Jurnal Matematika dan Pengetahuan Alam
Vol. 5, No. 2, Th. 1996 ISSN: 0853-0033

IMPROVED ANALYTICAL PERFORMANCE FOR THE DIRECT DETERMINATION OF TIN BY GRAFITE FURNACE ATOMIC ABSORPTION SPECTROMETRY USING MATRIX MODIFIERS

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ABSTRACT

The direct determination of tin by graphite furnace atomic absorption spectrometry is described. Several combinations of organic and inorganic substances such as saccharose with potassium dichromate, potassium tungstate or ammonium nitrate were investigated as the matrix modifiers for the enhancements of the absorbance signal of inorganic and organic tin. The sensitivity was increased by a factor of 17 when the combination of 10% saccharose with 10% potassium dichromate was used as the modifier, compared with that observed without the modifiers. On the other hand, the signal sensitivity was enhanced by a factor of 15 and 8 when saccharose was added with potassium tungstate and ammonium nitrate, respectively.

Interferences from several ions were eliminated, and the sensitivity was greatly improved. The calibration graph was linear up to 100 µg/L.

Key words : tin determination, grafite furnace atomic absorption spectrometry, matrix modifiers.

ABSTRAK

Penentuan timah secara langsung secara spektrometri serapan atom tungku grafit telah dipelajari. Beberapa kombinasi senyawa organik dan anorganik seperti sakarosa dengan kalium dikhromat, kalium tungstat dan amonium nitrat telah diperiksa sebagai pemodifikasi matrik untuk menambah signal absorban dari anorganik tin dan organik tin.

Kesensitifan meningkat 17 kali jika digunakan kombinasi sakarosa 10% dengan kalium dikhromat 10% sebagai modifier. Sebaliknya jika sakarosa dikkombinasikan dengan kalium tungstat atau amonium nitrat, kesensitifan signal bertambah masing-masingnya 15 dan 8 kali. Gangguan dari beberapa ion dapat dieliminasi dan kesensitifan dapat diperbaiki secara memuaskan. Kurva kalibrasi linear hingga konsentrasi 100 µg/L.

INTRODUCTION

The determination of tin compounds in the environment is becoming more and more important as their production increase. Tin compounds are used as stablizers for PVC, biocides in anti fouling paint, pesticides, fungicides, etc. (Blunden and Chapman, 1986, Vrijhof, 1985 and Donard and Pinel, 1989). As their compounds especially organotin compounds in the environment are degraded into a toxic compound, it is important to control their concentration levels in the environment.

Several techniques such as high performance liquid chromatography (Woollins and Cullen, 1984), gas chromatography (Yu and Arakawa, 1983), polarography (Weber, 1986), and atomic absorption spectrometry (Kojima, 1979, Slavin, 1982, Delmonte and Luperi, 1977 and Trachman *et al*, 1977) especially using graphite furnace atomization have already been employed for the determination of tin compounds. However, several problems may arise during both the ashing and atomizing steps, from the formation of volatiles and interaction of tin with carbon of the furnace wall (Lundberg, 1982). Several approaches have been made for the solution to these problems, such as treatment of the furnace tube (Hansen *et al*, 1981, Soderquist and Crosbyy, 1978, Fritzsche *et al*, 1979) and addition of chemical modifiers to the sample (Tominaga and Umezaki, 1977, Parks *et al*, 1985, Pinel *et al*, 1986, Taga *et al*, 1987, Taga *et al*, 1988, Zhou *et al* , 1984, Vickrey *et al*, 1980 and Ueda *et al*, 1988). Chakrabarti *et al*. (1980) proposed to the term "matrix modifier" for the chemical modification.

The general aim of chemical modification is to facilitate the analysis through *in situ* changing (modifying) of the thermochemical behaviour of both the analyte and matrix. According to Tsalev *et al*. (1990), the modifier can act as the thermal stabilization of volatile analytes and increase the volatility of the analyte during atomization. In this case the modifiers act predominantly as a volatilizer. By adding suitable modifiers the atomization temperature and its duration can be decreased with resulting in positive effects on sensitivity, tube life time and long term stability.

