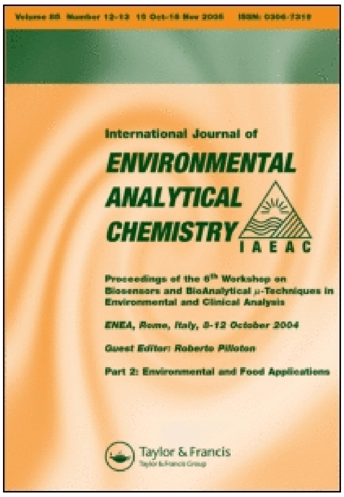

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Determination of Major Metals in Arctic Snow by Inductively Coupled Plasma Mass Spectrometry with Cold Plasma and Microconcentric Nebulization Techniques

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DETERMINATION OF MAJOR METALS IN ARCTIC SNOW BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY WITH COLD PLASMA AND MICROCONCENTRIC NEBULIZATION TECHNIQUES

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A method was developed for the determination of K, Ca, Mg, Na, Al and Fe in Arctic snow samples by inductively coupled plasma mass spectrometry. Shield torch system under cold plasma conditions was used to overcome the spectral interferences from the plasma gas on ^{39}K (^{38}ArH), ^{40}Ca (^{40}Ar) and ^{56}Fe (^{40}Ar^{16}O). Detection limits (3σ) were 1, 1, 2, 7, 6 and 3 ng/l for Na, Mg, Al, K, Ca and Fe, respectively. Reproducibility of measurements was better than 2% relative standard deviation (n=10) for all the elements of interest at 1.0 μg/l level. The sample consumption was ca. 60 μl per assay due to the use of a microconcentric nebulizer. Several Arctic snow samples were analysed and the reliability of the proposed method was confirmed by electrothermal atomic absorption spectrometry.

Keywords: Inductively coupled plasma mass spectrometry; cold plasma; microconcentric nebulizer; major metals; Arctic snow

INTRODUCTION

During the past two decades, great efforts have been devoted to the investigation of various constituents in the successively deposited snow and ice layers in Greenland and polar areas. These layers retain a unique, undisturbed and datea-

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ble record of the composition of the Earth's atmosphere in the past as much as 500 millennia. Among a wide variety of chemical species trapped in snow layers, the major ionic species, such as Ca^{2+}, K^+, Mg^{2+}, Na^+, Cl^- and NO_3^- et al., appear to be the most useful in tracing major natural and anthropogenic emission sources which ultimately govern the final composition of our atmosphere[1–3]. Measurement of their concentrations in polar ice cores will enable us to understand their global atmospheric circulation, to perceive the preindustrial environmental system of our planet, and to predict its future evolution in response to human activities.

The concentrations of these major ions in the polar snow and ice samples range widely, from sub µg/l to several hundreds µg/l [4–9]. Therefore, analytical techniques with both low detection limit and broad dynamic range are required for the accurate analysis of these samples. In addition, stringent contamination control is particularly important due to the ubiquity of these species. Up to now, ion chromatography has been solely used for the determination of major ions in polar ice samples due to its multispecies analysis capability. Early work by Legrand et al.[4] determined major ions (Na^+, NH_4^+, K^+, Cl^-, NO_3^-, SO_4^{2-}) at ng/g concentrations in Antarctic snow and ice cores. Mayewski et al.[5] analyzed trace level anions in a south Greenland ice core. Later on, Buck et al.[6] modified the method to separate mono- and divalent cations in a single isocratic run via column switching. Recently, Legrand et al.[7] successfully performed ion chromatographic measurement of major ions in the field. With this field measurement technique, contamination and breakage of fragile pieces of ice could be avoided during the transportation of ice core to conventional laboratory. However, with the ion chromatographic systems, unstable background conductivity was observed, which could deteriorate the accuracy of the results, particularly for the species (i.e., K^+, Ca^{2+}, Mg^{2+}) whose concentrations are only several times the detection limits[4,6,7]. A relatively long analysis time of 5–15 min per run could further aggravate the stability of the system. Since the concentrations of major ions may vary in 3–4 orders in some ice cores, dilution was necessary for the samples with high concentrations while for the samples with lower concentrations, a fairly large amount of sample (5 ml) was injected in order to achieve necessary sensitivity[7].

