

AAS

APPLICATION NOTES

The determination of trace elements (Ca, Mg, Sr, Ba, Al, Ni, Fe, Cr) in brine solution by graphite furnace AAS

AAS



Introduction

Sodium hydroxide and chlorine production by electrolysis is common practice in the chloro-alkali industry. Feed solutions containing concentrated sodium chloride and water are passed into an electrochemical cell. Here a voltage is applied to the cell causing passage of the sodium ions through a semipermeable membrane. Trace elements existing in solution will be excluded by the selective permeation. These metals form hydroxides on the surface of the membrane, reducing the efficiency of the ion passage in the cell.

To prevent this build-up occurring, the incoming solutions must be closely monitored to ensure that the trace metal content remains below 50 µg/L (ppb).

Because of the complexity of the matrix and the low concentration of metals present, graphite furnace atomic absorption offers the most realistic approach to the application.

Other methods include APDC extraction and ion exchange using chelex 100¹ followed by flame AA analysis. Furnace analysis using matrix modification² with NH₄ NO₃ has been used, but it should be noted that each extra handling step or chemical addition risks contamination. The method used for this study involved only the addition of 1% HNO₃.

Experimental

Instrumentation

A GBC atomic absorption spectrophotometer equipped with a GBC graphite furnace system and GBC SavantAA software was used for this application.

The water was purified (18 megohm resistivity), by a deionizing unit.

Sample and standard preparation

Samples were 30% w/v NaCl prepared in 1% nitric acid (Aristar grade). This retains the ions in solution and stabilises the analyte during the ash stage.

Standards were prepared from "Spectrosol" 1000 ppm stock solutions. A composite 5 ppm standard was prepared from these stocks and individual standards were prepared from the composite, the concentrations depending on the sensitivity of the element. The concentration of the intermediate standard used with each element is shown in Table 1. The AUTO MIX facility of the PAL autosampler was used to automatically prepare the additions in the furnace. The concentrations of the two additions used with each element are also shown in Table 1.

No attempt was made to matrix match standards to samples as the standard additions technique was selected.

Element	Intermediate Standard (ppb)	Addition Concentrations (ppb)	
		Addition 1	Addition 2
Cr	5	1.25	2.5
Ni	40	10	20
Ba	20	4	8
Al	20	2	4
Fe	20	4	8
Sr	20	2	4
Mg	5	0.5	1
Ca	50	12.5	25

Table 1: Standard concentrations

Optimisation of ash temperature in furnace AA

An important objective of this application was to reduce the background absorbance caused by the NaCl to a reasonable level so that, at the atomise stage, the analyte measurement was interference-free. By plotting analyte absorbance and background absorbance versus ash temperature, an ash temperature can usually be chosen that provides for both high analyte sensitivity and low background.

Figure 1 explains the basic concepts of method development. At point A, the background absorbance is too high for background correction to be used. (i.e. more than 2 Absorbance units). At point C, the background has been successfully reduced, but analyte losses are quite high and maximum sensitivity is not achieved. At point B, the background is at a workable level for the background correction system and maximum analyte sensitivity is obtained. This represents the ideal ash temperature for this theoretical model.