The utilization of nitric acid in sample preparation has been succesful in a number of instances, while the use of ascorbic acid or potassium dichromate as a matrix modifiers was only moderatelty successful (Tominaga and Umezaki, 1977, Pinel *et al*, 1986).

Although many organic or inorganic substances have already been used for chemical enhancement in tin determination , scarcely any author has investigated the effectivity of combination of organic and inorganic substances for the matrix modifier. This paper describes the use of combinations of organic and inorganic compounds as the modifier for the direct determination of inorganic and organic tin as studied by graphite furnace atomic absorption spectrometry.

EXPERIMENTAL

Apparatus

A Shimadzu model 640-13 atomic absorption spectrometry equipped with a Shimadzu model GFA-3 graphite furnace atomizer and a Shimadzu model U-235 recorder were employed. A tin single-element hollow cathode lamp from Hamamatsu Photonics KK, Japan was used as the light source. Sample solution was injected into the graphite tube by using a precision displacement pipette (Gilson, pipetman model P-20). The instrumental operating conditions are described in detail in Table 1.

Table 1. Instrumental Operating Conditions

AAS conditions [Shimadzu model 640-13]	
Analytical wavelength	: 224.6 nm.
Band width	: 3.48 Ao.
Mode	: Absorbance.
Graphite furnace operation [Shimadzu model GFA-3]	
Atomization tube	: Untreated tube
Inert gas	: Argon, 1 L/min, interrupt position for atomization
Colling water	: 2 L/min
Sample size	: 20 µL.
Program	: dry, 150 ^{o}C for 40 s; ash, 650 ^{o}C for 30 s; and atomize, 2,200 ^{o}C for 6s.
Recorder [Shimadzu model U-235].	

Reagents

All the reagents employed in this work were obtained from Wako Pure Chemical Industries (Osaka, Japan), unless otherwise noted. Hydrochloric acid was of super special grade. Sacharose, ammonium nitrate, potassium dichromate, and potassium tungstate (Katayama Chemicals Co., Osaka, Japan) were of reagent grade or better. Aqueous solutions of metal chlorides of iron(III), magnesium(II), zinc(II), cadmium(II), gold(II), platinum(IV), sodium(I), potassium(I), barium(II), nickel(II), antimon(II), and palladium(II) containing 1,000 mg/L of each metal for AAS were employed for studying the interferences. The inorganic tin working standard solution prepared in 1M hydrochloric acid, while organic tin (Aldrich Chemical Co. USA) was prepared in methanol, both from 1,0000 mg Sn/L of tin stock solutions. Purified water was prepared by using a Millipore, Milli water purification system (Nihon Millipore Kogyo, Japan).

Procedure

The optimized atomization programmme was used as listed in Table I. The argon gas flow was interrupted during the atomizing step to give the maximum sensitivity.

All tin peak height determinations were made on injection of 20 uL volume of sample into the graphite tube. The mean (relative standard deviation better than 4%) of at least three replicate injections was taken for each solution. The measurements were made at 224,6 nm resonance line with a band width of 3.48 A^{O}. For the enhancement procedure, 20 uL of tin solution was injected into the tube, followed by addition of the modifiers investigated. For the investigation of interference, 20 uL of each metal chloride interference was immediately injected into the tube after the sample solution. For the study of the elimination of their interference, suitable modifiers were injected last.

RESULTS AND DISCUSSION

Optimizations of operating conditions

It was found that the heating temperature, especially during the ashing and atomizing step, affected the obtained peak height intensity. The optimal conditions for the ashing and atomizing were investigated in this work. The ashing temperature was varied from 450 to 950 ^{O}C, while the drying and atomizing temperatures were kept constant as listed in Table I. For the

investigation of atomization temperature, the temperature programming was varied from 1,500 to 3,000 ^{o}C, in which the drying and ashing temperatures were kept constant as listed in Table I.