Inductively coupled plasma mass spectrometry (ICP-MS) has been widely used for the trace elemental analysis in a variety of matrices because of its excellent detection limits, broad calibration range and the capability for rapid multi-elemental determination. These features make ICP-MS an excellent technique for the determination of major ions in polar snow samples. Although one limitation of quadrupole-based, argon-plasma ICP-MS is the isobaric and polyatomic interferences that affect the low level determination of ^{39}K (^{38}ArH), ^{40}Ca (^{40}Ar) and ^{56}Fe (^{40}ArO), they can be significantly reduced under cold plasma conditions (namely lower RF power and higher central gas flow)[10–13]. Sakata et al.[11] proposed a so-called 'Shield Torch' technique under cold plasma conditions to eliminate the isobaric interferences caused by the plasma gas. The insertion of a grounded metal shield between the load coil and the torch led to the significant suppression of isobaric argide ions. This technique has been used in the semiconductor industry for the analysis of K, Ca and Fe together with other impurities[14]. Detection limits of several ng/l were achieved for K, Ca, Fe and other elements.

The most common sample introduction method in ICP-MS is pneumatic nebulization of the sample solution. Concentric, cross flow and Babington nebulizers are often employed to produce fine aerosols. However, relatively large sample amounts (usually 3 ml per run) are needed due to their poor nebulization efficiency, 1.5–3% at most. Recently a microconcentric nebulizer (MCN, CETAC Technologies, Omaha, NE, USA) has become commercially available. The MCN can be operated at µl/min sample delivery rate with an improved nebulization efficiency as high as 90%[15–17]. This feature is of particular interest in polar snow analysis where the amount of sample is very limited owing to the logistical problems of sample collection and transportation from the remote and hostile polar region.

In the present work, a method was developed for the determination of K, Ca, Mg, Na, Al and Fe in Arctic snow samples by ICP-MS. Al and Fe were included as they can be used to deduce the contributions of other major ions from rock and soil dust [18,19]. Shield torch system under cold plasma conditions was employed to eliminate the spectral interferences on K, Ca and Fe. A MCN was used to reduce the sample consumption down to sub millilitre per measurement.

EXPERIMENTAL

Instrumentation

A Hewlett Packard 4500 ICP mass spectrometer (Hewlett Packard – Yokogawa Analytical Systems, Tokyo, Japan) was used in this study, which was housed in a class-10,000 clean room. The instrument was operated in cold plasma conditions and a shield torch system was used to reduce isobaric and polyatomic interferences. Samples were introduced into the instrument using a MCN (MCN-100, CETAC Technologies). A Scott-type spray chamber was used and cooled at 1 °C, The surfaces of the MCN that contact samples are made of PEEK, polyimide and sapphire, and is free of major metals after adequate cleaning. The MCN was run in free aspiration mode to avoid potential contamination from using Tygon peristaltic pump tubing. To minimize any viscosity or aspiration effects between samples, the sampling volume and depth were kept constant and an internal standard of 10 μg/l Co was used. In free aspiration mode the nebulizer consumed ca. 30 μl/min. Cones, torch and spray chamber were cleaned prior to use. The optimized experimental conditions and instrumental settings are given in Table I.

TABLE I Typical operating conditions

ICP mass spectrometer	
RF power	750 W
Sampling depth	14 mm
Plasma gas	16.0 l/min
Auxiliary gas	1.0 l/min
Carrier gas	1.0 l/min
Blend gas	0.65 l/min
Nebulizer	MCN-100
Sampler-skimmer	Nickel
Spray chamber	Quartz
Spray chamber temperature	1°C
Data acquisition	
Points/peak	3
Integration time/mass	1 sec
Repetitions	3

The electrothermal atomic absorption (ETAA) spectrometric analyses were made using a Hitachi Model Z-9000 Zeeman multielement ETAA spectrometer. Na and K were measured simultaneously while Mg and Ca were measured individually by introducing 20 μl aliquots into the pyrolytic graphite coated tube. Al and Fe were analysed simultaneously by dosing triple 40 μl aliquotes into the furnace. An atomization temperature of 2100 °C was used for Na, K and Mg, 2700°C for Ca, and 3000°C for Al and Fe. No chemical modifiers were necessary. Peak height absorbance was used for quantification.

