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Analysis of Trace Elements in Salt Crystals by Secondary Ion Mass Spectrometry

Hiroyuki To, Yasushi Niino and Masatoshi Arita

Sea Water Science Research Laboratory, Japan Tobacco Inc., Odawarashi, Japan

ABSTRACT

The authors investigated the application of secondary ion mass spectrometry (SIMS) to the analysis of trace elements in salt crystals, using uniform standard samples prepared by either freeze dry or fusing methods. The results are as follows.

The positive and negative secondary ionic species derived from NaCl matrix and sea salt compounds and their relative ion intensities were defined. When O^- was used as the primary ion to detect positive secondary ions, the relative ion intensities of alkali metals, alkali earth metals and aluminium were high. When Cs^+ was used as the primary ion to detect negative secondary ions, the relative ion intensities of halogens, carbon, phosphorus and sulfur were high. The detection limits of the elements with high relative ion intensities were low. In particular, the detection limit of lithium was 4×10^{-4} ppm in the case of positive secondary ions.

The quantitative analysis of alkali metals, alkali earth metals, halogens and phosphorus was carried out by the calibration curve method. Although, the analytical values of SIMS differed little from those from usual methods, lithium, fluorine, iodine and phosphorus could be analyzed at levels which could not be detected by the usual methods.

INTRODUCTION

The impurities in salt were analyzed by chelatometric titration, atomic absorption spectrometry, inductively coupled plasma emission spectrometry (ICP) and ion chromatography (Japan Tobacco, 1989). Recently, consumer demand has become diverse, among others the demand for salt of high purity has become strong. This required the development of new analytical methods for trace elements because the amounts of impurities in high purity salt are so small that application of the usual methods to their analysis is difficult.

Secondary ion mass spectrometry (SIMS) is used to analyze solid samples. When the sample is bombarded with a beam of high energy primary ions, positive and negative secondary ions are sputtered from the sample surface. Both are drawn into a mass spectrometer and measured. All elements from hydrogen to uranium can be analyzed by SIMS without any complicated pretreatments. At the same time, SIMS can give also such information as surface composition, depth profile of the elements and bulk and local chemical characteristics. Quantitative analysis by SIMS has been pursued using theoretical (Andersen and Hinthorne, 1973; Plog et al., 1977) and empirical approaches (Ishizuka, 1974; Ray and Hart, 1982; Nesbitt et al., 1986). The theoretical approaches are less accurate than the empirical ones because the mechanisms of secondary ion emission are not completely understood and matrix effects have a great influence. The main empirical approach is a calibration curve method using standard samples. For this method, uniform standard samples in the same matrix must be prepared. As SIMS is an one of three dimensional analytical method, the standard samples must have three dimensional uniformity. We have reported that fusing and freeze dry methods are excellent for preparing these standard samples in a sodium chloride (NaCl) matrix (To et al., 1990, 1991).

We have investigated the application of SIMS to the analysis of trace elements in salt crystals. In this paper, the secondary ionic species from sea salt compounds, relative ion intensities, detection limits and quantitative analysis using the calibration curve are discussed.

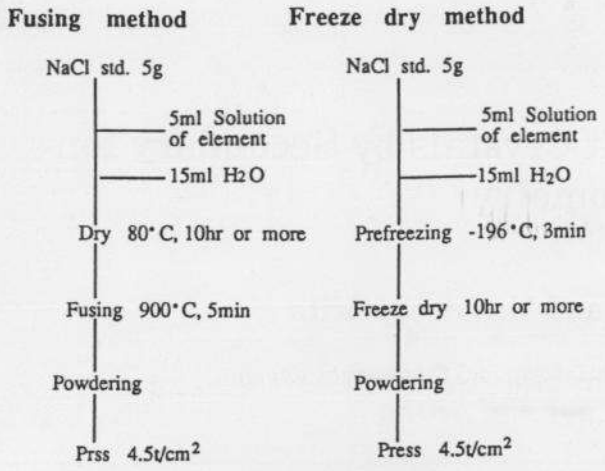

Fig. 1. Preparation procedures of standard samples.

