The Determination of Pb, Tl, Bi, Ga and Sn in High Purity Sulfuric Acid using Zeeman Graphite Furnace AA

Application Note

Atomic Absorption

Author

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Introduction

High purity acids are widely used in the semiconductor industry for a variety of purposes including use in etching solutions and in cleaning procedures. Suppliers of the acids must meet specific contaminant standards set for the semi-conductor industry. Specifications for many of the inorganic elements are in the part-per-billion range. Graphite furnace atomic absorption methods provide the necessary sensitivity and precision for the routine determination of metals at part-per-billion levels.

This study outlines graphite furnace methodology for the analysis of sulfuric acid. For this study, 500 grams of high purity sulfuric acid was diluted to 1000 mL. Unspiked and spiked samples of this solution were analyzed for five elements; Pb Tl, Bi, Ga and Sn. The spike level was 10 µg/L for all five elements.

Furnace Methodology

Graphite furnace analyses can be difficult due to chemical interferences. These interferences can be minimized by the use of platform atomization techniques and appropriate chemical modifiers. Platform atomization was utilized for all of the analyses. In addition a reduced palladium chemical modifier was used for the Sn determination. Zeeman background correction was utilized for all samples. Determination of the low part-per-billion levels in the sulfuric acid samples required maximum sensitivity. Peak height absorbance measurements provided greater sensitivity than peak area. Therefore peak height measurement was used. The SpectrAA-400 Zeeman spectrometer parameters are listed in Table 1. Argon was used as inert gas and the graphite tube was pyrolytic coated.

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Table 1. Instrument Parameters

Element	Lamp current (mA)	Wavelength (nm)	SBW (nm)
Pb	5	283.3	0.5
Tl	10	276.8	0.5
Bi	10	223.1	0.2
Ga	4	294.4	0.5
Sn	7	286.3	0.5

The temperature program and sampler parameters used for Pb, Tl, Bi and Ga are shown in Table 2. Hot inject was utilized for this analysis. Precision was improved by including a 50 second dry step from 350 ° to 400 °C. It was during this step that the evolution of sulfuric acid fumes occurred. After the removal of sulfuric acid fumes there was minimal background during the atomization step. A master standard of 100 µg/L Pb, Tl, Bi, Ga and Sn was prepared in 10% H_2SO_4. ACS laboratory grade sulfuric acid did not contain significant contaminants when diluted to this level. The automatic sampler was used to prepare calibration standards of 20, 40 and 100 µg/L of all elements (based on a 10 mL total volume). A 20 mL sample volume was used and therefore the standards for automatic calibration were 10, 20 and 50 µg/L of all elements. Calibration results and calibration graphs for Pb, Tl, Bi and Ga are shown in Figures 1–4.

Table 2. Furnace and Autosampler Parameters for Pb, Ti, Br, and Ga

Step no.	Temperature (C)	Time (sec)	Gas flow (L/min)	Gas type	Read command
1	200	30.0	3.0	Normal	No
2	350	20.0	3.0	Normal	No
3	400	50.0	3.0	Normal	No
4	400	10.0	3.0	Normal	No
5	600	5.0	3.0	Normal	No
6	600	5.0	3.0	Normal	No
7	600	1.0	0.0	Normal	No
8	2400	0.9	0.0	Normal	Yes
9	2400	2.0	0.0	Normal	Yes
10	2400	2.0	3.0	Normal	No
11	40	11.8	3.0	Normal	No

Sampler parameters volumes (µL)

	Solution	Blank	Modifier
Blank	-	20	
Standard 1	2	18	
Standard 2	4	16	
Standard 3	10	10	
Sample	20		

Recalibration rate	0
Reslope rate	0
Multiple inject	No
Hot inject	Yes
Pre inject	No
Temperature	140
Inject rate	7

The furnace and sampler parameters for the Sn determination are shown in Table 3. A reduced palladium chemical modifier was used. An alternate gas mixture of 5% hydrogen and 95% argon was introduced during the first 3 steps of the temperature program. A 400 mg/L Pd solution was pre-injected and dried prior to the introduction of the sulfuric acid. Standards were prepared in the same manner as discussed for the other elements. The calibration graph for Sn are shown in Figure 5.