Sample collection

Snow samples were collected in April, 1994, at the dome of the Agassiz Ice Cap on Ellesmere Island, Canadian Arctic. The sampling position is at 80.7°N and 73.1°W. Sampling procedures were described in detail elsewhere[20]. Sampling faces were scraped by a pre-cleaned plastic scoop before samples were transferred into pre-cleaned sample containers. Field blanks were collected at the same time as the samples, the designated bottles being opened and capped at the same time as the samples. Clean-room clothes were worn on regular Arctic clothing during sampling, as were plastic gloves, which were changed whenever sampling from a new layer was started.

500 ml wide-mouth screw capped high-density polyethylene bottles (Nalgene, Rochester, NY, USA) were used for the sampling operation. They had been cleaned through a rigorous and lengthy acid cleaning procedure which has been described elsewhere[22]. Following a final rinse with high purity de-ionized water, the bottles were wrapped in two layers of polyethylene bags and shipped to the sampling site empty. The samples were sent to the laboratory in a frozen state by rapid shipping in ice-packed containers and were stored at 4°C in a refrigerator before analysis.

Reagents and standards

The high purity water (>18 MΩ) was obtained from a commercial mixed ionexchange system (Barnstead Nanopure, Boston, MA, USA). Ultra-pure nitric acid (Tamapure-AA-100, Tama Chemicals, Kawasaki, Japan) was used for sample acidification and standard preparation. Multielement calibration standards were prepared freshly in 0.01 mol/l HNO_3 by serial dilution of 1000 mg/l stock solutions of Na, K, Ca, Mg, Al and Fe (Wako Pure Chemicals, Osaka, Japan). 10 µg/l Cobalt (Wako Pure Chemicals) was added in the calibration standards and snow samples as the internal standard. Reagent grade nitric acid and hydrochloric acid (Kanto Chemicals Co., Tokyo, Japan) were used for vessel washing.

Procedure

The containers used for handling or storage of standards and samples were either high-density polyethylene or Teflon FEP (Nalgene). They were cleaned by soaking successively for over 1 week in 1–2 mol/l reagent-grade HCl, 1–2 mol/l reagent-grade HNO_3 and 1M ultra-pure HNO_3, with rinses of de-ionized water after each step. After cleaning they were stored for more than 1 week filled with 0. 1 mol/l ultra-pure HNO_3 and rinsed with de-ionized water immediately before use.

All standard and sample preparation operations were conducted in class 100 clean draft. Plastic gloves and PTFE sleevelets were worn during operation. The snow samples were acidified to pH 2 by addition of ultra-pure HNO_3. An aliquot of each sample was then transferred into a 30 ml pre-cleaned high-density polyethylene screw capped bottle for subsequent analysis. The sub-samples were weighed. In order to assess the field blank, 200 ml of 0.01 mol/l HNO_3 were added to the empty bottles and carried through all operations. 10 μg/l Co was added into samples as internal standard.

RESULTS AND DISCUSSION

ICP-MS optimization

With quadrupole-based argon plasma ICP-MS instrument, the analysis of trace level K, Ca and Fe is hampered due to the isobaric interferences derived from argon and oxygen present in the plasma under normal analytical conditions. In order to eliminate these interferences, a shield torch system under cold plasma conditions was used in this work. Plasma and mass spectrometer conditions were optimized using a tuning solution containing 10 μg/l Co. The RF power and spray chamber temperatures were fixed to 750 W and 1 °C respectively. Other conditions, particularly the carrier gas and blend gas flow-rates, and the sampling positions, were optimized daily to achieve an argon dimmer (m/z 80) background less than 300 counts per second (cps) and the Co signal more than 100,000 cps. High purity water was aspirated to determine the ArO^+ background level that should be less than 300 cps. The typical operating parameters are shown in Table I.

In order to reduce the sample consumption, a MCN was used in the present work. The nebulizer was operated in free aspiration mode so as to avoid the potential contamination from Tygon pump tubing. However it was suspected that the amount of sample introduced might vary with the level of a sample liquid. Therefore, the effects of the sample level on the sensitivity were studied. No significant differences in sensitivity with varying sample levels were observed; less than 10% increase in sensitivity for all the elements when the distance from the nebulizer to the sample liquid level decreased from 40 cm to 10 cm. Nevertheless the distance was kept at 15 cm to eliminate any of this minor variation. Although the snow sample matrix is fairly simple, the individual sample's physical properties, such as viscosity and total dissolved solid, are different, which may cause slight difference in nebulization efficiency. Thus, Co was used as the internal standard (10 μg/l in sample) to correct for this discrepancy.

