

Determination of Tin by Hydride Generation AA

Application Note

Atomic Absorption

Author

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Introduction

Hydride generation techniques are used routinely for the determination of As, Se, and Sb in atomic absorption and atomic emission spectroscopy. Low level concentrations of Sn can also be determined by hydride generation. The gaseous stannane is generated by NaBH_4 reduction of tin in the acidified sample solution. High sensitivity and low detection limits can be achieved. However, current methodology suffers from several difficulties. These include pH dependency, potential contamination problems, poor standard stability and severe metal interferences. This AA-at-Work describes the development of a relatively simple tin hydride generation method. Problems associated with hydride generation determination of tin were investigated. The use of L-cysteine was of particular interest since it not only minimized interferences but also improved sensitivity and signal stability. A simple HNO_3 /L-cysteine method was evaluated for the analysis of digested environmental samples.



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Factors Affecting Tin Hydride Generation

There are a number of important factors that must be considered in tin determination by hydride generation. They include:

- Standard stability—this is a pre-requisite for accurate analysis. In this study, tin standards at the part-per-billion level were found to be unstable with acid concentrations typically used such as 1% HNO₃ or 1% HCl. Signals deteriorated in 24 hours. Methods for improving standard stability were investigated in this study.
- Contamination—tin can be a significant contaminant in analytical reagents. In this work contamination was not a major problem. However, blanks were always prepared with careful matching of reagents. Blank absorbances were usually below 0.040 abs.
- Metal interferences—hydride generation techniques are sensitive to high concentrations of metals. The use of L-cystine and L-cysteine has shown particular promise in the reduction of these types of interferences. Brindle, Xiao-chun Le and Boampong have reported significant reductions in metal interferences in the hydride determination of arsenic, germanium and tin when these reagents are used [1,2,3].
- pH dependency—the determination of tin by hydride generation has been an undesirable technique due to the considerable amount of sample preparation that must be performed to adjust the pH within a narrow range.

It was the purpose of this study to develop an easier, yet accurate tin hydride generation method.

Experimental

A SpectrAA-400 equipped with a VGA-76 Vapor Generation Accessory was used for this work. In the comparative study, a GTA-96 with platform atomization was used. The design and operation of the VGA-76 have been described in Varian AA-at-Work No. 38 [4].

Results

Methodology Development

The original method developed for VGA-76 tin determinations is outlined in Table 1. The acid channel contained 0.5 M HCl which was added at a rate of 1 mL/min. The reductant channel contained 0.6% NaBH₄ and 0.5% NaOH. This solution was introduced at a rate of 1 mL/min. Standards were prepared in 1% tartaric acid. The dropwise addition of 5% NaOH was used to adjust the pH to 2.0–3.0. The standard and sample solutions were introduced at a rate of 6–8 mL/min.

Table 1. Original Method—VGA Configuration

Solution	Concentration	Flow rate
Acid channel	0.5 M HCl	1 mL/min
Reductant channel	0.6% NaBH ₄ 0.5% NaOH	1 mL/min
Sample 1%	Tartaric acid controlled pH	6–8 mL/min

A blank, 20 µg/L, 50 µg/L, and 100 µg/L Sn standards were prepared by the tartaric acid method. The absorbance measurements of the standard solutions were very noisy. The higher the tin concentration, the more severe the instability became. Also, the resulting calibration graph was excessively curved. Signal graphics obtained from these standard solutions are illustrated in Figure 1.

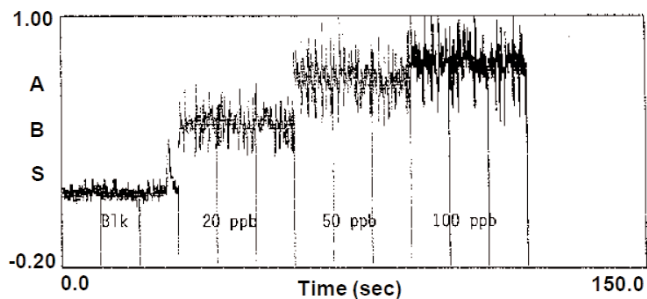


Figure 1. Sn by hydride—original tartaric acid method.

L-cystine and L-cysteine have been used to reduce metal interferences in the hydride generation determination of tin. L-cystine is a simple amino-acid. It is non-toxic and inexpensive. One disadvantage is that it is relatively insoluble in water. It dissolves more readily in 5 M HCl. L-cysteine was chosen for this work. It is freely soluble in water and acidic solutions. It was added directly to the standard and sample solutions.

