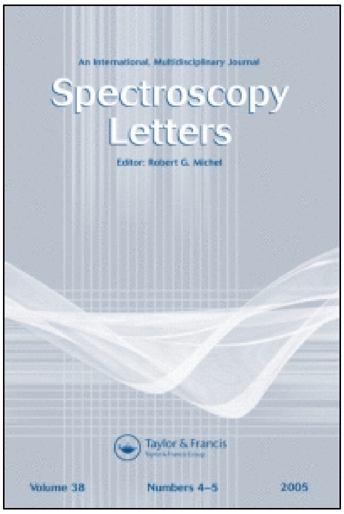

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# Determination of Tin in Pure Copper by Flow-Injection Hydride Generation Atomic Absorption Spectrometry

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# Determination of Tin in Pure Copper by Flow-Injection Hydride Generation Atomic Absorption Spectrometry

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**Abstract:** A reliable method was established for the determination of tin in pure copper by flow-injection hydride generation atomic absorption spectrometry. The determination of tin in pure copper often suffers from interference from the copper matrix. In this work, cupferron was used as a chelating reagent to separate the copper from the tin. At pH 3.0, copper ion could form stable cupferron complex and could be removed from sample solution by chloroform extraction without loss of tin. After most of the chloroform dissolved in the aqueous solution had been removed, tin could be determined at 224.6 nm with the optimized conditions of 1.0% HCl as carrier solution and 0.8% m/v $NaBH_4$ as reductant. A pure copper standard reference material, SRM 396 unalloyed copper, was analyzed with the proposed method. A calibration curve was obtained with a linear range of $1 \sim 13\ \mu g\,L^{-1}$ and a detection limit of $0.25\ \mu g\,L^{-1}$. The experimental results obtained for certified values were $0.76 \pm 0.3$ and $0.8 \pm 0.03\ \mu g\,g^{-1}$, respectively. A recovery of $93.7 \pm 2.6\%$ ($n = 5$) was obtained. This established that the method was applicable to the determination of tin in pure copper with good accuracy and precision.

**Keywords:** Atomic absorption spectrometry, Flow-injection, Hydride generation, Pure copper, Tin

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## INTRODUCTION

Pure copper is one of the most important metal materials for high-tech industries. It has a variety of important properties including thermal and electric conductivity, good anti corrosive properties, and it is easy to weld. Pure copper is also good for metal-centered liquid crystal materials.[1,2] Copper often replaces aluminum in oversize integrated circuits for a better electron-transfer effect.[3] However, trace amount of contaminants, especially the presence of volatile elements such as As, Ge, Sb, and Sn, in pure copper will degrade the electric and chemical properties of pure copper.[4,5] Because the total content of the impurities including Se, As, Bi, Co, Sb, Pb, and Sn is less than 1 $\mu g\,g^{-1}$, an analytical method with relatively high sensitivity and selectivity is required for determining those trace elements.

Although graphite-furnace atomic absorption spectrometry (GFAAS) has widely been employed for trace analysis, there were difficulties when tin was determined by GFAAS.[6,7] Those included interferences from chlorides and nitrates and the loss of tin as tin oxides.[8] Coating of Zr, Nb, Ta, and W on graphite platforms could reduce the loss of tin before atomization.[9] Using neutron activation analysis could avoid these problems, however, relatively low sensitivity and serious spectral interference are drawbacks.[8] Atomic fluorescence spectrometry also has the problem of relatively low sensitivity when dealing with tin, the detection limit being only 50 $ng\,ml^{-1}$. The tin contents in steel, ranging from 0.0073% to 0.085% m/m, have been determined with hydride-generation ICP.[10]

Flow-injection HGAAS is good for hydride-forming elements such as As, Sb, Bi, Se, Te, and Sn.[11–13] However, effective pretreatments were often required to determine trace amounts of tin in copper matrices (99.99%) accurately and precisely. Adsorption,[14] ion-exchange,[15] and solid-phase extraction methods[16] were often employed for this purpose. Masking agents[17,18] and coprecipitation[19] had also been proposed for reducing the matrix interferences. However, loss of tin was another potential problem. The chelation and extraction of analytes before determination with hydride generation atomic absorption spectrometry (HGAAS) could be an alternative method. The separation of analytes from interfering elements chromatographically with or ion-exchange method before high-performance liquid chromatography (HPLC) determination with HGAAS were reported.[12,20,21]

Because cupferron (*N*-nitroso-*N*-phenylhydroxylamine) had successfully been used for removing copper for Te determination,[22] the applicability of cupferron for tin was explored as the chelating reagent to react with copper. The aim of this work is to develop an efficient method for the separation of tin from the interfering copper matrix. The separation of tin from copper was accomplished with a chloroform extraction. The resultant sample solutions were analyzed for tin with flow-injection hydride generation atomic absorption spectrometry (AAS). The established method was evaluated for its precision and accuracy by analyzing tin in a standard reference material of pure copper.

