

Determination of Bromine and Iodine in Salt with Inductively Coupled Plasma - Mass Spectrometry

Salt Production

Keywords: Bromine, Iodine, ICP-MS, Analysis

Abstract:

A specific determination of the bromine and iodine in salt by inductively coupled plasma - mass spectrometry (ICP-MS) is described. The salt sample of 1.0 g was dissolved by 1 % tetramethyl ammonium hydroxide (TMAH) solution of 50 mL including 0.1 mg/L thallium solution as an internal standard. When the sample was iodized salt, the sample concentration was diluted to 1/10. Bromine and iodine occur in different chemical forms such as bromide, bromate, iodide, and iodate. There is no noticeable difference in the ICP-MS response among these. The influences of the concentration of the sodium chloride as a matrix, as well as internal standard elements, were investigated to quantitatively determine a reasonable detection limit. When a salt sample contains more than 1% magnesium, magnesium oxide precipitates as a build-up on the nebulizer and skimmer cone in ICP-MS. A supernatant solution that gives rise to precipitation, and therefore instability, was used as the measured solution. The detection limits for bromine and iodine were 1 mg/kg and 5 µg/kg, respectively. A good agreement was obtained for determined values by ICP-MS and the conventional method of ion chromatography or ICP-atomic emission spectroscopy. The proposed method is simple and high sensitivity, and this can be used to determine the bromine and iodine in several salt samples, including solar salt, rock salt, and iodized salt.

Introduction

Bromine and iodine are natural contaminants that occur in varying amounts depending on the origin and the method of salt production.

Conventionally, the bromine concentration in typical salt is about 0.1 g/kg. Recently, low-bromine salt has been developed. The bromine concentration of low-bromine salt is less than 0.1 g/kg, and it can also be infinitesimally, for example under 0.02 g/kg.

Bromide is the major chemical form of bromine in salt. To date, the most common analytical method used to identify the bromide in a salt sample has been ion-chromatography (IC) with ultraviolet detector¹⁻²⁾. However, this method of a detection limit was 20 mg/kg, which is rather unsatisfactory. Although IC with an ultraviolet detector offers a high level of sensitivity, it is affected by the large chloride ion peak, requiring the sample salt to be diluted 1000 times for use in an ion-exchange column capacity, and then the detection limit for a sample solution was 20 µg/L.

The iodine concentration in a typical salt is about 50 µg/kg or less. Several methods of iodine determination have been proposed, including Atomic Absorption Spectrometry³⁾, Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES)⁴⁾ with the reduced iodate to iodide using sodium sulfide^{5,6)}, HPLC⁷⁾, and ion chromatography (IC)^{8,9)}. These analytical methods have been developed for the estimation of iodine in iodized edible salt. Iodine is an essential trace element for humans, in that it is essential to the production of thyroid hormones. On the other hand, determination of trace (no more than 1 mg/kg) iodine in salt is important to ensuring the quality of soda chemicals. Trace iodine has been determined by Inductively Coupled Plasma - mass spectrometry (ICP-MS), applied to environmental samples¹⁰⁻¹⁴⁾ and food¹⁵⁻¹⁷⁾. Zhang et al. applied IC-ICP-MS to iodized salt¹⁸⁾. These methods require a pretreatment process such as on-line coupling IC, or acid digestion in a high matrix sample, e.g. urine, seawater, because ICP-MS cannot be applied to a high matrix sample.

A simple procedure for the determination of bromine and iodine, taking advantage of the high sensitivity of ICP-MS, is presented in this paper.

Materials and methods

Salts

The sodium chloride for the matrix effect test sample was pretreated to remove any iodine. In a beaker with a watch glass, 10 g of salt (sodium chloride, 99.99%, Sigma Aldrich) was dissolved in 30 mL of Milli-Q water (Millipore SA). To this solution was added 10 mL of hydrochloric acid (32–35%, Optima grade, Thermo Fisher Scientific), after which the salts were re-crystallized by evaporation to dryness. This cycle was repeated three times.

The samples were edible salts and crude salt. The edible salts were purchased in Japan (not iodized), Greece, the UK, and China (iodized). The crude salt was solar salt imported into Japan from Mexico, Australia, and India.

