Evaluation of Deuterium and Zeeman Background Correction with the Presence of Spectral Interferences Determinations of Arsenic in an Aluminium Matrix and Selenium in an Iron Matrix by GFAAS

Application Note

Atomic Absorption

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Introduction

In graphite furnace atomic absorption analysis background interferences frequently occur. Normal background interferences caused by molecular absorption and light scatter are common. These effects can be accurately corrected by most high speed background correctors.

Spectral interferences, which are caused by atoms with absorption lines very close to the analyte absorption line or by fine structure in the molecular absorption profile, can result in either positive or negative errors in the measurement of the concentration of analyte. Fortunately for the analyst, spectral interferences are rare. In fact, one of the distinct advantages of atomic absorption over emission techniques is its freedom from spectral interferences. There are, however, a few well documented instances where spectral interferences do occur in graphite furnace atomic absorption.

Arsenic and selenium are commonly determined by graphite furnace atomic absorption. Arsenic is normally determined at a wavelength of 193.7 nm and selenium at 196.0 nm. In complex matrices spectral interferences can be present for both of these elements. Aluminium interferes with arsenic at 193.7 nm and iron interferes with selenium at 196.0 nm.

This paper explores the effect of the aluminium concentration on arsenic results and iron concentration on selenium results. Deuterium and Zeeman background correction systems were used to illustrate their ability to correct for these spectral interferences.

Agilent Technologies

Experimental

The instrumentation used for the background evaluation was an Agilent SpectrAA-880 with deuterium background correction and an Agilent SpectrAA-880Z with Zeeman background correction. Both spectrometers were equipped with an Agilent GTA-100 graphite tube atomizer and PSD-100 programmable sample dispenser.

Reagents required

- 10,000 µg/mL stock aluminum solution (Al)
- 10,000 µg/mL stock iron solution (Fe)
- 1000 µg/mL stock arsenic solution (As)
- 1000 µg/mL stock selenium solution (Se)
- 1000 µg/mL stock nickel solution (Ni)

Atomic absorption standards can be purchased from any major chemical supplier.

Solution preparation

The stock Al and Fe stock standards were used to prepare the following solutions preserved with 2% nitric acid to be run as samples:

- 500 µg/mL – 5 mL stock standard diluted to 100 mL
- 300 µg/mL – 3 mL stock standard diluted to 100 mL
- 100 µg/mL – 1 mL stock standard diluted to 100 mL
- 50 µg/mL – 0.5 mL stock standard diluted to 100 mL
- 20 µg/mL – 4 mL of 500 mg/mL diluted to 100 mL
- 10 µg/mL – 2 mL of 500 mg/mL diluted to 100 mL
- 5 µg/mL – 1 mL of 500 mg/mL diluted to 100 mL

1000 µg/mL stock standards of As and Se were used to prepared a 1 µg/mL As and Se intermediate standard (1 mL stock As standard and 1 mL stock Se standard diluted to 1000 mL). The calibration standard used was prepared as follows:

> 60 µg/L Calibration Standard = 6 mL intermediate standard and 2 mL nitric acid diluted to 100 mL

All solutions were diluted to volume with Type 2 de-ionized water.

Instrumental

The Al and Fe solutions were analyzed using both deuterium and Zeeman systems. All furnace parameters were optimized on each instrument for platform atomization. Measurements were simultaneously taken in peak height and peak area. A 1000 µg/mL stock Ni standard was used as the matrix modifier. Hot injection shortened the dry time for the samples.

The PSD-100, Programmable Sample Dispenser, was programmed to auto-mix the standards and co-inject 3 µL of the matrix modifier to all solutions. The calibration standard concentrations were auto-mixed from the 60 µg/L bulk standard for As and Se to make 12 µg/L, 36 µg/L and 60 µg/L standards for calibration. The sample volume was 10 µL. Table 1 lists the instrument parameters for both the Zeeman and deuterium background correction systems.

