

Determination of As, Sb and Se in Difficult Environmental Samples by Hydride Generation

Application Note

Atomic Absorption

Author

Lucinda M. Beach

Introduction

Hydride generation techniques are used routinely for the determination of As, Se, and Sb in environmental samples. Advantages include high sensitivity, simplicity and relative freedom from interferences. The current method for the hydride generation determination of As and Se, as outlined in the USEPA manual SW-846, utilizes zinc slurry methodology. A batch type method is described. Batch type hydride generators are inherently slow and prone to interferences. These problems can be overcome with continuous flow systems which are faster, simpler to use and more reliable. Also, interferences are more easily managed.

The USEPA is updating SW-846 with alternative hydride methods for As and Se, while establishing a new method for Sb. The new methods will include the use of NaBH_4 rather than zinc slurry reduction and the utilization of continuous flow rather than a batch type apparatus. Lockheed Engineering and Sciences Company (LESC), Las Vegas, NV, wrote and evaluated the new methods. They also investigated the use of complexing reagents such as L-cystine to reduce transition metal interferences. The Agilent AA Resource Center in Wood Dale, Illinois was involved in the analysis of the referee samples. Although LESC utilized a "homemade" continuous flow apparatus, all of the work done at Agilent utilized the Agilent VGA-76 Vapor Generation accessory.

The VGA-76 features a continuous flow technique in which samples and liquid reagents are pumped and allowed to mix. The gaseous reaction products are then swept into an absorption cell located in the optical path of the AA. The VGA-76 can be readily connected to the PSC-56 programmable sample changer to provide total automatic presentation of up to 67 samples plus up to five calibration standards. Sixty determinations per hour can be made with 1% or better RSD. The VGA-76 has been described in more detail in Varian AA-at-Work No. 38 [1].



Agilent Technologies

This paper discusses the hydride generation analysis of several complex environmental samples. Numerous factors influence accuracy. Sample digestion methods and preparation procedures are of critical importance.

Digestion must adequately solubilize the elements of interest without loss by volatilization. Preparation procedures that guarantee the proper analyte oxidation state and eliminate the nitric acid and inter-element interferences are needed.

Five solid samples and a blank water sample were selected for this study. 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 – Water Blank

These were very difficult samples containing high levels of potential interferents.

Experimental

Methodology

The samples were digested according to SW-846 Method 3050 (solid samples) and Method 3010 (water samples). The digestion procedures are outlined in Table 1 and Table 2. Each solid digestion (Method 3050) required the addition of 1.0 gram of sample plus 10 mL of 1:1 nitric acid into a 250 mL beaker. The beaker was covered with a ribbed watchglass and the contents heated and refluxed without boiling at 95 °C for 10–15 minutes. The contents were allowed to cool. Five mL of additional nitric acid was added and the mixture was refluxed under the watch-glass cover for 30 minutes. This step was repeated once, after which the volume was reduced to approximately 5 mL. The mixture was allowed to cool. Two mL of Type 2 water and 3 mL of 30% H₂O₂ were added and the mixture was heated until effervescence subsided. More hydrogen peroxide was added in 1 mL portions until the sample appearance remained unchanged. At this point, the furnace analysis option of Method 3050 was followed, wherein the acid-peroxide- sample mixture was evaporated to approximately 5 mL. The beaker contents were filtered along with Type 2 water rinsings of the beaker into a 100 mL volumetric flask, and diluted to volume with Type 2 water. During the study, LESC found it necessary to concentrate the original digests to near-dryness after addition of an extra 5 mL of concentrated HCl. This extra step effectively removed peroxide interferences.