Three reagent grade sodium chloride samples were used, namely, Sigma-Aldrich “TraceCERT” grade (99.999% metal based purity) and “Redi-Dri” grade (99%+ purity), as well as Wako pure chemical “JIS special grade” (99.9%+).

Instrumentation

The ICP-MS used for this study was the 7900 (Agilent, Japan). This machine has a high matrix tolerance due to its aerosol dilution system on spray chamber. This system, which Agilent refers to as the “UMHI,” allows 2% total dissolved solids and can be used for salt samples. The standard operational primary conditions are as follows:

Plasma incident power: 1600 W

Flow rate of Argon as carrier gas: 0.92 L/min, Flow rate of dilution gas: 0.20 L/min

Torch sampling depth: 9 mm

Ion monitored m/z: 79, 127, and 205.

Reagents

The reagent grade chemicals were used without further purification except sodium chloride. High purity 25 wt% tetramethyl ammonium hydroxide (TMAH) was acquired from Tama Chemicals (Kanagawa, Japan).

Potassium iodate was purchased from Wako Pure Chemical Industry (Osaka, Japan).

Bromate and bromide solutions were purchased from Wako Pure Chemical. An iodide solution was obtained from Sigma-Aldrich (Tokyo, Japan). These solutions (1000 mg/L) were all of ISO traceable grade. These standard solutions were diluted in 1.0% TMAH.

Method

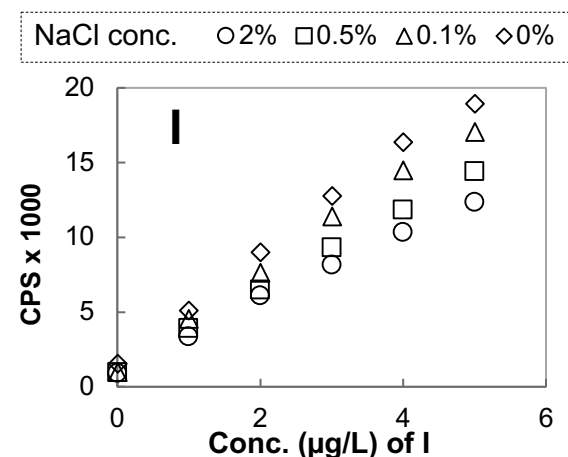
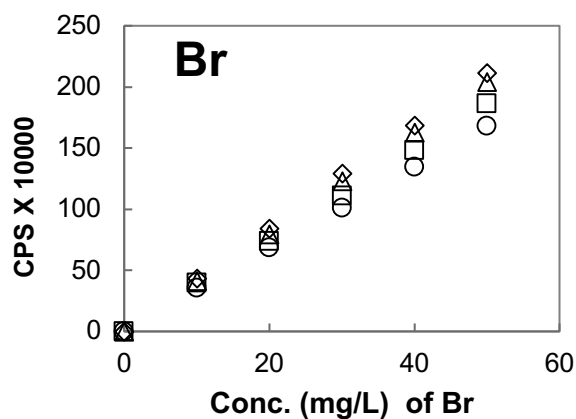
A salt sample of 1.0 g was dissolved in 50 mL of 1.0% TMAH including 0.1 mg/L thallium solution as an internal standard. When the sample was iodized salt, the sample amount was reduced to one-tenth, that is, 0.10 g. All these sample solutions was used polyethylene tubes, DigiTUBES (SCP Science, Canada).

