AAS
APPLICATION NOTES

The analysis of selenium in the presence of iron using the GBC graphite furnace system

GBC

Introduction

There are a number of papers detailing the problems caused by iron during the determination of selenium by graphite furnace.[1-4] The major problem is associated with an overcorrection of the total absorption signal when using deuterium arc background correction. This overcorrection is supposedly caused by iron spectral lines that adjoin the selenium resonance line at 196.0 nm.[5] Droessler and Holcombe[6] suggested that the problem was not due to spectral interference caused by adjoining iron lines but to entrained oxygen reacting with the iron. Consequently a method has been developed that overcomes this problem in water samples that contain up to 2000 μg/mL of iron.

Experimental

Instrument parameters

The GBC atomic absorption spectrophotometer, equipped with the unique HYPER-PULSE deuterium arc background correction system and the GBC automated graphite furnace system were used. The GBC graphite furnace system comprises the graphite furnace (GF) and programmable automatic sample loader (PAL). The GBC software was used to develop a furnace method and to collect and store data. Real-time colour graphics of absorbance and background peaks allowed the operator to optimise furnace conditions. The instrumental conditions are given in Figure 1. The inert gas was a mixture of argon and 5% hydrogen at a flow rate of 2.6 L/min, whilst the auxiliary gas was carbon monoxide at a flow rate of 0.1 L/min.

The samples were atomised from a pretreated solid pyrolytic graphite platform positioned inside a standard pyrolytic graphite coated tube.

A Super Lamp was used in preference to a normal hollow cathode lamp. The output of a Super Lamp has a narrower line width and is significantly brighter than that of a normal hollow cathode lamp. This results in better sensitivity, more linear calibration curves, lower baseline noise and hence improved detection limits.[8] The cleaner spectral output also allows wide slits to be used, giving even lower baseline noise, without loss of sensitivity. The wide band pass also means that any spectral interference appearing in the band pass will be averaged over a greater area by the background corrector and hence reduce any overcorrection effects.

Reagents

Selenium standard solution
1000 μg/mL.

Iron standard solution
10,000 μg/mL, prepared by dissolving 2.000 g of ultrapure iron in 20 mL of nitric acid, and diluting to 200 mL.

Nitric acid
Aristar grade.

Chloroplatinic acid
General Purpose Reagent Grade.

Deionised water
Reverse osmosis, mixed bed deionised Type 1 ultrapure water.

Platform pretreatment solution
Chloroplatinic acid was dissolved in Type 1 ultrapure water to give a 1% m/V platinum solution.

Selenium standard solution

200 ng/mL selenium solution was prepared fresh daily in 2% V/V nitric acid in Type 1 ultrapure water.

Sample preparation

Two sets of samples were prepared. One set was used for the method development and consisted of:

1. 1000 µg/mL iron in 2% V/V nitric acid;
2. 50 ng/mL Se in 1000 µg/mL iron and 2% V/V nitric acid; and
3. 50 ng/mL Se in 2% V/V nitric acid.

The second set of samples were used for verification of the method and consisted of six solutions of 70 ng/mL of Se in 2% V/V nitric acid with iron concentrations of 50, 100, 200, 500, 1000 and 2000 µg/mL. A calibration curve was developed by the autosampler taking 2, 4 and 6 µL aliquots of the 200 ng/mL standard selenium solution, diluting them to 16 µL with a 2% V/V nitric acid solution, then depositing them in the furnace.

Graphite furnace applications report

These samples of water contain Fe from concentrations 50 to 2000 mg/L. The Se concentration is 70 µg/L. The analysis is performed from a platform that has been previously coated in the furnace with 2 mg of platinum.

Element	Se
Matrix	Aqueous iron solutions
Instrument Mode	Absorbance BC on
Beam Mode	Double Beam
Measurement Mode	Peak Area
Wavelength (nm)	196.0
Slit Width (nm)	2.0
Slit Height	Reduced
Lamp 1 Current (mA)	18.0
Lamp 2 Current (mA)	0.0
Integration Time (sec)	5.0
No. of Replicates	2
Calibration Mode	Concentration
Recal. Std No.	3

Graphite Furnace Parameters					
Step No.	Final Temp ˚C	Ramp Time (sec)	Hold Time (sec)	Gas Type	Read On
1	110	10.0	30.0	Both	No
2	250	10.0	10.0	Both	No
3	1000	5.0	10.0	Both	No
4	1000	1.0	1.0	Inert	No
5	1000	0.5	0.5	None	No
6	2100	0.6	5.4	None	Yes
7	2400	1.0	2.0	Inert	No

