

AAS

APPLICATION NOTES

Quality control procedures for graphite furnace AAS using SavantAA software

AAS



Introduction

With the arrival of quality standards in the analytical laboratory, an ever increasing emphasis is being placed on quality control software and the verification of the results produced. To address these requirements, GBC has developed SavantAA software, an automated quality control software package which allows Intelligent Quality Control systems to be activated automatically within an analytical run.

This application note introduces three quality control procedures for graphite furnace atomic absorption spectrometry (GFAAS) to illustrate their capability to enhance analytical accuracy and precision, whilst allowing improvements in productivity. These automatic procedures are Spike Recovery, Sample Blank Correction and Automatic Sample Dilution.

1. Spike recovery

This provides a useful way to check the validity of an analytical method, particularly where a suitable Certified Reference Material is not available.

SavantAA software allows the PAL automatic sample loader to automatically spike a sample with a known amount of standard. The software then compares results for the spiked and un-spiked sample and calculates the percentage recovery achieved. The frequency of samples spiked can be set by the operator. This system provides a simple automated facility for the verification of graphite furnace results. The example given in this note is the analysis of lead in river water by GFAAS.

2. Sample blank correction

In AAS a calibration blank is routinely measured as part of the calibration. However, in some applications this calibration blank is inappropriate for the samples. Whilst it is desirable to keep standards and samples in the same matrix, this is not always practicable in the routine laboratory environment.

Acids from different containers can give varying blank values due to contamination or the leaching of metals from containers, and it may not be possible to prepare all samples and standards in a single container. If sample and standard matrices differ, a sample blank correction may be necessary.

To enable the analyst to correct for matrix differences between samples and standards, GBC has incorporated Sample Blank Correction into the SavantAA software. This facility allows separate blanks to be used for calibration and sample runs, thus eliminating the need for sample and standard matrices to be perfectly matched, as each can be corrected against its own blank value.

The example given is the analysis of zinc by GFAAS. The standards and samples in this case were prepared using nitric acid from two different containers.

3. Automatic sample dilution

As increased sample throughput is critical in modern laboratories, SavantAA software is designed to transfer much of the sample handling role to the instrument. This allows the analyst to focus on tasks requiring more specialised technical knowledge.

The Automatic Sample Dilution facility allows the PAL programmable auto loader to automatically dilute samples whenever the absorbance is greater than the highest calibration standard.

SavantAA software allows the furnace system to perform serial dilutions on a sample. Thus, if the undiluted sample signal is greater than the highest calibration standard, the sample will be diluted by a pre-determined factor. If the diluted sample signal is still greater than the high calibration standard, the sample will be diluted a second time by the same pre-determined factor. This sequence of dilutions continues until a signal within the calibration range is achieved or the sample volume limit of 1 μL is reached. This ensures that samples are measured within the optimum or linear range of the calibration curve. Automatic Sample Dilution typically extends the working concentration range by a factor of 20.

Experimental

Instrumentation

A GBC atomic absorption spectrophotometer, equipped with the unique Hyper-pulse deuterium arc background correction system and GBC automated graphite furnace system may be used for the analysis. The graphite furnace system consists of the graphite furnace power supply (GF) and programmable automatic sample loader (PAL).

SavantAA software provides control of the entire system: spectrometer, furnace and autosampler, allowing the operator to develop furnace methods and to collect and store data. The facility to display real-time colour graphics of simultaneous signal absorbance and background traces and temperature profile traces allows the operator to optimise furnace conditions. Graphics traces for all standards and samples are stored on the computer, together with all files, allowing recall for method assessment and refinement.

Cleaning of apparatus

All containers and apparatus coming into contact with very dilute solutions were thoroughly cleaned before use. Preferably these containers should not have been in contact with high concentration metal solutions. All glassware was soaked for a minimum of 16 hours in 50% nitric acid and then rinsed in 18 $\text{M}\Omega/\text{cm}^2$.

Reagent preparation

Analytical reagent grade chemicals were used throughout, unless specified. High purity 18 $\text{M}\Omega/\text{cm}^2$ quality water was used.

Working standard solutions for lead and zinc were prepared from 1000 mg/L stock solution by dilution in 0.5% v/v and 1% v/v nitric acid respectively. Standard analytical conditions were used throughout as specified in the GBC Furnace Methods Manual¹ and AA Application Note 'The Analysis of Lead in Drinking Water'² unless otherwise specified.