EXPERIMENTAL

Sample preparation

The standard samples were prepared by the fusing or the freeze dry method. These procedures are outlined in Fig. 1. For example, the standard sample of 10 ppm (wt/wt) of calcium was prepared as follows: Five grams of NaCl standard reagent grade (Manakku Co., Ltd. Purity = 99.99%) were mixed with 5 ml of the solution of 10 ppm calcium and then the volume of the mixture was increased to 20 ml by adding ultra pure water. This solution was treated by the fusing or the freeze dry method. The resulted dryness was powdered in an agate mortar and about 0.2 g of the powdered samples was pressed at 4.5 t/cm^2 with an instrument to make tablet (Hitachi Co., Ltd.). A tablet of 10 mm diameter and about 1 mm thickness was obtained. In order to prevent the electric charge, when trying to detect negative secondary ions, a gold coating was put on the surface of sample of about 100 nm thickness using a sputter coater (1030 Model, Hitachi Co., Ltd.). The solution of the elements for analysis was prepared using sodium salts or chlorides of theirs. Halides, sulfates, carbonates, phosphates and nitrates of alkali and alkali earth metals were selected as the reference standard for the sea salt compounds. These reagents were powdered in an agate mortar. The samples were obtained by pressing the powdered samples at 4.5 t/cm^2 with the instrument to make the tablets. The reagents used were of special or maximum purity grades (Wako Pure Chemical Ind. Ltd.).

SIMS analysis

A Hitachi IMA-3 model was used. The schematic diagram of the apparatus is shown in Fig. 2 and the analytical conditions are listed in Table 1. In order to detect positive secondary ions, O^- was used as the primary ion. To detect negative secondary ions, Cs^+ was used as the primary ion and electrons were irradiated onto the sample to neutralize the electric charge. The current density of primary ions was set to a maximum. In case of measurements of relative ion intensities, detection limits and quantitative analysis, the analytical values were calculated as an average of measured values at 5 points of the sample.

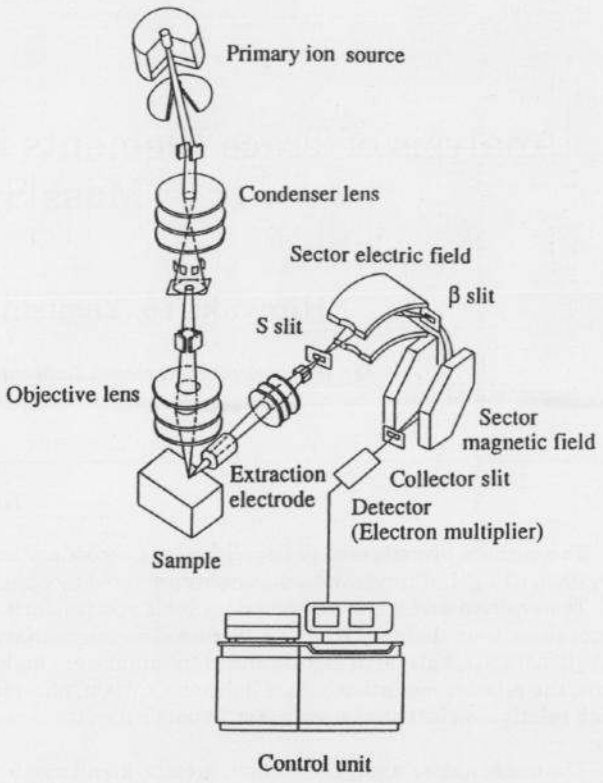

Fig. 2. Schematic diagram of apparatus for SIMS analysis.

TABLE 1
Analytical conditions

	Secondary ion	
	Positive	Negative
Primary ion		
Source	O^-	Cs^+
Energy	–13 keV	13 keV
Current	50 nA	100 nA
Diameter	300 μm	300 μm
Secondary ion		
Accelerating voltage	+3 kV	–3 kV
Mass range	0–250 m/e	0–250 m/e
Detector	Multiplier	Multiplier