## EXPERIMENTAL

### Materials and Reagents

All chemicals used in this work were analytical reagent grade from Merck (Darmstadt, Germany), except suprapur hydrochloric acid (30%) and nitric acid (65%). Deionized distilled water (17.8 MΩ $cm^{-1}$) was used for dilution. Sodium borohydride solution (0.8% $NaBH_4$) was freshly prepared and filtered to 0.45 μm before use. The standard metal solutions $SnCl_4$ in 0.4% HCl and $Cu(NO_3)_2$. $3H_2O$ in 0.5 M $HNO_3$ were prepared. A standard reference material of pure copper (SRM396 unalloyed copper Cu III) was obtained from the U.S. National Institute of Standards and Technology (NIST).

### Apparatus

All the chemicals were weighed with microbalance MT-5 (Mettler Instrument AG, Gteifensee, Switzerland), with a maximum capacity of 5.1 g to a precision of 0.001 mg. The investigations were performed with a 5100ZL atomic absorption spectrophotometer and a Perkin-Elmer FIAS-400 Flow-Injection Analyzer (Perkin-Elmer, Norwalk, CT, USA). The experimental conditions are shown in Table 1. The reductant flow rate was 1.0 mL $min^{-1}$ A CEM model MDS-2000 microwave digestion system was used (CEM Matthews, NC, USA).

### Procedure

Sample Pretreatment

An amount of 30∼70 mg pure copper was precisely weighed in a 7 mL digestion vessel and dissolved with an acid mixture of 1.5 mL 30% HCl and 0.5 mL 65% $HNO_3$. Polypropylene (PP) containers were used in the sample pretreatment. The copper sample was digested in a microwave digestion system according to the condition given in Table 2. The pH of the sample solution was adjusted to 3.0 with phosphate buffer and then treated with 3.0 mL cupferron solution (5%, m/v). The copper–cupferron complexes were extracted with 20 mL chloroform three times. Most of the chloroform dissolved in the aqueous solution was removed by heating on the hot plate at 50°C for 30 min. The resultant aqueous sample solution was diluted to 10 mL with 1.0% HCl, which was prepared in saturated boric acid, and the tin content was measured by flow injection analysis-hydride generation AAS (FI-HGAAS).

**Table 1.** Instrumental parameters for FIAS-HGAAS[a]

| | |
|---|---|
| Light source | Electrode discharge lamp (EDL) |
| Wavelength (nm) | 224.6 |
| Light current (mA) | 380 |
| Slit width (nm) | 0.7 |
| Measurement (s) | 15 |
| Signal measurement | Peak height |
| Sample volume ($\mu$L) | 500 |
| Atomizer | Quartz tube |
| Gas–liquid separator | Mercury hydride system (MHS-20) |
| Quartz tube atomizer temperature (°C) | 900 |
| FIAS fill time (s) | 10 |
| FIAS injection (s) | 15 |
| Measurement time (s) | 15 |
| NaBH4 reduction solution (m/v, %) | 0.8 |
| HCl carrier solution (v/v, %) | 1.0 |
| Carrier solution flow rate (mL $\text{min}^{-1}$) | 10 |
| Carrier gas flow rate (mL $\text{min}^{-1}$) | 100 |

[a] Flow injection analysis-hydride generation AAS.