1. Spike recovery

Experimental

Two samples of river water (SRO1, SRO2) were analysed using two graphite furnace methods. The temperature program for the furnace is shown in Table 1. Method 1 used no matrix modifier. Method 2 used 5% w/v diammonium hydrogen orthophosphate as a matrix modifier. Both methods utilised a pyrolytic platform in the graphite tube and the measurements were made using peak area. The standards were prepared in 0.5% v/v nitric acid. Sample volume was 5 μL and modifier volume was 5 μL .

Program Step	Final Temp. (°C)	Ramp Time (s)	Hold Time (s)	Gas Type
1	140	10.0	30.0	Argon
2	250	30.0	5.0	Argon
3	1000	10.0	10.0	Argon
4	1000	1.0	2.0	None
5	1600	0.5	3.5	None

Table 1: Furnace program used for the determination of lead in river water

Results and discussion

The results show significantly higher results for Method 1, with the spike recoveries being unacceptably high. The spike recoveries for Method 2 are within an acceptable range.

The high results and recoveries for Method 1 are due to the absence of a matrix modifier, causing some of the analyte in the standards to be lost during the ashing stage. This results in a calibration plot with a smaller gradient (and sensitivity) due to the low absorbance values obtained for the standards. The samples, however, contain dissolved salts. These salts act as a modifier, reducing the loss of analyte from the samples during the ashing stage. These effects cause falsely high sample results and percent recovery values.

Analysis Method	River Water Sample	Sample Result (µg/L)	Spike Added (µg/L)	Sample Spike (µg/L)	Spike Recovery (%)
1	SRO1	42.39	25.00	91.76	197.5
1	SRO2	195.32	25.00	248.97	214.6
2	SRO1	19.72	25.00	43.31	94.4
2	SRO2	74.15	25.00	100.10	103.8

Table 2: Results for the determination of lead in two samples of river water, determined against aqueous standards

The use of spike recoveries allows the analyst to determine whether or not a furnace program is suitable for the type of sample being analysed. Although the literature quotes ashing temperatures and suitable matrix modifiers, it may be necessary to determine the maximum ashing temperature and most suitable modifier for each sample type. Also, variation in peak shape between samples due to matrix variation will result in inaccurate results. These processes require the use of spike recovery for method development and for the continual automated monitoring of real samples to obtain accurate results within the day-to-day running of a QC laboratory.

2. Sample blank correction experimental

A working standard containing 5 mg/L zinc was prepared by serial dilution of a commercially available 1000 mg/L zinc standard. The working standard was acidified with very high purity nitric acid (Aristar grade) to give a final acid concentration of 1% v/v. Two water samples were prepared so as to contain 0.25 and 0.75 µg/L of zinc respectively. The sample solutions were acidified using analytical grade nitric acid to give a final acid concentration of 1% v/v.

The two samples were then analysed by GFAAS using a pyrolytically coated graphite tube, with a single calibration blank prepared from the very high purity acid. The furnace program used is given in Table 3. The samples were analysed a second time using separate blanks for the standards and samples. The

standard blank was prepared from very high purity acid and the sample blank was prepared from analytical grade acid. The sample volume was 15 μ L and the measurement mode was peak height. The results from the two furnace runs are given in Table 4.

Program Step	Final Temp. ($^{\circ}$ C)	Ramp Time (s)	Hold Time (s)	Gas Type
1	125	10.0	30.0	Argon
2	250	30.0	5.0	Argon
3	400	10.0	10.0	Argon
4	400	1.0	2.0	None
5	1800	1.0	3.0	None
6	2200	1.0	2.0	Argon

Table 3: Furnace program used for the determination of zinc in water using a pyrolytically coated graphite furnace tube

Results and discussion

The results in Table 4 show that the use of a separate sample blank can be useful where sample and standard preparations vary. The samples were known to contain 0.25 and 0.75 ng/mL of zinc respectively. In the first analysis, where a separate sample blank was not used, the measured concentrations were high, giving a large percentage error in the sample results. This was due to a higher level of zinc in the analytical grade acid than in the very high purity acid. In the second analysis where a separate sample blank was used and corrected for, the sample results were very close to the theoretical values and the percentage error is within an acceptable range.

