広島大学学位論文

Development of Tungsten Boat Furnace Electrothermal Vaporisation-Inductively Coupled Plasma Atomic Emission and Mass Spectrometric Method for the Determination of Non-metal Elements

（非金属元素の定量のためのタングステン炉
電気加熱気化－誘導結合プラズマ原子発光
分光分析法および質量分析法の開発）

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化学専攻

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目次

１．主論文

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２．公表論文

(1) Sensitive Determination of Iodine by Tungsten Boat Furnace Vaporization with Inductively Coupled Plasma Mass Spectrometry Using Tetramethylammonium Hydroxide as a Chemical Modifier.

Yasuaki Okamoto, Hiroko Kataoka, Chie Konishi, Terufumi Fujiwara and Kazuaki Ito

Rapid Communications in Mass Spectrometry, **18**, 2351-2353 (2004).

(2) Sequential Determination of Boric Acid and Boron Nitride by Electrothermal Vaporisation Inductively Coupled Plasma Atomic Spectrometry.

Yasuaki Okamoto, Hiroko Kataoka, Satoshi Tsukahara and Terufumi Fujiwara

Journal of Analytical Atomic Spectrometry, **20**, 383-384 (2005).

(3) Separate Vaporisation of Boric Acid and Inorganic Boron from Tungsten Sample Cuvette-Tungsten Boat Furnace Followed by the Detection of Boron Species by Inductively Coupled Plasma Mass Spectrometry and Atomic Emission Spectrometry (ICP-MS and ICP-AES).

Hiroko Kataoka, Yasuaki Okamoto, Satoshi Tsukahara, Terufumi Fujiwara and Kazuaki Ito

Analytica Chimica Acta, **610**, 179-185 (2008).

(4) Sensitive Determination of Bromine and Iodine in Aqueous and Biological Samples by Electrothermal Vaporization Inductively Coupled Plasma Mass Spectrometry Using Tetramethylammonium Hydroxide as a Chemical Modifier.

Hiroko Kataoka, Sachiko Tanaka, Chie Konishi, Yasuaki Okamoto, Terufumi Fujiwara and Kazuaki Ito

Rapid Communications in Mass Spectrometry, **22**, 1792-1798 (2008).

(5) Magnetic Drop-In Tungsten Boat Furnace Vaporisation Inductively Coupled Plasma Atomic Emission Spectrometry (MDI-TBF-ICP-AES) for the Direct Solid Sampling of Iron and Steel

Hiroko Kataoka, Yasuaki Okamoto, Takaya Matsushita, Satoshi Tsukahara, Terufumi Fujiwara and Kazuaki Wagatsuma

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(1) Determination of Iron in Calcium-Rich Samples by Tungsten Boat Furnace Vaporization with Inductively Coupled Plasma Mass Spectrometry Using Calcium(II) Ion as a Chemical Modifier.

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(2) Direct Determination of Zinc in Steel Samples by Electrothermal Vaporization Inductively Coupled Plasma Atomic Emission Spectrometry.

Yasuaki Okamoto, Takaya Matsushita, Hiroko Kataoka, Satoshi Tsukahara and Terufumi Fujiwara

Applied Spectroscopy, **60**, 339-342 (2006).

主 論 文

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CONTENTS

1 INTRODUCTION

Atomic spectrochemistry, or simply atomic spectrometry, was created in 1860 by the famous scientists, R. Bunsen and G. Kirchhoff. In the atomic spectroscopist's bible, "Die Spectren der Alkalien und alkalischen Erden, (*Fresenius' Zeitchrift für Analytische Chemie*, **1**, 1-2, published in 1862), they colour-illustrated the line spectra of alkali and alkaline earth metals. [1] They used a chemical flame as an excitation or emission source. The flame is nowadays called "bunsen burner" as a common noun and is conveniently used in a beginners chemical experiment. Afterwards, a numerous number of improvement has been performed in order to detect elements more sensitively, more rapidly, more exactly, more conveniently, more and more...

Concerning the excitation source of analyte, inductively coupled plasma (ICP) developed by V. A. Fassel and S. Greenfield is the most sophisticated atomic emission source. [2,3] The meaning of the plasma is in this case gas-phase ions, that is made by an electrical discharge of argon under the atmospheric pressure. Inductively coupled plasma atomic emission spectrometry (ICP-AES) has various excellent features compared to the traditional flame-AES, and those include as follows: (1) Almost all the metal elements can be determined with wider calibration ranges. (2) The discharges are very stable, e.g. higher robustness, less drift. (3) Few background emissions are observed in the wider wavelength range. And (4) as the results, obtained detection limits for metal ions are superior. The most remarkable feature of ICP-AES is its robustness, since among a numerous number of emits only a selected light passes through the spectrometer and reaches a photomultiplier detector. Therefore, there is no damage to the detector even if samples contain a large amount of impurities or have a high matrix component. As an extreme case, aqueous samples contain a large amount of salts can be analysed by the

ICP-AES. An alternative feature of the ICP is that not only excited neutral atoms but also ionised atoms (atomic ions) are formed in the argon plasma, since the plasma temperature is excellently high (approximately, 8000 K, [4]). Focussing on the feature, R. S. Houk, V. A. Fassel and coworkers established the ICP mass spectrometry (ICP-MS). [5] In ICP-MS, the plasma is used as an ionisation source. Therefore, easily ionisable elements, e.g. metal elements, form their respective singly charged atomic ions. The detectability of ICP-MS is superior to that of ICP-AES. However, during the measurement operations by ICP-MS, there are the deterioration of the detector, etc. Co-existing materials cause other damages. The damages include deterioration of the detector, deposition on the surface of ion optics, clogging of orifices of sampling cone and skimmer, etc. Therefore, analysable samples are limited in the ICP-MS. Taking advantages of each method, both ICP-AES and ICP-MS are utilised for the trace element determination, depending on the properties of samples and the concentrations of analytes to be determined

Regarding the sample properties, solution samples, more preferably aqueous solution samples are suitable for ICP-AES and ICP-MS measurements because a nebuliser is commonly used to introduce sample solutions into the plasma. However, its sample introduction efficiency is not sufficient. According to Sharp, [6,7] pneumatic nebulisation allows approximately 3-12% of the nebulised solution to actually reach the plasma, and the value is further decreased with any increase in viscosity or salt-content of the solution. Moreover not only the analyte but also a mist of water spray are introduced into the plasma. The accompanying water reduces the plasma temperature. The lower the temperature, the lower the both efficiencies of excitation and ionisation. As the result, poorer detection limits are obtained for both spectrometries. The electrothermal vaporisation (ETV) techniques were used as the alternative sample introduction method. The advantages of the ETV are usually higher introduce efficiency of analytes, higher sensitivity and lower sample consumption compared to the nebulisation of sample solutions. [8-10] According to the literature, [8,9,11-14] for the determination of metal elements, the transport efficiency of ETV was 10-76%, while the efficiency of pneumatic nebulisation was 1-2%. [9] Moreover, the efficiency of ETV is increased to 40-100% by applying chemical modification techniques, which include that palladium, sodium chloride, etc. [14] are added to the sample prior to the vaporisation or that small quantities of gaseous carbon tetrachloride [11] or trifluoromethane [9] are mixed into a carrier gas stream. The function of the modifiers are to suppress the deposition of analytes at the inside surface of a furnace, a tube and a torch, and to facilitate the introduction by forming more or less volatile components and enough smaller particles that will decompose easily in the plasma. [9,11,13,15] As for the sample pretreatment, there are the possibilities of direct analysis of solid samples. [8,9,16] As a result, the time saving for sample pretreatment, the reduction of the risk of contamination and the avoidance of hazardous reagents are achieved which are difficult in the nebuliser system. [9,10] Because of the separate vaporisation and introduction of the analyte and matrix, physical and spectral interference are reduced.

In the commonly used ETV procedure, chemical modification techniques have been applied. The atomic spectrometry with the ETV can determine not only metal elements but also semi-metal and non-metal elements at low concentrations. Especially, for elements with high ionisation potentials, more efficient ionisation is achieved with an ETV system. The improved sensitivity can be attributed to both the high introduction efficiency and the elimination of the accompanying water mist. However, in the ETV application, there is a problem that the species of non-metal elements are fairly volatile. To prevent losses of such analytes during a drying stage, it is necessary to add suitable chemical modifier(s) to the sample solution in order to retain the analyte on the furnace prior to the vaporisation step. In this thesis, by applying the proposed chemical modification techniques, sensitive and selective determination of non-metal elements such as halogens, boron, sulphur, selenium and antimony by ETV-ICP-MS and ETV-ICP-AES is developed.

2 EXPERIMENTAL

2.1 Apparatus

A Seiko II (Chiba, Japan) Model SPQ9000 ICP mass spectrometer incorporating a Seiko II Model EV-300 metal furnace vaporiser unit and a Seiko II Model SPS4000 ICP atomic emission spectrometer, attached to a Seiko II SAS-705V metal furnace atomiser unit, were used. Electric currents to the two vaporiser heads were supplied with the vaporiser unit and the atomiser unit, respectively. Regarding temporary signal acquisitions for the ETV technique using this ICP mass spectrometer, up to 20 atomic ions or atomic mass/charge values were simultaneously measurable. By means of an MS-Windows workstation attached, a maximum ion count (peak height) and/or an integrated ion intensity (peak area) could be estimated for each element ion. On the other hand, the ICP atomic emission spectrometer incorporated two radial-view monochromators, by which two analytical elements or wavelengths could be measured simultaneously. The correction of background emission was accomplished by using an oscillating quartz refractor plate, with which the spectrometer was equipped. The pressure inside the spectrometer housing was maintained at 50 Pa or better by evacuating with a rotary vacuum pump throughout.

A Seiko II Model EV-300 metal furnace vaporiser combined with ICP-MS was used after modification. The modified parts were as follows: Both the autosampler device and the vaporiser head unit equipped with a TBF (small-type, 6 mm × 70 mm) were removed. Instead of the vaporiser head, an atomiser head of a Seiko II Model SAS-705V was newly attached to be used in combination with the ICP mass spectrometer. The atomiser head had originally been developed for electrothermal atomic absorption spectrometry (AAS). The furnace electrodes and a TBF (large U-type, 10 mm × 60 mm) were covered with a handmade glass dome (78 mm i.d., 50 mm high) instead of a quartz window holder for AAS. The sample introduction port was closed with a silicone rubber stopper. Another SAS-705V atomiser head of ICP atomic spectrometer was modified in the similar manner. Poly(tetrafluoroethylene) (PTFE) tubes (4 mm i.d. × 50 cm long) were used for connecting the ICP torches of the mass or atomic emission spectrometer with each outlet port of the atomiser heads. Details of the TBF and the head of the vaporiser are illustrated in Fig. 1.

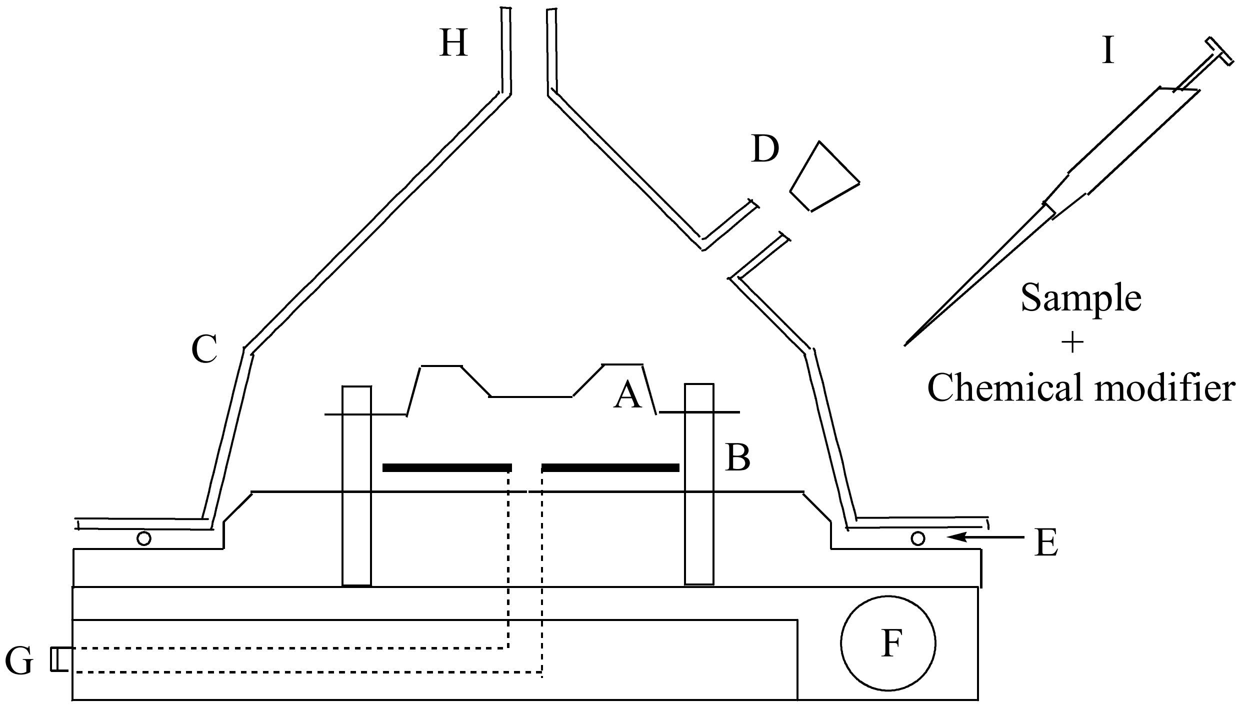

Figure 1. Schematic diagram of the apparatus and experimental procedure. A, tungsten boat furnace; B, furnace electrode; C, glass dome; D, silicone rubber stopper; E, O-ring; F, electric terminal; G, argon carrier gas inlet port; H, outlet port to ICP; I, digital micropipette.

In section 3.2 and 3.3, the small sample cuvettes (10 mm × 20 mm) were shaped by cutting both edges of the tungsten boats. The cuvettes were used as sampling dishes, sample carriers, crucibles for fusion and furnaces for electrothermal vaporisation. If necessary, up to 100 μL of an aqueous sample solution could be placed into each cuvette.

Gilson Medical Electronics (Villiers-le-Bel, France) Model Pipetman P-200 and Model Microman M-25 digital pipettes were used for standards and reagent injections, respectively.

2.2 Reagents

In section 3.1, an iodate(V) standard stock solution was prepared by dissolving 3.3726 g of potassium iodate (analytical reagent grade, purchased from Sigma-Aldrich Japan, Tokyo, Japan) in deionised water and making up the solution to 100 mL with the water. The resulting solution has a concentration of 20.000 g L^{-1} iodine. For comparison of sensitivities, an aqueous iodide solution was prepared by dissolving ammonium iodide (Sigma-Aldrich Japan) in the same manner. Standard solutions of bromate(V) and bromide were prepared by dissolving potassium bromate (Sigma-Aldrich Japan) and ammonium bromide (Nacalai Tesque, Kyoto, Japan), respectively. Working solutions were freshly prepared by dilution of the stock standards or previously diluted solutions with water. The extra-pure grade tetramethylammonium hydroxide (TMAH, 25% aqueous solution, Tama Chemical, Tokyo, Japan) and the Suprapur-grade ammonium dihydrogenphosphate (Merck, Darmstadt, Germany) were used as a chemical modifier and a masking reagent, respectively. The ammonium dihydrogenphosphate 1.2112 g was dissolved with 500 mL water. 1 mL of the ammonium dihydrogenphosphate aqueous solution and 40 mL of the 25% TMAH were mixed and made the volume to 50 mL with water in a PFA bottle. The resulting concentrations of TMAH and phosphate were 20% and 40 mg L^{-1}, respectively.

In section 3.2, standard solutions of boric acid were prepared by diluting the Certipur-grade 1000 mg L^{-1} boron(III) stock solution (Merck) with water. Sodium tetraborate (Aldrich Chemical, Milwaukee, USA) and sodium metaborate tetrahydrate (Aldrich Chemical) were dissolved and diluted with water, respectively. An aqueous slurry solution of boron nitride was prepared by suspending 1.1478 mg of boron nitride (Merck) with 50 mL of water in a 50-mL quartz vessel with a quartz plug. The resulting solution has a concentration of 10 mg L^{-1} boron(III). Slurry solutions of chromium boride (Strem Chemicals, Newburyport, USA) and boron carbide (Mitsuwa's Pure Chemicals, Osaka, Japan) were prepared in the same manner, respectively. On sampling, these slurry solutions were stirred continuously with a magnetic stirrer and a stirring bar made from quartz glass. The extra-pure grade 25% TMAH aqueous solution and a 2.5% sodium hydroxide solution were used as chemical modifiers. The latter solution was prepared by dissolving 1.813 g of the sodium hydroxide monohydrate (Suprapur-grade, Merck) in 50 g water. For the analysis of steel samples, a 15% aqueous solution of ammonium dihydrogenphosphate (Merck) was used as a masking reagent.