Table 3. Furnace and Autosampler Parameters for Sn

Step no.	Temperature (C)	Time (sec)	Gas flow (L/min)	Gas type	Read command
1	200	30.0	3.0	Alternate	No
2	350	20.0	3.0	Alternate	No
3	400	50.0	3.0	Alternate	No
4	400	10.0	3.0	Normal	No
5	800	5.0	3.0	Normal	No
6	800	5.0	3.0	Normal	No
7	800	1.0	0.0	Normal	No
8	2500	0.9	0.0	Normal	Yes
9	2500	2.0	0.0	Normal	Yes
10	2500	2.0	3.0	Normal	No
11	40	12.3	3.0	Normal	No

Sampler parameters volumes (µL)

	Solution	Blank	Modifier
Blank	–	20	20
Standard 1	2	18	20
Standard 2	4	16	20
Standard 3	10	10	20
Sample	20		

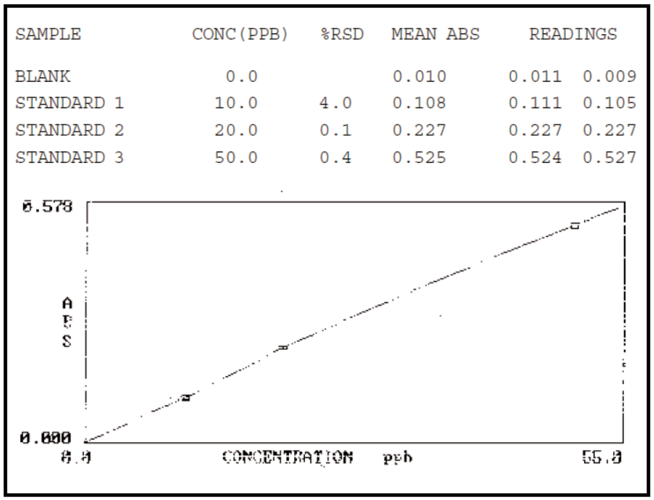
Recalibration rate	0
Reslope rate	0
Multiple Inject	No
Hot inject	Yes
Pre inject	Yes
Temperature	140
Inject rate	7

Results

The results of the analysis of the sulfuric acid samples are given in Table 4. Samples 2287–14 and 2287–23 are a split of one sample. One portion was spiked with 10 µg/L of the element of interest and the other portion was not spiked. Also listed is the characteristic concentration or sensitivity for each determination (based on 20 µL). Detection limits were not determined in this study, but detection limits are typically equal to or lower than the characteristic concentration.

Table 4. Results (µg/L)

Sample type	Pb	Tl	Bi	Ga	Sn
2287-14	≤ 0.1	≤ 0.2	10.9	10.9	≤ 0.3
2287-23	10.1	10.1	≤ 0.3	≤ 0.1	9.9
Characteristic concentration (µg/L, based on 20 µL volume)	0.4	0.5	0.6	0.3	0.6
Characteristic mass (pg)	8	10	12	6	12



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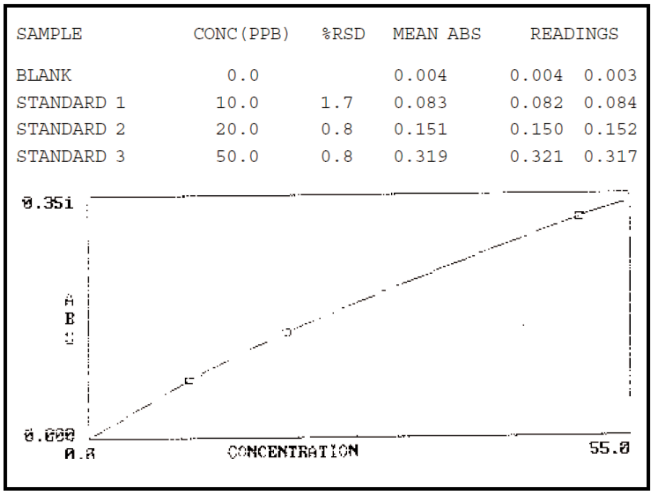
SAMPLE          CONC(PPB)   %RSD   MEAN ABS      READINGS

BLANK              0.0             0.010      0.011  0.009
STANDARD 1        10.0      4.0    0.108      0.111  0.105
STANDARD 2        20.0      0.1    0.227      0.227  0.227
STANDARD 3        50.0      0.4    0.525      0.524  0.527
```

Figure 1. Pb calibration.



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SAMPLE          CONC(PPB)   %RSD   MEAN ABS      READINGS

BLANK              0.0             0.004      0.004  0.003
STANDARD 1        10.0      1.7    0.083      0.082  0.084
STANDARD 2        20.0      0.8    0.151      0.150  0.152
STANDARD 3        50.0      0.8    0.319      0.321  0.317
```
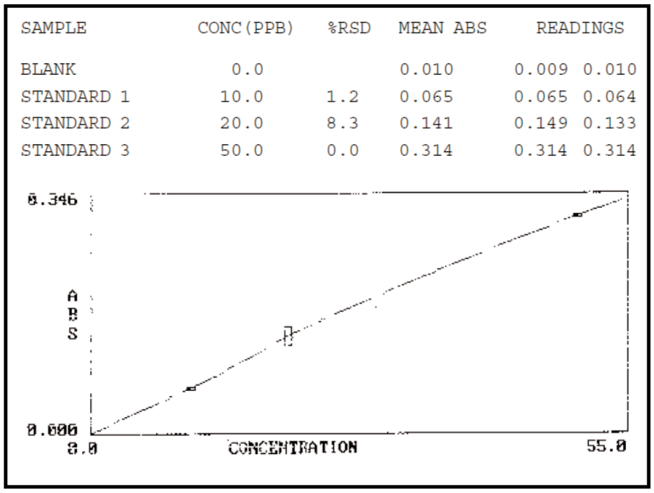

