Application Note

Application of the GBC HSA3000 to Samples with High Dissolved Solids

Introduction

The analysis of samples with high dissolved solids content may create several potential difficulties for atomic absorption analysis. The most significant of these is build-up of salt within the burner and possible blockage of the burner slot. Analytical considerations that must be considered are; (a) a suitable sample volume to provide sensitivity, accuracy and precision of the analytical signal, (b) the volume of flushing solution required, (c) avoidance of contamination of spray chamber and burner, and (d) sampling rate.[1]

Difficulties may occur when the sample matrix contains more than 2% dissolved solids, and the subsequent flushing action of a rinsing solution may be insufficient to prevent sample carryover. Also, the physical properties of the sample may cause changes in drop size distribution, sample transport and sensitivity.[2] At a concentration of 5% dissolved solids, contamination of subsequent samples, residual salt build-up and deposition of salt on the inside of a hot burner jaw may occur.

To overcome these problems, such samples can only be introduced as a small volume. Subsequently a rinsing solution must be aspirated for cleaning purposes. If a sample was introduced as a discrete volume in a continuously flowing rinse solution, the previously mentioned difficulties could be overcome. Variations in uptake rate would not affect the absolute amount of element seen via the signal trace, due to fast signal processing and the transient nature of the peak formed. The concept of the GBC HSA3000 High Solids Analyser is to take up a discrete sample volume and release it into a continuously rinsing stream. This accessory has been designed to overcome the analytical difficulties mentioned above and as such is ideal for these types of sample.

This report describes the application of the GBC HSA3000 for the analysis of samples containing dissolved solids at levels up to 30% m/V. This device provides a continuously flowing stream of rinse liquid to the nebulizer of an atomic absorption spectrometer. A switching valve, incorporating a sample loop, allows the introduction of a small volume of sample into the rinse stream, and passage of the sample into the spray chamber with minimal diffusion. The sample produces a transient absorbance signal with a peak height similar to the absorbance of a continuously aspirated sample. The number of sample replicates is set within the operating software of a GBC 906 atomic absorption spectrometer, and the switching valve is software-controlled.

Experimental

The analyses were performed using a GBC 906 automatic atomic absorption spectrometer with Ultra-Pulse deuterium arc background correction system in conjunction with the GBC HSA3000 High Solids Analyser accessory. A GBC Data Station (AT-compatible computer with 40 megabyte hard disk drive) with 906 software installed was used to control the operation of both the HSA3000 and a GBC FS3000 flame auto-sampler. The software allowed flame applications to be developed, data to be collected and stored, and graphics traces to be displayed. The real time colour graphics traces allow the analyst to optimise the analytical conditions. The measurement mode can be either peak height or peak area. Post-run editing allows data to be presented in either mode. The analysis of samples with high dissolved solids does require that the spray chamber/burner system (including burner slot) be cleaned prior to the beginning of the analysis. The instrument electronics take 200 (at 50 Hz) or 240 (at 60 Hz) sample measurements per second with a delay of less than I millisecond between measurements of background and total absorbance. Also, interpolation of background measurements is used to calculate background absorbance when the total absorbance signal is measured. Smoothing or damping of the signal trace was not used for any of these experiments (time constant set to zero).

Reagent Preparation

All chemicals used were analytical grade. Atomic absorption standards for barium, copper and iron of 1000 µg/mL (BDH Chemicals, Australia) were used to prepare working standards of 5, 10, 15 and 20 µg/mL for barium; 1, 2, 3, 4, 5 and 6 µg/mL for copper; and 2 and 4 µg/mL for iron. All standard solutions were prepared appropriately for the respective percentage m/V sodium chloride (Univar, Ajax Chemicals, Australia). Deionized water used for reagent preparation and analysis was obtained from a mixed bed deionizing unit (Continental Water Systems Pty Ltd, Australia). Sodium chloride was used for the salt matrix due to its high solubility at room temperature.

Results and Discussion

The HSA3000 provides a continuously flowing stream of rinse liquid to the nebulizer. The switching valve incorporates a. sample loop of predetermined volume (100 µL) to allow a discrete volume of sample to be flushed into this rinse stream. The aspiration rate of the sample is determined by the nebulizer uptake control which is set so that the sample is transferred into the atomization system in minimum time.[2]

The HSA3000 control parameters window in the GBC 906 operating software, allow a precise time to be entered for initial sample uptake and for the uptake of subsequent sample replicates. The Initial fill time was set to 15 seconds. This includes priming time plus 8 seconds filling time for the sample loop. The replicate fill time, that is, the time to fill the loop for each replicate, was set to 8 seconds. For each sample of 5 replicates the analytical time per sample is 95 seconds. The accessory ensures the same absolute quantity of sample each time.