In section 3.3, for the construction of the calibration curve, standard iron plates were used instead of the sample piece(s). The plates were prepared according to the literature [17] by using standard solutions diluted with diluted nitric acid from the stock solution of iron (1000 mg L^{-1}, Certipur-grade, Merck). Briefly, an aliquot of the standard solutions was placed on each pure iron plate (99.998%, 0.075 mm thick and 3.2 mm o.d., Nilaco, Tokyo, Japan). These plates were dried on a hot plate kept at 80ºC prior to the measurement.

Biological certified reference materials were purchased from the NIST (National Institute of Standards and Technology, US Department of Commerce) and the NIES (National Institute for Environmental Studies of Japan, Ibaraki, Japan). A pair of Standard River Water standards JAC0031 and JAC0032, were purchased from the Japan Society for Analytical Chemistry

(JSAC, Tokyo, Japan). Steel certified reference materials were purchased from the NIST and the ISIJ (Iron and Steel Institute of Japan, Tokyo, Japan).

2.3 Conventional ETV Procedure Followed by the Detection with ICP-AES and ICP-MS

For the conventional routine analysis using ETV, an aliquot of the chemical modifier solution and an aqueous sample solution were pipetted directly into the depression of TBF and the TBF was then warmed gently at a relatively low temperature to expel the solvent. During the drying stage, the sample insertion port was left open to allow the moisture to escape from the TBF. After the TBF had dried completely, the port was closed with a silicone rubber stopper. The temperature was gradually ramped and maintained at an ashing temperature to pyrolyse the dried matrix. Then the temperature rose up and set to the suitable vaporisation temperature to generate a transient cloud of the analyte vapour. The vapour was transported to the ICP spectrometer by a carrier gas stream of argon through Teflon (PTFE) tubing. The transient signals were recorded and the peak areas were estimated.

2.4 Sample Preparation

The biological sample was prepared by alkali-digestion with TMAH. Briefly, in this experiment, approximately 200-400 mg of the powdered sample were weighed into a PFA vessel and 3 mL of the 25% TMAH solution was placed. Then the vessel was closed tightly, and set in a double-vessel digestion bomb whose interior was sealed with PTFE. The vessel was heated at 90ºC for a suitable period (typically 1 h) in an air oven. After cooling to room temperature, the contents were diluted without filtration and/or centrifugation by adding water as required.

The steel sample could not dissolve with TMAH, therefore it was digested by using hydrochloric acid. Approximate 100-200 mg aliquot of the steel sample and 3 mL hydrochloric acid were put into the PFA vessel and it was set in the double-digestion bomb. After heating at 90ºC overnight, the digested contents were diluted with water as required.

3 RESULTS AND DISCUSSION

3.1 Determination of Halogens

By using ICP-AES and ICP-MS, sufficient analytical performances can be achieved for the determination of metal, semi-metal and even for some of the non-metal elements. However, these atomic spectrometries have not been used commonly for the determination of halogens. Because of the high excitation and ionisation potentials, extremely poor sensitivities have been obtained for the determination of halogens by ICP-AES and ICP-MS. The sensitive and simultaneous determination of all halogens (iodine, bromine, chlorine and fluorine) was tried by using the advantages of TBF, that are the high introduction efficiency and the high plasma temperature due to the elimination of the accompanying water mist. As for the practical applications, the determinations of halogens in aqueous samples, salts and biological samples were carried out.

3.1.1 Analytical procedures for the determination of bromine and iodine

A 4 µL aliquot of the TMAH solution and up to 95 µL of an aqueous sample solution were pipetted in the TBF. The TBF was then heated for 30 s at 150ºC to expel the solvent through the open sample insertion port. After the sample was dried completely, the insertion port was closed with a silicone rubber stopper and the TBF was maintained at 180ºC for 30 s to pyrolyse the dried matrix. The temperature was raised to 1400ºC with a ramp time of 8 s and a hold time of 15 s for vaporisation. The generated analyte vapour, probably the TMA salt of each halide, was introduced into the plasma ion source by the argon carrier gas stream. The integrated ion intensities (peak areas) of $^{19}F^+$, $^{35}Cl^+$, $^{79}Br^+$, $^{81}Br^+$ and $^{127}I^+$ were measured. When the sample included a lot of metal ions and/or contained a complex matrix, the TBF temperature was taken up to 2000ºC for 5 s to clean-up the surface of TBF. The recommended operating conditions are summarised in Table 1.

Table 1. Instrument operation conditions for the determination of bromine and iodine

ICP mass spectrometer (Seiko II SPQ9000)	
R.F. incident power	1.2 kW
Measuring mode	Peak hopping
Analytical mass number	79, 81 and 127
Dwell time	33 ms
Sampling depth	11 mm
Plasma argon gas	16 L min^{-1}
Auxiliary argon gas	1.0 L min^{-1}
Lenses	Tune on ^{204}Hg (vapour)
Integration time	10 s
Tungsten boat furnace vaporiser (Seiko II EV-300)	
Sample injection	~95 µL
Modifier injection	
$(CH_3)_4NOH$ (TMAH)	1.0 mg
$NH_4H_2PO_4$	240 ng
Drying	150ºC for 30 s (ramp 10 s)
Ashing	180ºC for 30 s (ramp 10 s)
Vaporisation	1400ºC for 15 s (ramp 8 s)
Carrier gas flow rate	
Argon gas	0.85 L min^{-1}
Hydrogen gas	0.03 L min^{-1}

3.1.2 Evaluation of standards

To prepare the standard solutions of iodine, potassium iodide has been used. [18-20] However, the iodide solutions turned yellow with time, and this could not be prevented even on storage in a dark cool place. On the contrary, potassium iodate solutions do not have this problem. Since the iodate ion is easily reduced to the iodide ion by the TMAH added as a chemical modifier, the iodate ion showed similar vaporisation properties, identical peak profiles and essentially the same sensitivity. Moreover, crystalline potassium iodate is more stable and highly pure. It is also preferable for the more accurate weighing operation since potassium iodate has a larger gravimetric factor. Therefore, as Okamoto et al. [21] and Resano et al. [22] reported previously, standard solutions were prepared with potassium iodate. For the similar reasons, potassium bromate is adopted as standards throughout, though no change in colour of the bromide solutions was observed. Regarding the standard solutions of chlorine and fluorine, potassium chloride and ammonium fluoride were used to prepare the respective standard solutions.

3.1.3 Optimisation for the determination

It is well known that hydrogen halide and halogen molecules are fairly volatile. Therefore, even in the traditional wet sample preparation procedure, it is necessary to prevent the loss of analytes. For this reason, the wet-digestion procedure had to be carried out using closed vessels or high-pressure bombs. [23] Especially, in the case of fluorine, the fluoride ion was often distilled or expelled from aqueous solutions as hexafluorosilicic acid or hydrofluoric acid under strongly acidic conditions. In the ETV procedure, it is necessary to add some chemical modifier(s) to retain the analytes during the drying and ashing processes. However, the application of acids and oxidative reagents is not preferred, since a TBF is not a closed and pressure-tight system. Under the TBF system without any modifiers, the analytes would vaporise and cause a loss prior to their introduction into the ICP. Resano and co-workers [22] examined various kinds of palladium species as the chemical modifier in order to retain the analyte iodide. The use of a large excess amount of metal hydroxides and/or metal salts should be avoided in atomic spectrometry. During the measurement, there is the deterioration of the detector, etc. Co-existing materials cause other damages. The damages include deterioration of the detector, deposition on the surface of ion optics, clogging of orifices of sampling cone and skimmer, etc. Therefore, in this work, TMAH was applied as a suitable modifier to retain all the halide ions on the surface of the TBF during the drying and ashing processes. TMAH is sufficiently strongly basic to form thermally stable TMA salts with halide ions. Especially, it is the most remarkable advantage that an excess amount of the reagent could be decomposed and expelled as methanol and trimethylamine from the TBF device during the drying procedure. As shown in Fig. 2, for the determination of halogens, 1.0 mg of TMAH was sufficient to form the halide salts with the TMA ion and to retain them until the vaporisation stage. The added amount corresponds to a 4.0 μL injection of the commercially available 25% TMAH aqueous solution.

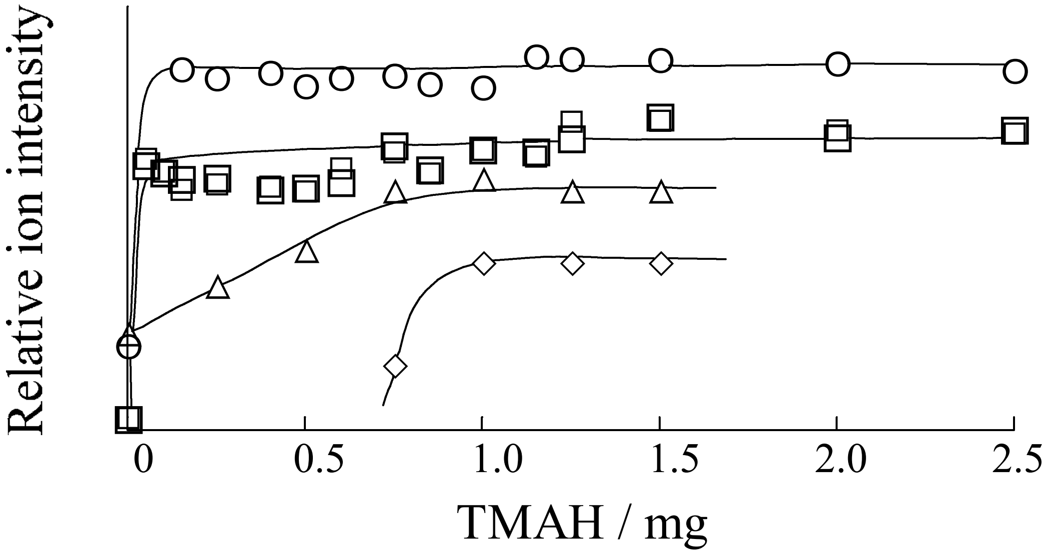

Figure 2. Effect of tetramethylammonium hydroxide (TMAH) amount on the ion intensities of halogens.

F^-, 0.1 mg; Cl^-, 10 ng; Br(V), 2.0 ng; I(V), 500 pg; drying, 150℃ for 30 s (ramp 10 s); ashing, 180℃ for 30 s (ramp 10 s); vaporisation, 1400℃ for 15 s (ramp 8 s); flow rate of carrier gas, 0.85 dm^3 min^{-1}; $NH_4H_2PO_4$, 240 ng.

◇: ^{19}F; △: ^{35}Cl; □ : ^{79}Br; □ : ^{81}Br; ○: ^{127}I.

The effects of ashing and vaporisation temperatures on the ion intensities of bromine and iodine were examined, and the results are shown in Fig. 3 and 4, respectively. The analytes added as bromate(V) and iodate(V) were retained completely on the surface of the furnace up to approximately 200ºC and a large portion of the halogens vaporised at a temperature higher than 400ºC. The presence of ammonium dihydrogenphosphate as a masking reagent did not affect the optimum vaporisation temperatures and the sensitivities of both bromine and iodine. The optimised ashing and vaporisation temperatures were 180ºC and 1400ºC, respectively. Figure 5 shows the peak profiles of bromine and iodine under the optimised conditions.

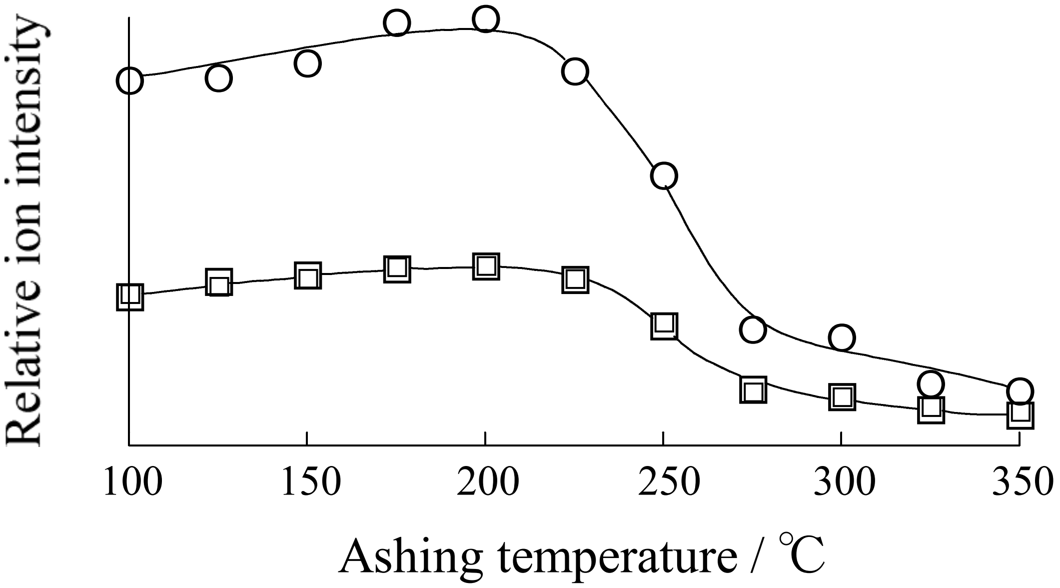

Figure 3. Effect of ashing temperature on the ion intensities of iodine and bromine.

I(V), 500 pg; Br(V), 2.0 ng; drying, 150℃ for 30 s (ramp 10 s); vaporisation, 1400℃ for 15 s (ramp 8 s); flow rate of carrier gas, 0.85 dm^3 min^{-1}; TMAH, 1.0 mg; $NH_4H_2PO_4$, 240 ng.

○, ^{127}I; □ , ^{79}Br; □ , ^{81}Br.

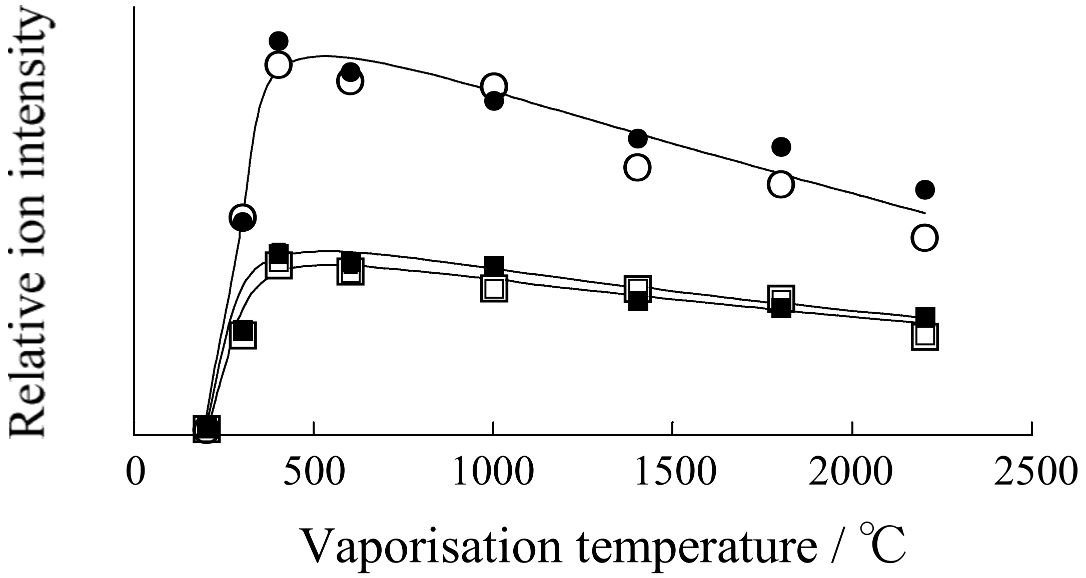

Figure 4. Effect of vaporisation temperature on the ion intensities of iodine and bromine. I(V), 500 pg; Br(V), 2.0 ng; drying, 150℃ for 30 s (ramp 10 s); ashing, 180℃ for 30 s (ramp 10 s); flow rate of carrier gas, 0.85 dm^3 min^{-1}; TMAH, 1.0 mg; $NH_4H_2PO_4$, 240 ng. ○, ^{127}I with $NH_4H_2PO_4$; ●, ^{127}I without $NH_4H_2PO_4$; □ , ^{79}Br with $NH_4H_2PO_4$; ■, ^{79}Br without $NH_4H_2PO_4$; □ , ^{81}Br with $NH_4H_2PO_4$; ■, ^{81}Br without $NH_4H_2PO_4$.