## RESULTS AND DISCUSSION

### Matrix Effect

When trace tin in pure copper was measured with HGAAS, the presence of copper would reduce the hydride formation efficiency of tin and cause serious interferences.[5,20,22] Thus, the atomic absorption signal was not detectable in the pure copper solution. References[5,20,22] did not describe the precipitates. However, in our flow-injection system, purplish black precipitate was found when copper sample solutions were treated with $NaBH_4$ solution. The copper precipitate was deposited and accumulated within the conduits. This indicated the necessity of the separation of tin from the bulk copper matrix.[23,24] Table 3 summarizes the effect of copper on the atomic signal of tin. A negative error was observed when the copper to tin ratio

**Table 2.** The heating program for CEM MD-2000 microwave digestion system

| Stage | Power (%) | Pressure (psi) | Run time (min) | Time@P[a] (min) | Temperature (°C) |
|---|---|---|---|---|---|
| 1 | 50 | 40 | 15 | 10 | 35 |
| 2 | 55 | 45 | 15 | 10 | 45 |

[a] Hold time.

**Table 3.** Copper ion effects on the relative atomic absorbance of Sn

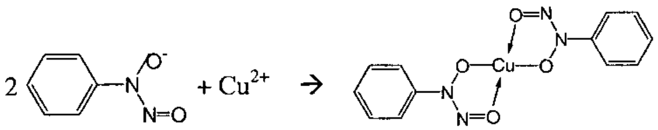
| Cu (ppm) | Relative atomic absorbance of Sn (%)[a] |
|---|---|
| 0.00 | 100 |
| 0.01 | 99 |
| 0.05 | 94 |
| 0.10 | 90 |
| 0.50 | 85 |
| 1.00 | 82 |
| 5.00 | 78 |
| 10.00 | 75 |
| 50.00 | 70 |
| 100.00 | 68 |

[a] The relative atomic absorbance of Sn in the sample solution was measured with 10 ppb Sn standard solution as the reference signal. Copper was added as $Cu(NO_3)_2$.

was greater than 10. The concentration ratio of Cu to Sn in the pure copper was more than $1.25 \times 10^5$. Consequently, a serious matrix effect was observed. In order to remove the matrix interference, $La(NO_3)_3$ coprecipitation, EDTA,[25] and Zincon[26] chelating methods had been tried; however, none of them gave satisfactory results. Irreproducible atomic profiles with relatively high background absorption and low sensitivity were obtained in these methods.

## Cupferron Chelation–Extraction Pretreatment

Nonpolar chelates were formed between copper and cupferron according to Scheme 1. Tin ions were separated from the interfering matrix after copper–cupferron chelates were extracted from the aqueous phase with chloroform.



**Scheme 1.** Formation of nonpolar chelate.

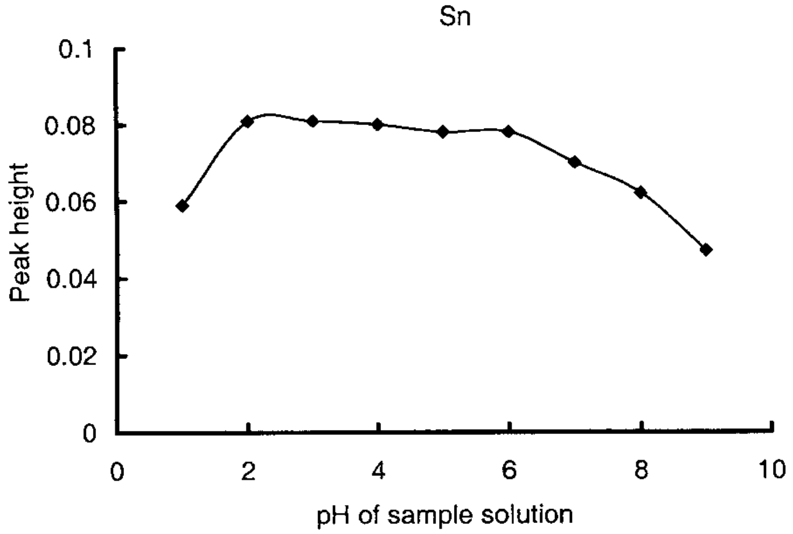


Figure 1. Effect of the pH of pure copper solution (7.7 mg mL$^{-1}$ Cu and 0.112 mol L$^{-1}$ cupferron).