In this work, L-cysteine was found to have a beneficial effect on precision. Improvements in precision and calibration linearity are apparent in the signal graphics shown in Figure 2. In further work, tartaric acid was eliminated and 1% HNO₃ was added. Precision further improved with optimized methodology.

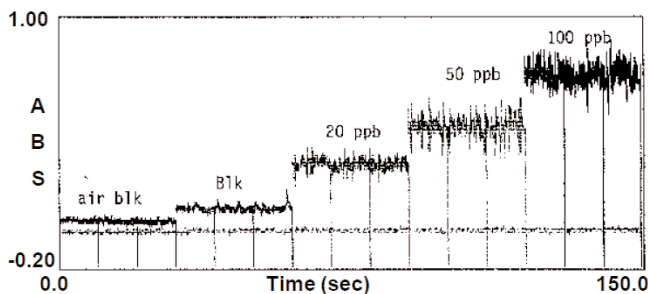


Figure 2. Sn by hydride—effect of tartaric acid and L-cysteine.

High levels of transition metals can cause severe interferences in hydride generation techniques. Typical behavior when high metal concentrations are present is shown in Figure 3. The first group of signals was obtained with a tin standard. L-cysteine and copper were not present. For the second set of signals, 40 mg/L copper was added to the tin standard. The resulting suppressed signal continues to decrease. When the standard (next two sets of signals) was reanalyzed, the signal did not return to the expected level even though copper was not present. This indicated a carry-over effect that is common in hydride generation when metal interferences are present. The last set of signals was obtained from a tin standard containing both 40 mg/L copper and 1% L-cysteine. The L-cysteine reduced the interference from copper significantly.

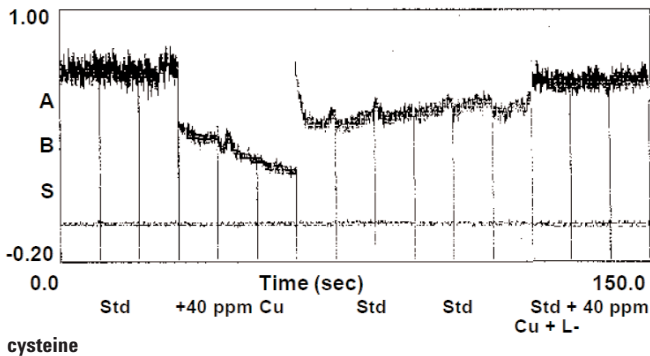


Figure 3. Cu interference—effect of L-cysteine.

The effect of pH was investigated. The study was done at two different wavelengths. The results shown in Figure 4 were obtained at 235.5 nm. (Absorbance signals were approximately 40% lower at 235.5 nm when compared to the absorbances obtained at the recommended 286.3 nm.) For this study, a series of standard solutions were prepared with varying amounts of HNO₃, ranging from 0.1% to 3.0% (0.015–0.45 molar). All solutions contained 1% L-cysteine.

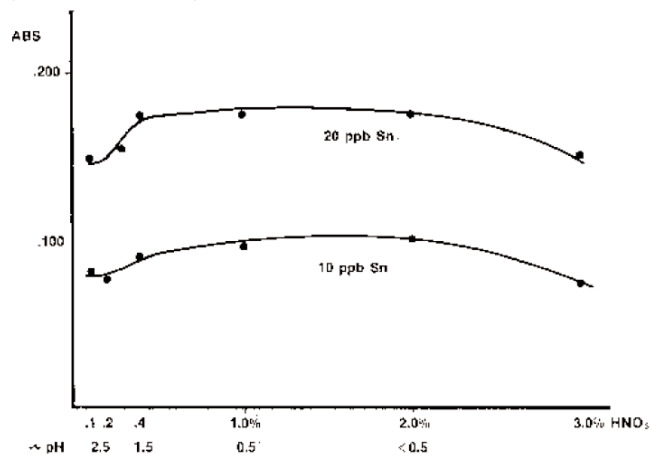


Figure 4. Effect of HNO₃ concentration on Sn signal at 235.5 nm.

Between 0.5% and 2.0% HNO₃, the tin absorbance signals remained essentially constant. Previous methods have recommended a pH of 2.0–2.5. Although pH dependency was minimized with the L-cysteine method, standard and sample acid matrix matching is recommended.