Sample acidification

In this study, samples were acidified with ultra-pure HNO_3 to dissolve and release major metals associated with dust particles in the sample meltwaters and adsorbed on the walls of the container. There is a trade off between contamination and acid concentration, as pointed out by several other authors[22,23] in the analysis of trace elements in snow samples. Moreover, it was noticed in this study that the sample acidity could significantly affect the sensitivity of ICP-MS under cold plasma conditions. As shown in Figure 1, sensitivity decreases as acidity increases. This is due to the space charge effects which are the major cause of matrix interferences[24]. These effects become more significant as the total ion beam currents increase. Under cold plasma conditions, the dominant ions are H_3O^+, NO^+ and O_2^+[12]. As more HNO_3 is introduced to the plasma, the population of NO^+, derived from HNO_3, increases, and total ion beam currents increase subsequently. This caused the decreased sensitivities. Table II presents the blank values at different acidities. Blank values for higher acidity are greater than those for lower acidity since more impurity was introduced as more HNO_3 was added. Although higher sensitivity and lower blank value could be obtained with lower acidity, it was observed that the results for Al and Fe were not reliable at acidity lower than 0.001 mol/l HNO_3. This was probably caused by their hydrolysis and adsorption on the walls of the container. Therefore 0.01 mol/l HNO_3 was chosen as the sample acidity.

TABLE II Blank values at different acidities

Element	*Blank values (ng/l)* *			
	0.5 mol/l HNO_3	*0.1 mol/l HNO_3*	*0.01 mol/l HNO_3*	*0.001 mol/l HNO_3*
Na	151	25	17	11
Mg	42	18	15	7
K	270	32	15	6
Ca	195	75	12	14
Al	233	95	81	NR†
Fe	50	42	22	NR†

*. Concentrations were obtained by method of standard additions.

†. Results were not reliable.

After the acidification of snow sample, it was reported that heavy metals could be dissolved by 0.1% v/v HNO_3 within 48 h[22]. However it was also reported that Fe concentrations of acidified Antarctic snow samples increased for up to 3 months following acidification by 0.1% v/v HCl[23]. In this study, the concentrations of the elements of interest were monitored over a period of one month after acidification by 0.01 mol/l HNO_3. It was observed that steady concentrations of these elements could be reached within 30 min following acidification.

This indicated that the major elements adsorbed on the walls of the container could be desorbed fairly quickly. In addition, any particles transferred into the ICP would be vaporised and ionised, given that the particles are typically < 10 μm in diameter[23,25].

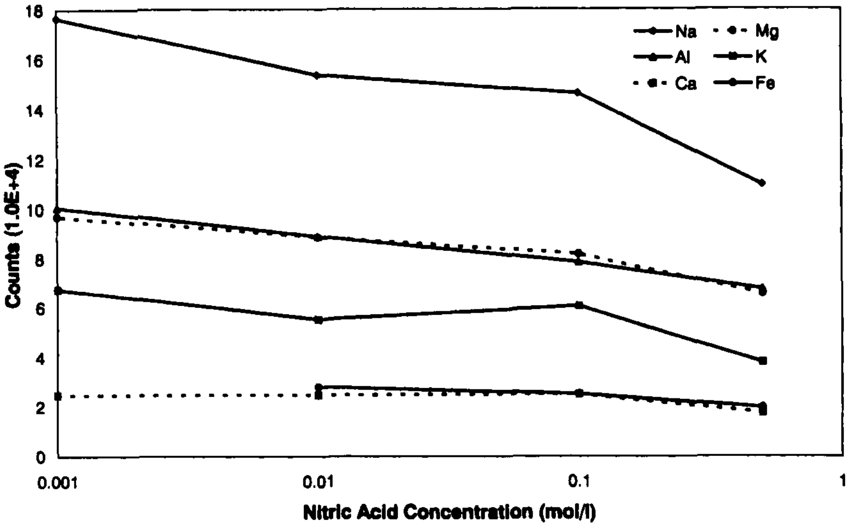

FIGURE 1 The effects of sample acidity on the sensitivity. The concentrations were 1.0 μg/l for all the elements. Other conditions used are shown in Table I