Results and discussion

Evaluation of ICP-MS conditions

In salt, bromine and iodine presumably are in different chemical forms such as bromide, bromate, iodide, and iodate. In ICP-MS, the sample solution was induced to plasma as the ionization source, and bromine and iodine were detected as cations Br^+ and I^+ (hereinafter Br, I) In the mass spectrometer, Br was monitored mass-to-charge ratio (m/z) 79, I was monitored m/z : 127. Thus, the effects of the chemical forms on the ICP-MS signal intensity were measured. The signal intensities for bromide and iodide were compared with those for bromate and iodate. The bromide standard solution (certified, 1.002 mg/L, 12.54 $\mu\text{mol/L}$) and bromate standard solution (certified, 1.997 mg/L, 15.61 $\mu\text{mol/L}$) were diluted to 0.1 mg/L, respectively, giving a bromide/bromate intensity ratio of 1.01 ± 0.008 . Meanwhile, when the solutions were diluted to 1 mg/L, the ratio was 1.01 ± 0.006 . The ratios of the iodine/iodide signal intensities were 0.99 ± 0.009 , 1.01 ± 0.005 , and 1.00 ± 0.05 for 1 mg/L, 0.1 mg/L, and 0.01 mg/L solutions, respectively. In this system, the signal intensities for both the bromide and bromate forms, and iodide and iodate forms, were the same and stable.

Figures 1 shows the variation in the Br and I intensities as working curves with a difference of NaCl concentration of 2.0%, 0.5%, 0.1%, and 0%. The matrix effect of the NaCl is very apparent, and can be quantified using the internal standard method. To identify an internal standard for which the need for adjustment was negligible, a recovery test was performed. The elements used for the internal standard were scandium (Sc), gallium (Ga), germanium (Ge), ruthenium (Ru), rhodium (Rh), indium (In), tellurium (Te), terbium (Tb), holmium (Ho), and thallium (Tl). Sc, Tb, and Ho are rare earth metals, and are commonly selected for use as the internal standard in ICP-MS. Yttrium is frequently used as an internal standard but could not be used in this case because it would precipitate in an alkaline solution. Ru and Rh are rare metals that are not expected to be found in a salt sample. Ga, Ge, In, Te, and Tl are representative elements, that are able to dwell as ions in an alkaline solution. In particular, Te is frequently used as an internal standard for I, with the mass number and first ionization energy of Te being near those of I. The bromine and iodine in the 2% NaCl solution (1.0 g/50 mL) and 1.6% NaCl solution were measured and both were found to exhibit spikes above the internal standards. All the elements were used for an internal standard except indium (Fig. 2). Indium is not stable in a TMAH solution.



