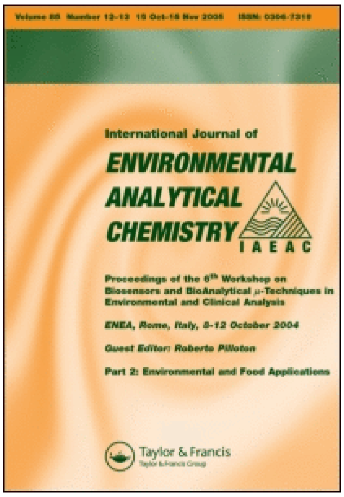

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The Determination of Sulphur and Heavy Metals in Snow by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)

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The concentrations of sulphur, phosphorous, magnesium, calcium and twelve heavy metals were determined in snow samples gathered from Montreal using ICP-AES techniques without prior preconcentration methods. The advantages of this method are discussed in relationship to wet atmospheric deposition studies. The accuracy and precision of the ICP-AES technique was demonstrated using a certified water standard from the National Bureau of Standards.

1. INTRODUCTION

The detection of trace elements in wet atmospheric deposition (rain and snow) has received a great deal of attention in the last several years[1–2] including a recent and very comprehensive review article[3]

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in this field. Because of the important significance the atmosphere has in the redistribution and biogeochemical cycling of elements (in particular sulphur and heavy metals) various techniques are presently being employed to detect the usually very low elemental concentrations. Methods such as graphite-furnace atomic absorption spectrophotometry,[4-6] instrumental neutron activation analysis,[7-9] and proton-induced X-ray emission[9,10-13] have all been successfully used in the recent past to detect potentially toxic and non-toxic elements in either rain or snow.

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) has become a very useful multi-elemental analytical tool rivalling traditional and new nuclear methods. ICP-AES has been used to determine a wide range of elements in various matrices including sea-water,[14] coal,[15] natural waters,[16,17] and marine sediments.[18] Two other review articles[19,20] have outlined the other salient features and wide range of applicabilities of ICP-AES.

Surprisingly, other than several preliminary studies to determine S, Mg and P in snow,[9,21] and Na, Mg, Al, Ca, Fe, Cu and Zn in rain,[7] it appears that the employment of ICP-AES to determine other elements in either rain or snow has received little attention.

The aim of this study is to investigate the use of ICP-AES to determine which elements may be routinely analyzed in wet atmospheric depositions without prior preconcentration techniques.

2. EXPERIMENTAL PROCEDURES

Snow samples were collected from the island of Montreal. The complete sampling procedure and experimental work-up has already been fully described in previous studies.[4,9-11] All samples were filtered through a triply pre-rinsed 0.40 μm Nuclepore filter as to distinguish between soluble and insoluble fractions and subsequently acidified to 1% using high purity nitric acid (Ultrex HNO_3).

For the analytical purpose of this paper only three snow samples were analyzed. The accuracy of the ICP-AES method was determined using a certified water standard reference material from the National Bureau of Standards (NBS 1643a: trace elements in water).

ICP-AES experiments were conducted at the Institute of Environmental Studies at the University of Toronto. The ICP-AES system used was an ARL 34000 vacuum spectrometer operating under the following conditions: (a) plasma gas rate 12 L/min (b) auxiliary plasma gas rate 0.8 L/min (c) carrier gas rate 1 L/min and (d) incident power 1.2 Kw.

The analytical wavelengths in nm for elemental analyses were: Al (308.2), As (189.0), Ca (317.9), Cu (324.8), Cd (226.5), Co (228.6), Cr (267.7), Fe (259.9), Mg (279.1), Mn (257.6), Mo (202.0), Ni (231.6), P (178.3), Pb (220.3), S (180.7), V (292.4), and Zn (213.9).

All these wavelengths, although some not the most sensitive for ICP-AES analysis, were chosen since they exhibited the least amount of spectral interference. Special consideration was given to the possible spectral overlap of phosphorous and sulphur. Considering the low phosphorous values (two concentration less than the 50 ng/g detection limit) and the high sulphur concentrations (800–2000 ng/g), the interference should be negligible. Indeed, a spectral scanning of the ICP-AES system using synthetic solutions proved our assumption.

Blanks of acidified deionized and distilled water were also analyzed and proved to be negligible.

