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A METHOD OF CONCENTRATING THE MAJOR IMPURITIES CONTAINED IN ICE BY ION EXCHANGE

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Abstract. This note describes a method for concentrating Na, K, Ca, and Mg impurities in samples of snow and ice for analysis by atomic absorption in flame photometry. The cations are fixed on a Dowex 50 ion-exchange resin then selectively released and separately analysed by atomic absorption. This method allows the simultaneous treatment of a large number of specimens with concentration factors which can reach 60 to 75 and with very low risk of contamination or loss of the specimens.

Résumé. *Methode de concentration des impuretés majeures de la neige et la de glace par échange d'ions.* Une méthode de concentration des échantillons de neige et de glace, en vue du dosage de Na, K, Ca, Mg par absorption atomique avec flamme, est décrite dans cette note. Les cations sont fixés sur une résine échangeuse d'ions Dowex 50 puis élués sélectivement et dosés séparément par absorption atomique. Cette méthode permet le traitement simultané d'un grand nombre d'échantillons avec des facteurs de concentration pouvant atteindre 60 à 75 et des risques de contamination ou de perte d'échantillon faibles.

Zusammenfassung. *Ein Ionenaustauschverfahren zur Konzentration grösserer im Eis und Schnee enthaltener Verunreinigungen.* In diesem Beitrag wird ein Verfahren zur Konzentration von Na-, K-, Ca- und Mg-Verunreinigungen in Schnee- und Eisproben im Hinblick auf die Messung durch Atomabsorption in offener Flamme beschrieben. Die Kationen werden an einem Dowex 50-Austauschnetz fixiert, dann selektiv freigelassen und getrennt mittels Atomabsorption gemessen. Diese Methode erlaubt die gleichzeitige Behandlung einer grossen Zahl von Proben mit Konzentrationsfaktoren, die 60–75 erreichen können, wobei das Risiko der Kontamination oder des Verlustes der Probe gering ist.

Introduction

Analysis using atomic absorption with flame photometry of the major impurities (Na, K, Ca, Mg) contained in snow and ice requires the prior concentration of specimens. The most recent published work (Murozumi and others, 1969; Boutron and others, 1972) have shown that the concentration of these impurities in ice and polar snow varies from several parts per billion (10^{-9} by weight) to several tens of parts per billion. Such concentrations are not directly analysable in atomic absorption by flame photometry. Few results have so far been published for temperate ice. According to Gorham (1958) and Souchez and others (1973), the concentrations there are much higher. The latter authors indicate for "glacier ice" taken from the Glacier d'Argentière (Mont-Blanc) values of from 100 to 400 parts per billion for Na, K, and Ca and several tens of parts per billion for Mg. On the other hand Boutron (unpublished) measured, for two samples of ice from the Glacier St Sorlin, concentrations significantly lower, of the order of magnitude of those found for the polar ices. The preliminary results which we have obtained on the Glacier d'Argentière and on the Glacier des Bossons (Mont-Blanc) confirm these latter values.

Two methods for concentrating impurities in ice samples have been described. One, used by Murozumi and others (1969), consists in two or three melting and refreezing operations on 90% of the ice followed by analysis of the brine in which the impurities have been concentrated. The other, recommended by Boutron (1972), consists in an evaporation of the specimens at 60°C in the presence of acid, in a dust-free atmosphere. The factor of concentration is then from 20 to 50. Both of these techniques require considerable experimental skill, and the risk of contamination in the course of operation is serious. Furthermore, the second process requires expensive equipment. For these reasons we have sought to develop a simpler method based on ion exchange.

METHOD

Principle

The sodium, potassium, calcium, and magnesium contained within the snow or ice are fixed, after melting of the specimen, on a cationic resin column then eluted selectively and analysed, separately in their own eluent, by atomic absorption in a flame. The atomic absorption equipment used, Perkin Elmer 103 with an air-acetylene flame, and potentiometric measurement, allows direct determination for water in which the concentrations are above 100 parts per billion for sodium, 50 parts per billion for potassium, 100 parts per billion for calcium, and 20 parts per billion for magnesium. Our own exchange techniques have been used previously for the concentration, starting from very dilute solutions, of cations such as Cr, Cu, Co, and Ni, for which the values of K_d are large* (Davies and others, 1972; Dingham and others, 1972). But up to now this technique has not been used for the concentration of trace cations of low K_d, such as Na and K.