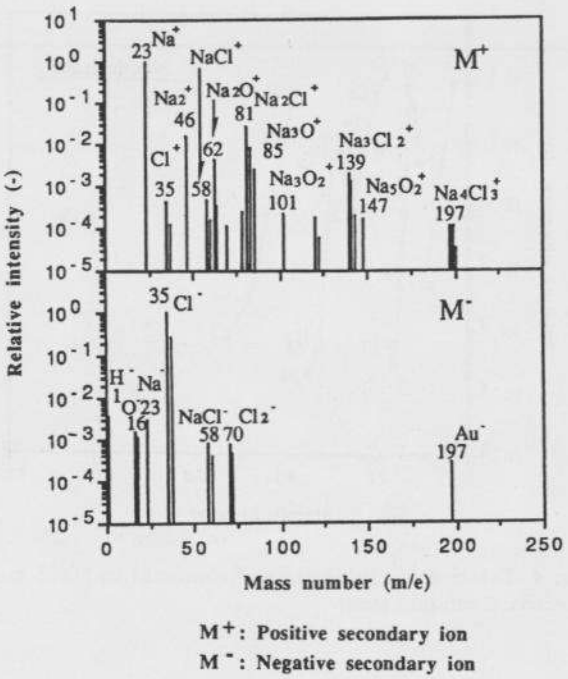

Fig. 3. Reference mass spectra from NaCl.

RESULTS AND DISCUSSION

Secondary ionic species from sea salt compounds

To establish a background reference depending on a matrix for analysis, the mass spectra from NaCl standard reagent grade were measured. The mass spectra of positive and negative secondary ions are shown in Fig. 3.

When using O^- as the primary ion for detection of positive secondary ions, Na^+ was the most intense species of ions. Moreover, various secondary ionic species were detected. The species were the singly charged monatomic ion (Cl^+), the singly charged multi-atomic ion (Na_2^+), the molecular ions ($NaCl^+$, Na_2Cl^+, $Na_3Cl_2^+$) and oxide ions (Na_2O^+, Na_3O^+) and so on.

When using Cs^+ as the primary ion to detect negative secondary ions, the Cl^- was the most intense species of ions. The other species were the singly charged monatomic ions (H^-, O^-, Na^-, Au^-), the singly charged multi-atomic ion (Cl_2^-) and the molecular ions (OH^-, $NaCl^-$) and so on. The negative mass spectra were simpler than the positive ones.

Positive oxide ions were derived from O^- of the primary ion, H^-, O^- and OH^- were derived from moisture in the sample and sample chamber and Au^- was derived from the gold coating on the surface of the samples. These species of ions are present as background when analyzing the impurities.

TABLE 2

Positive secondary ionic species from various sea salt compounds and their relative ion intensities

Ionic species	Relative ion intensity	
	Li, Na, K Salts	Mg, Ca, Sr Salts
M^{+*1}	100	100
M^{2+}	–*3	0.04–1
M_2^+	1–2	0.1–1
MO^+	–	1–20
M_2O^+	0.1–10	0.3–5
M_3O^+	0.01–8	–
MX^{+*2}	–	4–20
M_2X^+	2–10	–
$M_3X_2^+$	0.2–2	–
MS^+	–	0.1–0.5
M_2S^+	0.1	–
$M_3SO_3^+$	0.2–1	–
MPO_2^+	–	0.3
$M_2PO_2^+$	0.2	–

*1 M: Li, Na, K, Mg, Ca and Sr.
*2 X: F, Cl, Br and I (Halogens).
*3 –: <0.01 ppm.

TABLE 3

Negative secondary ionic species from various sea salt compounds and their relative ion intensities

Halide		CO_3, NO_3, PO_4, SO_4 Salts	
Species	Intensity	Species	Intensity
X^{-*}	100	O^-	100
X_2^-	0.03–0.05	C^-	1–4
MX^-	0.02–0.1	P^-	2–3
O^-	0.07–2	S^-	20–30
		PO^-	0.01–0.4
		SO^-	0.03–0.1

* X: F, Cl and I (Halogen).

Furthermore, at maximum sensitivity, other large or small peaks were detected at all mass numbers.

Alkali metals, alkali earth metals and halogens often exist as impurities in salt. In order to clarify their secondary ionic species, the mass spectra from various sea salt compounds were measured. The positive secondary ionic species are shown in Table 2 and the negative secondary ionic species are shown in Table 3.