Table 1. Instrument Parameters

Instrument mode	Absorbance
Calibration mode	Concentration
Calibration algorithm	New rational
Sampling mode	Auto-mix
Replicates	2
Background correction	On
Standard 1 concentration	12.00
Standard 2 concentration	36.00
Standard 3 concentration	60.00
Smoothing	5 point
QC protocol	On
Bulk standard concentration	60.00
Sample volume	10 µL
Total volume	18 µL
Modifier volume	3 µL
Standard 1 volume	2 µL
Standard 2 volume	6 µL
Standard 3 volume	10 µL
QC spike bulk concentration	60.00
Rate	1
Volume injected	5 µL
Action	Flag and continue
Recovery limits	85—15%

Table 2 lists the furnace parameters for As in the aluminium matrix. Table 3 lists the furnace parameters for Se in the iron matrix.

Table 2. Furnace Parameters – Arsenic in Aluminium

Hot injection	Yes
Temperature °C	135
Injection rate	1

Step type	**Temp (°C)**	**Time (secs)**
Dry	300–500	15
Ash	850–1400	25
Atomize	2600	3
Cool down	60	20

Table 3. Furnace Parameters – Selenium in Iron

Hot injection	Yes
Temperature °C	135
Injection rate	1

Step type	**Temp (°C)**	**Time (secs)**
Dry	300–500	15
Ash	650–1000	15
Atomize	2500	3
Cool down	60	20

Results and discussion

Deuterium Background Correction

A common, rather inexpensive, background correction technique is continuum source background correction. The continuum source commonly used in present day atomic absorption, is a deuterium lamp. The deuterium lamp is effective over the wavelength range of 180 nm to 420 nm. As was previously mentioned, the background becomes more significant as the wavelength decreases. Therefore the deuterium lamp can be used at the wavelengths most in need of background correction. Figure 1 illustrates the optical configuration of a single beam Agilent spectrometer with deuterium background correction. Accurate measurements depend on directing the deuterium lamp radiation and the hollow cathode lamp radiation along coinciding optical paths. Therefore, careful alignment of both lamps is critical.

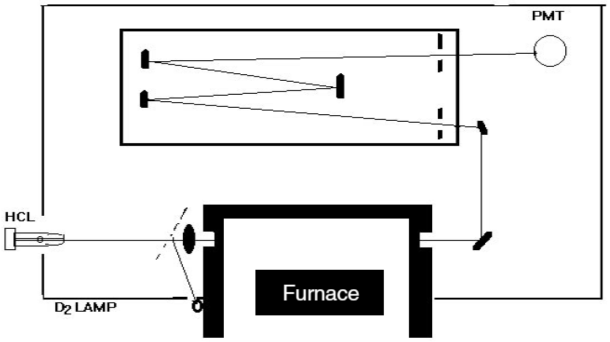

Figure 1. Schematic of a typical single beam optical system fitted with deuterium background correction.

In this configuration, the hollow cathode lamp (HCL) and the deuterium (D_2) lamp are sequentially pulsed on and off with a 2 ms delay between total and background measurements. When the HCL is on and the D_2 lamp is off, the total absorbance (TA) at the analytical wavelength is measured (AA + BG). When the HCL is off and the D_2 lamp is on, the D_2 continuum energy fills the slit and the background (BG) is absorbed. The atomic signal is calculated by subtracting the background absorbance from the total absorbance (TA-BG) (Figure 2).

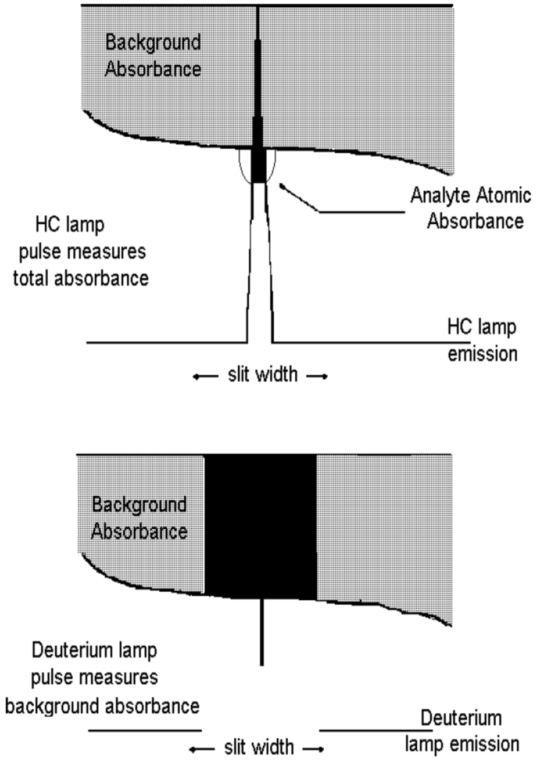

Figure 2. The attenuation of the narrow band hollow cathode lamp profile represents the total absorbance measurement (background and atomic), the attenuation of the broad band deuterium profile is caused primarily by background alone.

