JAAS
Journal of Analytical Atomic Spectrometry

Determination of Boron Using Mannitol-assisted Electrothermal Vaporization for Sample Introduction in Inductively Coupled Plasma Mass Spectrometry

WEN-CHING WEI, CHIH-JUNG CHEN AND MO-HSIUNG YANG*

Institute of Nuclear Science, National Tsing Hua University, Kuang-Fu Road, 30043 Hsinchu, Taiwan

The possibility of improving the detection sensitivity for boron with the use of mannitol as a chemical modifier in electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS) is presented. Experiments were performed by adding mannitol to a boron analyte solution to form a boron–mannitol complex and then injecting the resulting product into the ETV-ICP-MS system for determination. The effect of mannitol on the signal pulse of boron was investigated by monitoring the analyte through a heating cycle from 150 to 2600 °C. The appearance of several marked signal pulses at temperatures between 425 and 1500 °C was observed and assumed to result from the vaporization of boron–mannitol complexes. The signal intensity of boron in the presence of mannitol was found to be considerably enhanced in comparison with that in its absence. The optimization of the ETV and ICP parameters and the amount of mannitol added and the comparison of mannitol with different modifier systems were subsequently investigated. It was found that by following the established method the sensitivity for boron in the presence of mannitol can be improved by a factor of 84 compared with that without the modifier, and the limits of detection (3 *s*) achieved in the presence of mannitol can be as low as 0.2 ng ml^{-1} with a 20 µl injection. The large boron sensitivity enhancement in the presence of mannitol in ETV-ICP-MS is attributed to the formation of a boron–mannitol complex that is subsequently vaporized from the graphite surface and transported with the assistance of mannitol to the plasma. A novel application with mannitol, which acts both as a preconcentrating agent for boron in the chemical separation process and as a modifier in the ETV-ICP-MS for the determination of boron in trichlorosilane, is also presented.

Keywords: *Boron; electrothermal vaporization inductively coupled plasma mass spectrometry; mannitol chemical modifier*

Electrothermal vaporization (ETV) as a means of sample introduction for inductively coupled plasma spectrometry promises to be an important analytical technique in ultra-trace and microlitre-scale analyses. Because volatilization of the analyte occurs in the ETV device, the plasma is not required to desolvate the sample and, therefore, the plasma has more energy available for atomization, ionization and excitation. The furnace also offers the ability to separate sample matrix components from the analyte of interest, which causes a decrease in interferences in the emission or mass spectrum and improved sample transport efficiency of the analyte, compared with nebulization, to the argon plasma.[1] Both of these advantages allow improved detectability for most elements. Despite the above advantages, however, this ETV technique has limited application in the determination of boron because of its tendency to form refractory carbides with the carbon of the graphite tube before atomization occurs.[2] Among the problems associated with the formation of refractory carbides are loss of sensitivity and the occurrence of memory peaks due to the vaporization of residual boron carbides formed during previous determinations.

In an attempt to solve this problem of carbide formation, in several studies ETV as a sample introduction technique for inductively coupled plasma atomic emission spectrometry (ICP-AES) has been used to investigate the halogenating vaporization behaviour of boron in a graphite furnace. The results indicated that addition of halogenating agents such as trifluoromethane,[3] chlorine[4] and polytetrafluoroethylene (PTFE)[5,6] was effective in preventing carbon from reacting with boron and converting refractory carbides into volatile halides. Typical improvements in the detection limits obtained with this technique are between one and two orders of magnitude compared with those of ICP-AES without the halogenating agents.[3,5]

In addition to studies on the ICP system as described above, many improved methods for the determination of boron by electrothermal (graphite furnace) atomic absorption spectrometry (ETAAS) have been developed. Most of these studies attempted to prevent the formation of refractory boron carbides by means of chemical modifiers such as Mg,[7] Ni[8] and Ti with ascorbic acid.[9] Some methods involve pre-treating the graphite tube with elements that form carbides that are more thermodynamically stable than boron carbides, such as Zr,[8] or *in situ* coating of the tubes with pyrolytic graphite.[10] Although these methods are effective in preventing the formation of boron carbides and improve the detection limit of boron in ETAAS to the range 20–70 ng ml^{-1},[11] these values are still around two orders of magnitude higher in comparison with many elements determined routinely by ETAAS.

The results from ETAAS indicate that carbide formation cannot be the only factor causing the poor sensitivity of boron and other responsible factors may also be involved. Among these studies, Slavin[12] suggested that pre-atomization loss of volatile B_2O_3 could be responsible for the low sensitivity of boron, although no direct evidence for this was reported. The evidence of low-temperature loss of boron was recently reported by Wiltshire *et al.*[13] using dynamic secondary ion mass spectrometry and confirmed that vaporization of boron species occurs above 900 °C. More intensive work using ETV-ICP-MS to investigate the vaporization and atomization of boron in the graphite furnace was recently reported by Byrne *et al.*[11] They explained, based on their ETV-ICP-MS data, that the majority (>95%) of the boron is vaporized in molecular form, possibly as gaseous HBO_2 and BO, and removed from the furnace at temperatures between 900 and 2100 °C, which is well below the appearance temperature of boron atoms. As the onset of this vaporization is at around 800 °C, far below the temperature at which boron carbide would be expected to form, they concluded that carbide formation is not

* To whom correspondence should be addressed.

the major cause of the lower sensitivity of boron in ETAAS. Based on all evidence obtained so far, it may conclude that the loss of volatile molecular species from the furnace prior to atomization and the formation of refractory compounds are two major causes of lower sensitivity in ETAAS.