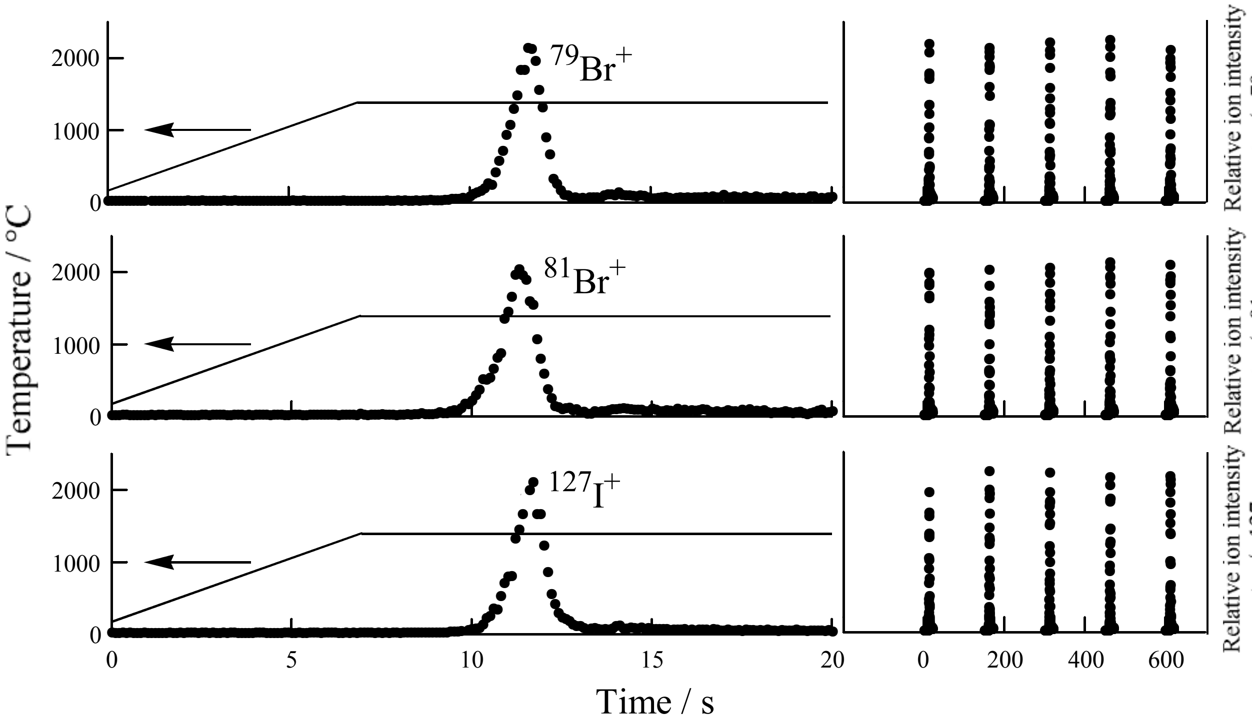

Figure 5. Peak profiles for bromine and iodine.

The usage of plastic bottles to stock solutions or disposable tips of digital pipettes often caused the bromine contamination. As for the storage vessels for standard and sample solutions, the solutions stocked in polyethylene bottles were contaminated especially under the alkali conditions (for example, 0.1 mol L^{-1} ammonia water). When the disposable tips were used for pipetting the basic TMAH solution, the serious contamination was observed. As some kinds of plastics contain the brominated retardants, bromine may be leached out easily from the surface. Therefore, the bottles and the tips made of glass or polytetrafluoroethylene are preferable as their materials.

3.1.4 Interference study

Because of the low vaporisation temperature, few foreign anions and cations, especially no metal ions, are vaporised and introduced into the plasma. Reduced interference is also expected because almost all the metal ions are precipitated as their hydroxide salts in the strongly basic TMAH medium. The effect of ubiquitous cations and anions on the vaporisation of bromine and iodine was investigated according to the recommended procedure. Tolerable amounts of foreign ions, which gave less than a 10% error for the determination of bromine and iodine were evaluated. The results are summarised in Table 2, 3 and 4. Fortunately, when an aliquot of 240 ng ammonium dihydrogenphosphate was added in each batch, tolerance limits against 200 pg of bromine were improved to 3000:1 or more for all the foreign ions tested. While by adding the phosphate ion the limits were improved to 12000:1 or more against 50 pg of iodine, excepting Fe^{3+} and Co^{2+}. Concerning the interference of Fe^{3+} and Co^{2+}, the limits were 6000:1 and 7000:1, respectively.

Table 2. Tolerance limits of foreign ions for the determination of iodine[a] (results within 10% error)

	Mass ratio[b] (foreign ion / iodine)	
	No addition	With $NH_4H_2PO_4$[c]
Na^+	>4000	>12000
K^+	6500	>12000
Mg^{2+}	11000	>12000
Ca^{2+}	7000	>12000
Mn^{2+}	10000	>12000
Fe^{3+}	650	6000 5000[d] 8000[e]
Co^{2+}	4500	7000
Ni^{2+}	8000	>12000
Cu^{2+}	9000	>12000
Zn^{2+}	>12000	>12000
Al^{3+}	>12000	>12000
NH_4^+	>3000	>40000
NO_3^-	>7500000	>7500000
SO_4^{2-}	10000	>100000
PO_4^{3-}	300	-
Cl^-	>10000	>20000
Br^-	100	>12000

a. Analytical mass number, I-127.

b. I(V), 50 pg. With TMAH, 1.0 mg.

c. $NH_4H_2PO_4$, 240 ng.

d. Vaporisation temperature, 2000ºC.

e. Vaporisation temperature, 600ºC.

Table 3. Tolerance limits of foreign ions for the determination of bromine[a] (results within 10% error)

	Mass ratio[b] (foreign ion / bromine)			
	No addition		With $NH_4H_2PO_4$[c]	
	^{79}Br	^{81}Br	^{79}Br	^{81}Br
Na^+	750	750	>3000	>3000
K^+	>3000	>3000	>3000	>3000
Mg^{2+}	1500	1500	>3000	>3000
Ca^{2+}	1000	1000	>3000	>3000
Mn^{2+}	2500	>3000	>3000	>3000
Fe^{3+}	750	750	1500	1500
			2000[d]	2000[d]
Co^{2+}	750	800	2000	2500
Ni^{2+}	2000	2000	>3000	>3000
Cu^{2+}	1000	2000	>3000	>3000
Zn^{2+}	>3000	>3000	>3000	>3000
Al^{3+}	3000	2500	>3000	>3000
NH_4^+	>3000	>3000	>15000	>15000
PO_4^{3-}	250	200	-	-
NO_3^-	>2000000	>2000000	>2000000	>2000000
SO_4^{2-}	1000	1000	>25000	>25000
Cl^-	>1500	>1500	>5000	>5000
I^-	200	150	>100000	>100000

a. Analytical mass number, Br-79, Br-81.

b. Br(V), 200 pg. With TMAH, 1.0 mg.

c. $NH_4H_2PO_4$, 240 ng.

d. Vaporisation temperature, 2000°C.

Table 4. Tolerance limits of foreign ions for the determination of chlorine[a] (results within 10% error)

	Mass ratio[b] (foreign ion / chlorine)	
	No addition	With $NH_4H_2PO_4$[c]
Li^+	750	>3000
Na^+	500	>3000
K^+	200	2000
Mg^{2+}	>3000	>3000
Ca^{2+}	>3000	>3000
Sr^{2+}	1500	>3000
Ba^{2+}	>4500	>4500
NH_4^+	>3000	>3000
NO_3^-	>200000	>200000
SO_4^{2-}	200	2000
PO_4^{3-}	>3000	>3000
Br^-	>3000	>3000
I^-	3000	>17000

a. Analytical mass number, Cl-35.

b. Cl^-, 10 ng. With TMAH, 1.0 mg.

c. $NH_4H_2PO_4$, 240 ng.

3.1.5 Determination of halogens in practical samples

To evaluate the usefulness of the proposed method, various reference materials were analysed. The samples were prepared by alkaline digestion with TMAH according to the experimental section. The alkaline digestion using TMAH was firstly applied and recommended by Fecher and Magengast [25] to the determination of bromine and iodine in biological samples by ICP-MS. The resulting solution is fairly basic as a result of the remaining TMAH. For the subsequent analysis by TBF-ICP-MS, this digestion method is more favourable than the common acid digestion procedure, since the remaining TMAH will act as a chemical modifier. Therefore a minimal or no additional amount of TMAH is needed. If acid digestion procedures were applied, a large amount of TMAH should be added not only as the modifier but also for neutralisation of the remaining acids. Analytical results for bromine and iodine in various certified reference materials are summarised in Table 5 together with the results of recovery tests. The recovery values were in good agreement with the expected values.

Table 5. Analytical results for bromine and iodine in biological samples

Sample	Bromine ($\mu g\ g^{-1}$)				Iodine ($\mu g\ g^{-1}$)		
	Added	Measured[a]		Certified[b]	Added	Measured[a]	Certified[b]
		^{79}Br	^{81}Br				
NIST SRM 1549 (Non-fat Milk Powder)							
	0	12±1	12±1	(12)	0	3.4±0.1	3.38
	4.6	16±1	17±1		2.3	5.6±0.3	
	9.2	21±1	21±1		4.6	7.9±0.2	
	13.9	26±2	25±1		6.9	10.2±0.3	
NIES No. 9 (Sargasso)							
	0	290±20	300±10	(270)	0	500±10	(520)
	140	410±20	460±10		280	800±20	
	280	560±40	590±10		560	1090±30	
	420	690±40	720±10		850	1350±40	
NIST SRM 1566 (Oyster Tissue)							
	0	56±1	57±2	(55)	0	2.8±0.2	(2.8)
	30	87±6	89±4		3.0	5.7±0.1	
	60	125±2	124±1		6.0	9.0±0.3	
	89	163±3	153±1		8.9	11.2±0.5	

Table 5. Analytical results for bromine and iodine in biological samples (continue)

	Bromine (μg g^{-1})				Iodine (μg g^{-1})		
Sample	Added	Measured[a]		Certified[b]	Added	Measured[a]	Certified[b]
		^{79}Br	^{81}Br				
NIST SRM 1547 (Peach Leaves)							
	0	12±2	11±1	(11)	0	0.5±0.1	(0.3)
	3	11±1	13±1		0.3	0.8±0.1	
	5	17±3	16±1		0.5	1.1±0.1	
	11	23±2	21±1		0.8	1.3±0.1	
NIST SRM 1573a (Tomato Leaves)							
	0	1500±100	1500±100	(1300)	0	1.0±0.1	(0.85)
	200	1700±100	1600±100		1.2	2.4±0.1	
	500	2100±100	2100±100		2.4	3.6±0.1	
	1000	2500±100	2400±100		3.6	4.6±0.2	
	2400	4100±100	4000±100				
NIST SRM 1515 (Apple Leaves)							
	-	-	-	-	0	0.5±0.1	(0.3)
					0.3	0.8±0.1	
					0.5	1.1±0.1	
					0.8	1.4±0.1	

a. Mean ± standard deviation, 3 results.

b. Values in parentheses are not certified.

An alternative attempt was made to apply this method to the determination of bromine and iodine in various commercially available table salts for cooking and mineral water samples. Since the concentration of iodine is too low to be determined, the analytical results of bromine are listed in Table 6. The table salt J, made by my teacher, is a crude salt prepared from sea water according to the ancient method performed from B.C. 3rd century through A.D. 3rd century in Japan. The table salts A, D, E, F and I are supposed to be made of sea water, since the concentrations of bromine are similar to the table salt J. On the other hand, the bromine contents of the table salts B, C, G and H are high and these salts are supposed to be added bromine artificially. The analytical results of mineral water samples are listed in Table 7 together with the analytical results obtained by the ion chromatography with UV detection (IC-UV). [36] As for the mineral water F and I, however, only the nominal data showed contradictory to the results obtained by the proposed method and IC-UV, which gave the similar results. This discrepancy should result from the measurement error of the nominal data.

Table 6. Analytical results for bromine in table salts

Sample	Bromine (mg g^{-1}) Added	Measured[a] ^{79}Br	 ^{81}Br
Table salt A	0	0.13±0.01	0.13±0.01
	0.03	0.17±0.01	0.16±0.01
	0.07	0.20±0.01	0.20±0.01
	0.13	0.26±0.01	0.26±0.01
Table salt B	0	2.0±0.1	1.9±0.1
	0.67	2.6±0.2	2.4±0.2
	1.33	3.4±0.1	3.3±0.1
	2.67	4.6±0.1	4.5±0.1
Table salt C	0	1.3±0.1	1.1±0.1
Table salt D	0	0.40±0.01	0.38±0.02
Table salt E	0	0.29±0.01	0.30±0.02
Table salt F	0	0.47±0.05	0.45±0.06
Table salt G	0	0.87±0.05	0.82±0.02
Table salt H	0	1.2±0.1	1.1±0.1
Table salt I	0	0.40±0.04	0.40±0.02
Table salt J[b]	0	0.25±0.01	0.25±0.01

a. Mean ± standard deviation, 3 results.

b. Home-made table salt.

Table 7. Analytical results for bromine and iodine in mineral water made of deep-sea water

Sample	Bromine (μg g^{-1})			Iodine (ng g^{-1})			
	Added	Measured[a]		Added	Measured[a]	Nominal	IC-UV[c]
		^{79}Br	^{81}Br				
Mineral water A	0	0.68±0.05	0.67±0.08	0	0.43±0.02	-	-
	0.24	0.89±0.07	0.94±0.06				
	0.50	1.2±0.1	1.1±0.1				
	1.00	1.7±0.1	1.8±0.1				
Mineral water B	-	-	-	0	0.26±0.01	0.26	-
				0.125	0.40±0.02		-
				0.250	0.51±0.01		-
				0.500	0.77±0.04		-
Mineral water C	0	0.79±0.02	0.78±0.03	0	1.9±0.1	-	-
Mineral water D	0	3.4±0.1	3.5±0.1	0	3.0±0.1	2.2	4.1±0.7
Mineral water E	0	0.038±0.001	0.037±0.001	0	3.2±0.1	-	-
Mineral water F	0	1.4±0.1	1.3±0.1	0	12±1	200	14±1
Mineral water G	0	0.24±0.01	0.24±0.01	-	-	-	-
Mineral water H	0	0.28±0.01	0.28±0.01	-	-	-	-
Mineral water I	-	-	-	0	5.5±0.2	0.84	5.3±0.8
Mineral water J	-	-	-	0	9.6±0.2	9.0	12±2
Tap water	0	0.021±0.001	0.020±0.001	0	1.9±0.1	-	-
Sparkling natural mineral water	(0.40)[b]	0.55±0.01	0.55±0.02	0	11±1	-	10±1

a. Mean ± standard deviation, 3 results.

b. Nominal value.

c. Iodine concentration measured by ion chromatography with UV detection. [36]

3.1.6 Basic analytical performance characteristics

The analytical performance characteristics are listed in Table 8. The detection limits were 0.086 pg, 0.77 pg, 0.89 ng and 290 ng for iodine, bromine, chlorine and fluorine, respectively, when ^{127}I, ^{79}Br, ^{35}Cl and ^{19}F were used for the measurement. The limit of detection was defined as the absolute amount of each analyte required to yield a net peak area that was three times the standard deviation of the blank in the presence of a suitable amount of TMAH. The detection limits represented in concentration are summarised in Table 8, when a sample injection volume of 90 - 95 μL is placed in the TBF. With larger sample volumes, lower detection limits could be attained proportionally. For this purpose, repeated injection would be effective. Table 9 also lists the analytical performances of alternative methods. In comparison with other detection techniques used for routine halogen determinations, better detection limits up to several orders magnitudes have been achieved with the proposed ETV-ICP-MS. The detection limit obtained by the proposed method is approximately 1000 times lower than that obtained using similar types of ICP mass spectrometer equipped with a nebuliser. Linear calibration graphs for $^{79}Br^+$, $^{81}Br^+$ and $^{127}I^+$ ions almost intersecting the origin of the coordinate axis and covering absolute amount of up to at least 200 ng of bromine and 200 ng of iodine with correlation coefficients of 0.996, 0.994 and 0.997 were established for $^{79}Br^+$, $^{81}Br^+$ and $^{127}I^+$, respectively. The relative standard deviations obtained for eight replicate measurements of 20 pg of bromine and 2.0 pg of iodine was 2.2% and 2.8%, respectively. Approximately 25 batches were vaporisable per hour.