The deuterium background corrector cannot accurately correct for some structured molecular background. The structure in the background means that the background is not uniform across the slit. Therefore, the average of the background absorbance measurements may not be representative of the background at the analytical peak. As a result the calculated atomic absorbance may show either positive or negative error.

D_2 background correction cannot correct for such spectral interferences. Normally, the interfering element concentration is far greater than the concentration of analyte of interest.

Zeeman Background Correction

One alternative to deuterium background correction is Zeeman background correction. The Zeeman effect is the splitting of atomic spectral lines in the presence of a magnetic field. In practice, the best implementation of the Zeeman effect is to place a modulated electromagnet around the atomizer. Figure 3 illustrates the optical system for the Agilent Zeeman background correction system. This uses a transverse Zeeman effect background correction system. All Zeeman systems are optically single beam instruments and require only a single energy source.

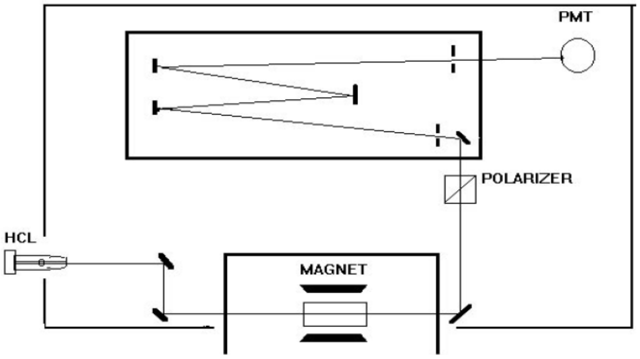

Figure 3. Schematic of the optical system used in the Agilent Zeeman systems.

Just as with the D_2 background correction system, when the HC lamp is on, the total absorbance is measured at the analytical wavelength with the Zeeman magnet turned off. In the simple or normal Zeeman effect, when the magnet is on, the analyte absorption line is split into a π component and two σ components. The π component is at the analytical wavelength and the σ components are symmetrically shifted by a few picometers around the central π component. The degree of the shift is dependant on the strength of the magnetic field. The π and σ components can be distinguished because they exhibit polarizations of light; the π components are polarized parallel to the magnetic field and the σ components from light polarized perpendicular to it. A polarizer is positioned in the optical system to remove the π component of the transmitted radiation. Therefore, the background measurement can be made at the exact analyte wavelength when the magnetic field is applied (Figure 4).