For the purpose of developing ETV-ICP-MS as a highly sensitive method for determination of boron, information acquired from ETAAS can provide some useful insights into sample vaporization mechanisms and optimum operating conditions for ETV. However, it should be emphasized that unlike ETAAS, where efficient formation of atomic species is paramount, in ETV-ICP-MS efficient vaporization of the sample and transport to the plasma are necessary.[14] This is because in ETV-ICP-MS any molecular or atomic species removed from the furnace, either during the pyrolysis step or the temperature ramp to atomization, will be totally or partially dissociated by the plasma and detected as atomic ions by the mass spectrometer. Therefore, some of the problems associated with poor atomization efficiency in ETAAS may not be directly applicable to ETV-ICP-MS. In view of the results of Byrne *et al.*[11] indicating a substantial enhancement of transport efficiency of boron in the ETV-ICP-MS system in the presence of nickel nitrate as modifier and also the success of applying halogenating agents for preventing carbide formation in the ETV-ICP-AES system, it may be expected that a further increase in detection sensitivity of boron by ETV-ICP-MS will be possible, provided that the formation of boron carbides and transport losses of boron can be more effectively prevented by the use of some special chemical modifiers.

In our studies on the analysis of silicon semiconductor materials,[15–17] mannitol, $CH_2OH(CHOH)_4CH_2OH$, was used as a reagent to separate boron from the hydrolysed silicon matrix by vaporization through the formation of a non-volatile boron–mannitol complex. The results indicated that the quantitative recovery of boron from various acidic solutions (including HF, HCl and HNO_3) in the presence of mannitol could be achieved, and the boron–mannitol complex formed could completely resist vaporization losses in the subsequent evaporation process. The treated sample solution so obtained can be used for the determination of boron by ETAAS, ICP-AES or spectrophotometric methods. In an attempt to inject the treated sample solution which contained mannitol into the ETV-ICP-MS system for boron determination, we surprisingly found a substantial increase in the intensity of boron (about 80-fold) compared with boron solution without mannitol added. This observation led us to consider that mannitol may be a very effective chemical modifier for boron in ETV-ICP-MS. In this study, the effect of the boron–mannitol complex in assisting the determination of boron by ETV-ICP-MS was investigated. The analytical characteristics of the technique and the optimization of the experimental conditions were also studied. The method established was tested for its applicability to the determination of boron in a trichlorosilane sample.

EXPERIMENTAL

Containers and Reagents

Polytetrafluoroethylene (PTFE) and polypropylene containers were used throughout. The vessels were cleaned by immersion in concentrated nitric acid overnight and steaming successively with nitric acid and water vapour before use.

All chemicals were of analytical-reagent grade. High-purity water, which was purified by demineralization, two-stage quartz distillation and subsequent sub-boiling distillation, was used throughout. HNO_3 and HF were also purified by sub-boiling distillation. A stock solution of boron (5.000 ± 0.005 g l^{-1}) from Merck was diluted to the desired concentrations with water prior to use. Mannitol was of analytical-reagent grade from Merck. Mannitol solution of 1% m/v was prepared by dissolving 1 g of mannitol in 100 ml of water and further diluted prior to use.

Sample Pre-treatment

The pre-treatment of trichlorosilane followed basically the procedures described in previous papers[15–17] and was performed in a clean laboratory with class 100 clean bench. For the dissolution of silane samples, 10 ml of sample were transferred into a 100 ml PTFE beaker and the system was cooled with liquid nitrogen. Then, 1 ml of 1% mannitol solution was added, followed by the slow addition of 50 ml of water to hydrolyse the silane sample. The hydrolysed product was dissolved in 15 ml of HF and the resulting solution was then evaporated nearly to dryness at about 80 °C. The residue was dissolved in 0.5 ml of 0.5 mol l^{-1} HNO_3 and diluted to 1 ml for determination by ETV-ICP-MS. Blanks and standards were tested followed the same procedures as for samples.

ETV-ICP-MS Instrumentation

The instrumentation consisted of a Perkin-Elmer SCIEX Elan 5000 ICP mass spectrometer and an electrothermal vaporization unit from a Perkin-Elmer HGA-600MS graphite furnace. A Perkin-Elmer AS-60 autosampler was used for sample introduction. Pyrolytic graphite-coated tubes were used throughout.