When the positive secondary ions were measured, the singly charged monatomic ions of alkali and

alkali earth metals (M^+) were the most intense for all samples. The double charged monatomic ion (M^{2+}) appeared in the compounds of alkali earth metals. The intensities of the singly charged diatomic ion (M_2^+) from alkali metal compounds was higher than those from alkali earth metal compounds. Among oxide ions, following ionic species were intense: M_2O^+ and M_3O^+ from alkali metal compounds and MO^+ and M_2O^+ from alkali earth metal compounds. Among halide ions from alkali metal compounds. M_2X^+ and $M_3X_2^+$ were intense and M_2X^+ were about 10 times as intense as $M_3X_2^+$. And then among halide ions from alkali earth metal compounds, MX^+ was intense. Moreover M_2S^+, $M_3SO_3^+$ and $M_2PO_2^+$ also appeared from alkali metal compounds and MS^+ and MPO_2^+ appeared from alkali earth metal compounds. In the majority of cases, M^+ of alkali and alkali earth metals which are impurities were detected.

When the negative secondary ions were measured, the singly charged monatomic ions of halogen (X^-) were the most intense in case of halides and O^- was the most intense in case of sulfates, carbonates, phosphates and nitrates. Moreover X_2^-, MX^- and O^- were detected from halides; S^- and SO^- were detected from sulfates; C^- was detected from carbonates; and P^- and PO^- were detected from phosphates. However, ions on nitrogen were not detected from nitrates. H^-, O^- and OH^- were detected from the samples in which there were no hydrogen and oxygen atoms, but these intensities varied with the moisture in the samples and the vacuum conditions in the sample chamber.

Relative ion intensities and detection limits

Storms et al. (1977) measured relative ion intensities of elements using the elements themselves, or compounds containing them. However, alkali metals and halogens were not measured. Besides, in this study, the influence of the matrix of NaCl has to be considered. Therefore, we measured the relative ion intensities of elements in an NaCl matrix. The standard samples of each element were measured and the measured values were corrected on the basis of the relative isotopic abundance in nature. The relative intensities of positive secondary ions based on Na^+ are shown in Fig. 4 and those of negative secondary ions based on Cl^- are shown in Fig. 5.

The ion intensities of alkali metals, alkali earth metals and aluminium were high for the positive secondary ions and those of halogens, carbon, oxygen, phosphorus and sulfur were high on the negative secondary ions. In accordance with the data of Storm et al. (1977), the ion intensities of positive secondary ions were found to decrease gradually with an increase of the ionization potential and those

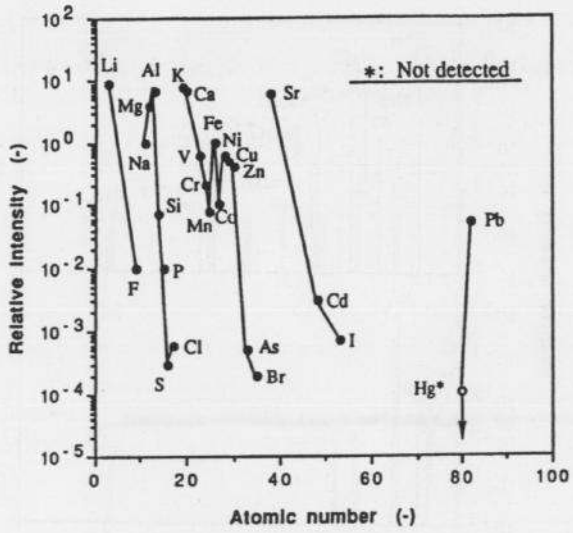

Fig. 4. Relative ion intensities of elements in NaCl matrix (positive secondary ions).

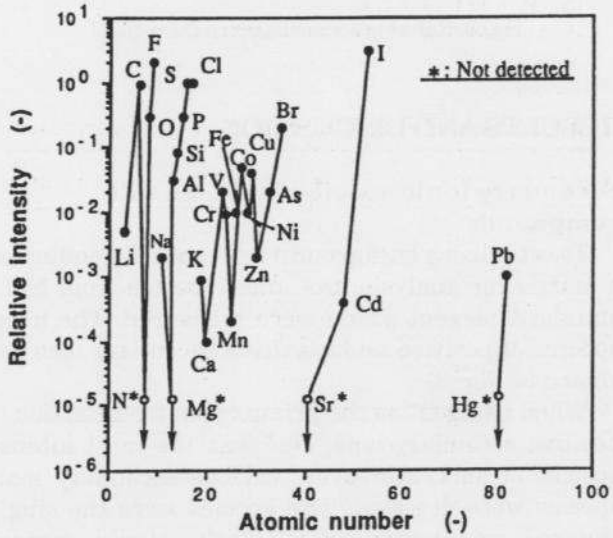

Fig. 5. Relative ion intensities of elements in NaCl matrix (negative secondary ions).