Sampling Mode	Auto Sampling
Standards Preparation	Auto-calculated

Autocalc Sampler Volumes	
Std 1 Volume (µL)	2
Sample Volume (µL)	16
Modifier Volume (µL)	0
Total Volume (µL)	16
No. of Injections	1
Inject before Step No.	1
Recalibration Rate	6

Figure 1: Operating parameters for determining selenium in the presence of iron

Platform pretreatment

The pyrolytic graphite platform was pretreated with 2 mg of platinum, attained by depositing with the autosampler ten 20 µL aliquots of the platform pretreatment solution. The platform was then heated in the furnace tube under the conditions shown in Figure 2.

Graphite Furnace Parameters					
Step No.	Final Temp ˚C	Ramp Time (sec)	Hold Time (sec)	Gas Type	Read On
1	110	10.0	30.0	Inert	No
2	250	10.0	10.0	Inert	No
3	1000	5.0	10.0	Inert	No
4	1000	0.5	0.5	None	No
5	2100	0.6	4.0	None	Yes
6	2500	1.0	2.0	Inert	No

Sampling Mode	Auto Sampling
Standards Preparation	Auto-mixed

Auto-mix Sampler Volumes				
	Blank Volume	**Std Volume**	**Sample Volume**	**Modifier Volume**
Sample	0	0	0	20

No. of Injections	10
Dry to Step No.	3
Inject before Step No.	1
Recalibration Rate	10

Figure 2: Furnace program for platinum pretreatment of platform

Discussion

As a result of the work done by Droessler and Holcombe[6] it was decided that a means of scavenging entrained oxygen in the furnace needed to be developed. Consequently it was decided to use carbon monoxide as an auxiliary gas. Argon was chosen as the carrier gas. It was also decided to use the matrix modifier proposed by Saeed[7] of 0.1% m/V Ni + 3.5% V/V HNO_3 + 0.8% m/V Pt, to facilitate the use of an ashing temperature in the region of 1000°C. This high ashing temperature removes most of any matrix components that can interfere with the analysis.

The carrier gas flow rate was set at 2.6 L/min whilst the carbon monoxide flow rate was varied from 0.1 L/min to 2.0 L/min. It was found that the minimum flow rate of 0.1 L/min provided the best results. At higher flow rates the hot carbon monoxide would ignite once it came in contact with the atmosphere. For this reason, a step was incorporated into the furnace program to flush out any carbon monoxide remaining in the furnace, before atomising the sample.