Table 1. Method 3050

1. Transfer 1.0–2.0 g of homogeneous sample to beaker.
2. Add 10 mL 1:1 HNO₃, heat at 95°C for 10–15 minutes.
3. Cool, add 5 mL conc. HNO₃. Reflux for 30 minutes then evaporate to 5 mL.
4. Add 2 mL water and 3 mL H₂O₂, heat sample.
5. Continue to add 1 mL H₂O₂ aliquots until clear.
6. For flame: Add 5 mL HCl and 10 mL water. Heat 15 minutes, dilute to 100 mL.
7. For furnace: Heat to reduce volume to 5 mL. Cool, dilute to 100 mL.

Table 2. Method 3010

1. Transfer 100 mL aliquot to a beaker.
2. Add 3 mL HNO₃, heat and reduce volume to 5 mL.
3. Repeat step 2 until digestate is clear.
4. Wash beaker and add 1:1 HCl. Heat 15 minutes.
5. Cool, wash beaker and filter if necessary.
6. Adjust to 100 mL final volume with Type 2 water.

Two 1.0 gram portions of each sample were prepared. One portion was digested “neat”. The second portion was spiked with the analytes of interest before digestion and was identified with an ‘S’ suffix in the sample name. Spiking levels were adjusted so that each sample contained, in addition of the indigenous levels, 100 µg/L Sb, 40 µg/L As, and 10 µg/L Se. The aqueous digestion is outlined in Table 2. It was used to digest the blank water sample. This sample was also spiked with 100 µg/L Sb, 40 µg/L As, and 10 µg/L Se.

These digested samples were provided to Agilent by LESC. Further preparation was necessary for vapor generation. The procedure for As and Sb is listed in Table 3. The samples were further diluted 1:10 with additional reagents. The final solution contained 50% HCl, 2% urea, and 1% KI. As and Sb determinations can be done with the same sample solution. The addition of KI guarantees that As and Sb are in the +3 oxidation state and urea minimizes the nitric acid interference [2].

Table 3. Sample Preparation for As and Sb

- One sample preparation for both elements 5 mL sample placed in 50 mL volumetric. 25 mL HCl added.
- Mixed and cooled. 5 mL 20% urea added.
- Mixed and cooled. 2.5 mL 20% KI added.
- Diluted to mark with D.I. water.
- Analyzed for As and Sb after 30 minutes.

The Se determination required a separate sample preparation which is outlined in Table 4. Again, the digested samples were diluted 1:10 with additional reagents. The final solution contained 60% HCl and 0.4% urea. The 30 minute hot water bath step was required to reduce Se^{+6} to Se^{+4} . The sample degassed with the addition of urea. Dissolved gas can cause poor precision in hydride analysis. Allowing the samples to degas before analysis improved precision.

Table 4. Sample Preparation for Se

5 mL sample placed in 50 mL volumetric. 30 mL HCL added.*
Placed in hot water bath (boiling) for 30 minutes.
Samples cooled.
1 mL 20% urea added.
Samples cooled and periodically shaken to degas over next 30 minutes.
Samples diluted to mark with D.I. water and analyzed for Se after they had stopped degassing.

* For standard preparation 3 drops of HNO_3 were also added.

The VGA-76 was configured with the same conditions for all 3 elements. The acid channel contained concentrated HCl and the uptake rate was 1 mL/min. The reductant channel contained 0.3% NaBH_4 and 0.5% NaOH and the uptake rate was 1 mL/min. The prepared sample uptake rate was 6–7 mL/min. (The exact uptake rates were not determined. They remained constant for samples and standards.)

Results

Arsenic

The VGA-76 As calibration is shown in Table 5. The sensitivity and precision were excellent. Although the sample digest was diluted 10-fold in our sample preparation procedure, the excellent sensitivity of the VGA-76 allowed the determination of less than 1 $\mu\text{g/L}$. For example, 0.2 $\mu\text{g/L}$ As would result in an absorbance of 0.006.