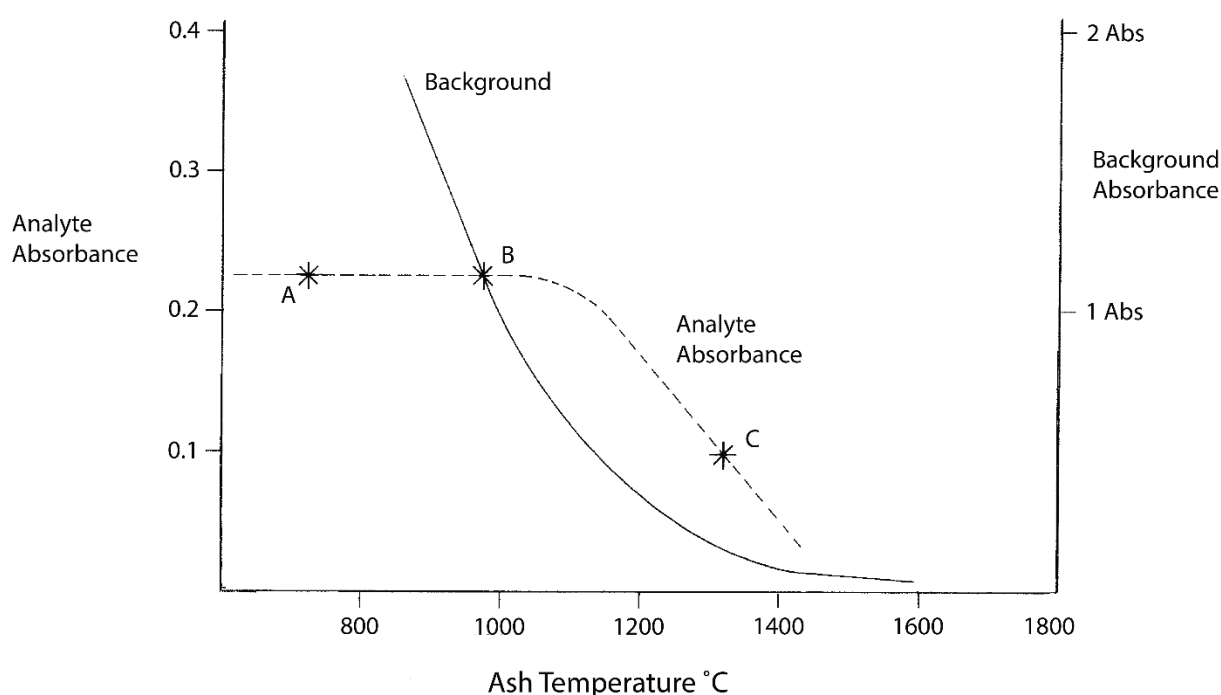


Figure 1: Theoretical model for optimisation of ash temperature

Optimisation of ash temperature with brine solution

Figure 2 shows the reduction of the background absorbance with increasing ash temperature (30 sec ramp, 30 sec hold). An ash temperature of 1200°C was selected for all elements. If a higher ash temperature was used, elements such as magnesium and iron were volatilised as chlorides during the final stages of the ash. Even at 1200°C significant losses were seen (Note: 800°C is the recommended maximum for these elements). At 1200°C the background levels were found to be negligible and background correction was quite simple. For elements with higher atomise temperatures, 1400°C could be used for ashing with no analyte losses and no background correction necessary.

Intermediate stages in the ashing procedure represent the various stages of the decomposition of the brine. Evaporation of the water leaves a dry residue of sodium chloride crystals which must be gradually distilled from the furnace wall. Any violent ashing seen during this distillation indicates the need for slower ramp rates and longer hold times at this point. The program must allow for both smooth melting and slow volatilisation of the NaCl. If the concentration of the element being determined is high enough, the program can be simplified by diluting the brine with deionized water, thereby reducing the necessity for long ashing procedures.

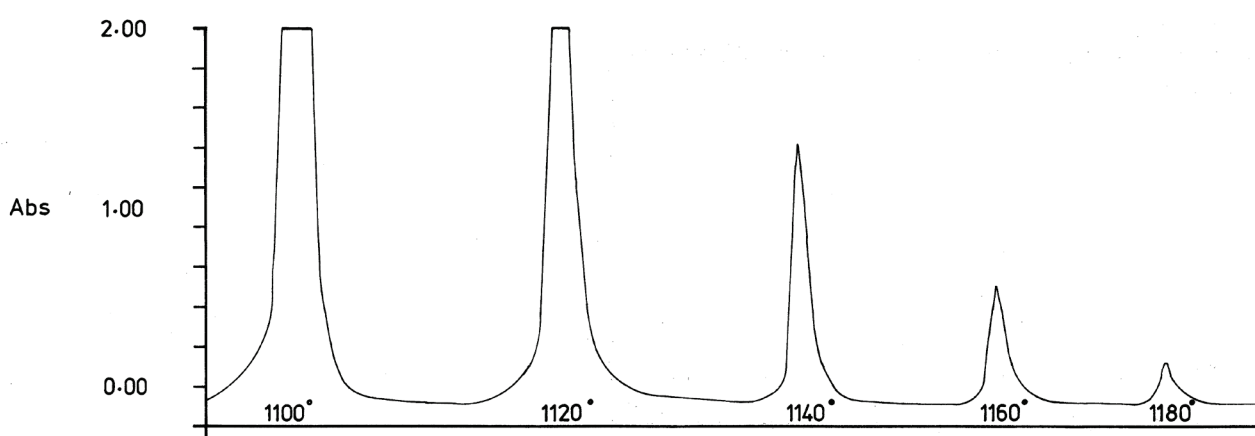


Figure 2: Effect of ash temperature on background absorbance due to brine solution at the iron wavelength (248.3 nm)

Table 2 shows the ash and atomisation temperatures used for the eight elements studied.