Chromatographic apparatus

A method was first tested with experimental apparatus consisting of a column of "altuglass" connected to a polyethylene reservoir using a rubber bung. But it has subsequently been necessary to construct the entire apparatus in "altuglass" which is more convenient to use and permits routine work. The "altuglass" (a plastic material of the polymethylmethacrylate type) is easily machineable and has, for this reason, been preferred to polyethylene. We did not initially think that this change in material should modify the results noticeably. The chromatographic apparatus consists of: a 1.5 l cylindrical reservoir with a lid and reducing at the base into a tapering tube, and a tube 200 mm high, 7 mm in interior diameter, containing 2 ml of the resin Dowex 50X12, 100–200 mesh. This tube tapers at its lower end and has a needle valve at the top. It is fixed to the reservoir by a threaded section.

Mode of operation

The sample (500–1 500 ml) previously filtered through a Millipore filter of 0.3 μm, is poured into the reservoir and then introduced into the column through the needle valve to a height such that its speed of traversing the resin remains below 60 ml/h. The cations fixed in the resin are subsequently released: the sodium by 20 ml of 0.6*N* HCl (prepared starting with HCl R.P. from Prolabo or Suprapur HCl from Merk and water twice distilled in quartz and ion-exchanged) the potassium by 25 ml of 0.6*N* HCl, the magnesium by 25 ml of 1*N* HCl and the calcium by 20 ml of 4*N* HCl. The different cations are finally analysed in each section by atomic absorption and the true concentrations deduced from the measured concentrations using the calibration lines (Fig. 1). The chromatographic apparatus, as well as all the vessels used in the course of the experiment, are carefully washed in hydrochloric acid and rinsed many times with water twice distilled in quartz and ion-exchanged.

DISCUSSION

Fixation of the cations

We have verified the absence of cations in the filtrates obtained after the passage through the columns of synthetic solutions containing up to 0.40 mmol/l of cations. This shows that the amount of Dowex 50 used (2 ml) is sufficient.

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* Some values of K_d in 0.1*N* HCl (Strelow, 1960) are: Na, 52; K, 106; Cu^{2+}, 1 510; Co^{2+}, 1 650; Ni^{2+}, 1 600; Cr^{3+}, 1 130.