The success of this combination of modifier and gases in eliminating overcorrection is illustrated by comparing Figures 3 and 4. Figure 3 shows three replicates of the overcorrected signal caused by the presence of iron when analysing for selenium at the 196.0 nm selenium resonance line, when no carbon monoxide is used. This overcorrection occurs because more of the radiation from the deuterium lamp is absorbed than from the selenium hollow cathode lamp. Thus when the absorbance of the deuterium lamp is subtracted from the absorbance of the hollow cathode lamp a negative result is obtained. Hence the term overcorrection of the signal. The magnitude of this overcorrection is less than has been reported by other workers.[1-4] Figure 4 shows the signals produced when three different solutions were analysed for selenium, using the matrix modification solution and carbon monoxide. The first set of traces was produced by 16 µL aliquots of a 1000 µg/mL iron solution, while the second set resulted from analysing 16 µL of a selenium-iron solution containing 50 ng selenium plus 1000 µg iron per mL. These two sets of traces show that signal overcorrection did not occur despite the presence of 16 µg of iron in the sample. The third set of traces in Figure 4 shows the results for 16 µL aliquots of a 50 ng/mL selenium solution. As is evident, the signal resulting from the selenium solution containing iron is much greater than that for the selenium solution without iron. Moreover, when analysing the selenium-only solution, the signal appeared to be suppressed compared to results obtained in earlier work.[8] As a result, a number of different modifiers were tried in an attempt to overcome this problem. The best was a solution of 1% m/V Pt. Unfortunately there was still some discrepancy between the sensitivity for the solutions containing iron and those without; however, there was no sign of any overcorrection, even for solutions containing 5000 µg/mL of iron.
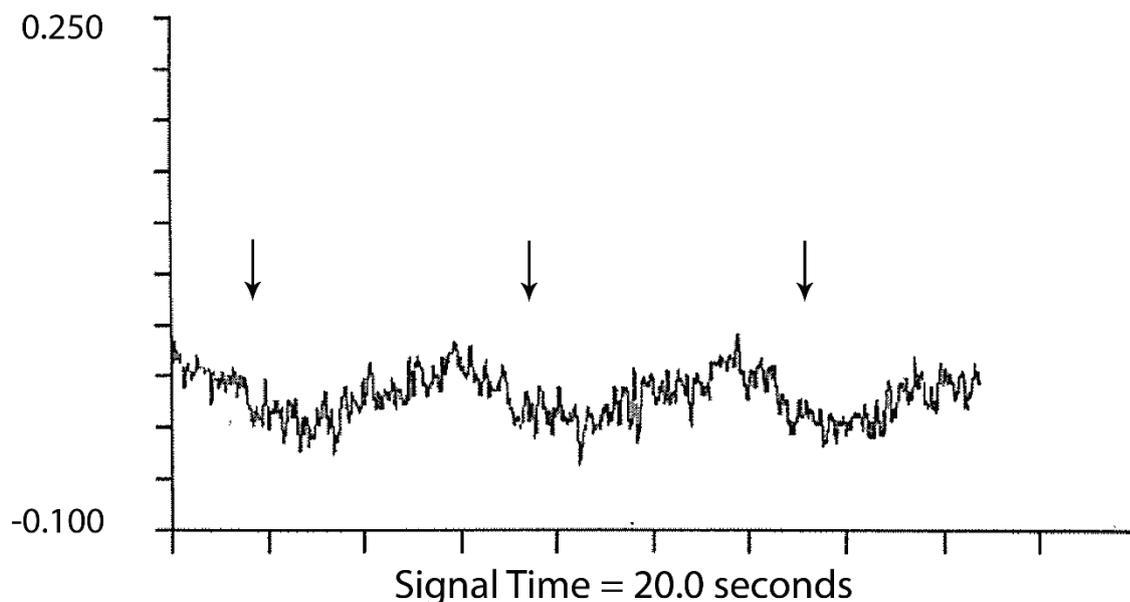
Figure 3: Effect of overcorrection caused by 16 µg of iron on a selenium measurement when there is no modification
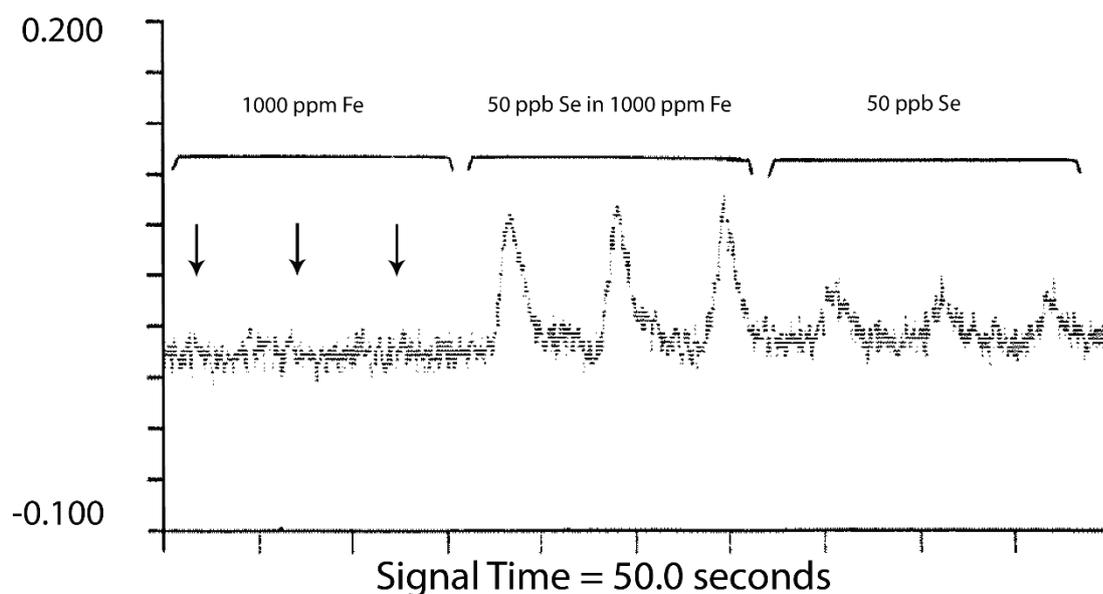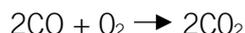