NaCl conc. ○2% □0.5% △0.1% ◇0%

Figures 1: Working curves of Br and I with some NaCl concentration in matrix

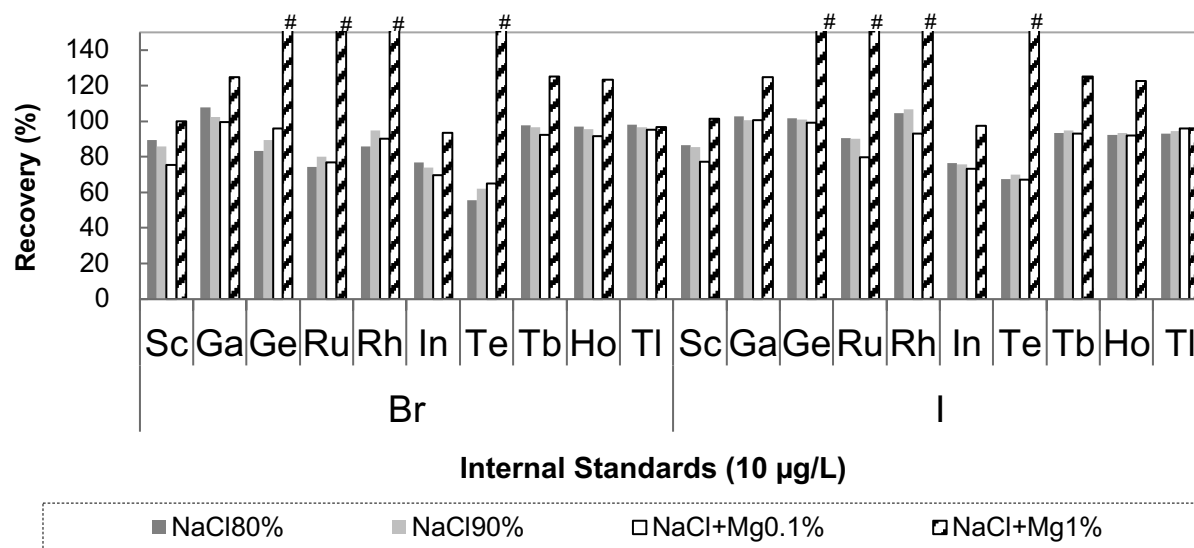
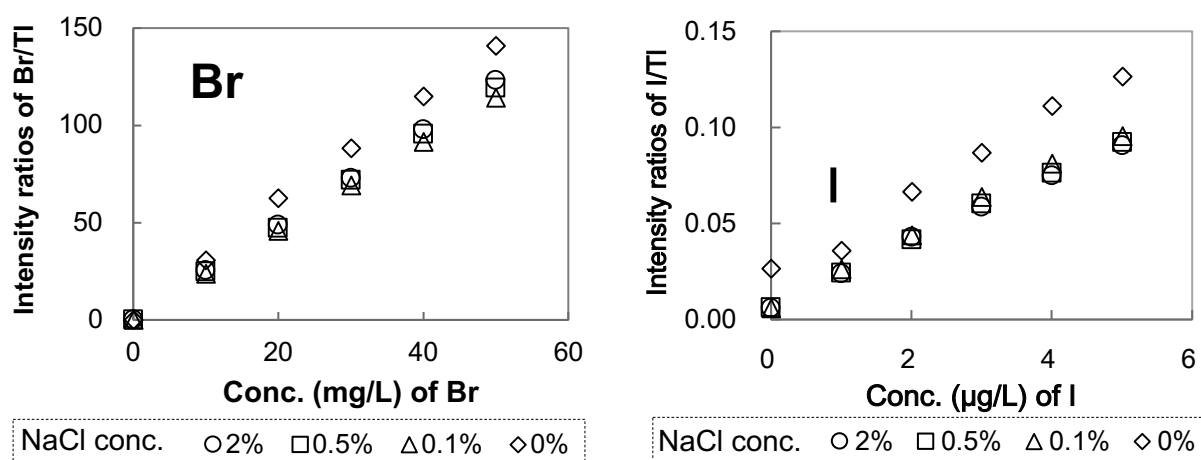


Figure 2: Recoveries of ratios of bromine or iodine determined by internal standards with NaCl 100%.

Here, a pound symbol (#) indicates a recovery of more than 150%.

Typical salt incorporates a small amount of each alkaline earth metal as an impurity. In Japan, wet salt made from the seawater to cut dry process and water contents about 3%~5%, is the preferably used for cooking. Wet salt, including bittern, is rich in alkaline earth metals. In bittern, the magnesium, calcium, and potassium constitutes as much as 3% of sample, we inspected effect of bittern for quantity of Br and I. The presence of calcium and potassium did not affect the recoveries of the Br and I, nor the intensities of the internal standards. Magnesium, however, affected the intensity of the internal standards, except thallium (Tl), as shown in Fig. 2. Magnesium was found to form a precipitate as magnesium hydroxide, in a high pH solution of TMAH. Many of the elements were co-precipitated and removed from the sample solution. This is unavoidable in the case of wet salt. The intensity showed that the Br and I did not catch up to the precipitation, nor did the Tl. In those samples incorporating magnesium at concentrations of 1% and 0.1%, the recoveries of Br were $95 \pm 0.2\%$ and $97 \pm 1.2\%$, respectively. Meanwhile, the recoveries of I were $96 \pm 0.6\%$ and $96 \pm 0.8\%$, respectively. Thus, we chose to use Tl, despite its being very toxic, for the internal standard of Br and I.



Figures 3: Working curves of Br and I with Tl to correct matrix effect.

Figures 3 shows the working curves for Br and I, corrected by the Tl internal standard. The concentrations of the NaCl were not affected, except in the case of the 0% NaCl solution. When the sodium or chloride ion concentrations were less than the concentration of Tl, the intensity of the Tl was observational decreasing (Fig. 4). This phenomenon has not yet been solved.