3. RESULTS AND DISCUSSION

Results for the concentrations of sixteen elements in the snow soluble fraction as determined by ICP-AES are shown in Table I. The accuracy of the ICP-AES technique as demonstrated by analyzing the certified water standard reference material NBS 1643a is revealed in the results of Table II. Errors on the concentration values were determined as the standard deviation for three separate determinations for the snow samples and five separate determinations for the NBS water standard. Typical detection limits, as indicated in the last column of Table I, have been determined by the automatic program of the ARL 34000, which is twice the standard deviation of the signal of the background of the analytical blank. If other more complex matrices were being investigated these detection limits would have to be increased by a factor of at least three or four fold. Precipitation (rain or snow) and water samples in general are not nearly as complex as geological, coal or aerosol samples, and hence these detection limits are indeed a very good indication of what one

TABLE I

Concentrations and detection limits of elements in three Montreal snow sites as determined by ICP-AES[a].

Element	Site 1 (ng/g)	Site 2 (ng/g)	Site 3 (ng/g)	Detection Limit (ng/g)
Al	92±6	506±23	458±8	25
As	<70	<70	<70	70
Ca[b]	51.6±1.3	5.9±0.1	2.2±0.1	1
Cd	<3	6±2	7±2	3
Cr	<4	9±1	10±2	4
Co	4±1	8±2	7±1	4
Cu	26±1	62±2	37±1	4
Fe	10±1	65±1	72±1	2
Mg	<20	372±13	335±9	20
Mn	<5	12±1	22±1	5
Mo	<7	8±2	12±2	7
Ni	11±2	70±4	39±3	10
P	<53	<53	70±11	53
Pb	<50	<50	62±17	50
S	1800±160	893±30	2000±30	4
V	4±2	5±2	2±2	2
Zn	5±3	161±3	109±3	4

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

[b]Calcium is shown in parts per million

might expect in such aqueous samples. However, in actual precipitation studies[3] the concentrations of certain elements notably, cadmium, chromium, cobalt, phosphorous and lead many be below achievable detection limits.

In such cases the use of graphite-furnace atomic absorption spectrometry, especially for lead, cadmium and chromium, can yield superior detection limits; typically less than 1 ng/g, for water samples.

The agreement of the NBS values (Table II) with those of ICP-AES are in very good agreement. This is very gratifying since it adds a lot of confidence to the analytical procedures used to obtain our results in snow samples.

TABLE II

Concentrations of Elements in NBS-SRM 1643a as determined by ICP-AES.

Element	Measured Value[a]	NBS Value
As	<70	76±7
Cd	12.2±1.6	10±1
Cr	14.2±3.4	17±2
Co	21.5±2.0	19±2
Cu	19.3±3.1	18±2
Fe	84.5±1.8	88±4
Pb	<50	27±1
Mn	32.0±0.7	31±2
Mo	95.6±3.1	95±6
Ni	50.4±6.3	55±3
V	51.1±4.8	53±3
Zn	69.7±2.4	72±4
Ca	27.6±0.7 (μg/g)	(27)
Mg	9.0±0.2 (μg/g)	(8)

[a] Errors based upon the average of five determinations and their respective analytical standard deviations. All NBS values certified except those in parenthesis.

Of prime analytical importance is the readily detectable concentrations of sulphur in snow. Sulphur's importance in studying acid precipitation is now well-known. As well, manganese whose presence in the atmosphere has been postulated to act as a catalyst on sulphur to help accelerate the oxidation of SO_2, [22-26] can also be detected at concentrations as low as 5 ng/g. The inter-elemental correlations between Mn and S have also been studied in detail.[21-23] In fact, it would appear that ICP-AES can be routinely used to detect the presence of these two important elements in precipitation. The detection of aluminum and iron in wet atmospheric deposition is also of interest since these elements can be used as a "normalizing elements" in enrichment factor calculations[2,4].

Other elements which are also of environmental importance and can be routinely analyzed by ICP-AES include, copper, nickel and zinc. If, however concentrations for these elements are at or below the detection limits of 4, 10 and 4 ng/g, respectively, graphite furnace atomic absorption spectroscopy or a preconcentration technique should be employed instead. It is clear from Table I that the use of a reliable preconcentration technique would be very useful in assuring that more elements can be determined in precipitation samples not only in urban, but as well as, rural and remote areas.

4. CONCLUSIONS

We have demonstrated that inductively coupled plasma-atomic emission spectroscopy can serve to be a very reliable tool in the determination of sulphur and other heavy metals in wet atmospheric deposition studies. The analytical procedures used to obtain our results have been well justified by using a NBS certified water reference material. We hope to continue our research investigating other precipitation and water samples by employing inductively coupled plasma-mass spectrometry (ICP-MS) in the very near future, along with simple evaporation or freeze-drying preconcentration methods.

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