WORLD SALT SYMPOSIUM
June 19-21, 2018 Park City UT, USA

Determination of Bromine and Iodine Content of Salt using Inductively Coupled Plasma - Mass Spectrometry

Research Institute of Salt and Sea Water Science,
The Salt Industry Center of Japan

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Research Institute of Salt and Sea Water Science

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Introduction

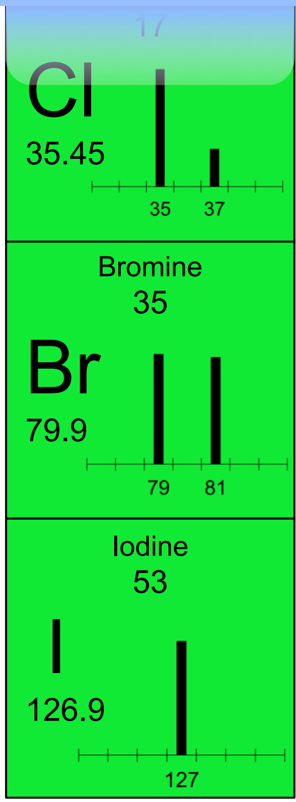
Salt includes bromine and iodine impurities as chloride.

Approximate bromine and iodine contents

	Bromine	Iodine
Solar salt	100 mg/kg	20 μg/kg
Rock salt	200 mg/kg	20 μg/kg
Ion-exchange membrane salt *	500 mg/kg	<10 μg/kg
Seawater	60 mg/kg	30 μg/kg

*In Japan, edible salt is produced using a method based on an ion-exchange membrane. With this method, seawater is concentrated by electro-dialysis that uses an ion-exchange membrane, and then the obtained brine is crystallized. The use of the ion-exchange membrane causes bromide to be concentrated in the brine.

Introduction



Bromine

Bromide is usually measured by ion-chromatography (IC).
The limit of quantitation by IC is
15 mg/kg (Eusalt/AS 018-2005), 20 mg/kg (SIC-Japan).
A reagent salt is used with the IC method for matrix matching.
So, what is the bromine concentration in the reagent sodium chloride?

Iodine

Iodine is usually measured by ICP-AES with the reduced iodate to iodide using sodium sulfide. These methods have been developed to estimate the iodine levels in iodized edible salt. The limit of quantitation by ICP is about 5 mg/kg level.

The determination of trace iodine in salt is important to ensuring the quality of soda chemicals, and so on.

The following presents a simple procedure for the determination of bromine and iodine in salt with ICP-MS.

Materials and Methods

Salt sample 1.0 g †

† : Iodized salt sample 0.1 g

← 10 % tetramethyl ammonium hydroxide 5 mL

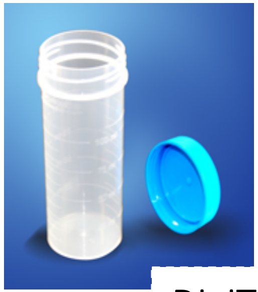
← 10 mg/L thallium solution 0.5 mL

↓

Dissolved 50 mL of water

↓

ICP-MS



DigiTUBES

ICP-MS (Agilent 7900)

Plasma incident power: 1600 W
Flow rate of argon
as carrier gas: 0.92 L/min
as dilution gas: 0.20 L/min
Torch sampling depth: 9 mm
Monitoring ion: m/z: 79 for Br, 127 for I, 205 for Tl

Lower limit of quantitation
Br 50 μg/kg
I 5 μg/kg

ICP-MS conditions

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Typical available forms of bromine & iodine in salt

Bromine	Bromide	Br^-
	Bromate	$BrO3^-$
Iodine	Iodide	I^-
	Iodate	$IO3^-$

Into plasma

Ionization

Detected

m/z:79 (81) Br^+

m/z:127 I^+

ICP-MS signal intensity ratios

	Bromide/Bromate		Iodide/Iodate
1 μmol/L	1.01 ± 0.01	1 μmol/L	1.01 ± 0.01
10 μmol/L	0.99 ± 0.01	10 μmol/L	0.99 ± 0.01

ICP-MS detected without distinction of forms and achieved stable quantitation.