Table 5. Arsenic Calibration VGA-76

Sample	Conc. (ppb)	%RSD	Mean abs
Blank	0.0		0.008
Standard 1	2.0	2.0	0.062
Standard 2	5.0	0.9	0.148
Standard 3	10.0	0.6	0.262
Standard 4	20.0	1.0	0.455
Standard 5	40.0	0.4	0.700

The results of As determinations in the digested samples are listed in Table 6. Recall that each of the six samples had a pre-digestion spike of 40 $\mu\text{g/L}$ As (designated with an "s"). The difference between the unspiked and spiked sample was often not equal to the spike level. This variability was probably due to error introduced during digestion and sample handling rather than errors in the instrument analytical method. Graphite furnace results are shown for comparison. There was good agreement between the two methods except for sample 2. Standard additions calibration was not used. There appeared to be a matrix interference in the graphite furnace analysis of this sample (the electroplating sludge).

Table 6. Arsenic Results ($\mu\text{g/L}$)

Sample	Hydride generation	Graphite furnace
1	245	260
1s	281	294
2	143	116
2s	195	150
3	54	56
3s	79	82
4	45	47
4s	75	78
5	527	530
5s	582	595
6	0	0
6s	36	40

A spike recovery study was done and the results are shown in Table 7. The sample solutions were spiked with 8 $\mu\text{g/L}$ As (samples 5 and 5s had been further diluted 1:2). Recoveries of the 8 $\mu\text{g/L}$ As were excellent, ranging from 87% to 108% or 7.0 to 8.6 $\mu\text{g/L}$. This indicated minimal interference in the VGA analysis of properly prepared samples.

Table 7. Arsenic Spike Recovery Study

Sample	Expected results	Found (ng/mL)	Recovery of 8 ng/mL spike (%)
1	32.5	33.1	108
1s	36.1	36.6	106
2	22.3	22.6	104
2s	27.5	28.2	109
3	13.4	14.0	108
3s	15.9	16.5	108
4	12.5	12.7	102
4s	15.5	16.0	106
5*	34.4	33.3	87
5s*	37.1	37.0	99

All samples diluted 1:10

* Samples 5 and 5s further diluted 1:2

Antimony

The VGA-76 antimony calibration is shown in Table 8. The sensitivity was excellent. The highest standard was 20 µg/L Sb and it gave an absorbance of 0.846. The precisions of 3 replicate readings were excellent (< 1.5%). With this sensitivity and precision, 0.1 µg/L Sb could be easily determined.

Table 8. Antimony Calibration VGA-76

Sample	Conc. (ppb)	%RSD	Mean abs
Blank	0.0		0.000
Standard 1	2.0	1.5	0.086
Standard 2	5.0	0.7	0.216
Standard 3	10.0	0.5	0.425
Standard 4	20.0	1.5	0.846

Shown in Table 9 are the absorbance and concentration results of the actual samples. Sample preparation involved a 1:10 dilution. Even with the dilution the precisions in the VGA determinations were 3 %RSD or better for all samples except the blank (sample 6). Sample 4 contained 3.0 µg/L Sb (0.3 µg/L Sb with dilution). The precision was excellent at 2.9 %RSD.

Table 9. Antimony Results VGA-76

Sample	Conc. (ppb)	%RSD	Mean abs
1	6.4	2.2	0.276
1s	10.9	1.1	0.463
2	3.0	1.4	0.130
2s	6.8	2.3	0.295
3	1.6	1.6	0.071
3s	3.7	0.2	0.160
4	0.3	2.9	0.015
4s	4.2	1.6	0.182
5	0.4	3.0	0.017
5s	4.0	1.0	0.171
6	0.0	51.9	0.001
6s	10.5	0.8	0.445

The results for Sb in the digested samples are listed with graphite furnace results in Table 10. Each of the six samples had a predigestion spike of 100 µg/L Sb (designated with an "s"). This predigestion spike was not recovered for any of the samples except number 6 which was a blank water. This indicated severe losses of Sb in the digestion procedure.