of negative secondary ions increased gradually with an increase of electron affinity. However, in case of positive secondary ions, the ion intensity of aluminium was higher than the data of Storms et al. (1977), and those of vanadium, chromium and manganese were lower than their data. Also, in the case of negative secondary ions, the ion intensity of phosphorus was higher than their data and that of arsenic was lower. These differences are considered to be the result of the influence of the matrix effects of NaCl.

Detection limits of elements in an NaCl matrix were measured using two standard samples in which there were elements in differing concentrations. In

TABLE 4

Detection limits of elements in NaCl matrix (positive secondary ion)

Element	m/e	Detection limit (ppm)	Remarks[*5]	Element	m/e	Detection limit (ppm)	Remarks[*5]
Li	7	4×10^{-4}		Fe	56	0.05	
F	19	0.7		Co	59	0.1	
Mg	24[*1]	9×10^{-3}	0.9	Ni	58[*1]	0.02	>10000
Al	27	0.05		Cu	65	4	
Si	28	20		Zn	64	4	
P	31	0.9		As	75	30	
S	48[*2]	10	30	Br	125[*3]	30	3000
K	39[*1]	0.07	0.8	Sr	88	0.4	
Ca	40[*1]	0.02	2	Cd	114	10	
V	51	3×10^{-3}		I	173[*4]	3	400
Cr	52	4×10^{-3}		Hg	202	>10000	
Mn	55	0.03		Pb	208	30	

[*1]: Detection on the high resolution mode.
[*2]: Measurement of SO^+.
[*3]: Measurement of Na_2Br^+.
[*4]: Measurement of Na_2I^+.
[*5]: Measurement of M^+ on the standard mode.

TABLE 5

Detection limits of elements in NaCl matrix (negative secondary ion)

Element	m/e	Detection limit (ppm)	Remarks[*5]	Element	m/e	Detection limit (ppm)	Remarks[*5]
Li	7	0.1		Fe	56	7	
C	12	0.6		Co	59	2	
F	19	0.02		Ni	58	>10000	
Mg	40[*1]	0.5	>10000	Cu	65	0.2	
Al	27	0.5		Zn	64	0.5	
Si	28	0.1		As	75	20	
P	31	8×10^{-3}		Br	79[*2]	0.03	3
S	34	1		Sr	104[*3]	0.4	>10000
K	39	80		Cd	130[*4]	40	1000
Ca	40	400		I	127	0.5	
V	51	7		Hg	202	>10000	
Cr	52	2		Pb	208	200	
Mn	55	100					

[*1]: Measurement of MgO^-.
[*2]: Detection on the high resolution mode.
[*3]: Measurement of SrO^-.
[*4]: Measurement of CdO^-.
[*5]: Measurement of M^- on the standard mode.

case of elements of which the intensities of singly charged monatomic ions were low, the molecular ions were measured. When the background peaks of the NaCl matrix were high, the peaks of elements were separated from the background peaks by measurement at a high resolution mode of mass. The detection limit was defined as the concentration of the element which shows a signal equal to the three times the value of the background fluctuation. The detection limits of positive secondary ions are shown in Table 4 and those of negative secondary ions are shown in Table 5.