Figure 4: Screen showing signals obtained using carbon monoxide and platinum added with the samples

The overcorrection problem had been solved by the use of carbon monoxide to scavenge oxygen by way of the reaction

$$2CO + O_2 \rightarrow 2CO_2$$

Platinum was thought to catalyse this reaction, so to test this theory the platform was pretreated with platinum in the way described in the previous section. A gas mixture of 5% hydrogen in argon was then used to reduce the platinum to its elemental state. The same gas mixture was also used throughout the subsequent analysis to help maintain the platinum in its reduced form. (Metallic platinum has a boiling point of over 3600°C and so it will not be easily volatilised out of the furnace at temperatures up to 2400°C). The results of this procedure are shown in Figure 5 which includes traces of the same three samples used previously (iron-only, selenium-iron, and selenium-only). The flat baseline from the first solution indicates that there is no overcorrection, whilst the peaks for the two solutions containing selenium are the same shape and have the same area. Peak area values are shown in Figure 6.
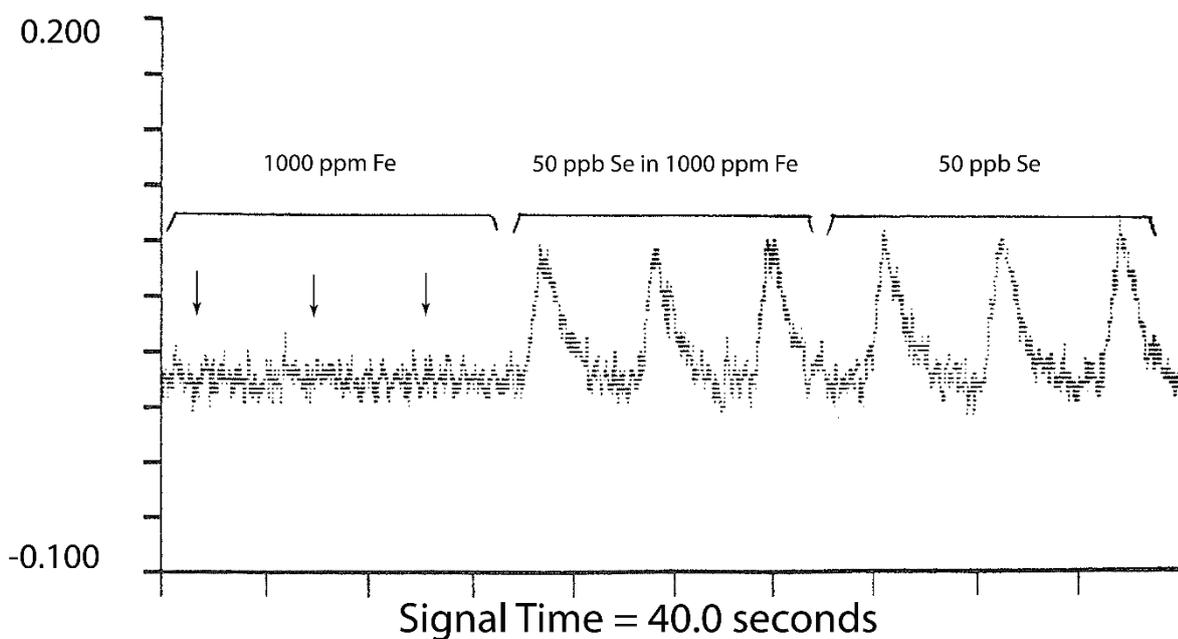
Figure 5: Screen showing signals obtained using carbon monoxide and platinum pretreatment

1000 ppm Fe	0.020	0.022	0.020
0.21 ppb	RSD = 5.61%	Mean Abs. = 0.021	
1000 ppm Fe + Se	0.104	0.095	0.102
0.99 ppb	RSD = 4.93%	Mean Abs. = 0.100	
50 ppb Se	0.100	0.101	0.100
0.99 ppb	RSD = 0.38%	Mean Abs. = 0.100	

Figure 6: Peak area results for selenium with and without iron

It was further thought that when the platinum was added as a modifier it bound with both the iron and the selenium, resulting in only a slight excess of platinum. However when there was no iron in the sample there was a large excess of platinum which was causing a suppression of the selenium signal. Consequently when the platinum was added as a coating it was not present in excess and so did not suppress the selenium signal. Tests were then carried out to evaluate the lifetime of the platinum coating. There was no significant degradation of the signals after 100 firings of the tube, and it required close to 200 firings before there was any sign of overcorrection occurring, i.e. at this point the carbon monoxide was not scavenging all of the oxygen. The number of firings achievable before needing to reapply the platinum can be extended by increasing the amount of platinum deposited initially.