Table 8. Detection limits and precision of halogens

	^{19}F	^{35}Cl	^{79}Br	^{81}Br	^{127}I
Proposed ETV-ICP-MS					
D. L. (3σ) / pg	290000	890	0.77	1.1	0.086
D. L. (3σ)[a] / pg cm^{-3}	3.2×10^6	9300	8.1	11	0.91
R. S. D., %	3.6[b]	3.3[c]	2.2[d]	2.7[d]	2.8[e]
Linearity / ng	~100000	~1000	~200	~200	~200
Throughput / h^{-1}	25	25	25	25	25
Nebuliser ICP-MS					
D. L. (3σ) / pg cm^{-3}	-	730000	1400	22000	310
R. S. D., %	-	-	12[f]	3.4[f]	8.6[g]
Throughput / h^{-1}	-	40	40	40	40

a. Sampling volume, 95 mm^3.

b. F^-, 5.0 μg; n=10.

c. Cl^-, 10 ng; n=10.

d. Br(V), 20 pg; n=8.

e. I(V), 2 pg; n=8.

f. Br(V), 2 ng cm^{-3}; n=10.

g. I(V), 20 ng cm^{-3}; n=10.

Table 9. Detection limits of halogens by various analytical methods

	Detection limit[a] / ng g^{-1}			
Analytical method	F	Cl	Br	I
Proposed ETV-ICP-MS	3200 (290 ng)	9.3 (0.89 ng)	0.0081 (0.00077 ng)	0.00091 (0.000086 ng)
Nebuliser ICP-MS[b]	-	730	1.4	0.31
Nebuliser ICP-MS	5000[24]	-	0.30[25]	0.07[25]
Microwave induced plasma AES	-	6.8[26], 17[27]	24[27]	55[27]
X-ray fluorescence spectrometry	-	700[28]	90[28]	510[28]
Luminol chemiluminescence[c]	-	-	-	0.02[29]
Instrumental neutron activation analysis[d]	300[30]	-	-	~300[31]
Epithermal neutron activation analysis[c]	-	(6000 ng)[32]	(23 ng)[32]	(2 ng)[32], 10-40[33]
Thermal neutron activation analysis[d]	-	50[34], (2000 ng)[32]	3[34]	10[34]
Radiochemical neutron activation analysis[d]	-	-	-	0.5[33]
Ion chromatography[c]	9.7[35]	5.4[35]	22.7[35]	163[35]
Ion chromatography (UV)[e]	-	-	-	0.2[36]
Capillary electrophoresis (UV)[c]	-	-	-	0.4[37]

a. 3 σ. Values in parentheses are absolute amounts.

b. Detection limits obtained with the same instrument of the proposed ETV-ICP-MS, but the sample was nebulised.

c. S/N=3.

d. Solid base.

e. S/N=2.

3.1.7 Potential of halogen determination by TBF-ICP-MS simultaneously

The multi-element trace determination by ICP-MS is not so difficult. Concerning the determination of halogens, however, there is limited scope using the argon ICP in ICP-MS because these non-metals have high ionisation energies (I, 10.46 eV; Br, 11.85 eV; Cl, 13.02 eV; and F, 17.42 eV), while the ionisation energy of argon is only 15.76 eV. [38] The degree of elemental ionisation gives a measure of ionisation efficiency. The value is calculated by dividing the number of analyte ion by the sum of those of corresponding ion and neutral atom. [4] According to the calculation by Gray (the data were included in the Ref. [38]) the degrees of elemental ionisation for iodine, bromine and chlorine were 33.9%, 4.5% and 0.9%, respectively, whereas those for the other 53 elements were greater than 90%. According to the Houk, the degree for fluorine was only 0.0009%. [4] Moreover, for the determination of halogens by the conventional nebuliser ICP-MS, there is isobaric interference except the measurement of the iodine ion. For example, due to the formation of molecular ions such as $^{16}O^{18}OH^+$ and $^{36}ArH^+$ in the argon plasma, the detection of $^{35}Cl^+$ and $^{37}Cl^+$ is significantly disturbed. The polyatomic ions, $^{38}Ar^{40}ArH^+$ and $^{40}Ar^{40}ArH^+$, have the same nominal masses as $^{79}Br^+$ and $^{81}Br^+$ have, respectively. The ions of $^{38}Ar^{2+}$ and $^{18}OH^+$ will interfere with the detection of the $^{19}F^+$ ion. Especially, the isobaric interference on measuring the $^{35}Cl^+$, $^{37}Cl^+$, $^{81}Br^+$ and $^{19}F^+$ was severe when a sample solution was introduced via a nebuliser.

In ETV system, the plasma having the special conditions namely a dry plasma and little co-existing molecular and atomic ions, namely a matrix free plasma can be obtained. Under the plasma conditions, isobaric interference especially caused by the elements such as ^{1}H, ^{16}O and ^{18}O is extremely reduced. Figure 6 shows the relationship of the ionisation degrees [4,38] with the detection limits obtained by both the sample introduction systems of the proposed ETV and a conventional nebuliser. Excepting the chlorine, a plot of the detection limits of the four halogen species obtained by the ETV against the ionisation degrees is found to be linear. The molecular ions such as $^{16}O^{18}OH^+$ and $^{36}Ar^+$ disturbed the detection of the $^{35}Cl^+$ ion. As for the fluorine, it cannot be determined by the conventional nebuliser ICP-MS because of extremely low sensitivity and the intense spectral interference caused by water solvent. The detection of fluorine was attempted by nebulising a highly concentrated solution of ammonium fluoride, however no signal was observed. The detection limit of fluorine with quadrupole ICP-MS using the nebuliser could be evaluated by extrapolating the line B to the ionisation degree of fluorine, 0.0009% in Fig. 6, and the value is estimated to be ca. 3000 mg L^{-1}. By the best search of literature, there is the only one paper concerning the determination of fluorine ion by a nebuliser sample introduction using a double focusing sector field high-resolution ICP mass spectrometer, and the reported detection limit in solution is 5 mg L^{-1}. [24] Similar detectability of the fluorine ion are achieved by the proposed method despite a quadrupole type ICP mass spectrometer. [39] The detection limits of $^{35}Cl^+$, $^{79}Br^+$ and $^{127}I^+$ obtained by the ETV were better than those by the nebuliser with a factor of approximately three orders of magnitudes as shown in Fig. 6. By the sample introduction using the nebuliser, the detection limit of $^{81}Br^+$ was about 10-times worse than that of $^{79}Br^+$, whereas by the ETV the detection limit of $^{81}Br^+$ was similar to that of $^{79}Br^+$ because of no isobaric interference caused by the $^{40}Ar^{40}ArH^+$ ion which generates in the presence of water mist.

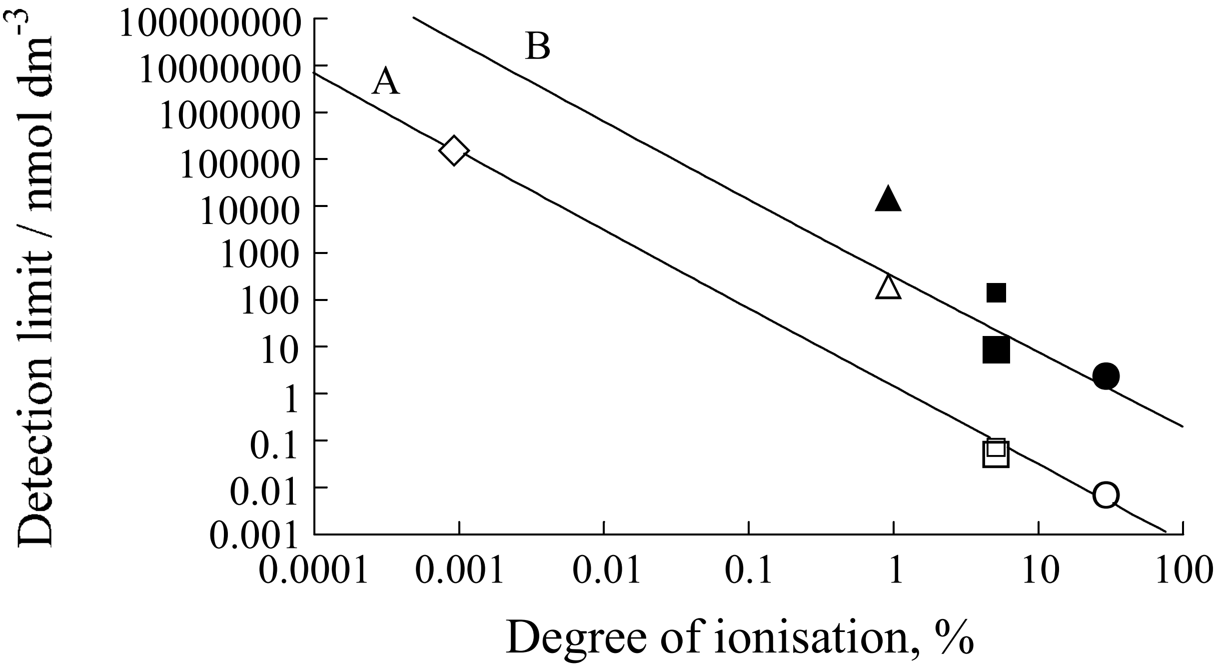

Figure 6. Correlation between ionisation efficiency[a] and detection limits measured by ICP-MS.

◇: ^{19}F; △▲: ^{35}Cl; □■: ^{79}Br; □■: ^{81}Br; ○●: ^{127}I.

A: ETV method; B: Nebuliser method.

a. Ref. [4].

3.2 Differential Determination of Boric Acid and Inorganic Boron

In this section, the separable determination of nonmetallic boron was attempted by TBF-ICP-MS and TBF-ICP-AES focusing on the significant difference of vaporisation properties of boron species.

Atomic spectrometry is sensitive for metal and semimetal elements. The atomic spectrometry with the ETV can determine not only these elements but also non-metal elements at low concentrations. In the commonly used ETV procedure, chemical modification techniques have been applied. Wei et al. [40,41] and Pozebon et al. [42] proposed a mannitol assisted ETV-ICP-MS. According to the Wanner's paper, [43] NH_4F was also effective to retain boron species. For the vaporisation of boron in the graphite furnace atomic absorption spectrometry, calcium, [44] zirconium [45] and combination uses of citric acid and zirconium [46] or tungsten [47] were also available. For the solid sample decomposition in a graphite furnace, ammonium nitrate [47] or fluorinating agents were also used. The fluorinating agents include ammoniacal hydrofluoric acid [48] and polytetrafluoroethylene. [49] However, their usage as chemical modifiers was mainly to unify the analyte species vaporised, to separate boron from the matrix, to prevent the formation of non-volatile boron carbide or to improve the detectability. It is well known that boric acid and its salts (sodium tetraborate, sodium metaborate) show a relatively high toxicity. These are all volatile and especially in acidic media, the volatility is extremely increased. On the contrary, other boron species such as boron nitride, chromium boride, boron carbide, etc. are thermally quite stable and show non-volatility.

This section describes the two parallel sampling procedures; the one is for the more volatile boron species such as boric acid and its salts in distinction from non-volatile boron species, and the other for the total amount of the volatile and non-volatile boron species including the former. For the determination of the volatile boron species, the analyte is electrothermally vaporised and introduced into an ICP mass spectrometer. For the total boron determination, the sample is fused with sodium hydroxide on the TBF prior to the vaporisation and introduction into an ICP-AES. From the difference of these two analytical results, the amount of the non-volatile boron species can be estimated.

3.2.1 Analytical procedures for the separate determination of boric acid and inorganic boron

For routine analysis, there are two vaporisation procedures. As shown in Fig. 7, the procedure I is for the determination of the volatile boron by TBF-ICP-MS, and the procedure II is for the total boron by TBF-ICP-AES. As for the procedure I, a 10 µL aliquot of the TMAH solution and up to 90 µL of an aqueous sample solution were pipetted into the sample cuvette superposed on the TBF. It was warmed to expel the solvent through the open sample insertion port. After the sample had dried completely, the insertion port was closed with a silicone rubber stopper. During the ashing step, excess TMAH was expelled from the furnace. Then, the temperature was taken up to 800ºC for vaporisation. The generated analyte vapour, mainly $TMA{\cdot}B(OH)_4$, was transported into the ICP through the PTFE tube by the carrier gas. The transient signal of the $^{10}B^+$ ion was integrated and the peak area was estimated.

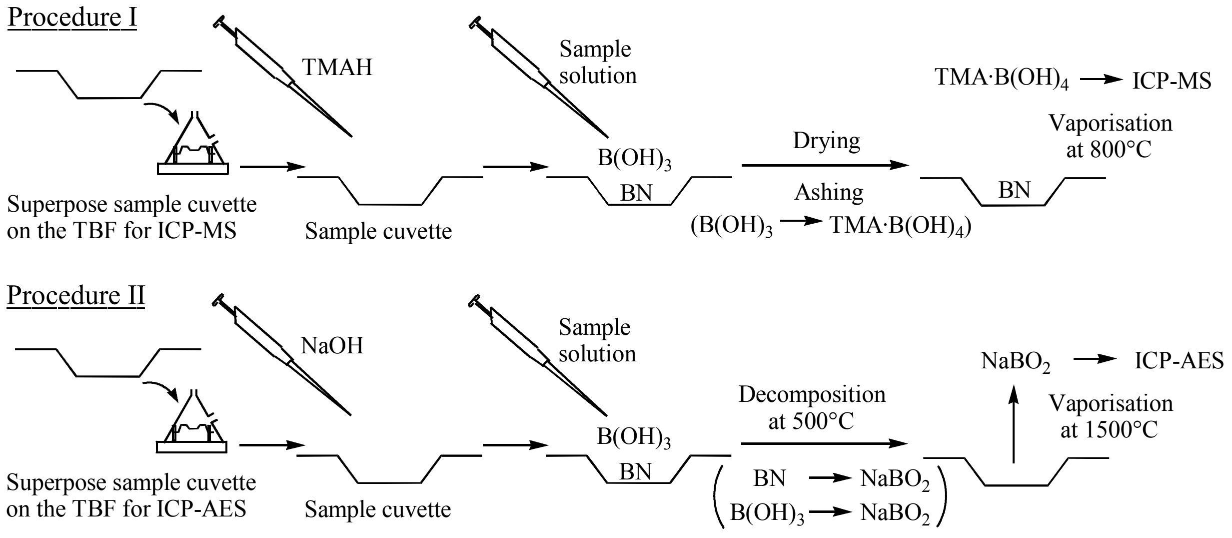

Figure 7. Schematic diagram of the sample cuvette-tungsten boat furnace vaporisation method. Procedure I, determination of volatile boron by TBF-ICP-MS; procedure II, determination of total boron by TBF-ICP-AES.

For the determination of the total boron, the procedure II was carried out. A 4.0 μL aliquot of the sodium hydroxide solution as another modifier and up to 96 μL of an aqueous sample solution were pipetted into the sample cuvette superposed on the TBF vaporiser for the ICP-AES. If necessary, a 30 μL aliquot of ammonium dihydrogenphosphate may be added as a masking reagent when steel samples were analysed. The temperature was ramped up for drying and ashing in the similar manner. During the ashing stage, non-volatile boron species as well as the volatile boron were fused with sodium hydroxide to produce sodium metaborate quantitatively. Finally, the resultant analyte in the cuvette was vaporised and introduced into the plasma. The momentary emission signal at 249.773 nm (B I) was recorded and the peak height was measured. In order to avoid memory effects, the sample cuvette used in each run was exchanged with a fresh cuvette, which had been preconditioned by heating to expel boron impurities and to confirm a blank signal level. The recommended operating conditions are listed in Table 10.

Table 10. Instrument operation conditions for the determination of boron

	Procedure I (for volatile boron)	Procedure II (for total boron)
TBF vaporiser	SII EV-300	SII SAS-705V
Sample amount	~90 µL	~96 µL
Chemical modifier	TMAH (2.5 mg)	NaOH (0.10 mg)
Heating programme		
Drying	135ºC, 30 s (ramp 10 s)	150ºC, 30 s (ramp 10 s)
Ashing	180ºC, 10 s (ramp 20 s)	500ºC, 20 s (ramp 25 s)
Vaporisation	800ºC, 10 s (ramp 0 s)	1500ºC, 10 s (ramp 5 s)
Carrier gas flow rate		
Argon gas	1.15 L min^{-1}	1.15 L min^{-1}
Hydrogen gas	0 L min^{-1}	0.05 L min^{-1}
ICP spectrometer	SII SPQ9000 mass spectrometer	SII SPS4000 atomic emission spectrometer
R.F. power	1.7 kW	1.6 kW
Argon gas flow rate		
Plasma gas	16 L min^{-1}	16 L min^{-1}
Auxiliary gas	1.0 L min^{-1}	1.0 L min^{-1}
Analytical mass	10 ($^{10}B^+$)	-
Sampling depth	10.0 mm	-
Analytical line	-	249.773 nm (B I)
Observation height	-	5.0 mm
Integration time	10 s	15 s

3.2.2 Optimisation for the determination by TBF-ICP-MS

The operating conditions for the two vaporisation procedures were optimised. Regarding the procedure I for the determination of the volatile boron (boric acid, sodium tetraborate and sodium metaborate), the heating program for drying, ashing and vaporisation stages was investigated by obtaining signals with 5.0 μL aliquots of the boric acid solution containing 100 pg of boron species.