Percent Salt	Copper Conc. µg/mL	Relative Absorbance %	
		Flame alone	Flame with HSA3000*
10	2	86.9	86.6
10	4	84.5	86.8
10	6	88.0	85.1
20	2	72.3	75.2
20	4	75.2	76.2
20	6	75.2	78.6
30	2	**	68.7
30	4	**	73.1
30	6	**	72.1

* Peak height measurement
** Nebulizer blocked

Table 1*: Relative absorbance of copper in NaCl compared to copper in aqueous standards (0% m/V NaCl) at the same concentration. Aqueous standards were set as the reference of 100%. Each reading was determined from the mean absorbance of 3 replicates converted to a percentage relative to aqueous standards.*

Table 1 compares standard flame analysis with the use of the HSA3000 coupled to a flame system. For flame analysis in samples up to 20% m/V NaCl the nebulizer system remains operational, however sensitivity diminishes as the salt concentration increases. Also, the nebulizer and burner quickly become blocked. The data for the HSA3000 shows a sensitivity loss similar to that for flame analysis alone, however the low sample volume and continuous rinsing allow samples with much higher salt concentrations to be analysed. The sensitivity suppression for both systems highlights the requirement for matrix matching or standard additions calibration. It is likely that this loss is due to a reduction in the atomization efficiency of large particles produced after desolvation.

A sample loop of 100 µL was chosen to provide a suitable volume for absorbance measurement. At 0% NaCl this produced a transient signal with a peak height of approximately 80% (ratio 0.80) of the equivalent steady state signal (See Table 2). At 20% m/V NaCl the ratio was slightly higher at 86%

thus indicating that the sensitivity of the HSA3000 improves relatively compared to a conventional steady state signal.

Percent Salt	Cu Conc. μg/mL	Ratio
0	2	0.79
0	4	0.80
0	6	0.81
10	2	0.77
10	4	0.81
10	6	0.81
20	2	0.85
20	4	0.86
20	6	0.86

***Table 2**: Ratio of copper absorbance for the HSA3000 (peak height measurement) compared to steady state signal for the same solutions. Each ratio was calculated from the mean absorbance values of 3 replicates of each sample using each*

Figure 1 illustrates the suppression of the copper signal when comparing the signal traces for 3 standards in a deionized water matrix with the same concentration values in 10% m/V NaCl.

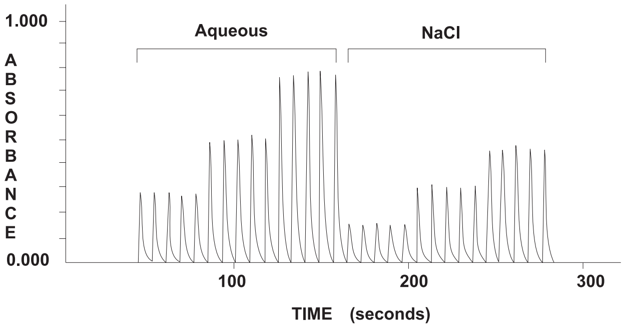

***Figure 1**: Comparison of 2,4 and 6 mg/mL Cu standards in aqueous solution and 10% m/V NaCl.*

Using standard parameters for operation, 120 samples and 36 individual standards (12 recalibrations of each of 3 standards) were analysed over a period of 247 minutes (Table 3). The absorbance for sample number 120 when compared with the initial measurement of standard 3 (both of which had the same concentration) was almost the same value. The percent relative standard deviations for samples 118, 119 and 120 are all about 2%, indicating that this accessory is able to provide accurate and precise measurements over a long period.

Sample Type	Conc. mg/mL	Mean Abs.	RSD%
Standard 1	2.00	0.16	2.2
Standard 2	4.00	0.30	2.4
Standard 3	6.00	0.47	1.3
Standard 118	4.92	0.38	1.2
Standard 119	3.31	0.26	1.8
Standard 120	6.02	0.47	2.1

***Table 3**: Results for Cu in a 10% NaCl solution. Sample 120 is an identical solution to Standard 3. Peak measurements were used.*

An additional experiment (Figure 2) shows excellent precision for 50 replicates of copper at a concentration of 4.8 μg/mL in 30% m/V sodium chloride.

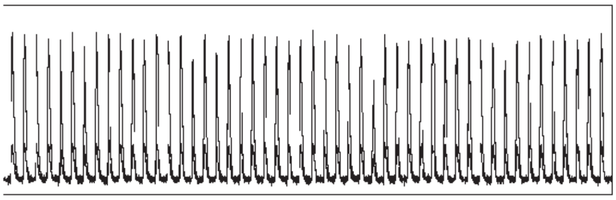

***Figure 2**: Trace for 50 measurements of 4.8 mg/mL Cu in a 30% NaCl solution (2.4% RSD).*

Matrix matching for standards and samples is crucial in this type of sample due to the suppression of the absorbance signal observed in the presence of dissolved solids.[4] In general, standard additions may need to be considered if the components of the sample are not fully known.