Element	Ash	Atomise
Strontium	1200 – 1300	2600
Nickel	1200 – 1300	2600
Magnesium	1200	2300
Iron	1200	2300
Calcium	1200 – 1300	2600
Chromium	1200 – 1300	2600
Barium	1200 – 1400	2600
Aluminium	1200 – 1400	2600

Table 2: Recommended ash/atomise temperatures (°C) for brine solutions

Contamination

When working near the detection limit, furnace applications present problems that would not normally be experienced with flame work. Contamination from dust particles falling into the furnace or sample cups can lead to erroneous results. For best results, a class 100 clean room with a laminar flow filtration system should be provided. However, if this is not possible, precautions should be taken to ensure that a clean environment is achieved and maintained.

Cleaning procedure

Beakers, disposable pipette tips and sample cups were soaked for a minimum of 16 hours in high purity 2% EDTA solution followed by rinsing in 18 megohm deionized water. They were then left for a minimum of 16 hours in high purity 50% HNO₃ followed by rinsing in deionized water again.

Handling of samples and standards should be minimised to avoid further contamination. Automatic pipettors with clean disposable tips are preferable to glass pipettes and volumetric apparatus. Calcium and magnesium were found to be the main contaminants. The above procedure provided good results for both of these elements.

Standard additions

Calculations used in the standard additions method assume absolute linearity of the calibration plot. Curvature is element dependent, but there will typically be some curvature between 0.3 and 0.7 absorbance units. The top standard should always be below this point. In Figure 3, the dashed line illustrates the error which occurs if the standard additions method is used with a curved calibration graph.

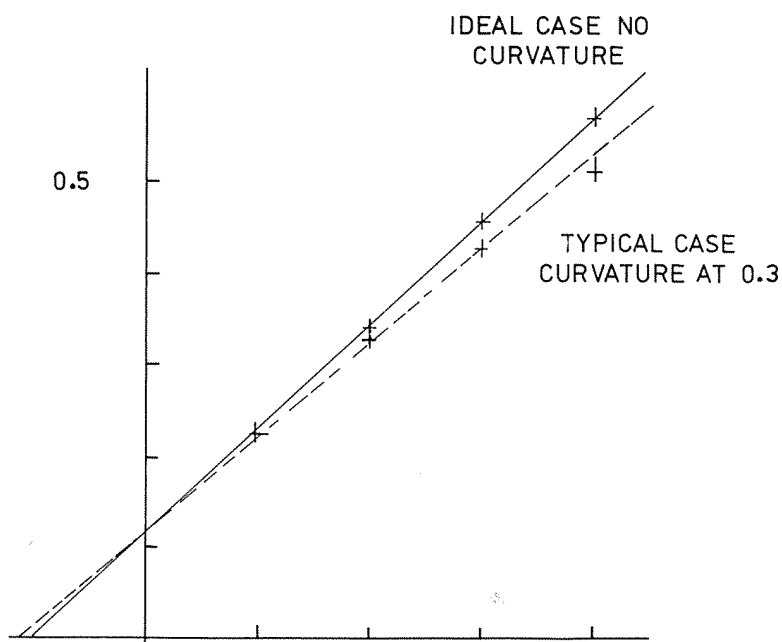


Figure 3: Error in standard additions method caused by curvature

Results

Figure 4 shows the operating conditions for the GBC atomic absorption spectrophotometer, the furnace temperature program and the results of the standard additions measurement for iron. Iron was also determined by the normal calibration method using matrix-matched standards. The measured concentration of 11.4 µg/L agreed well with the value of 11.6 µg/L measured by standard additions. The characteristic mass for iron was calculated to be 1.8 pg. Comparison with the value of 1.5 pg quoted in the GBC Furnace Methods Manual indicates that there is a slight loss of sensitivity with the brine solution.

Poor reproducibility for magnesium led to further method development for this element. It was found that by using a pyrolytic graphite platform³ acceptable results could be obtained. The modified temperature program used for platform atomisation is shown in Figure 5. It is necessary to carefully align the autosampler injection probe when using the platform. GBC AAS Application Note⁴ outlines the correct procedure.

Table 3 shows the concentrations found for the eight elements studied. The total trace element concentration for this brine solution was approximately 25 µg/L. Only calcium and iron were present at significant levels. All the other elements were close to detection limit levels.