The ICP-MS instrument was initially optimized using conventional pneumatic nebulization, then converted to operate with the ETV. The HGA-600MS was interfaced to the argon plasma via a 50 cm length of 6 mm i.d. PTFE tubing. The operation of the HGA-600MS was completely computer controlled. During the drying and ashing stages of the temperature programme, opposing flows of argon gas (300 ml min^{-1}) originating from both ends of the graphite tube removed water and other vapours through the dosing hole of the graphite tube, while during the high-temperature vaporization step, the dosing hole was sealed pneumatically with a graphite probe. Once the graphite tube had been sealed, a valve located at one end of the HGA workhead directed the carrier argon flow from one end of the graphite tube directly to the argon plasma at a flow rate of 1.2 ml min^{-1}. The peak hop transient mode of data acquisition was used with a range of 25–45 ms dwell time for each ion monitored. The masses of 10 and 11 were simultaneously monitored throughout this work. The instrumental parameters and operating conditions used are summarized in Table 1.

Table 1 Instrumental parameters and operating conditions

Conditions for ICP-MS	
ICP radiofrequency power	1.0 kW
Coolant argon flow rate	15 l min^{-1}
Auxiliary argon flow rate	0.8 l min^{-1}
Carrier gas flow rate	1.2 l min^{-1}
Sampler/skimmer	Nickel
HGA-600 electrothermal vaporizer	
Sample volume	20 μl
Heating cycle	
Drying	10 s ramp to 150 °C 50 s hold at 150 °C
Vaporization:	
for the signal profile	(1) 20 s ramp to 1500 °C 30 s hold at 1500 °C 0 s ramp to 2600 °C 5 s hold at 2600 °C (2) 40 s ramp to 2600 °C
for the determination of boron in sample	0 s ramp to 2500 °C 8 s hold at 2500 °C

RESULTS AND DISCUSSION

Effect of Mannitol Chemical Modifier

The remarkable complex-forming ability of boric acid with mannitol (b.p. 290–295 °C) in solution has been reported by many researchers.[18–23] The stoichiometry and equilibria of the boric acid–borate–mannitol system have been intensively studied. It is generally thought that mannitol reacts with boric acid to yield complexes with mannitol (M)-to-boron (B) ratios of 1:2 ($[BMB]^{2-}$), 1:1 ($[BM]^{-}$) or 2:1 ($[BM_2]^{-}$), or even polymerized forms such as $[BM]_n^{n-}$, depending strongly on the mannitol-to-$B(OH)_3$ mole ratio.[20,22] Despite extensive work devoted to the stoichiometry and equilibria of boron–mannitol complexes in aqueous systems, there is still a lack of information on the boiling points, melting points and other thermochemical data of the respective complexes.

The general effect of mannitol as a chemical modifier on the signal profile of boron in ETV-ICP-MS was first investigated by monitoring the analyte throughout a heating cycle from 150 to 2600 °C. Fig. 1 shows the signal pulses of 10 ng of boron in the presence of 40 μg of mannitol and 10 ng of boron without mannitol. $^{10}B^+$ and $^{11}B^+$ were simultaneously monitored and the results indicated no significant difference between them. Considering the relatively high abundance of boron-11 (80.2%), only the data for $^{11}B^+$ are reported in this paper. In order to ascertain if the possible contamination of boron in the mannitol reagent and also the $^{12}C^+$ signal due to the presence of mannitol may constitute serious background interferences for the detection of boron, a mannitol solution of 2000 μg ml^{-1} was injected into the ETV system to serve as a reference. The signal profile of boron shown in Fig. 1 was obtained with a heating programme consisting in increasing the temperature from 150 to 1500 °C in 20 s and holding at 1500 °C for 30 s, then re-vaporizing from 1500 to 2600 °C at maximum power heating (0 s ramp) and holding at the latter temperature for 5 s. As can be seen, there are four signal pulses for boron in the presence of mannitol, whereas there is no appreciable signal pulse for boron in the absence of mannitol and in the reference mannitol solution. In the presence of mannitol, boron exhibits three peaks in the temperature range 150–1500 °C, the first peak beginning to appear at 425 °C (4.5 s), and a fourth peak appears as the temperature is further increased to 2600 °C (50.5 s). From the striking difference in the signal profiles in the presence and absence of mannitol, it is concluded that mannitol must play an important role in the ETV process.

The question then arises as to why several peaks should be observed in the temperature range 425–1500 °C in the presence of mannitol when none is observed in its absence. The latter case is obviously not consistent with the observation of Byrne *et al.*[11] in their ETV-ICP-MS experiments on boron with no modifier addition. They found a broad boron signal at vaporization temperatures between 800 and 2600 °C with a peak maximum at 1800 °C, and suggested that gaseous HBO_2 and BO are formed at 900–2100 °C, which accounted for the low sensitivity towards boron in ETAAS. In order to confirm if the boron signal observed by Byrne *et al.*[11] exists, the heating cycle used in Fig. 1 was modified by increasing the vaporization temperature from 150 to 2600 °C, instead of only to 1500 °C as in Fig. 1, in 40 s. Fig. 2 shows the signal pulses of boron obtained in the presence and absence of mannitol. As can be seen, there now appears a distinct signal pulse, although of much lower intensity compared with others in the same figure, between 1068 °C (15 s) and 1500 °C (22 s) for boron in the absence of mannitol, and three signal pulses again similar to those seen in Fig. 1 in the presence of mannitol, but no fourth signal pulse is observed. The distinct appearance of the boron signals between 1068 and 1500 °C in the absence of mannitol as seen in Fig. 2 basically agrees with the previous report,[11] except for some difference in the signal appearance, possibly due to the different heating programmes applied. This may further support Byrne *et al.*'s conclusion that the poor sensitivity for the determination of boron by ETAAS is attributable to extensive pre-atomization loss of molecular species from the graphite furnace at temperatures well below the appearance temperature (about 2200 °C) of boron.[11]