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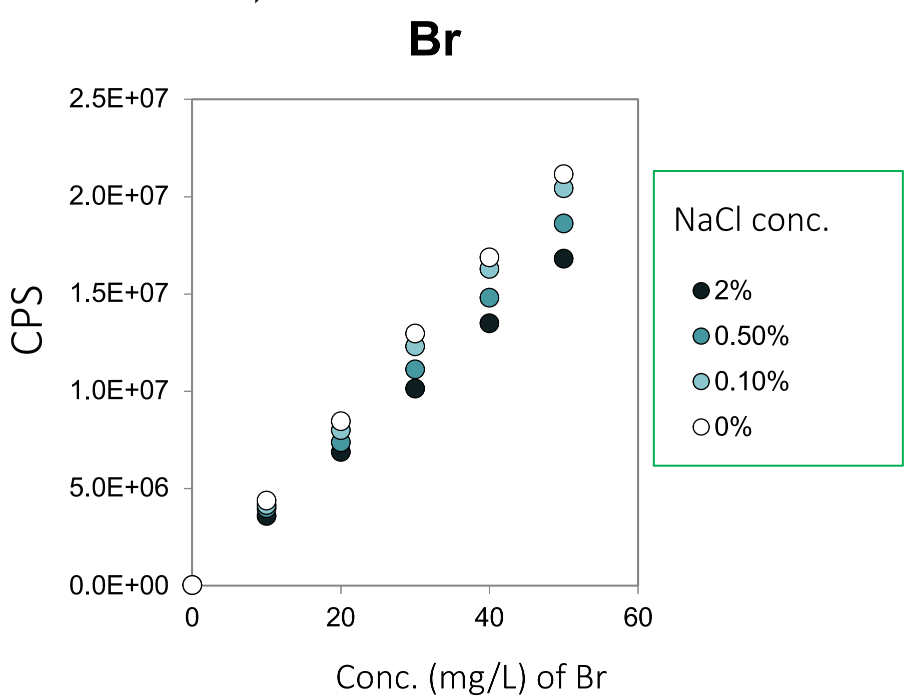
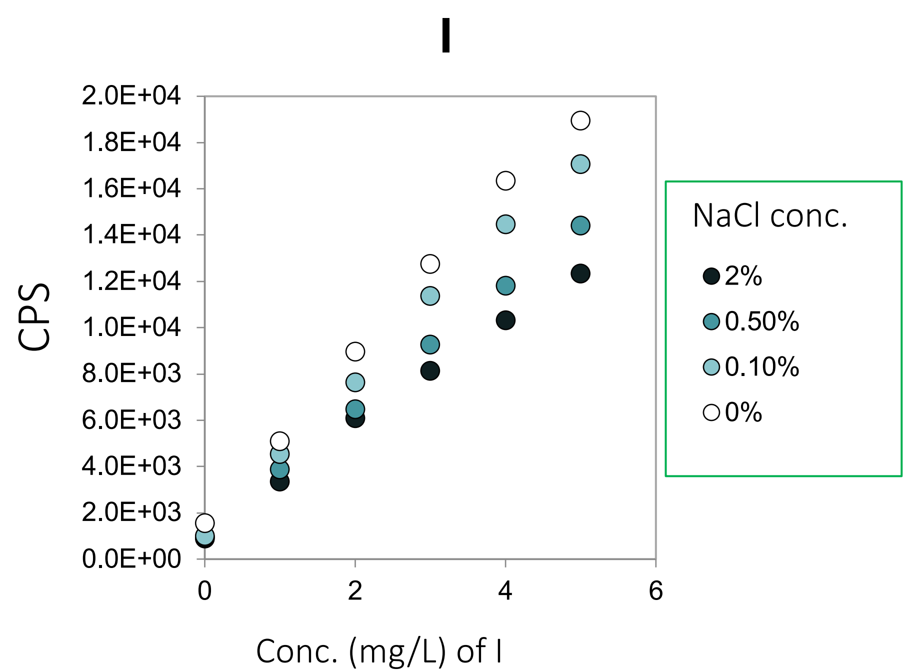
Matrix effects

NaCl concentration has a profound effect on the signal intensity of ICP-MS.