The optimum pH ranged from pH 2.0 to 6.0 as shown in Fig. 1. The cupferron chelation was not completed when pH was lower than 2.0,[27] consequently, less tin was recovered; this resulted in a smaller peak height. The formation of $Cu(OH)_2$ precipitate would cause the loss of tin at pH higher

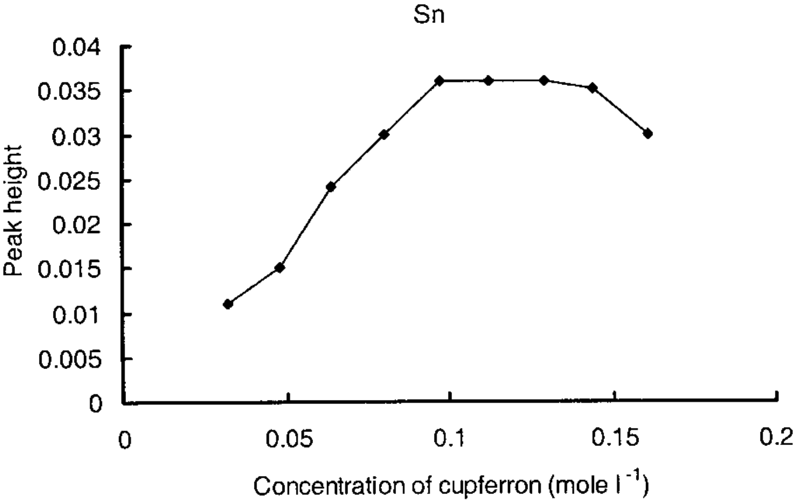


Figure 2. Effect of cupferron on the peak height of tin in pure copper solution (2.7 mg mL$^{-1}$ Cu, pH = 3.0).

than 7.0. The reduction in tin absorption could be due to the presence of residual copper or the coprecipitation of tin in $Cu(OH)_2$ precipitate. Figure 2 shows the effect of cupferron concentration on the peak height of tin. The maximum peak height was obtained when the concentration ranged from 0.032 to 0.128 mol $L^{-1}$. Further increase in the cupferron would bring a decrease in tin atomic absorption. Thus, the following experiments were performed at pH 3.0 and 0.112 mol $L^{-1}$ cupferron solution.

Cupferron chelation–extraction pretreatment was effective in reducing copper matrix interference for tin determination. However, the analytical results were highly susceptible to the amount of chloroform dissolved in the aqueous solution (upper layer). With the presence of chloroform, the absorption signal went over-scale as shown in Fig. 3a. Because CO, $CO_2$, HCl, and phosgene produced from the decomposition of $CHCl_3$ did not give molecular absorption in the UV region, the relatively broad, irreproducible absorption profiles could be attributed to the scattering of black carbon residues that deposited on the inner wall of the quartz atomizer. This would cause serious interference and some degree of damage to the tube. By heating the sample solution on the hot plate for 30 min, the excess chloroform would be removed and a reproducible absorption profile, Fig. 3b, was obtained. The cupferron chelation–extraction pretreatment was selective, as no tin was detectable in the organic phase ($CHCl_3$ layer) by FAAS. After extraction, no copper was detectable in the aqueous solution by FAAS.

## Reduction by Sodium Borohydride, $NaBH_4$

$Sn^{2+}$ and $Sn^{4+}$ are the two most common oxidation states of tin in aqueous solution. These ions were reduced to $SnH_4$ with comparable efficiency by reaction with sodium borohydride.[9] Therefore, prereduction for the determination of tin was not required.[28] In our work, the calibration curves were established from standard $SnCl_4$ solution. $NaBH_4$ is the most common reductant for HG. The absorption signal of $SnH_4$ was monitored as a function of $NaBH_4$ from 0.2 to 2.0% m/v with a carrier solution of 1.0% HCl. The peak heights of atomic absorption profiles thus obtained were recorded (Fig. 4). The optimal concentration of $NaBH_4$ ranged from 0.8% to about 1.0% m/v. For 7.0 ppb tin standard solution, the peak height was decreased after 1% m/v. In contrast, the tin peak height for the copper sample solution remained constant with wider concentration range, which was from 0.7% to 1.6% m/v. The diverse effects of the concentration of $NaBH_4$ on the peak height implied a matrix effect from copper. Tin reacted with hydrogen radicals provided by $NaBH_4$ to form $SnH_4$. When the concentration of $NaBH_4$ was lower than 0.8%, the hydrogen free radical thus produced was not enough for the generation of $SnH_4$, whereas with