By comparing Figs. 1 and 2, it is found that in the absence of mannitol no perceivable boron signal can be observed at a vaporization temperature of 1500 °C (Fig. 1), which far exceeds the temperature for pre-atomization loss of molecular boron species,[11] whereas a distinct signal of boron is observed as the vaporization temperature is further increased to 2600 °C (Fig. 2). This may indicate that the vaporized boron species in the absence of mannitol, even at a vaporization temperature as high as 1500 °C, still cannot be effectively transported from ETV to the ICP through the transportation line. If this is indeed the case, the appearance of the three signal pulses of boron in Fig. 1 at temperatures between 425 and 1500 °C in the presence of mannitol may thus be explained by the fact that these species resulting from reaction between boron and mannitol should possess special properties of high volatility and easy transportability.

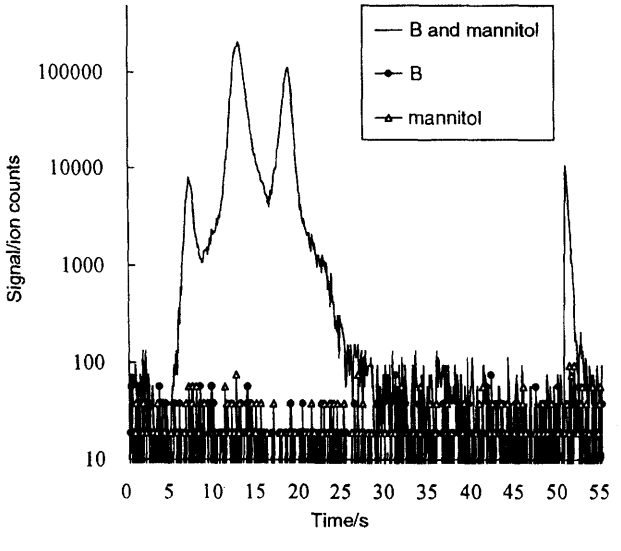

Fig. 1 Comparison of signal profiles for 10 ng of B with and without mannitol (40 μg). Vaporization 150–1500 °C (20 s), hold at 1500 °C (30 s), re-vaporization 1500–2600 °C (0 s), hold at 2600 °C (5 s)

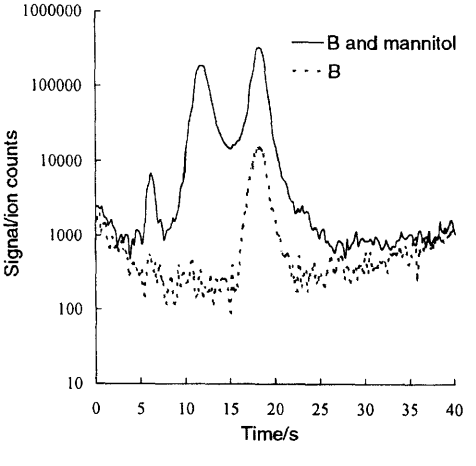

Fig. 2 Comparison of signal profiles for 10 ng of B with and without mannitol (40 μg). Vaporization temperature was increased from 150 to 2600 °C in 40 s

As previously discussed, boron can react with mannitol to form various boron–mannitol complexes which depend strongly on the complex formation conditions.[20–23] Since no information on the volatility and thermal stability of these boron–mannitol complexes is available, no detailed discussion or identification of the respective species from the signal pulses of the vaporization curve is possible. However, it is reasonable to assume that the appearance of each signal pulse shown on the vaporization curve may correspond to specific molecular precursors of boron. The molecular precursors of boron can be either certain specific boron–mannitol complexes evaporated directly from the graphite surface or certain reaction products of the complex that evaporated from ETV surface and were then transported to the ICP for detection. As a consequence, the first three overlapped signal pulses that appeared between 425 and 1500 °C, which were found to change their relative intensities on varying the ratio of boron to mannitol in the injected solution, may represent three relatively easily vaporized boron-containing species, while the fourth peak that appeared at 2600 °C may consequently correspond to less volatilized species. From the shape of the fourth signal pulse, which shows no peak tailing, and also its disappearance from Fig. 2 when the vaporization temperature was increased to 2600 °C, it may be assumed that the species corresponding to this signal pulse should not be a boron carbide. This is because boron carbide (b.p. 3500 °C) cannot be completely vaporized at 2600 °C[5] and normally shows a memory effect during subsequent blank firings.[2] Consequently, it may be reasonable to assume that this less volatilized species is most likely the reaction product resulting from decomposition of the boron–mannitol complex on increasing the heating temperature from 1500 to 2600 °C. This part of the boron-containing species can later be completely evolved and transported to the plasma and contributes to the overall signal intensity in ETV-ICP-MS. Further investigations on the possible reaction process of these species in the ETV system are in progress.