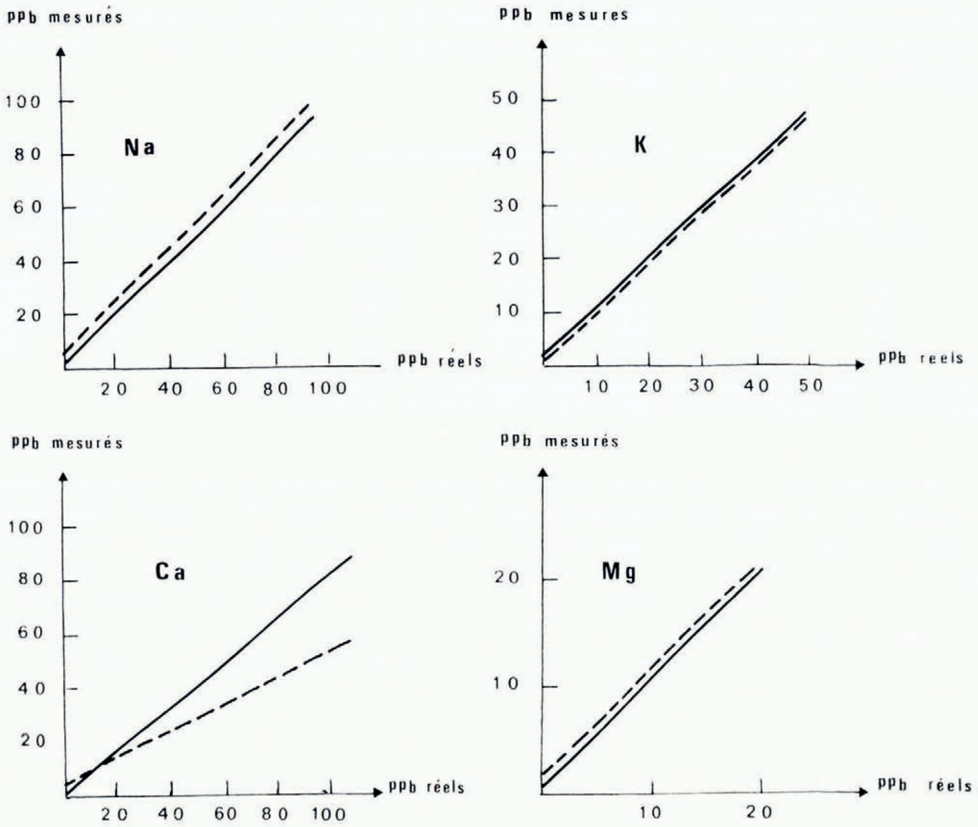

Fig. 1. Calibration curve for the analysis of cations in ice. Measured concentrations plotted against the known content of synthetic solutions. Dashed lines represent experiment 1 using the experimental apparatus of "altuglass" and polythene. Solid lines represent experiment 2 using the apparatus intended for routine analysis made wholly of "altuglass".

Separation of the cations

The separated eluants produced as described above have been retained for a series of tests. These show that the separations were complete. Only K and Mg showed any interference in the case of "strong" concentrations of magnesium (200 parts per billion). But even in this case a maximum of 3% of magnesium is removed with the potassium which is negligible. On the other hand moderately high magnesium contents have been analysed directly on the specimen.

Correlations between true and measured values

These correlations (Fig. 1) have been established using synthetic solutions prepared from standard solutions of 1 g/l (NaCl and KCl standard solutions from Merk, $CaCO_3$ standard solution from Merk, Mg standard titrisol Merk). The linear regressions have been calculated for each element in the two series of experiments with apparatus made of "altuglass" and polyethylene and with apparatus entirely from "altuglass" (Table I and Fig. 1). These results call for certain comments: the correlation coefficients are high (0.90 to 0.99), the behaviour of sodium, potassium, and magnesium are comparable whatever the apparatus used (the differences in initial ordinates are due to a change in hydrochloric acid), whereas the behaviour of calcium is very different, and finally the slopes of the regression lines are close to 1 except for calcium where the values of 0.50 and 0.84 indicate a systematic loss of this element that we have tried to explain.

TABLE I. RESULTS OF EXPERIMENTS TO SEPARATE CATIONS

	Number of measurements		*Slope of curve*		*Initial ordinate*		*Correlation coefficient*	
	Expt. 1	Expt. 2	Expt. 1	Expt. 2	Expt. 1 p.p.b.	Expt. 2 p.p.b.	Expt. 1	Expt. 2
Na	21	18	0.99	1.00	4.3	0.5	0.90	0.91
K	34	20	0.92	0.95	0.9	1.5	0.98	0.99
Ca	23	16	0.50	0.84	3.8	−0.2	0.99	0.98
Mg	33	16	1.00	0.98	1.8	0.7	0.95	0.98

Experiment 1 was performed with experimental apparatus of "altuglass" and polythene.
Experiment 2 was performed with routine apparatus wholly of "altuglass".

From the very first we have established the absence of calcium in the synthetic solutions after the passage through the resin, in the first fractions eluted ($0.6N$ and $1N$), and on the resin after passage of the last eluent (20 ml of $4N$ HCl). The calcium seems to be partly absorbed on the walls of the chromatographic apparatus, and comparison between the results of tests 1 and 2 indicates that it is absorbed more on the polyethylene or the rubber than on the "altuglass". We have tried to demonstrate this phenomenon in two ways. First we have analysed the acidic washing solutions (20 ml of $4N$ HCl and 20 ml of $6N$ HCl) from the reservoirs in polyethylene equipped with their bungs and reservoirs in "altuglass". We have been unable to discover calcium in these solutions, which indicates that it is absorbed in an irreversible way. We have, therefore, prepared a synthetic solution (2 ppm Na, 2 ppm K, 2.5 ppm Ca, 0.5 ppm Mg) which is directly analysable on the Perkin Elmer 103 spectrophotometer. This solution has been divided into four parts, which have been transferred respectively into a "Pyrex" beaker, a polyethylene flask, a beaker containing fragments of "altuglass", and a "Pyrex" beaker containing a rubber bung. (Each vessel having been previously washed in dilute HCl and rinsed with twice-distilled water.) After 24 h each fraction has been analysed. In the fourth vessel the concentrations of Na (2.3 ppm) and Ca (3 ppm) were higher than those initially, which explains, as well as the use of Prolabo HCl, the high values of the initial ordinates in test 1. On the other hand in the first three vessels the concentrations were identical to the initial ones for all four cations. Thus, if there is absorption of calcium, it is, in this case, below the errors of analysis. On the other hand for low concentrations it corresponds to a loss of 16% in the "altuglass" apparatus and occurs in a manner proportional to concentration following the Langmuir isotherm. Nevertheless the correlation coefficients of the sample lines allow us to deduce that for calcium, as for sodium, potassium, and magnesium, the true values from the measured values.