Table 10. Antimony Results (µL)

Sample	Hydride generation	Graphite furnace
1	64	66
1s	109	102
2	30	25
2s	68	54
3	16	17
3s	37	32
4	3	4
4s	42	41
5	4	4
5s	40	36
6	0	0
6s	105	102

A spike recovery study was done and these results are listed in Table 11. The diluted samples solutions were spiked with 8 µg/L Sb. Recoveries of the 8 µg/L spike were excellent ranging from 90% to 101% or 7.2 to 8.1 µg/L. There was no indication of interference in the VGA analysis of the prepared samples.

Table 11. Antimony Spike Recovery Study

Sample	Expected results	Found (ng/mL)	Recovery of 8 ng/mL spike (%)
1	14.4	14.5	101
1s	18.9	18.1	90
2	11.0	10.8	98
2s	14.8	14.1	91
3	9.6	9.5	99
3s	11.7	11.6	99
4	8.3	8.0	96
4s	12.2	11.8	95
5	8.4	8.1	96
5s	12.0	11.3	91

All samples diluted 1:10 + 8 ng/mL spike

Selenium

The selenium concentrations in the samples were very low. The selenium predigestion spike concentration was also low at 10 µg/L. Therefore, a low level calibration was used and is shown in Figure 1. The precisions for three replicate readings of the standards were excellent at 1.6 %RSD or better. A predigestion spike of 10 µg/L resulted in a spike concentration of 1.0 µg/L Se in the analysis solution after the 10 fold dilution from sample preparation. This concentration can be easily determined by the VGA and would give an absorbance of approximately 0.030.

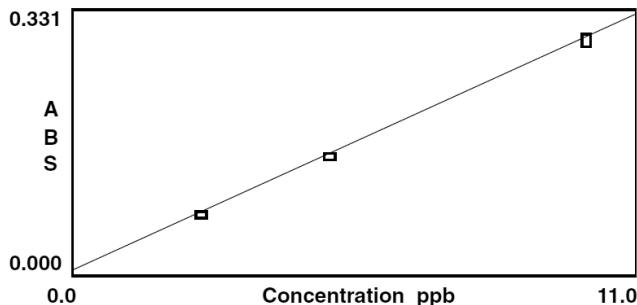


Figure 1. Low level selenium calibration VGA-76.

Results for Se in the digested samples are listed in Table 12. There was good agreement between hydride generation and graphite furnace determinations. The predigestion spike of 10 µg/L Se was not recovered except in the blank water sample (number 6). Again, this reflected problems which occurred during digestion.

Table 12. Selenium Results (µg/L)

Sample	Hydride generation	Graphite furnace
1	4	5
1s	9	9
2	5	7
2s	14	13
3	6	5
3s	12	11
4	< 2.0	< 0.5
4s	7	7
5	37	32
5s	43	37
6	0	0
6s	9	10

A spike recovery study was also done for selenium. The sample solutions were spiked with 2.0 µg/L Se. Recoveries of the 2.0 µg/L Se were excellent, ranging from 95% to 105% or 1.9 to 2.1 µg/L Se. The results of this study are shown in Table 13.

Table 13. Selenium Spike Recovery Study

Sample	Expected results	Found (ng/mL)	Recovery of 2 ng/mL spike (%)
1	2.4	2.5	105
1s	2.9	3.0	105
2	2.5	2.6	105
2s	3.4	3.4	100
3	2.6	2.7	105
3s	3.2	3.3	105
4	2.2	2.1	95
4s	2.7	2.6	95
5	5.7	5.6	95
5s	6.3	6.2	95

All samples diluted 1:10 + 2.0 ng/mL spike

Data Comparison from Two Hydride Generation Systems

In the following portion of this paper the Agilent methodology and results will be compared to that of Lockheed Engineering and Sciences Company (LESC). Hydride generation systems, reagent concentrations, and results will be considered.