A moderate elevation of temperature throughout the heating process was essential. The quantitative release of boron species assignable to boric acid can be achieved at the vaporisation stage, permitting the complete retention of the non-volatile boron in the furnace. Because of the volatility of boric acid, it is necessary to add a chemical modifier to retain the analyte during the ashing stage. For the chemical modifier sodium hydroxide was suitable to determine all the boron species by TBF-ICP-AES as described below. On the contrary, the use of sodium hydroxide as a chemical modifier was not recommended for the ICP-MS measurements. When the modifier vaporise and is introduced into the ICP mass spectrometer together with the analyte, it will cause damages such as clogging of orifices of a sampling cone and a skimmer, its deposition on the surface of ion optics and quadrupoles, as well as deterioration of the ion detector. In the ICP-MS measurements, TMAH was used as a modifier to retain boric acid. TMAH was sufficiently basic to form its borate salt. Especially, it is most remarkable that an excess of the reagent could be expelled from the device during the drying and ashing procedure. As Fig. 8 shows, when no modifier was added, almost all the analyte was lost, even at a drying temperature of 135ºC. The sensitivity increased with increasing the added amounts of TMAH, and remained almost constant over the range of 2 mg or more. Therefore 2.5 mg was selected as the suitable amount of modifier, i.e., each 10 μL aliquot of the 25% TMAH aqueous solution was added to the cuvette before a sample aliquot was injected. The effect of ashing temperature on the ion intensity of various boron species (boric acid, sodium tetraborate, sodium metaborate, boron nitride, chromium boride and boron carbide) in the presence and absence of TMAH was examined. In the presence of TMAH, signals of boric acid, sodium tetraborate and sodium metaborate were observed (Fig. 9). This suggests that the species are retained completely on the surface of the furnace up to approximately 200ºC (Fig. 10). This is because TMAH was sufficiently basic to form the borate salt, presumably tetramethylammonium borate ($TMA\cdot B(OH)_4$), and the product was thermally stable enough to retain in the furnace prior to the vaporisation stage. The effect of the vaporisation temperature on the peak signal was investigated (Fig. 11). The appearance temperature for the signal assignable to the boron ion was found to be 600ºC. At higher temperatures, the analyte was expected to be vaporised more rapidly. Thus, the vaporisation temperature of 800ºC was chosen as an optimal. The non-volatile boron species were not vaporised at the vaporisation temperature of 800ºC. When no modifier was added, no signal attributed to the volatile boron was observed, because these boron species were almost lost, even at a drying temperature. Although TMAH released the $^{12}C^+$ ion, which might increase the background level at m/z 11, the interference was completely avoidable by recording the ion intensity of boron at m/z 10.

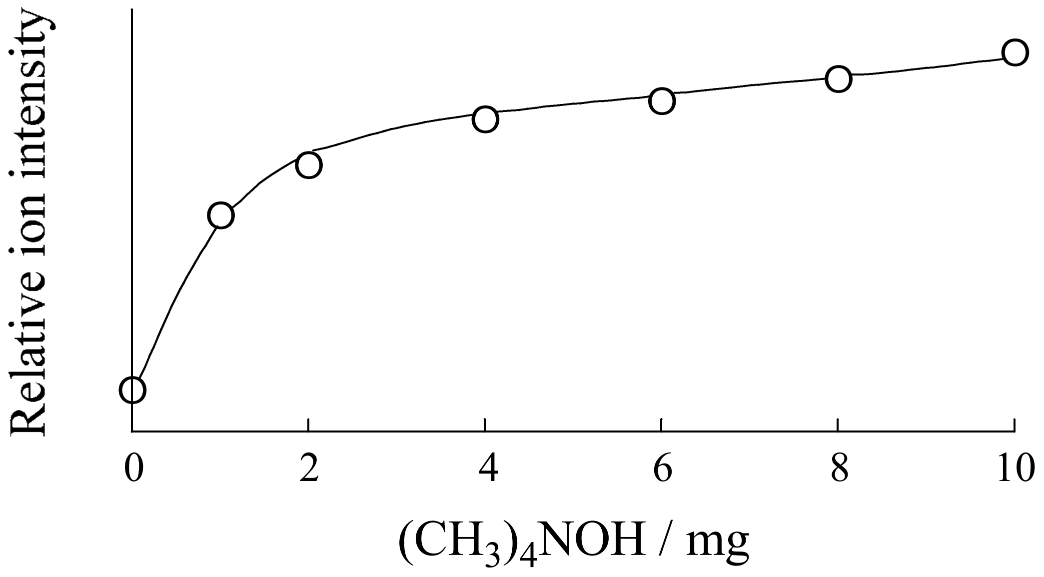

Figure 8. Effect of TMAH on the ion intensity of ^{10}B measured by the procedure I (TBF-ICP-MS).

Boron, 200 pg; drying, 135℃ for 30 s (ramp 10 s); ashing, 180℃ for 10 s (ramp 20 s); vaporisation, 800℃ for 10 s (ramp 0 s); flow rate of carrier gas, 1.15 dm^3 min^{-1}.

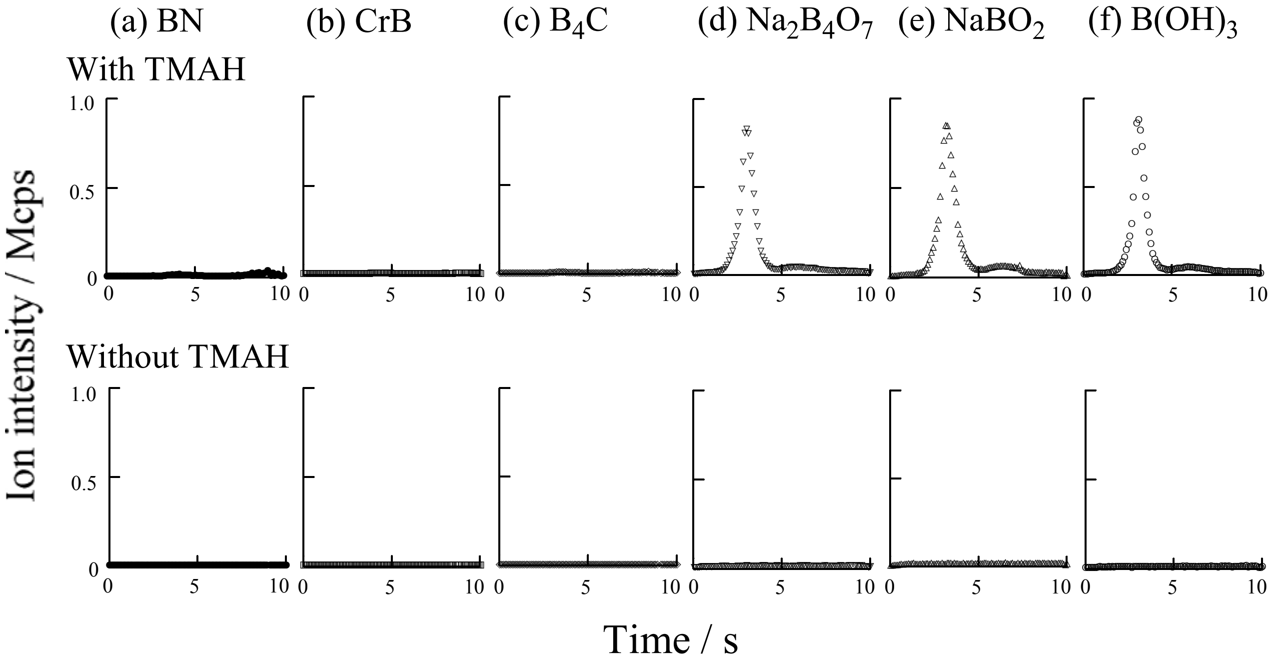

Figure 9. Peak profiles of various boron compounds measured by the procedure I (TBF-ICP-MS). TMAH 2.5 mg; drying, 135℃ for 30 s (ramp 10 s); ashing, 180℃ for 10 s (ramp 20 s); vaporisation, 800℃ for 10 s (ramp 0 s); flow rate of carrier gas, 1.15 $dm^3\ min^{-1}$.

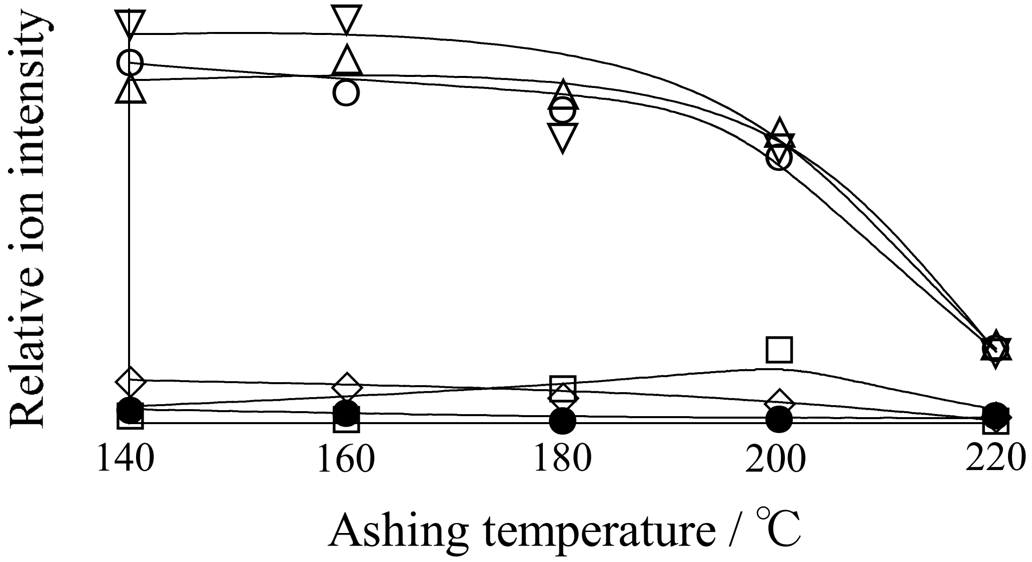

Figure 10. Effect of ashing temperature on the ion intensity of ^{10}B measured by the procedure I (TBF-ICP-MS).

Boron, 100 pg; drying, 135℃ for 30 s (ramp 10 s); vaporisation, 800℃ for 10 s (ramp 0 s); flow rate of carrier gas, 1.15 dm^3 min^{-1}; TMAH, 2.5 mg.

●, boron nitride; □ , chromium boride; ◇, boron carbide; ▽, sodium tetraborate; △, sodium metaborate; ○, boric acid.

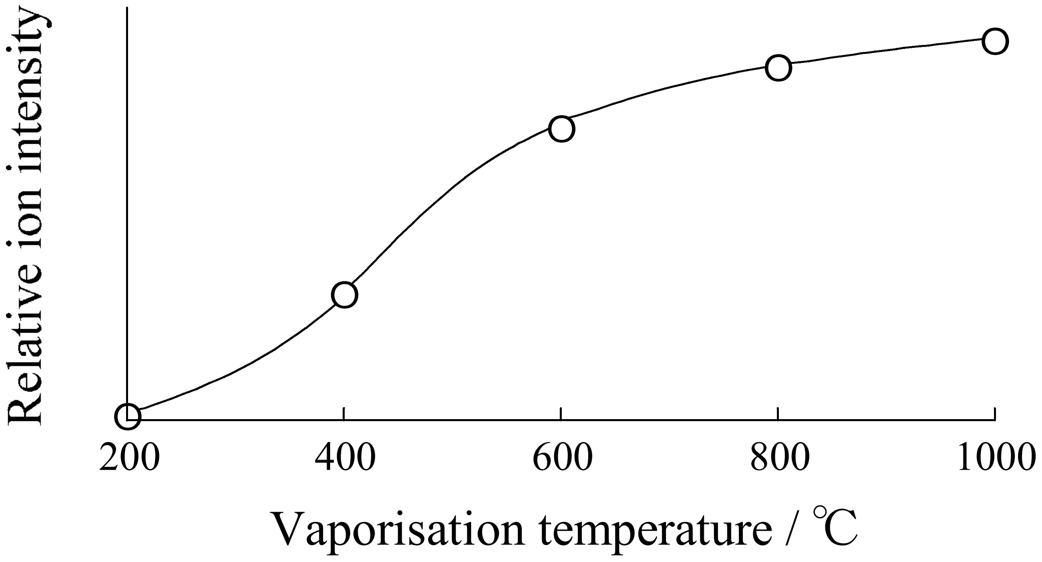

Figure 11. Effect of vaporisation temperature on the ion intensity of ^{10}B measured by the procedure I (TBF-ICP-MS).

Boron, 200 pg; drying, 135℃ for 30 s (ramp 10 s); ashing, 180℃ for 10 s (ramp 20 s); flow rate of carrier gas, 1.15 dm^3 min^{-1}; TMAH, 2.5 mg.

3.2.3 Optimisation for the determination by TBF-ICP-AES

As shown in Table 11, in contrast to the boric acid, sodium tetraborate and sodium metaborate, boron nitride has an extremely high melting point (3000ºC [50]) and probably a higher boiling point (not measured). Boron carbide (m.p. 2350ºC, b.p. >3500ºC) and chromium boride (m.p. 2760ºC, b.p. not measured) are also thermally stable. [50] Without any chemical pretreatment, these boron species are too non-volatile to vaporise quantitatively by the ETV procedure. It is necessary to add another chemical modifier in procedure II. According to the reference, [50] boron carbide and also chromium boride can dissolve in fused alkali. Therefore in the procedure II, sodium hydroxide was added as a chemical modifier. For the optimisation of experimental conditions in the procedure II, boron nitride had been used as the non-volatile boron. As Fig. 12 shows, when sodium hydroxide was not added, no emission signals of boron were observed even at an adequate vaporisation temperature. The emission intensity increased with increasing the added amount up to 0.024 mg, and remained almost constant over the range of 0.024-0.140 mg. The effect of ashing temperature on the atomic emission of boron was examined (Fig. 13). Fortunately, the volatile boron species, i.e., sodium tetraborate, sodium metaborate and boric acid, showed the same behaviour. Almost the same maximum and constant emission intensities for all the boron species were obtained in a wider range of up to 700ºC of the ashing temperature regardless of different thermal properties of the boron species. This suggests that the reactions of all the boron species with sodium hydroxide may result in the formation of the same species during the ashing stage. The effect of vaporisation temperature was examined (Fig. 14). Boron nitride was not vaporised at a high temperature of 2400ºC when no sodium hydroxide was added. In the presence of sodium hydroxide, the emission signal was appeared at 1200ºC and remained nearly constant over the range of 2400ºC or more. Under the same conditions, boric acid and boron nitride showed the same behaviour.

As Fig. 15 shows, both the calibration graphs were the same. By this procedure II using sodium hydroxide as a chemical modifier, the same signals of not only the non-volatile boron but also the volatile boron (boric acid, sodium metaborate and sodium tetraborate) appeared (Fig. 16). Even if the detectability is superior, detection with an ICP mass spectrometer is not recommended because a large amount of alkali metal salts will cause an overload. The residue of sodium hydroxide remained after each firing. Removing it by a conventional bake out is not recommended, because such a high temperature will deteriorate the sample cuvette and TBF in the presence of the alkali residue. Repeated use of the sample cuvettes was possible when the residue was washed out by soaking in dilute hydrochloric acid.