The ashing and atomizing conditions should be optimized. At higher ashing temperature, the formation of carbide with graphite wall might decrease the signal intensity. From the experimental results, the optimal ashing and atomizing temperature in this work have been chosen as follows: ashing and atomizing temperatures were 650 ^{o}C and 2,800 ^{o}C, respectively.

The flow rate of argon gas also affected the signal intensities. When the flow rate of the argon gas was varied from 0.5 to 2.0 L/min, a virtually constant signal response was observed at the flow rate higher than 1.0 L/min. Therefore 1.0 L/min of argon gas flow rate was chosen for further studies.

The influence of the hydrochloric acid concentration on the signal intensity was investigated. The result is shown in Figure 1. The similar signal intensity was obtained when the hydrochloric acid concentration varied from 1.0 to 6.0 M, though less intense peaks were observed without adding the acid.

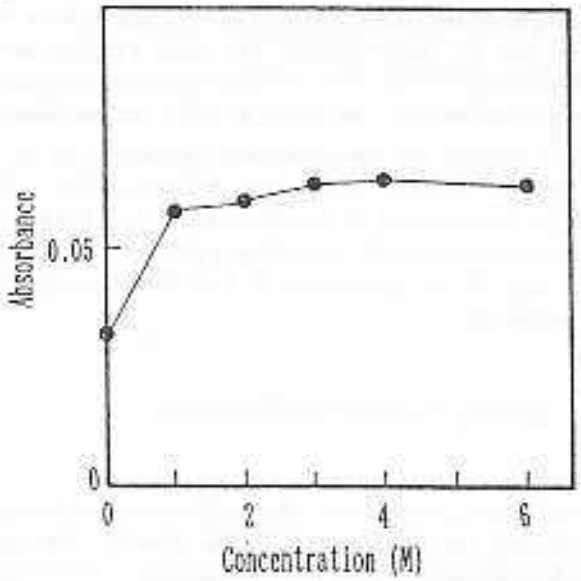

Figure 1. Effect of hydrochloric acid concentration on the tin determination (10 ng).

Enhancement of tin sensitivity by using matrix modifier

Figure 2 illustrates the effect of addition of modifiers on signal enhancements for the determination of tin by graphite furnace atomic absorption spectrometry (GFAAS). Three kinds of combinations of organic and inorganic substances, i.e., saccharose-potassium dichromate, saccharose-potassium tungstate, and saccharose-ammonium nitrate were chosen as modifiers. From this figure it is shown that when the combination of 10% saccharose and 10% potassium dichromate was used as the modifier, the signal absorbance of tin was enhanced by a factor of 17 compared with that without adding any modifier. On the other hand, by using the same level concentrations, the combination of saccharose-potassium tungstate and saccharose-ammonium nitrate gave enhancements on the signal absorbance by a factor 15 and 8, respectively.

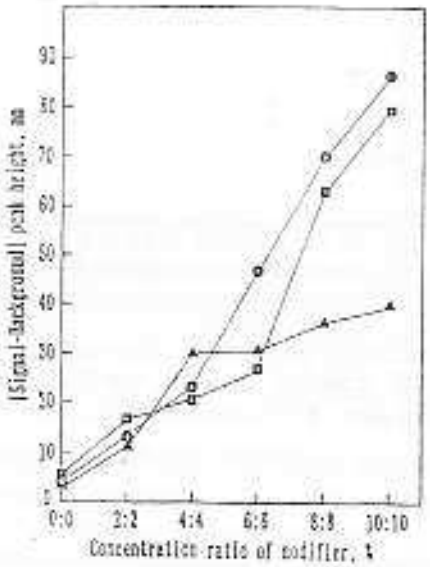

Figure 2. Effect of modifiers on the sensitivity enhancements of tin. Modifier used : ● = saccharose - $K_2Cr_2O_7$; ■ = saccharose - K_2WO_4; ▼ = saccharose - NH_4NO_3. Tin concentration = 100 µg/L.