Hydride methodologies are compared in Table 14. LESC utilized a four channel system, however only three channels were used. The samples were introduced through channel 1 at a flow rate of 4.2 mL/minute. The reductant channel or channel 2 was used to introduce a solution of 4.0% NaBH₄. The acid channel was not used. The fourth channel was used to add KI for As and Sb determinations. The Agilent VGA-76 conditions are also listed. The VGA-76 used 3 channels with the KI added to the sample solutions for As and Sb determinations. Both systems used sample solutions of high HCl content. (LESC further prepared the Method 3050 solutions by adding HCl to make the analysis solutions 40% HCl.) The Agilent VGA-76 sample flow rate was almost double that of the LESC's system. LESC used a NaBH₄ solution 13 times more concentrated than that used in the VGA-76. This solution was also added at twice the rate of the VGA-76. Considering that the LESC sample flow rate was half that of Agilent, the ratio of NaBH₄ to sample volume was 52 times greater in the LESC system than in the Agilent system. LESC added the KI solution automatically while the Agilent method involved addition of 1% KI to the samples.

Table 14. Comparison of Hydride Conditions

Channel	LESC	Agilent
Sample	40% v/v HCl 4.2 mL/min	50% v/v HCl 7 mL/min
Reductant	4.0% NaBH ₄ 2.1 mL/min	0.3% NaBH ₄ 1.0 mL/min
Acid	—	Conc HCl 1.0 mL/min
KI (As, Sb only)	20% * 0.5 mL/min	

* 1% in samples

LESC added L-cystine to the prepared samples making the final analysis solution 3% L-cystine.* This resulted in much better recoveries in studies of transition metal interferences. LECS had metal precipitation problems and severe interferences with high concentrations of transition metals. With the conditions used in the VGA-76 there was no improvement with L-cystine in this study. Higher NaBH₄ concentrations are associated with greater transition metal interferences [2]. With higher levels of NaBH₄ L-cystine appears to suppress the metal interferences in As and Sb determinations. L-cystine could not be used in the determination of Se. It caused complete suppression of the signal.

Analytical results from both labs are compared in Table 15. Agilent results by hydride generation and graphite furnace are shown. Two data sets are shown for LECS: before and after an extra evaporation step at the end of the digestion. It appeared that residual H₂O₂ caused a synergistic interference with nitric acid resulting in a large background signal that could not be corrected for by the AA instrument used. The results listed in the “BEF” (before) column are often very high. This problem was not encountered with the VGA-76 and the Agilent SpectrAA-20 and SpectrAA-400. An extra evaporation step was not necessary. The samples were diluted further than LECS, however, detection limits were not compromised due to the excellent sensitivity of the instrumentation. The extra dilution minimized the H₂O₂ interference and results compare very well with the LECS “AFT” (after) results. In the graphite furnace determination of As in sample 2 matrix interferences were encountered. Standard additions calibration was not done and lower results were obtained. Detection limits were not determined, therefore no results were reported for sample 6. Sample 6s was the blank water spiked with 40 µg/L As. The problems that LECS was having with high background are apparent in the “BEF” results. With sample 6 the background corrector was overranged or “saturated” in the As determination. LECS’s “AFT” results were considerably lower. Agilent results by graphite furnace and hydride compare fairly well with LECS’s “AFT” results.

* **Warning** Care should be taken when L-cystine is added to high concentration HCl solutions. Excessive degassing can result in the “boiling over” of strongly acidic solutions. Adequate face and eye protection is required.

Table 15. Arsenic Data Comparison mg/L

Sample	Agilent GFAA	Agilent hydride	AFT LESC hydride	BEF LESC hydride
1	260	245	267	281
1s	294	281	310	315
2	116*	143	167	203
2s	150*	195	196	243
3	56	54	40	340
3s	82	79	64	212
4	47	45	36	164
4s	78	75	58	259
5	530	527	505	1326
5s	595	582	559	624
6	0	0	1.6	SATD
6s	40	36	28	1018

* Standard additions calibration not performed

The antimony results are shown in Table 16. Again some of the results without the extra evaporation step are high (BEF LECS HYD). Agilent results by graphite furnace and hydride compare fairly well with LECS’s “AFT” results.

