Application Note

Improved Accuracy in Atomic Absorption Analysis using Automatic Sensitivity Correction

Introduction

The very nature of the atomic absorption principle has made possible the accurate analysis of metals in solution. In the analytical laboratory, the measurement of sample absorbance may suffer from small changes over time, due to sample matrix effects, analyte-specific conditions or analytical circumstances that are beyond operator control.

For the three forms of analysis, flame, furnace (electrothermal atomization) and hydride, there are well defined conditions responsible for this alteration in absorbance. Analysts are aware of these but may be puzzled how best to negate their effect on analytical *accuracy* and *precision*.

In flame analysis, absorbance changes can occur due to:

- Alteration of the nebulization rate e.g., blockage by particulate matter or high solids deposit.
- Changes to the burner temperature over time.
- Deposition of sample matrix (e.g., salt material or carbon build-up due to carbohydrates in samples) on the interior of the burner jaw.
- Carbon build-up on the burner lips when nitrous oxide-acetylene is used.

In furnace analysis, the fact that the graphite tube is heated to temperatures up to 3000°C results in degradation of the interior graphite tube surface, which may affect the analytical absorbance. Any of the following may occur:

- Changes to graphite tube wall integrity after long term use.
- Matrix build-up (e.g., blood matrix and carbon waste) on the wall or the surface of a pyrolytic platform.

In hydride analysis, absorbance changes may be caused by:

- Chemical deterioration of the sodium borohydride reducing reagent, which occurs spontaneously.
- Chemical build-up on the interior surface of a hydride cell, which may cause alteration in the availability of free ground state atoms.

To maintain analytical *accuracy* and *precision*, analysts have resorted to re-calibration and rescale (normalization) routines. However these procedures cannot correct results for samples previously analysed, but only for samples about to be analysed. The objective of this paper is to present a procedure which improves analytical *accuracy* for samples between calibrations, recalibrations or rescale measurements, even though a change in sensitivity has occurred over time.

GBC has incorporated a procedure called *Automatic Sensitivity Correction* into the *Intelligent Quality Control* parameters of the *Avanta* software for use on GBC Avanta Σ, Avanta, 932 and 933 atomic absorption spectrometers.

The Principle of Automatic Sensitivity Correction

The selection of 'Sensitivity Correction ON' in the Method Properties menu of the *Avanta* software activates the proportional correction procedure for the current results. This causes a 'Rescale Standard' measurement to be performed automatically (provided that a recalibration has not been performed) after all samples have been measured in a sample run, and it is designated as the reference value. The correction procedure is calculated in three parts:

1. Baseline Correction for absorbance change in successive calibrations or rescale blank measurements. All sample measurements between these blank measurements are corrected proportionally.

2. Sensitivity Correction for a change in absorbance between successive calibration, or rescale standard, measurements using a predefined standard as the reference point. All measurements, including standards, are corrected proportionally.

3. A correction factor is determined for each sample result and stored as part of the results parameters in the results file. The greatest correction applies to the last sample measurement. The correction calculation remains disabled until the analyst decides to activate 'sensitivity correction' for the analytical run. If, upon studying the run, the results do not require correction, the analyst may choose to accept the results uncorrected.

Experimental

Instrumentation

A GBC Avanta atomic absorption spectrometer with programmable flame control, Ultra-Pulse deuterium-arc background correction system, and motorized 4-lamp turret to allow sequential multi-element analysis was used. Accessories used for the generation of experimental data included an SDS-270 flame autosampler, System 3000 graphite furnace and *Avanta* software incorporating *Intelligent Quality Control* with the *Automatic Sensitivity Correction* parameter.

Reagents and Sample Preparation

All chemicals were analytical grade or designated manufacturer high purity grade. Nitric acid for sample preparation was Aristar grade (BDH, Merck Pty Ltd, Australia). Atomic Absorption Standards for lead, vanadium, silicon and mercury were 1000 μg/mL (BDH, Merck Pty Ltd, Australia).

De-ionized water for washing and rinsing was obtained from a mixed-bed de-ionizing unit (Service Exchange De-ionization System, Continental Water Systems Pty Ltd). De-ionized water used for reagent preparation and analysis was from a reverse osmosis, mixed bed de-ionizing unit that supplies type 1 Ultrapure water (Modulab, Reagent Grade Model Water System, Continental Water Systems Pty Ltd).

Analytical standards and samples were prepared freshly each day at the appropriate concentration for each element. Quality Control material for lead in blood analysis was obtained from State of New York, USA, Department of Health, Lot #18 (cow blood) and Contox whole blood – lead control, Kaulson Laboratories Inc, N.J., USA. Both samples were prepared with type 1 Ultrapure water according to the instructions provided.

Unless otherwise stated, measurements were made using recommended operating parameters and sample treatment procedures.

Results and Discussion

1. Flame Analysis

Flame analysis using an air-acetylene flame does not generally suffer from difficulties, however when using the nitrous oxide-acetylene flame, consideration should be given to both the type of sample matrix and the analytical parameters to ensure analytical *accuracy*. A common minor inconvenience of the nitrous oxide-acetylene flame is that the temperature of the burner must be stable to ensure accurate results. In Figure 1, results for a 100 μg/mL silicon solution have been depicted as multiple samples that were measured with a relatively cold burner. The uncorrected results show an increasing reduction in concentration as the sample number increases.

Corrected results show a higher accuracy since they more closely approach the nominal concentration value.