Figure 3 shows the effect of the combination concentration ratio of the modifiers. As illustrated in Figure 3, by using a single modifier *i.e.*, potassium dichromate or potassium tungstate alone gave a signal much better than saccharose alone. The optimum concentration was determined by comparing the peak heights observed for tin solution containing modifiers with various concentrations and the corresponding to blank signal.

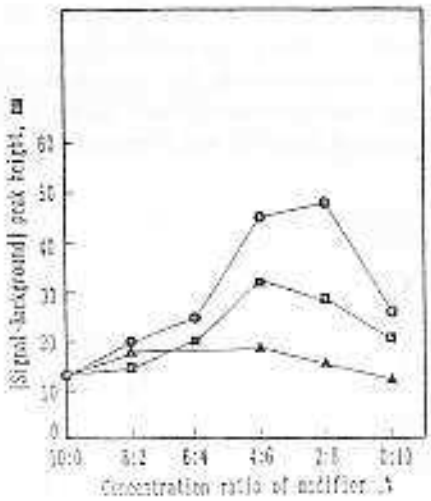

Figure 3. Effect of modifiers on the sensitivity enhancements of tin.Modifier used : ● = saccharose - $K_2Cr_2O_7$; ■ = saccharose - K_2WO_4; ▽ = saccharose - NH_4NO_3. Tin concentration = 100 ug/L.

The use of higher than 10% concentration of saccharose, resulted a carbon residue on the tube wall. This residue can undoubtedly lead to erroneous results. Therefore, the concentration of saccharoce modifier higher than 10% has not been investigated. High-purity reagents as well as ready-made solutions of chemical modifiers are commercially available but intolereable blanks can be experienced with some analytes and modifiers. Figure 4 shows the blank signals resulted from the modifier used. In our work, with the modifier proposed, saccharose-ammonium nitrate gave no

signal absorbance in the blank solution. However, small signal was appeared when higher concentration of saccharose-potassium tungstate modifier was used. Moreover, as shown in Figure 4, the blank signal from tin impurities in the saccharose-potassium dichromate modifier becomes too great if the concentration is increased. This is due to potassium dichromate, since the saccharose it self gave no signal blank. This result is in agreement with that reported by Pinel *et al.* (1986).

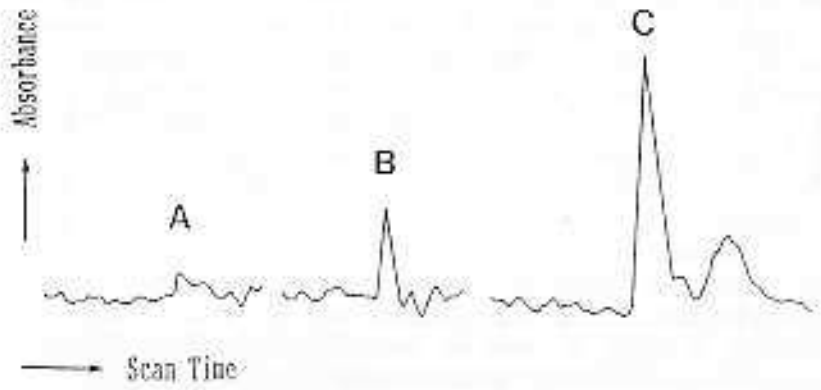

Figure 4. Background absorbance of modifiers. A. saccharose - NH_4NO_3; B = saccharose - K_2WO_4; C = saccharose - $K_2Cr_2O_7$

In view of the successfull GFAAS enhancement method described above, we decided to investigate the linearity of the calibration graph of inorganic and organic tin, without addition of any matrix modifier (Figure 5A) and with addition of matrix modifier (Figure 5B). Without additional modifier, the calibration graph for tin(II) chloride and organic tributhyltin chloride was linear up to 1,000 ug Sn/L, with the detection limit is about 50 ug/L. In the presence of modifiers, the calibration graph was linear up to 100 ug Sn/L with the detection limit around 3 ug/L for saccharose-potassium dichromate and saccharose-potassium tungstate modifiers. On the other hand saccharose-ammonium nitrate modifier gave detection limit around 8 ug/L.

