limits for Sr which can be measured well with PIXE. Strontium analysis was not carried out with AAS which is known to yield good precision and accuracy.

Cd. The agreement between PIXE and AAS is very good whereas INAA yields poor sensitivities.

Pb. This metal shows the best correlation between PIXE and AAS of all the elements measured. It is well known that INAA is not applicable to Pb.

4. CONCLUSION

The results presented in this paper indicate that many of the environmentally interesting elements present in snow samples can be detected and analyzed more advantageously in a multi-elemental study made by PIXE than with INAA or AAS. Only in the determination of Na and Al was PIXE not found to be adequate, while the results yielded by PIXE on Ti would probably have to be compared with other methods. The analysis and detection limits of Na, Al, Mg, Ti and V could be further improved by the use of ultra-thin targets which would decrease the low-energy background on the X-ray spectra.

For Br and Cr, the PIXE method can still be very advantageous. However, to fully exploit its advantages, filters of other types than Nuclepore should be used as target backing to reduce interference effects from contaminations. Finally we found that the elements Mg, P, S, K, Ti, Cr, Fe, Ni, Sr, Cd and Pb (and to some degree Ca, Cu and Zn) cannot be efficiently detected in the ng/g range in filtered snow samples by the INAA method. Although INAA techniques seem to be less suitable for multi-elemental analysis of the aqueous precipitation samples, the technique does offer very reliable results for Na, Al, Cl, V, Mn and Br. All these elements may be analysed effectively without any prior preconcentration methods using short irradiations. Thus a judicious use of PIXE and INAA may yield excellent results in analysing a wide range of trace elements present in soluble precipitation. This in turn does not negate the usefulness of AAS, where preconcentration is necessary though multi-elemental analysis of samples cannot be done, with AAS. To this end the present authors are in the process of exploring the further possibilities of ICP spectrometry for multi-elemental analysis of rain and snow samples.

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