A study of HNO₃ concentration was carried out at 286.3 nm. A series of 10 µg/L Sn standards were prepared in varying concentrations of HNO₃. All solutions contained 1% L-cysteine. The signal graphics are shown in Figure 5. In this study, the 0.1% and 0.2% HNO₃ solutions did not result in lower absorbance signals. However the Sn signal in the 0.1% HNO₃ was particularly noisy. (A minimum amount of acid is necessary to produce hydrogen efficiently from the NaBH₄. Since the sample acid is the only acid added in this method, 0.1% HNO₃ may be less than this amount.) As with the previous study, sensitivity decreased when HNO₃ concentrations approach 3.0%. For the standard solutions containing 0.2%–2.5% HNO₃ and 10 µg/L Sn, the signal range was ± 6.5% of the mean absorbance (0.168 abs). This was excellent reproducibility over more than a 10 fold HNO₃ concentration range.

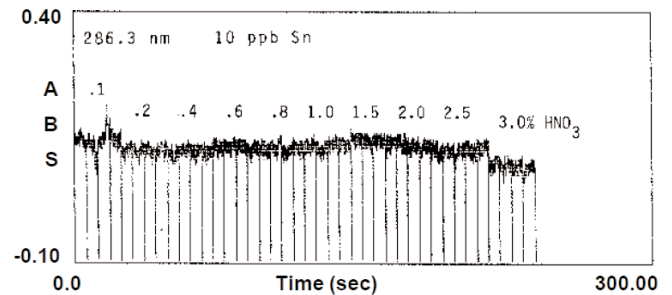


Figure 5. Effect of HNO₃ on Sn signal at 286.3 nm.

A pre-requisite of any AA method is accurate and stable analytical standards. This is of particular concern in hydride methods, where specific chemical forms of the element are required for the formation of the hydride compound. It was found in this work, Sn standards prepared in either 1% HCl or 1% HNO₃ deteriorated within a few hours. However, an intermediate standard of 2.0 mg/L Sn in 1% HNO₃ and 1% L-cysteine was stable for several weeks. Part-per-billion standards were prepared from this intermediate standard daily.

New Hydride Generation Methodology

A new method for Sn determination by hydride generation was developed for the VGA-76. This method is outlined in Table 2. The acid channel contained only D.I. water. The reductant channel contained 0.5% NaBH₄ and a minimum of NaOH. This solution was made fresh daily. Lower concentrations of NaBH₄ (0.3% recommended for As, Se, and Sb) produced noisy, suppressed tin signals. The samples and standards were prepared in 1% HNO₃ and 1% L-cysteine. The pH of standard and sample solutions was < 1 and pH adjustment did not appear to be necessary with this method. The VGA-76 was conditioned prior to an analytical run. Conditioning can be done by alternating a blank and standard solution until a stable signal is obtained. Alternately, one or two initial calibrations can be performed prior to an actual analytical run.

Table 2. New Method—VGA Configuration

Solution	Concentration	Flow rate
Acid channel	D.I. H ₂ O	1 mL/min
Reductant channel	0.5% NaBH ₄ 0.1% NaOH	1 mL/min
Sample	1% HNO ₃ 1% L-cysteine	6-8 mL/min

A calibration obtained with the HNO₃, L-cysteine method is shown in Table 3 and Figure 6. Sensitivity was excellent. A 5.0 µg/L Sn standard gave an absorbance of 0.085. Precisions were also excellent with %RSD levels of 2% or better.

Table 3. Sn Calibration - HNO₃, L-cysteine Method

Sample	Conc. ppb	%RSD	Mean ABS	Readings		
Blank	0.0		-0.002	-0.001	-0.003	-0.002
Standard 1	5.0	1.0	0.065	0.085	0.084	0.085
Standard 2	10.0	0.7	0.165	0.166	0.166	0.164
Standard 3	20.0	2.1	0.300	0.297	0.295	0.307
Standard 4	40.0	0.8	0.494	0.499	0.491	0.492

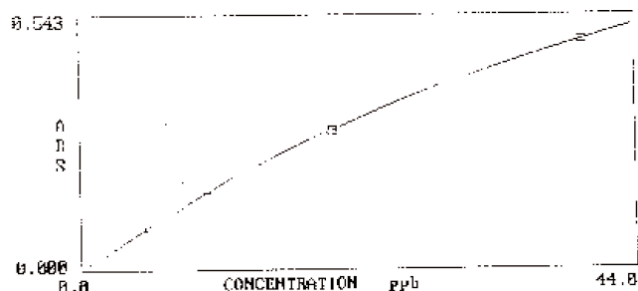


Figure 6. Sn calibration—HNO₃, L-cysteine method.

This method was applied to the determination of Sn in several digested environmental samples. They included five solid samples and a preparation blank (blank water sample).