Figures of merit

The characteristic data, i.e., sensitivity, precision, background equivalent concentration and detection limit, are summarized in Table III. Low detection limits were achieved for ^{39}K, ^{40}Ca and ^{56}Fe because the backgrounds for these isotopes, mainly caused by argon and oxygen present in the plasma, were substantially reduced due to the cold plasma technique used. With the use of the MCN, the sample consumption per three-replicate measurement was about 60 μl and memory effects were significantly reduced. After aspiration of 10 μg/l analytes, the signals could reach the baseline (<5% counts of 10 μg/l analytes) in 20 sec, while with Tygon pump tubing, 45 sec were usually required. Simultaneous measurement of six elements could be made in 60 sec with precision better than 2% relative standard deviation. Compared to other techniques, such as ion chromatography, ICP-MS offers a rapid multi-element measurement technique for the determination of major metals in Arctic snow samples with minimal sample consumption.

TABLE III Characteristic data of the ICP-MS system

Isotope	*BEC(ng/l)**	*Sensitivity (cps per µg/l)*	*RSD (%)†*	*LOD (ng/l)‡*
^{23}Na	17	154000	1.3	1
^{24}Mg	15	89000	1.0	1
^{39}K	16	56000	1.5	7
^{40}Ca	12	25400	1.8	6
^{27}Al	81	89000	1.1	2
^{56}Fe	22	28000	1.3	3

*. BEC, background equivalent concentration

†. RSD, relative standard deviation, calculated from 10 replicates measurements of 1.0 µg/l standard solution.

‡. LOD, limit of detection (3σ).

Results for Arctic snow samples

Table IV shows the results for the determination of Na, Mg, K, Ca, Fe and Al in four snow samples collected from varying depths. Comparative results obtained by ETAAS are also included. The results of analysis by ICP-MS are in good agreement with those by ETAAS. Determination of major metals along a deep ice core from the same site is under way in this laboratory. Their concentrations vary with seasons and changing sources. A detailed geochemical interpretation of variations in their concentrations will be discussed in a future publication.

TABLE IV Results for some representative snow samples*

Sample	*Depth (cm)*	*Concentration (ng/g)*					
		Al	*Ca*	*Fe*	*K*	*Mg*	*Na*
1	16–24	4.07±0.04	12.1±0.06	4.83±0.03	2.09±0.01	4.01±0.02	4.96±0.09
		(4.00±0.09)	(12.5±0.36)	(4.70±0.10)	(2.16±0.11)	(4.00±0.18)	(5.12±0.03)
2	24–30	1.65±0.06	4.42±0.03	3.92±0.02	0.83±0.04	1.40±0.01	1.27±0.01
		(1.78±0.12)	(4.60±0.02)	(4.02±0.09)	(0.84±0.06)	(1.32±0.09)	(1.32±0.02)
3	41–49.5	1.99±0.04	5.72±0.04	3.23±0.10	1.42±0.03	2.05±0.02	2 20±0.02
		(1.98±0.06)	(5.54±0.21)	(3.18±0.03)	(1.47±0.05)	(1.95±0.10)	(2.09±0.02)
4	92.5- 101.5	3.84±0.04	10.3±0.01	6.49±0.03	2.17±0.04	4.08±0.02	8.38±0.03
		(4.05±0.15)	(11.4±0.44)	(6.49±0.09)	(2.15±0.12)	(3.92±0.12)	(8.25±0.05)

* Mean values ± standard deviation based on three replicate measurements. Values in parentheses were obtained by ETAAS analyses.

CONCLUSIONS

It has been shown that ICP-MS is a rapid and reliable technique for the analysis of major metals in Arctic snow samples. Potential isobaric interferences on Ca, K and Fe were virtually eliminated due to the cold plasma conditions used. Low detection limits at several ng/l level were therefore achieved. With microconcentric nebulizer, less than 100 µl of snow sample is required for each assay. This provides a unique tool for the high-resolution measurement of major ions along ice cores.

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