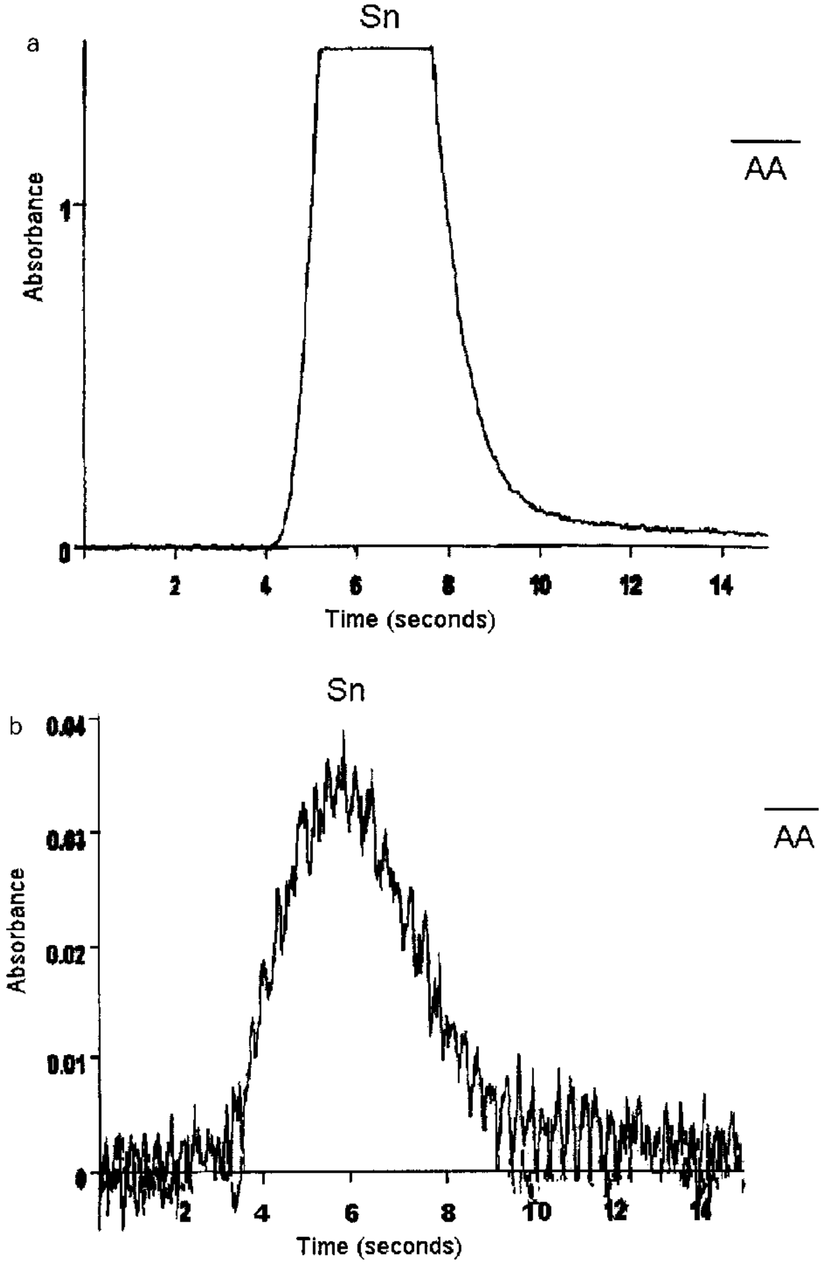


**Figure 3.** Representative absorption profiles of tin in pure copper solution (3.6 mg $mL^{-1}$) with reductant solution 0.4% $NaBH_4$, carrier solution 1.0% HCl in saturated boric acid (a) with excess amount of chloroform; (b) chloroform was removed.