The samples were:

Sample #1	NIST 1645 River sediment
Sample #2	USEPA (WP286) Electroplating sludge
Sample #3	USEPA (1-884) Hazardous waste soil
Sample #4	USEPA (EC-4) Industrial sludge
Sample #5	NIST 1633 Fly ash
Sample #6	Preparation blank

These were difficult solid environmental samples that were taken through the EPA digestion 3050 [5].

Two 1 gram portions of each sample (prepared and digested) were provided to Agilent by Lockheed Engineering and Sciences Company (LESC), Las Vegas, Nevada, USA. They were labelled 1, 1s up to 6, 6s. ("s" indicates a pre-digestion spike.)

The final digestate contained approximately 5% HNO₃ and 5% HCl. This solution was diluted 1:10 and 1% L-cysteine was added. Sample 1 contained a very high concentration of Sn and was diluted 1:20. After the addition of 1% L-cysteine, HNO₃ was added to maintain the HNO₃ concentration in the 0.8–1.8% range. Although pH dependency was minimized with this method, acid matrix matching was still required for best results.

Shown in Table 4 are the concentration results on the six digested samples. The efficiency of the digestion process has not been evaluated in this study although there is evidence that the digestion process did not yield full recovery of analyte.

Table 4. Sn Results in Digested Environmental Samples

Sample	Conc (µg/L)	%Spike recovery
1	1164	91
1s	1177	86
2	108	94
2s	147	98
3	88	96
3s	186	96
4	66	96
4s	96	96
5	35	91
5s	61	100
6	8	101
6s	5	96

However, a spike recovery study was performed on the digested samples (as supplied) to evaluate the validity of the analytical method.

The spike level was 10 or 20 µg/L in the analysis solution. When necessary, the digested solutions were diluted to fall in the method calibration range. Spike recoveries are listed in Table 4. The recoveries were excellent. Only sample 1s had a recovery of < 90%.

Comparison with Graphite Furnace

Tin graphite furnace methodology was also investigated in this study. The digested environmental samples were mixed and analyzed by both hydride generation and graphite furnace AA. The graphite furnace temperature program is shown in Table 5. Platform atomization and peak area measurements were used. Hot inject parameters are also listed. Tin calibration standards contained 5% HCl and were prepared fresh daily. Standards prepared in 1% HNO₃ were found to be unstable. Two modifier solutions were investigated. (A modifier volume of 8 µL was used for both.)

PO₄/Mg Modifier: 2% NH₄H₂PO₄ / 0.1%Mg (NO₃)₂

Pd Modifier: 500 mg/L Pd / 2.0% Citric Acid

Table 5. Sn Graphite Furnace Temperature Profile

Step no.	Temperature (°C)		Time (sec)	Flow rate (L/min)	Gas type	Read command
	PO ₄ /Mg	Pd				
1	350	350	40.0	3.0	Normal	No
2	900	1000	25.0	3.0	Normal	No
3	900	1000	15.0	3.0	Normal	No
4	900	1000	2.0	0.0	Normal	No
5	2200	2500	0.7	0.0	Normal	Yes
6	2200	2500	2.5	0.0	Normal	Yes
7	2200	2500	2.0	3.0	Normal	No
Hot inject	Yes					
Temperature	130					
Inject rate	5					

Ash and atomize temperatures are typically higher with palladium modifiers. Temperature parameters for both modifiers are listed in Table 5.

Tin results from both hydride generation and graphite furnace determinations are listed in Table 6.

The hydride generation results were obtained from three different runs. The first three graphite furnace results were obtained using the phosphate/ magnesium modifier. The fourth result was obtained using the palladium/citric acid modifier [6]. There was excellent agreement between all analytical methods.

Table 6. Sn Data Comparison in Mixed Digestion Environmental Sample

	Hydride generation	GFAAS
Run 1	188 µg/L	192 µg/L
Run 2	196 µg/L	225 µg/L
Run 3	195 µg/L	211 µg/L
Run 4	–	215 µg/L
Average (\bar{x})	193 µg/L	211 µg/L

Conclusion

The addition of L-cysteine greatly improves the determination of tin by hydride generation. It reduces metal interferences and improves precision and sensitivity. A new method was developed for the VGA-76. The acid channel contained only D.I. water and the reductant channel contained 0.5% NaBH₄ in a minimum of NaOH. Samples and standards were prepared in 1% L-cysteine and 1% HNO₃. The pH dependency typical of tin hydride determinations was minimized. Several difficult digested environmental samples were analyzed. In spike recovery studies, excellent results were obtained. There was good agreement between the graphite furnace and hydride generation results obtained for the analysis of a mixture of the digested environmental samples.

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