From the signal pulses shown in Fig. 2, it is seen that the signal of boron in the presence of mannitol is much higher than that in the absence of mannitol. This increase in signal intensity can be attributed to the role of mannitol, which may act as both a physical carrier and a chemical carrier. As previously described, mannitol is a specific reagent that reacts with boron to form various boron–mannitol complexes. The complexes so formed can be easily vaporized, as evidenced by the high signal intensity of the corresponding peaks on the vaporization curve. It may therefore be concluded that mannitol modifier not only plays a role in producing the analyte vapour of boron–mannitol complexes but also plays a second role as a physical carrier, improving the transport of the vaporized materials to the detection system.

Optimization of Analytical Parameters

With the knowledge that the presence of mannitol has a large enhancing effect on boron in ETV-ICP-MS, the following experiments were performed to optimize several important parameters that may influence the analytical performance of this method. Various factors, such as ETV temperature programme, carrier gas flow rate and amount of mannitol added, were systematically investigated.

Effect of ETV parameters

Thermal pre-treatment–vaporization curves can provide useful information about vaporization processes and optimum conditions for atomic ion formation in ETV-ICP-MS. In the ETV-ICP-MS experiments the atomic ions detected by the mass spectrometer could be formed from molecular species vaporized from the graphite furnace and subsequently dissociated in the plasma. For a given thermal pre-treatment temperature, the ashing and vaporization curves show the variation of atomic ion intensity with ashing and vaporization temperature.

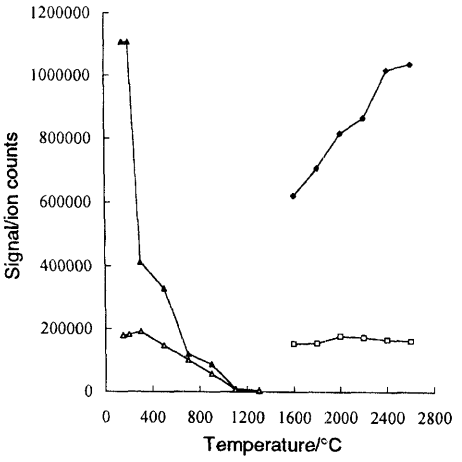

Fig. 3 Ashing and vaporization curves for boron with and without mannitol. In the presence of mannitol (40 μg), 10 ng of boron were used, and in the absence of mannitol, 150 ng of boron were used. Temperature programme for ashing curves: drying at 150 °C (10 s ramp, 50 s hold); ashing at prescribed temperature (20 s ramp, 60 s hold); vaporization 2600 °C (0 s ramp, 8 s hold). Temperature programme for vaporization curves: drying at 150 °C (10 s ramp, 50 s hold); vaporization at prescribed temperature (0 s ramp, 8 s hold). Ashing curve: △, without mannitol; and ▲, with mannitol. Vaporization curve: □, without mannitol; and ■, with mannitol

Fig. 3 shows the ashing and vaporization curves for boron with and without the presence of mannitol. The ashing curves shown were obtained by a heating programme of drying at 150 °C (10 s ramp, 50 s hold), ashing at the prescribed temperature (20 s ramp, 60 s hold) and vaporization at 2600 °C (0 s ramp, 8 s hold); while the vaporization curves were obtained with a programme of drying at 150 °C (10 s ramp, 50 s hold) and then vaporization directly at the prescribed temperature (0 s ramp, 8 s hold). The reason for extending the hold time at the ashing temperature to as long as 60 s at each prescribed temperature is simply to observe more obviously the loss of boron occurring at that specific temperature.

The most striking feature in Fig. 3 is the marked difference in the signal intensity for boron in the presence and absence of mannitol modifier. As can be seen, in the presence of mannitol the ashing curve decreases abruptly with increase in temperature from 200 to 1100 °C, indicating that boron begins to be lost at an ashing temperature somewhere between 200 and 300 °C, and this decreasing tendency persists to at least 1100 °C. In the absence of mannitol the ashing curve decreases after 300 °C but with a much lower tendency until 1100 °C, which is somewhat different from the pre-atomization loss temperature of 800 °C in the vaporization curve reported by Byrne *et al.*

Concerning the vaporization curves, it can be seen from Fig. 3 that in the presence of mannitol the signal of boron steadily increases from 1600 to 2500 °C and then levels off up to 2600 °C, which seems to be in reasonably good agreement with the appearance temperature of 2600 °C for the fourth peak as shown in Fig. 1. In the absence of mannitol, the signal of boron shows a slight increase from 1600 °C to a maximum at about 2000 °C and then gradually decreases again to 2600 °C, which is also in reasonable agreement of the optimum vaporization temperature of 1800 °C suggested for the determination of boron by Byrne *et al.* From the point of view of achieving maximum detection sensitivity for boron, the optimum heating cycle in the presence of mannitol is suggested to be drying at