Sample Number Used	Sample Blank (ng/mL)	Theoretical Conc. (ng/mL)	Measured Conc. (ng/mL)	% Error
1	No	0.25	0.81	224
2	No	0.75	1.38	84
1	Yes	0.25	0.26	4
2	Yes	0.75	0.74	1.3

Table 4: Results for the determination of zinc in water samples

The error incurred in the first analysis will be equivalent to the difference in concentration of zinc between the very high purity acid and the analytical grade acid. To confirm this, the zinc concentration was determined for a 1% v/v solution of the analytical grade acid, using the standard blank and standards prepared in the very high purity acid. The concentration was 0.57 μ g/L.

As expected, the error in the first analysis was due to contamination of the samples by the lower purity analytical grade acid. The use of a separate sample blank will correct this discrepancy. SavantAA software allows this sample blank to be programmed into the stored application, and the sample results to be automatically corrected for the sample blank. This removes the need to manually measure sample blanks or calculate the sample results at the end of an automated run.

3. Automatic sample dilution experimental

The experimental conditions were identical to those used for Sample Blank Correction (# 2 above). However, very high purity nitric acid was used to prepare the calibration blank.

Results and discussion

Table 5 shows a typical analysis report for the determination of zinc in river water by GFAAS. The calibration range is up to 2 µg/L, however sample concentrations up to 14 µg/L have been determined without any need for the operator to dilute samples or be present during the analysis run.

For samples 1 and 4, as the analyte concentration range for the undiluted sample falls within the calibration range, no sample dilution was carried out. For samples 2 and 3, the analyte concentration in the undiluted samples falls outside the calibration range. In these cases, the sample was automatically diluted by the PAL to achieve an analyte concentration which was within the calibration range. Note that for sample 2, two dilutions were necessary to obtain a result.

In each case all data is output to the report, regardless of whether or not it was possible to calculate a result. This allows the analyst to readily assess the validity of results and monitor the operation of the system.

Sample	Dilution Factor	Mean Abs	%RSD	Conc. (µg/L)
Blank		0.026		
Std 1		0.146	1.04	0.5
Std 2		0.256	0.98	1.0
Std 3		0.347	0.73	1.5
Std 4		0.421	0.71	2.0
Sample 1		0.383	0.30	1.7
Sample 2		1.133	0.84	Error
Sample 2	0.25	0.574	0.61	Error
Sample 2	0.05	0.197	0.88	14.4
Sample 3		0.761	0.29	Error
Sample 3	0.25	0.318	1.40	5.3
Sample 4		0.191	0.71	0.7

Table 5: Typical analysis report for Zinc in water by GFAAS using automatic sample dilution

Summary

SavantAA software enables the analyst to obtain spike recovery data for both method development and routine sample checking, without the need for labour intensive spike preparations. The use of the PAL to prepare standards and spike solutions ensures the maximum utilisation of analytical time, whilst maintaining good analytical practice.

SavantAA software allows a separate sample blank to be run, in addition to the calibration blank. This allows samples and standards to be prepared in different matrices, and for the analyte concentrations determined in the samples to be automatically corrected against their own matched blank. This facility is applicable to both flame and furnace work, and removes the need for manual correction calculations to be performed at the end of a sample run.

The use of automatic sample dilution in graphite furnace analysis allows for the analysis of samples containing a wide range of analyte concentrations, without the need for lengthy sample dilutions. For laboratories needing to analyse samples overnight to maximise instrument use, automatic sample dilution greatly increases the chances of having a full set of sample results the following morning ready for reporting. It is no longer necessary to prepare sample solutions based on your 'best guess' for the concentration range the analyte of interest may fall into.

SavantAA software introduces new levels of automation in atomic absorption spectroscopy, allowing laboratories to increase sample throughput, whilst still maintaining confidence that the results are accurate. SavantAA's unsurpassed level of automation provides efficient fully automated sample analysis, allowing laboratory staff to be utilised to the maximum on tasks requiring their specialist knowledge.

References

1. Graphite Furnace Methods Manual, GBC Scientific Equipment Pty Ltd, Braeside, Australia.
2. Gill, R., Ashton, P. and Jankowski, S. The Analysis of Lead in Drinking Water, GBC AAS Application Note.