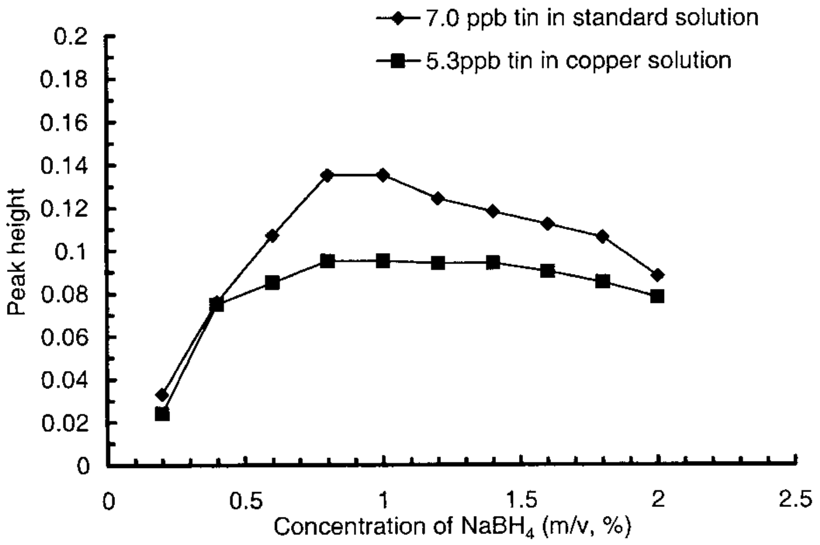


**Figure 4.** Effect of $NaBH_4$ on the peak height of tin.

higher reactant, 1.2%, the reaction would be violent, and the gas–liquid separator would splatter to cause the loss of tin. With a constant injection volume (500 μL), the dilution of tin with hydrogen gas could cause the reduction of tin signal.[22] Besides, shorter residence time of tin atom in quartz cell could also reduce the tin signal. The concentration of 0.8% $NaBH_4$ was used as the optimal concentration.

## Effect of Carrier Solution, HCl Solution

The efficiency of the formation of $SnH_4$ was quite susceptible to the concentration and the composition of the carrier solution.[29] Hydrochloric acid solution with saturated boric acid was often employed as the carrier solution to reduce the competition for free radicals from $Se^{4+}$.[30] Figures 5(a) and 5(b) show the absorption profiles obtained without and with 1% HCl, respectively. Reproducible absorption profiles were obtained in the presence of 1% HCl. In addition, the calibration curve established without HCl gave poor linearity. This agreed with the work in the literature.[13,20,28] When using HCl and saturated boric acid as the carrier solution, the tin absorption signal in standard solution decreased rapidly as the concentration of HCl increased, as shown in Fig. 6. At relatively low concentration, the absorption profile of tin became broader with a serious tailing effect. This might be caused by the deficiency of hydrogen free radical during the hydride formation step. As the concentration of HCl increased, the absorption signal