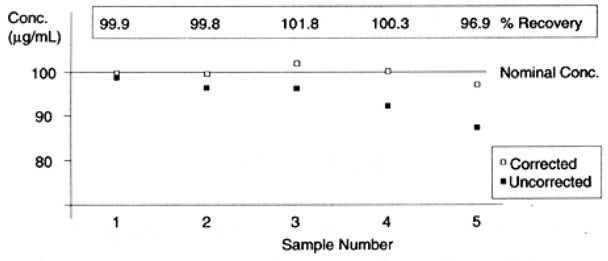

Figure 1: *Results of silicon analysis using a nitrous oxide-acetylene flame with a relatively cold burner. Note corrected and uncorrected data points.*

2. Furnace Analysis

Graphite furnace analysis can also be subject to sensitivity change. For example, to measure vanadium requires an atomization temperature of 2650°C. A furnace program was specifically set up to 'age' the graphite furnace tube. Figure 2 shows results for a vanadium standard with a concentration of 100 µg/L. The graph shows 40 consecutive measurements, plotted after 300 and up to 340 firings of a standard graphite furnace. This was performed to illustrate that the ageing graphite furnace tube suffers from a loss in sensitivity. The plot shows the original uncorrected data, with an obvious trend downward. The corrected results are also plotted to show the improvement in accuracy when the proportional sensitivity correction procedure is applied.

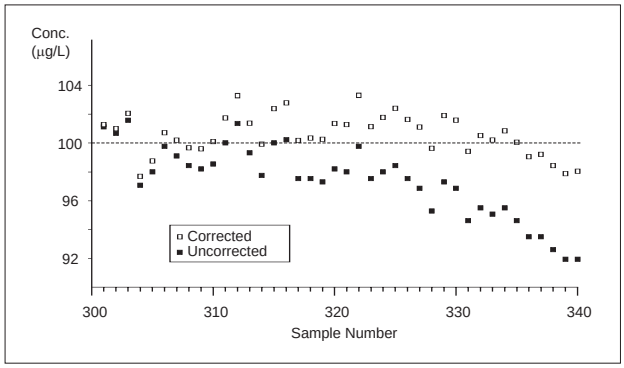

Figure 2: *Measurement of vanadium standard, 100 µg/L, using an aged graphite furnace tube. Tube firing results were plotted from 300 to 340 firings.*

The concentration of lead in whole blood is of major community concern and analysis is conducted in many clinical laboratories. A build up of carbon residue may occur if an unsuitable ashing temperature step is used. This residue may cause difficulties in obtaining accuracy. In addition, the effect of an ageing tube needs to be considered for accuracy to be maintained after a large number of furnace firings, i.e., 300 or more. A standard graphite furnace method for lead in whole blood was used[1] and modified to induce carbon build up.

The same blood sample (New York State Department of Health #18 (cow blood)) was measured over 49 consecutive firings. Using this well known reference material has allowed the monitoring of the effect of the absorbance-lowering factors which could not previously be accounted for. The plot in Figure 3 illustrates the improvement in *accuracy* for the blood sample when the sensitivity correction procedure is applied.

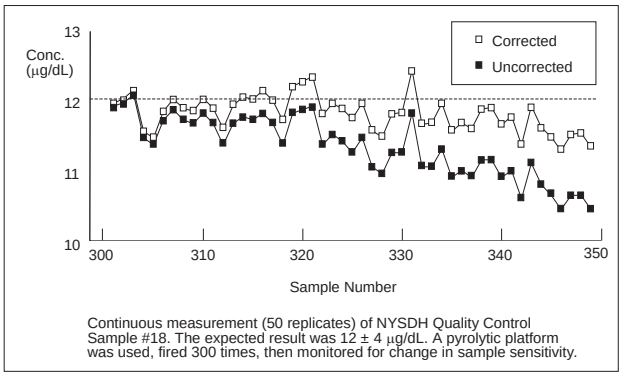

Figure 3: *Lead in whole blood, using porcine blood as a standard matrix, to illustrate the effect of induced matrix interference on analytical accuracy.*

3. Hydride Analysis

The hydride generation technique has the advantage of being a relatively simple procedure once the sample has been treated appropriately.[2] The tendency of analysts to use 'old' solutions can cause analytical difficulties. Sodium borohydride solution is the major reagent acting as the reductant in hydride generation and suffers deterioration over a relatively short time. Hence, fresh reagent should be prepared daily. *Automatic Sensitivity Correction* can be applied to combat the effects of ageing solutions or chemical deposition on the hydride cell.

Conclusion

The principle of *Automatic Sensitivity Correction* allows significant improvement in *accuracy* for all analytical modes of atomic absorption by automatically correcting sample results between recalibrations or rescales. Correction can be applied either before or after specific quality control monitoring.

For flame atomization, automatic sensitivity correction can be applied when using either air-acetylene or nitrous oxide-acetylene flames. Standard single burner angle or multi-angle analysis using Automatic Burner Rotation can be utilized, as well as hydride analysis and cold vapour generation for mercury. The use of a quality control check sample or sample blank in any analytical mode is treated in the same way as a sample result and hence also corrected accordingly.

For graphite furnace atomization, specific analytical parameters such as auto-dilution and spike recovery measurements on samples are included and corrected appropriately.

The ability of the GBC Avanta software to allow results editing to change the type of calibration plot to ‘Concentration’ (polynomial interpolation to connect data points) or ‘Concentration Least Squares’ and ‘Linear Least Squares’ (the same polynomial function with a least squares line of best fit for the data points) and the type of measurement, i.e., peak height, peak area or integration, where applicable, does not prevent *Automatic Sensitivity Correction* from being used to improve analytical *accuracy* and *precision* in any atomic absorption analysis.

References

1. Sinclair, D. and Chapple, G. *The Determination of Lead in Human Blood using Porcine Blood Standards,* GBC AA Application No 12, 1988.

2. Gerdei, T., Gill, R. and Wallis, N. A *Comparison between Flame-Heating and Electric-Heating Trace-Level Hydride Analysis*, GBC AA Application No. 25, 1993.