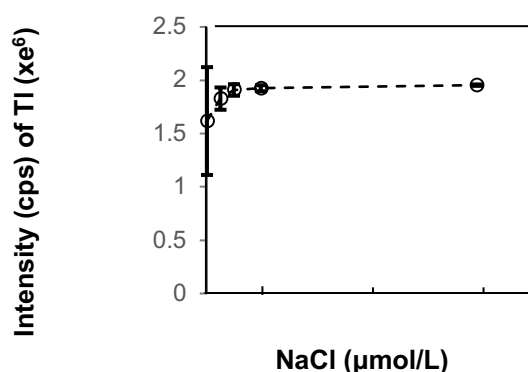


Figure 4: Change in Tl intensity with NaCl concentration

Detection limits

Validation

The Br and I detection limits were calculated. To the solution of Br with 2% NaCl (reagent No. 1, see Table 2) was added 1% TMAH, was measured by ICP-MS, the concentration of Br was found to be 0, 2, 4, 6, 8, and 10 µg/L. Because the Br could not be purified from the reagent grade NaCl, the working curve had an intercept. The detection limit, calculated as a concentration equal to seven times the standard deviation, was 1.0 µg/L. Thus, the method of detection limit was 50 µg/kg.

For I, the standard solution was treated with de-iodized sodium chloride, and concentrations of I of 0, 0.01, 0.1, 1, and 10 µg/L, were prepared in each of 1% TMAH and 2% de-iodized sodium chloride. The standard calibration curve was linear and the correlation coefficient was 1.0000 between 0–10 µg/L. The detection limit with ICP-MS was calculated to be ten times sigma of the blank solution, that is, 0.10 µg/L. This gave a method of detection limit was 5 µg/kg. These sensitivities were deemed satisfactory for salt analysis.

To evaluate the proposed method, the iodized salt sample made in the UK was also analyzed using the conventional IC for the Br and ICP-AES for the I. The concentration of Br determined by IC was 163 ± 5 mg/kg, while that determined by the proposed method was 166 ± 1 mg/kg, $n = 6$. The concentration of I as determined by ICP-AES was 29 ± 2 mg/kg, while that determined by the proposed method was 31 ± 2 mg/kg, $n = 6$. At the 95% confidence level, the differences between the results obtained by the proposed method and those obtained conventionally were not statistically significant. The concentration of iodate was found to be in good agreement with that claimed by the manufacturer. The concentration of bromide was typical for solar salt.

The results obtained for the iodized edible salt samples, analyzed by the proposed method were compared with those obtained by conventional methods. All the results (Table 1) obtained by each method were found to be in good agreement.

Sample No.	Br (g/kg)		I (mg/kg)	
	IC	ICP-MS	ICP	ICP-MS
1	0.18	0.16	25	23
2	0.17	0.16	32	29
3	0.14	0.14	8.7	11
4	0.17	0.16	20	18
5	0.23	0.21	6.9	10
6	0.086	0.083	17	19
7	0.15	0.14	6.7	7.6
8	0.070	0.066	27	29

Table 1 Bromine and iodine concentrations in commercial iodized salt

Sample volume of iodized salt

Normally, a sample weighing 1.0 g was dissolved in 50 mL of TMAH solution. However, iodized salt incorporates a high concentration of iodine, specifically, about 30 mg/kg. When using ICP-MS, this concentration was too high to measure; the dynamic range was about 0.1 – 100 µg/L. Thus, the sample solution had to be diluted ten times. For efficiency, we reduced the size of the sample to 0.1 g. This was done to potentially worsen the representation of the sample. We compared the repeatability with a 1 g of sample diluted ten times, using a 0.1 g

Research Institute of salt and sea water science, The salt industry center of Japan, Yasushi Noda, Determination of bromine and iodine in salt with Inductively Coupled Plasma - Mass Spectrometry sample with no dilution. The results of Br and I tests were repeated 10 times, were 165 ± 3 mg/kg and 32 ± 2 mg/kg for the 1 g sample with dilution, and 165 ± 3 mg/kg and 30 ± 1 mg/kg for the 0.1 g of sample with no dilution. The t-test did not reveal any difference between the two. The Br and I were also subjected to a similar analysis employing both sampling approaches. Thus, a 0.1 g sample of iodized salt was placed in 50 mL of TMAH solution.