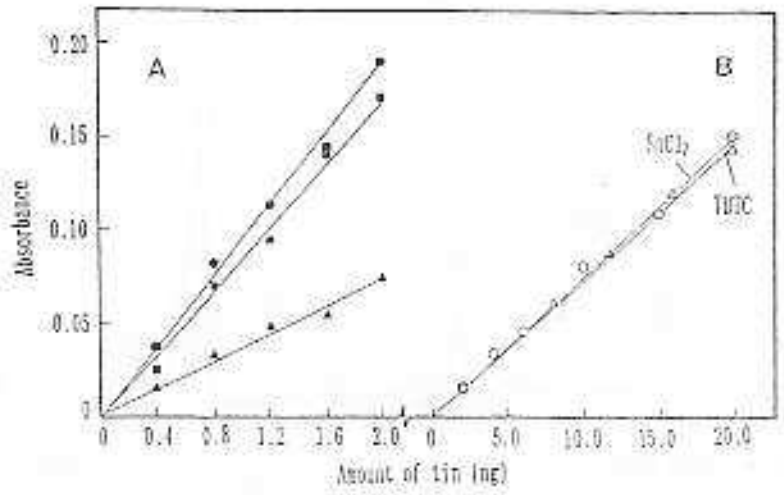

Figure 5. Calibration graph of tin with and without modifier. A. With modifiers; ● = saccharose - $K_2Cr_2O_7$; ■ = saccharose - K_2WO_4; ▼ = saccharose - NH_4NO_3. B. Without modifier

Effect of sample matrix on the tin signal

Matrix interference effects of the inter element type are known to occur in flameless atomic-absorption spectrometry. The direct determinations in real samples, however, are often subject to interference by matrix components. For the tin determination, problems may arise during both the ashing and atomizing steps, from formation of volatiles and interfere of tin with the carbon of furnace walls. Campbel and Ottawai (1974), reported that the

carbon tube itself plays a dominant role in the formation of the atomic vapour by assisting in the reduction of the metal oxide to metal.

The efficiency of free atom formation of tin in graphite furnace atomizers has been shown to be sensitive to both sample and sheath gas composition. Prevolatilization of molecular tin species (Delmonte and Luperi, 1977) gas phase molecular formation (Sturgeon and Chakrabarti, 1977), and surface interactions (L'Vov, 1978) have all been cited as causes for the absorbed interferences. The existence on the surface prior to atomization is reasonable because the metal oxide can result from the thermal decomposition of metal nitrite, sulfate and chlorides. The mechanism proposed for interferences in furnace atomization itself are not always in good agreement. The differences might result from the use of various atomizers size and heating rate, the properties of the analyte in different matricies of varying concentration, etc.

In our work the effect of several metal chlorides has been investigated. Figure 6 shows the effect of diverse metal ions on the tin determination. There are no interferences by nickel(II) and potassium(I) chlorides even in amounts of 2 ug with 20 ng of tin(II) solution. Moreover when 2 ug of each metal chloride, cadmium(II), sodium(I), and antimon(III) was added to a 20 ng of tin(II) solution, a peak reduction of 25%, 27% and 35% were observed, respectively. Furthermore, as shown in Figure 6, gold(III), iron(III), palladium(II), zinc(II) and platinum(IV) gave a strong reduction of peak height. About 50% for gold(III), 52% for iron(III), 62.5% for zinc(II), and 75% for platinum(IV), when 2 ug of each metal was present in 20 ng of tin solution.

Elimination of matrix interference

For suppression of matrix interferences, several organic and inorganic compounds such as ascorbic acid (Tominaga and Umezaki, 1977), citric acid (Trachman *et al*, 1977), ammonia (Lundberg, 1982), and dihydrogenphosphate (Kaiser *et al*, 1981) have been proposed. In the experimental results above, it was found that the mixture of saccharose and potassium dichromate gave much better enhancements than the other modifiers. For this reason we try to apply this modifier to eliminate the metal chlorides interference in the determination of tin. Platinum(IV) chloride interfere was chosen as a model because of its large on reduction of peak height.