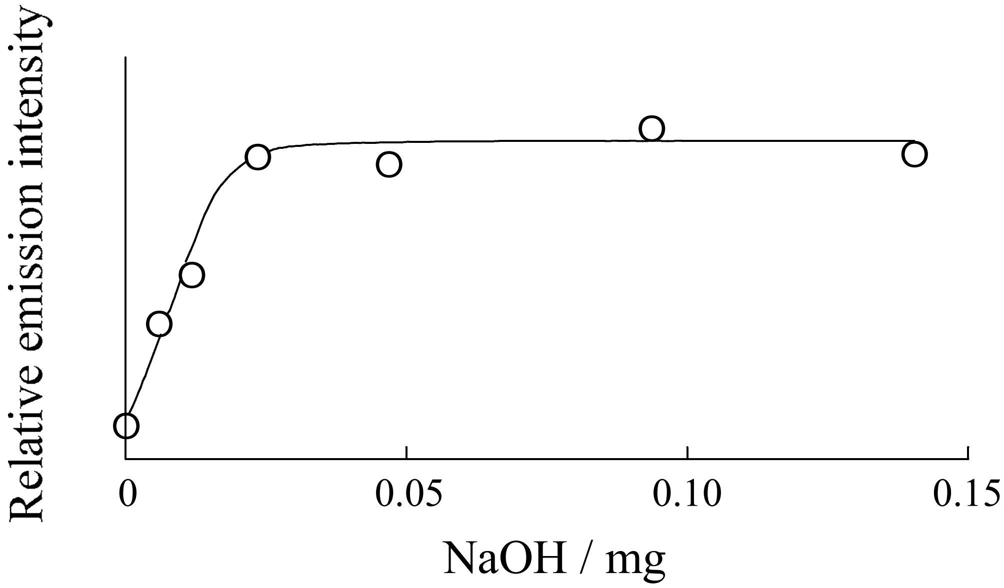

Figure 12. Effect of NaOH on the emission intensity of boron measured by the procedure II (TBF-ICP-AES).

Boron 10 ng; drying, 150℃ for 30 s (ramp 10 s); ashing, 500℃ for 20 s (ramp 25 s); vaporisation, 1500℃ for 10 s (ramp 5 s); flow rate of carrier gas, 1.2 dm^3 min^{-1}.

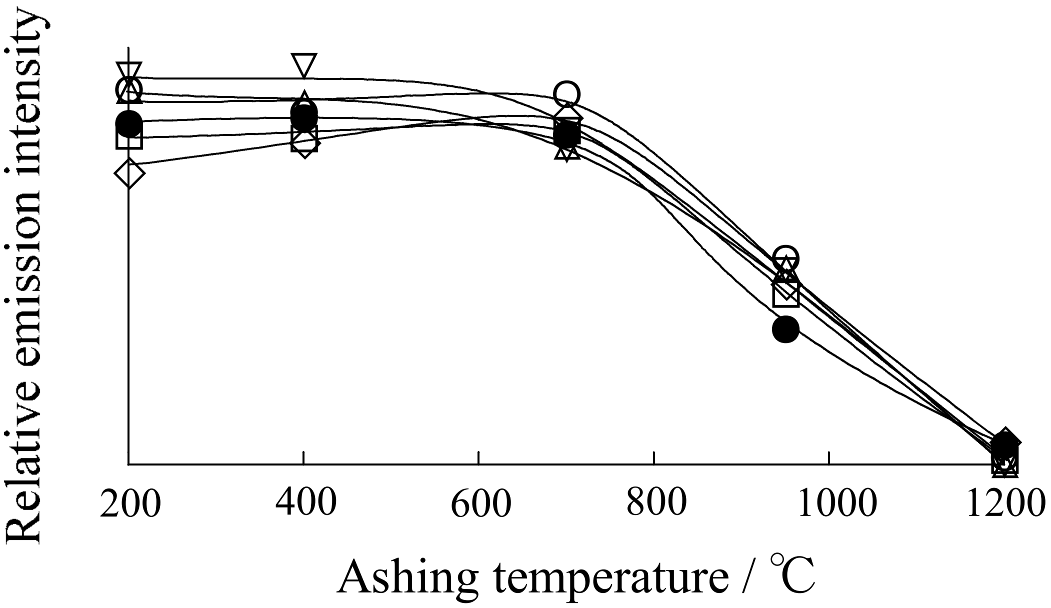

Figure 13. Effect of ashing temperature on the emission intensities of boron measured by the procedure II (TBF-ICP-AES).

Boron 10 ng; drying, 150℃ for 30 s (ramp 10 s); vaporisation, 1500℃ for 10 s (ramp 5 s); flow rate of carrier gas, 1.2 $dm^3\ min^{-1}$; NaOH, 0.10 mg.

●, boron nitride; □, chromium boride; ◇, boron carbide; ▽, sodium tetraborate; △, sodium metaborate; ○, boric acid.

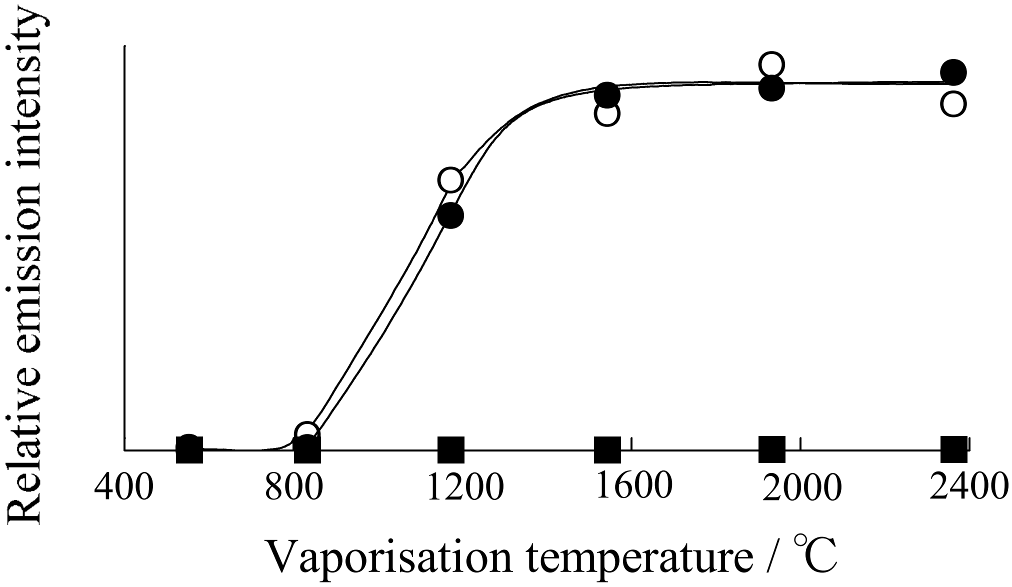

Figure 14. Effect of vaporisation temperature on the emission intensities of boron measured by the procedure II (TBF-ICP-AES).

Boron 10 ng; drying, 150℃ for 30 s (ramp 10 s); ashing, 500℃ for 20 s (ramp 25 s); flow rate of carrier gas, 1.2 dm^3 min^{-1}.

●, boron nitride with NaOH 0.10 mg;○, boric acid with NaOH 0.10mg; ■, boron nitride without NaOH.

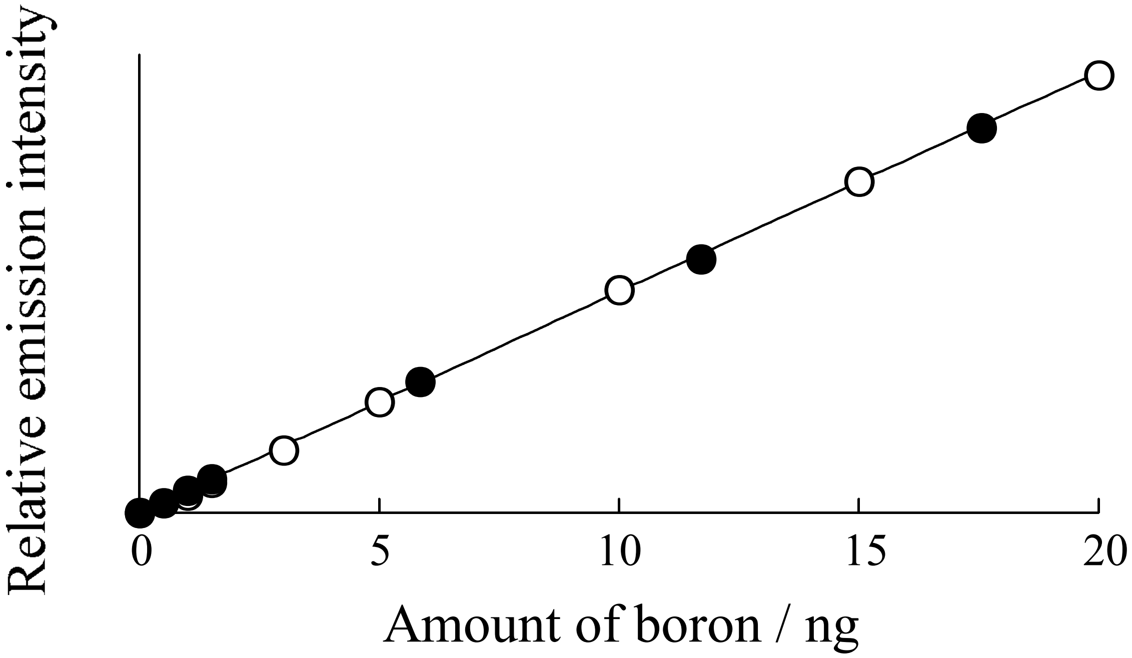

Figure 15. Calibration curves of boron measured by the procedure II (TBF-ICP-AES).

●, boron nitride; ○, boric acid.

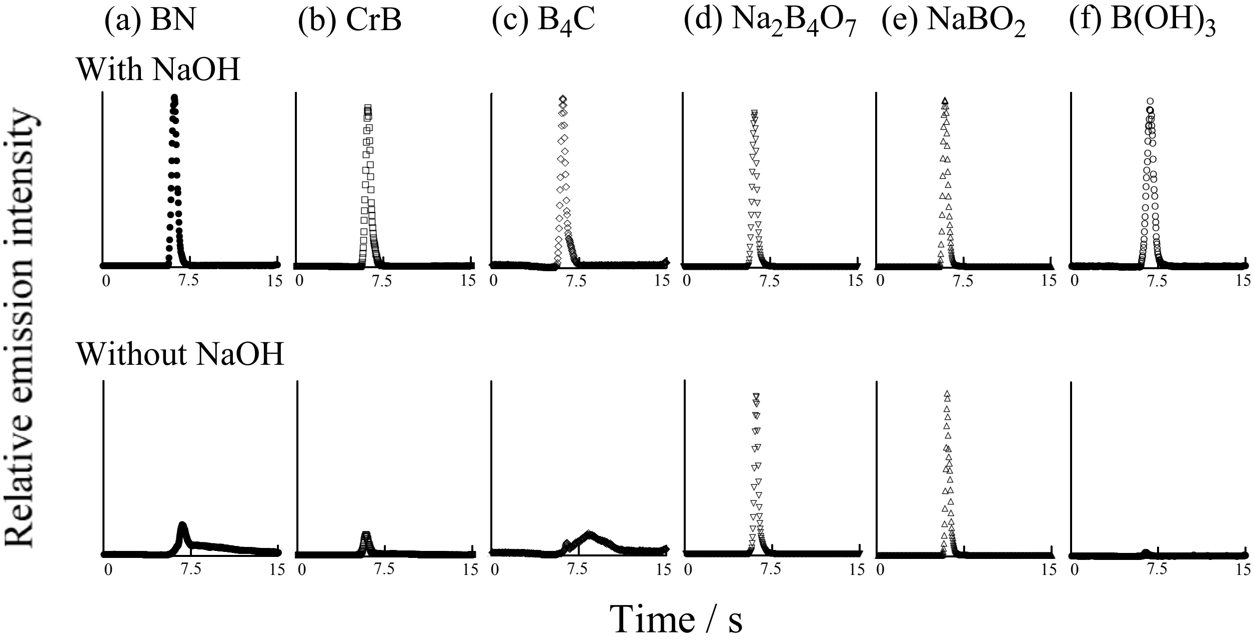

Figure 16. Peak profiles of various boron compounds measured by the procedure II (TBF-ICP-AES). NaOH 0.10 mg; drying, 150℃ for 30 s (ramp 10 s); ashing, 500℃ for 20 s (ramp 25 s); vaporisation, 1500℃ for 10 s (ramp 5 s); flow rate of carrier gas, 1.2 dm^3 min^{-1}.

Table 11. Properties of various boron compounds

Species	Melting point / ºC	Boiling point / ºC	Soluble in:
Boron nitride	subl ca 3000	-	hot acid (slightly)
Chromium boride	2760(?)	-	fused Na_2O_2
Boron carbide	2350	>3500	fused alkali
Sodium tetraborate	741	d 1575	water
Sodium metaborate	966	1434	water
Boric acid	(169)	(300)	water

subl, sublimes; d, decomposed. Reference [50].

3.2.4 Interference study

The effects of foreign cations and anions on the vaporisation of boron species were investigated. Tolerable amounts of foreign ions, which gave less than a 10% error for the determination of boron, were evaluated. The results are presented in Table 12. Excepting Cr^{3+}, Ca^{2+} and Pb^{2+}, all the foreign ion species tested were tolerated at a 1000:1 weight ratio or more for both the procedures (I and II). In the strongly basic TMAH or the sodium hydroxide medium, almost all the metal ions were formed into the non-volatile species, probably their hydroxide, while boron species were converted to the suitable species for the vaporisation in both procedures. For the determination of volatile boron species, which were measured by the procedure I, a severe interference caused by Cr^{3+} was observed. The phenomenon could be explained by assuming that the boron species converted into non-volatile chromium boride in the presence of chromium. When the vaporisation temperature was increased, fortunately, the tolerance limit for interference was improved to 700:1 weight ratio.

Table 12. Tolerance limits of foreign ions for the determination of boron (results within 10% error)

Ion	Mass ratio[a] Procedure I[b]	Procedure II[c]
Li^+	>8000	-
Na^+	4500	-
K^+	>8000	-
Mg^{2+}	2500	>1000
Ca^{2+}	4500	900
Ti(IV)	>8000	>1000
V(V)	>8000[d]	-
Cr^{3+}	200[d], 700[d, e]	-
Cr(VI)	-	>5500
Mo(VI)	>8000	>1000
Mn^{2+}	5000	>1000
Fe^{3+}	>10000	>10000
Co^{2+}	>8000	>1000
Ni^{2+}	>10000	>5500
Cu^{2+}	7500	1000
Zn^{2+}	>8000[d]	-
Cd^{2+}	5000	>1000
Si(IV)	6000[d]	-
Pb^{2+}	>8000	950
Al^{3+}	>8000[d]	>1000
NH_4^+	>70000	-

Table 12. Tolerance limits of foreign ions for the determination of boron (results within 10% error)(continue)

Ion	Mass ratio[a] Procedure I[b]	Procedure II[c]
F^-	5000[d]	-
Cl^-	>300000	-
Br^-	>8000	-
I-	24000	-
NO_3^-	>500000	-
CO_3^{2-}	>35000	-
SO_4^{2-}	>8000	-
PO_4^{3-}	4000	-

a. Foreign ion / boron.

b. Procedure I is for the determination of volatile boron.

c. Procedure II is for the determination of total boron. Reference [51].

d. TMAH, 10 mg.

e. Vaporisation temperature, 1600°C.

3.2.5 Determination of boron in practical samples

In order to prevent the volatilisation of boron species during the acid decomposition procedure, wet-digestion under the strongly acidic and oxidative media in a closed vessel has been used for the analysis of steel/iron samples. As the decomposition reagents, Shinohara et al., [52] Yamane et al. [53] and Uehara et al. [54] proposed combination of nitric acid with other oxidative acid. Coedo et al. recommended the use of aqua regia. [55] During such violent digestion processes, the steel samples were usually dissolved completely to unify the chemical forms of various boron species. In this work, steel samples were digested simply with hydrochloric acid only, the digestion conditions (90ºC - overnight) were milder than those used for the above-mentioned processes and thus the chemical forms of the boron species in the samples remained unchanged as they were. To prevent a loss of boron species during the hot acid-digestion procedure, a double-vessel digestion bomb was utilised. According to the literature, [50] it was concerned that boron nitride is slightly soluble in hot hydrochloric acid. The amount of boron nitride degraded to volatile species during the acid decomposition process was estimated by the procedure I. The examinations were carried out as follows: an aliquot of 1.34 μg boron nitride powder and 3 mL of hydrochloric acid were placed into the vessel. A series of these vessels were kept at 90ºC for 2 days or 20 days. After the digestion for 2 days and 20 days, the decomposition amounts were estimated to be 0.22% and 12.5%, respectively (Table 13). Therefore, it was concluded that during the digestion procedure mentioned in the section 2.4 the conversion of non-volatile boron species into volatile species occurred negligibly.

Table 14 shows the analytical results of several steel samples together with the various recovery examinations. As for the procedure I, the concentrations assignable to boric acid or volatile boron species in the NIST SRM 348, 362 and 364 were 3.9±0.3, 5.6±1.0 and 27±5 μg g^{-1}, respectively. Various known amounts of boric acid as a volatile boron species were added to each steel sample and the recovery values obtained are in good agreement with the expected values.

Table 13. Decomposition of boron nitride by digestion with hydrochloric acid

Heating time / day	Decomposed boron nitride, %
0	0
2	0.22
20	12.5

Boron nitride (1.34 μg) was decomposed at 90°C with hydrochloric acid (3.0 mL).