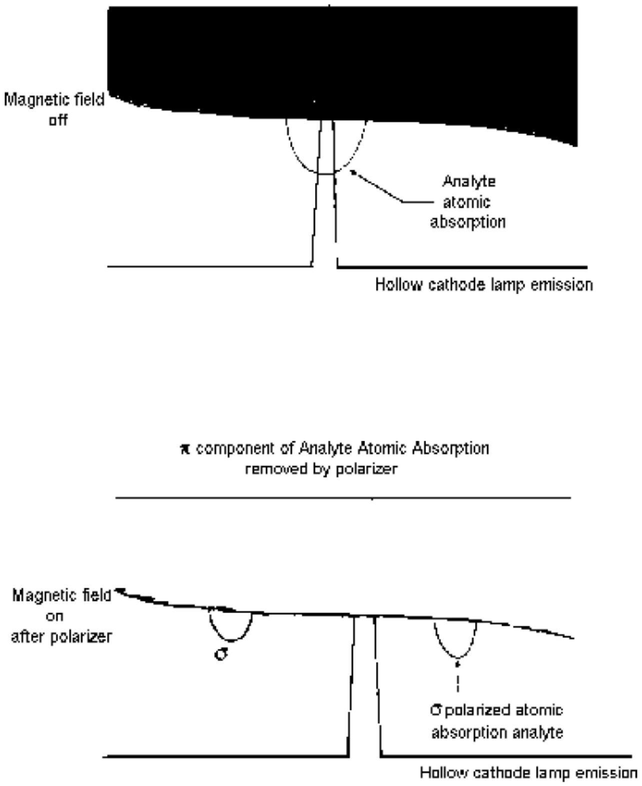

Figure 4. The principle of operation of Zeeman background correction is illustrated. With the magnetic field off (top), the total absorbance is measured. With the magnetic field on (bottom), the Zeeman splitting occurs and the central π component is excluded. This provides a measurement of the background absorbance. The atomic absorbance may be calculated by subtracting the background absorbance measurement from the total absorbance measurement.

Since the background is measured at the analyte wavelength and not averaged as in the D_2 system, structured molecular background and spectral interferences are easily corrected for. However, Zeeman effect does have disadvantages. One disadvantage is calibration roll-over. The calibration roll-over occurs when the sigma components of the analyte are not sufficiently shifted from the analyte line so that an overlap occurs at the source (hollow cathode) emission line. Roll-over can cause two different analyte concentrations to have the same absorbance.

To prevent such problems with roll-over occurring in practice, the maximum permissible absorbances have been determined for each element and these values are listed in the cookbook conditions and automatically recalled from the instrument operating conditions for each element wavelength. These cookbook values define the maximum peak height absorbances that can be achieved for that analyte without roll-over occurring at that specific wavelength.

It is good laboratory practice to ensure that the absorbances for the samples being determined do not exceed this maximum peak absorbance. The software controlling the SpectrAA 800 Zeeman constantly monitors the peak height absorbance (even when using peak area measurement mode) and if an absorbance exceeds this maximum permissible limit, a warning message is reported and that sample is flagged to highlight the error.

The Zeeman effect results in a loss of sensitivity for some elements. This can occur when the atomic line splits into several π and σ components that might overlap. The σ components may not be completely separated from the source (hollow cathode) emission profile. This attenuation of the source (hollow cathode) intensity reduces the sensitivity for some analyte wavelengths. The Magnetic Sensitivity Ratio (MSR) is calculated by dividing the Zeeman absorbance by the normal, non-Zeeman absorbance. The ratio is expressed as a percentage. The majority of analytes have MSR values greater than 80%. However, there are a few analytes, such as Li, which have MSR values as low as 49%.

Aluminium Matrix Effect on Arsenic

It has already been stated that deuterium background correction cannot correct for spectral interferences. One such case is the determination of As in the presence of Al. Part of this experiment was to determine how much Al can be present in the solution matrix without causing an erroneous As result. The same solutions were analyzed using AA systems fitted with Zeeman and D_2 background correction. Various Al solutions were programmed to be automatically spiked in-run with 30 µg/L As. Concentration values and % recoveries were calculated in both peak height and peak area. Since the US EPA contract required detection limit for As is 10 µg/L only results greater than or equal to 10 µg/L of As are considered of significance.

The data generated by the SpectrAA-880 system fitted with D_2 background correction is listed in Table 4. It would appear from the data that all solutions containing Al at concentrations greater than 20 mg/L also had significant quantities of As present. The majority of the % recoveries of the 30 µg/L As spike were very good for both peak height and peak area regardless of the Al concentration. Figure 5 represents the D_2 peak height and peak area % recoveries of the 30 µg/L As in graphic form. If one did not realize the presence of a spectral interference, based on the data presented, one would assume that there was actually more than 30 µg/L As present in these solutions or that some of the Al solutions analyzed were contaminated with As during sample preparation.