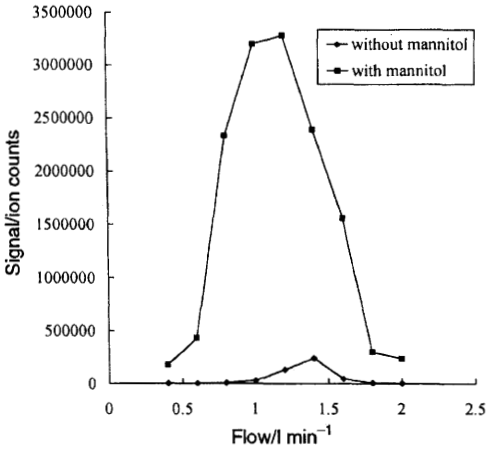

Fig. 4 Effect of carrier gas flow on the signals of 30 and 150 ng of B, in the presence and absence of mannitol (40 μg)

150 °C for 50 s, ramping at maximum power heating (0 s ramp) to 2500 °C and holding at that temperature for 8 s. The heating temperature programme established for the ETV system is summarized in Table 1.

Effect of carrier gas flow rate

The nebulizer gas flow rate is one of the most critical ICP parameters in ICP-MS and has a considerable influence on the analytical signal obtained.[24] Fig. 4 shows the effect of carrier gas flow rate on the signal intensity of 30 and 150 ng of boron in the presence and absence of mannitol (40 μg). It is seen that in the presence of the modifier the boron intensity increases abruptly with increasing flow rate from 0.4 to 1.2 l min^{-1}, then levels off, and after 1.2 l min^{-1} the signal decreases rapidly again with increasing flow rate. The flow rate of 1.0–1.2 l min^{-1}, which results in maximum signal intensity, is considered to be the optimal and was used throughout this study. In Fig. 4 it is also seen that the signal intensity of boron in the absence of modifier is much lower than the former, the maximum signal being observed at a flow rate around 1.4 l min^{-1}.

Effect of mannitol concentration

The signal enhancement caused by the presence of mannitol is primarily attributed to the increasing transport efficiency of boron between the vaporization surface and the ICP. The effect of the amounts of mannitol on the signal intensity of boron was therefore investigated. Fig. 5 shows the results of the addition of various amounts of mannitol to 10 ng of boron.

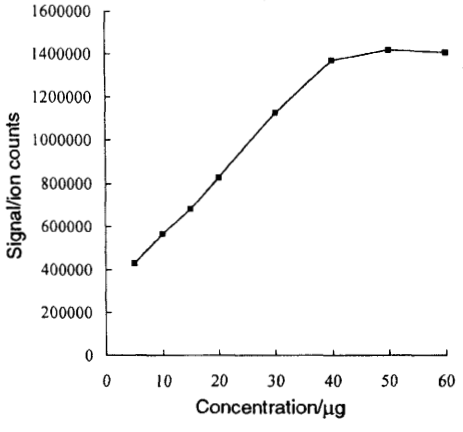

Fig. 5 Effect of mannitol amounts on the signal of B (10 ng)

It indicates that the signal intensity increases linearly with increasing addition of mannitol from 5 to 40 μg and then levels off until 60 μg. The possible effect of the $^{12}C^+$ signal originating from mannitol on the detection of the analyte ion ($^{11}B^+$) was checked, and the result indicated that only a limited increase in background was observed as the amount of mannitol added was lower than about 100 μg. However, in order to obtain a highly accurate result for the determination of ultra-trace levels of boron, suitable subtraction of the blank from the measured signal would be necessary. In this study, an amount of mannitol of 40 μg was considered suitable.

Analytical Performance

The notable effect of mannitol as a chemical modifier on the signal enhancement of boron in ETV-ICP-MS has been clearly indicated. With the use of the established experimental parameters given in Table 1, the analytical precision, sensitivity and limits of detection of the method were evaluated. The results showed that an analytical precision of less than 5% can generally be obtained by repeated determination of boron at a concentration of 50 ng ml^{-1}. The limits of detection, defined as the analyte concentration that gives a signal that is three times the standard deviation of the blank, was calculated to be at sub-ng ml^{-1} levels by injecting 20 μl of sample solution. Table 2 gives a comparison of the sensitivity and limits of detection of the present ETV-ICP-MS method for the determination of boron with and without mannitol addition. It can be clearly seen that with the modifier the limit of detection (3*s*) is improved by two orders of magnitude (34.2 *versus* 0.2 ppb) and the sensitivity is improved by a factor of 84 (16 versus 1344 ions per ppb) compared with that without the modifier. The effectiveness of mannitol on the sensitivity enhancement for boron is thus confirmed.