Table 14. Analytical results for boron in standard reference materials

Sample	Boron ($\mu g\ g^{-1}$) Added	Measured[a] Volatile boron (Procedure I)	 Total boron (Procedure II)	Certified
NIST SRM 348 Hi Temp Alloy (A286) (Ni-Cr)				
	0	3.9±0.3[c]	31±1[d]	31
NIST SRM 362 LA Steel (AISI 94B17 mod.)				
	0	5.6±1.0	26±1[d]	25
	2.2[e]	7.7±1.0	-	(7.8)[b]
	4.3[e]	10.2±1.1	-	(9.9)[b]
	8.6[e]	14.4±0.8	-	(14.2)[b]
NIST SRM 364 LA Steel, High C (mod.)				
	0	27±5	108±3[d]	106
	23[e]	81±13	-	(76)[b]
	46[e]	103±10	-	(99)[b]
	92[e]	142±8	-	(145)[b]

Table 14. Analytical results for boron in standard reference materials (continue)

Sample	Boron ($\mu g\ g^{-1}$) Added	Measured[a] Volatile boron (Procedure I)	 Total boron (Procedure II)	Certified
NIST SRM 1515 Apple Leaves				
	0	28±2	-	27±2
	15[e]	43±3	-	(42)[b]
	30[e]	56±2	-	(57)[b]
	60[e]	87±2	-	(87)[b]
NIST SRM 1547 Peach Leaves				
	0	30±2	-	29±2
	16[e]	45±1	-	(45)[b]
	32[e]	60±1	-	(61)[b]
	64[e]	93±2	-	(93)[b]
NIST SRM 1573a Tomato Leaves				
	0	19±1	35±2	33.3±0.7
	6.0[e]	24±2	-	(25)[g]
	12[e]	30±2	-	(31)[g]
	24[e]	42±1	-	(43)[g]

Table 14. Analytical results for boron in standard reference materials (continue)

Sample	Boron ($\mu g\ g^{-1}$)			
	Added	Measured[a]		Certified
		Volatile boron (Procedure I)	Total boron (Procedure II)	
NIST SRM 1573a Tomato Leaves				
	24[e]	-	56±3	(57)[b]
	47[e]	-	79±2	(80)[b]
	95[e]	-	127±3	(128)[b]
	300[f]	20±1	-	(19)[g]
	600[f]	17±1	-	(19)[g]
	1200[f]	20±8	-	(19)[g]
	10[f]	-	43±1	(43)[b]
	19[f]	-	53±2	(52)[b]
	38[f]	-	73±1	(71)[b]
	56[f]	-	92±1	(89)[b]

a. Mean ± standard deviation, 3 results.

b. Value in parentheses is expected value, i.e., the sum of certified value and added amount of boron.

c. Measured by standard addition method.

d. Reference [51].

e. Added as $B(OH)_3$ (volatile boron).

f. Added as BN (non-volatile boron).

g. Value in parentheses is expected value, i.e., the sum of the volatile boron amount measured and added amount of volatile boron.

To further evaluate the usefulness of this method, the Tomato Leaves (NIST SRM 1573a), Apple Leaves (NIST SRM 1515) and Peach Leaves (NIST SRM 1547) were analysed. The concentrations of total boron in the samples were shown as the certified values, but there is no information about the species of boron in the samples. The results in Table 14 suggest that the Apple Leaves and Peach Leaves contain boron in the form volatile boron species such as boric acid, while Tomato Leaves contains boron not only as boric acid but also as non-volatile species. The content of total boron in Tomato Leaves can be estimated by the procedure II. The analytical result was 35±2 μg g^{-1} which was in good agreements with the certified value of 33.3±0.7 μg g^{-1}. When several amounts of boric acid were added to the samples and the volatile boron species were measured according to the procedure I, the added amounts of boron were recovered completely. Further addition of non-volatile boron as nitride gave no effect on the final analytical results of the volatile boron. Similar recovery examinations were carried out in the procedure II. The added amounts of boric acid or boron nitride were recovered satisfactorily. Moreover, the analytical results listed in the Table 14 are all within the 95% confidence level. Therefore, the proposed method is suitable for the determinations of the volatile boron and the total boron in steel and botanical samples.

3.2.6 Basic analytical performance characteristics

The detection limits were defined as the absolute amount of boron required to yield a net peak area (procedure I) or a net peak height (procedure II) that was three times the standard deviation of the blank in the presence of TMAH (procedure I) or sodium hydroxide (procedure II). The detection limits of boron were estimated to be 1.2 pg (peak area) and 8.9 pg (peak height) for the procedures I and II, respectively. The values correspond to the volatile boron and total boron concentrations of 13 and 93 ng L^{-1}, respectively, when maximum sample injection volumes (90 and 96 μL for the procedures I and II, respectively) were applied. Concerning the measurement by ICP-AES, when the detection limit of total boron was estimated using the area of emission intensity, the detection limit became somewhat worse (630 ng L^{-1}).

The deterioration is attributed to the spectral interference, i.e., the emission line of tungsten (W II 249.748 nm) is close to the analytical line (B I 249.773 nm). Peak profiles measured at B I 249.773 nm and W II 245.148 nm which is the sensitive tungsten emission line are shown in Fig. 17. Even in the absence of boron, a very small signal was observed at the wavelength 249.773 nm. The signal should appear due to the spectral interference caused by the tungsten (W II 249.748 nm). For example, the signal appeared at approximately 8.0 s was not assigned to the emission signal of boron but to that of tungsten, because boron was appeared at approximately 6.5 s. Moreover, both the signals at 249.773 nm and 245.148 nm did not appear when no sodium hydroxide was added. Therefore, in the procedure II the surface of the sample cuvette was corroded by sodium hydroxide. A very small portion of the tungsten may be evaporated from the surface of the sample cuvette at the vaporisation step. Its emission would give the spectral interference to the determination of boron. Fortunately, the appearance times of boron and tungsten were slightly different, i.e., tungsten began to evaporate after the complete vaporisation of boron. Therefore, the emission peak of boron could be distinguished easily from that of tungsten when a peak height measurement mode was applied. The analytical performances are listed in Table 15. As for the linearities, linear calibration graphs for boron intersecting almost the origin of the coordinate axes and covering the absolute amounts of at least up to 100 ng of volatile boron and 1000 ng of total boron were established.

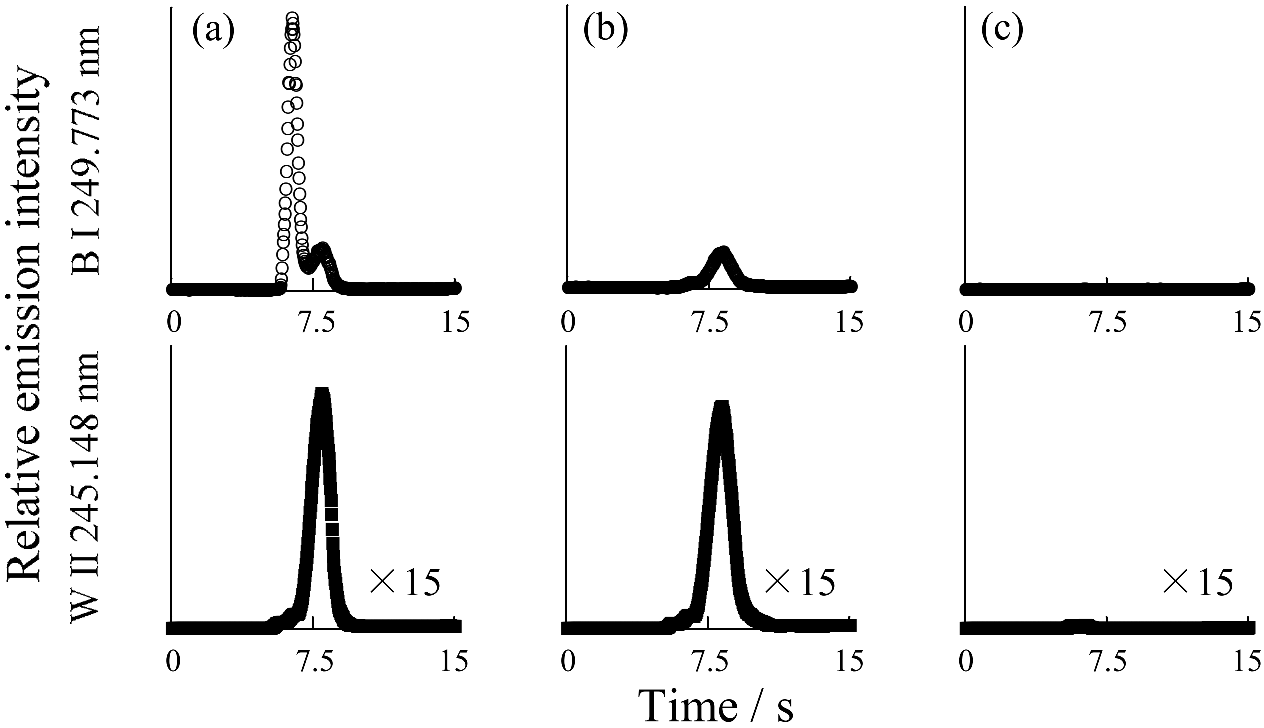

Figure 17. Peak profiles of boron and tungsten measured by the procedure II (TBF-ICP-AES). NaOH, 0.10 mg; drying, 150℃ for 30 s (ramp 10 s); ashing, 500℃ for 20 s (ramp 25 s); vaporisation, 1500℃ for 10 s (ramp 5 s); flow rate of carrier gas, 1.2 dm^3 min^{-1}.

(a), B 10 ng with NaOH; (b), B 0 ng with NaOH; (c), B 0 ng without NaOH.

Table 15. Detection limits and precision of boron

	Area	Height
ETV-ICP-MS[a] (procedure I)		
D.L. (3 σ) / pg	1.2	1.2
D.L. (3 σ) / pg cm^{-3}	13	13
R.S.D., %	3.1[b]	4.2[b]
Linearity / ng	~100	~100
ETV-ICP-AES[c] (procedure II)		
D.L. (3 σ) / pg	60	8.9
D.L. (3 σ) / pg cm^{-3}	630	93
R.S.D., %	1.6[d]	2.7[d]
Linearity / ng	~1000	~1000

a. Analytical mass number, B-10.

b. B(III), 10 pg; n=8.

c. Analytical line, B I 249.773 nm.

d. B(III), 200 pg; n=8.

As a vaporiser, use of furnaces made from graphite is common. For the determination of boron, however, the use of a graphite furnace is not recommended for both the procedures I and II. In the procedure I, boron reacts with the graphite and forms the thermally stable carbide. [42] Regarding the procedure II, when direct injection into the graphite furnace is applied, a plenty of sodium hydroxide added as a flux reagent cannot be removed easily by a conventional bake out procedure. Since the residue of sodium hydroxide in the cuvettes can be washed out easily by soaking the cuvettes in dilute hydrochloric acid, sampling on the removable sample cuvette made of tungsten is strongly recommended. There is no deterioration of both sample cuvettes and TBF, during the firing process, because of extremely lower vaporisation temperature.

3.2.7 Sequential determination

Boric acid and boron nitride can be determined selectively with a dual tungsten boat furnace (TBF) vaporiser system by ICP-MS and ICP-AES. Once an aliquot of the sample solution is pipetted into a sample cuvette made of tungsten, two boron species, the one having high volatility and the other low, can be determined sequentially by setting two different vaporisation temperatures. The volatile boron is determined by selective ICP-MS using TMAH, and the remaining non-volatile boron is determined by robust ICP-AES using sodium hydroxide. This sequential method allows selective determinations of the volatile boron and the non-volatile boron. However, for the determination of non-volatile boron there is an unsatisfactory performance in sensitivity, since the sample amount taken tends to be suitable not for ICP-AES but for ICP-MS. Therefore the two parallel sampling procedures mentioned above are superior.

3.3 Determination of Sulphur, Selenium and Antimony in Iron/steel Samples

In the steel working process, there are important elements, which can influence the positive or negative quality of steel both positively and negatively, by varying such as the ductility, brittleness, resistance to corrosion, machining quality, carbide stability, etc. [56-58] and their influences may be observed even at very low concentrations. [59] These elements include sulphur, selenium and antimony. Regarding the determination, ICPs are utilised for the excitation and ionisation sources for AES and MS, and pneumatic nebulisation has been widely applied for sample introduction. In order to increase the detectabilities for the trace sulphur, selenium and antimony in steel, more sensitive analytical techniques are preferable. Direct solid introduction schemes are very attractive from the view points of increasing the transport efficiency compared with the solution nebulisation, analysing small amounts of samples because of requiring only several milligram amounts and not suffering from contamination inherent to sample preparation. Considering the ETV technique combined with ICP atomic spectrometry, they have further advantages of increased selective vaporisation of analytes from matrix compounds. The object of this section is to propose a robust, high-throughput and easy to operate analytical technique for the determination of sulphur, selenium and antimony in iron and steel samples. For these purposes, a TBF vaporiser based on a new concept is designed. As Fig. 18 shows, the steel sample is hanged over a TBF with a needle-shape magnet. By increasing the temperature of the TBF, the sample is gradually warmed by the radiation from TBF. Just when the temperature of the sample is raised to its Curie point, it is dropped into the TBF. As the TBF is maintained at a higher temperature than the melting point of the sample, the dropped sample melts immediately to generate the vapour of analytes. The vapour is successfully introduced into the plasma to measure the transient emission signals of the analytes.

Regarding the rapid determination of sulphur in steel, Uchihara et al. [17] proposed a similar ETV technique using a graphite crucible vaporiser. The concept of their method is that high purified tin was added as a chemical modifier to the steel in order to decrease the melting point of the sample to the eutectic point with tin. The spheroidal shape of tin alloy and its lower temperature will inhibit the vaporisation of analyte species. Compared to the method proposed by Uchihara et al., since higher and more rapid temperature elevation of the furnace can be achieved by utilising the TBF vaporiser, no chemical modifier to reduce the melting point of the sample is necessary. Because the wettability of tungsten by various metals melted is superior to the graphite, the melted sample is spread out over the surface of the TBF. The analyte vapour will release very easily from the wide spread surface of sample. Therefore, not only sulphur but also selenium and antimony can be also determined with the same procedure.

3.3.1 Magnetic drop-in vaporiser

The schematic experimental procedure is shown in Fig. 18. The sample introduction port was closed with a silicone rubber stopper. A long needle (1.0 mm o.d. × 130 mm long) made of steel pierced through the stopper. By attaching a permanent magnet to the outer edge of the needle, the opposite edge allows the hanging of several pieces of iron sample. For comparison, a disposable graphite cup was used instead of the above-mentioned sample cuvette.

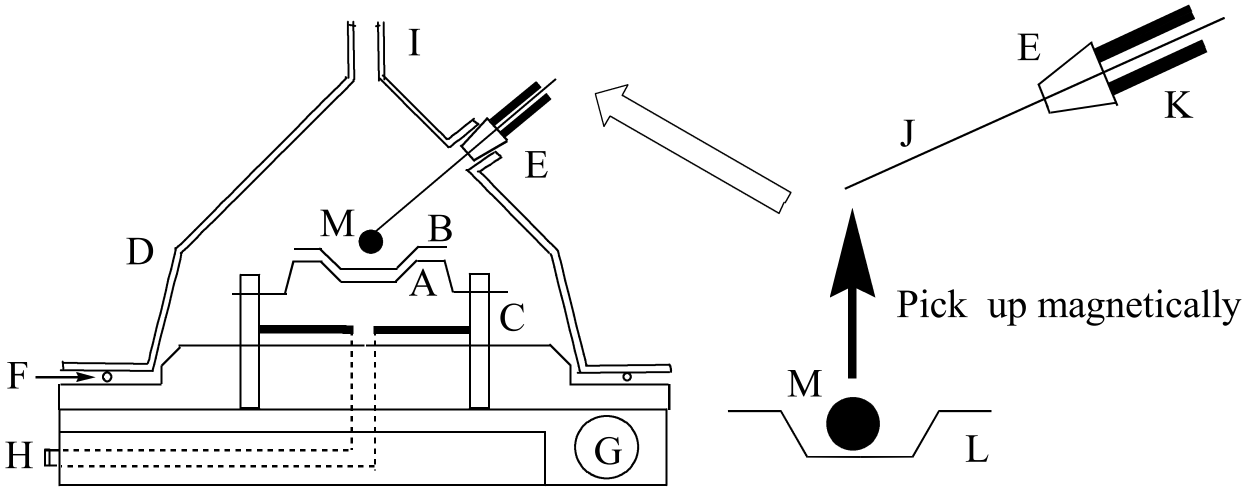

Figure 18. Schematic diagram of the apparatus. A, tungsten boat furnace; B, exchangeable sample cuvette; C, furnace electrode; D, glass dome; E, silicone rubber stopper; F, O-ring; G, electric terminal; H, argon carrier gas inlet port; I, outlet port to ICP; J, needle; K, permanent magnet; L, weighing dish; M, steel or iron sample.