Application

Low-bromine salt

Typically, the bromide concentration in solar salt is about 100–200 mg/kg. This method aims to detect bromine in low-bromine salt, with a concentration of less than 20 mg/kg, which was the detection limit of ion chromatography with a UV detector (IC). We used reagent grade sodium chloride as the sample instead of low-bromine salt.

The three kinds of reagent grade sodium chloride (Table 2) were analyzed by ICP-MS and IC (the bromide ion peak was deemed to be due to the total bromine). The concentrations of bromine as measured by this ICP-MS method were also found to be in good agreement with the results obtained by the conventional IC method. In the case of sample No. 3, the bromine could not be detected by IC due to the use of an ultra pure reagent. With the ICP-MS analysis method, however, it proved possible to detect the bromine, with the result being 2.5 mg/kg.

No.	Maker	Name (grade)	Purity	Determined (mg/kg)	
				ICP-MS	IC
1	Sigma-Aldrich	Redi dry	99+	73	73
2	Wako pure chemicals	JIS Special	99.5+	35	31
3	Sigma-Aldrich	TraceCERT	99.999+	2.5	< 20

Table 2 Bromine concentrations in reagent grade sodium chloride

Results obtained for different types of salt

For practical applications, the validated method was successfully applied to the study of several salt samples. The results are listed in Table 3.

Nation		Production		Bromine		Iodine		Additives	
Crude salts	Mexico	Solar		92	mg/kg	ND			
	Australia	Solar		0.11	g/kg	ND			
		Solar		94	mg/kg	ND			
		Solar		0.11	g/kg	ND			
		Solar		94	mg/kg	ND			
		Lake		86	mg/kg	11	μg/kg		
	India	Solar		87	mg/kg	23	μg/kg		
		Solar		65	mg/kg	26	μg/kg		
		Solar		76	mg/kg	11	μg/kg		
		Solar		52	mg/kg	37	μg/kg		
Edible salts	Japan	Solar (Wet type)		0.42	g/kg	0.18	mg/kg	Bittern	
		Ion-exchange Membrane		0.33	g/kg	ND			
		Re-crystallized solar salt		28	mg/kg	ND		Basic Magnesium carbonate	
	China	Rock (Substitute)		1.6	g/kg	26	mg/kg	KIO ₃ , KCl, KFeCN	
		Rock		1.1	g/kg	25	mg/kg	KIO ₃ , KFeCN	
		Solar		0.14	g/kg	26	mg/kg	KIO ₃	
		Rock (Seaweed)		42	mg/kg	21	mg/kg	KI, KFeCN, seaweed liquid	

Table 3 Analytical results for Br and I in crude and edible salts as obtained by ICP-MS

ND: not detectable, below 5 μg/kg

KFeCN: potassium ferrocyanide

In solar salt, the bromine content was found to be about 100 mg/kg. This result is in good agreement with the results of conventional analysis using IC.

Iodine is used as a measure of the required degree of quality of the crude salt used for electrolysis in the soda chemical industry. Therefore, there is a need to check for even minute amounts of I in salt, that is, at the µg/kg level. Mexican and Australian solar salts were found to have similar levels of iodine, at levels close to the lower limit of quantitation. Indian solar salt had a detectable iodine content, despite the bromine concentration being lower than the samples from Mexico and Australia. Regardless of the origin, the iodine concentration was sufficiently low to allow the industrial use of the salt.

The samples of iodized salt listed in Table 1 had been in long-term storage; those listed in Table 3 had been in short-term storage of less than 1 month. In the case of the iodized salt, the iodine was decreased as time.

Conclusion

The ICP-MS method for detecting Br and I was developed to provide a simple and high sensitivity means of analyzing salt samples. The detection limits for Br and I, as obtained with this method, are low enough to enable the checking of many actual samples without the need for any complicated sample pretreatment. The use of thallium as an internal standard is effective for correcting the matrix effect on ionization in an alkaline solution in ICP-MS. This technique is fast and easy, and can detect not only low level concentrations of Br and I, but also high level I concentrations such as those in iodized salt.

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