Graphite furnace system applications report

Element	Fe
Matrix	Brine
Instrument Mode	Absorbance BC on
Beam Mode	Double Beam
Measurement Mode	Peak Area
Wavelength (nm)	248.3
Slit Width (nm)	0.2
Slit Height	Reduced
Lamp 1 Current (mA)	7.0
Lamp 2 Current (mA)	0.0
Integration Time (sec)	3.0
No. of Replicates	3
Calibration Mode	Standard Additions
Recal. Std No.	2

Calibration Table		
	Standard or Added Concentration	Mean Standard Absorbance
Blank/Sample	0.000	0.134
Std 1	12.5	0.285
Std 2	25.00	0.423

Concentration Units	µg/mL
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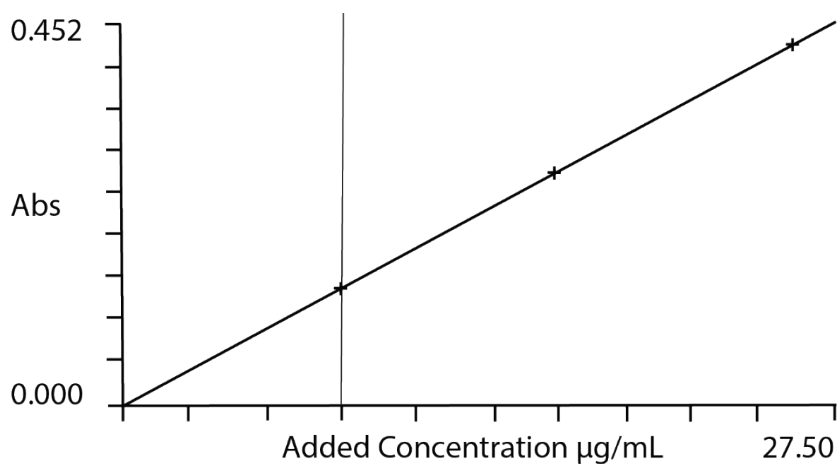
Graphite Furnace Parameters					
Step No.	Final Temp °C	Ramp Time (sec)	Hold Time (sec)	Gas Type	Read On
1	80	10.0	5.0	Inert	No
2	110	30.0	5.0	Inert	No
3	150	20.0	20.0	Inert	No
4	300	30.0	10.0	Inert	No
5	800	10.0	5.0	Inert	No
6	1200	30.0	30.0	Inert	No
7	1200	1.0	1.0	None	No
8	2300	0.8	2.0	None	Yes
9	2400	1.0	1.0	Inert	No

Sampling Mode	Auto Sampling
Standards Preparation	Auto-mixed

Auto-Mix Sampler Volumes				
	Blank Volume	Std Volume	Sample Volume	Modifier Volume
Sample	10	0	10	0
Blank	20	0	0	0
Std. 1	5	5	10	0
Std. 2	0	10	10	0

No. of Injections	1
Inject before Step No.	1
Recalibration Rate	2

Blank 0.000 µg/mL	0.030	0.022	0.017	RSD = HIGH	Mean Abs. = 0.023
Addition 1 12.50 µg/mL	0.295	0.278	0.282	RSD = 3.11%	Mean Abs. = 0.285
Addition 2 25.00 µg/mL	0.394	0.457	0.418	RSD = 7.47%	Mean Abs. = 0.423
Sample 1 11.59 µg/mL	0.132	0.132	0.137	RSD = 2.10%	Mean Abs. = 0.134



Graphite Furnace Parameters					
Step No.	Final Temp °C	Ramp Time (sec)	Hold Time (sec)	Gas Type	Read On
1	65	1.0	15.0	Inert	No
2	100	1.0	50.0	Inert	No
3	130	1.0	70.0	Inert	No
4	300	1.0	30.0	Inert	No
5	800	1.0	5.0	Inert	No
6	1175	10.0	20.0	Inert	No
7	1175	1.0	1.0	None	No
8	2300	0.6	2.0	None	Yes
9	2500	1.0	1.0	Inert	No

Figure 5: Temperature program for magnesium using platform atomisation

Cr	1
Ni	<1
Ba	<1
Al	1
Fe	12
Sr	1
Mg	1
Ca	8

Table 3: Results for brine analysis (ppb)

Conclusion

A method has been developed for direct quantitative analysis of trace metals in brine solution. The same program can be used for all elements, with minor adjustment for Fe and Mg where the atomise temperature is reduced from 2600°C to 2300°C. Better reproducibility can be obtained for magnesium by using a pyrolytic graphite platform.

References

1. Sturgeon, R.E., Berman, S.S., Desaulniers, A., Russell, D.S., Talanta 27,85 (1980).
2. Xuefeng Yin, Schlemmer, G., Welz, B., Anal Chem. 59, 1462 (1987).
3. Powell, L.A., Tease, R.L., Anal Chem. 54, 2154 (1982).
4. Sinclair, D., and Chapple, G., The determination of lead in human blood using porcine blood standards. GBC AAS Application Note.