⇨ Should be matrix match and internal standard calibration





Working curves of Br and I with some NaCl concentration in matrix.

ICP-MS conditions

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Matrix effects **Internal standards select**

- Sc, Ru, Rh, Tb, and Ho are rare metals that are not expected to be found in salt.
- Y, yttrium is frequently used, but it would precipitate in an alkaline solution.
- Ga, Ge, In, Tl, and Te are representative elements, that can exist as ions in an alkaline solution.
- Te is frequently used as an internal standard for I.

⇨ <u>All the elements, except In</u>, could be used for an internal standard.

In is not stable in a TMAH solution.

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg							
Lantanoid			La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinoid			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

ICP-MS conditions

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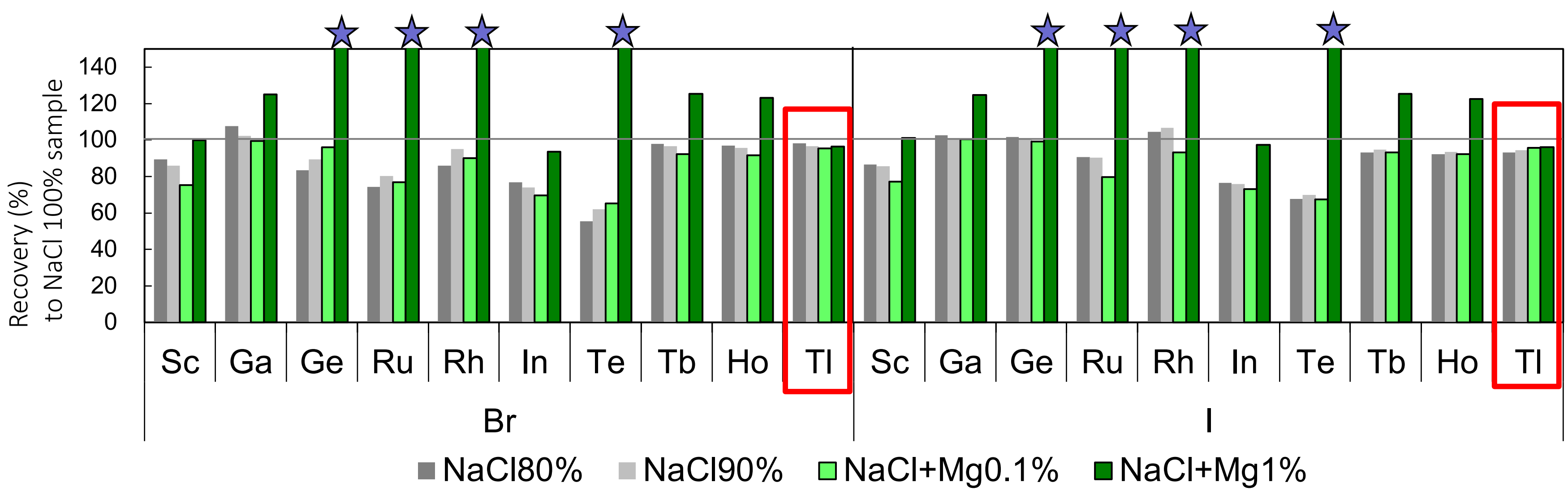
Matrix effects

Internal standards select

All the elements could be used as an internal standard for high-purity salt (100%)

Other matrix effects: Purity of sample salt and impurity elements (K, Mg, Ca)

K and Ca had no effect on the quantitation.
Purity was effected little, and Mg had the greatest effect except Tl.