CONCLUSION

The method which we have described seems well adapted to the concentration, at the parts per billion level, of major impurities contained in snow and ice.

The standardization curves established using synthetic solutions are valid for natural specimens. We have effectively indicated that the most pure snow and ice, for which it is, therefore, necessary to concentrate impurities, have always a pH between 4.3 and 6, a range of pH in which the K_d values, although variable, are sufficiently large to ensure fixation of the cations on the resin.

It is necessary however to draw attention to the fact that the standardization lines can vary sensibly with experimental conditions. It is therefore absolutely necessary to recalibrate for each modification of conditions. Furthermore we recommend interspersing between each series of samples from snow or ice to synthetic solutions which allow verification all the time of the calibration lines. However, concentration using ion exchange has many advantages: low cost of the apparatus, possibility of simultaneous treatment of up to a dozen specimens, elimination of any interference by the determination of each cation separately, low risk of contamination of the samples during concentration, and high concentration factor (60 for K and Mg, 75 for Na and Ca when treating 1 500 ml samples).

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REFERENCES

Boutron, C. 1972. Concentration of dilute solutions at p.p.b. level by non-boiling evaporation in quartz and teflon. *Analytica Chimica Acta*, Vol. 61, No. 1, p. 140–43.

Boutron, C. Unpublished. Contribution à la chimie des neiges de l'Antarctique: détermination d'éléments traces au niveau ppb par spectrométrie d'absorption atomique. [Doctorat du 3^{e} cycle thesis, Université de Grenoble, 1971.]

Boutron, C., *and others*. 1972. Chemistry of polar snows. Estimation of rates of deposition in Antarctica, [by] C. Boutron, M. Echevin and C. Lorius. *Geochimica et Cosmochimica Acta*, Vol. 36, No. 9, p. 1029–41.

Davies, M. B., *and others*. 1972. Atomic absorption/ion-exchange technique for the analysis of chromium complex multistage reactions, by M. B. Davies and J. W. Lethbridge and O. Nor. *Journal of Chromatography*, Vol. 68, No. 1, p. 231–44.

Dingman, J., *jr., and others*. 1972. Concentration and separation of trace metal cations by complexation on polyamine-polyurea resins, by J. Dingman, Jr., S. Siggia, C. Barton, K. B. Hiscock. *Analytical Chemistry*, Vol. 44, No. 8, p. 1351–57.

Gorham, E. 1958. The salt content of some ice samples from Nordaustlandet (North East Land), Svalbard. *Journal of Glaciology*, Vol. 3, No. 23, p. 181–87.

Murozumi, M., *and others*. 1969. Chemical concentrations of pollutant lead aerosols, terrestrial dusts, and sea salts in Greenland and Antarctic snow strata, [by] M. Murozumi, T. J. Chow and C. Patterson. *Geochimica et Cosmochimica Acta*, Vol. 33, No. 10, p. 1247–94.

Souchez, R. A., *and others*. 1973. Refreezing of interstitial water in a subglacial cavity of an Alpine glacier as indicated by the chemical composition of ice, by R. A. Souchez, R. D. Lorrain and M. M. Lemmens. *Journal of Glaciology*, Vol. 12, No. 66, p. 453–59.

Strelow, F. W. E. 1960. An ion exchange selectivity scale of cations based on equilibrium distribution coefficients. *Analytical Chemistry*, Vol. 32, No. 9, p. 1185–88.