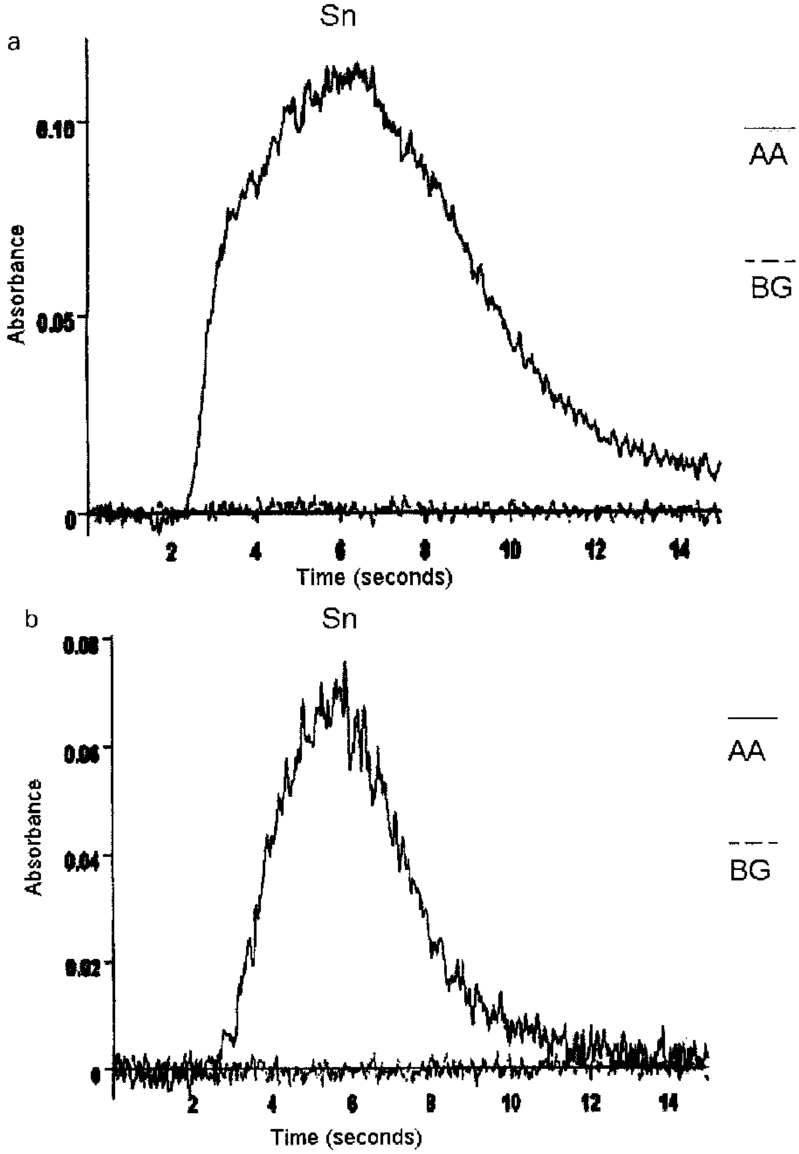


**Figure 5.** The effect of HCl on the absorption profile of Sn standard solution: (a) saturated boric acid without HCl; (b) 1.0% HCl in saturated boric acid.

decreased rapidly due to the formation of tin chloride and the dilution of tin in the presence of excess hydrogen gas.[28] A shorter residence time of tin with a carrier gas flow at about 100 mL min$^{-1}$ could also cause decreased peak height. Interestingly, the peak height of tin remained constant up to the

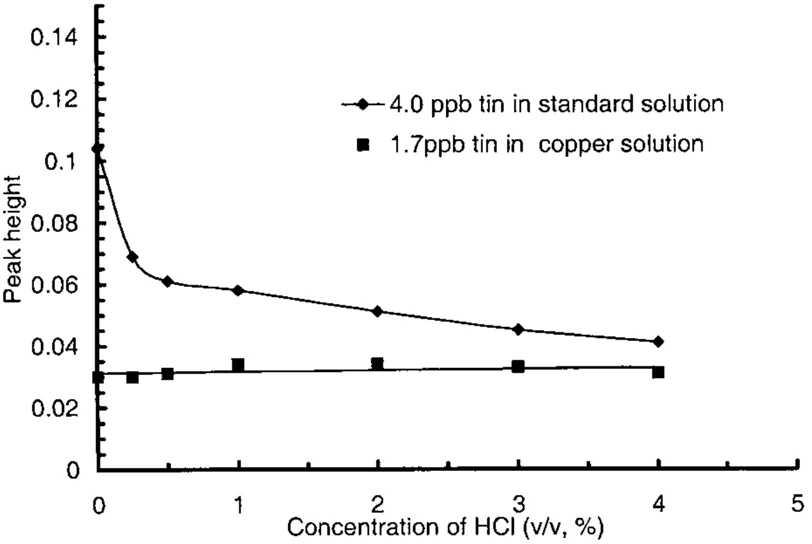


**Figure 6.** Effect of HCl carrier solution on the peak height of tin.

concentration of 4% HCl for copper solution. The change in the concentration of HCl resulted in negligible deviation for tin in the copper solution while greater deviation in the peak height for tin in the standard solution was observed.

## Analytical Characteristics

The proposed method was applied to the determination of tin in the standard reference material SRM396 unalloyed copper Cu III. The calibration curve was defined by the following equation:

$$\text{Peak height} = K \times (\text{concentration of Sn}) + B,$$

with $K = 0.012$, $B = 0.0093$, correlation coefficient = 0.9990, and a linear range of 1∼13 ppb established with the standard tin solution. The detection limit of 0.25 ppb was obtained as the concentration of the analyte corresponding to $3\sigma$ of the sample blank solution ($n = 20$) when 500 μL solution was injected for each measurement. The detection limit for the solid sample was 0.10 $\mu g\, g^{-1}$. The experimental result obtained in this method and the certified value were 0.76 ± 0.03 (with a recovery of 93.7 ± 2.6%, $n = 5$)

and 0.8 ± 0.3 $\mu g\, g^{-1}$, respectively. A close agreement between the experimental value and certified value established the accuracy of this method. The proposed method was applicable to the determination of tin in pure copper with good accuracy and precision. A standard addition approach would not have been applicable due to serious interference from copper, as the tin signal could not be detected in the presence of copper matrix.

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