3.3.2 Analytical procedures for the direct analysis of a solid sample

For routine analysis, each aliquot of the iron piece(s) (up to approximately 15 mg) was weighed accurately into a weighing dish. The weighed sample is hung on the edge of the needle. As Fig. 18 shows, the sample and the edge of needle are set over the upward of the TBF, on which a preconditioned sample cuvette is superposed prior to firing. For the vaporisation, the temperature of the TBF is maintained at 150°C for 10 s for the pre-heating, followed by immediate temperature elevation to 2300°C with a ramp time of 5 s and a hold time of 20 s. When the temperature of hung sample is above the Curie point of iron (770°C), the sample leaves from the needle to fall on the sample cuvette which allows to melt in place. The analytes vaporise from the surface of the melted sample. The generated vapour is transported into the ICP by the carrier gas stream. The momentary emission peak profiles are measured by the software attached to the spectrometer. The background-corrected integrated signal (net peak area) is estimated after each vaporisation. The recommended operating conditions are listed in Table 16. For the construction of the calibration curve, standard iron plates are used instead of the sample piece(s). The plates are prepared according to the literature [17] by using diluted standard solutions with dilute nitric acid, from the stock solution of iron. Briefly, an aliquot of the standard solutions is placed on each pure iron plate. These plates are dried on a hot plate kept at 80°C prior to the measurement. One of the plates is hung with the needle and the emission signal is measured in a similar manner.

Table 16. Instrument operation conditions for the determination of sulphur, selenium and antimony

ICP atomic emission spectrometer (Seiko II SPS4000)	
R.F. incident power	1.5 kW
Analytical line	S I 180.734 nm
	Se I 196.090 nm
	Sb I 217.581 nm
Observation height	8.0 mm above load coil
Plasma argon gas	16 L min^{-1}
Auxiliary argon gas	1.0 L min^{-1}
Integration time	25 s
Tungsten boat furnace vaporiser (Seiko II SAS/705V)	
Sample injection	~12 mg
Drying	150°C for 15 s (ramp 0 s)
Vaporisation	2300°C for 20 s (ramp 5 s)
Carrier gas flow rate	
Argon gas	0.85 L min^{-1}
Hydrogen gas	0.15 L min^{-1}

3.3.3 Optimisation of the vaporiser system

Uchihara et al. [17] proposed a chemical modification technique that a highly purified tin was added to iron or steel. One of the concepts of their method is that to achieve the effective release of sulphur species, the melting point of iron, which is 1535°C for pure iron, [60] is reduced to the eutectic point with tin. By applying their technique, the temperature was reduced to 500-700°C, depending on the mixing ratio of tin vs. sample (iron or steel). By using 0.5 g of tin as a modifier, for example, up to 0.8 g of the sample could be analysed. However, by the use of such a plentiful amount of tin, a spheroidal sample with a large diameter is formed. As Fig. 19C shows, less affinity between the graphite surface and melted alloy facilitated the formation of a complete spheroid. The diffusion of analyte from the inside of the spheroid to its surface was suppressed seriously. However, in the case of sulphur, even if the resulting alloy has a minimum surface area, the analyte sulphur was effectively released as volatile carbon disulphide by the reaction with the carbon from the inside wall of the graphite crucible. The above-mentioned is the other concept. In the case of selenium and antimony, however, formation of volatile species like carbon disulphide are not known. In fact, a similar attempts using graphite cup TBF vaporiser (Fig. 19A) resulted in failure. Even if a sufficient amount of selenium and antimony in the steel were vaporised and measured, a broader peak profile and a poorer sensitivity were obtained despite the addition of a suitable amount of tin as a chemical modifier. The poor detectability may be attributed to the minimum surface area of the alloy, to the low diffusion of analyte species, and to the low volatility of analyte at a low vaporisation temperature. Figure 20A shows the peak profile of selenium vaporised from a graphite cup furnace.

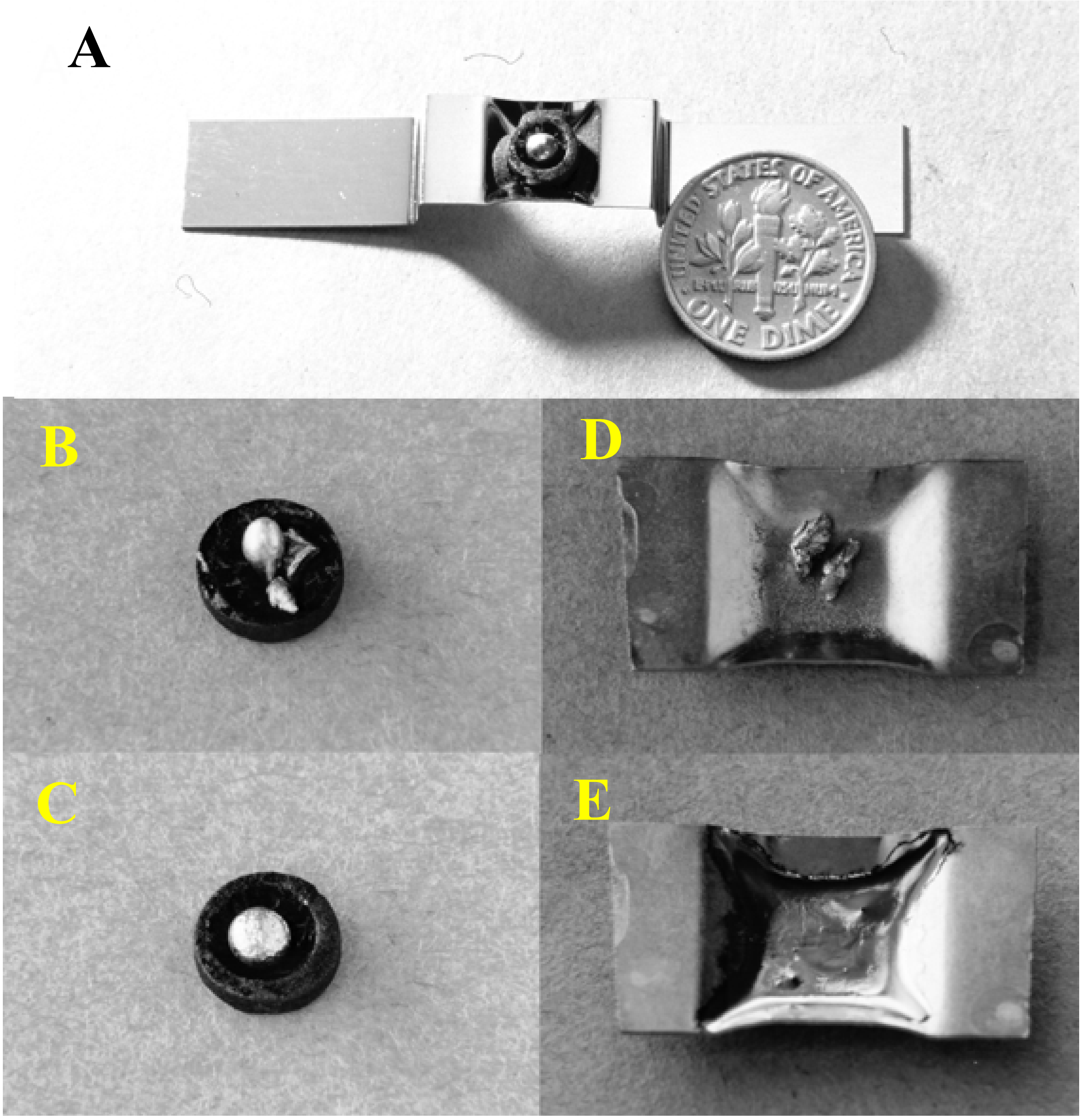

Figure 19. Photographs of separable graphite cup and small sample cuvette made of tungsten. A, tungsten boat furnace and graphite cup; B, graphite cup, steel sample and tin shot before vaporisation; C, the same of B after vaporisation (melted iron and tin form a small, complete spheroid); D, sample cuvette and steel sample before vaporisation; E, the same as D after vaporisation (melted iron spreads out in the bottom of cuvette).

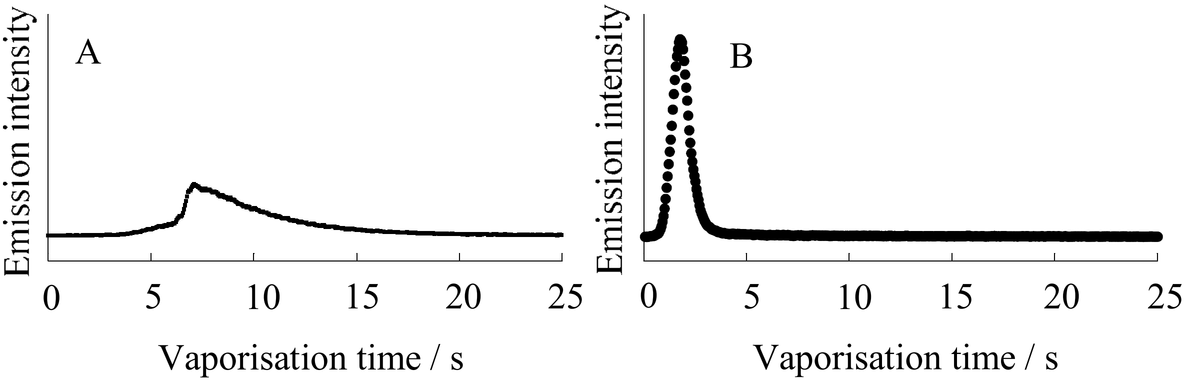

Figure 20. Peak profiles of selenium. A, vaporised from graphite cup; B,vaporised from sample cuvette made of tungsten. Sample, NIST SRM 339 Stainless Steel.

In contrast, the tungsten sample cuvette TBF vaporiser system has an advantage - the wettability between the surface of the sample cuvette made of tungsten and the melted iron is superior. As Fig. 19E shows, the melted iron spreads out over the surface of the sample cuvette. The widespread thin layer of the sample facilitates the vaporisation of analytes from the surface effectively. This is the most remarkable feature of merit using sample cuvette TBF. Actually, as Fig. 20B shows, a suitable peak profile for the determination of selenium was obtained even when no tin was added to the sample iron. Similar profiles can be obtained in the cases of sulphur and antimony. Therefore, no tin was added as a chemical modifier in the proposed vaporisation system. This reduced the operation time, since no extra procedure was needed in order to expel the impurities from the modifier of tin. When the vaporisation temperature is maintained at an intermediary temperature (2300°C) between the boiling point of the matrix iron (2750°C, [50] 3000°C, [60]) and the boiling points of potential species (e.g., -10°C for SO_2, [60] 46.5°C for CS_2, [60] 684±10°C for Se, [50] 315°C for SeO_2, [60] 260°C for H_2SeO_4, [60] 1425°C for SbO_3, [60] etc.), the quantitative generation and introduction of the analytes were achieved, permitting their effective separations from the iron matrix.

If the sample were dropped directly onto the TBF, the residue of steel remained on the surface of TBF after each firing. The use of exchangeable small sample cuvettes is strongly recommended. Although it was difficult to remove the residue by a conventional bake out procedure, it could be washed away easily by soaking it overnight in hydrochloric acid with a suitable concentration. In this manner, the same TBF is useable for several days or a week, exchanging the many sample cuvettes.

3.3.4 Basic analytical performance characteristics

The best attainable detection limits for sulphur, selenium and antimony were estimated to be 24 ng, 18 ng and 21 ng, respectively, which were defined as the absolute amounts of analytes required to yield net integrated signals (background-corrected peak areas) that were three times the standard deviation of the blank in the presence of highly purified iron foil. These values correspond to 1.6 mg kg^{-1}, 1.2 mg kg^{-1} and 1.4 mg kg^{-1} of the sulphur, selenium and antimony concentrations, respectively, when 15 mg of a sample is dropped on the sample cuvette. Regarding the sulphur and antimony, since several mg kg^{-1} or more of the analytes are contained in real steel samples, the obtained detectabilities are concluded to be sufficient. With a larger sample amount, a proportionally lower detection limit could be attained. If necessary, larger TBF (e.g., 25 mm × 100 mm; the size of bottom depression, 21 mm × 21 mm) and sample cuvettes are useable. Linear calibration graphs covering absolute amounts up to 12-16 μg and intersecting the origin of the coordinate axes with a typical correlation coefficient $r^2=0.992 \sim 0.999$ were established. The repeatabilities were estimated to be 3.1-5.1% using the NIST SRM samples. This acceptable precision includes overall sample introduction procedures, such as the weighing, the introduction of sample piece(s), the operation of hanging and dropping, vaporisation, etc. These values were much better than those obtained by the authorised analytical methods. [61,62] The analytical methods such as laser ablation ICP-MS, spark or glow discharge AES, etc., required solid standards to construct calibration curves. To perform this purpose, SRMs were commonly used. In these cases, the selection of the standards was very important, i.e. the analyte concentrations of the sample should be in the concentration range of the standards, also, the matrices of the standards should be similar to those of the samples. Compared to the methods, the proposed MDI-TBF-ICP-AES requires no solid standards. Quantitative determinations can be performed by using the aqueous standard solutions, even without any matrix matching and sample pre-digestion. For more accurate determinations, the standard additions method will be easily applicable by dropping samples together with standard iron plates simultaneously.

3.3.5 Determination of sulphur, selenium and antimony in practical samples

In order to evaluate the feasibility of direct analysis, the proposed technique was applied to the determination of sulphur, selenium and antimony in several certified reference materials of steel. The results are listed in Table 17. It is demonstrated that the direct analysis of sulphur, selenium and antimony by the proposed method is accurate even without any matrix matching, addition of chemical modifier and sample pre-digestion. The sample cuvette TBF technique makes it possible to measure a number of samples sequentially by preparing several sample cuvettes before. Regarding the sample throughput, approximately 60 samples could be vaporised per hour.

Table 17. Analytical results of sulphur, selenium and antimony in certified reference materials measured by calibration curve method

Sample	Found,[a] %	Certified, %
Sulphur		
NIST SRM 362 AISI 94B17 (mod.)	0.035±0.004	0.0360
NIST SRM 339 Stainless Steel	0.015±0.005	0.013
Selenium		
NIST SRM 339 Stainless Steel	0.248±0.002	0.247
NIST SRM 2165 Special Low Alloy	0.0032±0.0001	0.0035[b]
Antimony		
NIST SRM 362 AISI 94B17 (mod.)	0.013±0.001	0.013
JSS 173-3 Carbon Steel	0.0047±0.0003	0.0048

a. Mean ± standard deviation, n=4.

b. Reference value.

4 CONCLUSIONS

The simultaneous determination of halogens by an electrothermal sample introduction ICP-MS is demonstrated by using TMAH as a chemical modifier. The detection limits obtained by using the proposed ETV technique are improved approximately three orders of magnitude compared to those using a nebuliser. A graphite furnace vaporiser can be also possible for the same purpose. The detectabilities for bromine and iodine by ICP-MS were significantly improved by the present procedure, although the limitations are still remained for the determination of chlorine and fluorine in their sensitivities. The method shows great potential for the determination of bromine and iodine in aqueous and biological samples as well as foodstuffs.

Focusing on the significant difference of vaporisation properties of boron species, the selective determinations of volatile and non-volatile boron are established. TMAH is added as a chemical modifier for the determination of volatile boron, while sodium hydroxide is added as a flux for total boron including volatile species. When small quantity of a sample is analysed, an aliquot of sample solution is pipetted into a sample cuvette made of tungsten, two boron species, the one having high volatility and the other low, can be determined sequentially by setting two different vaporisation temperatures. If accurate determinations are needed, two parallel sampling procedures are superior. The analytical results of steel and botanical samples were agreement with their certified values (total boron). The recovery experiments in which boron was added as boric acid and/or boron nitride are satisfactory.

Applying to the magnetic drop-in TBF-ICP-AES technique, the quantitative generation and introduction of the sulphur, selenium and antimony could be achieved, permitting its effective separation from the iron matrix, since the vaporisation temperature is maintained at an intermediary temperature between the boiling points of sulphur, selenium and antimony species.

Thus, this method will be readily be extended to the direct determination of sulphur, selenium and antimony by ETV-ICP-MS, where it should be necessary to protect the mass spectrometer against an overload of matrix.

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Appendix

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