The HSA3000 can also be used to determine the concentration of metals that require the use of a nitrous oxide-acetylene flame. Barium was measured in ground water samples containing up to 30% m/V sodium chloride against matrix-matched standards. The procedure for this analysis consisted of 3 replicates of each sample using the HSA3000 parameters as described previously. Furthermore, there was no blockage of the nitrous-oxide burner with salt even though a nitrous oxide-acetylene flame may achieve temperatures up to 2800°C. Figure 3 shows the signal traces for the Ba standards as well as the resulting calibration curve used in this analysis.

The transient signal trace of iron in 10% m/V sodium chloride is illustrated in Figure 4. The background signal, due to the sodium chloride, is shown superimposed on the iron peaks. These traces are similar to what is sometimes seen for a graphite furnace analysis in a sodium chloride matrix. The Ultra-Pulse deuterium arc background correction system was able to easily correct the background signals.

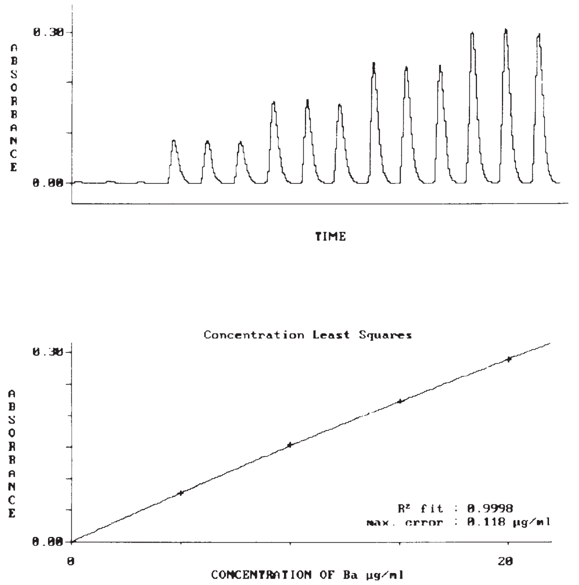

Figure 3: Standards traces and calibration curve for 5, 10, 15 and 20 µg/mL Ba in a 30% NaCl solution (peak height measurements).

The speed of analysis for the HSA3000 is dependent on factors such as manual or automatic sampling, initial fill time, replicate fill time, signal read time and rinsing time. The standard parameters for a typical analysis will allow a throughput of 50 samples per hour. In general, peak area measurement mode should be used.

The HSA3000 can analyse elements in matrices of high salt concentration up to 30% m/V. The combination of high speed data acquisition for the analyte signal and background signal, and the accurately timed introduction of a small sample volume into a continuously rinsing stream allows analysis in sample matrices previously considered to be extremely difficult due to salt build-up in the nebulizer, spray chamber and burner system.

Conclusion

The HSA3000 has been used to improve sensitivity and avoid sample dilution by the direct analysis of samples with high dissolved solids which may have previously caused severe problems and possible nebulizer or burner blockages. Also, sample throughput has been maintained at a high rate. The very short residence time for the undiluted sample in the nebulizer-atomization system combined with the flushing action of the rinsing solution, provide an extremely robust analytical procedure.

References

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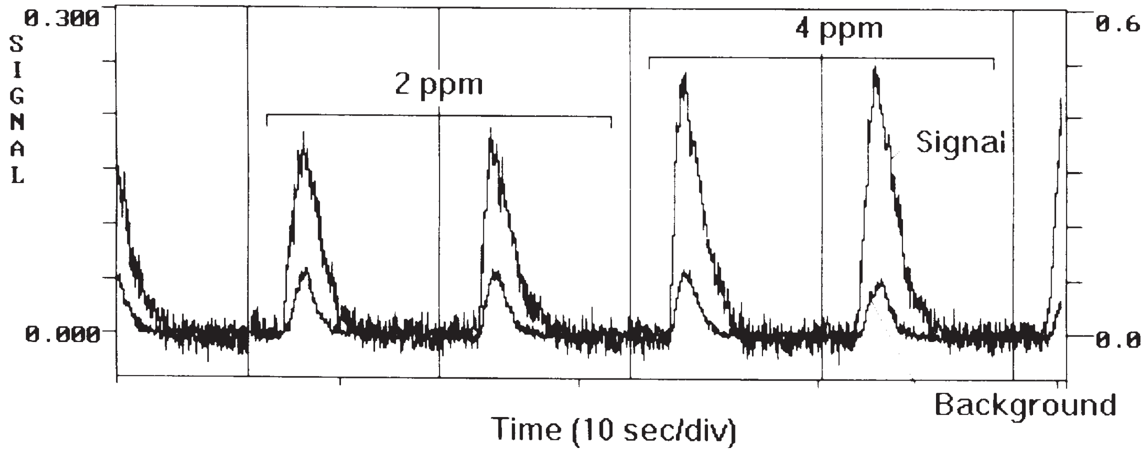

Figure 4: Signal and background traces for 2 and 4 µg/mL Fe in 10% m/V NaCl. Note different y-axis scales.