Recoveries of ratios of bromine or iodine determined by internal standards with NaCl 100%
Here, # indicates a recovery of more than 150%

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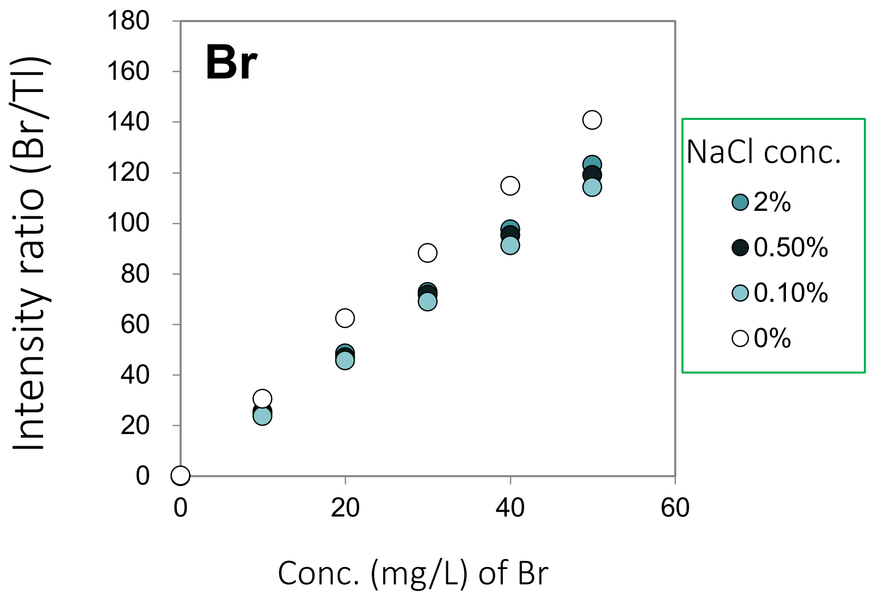
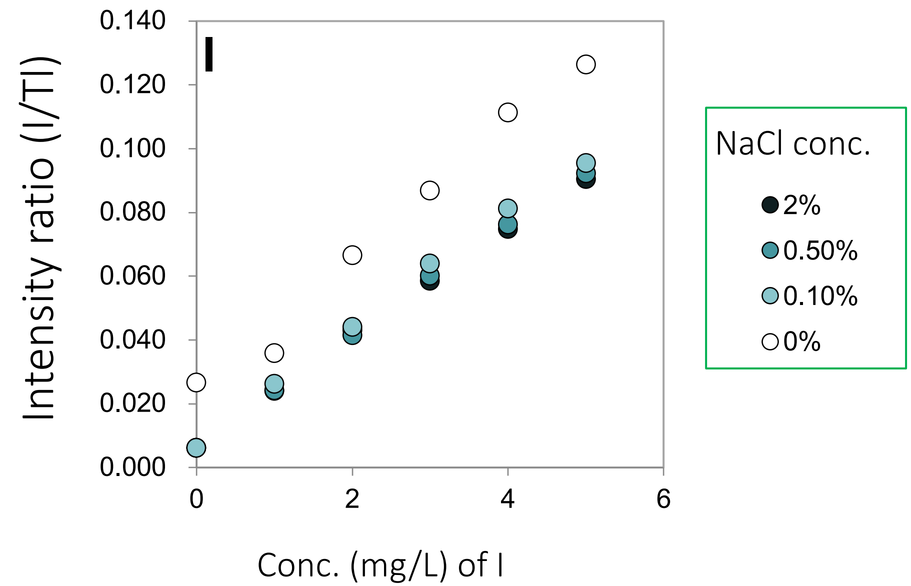
Matrix effects

Could internal standard calibration be reduced to tolerable levels?

Matrix match calibration was needed.

In the case of the no-salt matrix, the slope of the working curve was markedly elevated.