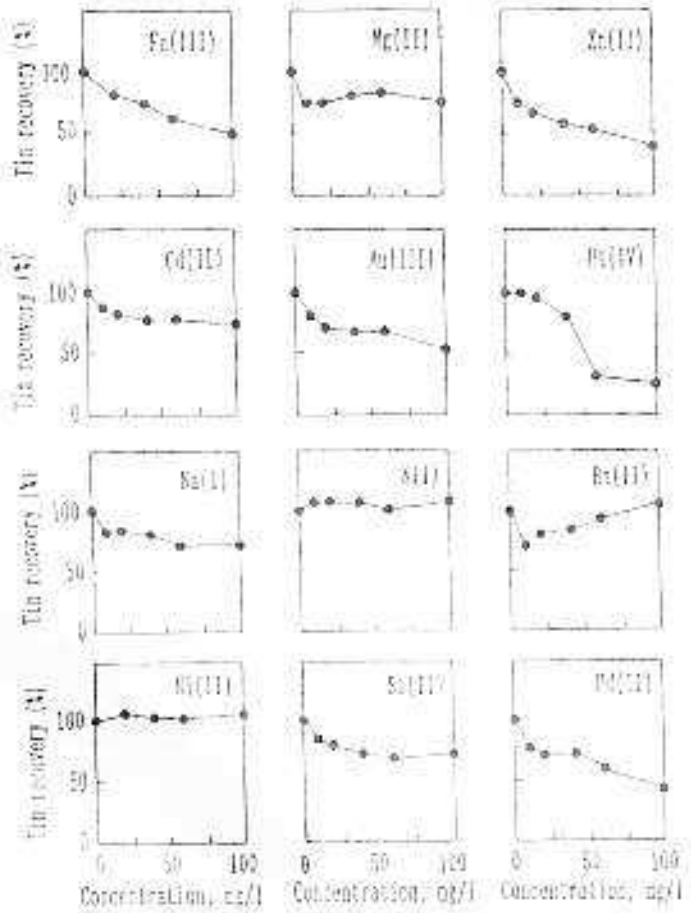

Figure 6. Effect of diverse metal chlorides on the tin determination (20 ng)

In this work the effect of saccharose-potassium dichromate modifier for the elimination of Pt(IV) chloride interference was investigated as a function of atomizing temperature. The results in Table II shows, at atomizing temperature 2,200 °C in the presence of 2 ug platinum in 20 ng tin solution the absorbance signal is reduced by a factor of about 3.4 compared with the absorbance signal of 20 ng of pure tin, and become 100 % (no interference) when combination of 2 ug of saccharose and 2 ug of potassium dichromate solution were added

Table II. Eliminations of Pt(IV) chloride interference by using a combinations of saccharose and potassium dichromate modifier.

Atomizing tempt : (oC)	Absorbance signal* : 20 ng Sn	: 20 ng Sn + 2 µg Pt	: 20 ng Sn + 2 µg Pt + 2 ug saccharose + 2 µg K2Cr2O7
1,500	0.006	0.006	0.006
1,800	0.036	0.006	0.020
1,900	0.070	0.014	0.046
2,000	0.114	0.028	0.084
2,200	0.134	0.040	0.134
2,400	0.114	0.048	0.316
2,600	0.086	0.040	0.310
2,800	0.070	0.040	0.312

*Mean of at least three injections. Rsd better than 4%.

In conclusion the proposed method can be applied for the direct determination of tin in water samples. It is emphasized that the addition of matrix modifier is simple, rapid and no pretreatment of the graphite tube is required.

Acknowledgement : The author wishes to thank Prof. Hiroki Haraguchi of Nagoya University Japan for kind help and suggestions during the course of this work.

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