Further comparison of mannitol with other modifier systems for boron in ETV-ICP-MS was also made. Mannitol, EDTA, Pd, Mg, Cu and Ni gave sensitivity enhancement factors of 84, 28, 0.95, 8.3, 9.0 and 5.7, respectively, compared with the absence of a chemical modifier. Mg and Ni were chosen because of their common use in ETAAS to prevent boron from forming refractory carbides, Pd was used because of its universal modifier feature in ETAAS and its beneficial effect in improving the transport efficiency of a large number of elements in ETV-ICP-MS[25] and EDTA was chosen simply in consideration of its organic nature. The test was made on a common basis based on the established heating cycle with a 10 s ramp to 150 °C for 50 s and a maximum vaporization temperature of 2600 °C for 8 s and subsequent determination by ICP-MS following basically the conditions shown in Table 1. Mannitol gave the highest sensitivity enhancement for boron (84-fold compared with no modifier addition). A sensitivity enhancement of up to a factor of 10 for boron in the presence of Ni modifier in ETV-ICP-MS was reported by Byrne *et al.*, but in this work a factor of 5.7 was obtained, possibly owing to the different vaporization process applied. It is interesting that addition of EDTA gave a sensitivity enhancement for boron of 28-fold. The explanation for this may be similar to the effect of citric acid modifier on Co, V and In,[26] i.e., EDTA would pyrolyse on heating to a vaporization temperature of

Table 2 Comparison of sensitivity and limits of detection for the determination of boron by ETV-ICP-MS in the presence and absence of mannitol

Conditions	Sensitivity (ions per ppb)	Detection limit (ppb)
Without mannitol	16	34.8
With mannitol	1344	0.2

2600 °C and result in the formation of a significant amount of carbon particles, that would serve as carriers of boron analyte vapour. Pd showed no enhancement for boron determination, and Mg and Ni, which exhibited a sensitivity enhancement effect for boron in ETAAS,[7,8] were not as effective as mannitol in ETV-ICP-MS. The enhancement effects of Mg, Ni and Cu for the determination of boron in ETV-ICP-MS can be attributed to the following two reasons: preventing the formation of boron carbide in the graphite furnace, although this has been clarified as not being the major cause for the reduced sensitivity,[11] and enhancing the transport efficiency between the ETV and the plasma, which is suggested to be most important because boron may be particularly prone to transport loss in ETV-ICP-MS.[11] As mannitol is much more effective than the other modifiers tested in enhancing boron determination in ETV-ICP-MS, this may imply that mannitol plays a unique role in assisting in the formation of volatile boron species from the vaporization surface, improving the mass transport efficiency of the volatile analyte to the plasma and reducing the formation of refractory boron carbide.

By applying the definition that 'chemical modifiers are compounds or mixtures of compounds which are used to change the chemical or physical properties of the sample matrix or the vaporizer/atomizer (or a combination of these) surface in such a way as to improve analysis',[25] mannitol can thus be considered as a specific modifier for boron that reacts with it to form boron–mannitol complexes, which further assist in transportation of the evaporated complex species from the graphite surface to the plasma for detection. In the vaporization process, mannitol may exist in various possible forms such as unreacted molecular species, as indicated by a report that about 93% of mannitol appears in the vapour phase at 420 °C,[23] and certain pyrolysis products resulting from reaction of mannitol during the heating process. It may therefore be concluded that the significant sensitivity enhancement for boron determination in the presence of mannitol by ETV-ICP-MS is possibly due to the more efficient transport of boron to the plasma through the formation of a boron–mannitol complex, which is expected to vaporize completely from the heated graphite surface, as was shown by the absence of a memory effect during subsequent blank firings. As mannitol, like the modifier nickel nitrate, is largely ineffective in preventing pre-atomization loss of boron in ETAAS, as was shown by the appearance of a boron signal in the temperature range 425–1500 °C (Fig. 1), it can be classified as a modifier that primarily acts to improve the production and/or transport of analyte (atoms and/or molecules) to the plasma.[27]

Application

Boron, being one of the Group III elements, existing at levels as low as sub-ng ml^{-1} in silicon materials, can profoundly affect the electrical properties of semiconductor products.[28] It has long been an important task in the semiconductor industry to determine ultra-trace levels of boron in silicon wafers and in starting materials such as dichlorosilane and trichlorosilane. In our studies on the development of methods for determining trace impurities in silicon and chlorosilanes, mannitol was found to be especially effective for the preservation of boron during chemical pre-treatment processes.[15–17] The trace amount of boron which remained in the treated sample solution was finally determined by spectrophotometry, ETAAS and ICP-AES. It was found, however, that the detection sensitivity achievable with these methods is only at the 5–100 ng ml^{-1} level,[15–17] which in certain circumstances cannot fully meet the analytical requirements for high-purity semiconductor materials.