Table 16. Antimony Data Comparison mg/L

Sample	Agilent GFAA	Agilent hydride	AFT LESC hydride	BEF LESC hydride
1	66	64	59	63
1s	102	109	95	107
2	25	30	23	43
2s	54	68	49	79
3	17	16	13	25
3s	32	37	27	48
4	4	3	8.2	28
4s	41	42	33	60
5	4	4	4.4	46
5s	36	40	28	25
6	0	0	1.8	ND
6s	102	105	90	192

A comparison of selenium results is shown in Table 17. Only one set of data from LECS was obtained for selenium. LECS was not able to use L-cystine for the selenium determination due to severe signal suppression. To minimize the transition metal interference the digested solutions were diluted 10 fold. This dilution minimized the H₂O₂/nitric acid gaseous background interferences. Therefore, the extra evaporation of the digest was not necessary. There was excellent agreement between all three methods of analysis.

Table 17. Selenium Data Comparison mg/L

Sample	Agilent GFAA	Agilent hydride	LESC hydride
1	5	4	4.3
1s	9	9	9.5
2	7	5	6
2s	13	14	17.5
3	5	6	5.5
3s	11	12	11.5
4	< 0.5	< 2	< 3
4s	7	7	8
5	32	37	34.5
5s	37	43	41
6	< 0.5	< 2	< 3
6s	10	9	10.5

In this study, predigestion spikes often were not recovered. The percent recoveries of the predigestion spikes are summarized in Table 18. They are calculated from the difference between results obtained from the spiked and unspiked samples. The % recovery is the percentage this number is of the actual spike. The average percent recovery of the 5 samples is shown. Sample 6s data was a blank water solution and is shown separately. Good recoveries were obtained from the blank solution for all three elements. Recoveries were poorer with real samples. Only 25–36% of the spiked Sb was recovered. The digestion used was known to result in poor antimony recovery due to poor solubility and retention of antimony in the non-solubilized portion of the sample. The digestion appeared to result in fairly good recoveries of As. Although Se recoveries were good for the spiked blank solution, they were poor for the real samples, the percent recoveries ranging from 56–74%.

Table 18. % Recoveries of Predigestion Spikes

	Agilent GFAA	Agilent hydride	AFT LESC hydride
Arsenic			
\bar{x} (1S–5S)	100	90	66
6S	100	90	66
Antimony			
\bar{x} (1S–5S)	30	36	25
6S	102	105	88
Selenium			
\bar{x} (1S–5S)	56	66	74
6S	100	90	105

Accurate results are very dependent on digestion procedures and sample handling that occurs before instrumental analysis. In the analysis of difficult solid environmental samples this may be the greatest source of error. It was the purpose of this study to investigate the accuracy of the NaBH₄ hydride technique and not the digestion procedures. For the most part there was very good agreement between Agilent’s data

obtained by graphite furnace and VGA-76 hydride analysis and LESC’s data obtained after an extra evaporation step (As and Sb). There was excellent agreement in the Se data.

Conclusion

Numerous factors affect the accuracy of the hydride generation technique. The digestion procedure can be a source of analyte loss. Residual HNO₃ and H₂O₂ can result in interferences. The nitric acid interference can be eliminated by the use of urea. Residual H₂O₂ can be removed by an extra evaporation step at the end of the digestion or simple dilution can minimize the interferences encountered.

Transition metal interferences can be minimized by the use of L-cytine, the use of high HCL concentrations and low NaBH₄ concentrations. Agilent VGA-76 results were obtained without the use of L-cystine. Comparable results were obtained without L-cystine with the VGA76 methodology. Of course, different hydride generator conditions can result in different conclusions in interference studies. Nonetheless, with proper sample preparation, hydride generation can be a very accurate technique for difficult samples.

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