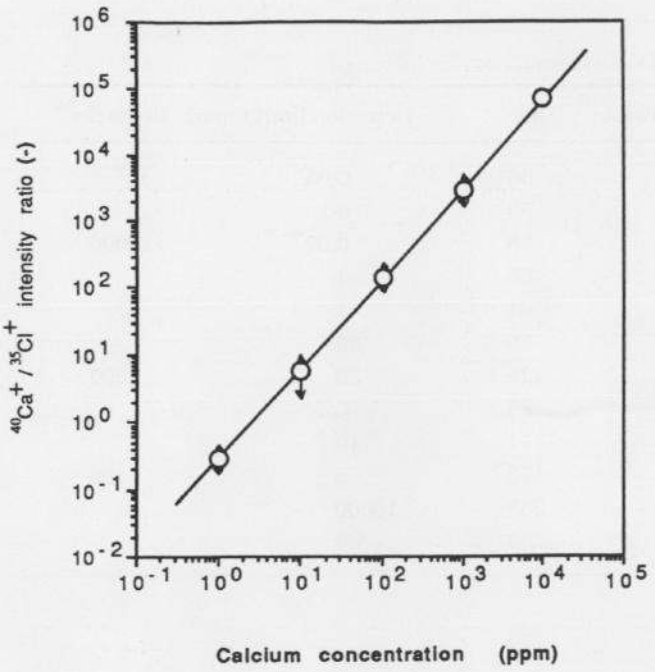

Fig. 6. Calibration curve for calcium in NaCl matrix (positive secondary ions). Arrows show deviation of measured values.

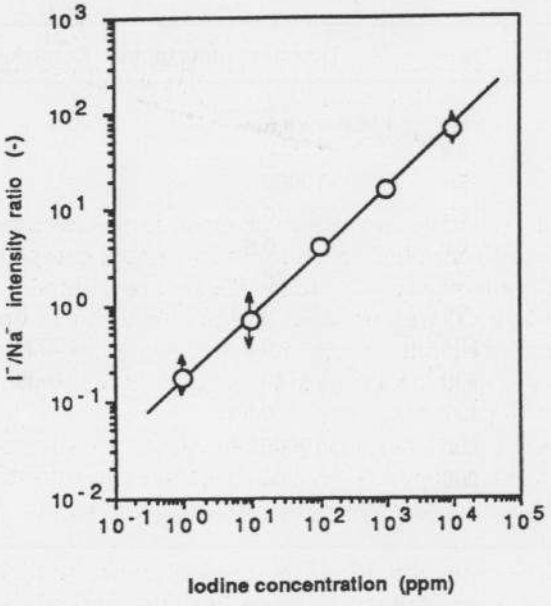

Fig. 7. Calibration curve for iodine in NaCl matrix (negative secondary ions). Arrows show deviation of measured values.

The detection limits of positive secondary ions ranged from 10^{-4} to 10^4 ppm (wt/wt). In particular, the detection limit of lithium was very low (4×10^{-4} ppm), because the ion intensity was very high compared with the background. Also, the ion intensities of the other alkali and alkali earth metals were low (10^{-3}–10^{-1} ppm). The detection limits of negative secondary ions ranged from 10^{-3} to 10^4 ppm. Phosphorus, fluorine and bromine gave very low (10^{-3}–10^{-2} ppm) values. Sulfur, of which relative ion intensity was high, showed a relatively high (1 ppm) vale, as the measurements were carried out at mass number 34 which was in low isotopic abundance, as O_2^- peak appears at mass number 32.

In the case of measurement of molecular ions in the high resolution mode, both detection limits of positive and negative secondary ions fell from 2 to 5 order of magnitudes. The deviations at the high resolution mode differed little from the deviations at the standard mode. However, it was difficult to apply quantitative analysis to the measurements of molecular ions as the deviations were larger than those of monatomic ions.

Quantitative analysis by calibration curve

The quantitative analysis by the calibration curve method was investigated. Lithium, potassium, magnesium and calcium were selected for the analysis of positive secondary ions. Fluorine, bromine, iodine, phosphorus and sulfur were selected for the analysis of negative secondary ions. The calibration curves were drawn up using standard samples. Their concentration ranged from the order of the background level at the measured mass number up to 1% (wt/wt). The analytical values were represented by the ratio $M^+/^{35}Cl^+$ in case of positive secondary ions and by the ratio M^-/Na^- in case of negative secondary ions. For example, the calibration curve for calcium is shown in Fig. 6 and for iodine in Fig. 7.

The calibration curves of elements except for sulfur were linear in the concentration range in the order of background level at the mass number up to 1% after correcting for the background. The measured value of sulfur varied largely at the low concentration and the calibration curve was not linear. The reason for this variation is a disturbance by the adjacent $^{35}Cl^-$ to $^{34}S^-$. When iodine was measured, the peak of iodine ($^{127}I^-$), which was present as an impurity in the gold coating showed an ionic intensity corresponding to about 1 ppm concentration. Therefore, other methods free from electric charge have to be devised for the analysis of samples of less than 1 ppm. The relative standard deviations of the analysis of each sample were between 5 and 30%. We think that this is largely attributable to the distribution of concentrations in the standard samples.