Results

To test the validity of the method a number of solutions, each containing 70 ng/mL of Se, were made up. These solutions had iron concentrations of 50, 100, 200, 500, 1000 and 2000 µg/mL. The solutions were then analysed against a standard calibration curve, constructed by taking 2, 4 and 6 µL of a 200 ng/mL solution of selenium, and diluting each of these aliquots to 16 µL with a 2% V/V nitric acid blank solution. This operation was carried out in-situ by the automatic sampler. A typical calibration curve is shown in Figure 7.
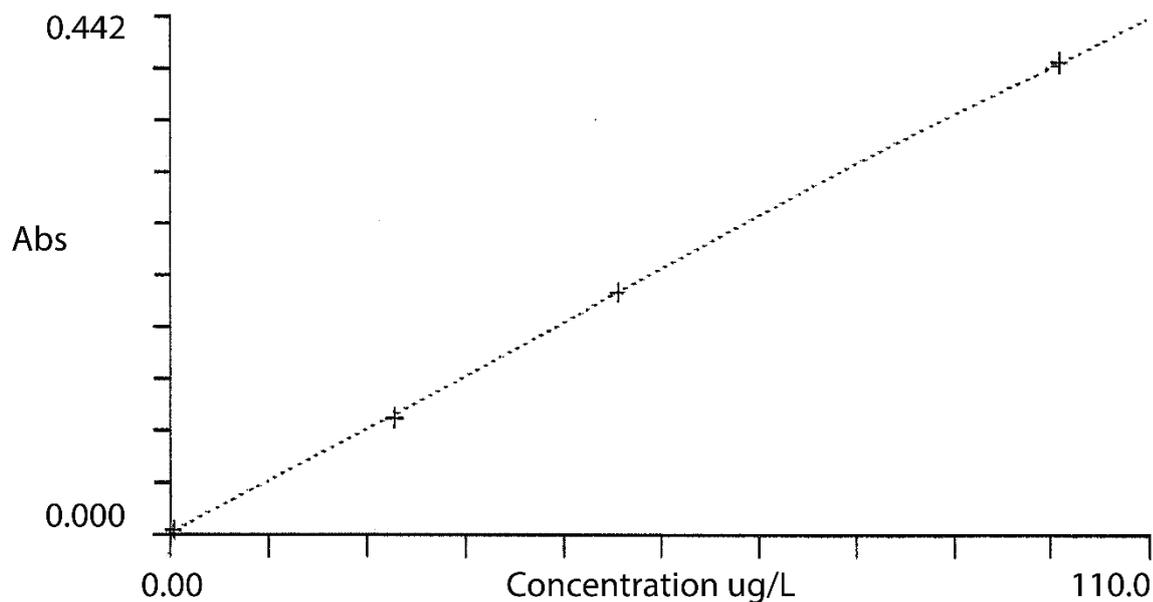
Figure 7: Screen showing typical calibration curve for selenium in 2% V/V nitric acid

The results of this analysis are shown in Table 1. Recoveries range from 98.0 to 104.7 percent.

Iron Content (µg)	Se Added (ng)	Recovery (%)
0.8	1.12	98.0
1.6	1.12	99.4
3.2	1.12	103.8
8.0	1.12	99.1
16.0	1.12	104.7
32.0	1.12	104.3

Table 1: Selenium recoveries with varying iron concentrations in the furnace

Conclusion

It has been shown that the overcorrection of the selenium signal that occurs when analysing selenium at 196.0 nm in the presence of iron is not caused by adjoining iron spectral lines. Further, it has been shown that the overcorrection problem can be solved with the use of carbon monoxide to scavenge oxygen from the furnace environment. As a result, a simple method has been developed that relies on aqueous calibrations and will analyse selenium in the presence of as much as 2000 µg/mL of iron. As well, this method does not suffer from the 12% reduction in sensitivity that occurs when a Zeeman background correction system is used.[9] A method with no loss in sensitivity is particularly important when analysing water samples that contain as little as 10 ng/mL or less of selenium.

References

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