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

ICP-MS conditions

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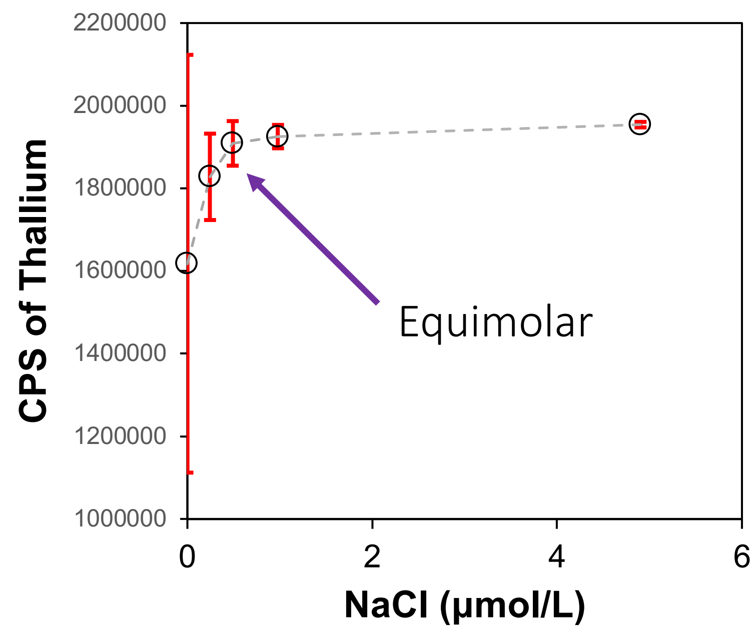
Matrix effects

Thallium exhibited a similar behavior to Br and I in ICP-MS.
In water, however, without the NaCl solution, Tl exhibits a different behavior.

When the Na^+ or Cl^- concentrations were lower than that of Tl, the intensity of the Tl was observed to decrease.

This phenomenon has not yet been solved.



Change in Tl (0.49 μmol/L) intensity with NaCl concentration

Validation

Upper limit of quantitation was about 50 mg/kg for I.
Iodized salt should be diluted or the sample amount decreased.

t-test

Sample; iodized salt made in the UK

Method;

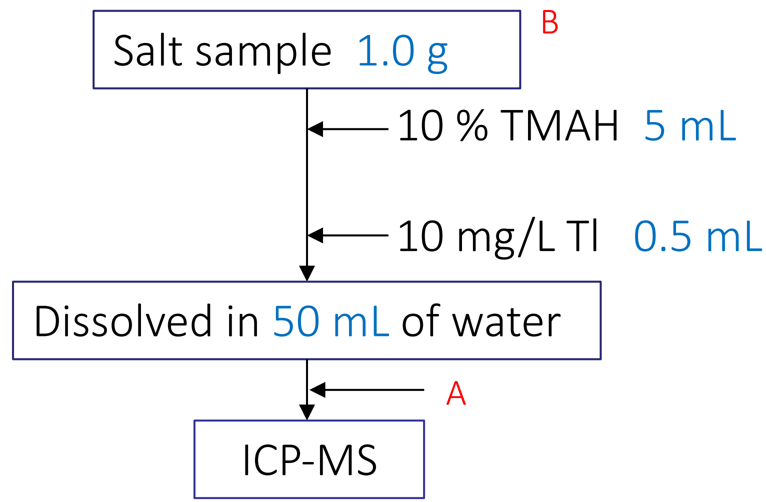
A: Diluted 10 times in water

B: Iodized salt sample change to 0.1 g

Each test, n = 10

Result (mg/kg)

Methods	Br	I
A	165 ± 3	32 ± 2
B	165 ± 3	30 ± 1



The t-test did not reveal any difference between the two.
We selected method B.

Validation

Sample: Iodized salt made in the UK

Test of significance (mg/kg) n = 6

Methods		Br	I
Proposed	ICP-MS	166 ± 1	31 ± 2
Conventional	IC	163 ± 5	
	ICP-AES		29 ± 2