Figure 2. Tl calibration.



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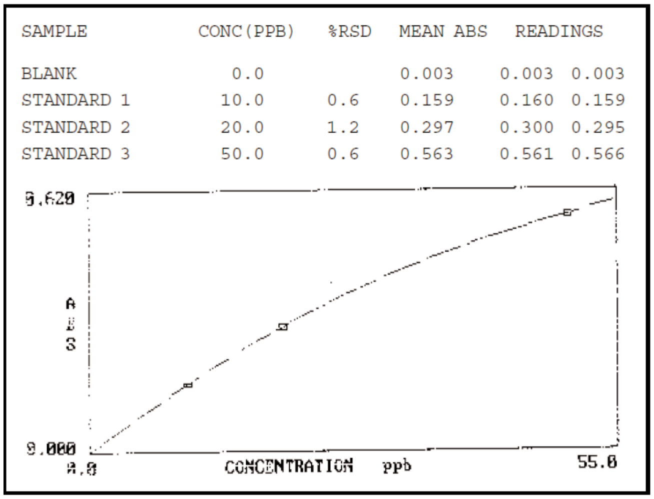
SAMPLE          CONC(PPB)   %RSD   MEAN ABS      READINGS

BLANK              0.0             0.010      0.009  0.010
STANDARD 1        10.0      1.2    0.065      0.065  0.064
STANDARD 2        20.0      8.3    0.141      0.149  0.133
STANDARD 3        50.0      0.0    0.314      0.314  0.314
```

Figure 3. Bi calibration.



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SAMPLE          CONC(PPB)   %RSD   MEAN ABS    READINGS

BLANK              0.0             0.003      0.003  0.003
STANDARD 1        10.0      0.6    0.159      0.160  0.159
STANDARD 2        20.0      1.2    0.297      0.300  0.295
STANDARD 3        50.0      0.6    0.563      0.561  0.566
```
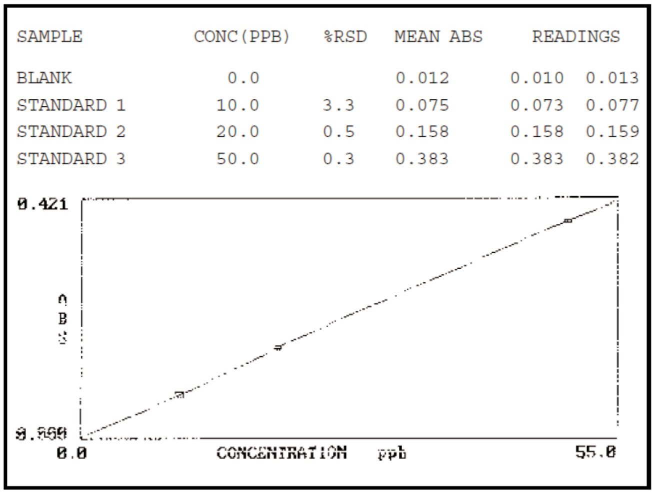

Figure 4. Ga calibration.



```
SAMPLE          CONC(PPB)   %RSD   MEAN ABS      READINGS

BLANK              0.0             0.012      0.010  0.013
STANDARD 1        10.0      3.3    0.075      0.073  0.077
STANDARD 2        20.0      0.5    0.158      0.158  0.159
STANDARD 3        50.0      0.3    0.383      0.383  0.382
```

Figure 5. Sn calibration.

Conclusion

Sensitive graphite furnace techniques are an excellent choice for the determination of trace elements in high purity acids. Results are reported for the determination of 5 elements in high purity sulfuric acid. The recovery of a 10 µg/L spike of the elements of interest ranged from 9.9 to 10.9 µg/L with the methods described. Time-consuming standard additions was not necessary. The characteristic concentration and detection limit for all elements were below 1 µg/L in the solutions analyzed.

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