By taking advantage of the high detection sensitivity of ETV-ICP-MS and the unique property of mannitol which acts as a preconcentrating agent for boron in the pre-treatment process and as a chemical modifier in the ETV system, it is expected to be possible to determine boron down to extremely low levels in trichlorosilane samples. Because ETV-ICP-MS is suitable for microlitre sample analysis, it can be expected to show a further gain in analytical sensitivity if the solution resulting from sample pre-treatment can be restricted to as small a volume as possible ($\leqslant$1 ml) from the originally large sample size ($\geqslant$10 ml). Repeated determination of blanks following the procedure described for the analysis of 10 ml of trichlorosilane as in the Experimental section shows that the limits of detection calculated based on three times the standard deviation of the blank ($n=3$) is 0.05 ng ml^{-1}, which is about two orders of magnitude lower than that of our previous ICP-AES method.[17]

The analytical reliability of the method was also evaluated. Because there are no silane samples with known boron contents available, the accuracy of the analytical result may alternatively be evaluated using different analytical methods. The analysis of a commercially available trichlorosilane sample by the present ETV-ICP-MS method and a previously developed ICP-AES method gave mean boron concentrations ($n=3$) of 44.9 ± 3.8 and 42.2 ± 3.7 ng ml^{-1}, respectively. The good agreement of the data provides an indication of the accuracy of the proposed method. In summary, the use of mannitol, which plays a dual role both in the sample pre-treatment step for preventing volatilization loss of boron and in ETV-ICP-MS for enhancing the detection sensitivity of boron, has resulted in the possibility of determination of ultra-trace levels of boron in trichlorosilane samples.

The authors are grateful to the National Science Council, Republic of China, for financial support.

REFERENCES

1 Carey, J. M., and Caruso, J. A., *CRC Crit. Rev. Anal. Chem.*, 1992, **23**, 397.
2 Barnett, N. W., Ebdon, L., Evans, E. H., and Ollivier, P., *Anal. Proc.*, 1988, **25**, 233.
3 Kirkbright, G. F., and Snook, R. D., *Anal. Chem.*, 1979, **51**, 1938.
4 Satumba, R. T., Bootes, R. A., and Matousek, J. P., *ICP Inf. Newsl.*, 1987, **13**, 22.
5 Huang, M., Jiang, Z., and Zeng, Y., *J. Anal. At. Spectrom.*, 1991, **6**, 221.
6 Hu, B., Jiang, Z., and Zeng, Y., *Fresenius' J. Anal. Chem.*, 1991, **340**, 435.
7 Van der Geugten, R. P., *Fresenius' Z. Anal. Chem.*, 1981, **306**, 13.
8 Laguera, M., Madrid, Y., and Camara, C., *J. Anal. At. Spectrom.*, 1991, **6**, 669.
9 Goyal, N., Dhobale, A. R., Patel, B. M., and Sastry, M. D., *Anal. Chim. Acta*, 1986, **182**, 225.
10 Norval, E., *Anal. Chim. Acta*, 1986, **181**, 169.
11 Byrne, J. P., Gregoire, D. C., Goltz, D. M., and Chakrabarti, C. L., *Spectrochim. Acta, Part B*, 1994, **49**, 433.
12 Slavin, W., *Graphite Furnace AAS a Source Book*, Perkin-Elmer, Norwalk, CT, 1984, p. 83.
13 Wiltshire, G. A., Bolland, D. T., and Littlejohn, D., *J. Anal. At. Spectrom.*, 1994, **9**, 1255.
14 Byrne, J. P., Hughes, D. M., Chakrabarti, C. L., and Gregoire, D. C., *J. Anal. At. Spectrom.*, 1994, **9**, 913.
15 Chen, J. S., Lin, H. M., and Yang, M. H., *Fresenius' J. Anal. Chem.*, 1991, **340**, 357.
16 Liu, C. Y., Chen, P. Y., Lin, H. M., and Yang, M. H., *Fresenius' Z. Anal. Chem.*, 1985, **320**, 22.
17 Chu, C. C., Chen, P. Y., and Yang, M. H., *Analyst*, 1990, **115**, 29.
18 Conner, J. M., and Bulgrin, V. C., *J. Inorg. Nucl. Chem.*, 1967, **29**, 1953.
19 Dawber, J. G., and Matusin, D. H., *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 2521.
20 Ishikawa, T., and Nakamura, E., *Anal. Chem.*, 1990, **62**, 2612.
21 Aruga, R., *Talanta*, 1985, **32**, 517.
22 Barbier, Y., and Rosset, R., *Bull. Soc. Chim. Fr.*, 1968, **12**, 5072.

23 Svarcs, E., Grundsteins, V., and Ievins, A., *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, 1967, **2**, 154.
24 Vaughan, M. A., Horlick, G., and Tan, S. H., *J. Anal. At. Spectrom.*, 1987, **2**, 765.
25 Gregoire, D. C., Al-Maawali, S., and Chakrabarti, C. L., *Spectrochim. Acta, Part B*, 1992, **47**, 1123.
26 Ediger, R. D., and Beres, S. A., *Spectrochim. Acta, Part B*, 1992, **47**, 907.
27 Gregoire, D. C., Lamoureux, M., Chakrabarti, C. L., Al-Maawali, S., and Byrne, J. P., *J. Anal. At. Spectrom.*, 1992, **7**, 579.
28 Lancaster, W. A., and Everingham, M. R., *Anal. Chem.*, 1964, **36**, 245.

Paper 5/01060H
Received February 21, 1995
Accepted July 24, 1995