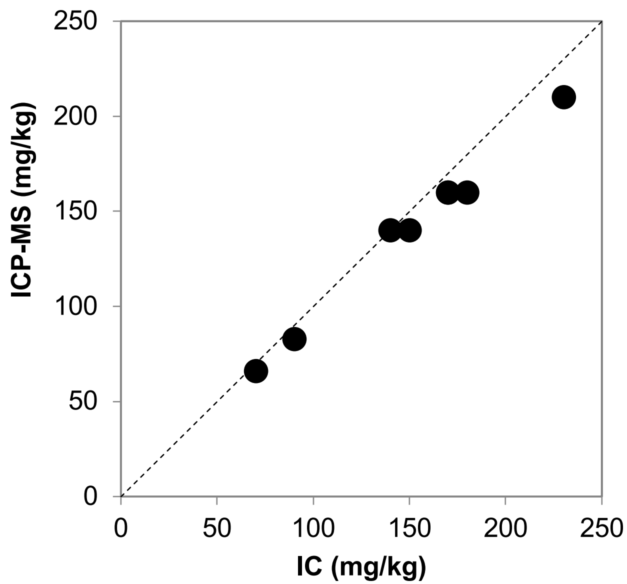
Confidence level (95%)
Not statistically significant

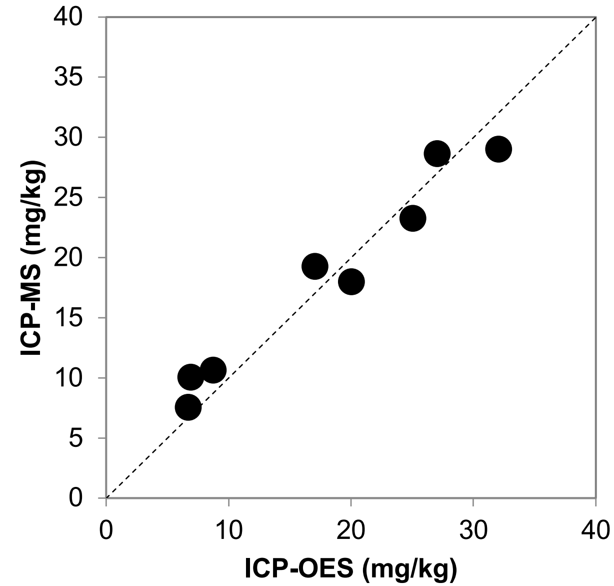
Bromine and iodine concentrations in the commercial iodized salt

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

Good agreement

Validation





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Good agreement

Bromine

Bromine concentrations in reagent grade NaCl were determined by proposed method and conventional method, IC.

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

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Every crude salt has a sufficiently low level of iodine for the soda chemical industry.
In edible salts, the bromine content may increase as a result of the presence of additives.

Results for Br and I in crude and edible salts as obtained by ICP-MS

	Nation	Production	Bromine		Iodine		Additives
Crude salts	Mexico	Solar	0.092	g/kg	ND		
Crude salts	Australia	Solar	0.11	g/kg	ND		
Crude salts	Australia	Solar	0.094	g/kg	ND		
Crude salts	Australia	Solar	0.11	g/kg	ND		
Crude salts	Australia	Solar	0.094	g/kg	ND		
Crude salts	Australia	Lake	0.086	g/kg	11	µg/kg	
Crude salts	India	Solar	0.087	g/kg	23	µg/kg	
Crude salts	India	Solar	0.065	g/kg	26	µg/kg	
Crude salts	India	Solar	0.076	g/kg	11	µg/kg	
Crude salts	India	Solar	0.052	g/kg	37	µg/kg	
Edible salts	Japan	Solar (Wet type)	0.42	g/kg	180	µg/kg	Bittern
Edible salts	Japan	Ion-exchange Membrane	0.33	g/kg	ND		
Edible salts	Japan	Re-crystallized solar salt	0.028	g/kg	ND		Basic magnesium carbonate
Edible salts	China	Rock (Substitute)	1.6	g/kg	26	mg/kg	KIO_3, KCl, YPS
Edible salts	China	Rock	1.1	g/kg	25	mg/kg	KIO_3, YPS
Edible salts	China	Solar	0.14	g/kg	26	mg/kg	KIO_3
Edible salts	China	Rock (Seaweed)	0.042	g/kg	21	mg/kg	KI, YPS, seaweed liquid

ND: Not detectable, below 5 µg/kg

Conclusion

The ICP-MS method for detecting Br and I was developed to provide a simple and highly sensitive 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 an effective means of 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 bromine and iodine, but also high level iodine concentrations such as those in iodized salt.