Table 4. Arsenic Results in Aluminium Matrix Deuterium Background Correction

Al soln conc (mg/L)	**As value (µg/L) pk ht**	**Spike (% rec) pk ht**	**As value (µg/L) pk area**	**Spike (% rec) pk area**
5	0.74	101	2.57	96
10	1.01	92	4.49	101
20	2.05	103	7.76	95
50	21.8	131	20.0	128
100	42.4	88	40.5	101
300	170.9	50	135.6	77
500	181.8	80	172.3	86

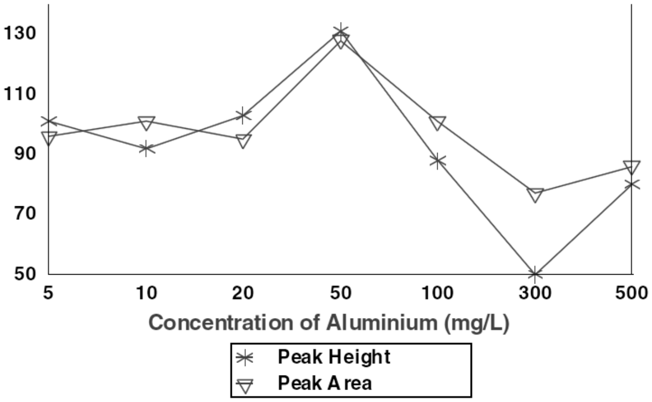

Figure 5. Spike recovery — 30 µg/L arsenic in Al matrix deuterium background correction.

Figure 6 compares the signal graphics of a 30 µg/L aqueous As standard with no Al present to a signal graphic of a 100 mg/L Al standard spiked with 30 µg/L As. The small shoulder on the Al peak is the As peak. Since there is no time separation between the peaks and the Al absorbs the source (hollow cathode) radiation, the correct As concentration is impossible to quantitate solely by using deuterium background correction system. However, there is a challenge to find a chemical modifier to sufficiently delay the atomization of the Al, thus separating the two analyte peaks, to make this determination possible.

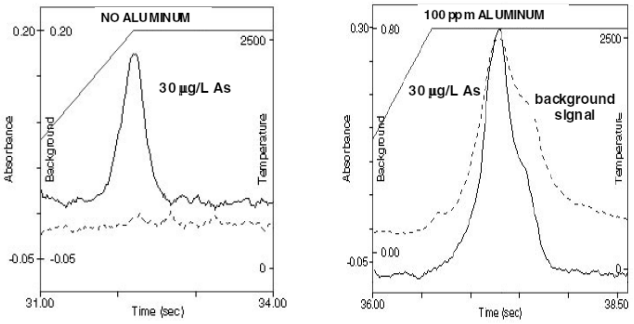

Figure 6. Arsenic in aluminium with deuterium background correction.

The data generated by the SpectrAA-880Z Zeeman system is listed in Table 5. For concentrations of Al less than 300 mg/L, As was not detected . The data indicated that above 300 mg/L Al, significant interference occurs even with Zeeman background correction. The 30 µg/L As spike recoveries were very good even for the higher Al concentrations. Figure 7 represents the % recoveries of the 30 µg/L As in graphic form for peak height and peak area results.

Table 5. Arsenic Results in Aluminium Matrix Zeeman Background Correction

Al Soln conc (mg/L)	**As value (µg/L) pk ht**	**Spike (%Rec) pk ht**	**As value (µg/L) pk area**	**Spike (%Rec) pk area**
5	1.49	106	1.79	106
10	1.66	105	2.66	102
20	1.92	105	3.23	99
50	1.91	103	4.03	97
100	4.19	72	3.68	86
300	19.3	108	1.11	80
500	19.7	83	16.2	84

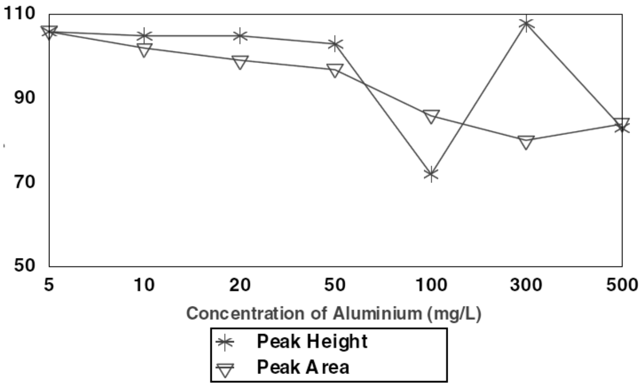

Figure 7. Spike recovery – 30 µg/L arsenic in Al matrix Zeeman background correction.