Several kinds of salts were analyzed using the calibration curves and the analytical values were compared with those derived from usual methods. The results are shown in Tables 6 and 7. The analytical values differed little from those derived from

TABLE 6

Comparison of analytical values between SIMS and usual methods (positive secondary ion) (ppm)

	Li		K		Mg		Ca	
Sample No.	ICP	SIMS	A[*1]	SIMS	(A[*1]) C[*2]	SIMS	(A[*1]) C[*2]	SIMS
1	N.D.[*3]	4×10^{-3}	2.5×10^{1}	2×10^{1}	(2.5)	2	(5.0)	6
2	N.D.	6×10^{-3}	6.5×10^{1}	4×10^{1}	(3.0)	4	(8.9)	9
3	6×10^{-2}	5×10^{-2}	1.2×10^{3}	1×10^{3}	2.0×10^{2}	2×10^{2}	1.3×10^{2}	2×10^{2}
4	2×10^{-1}	2×10^{-1}	1.9×10^{3}	1×10^{3}	4.7×10^{2}	5×10^{2}	3.1×10^{2}	3×10^{2}

[*1] A: Atomic absorption spectrometry.
[*2] C: Chelatometric titration.
[*3] N.D.: Not detected.

TABLE 7

Comparison of analytical values between SIMS and usual method (negative secondary ion) (ppm)

	F		Br		I		P	
Sample No.	IC[*1]	SIMS	IC[*1]	SIMS	IC[*1]	SIMS	IC[*1]	SIMS
1	N.D.[*2]	9×10^{-2}	4.4×10^{1}	4×10^{1}	N.D.	3×10^{-1}	N.D.	2×10^{-2}
2	N.D.	1×10^{-1}	6.5×10^{1}	5×10^{1}	N.D.	3×10^{-1}	N.D.	3×10^{-2}
3	N.D.	4×10^{-1}	5.4×10^{2}	5×10^{2}	N.D.	1	N.D.	4×10^{-2}
4	N.D.	4×10^{-1}	9.9×10^{2}	1×10^{3}	N.D.	6×10^{-1}	N.D.	6×10^{-2}
5	N.D.	4×10^{-1}	5.5×10^{2}	4×10^{2}	N.D.	4×10^{-1}	4.8×10^{2}	6×10^{2}

[*1] IC: Ion chromatography.
[*2] N.D.: Not detected.

usual methods. Lithium could be analyzed at a level which could not be detected by ICP. Besides, fluorine, iodine and phosphorus could be analyzed at levels which could not be detected by ion chromatography. However, it seems that the analytical values of iodine lacked reliability as the iodine content was less than 1 ppm in all the samples.

The relationship between concentration and intensity is linear at the concentration from order of ppb or ppm up to 1%, so it is possible to apply SIMS to the analysis of impurities in salt crystals over a large range of concentrations. In particular, this method is available for the detection of trace elements and the determination of content order, as it has a merit of being an analysis which can be carried out quickly yet of high sensitivity and not requiring pretreatment.

CONCLUSIONS

The application of SIMS to the analysis of trace elements in salt crystals has been studied and the following results were obtained.

The positive and negative secondary ionic species derived from NaCl matrix and sea salt compounds and their relative ion intensities were defined.

When O^- was used as the primary ion to detect positive secondary ions, the relative ion intensities of alkali metals, alkali earth metals and aluminium were high.

When Cs^+ was used as the primary ion to detect negative secondary ions, the relative ion intensities of halogens, carbon, phosphorus and sulfur were high.

The detection limits of the elements with high relative ion intensities were low. In particular, the detection limit of lithium was 4×10^{-4} ppm in the case of positive secondary ions.

The quantitative analysis of alkali metals, alkali earth metals, halogens and phosphorus was carried out by the calibration curve method. Although, the analytical values of SIMS differed little from those from usual methods, lithium, fluorine, iodine and phosphorus could be analyzed at levels which could not be detected by the usual methods.

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