Figure 8 compares the signal graphics of a 30 µg/L aqueous As standard with no Al present to a signal graphic of a 100 mg/L Al standard spiked with 30 µg/L As. The two signals are almost identical in shape. The peak area absorbance sec^{-1} numbers are the same but the peak height absorbance is slightly lower. The Zeeman background correction technique is effective in the determination of As when the Al concentration in solution is greater than 20 mg/L. However, if the concentration of Al is 300 mg/L or greater, a dilution of the sample may be necessary to achieve the correct result.

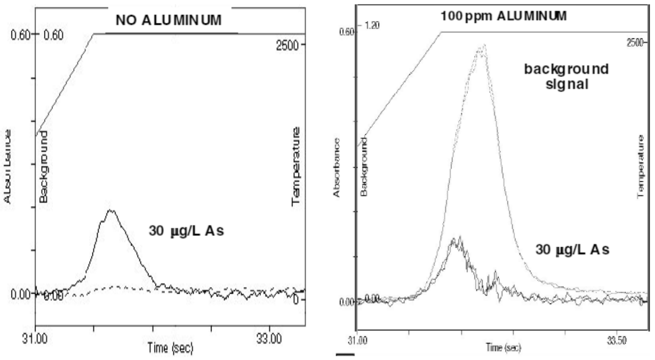

Figure 8. Arsenic in aluminium with Zeeman background correction.

Iron Matrix Effect on Selenium

The second part of the experiment was to evaluate the deuterium background correction system while determining Se in the presence of Fe. The same solutions were then analyzed on the Zeeman system. The Fe solutions were automatically spiked in-run with 30 µg/L Se. The US EPA contract required detection limit for Se is 5 µg/L. For the purpose of this study, only results greater than or equal to 5 µg/ L Se are considered of significance.

The data generated by the deuterium system is listed in Table 6. The spectral overlap caused by the Fe introduced a negative error on the Se results. This is the opposite effect to that which occurred for As in the presence of Al. The peak height Se data could be used for all Fe concentrations though the % recovery for the 1000 mg/L Fe solution was low. The results were slightly negative but not extreme. The % recoveries for the Se spike area measurements were very low for all of the Fe solutions with the exception of the 5 mg/L Fe sample. Figure 9 represents the % recoveries for the 30 µg/L Se spike in peak height and in peak area for the deuterium system.

Table 6. Selenium Results in Iron Matrix Deuterium Background Correction

Fe soln conc (mg/L)	Se value (µg/L) pk ht	Spike (% rec) pk ht	Se value (µg/L) pk area	Spike (% rec) pk area
5	–0.21	104	–6.02	80
10	–0.44	104	–9.24	79
20	–0.22	95	–12.9	95
50	0.15	95	–18.5	128
100	–0.72	92	–28.2	101
300	0.25	96	–44.7	77
500	–0.69	85	–60.1	1
1000	–0.31	63	–68.5	1

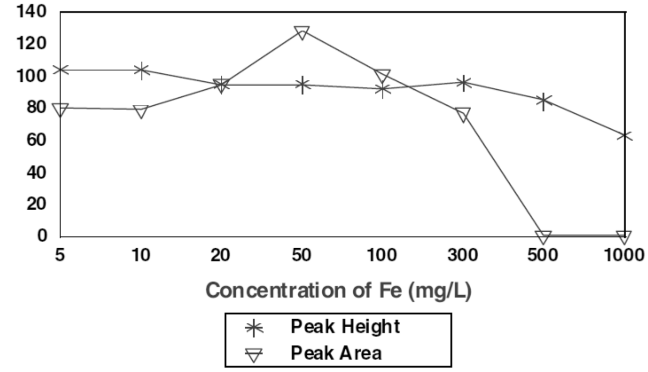

Figure 9. Spike recovery – 30 µg/L selenium in Fe matrix deuterium background correction.

Figure 10 compares the signal graphics of a 30 µg/L aqueous Se standard containing no Fe with the signal graphics of a 1000 mg/L Fe solution spiked with 30 µg/L Se. The negative deflection in the baseline and the Se peak suppression becomes more apparent as the Fe concentration increases. With careful programming of the graphite furnace thermal program including the peak read command and using peak height as the measurement mode, the deuterium background correction system could be used to determine Se in the presence of Fe.

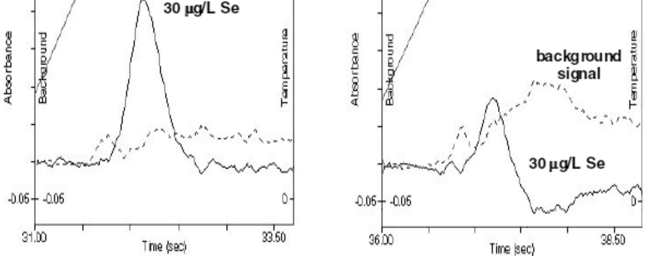

Figure 10. Selenium in iron with deuterium background correction.

The SpectrAA-880Z background correction system results appear in Table 7. The peak height concentration values and the peak area concentration values are both acceptable for Se. The % recoveries are very good for all Fe solutions. Figure 11 represents the % recoveries for the 30 µg/L Se spike in peak height and in peak area for the Zeeman system.

Table 7. Selenium Results in Iron Matrix Conclusions Zeeman Background Correction

Fe soln conc (mg/L)	Se value (µg/L) pk ht	Spike (% rec) pk ht	Se value (µg/L) pk area	Spike (% rec) pk area
5	–0.68	110	–2.85	102
10	–0.63	108	–2.74	100
20	2.22	103	–1.38	100
50	2.21	87	–0.74	97
100	3.14	102	–0.50	96
300	5.58	112	–5.91	89
500	11.3	81	–16.6	80
1000	2.09	95	–2.16	102

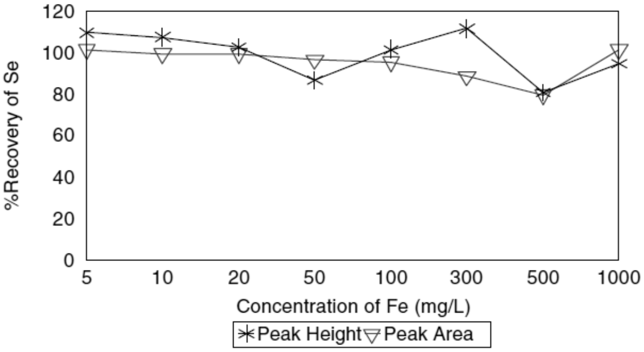

Figure 11. Spike recovery – 30 mg/L selenium in Fe matrix Zeeman background correction.

Figure 12 compares the signal graphics of a 30 µg/L aqueous Se standard containing no Fe with the signal graphics of a 5000 mg/L Fe solution spiked with 30 µg/L Se. The baseline in this instance is very flat with no negative deflection. The peak shapes are identical though the peak area of the Se in the Fe solution is slightly lower than the aqueous standard peak area.

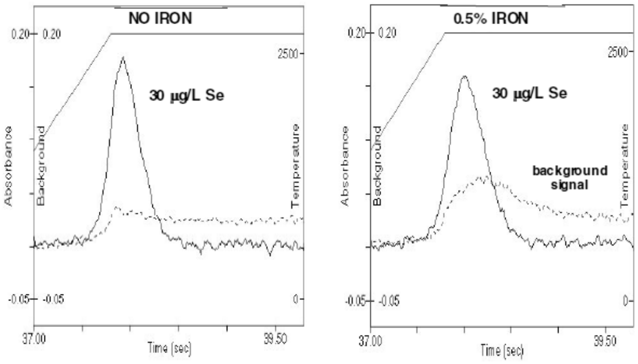

Figure 12. Selenium in Iron with Zeeman background correction.

Conclusions

The results of this experiment indicate that deuterium background correction can not be used to determine arsenic in the presence of Al concentrations greater than 20 mg/L. When using the deuterium background correction as the Al concentration increases the measured arsenic concentration increases.

The Zeeman background correction system can accurately determine arsenic in an Al matrix. However, there does seem to be some interference at Al concentrations equal to or greater than 300 mg/L.

The results for the determination of Se in the presence of Fe showed that deuterium background correction systems could be used. However, the graphite furnace parameters must be carefully programmed to ensure that maximum peak height of the Se peak is read. Peak area results were all unacceptable due to the negative baseline shift. The Zeeman background correction can accurately determine Se in an Fe matrix.

Future work would include trying to find a chemical or physical modifier to easily separate the As and Al peaks.

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