

# AAS

## APPLICATION NOTES

Why use Automatic Burner Rotation in flame AAS?

AAS



## Introduction

When samples of varying concentrations are analysed, more than one calibration range may be required to obtain the most accurate results.

Previously the analyst had three choices to overcome the problem.

1. Changing the analytical wavelength to a less sensitive resonance line. This may be a useful alternative provided that the working range of the 2nd or 3rd resonance line permits an appropriate analytical range for the individual samples. For zinc the sensitivity ratio may be as high as 8000 times when comparing the primary line (213.9 nm) to the secondary line (307.6 nm) and hence the latter line is unsuitable for most samples. For some metals, for example beryllium, mercury, phosphorus and strontium, a secondary line is not available for atomic absorption and an alternative method must be used.
2. Dilution of the sample to within a suitable concentration range, which may require many trial and error attempts to obtain an accurate answer. Dilution, even in the hands of a skilled chemist, is prone to introduce errors that may compound any other errors introduced during sample preparation or treatment. This procedure is time-consuming and labour intensive.
3. Manual rotation of the burner. This was often chosen as a suitable remedy because of its simplicity and the short time required to set the required sensitivity. The drawback was the inability to accurately reproduce the rotation angles within-run or between-run and the need for operator intervention.

GBC is the first atomic absorption manufacturer to have developed a programmable burner rotation accessory with full software control which automatically sets burner rotation. Angle settings are reproducible to within 0.1 degrees.

The analysis procedure uses an initial calibration performed at zero rotation angle, after which all samples are measured. If any sample result is over-range a "High" message is displayed in the concentration field and an error flag is set for the over-range sample. Once all the samples have been measured and any over-range samples have been found, the burner is automatically rotated to a pre-programmed angle for a second calibration to be performed. Any samples found to be in error (over-range) are re-run to obtain within-range readings. A complete analysis may involve up to five calibration ranges at five corresponding calibration angles. An example of this using two burner angles is shown in Figure 4.

The purpose of this paper is to demonstrate the benefits of Automatic Burner Rotation and its usefulness in expanding the working range for flame atomic absorption spectrophotometry.

## Experimental

### Instrumentation

A GBC atomic absorption spectrometer (AAS), equipped with the Hyper-Pulse deuterium arc background correction system and a flame autosampler were used. The programmable automatic burner rotation option was installed. GBC AAS software was used for developing the applications, collecting and storing the data and displaying the graphics traces. This software also provides complete control of automatic burner rotation whilst incorporating Intelligent Quality Control to ensure valid results. The instrumental conditions for aluminium, cadmium, calcium, copper, iron and silicon are listed in Table 1.

Element	Wavelength	Slit Width (nm)	Flame Type
Al	396.2	0.5	N <sub>2</sub> O/Acet
Ca	422.7	0.5	N <sub>2</sub> O/Acet
Cd	228.8	0.5	Air/Acet
Cu	324.8	0.5	Air/Acet
Fe	248.3	0.2	Air/Acet
Si	251.6	0.2	N <sub>2</sub> O/Acet

**Table 1: Instrument parameters for aluminium, cadmium, calcium, copper, iron and silicon**

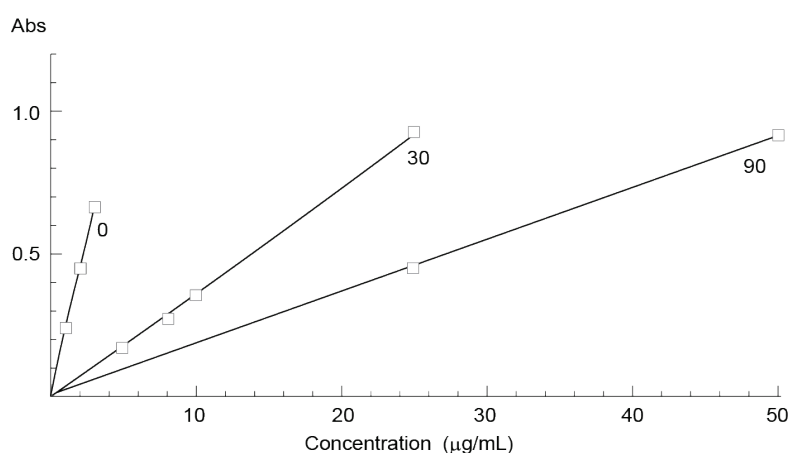
## Reagents and sample preparation

All chemicals were analytical reagent grade. Nitric acid (HNO<sub>3</sub>) and atomic absorption standards for copper, iron, cadmium, aluminium, silicon and calcium of 1000 µg/mL were used. De-ionized water for washing and rinsing was obtained from a mixed-bed de-ionizing unit. De-ionized water used for reagent preparation and analysis was from a reverse osmosis, mixed-bed deionizing unit that supplies Type 1 ultrapure water with a resistivity of 18 Mohms. Analytical standards were freshly prepared at the appropriate concentration for each element. Samples were prepared and measured against standards. For each sample run 3 replicates of 3 seconds duration were used to determine concentration. The mean values for three separate runs were used to calculate accuracy, as well as within-run and between-run precision. For aluminium, cadmium and silicon, real samples were used which had known analyte concentrations.

## Results and discussion

Calcium is generally measured using a nitrous oxide-acetylene flame to provide enhanced sensitivity compared to the air-acetylene flame.

The optimum working range is generally 1 to 5 µg/mL at 422.7 nm. Calcium, at concentrations up to 50 µg/mL, was measured by rotating the burner angle from 0 to 30 and then to 90 degrees (Table 2). The corresponding calibration curves for calcium were all linear (Figure 1), indicating that ABR allows the calcium working range to be extended beyond 100 µg/mL without sacrificing accuracy. The secondary line for calcium, 239.9 nm, is unsuitable because it has a working range of approximately 180 to 760 µg/mL. Automatic burner rotation allows an extended working range from 5 to 50 µg/mL.



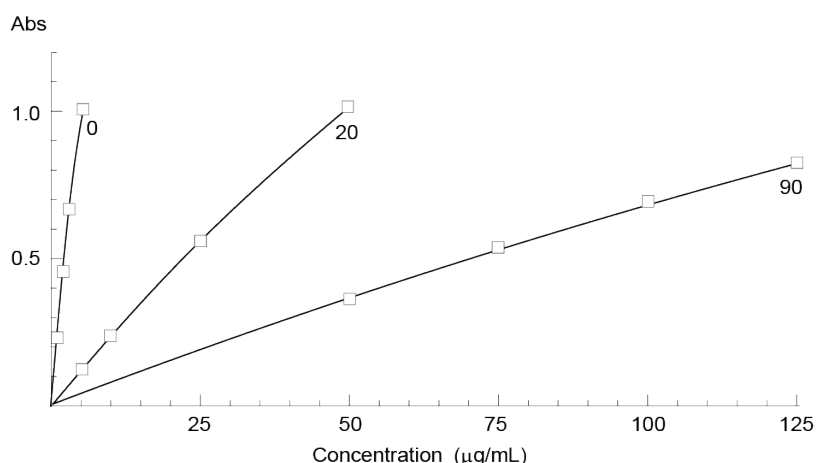
**Figure 1: Calibration curves for calcium measurement in samples at concentrations ranging from 1–50 µg/mL at burner angles of 0, 30 and 90 degrees**

For analysis using an air-acetylene flame for the measurement of calcium over an extended working range, similar results could be expected for precision, provided that chemical interferences were accounted for.

Burner Angle	Expected Conc. (µg/mL)	Actual Conc. (µg/mL)	% Recovery	% RSD
30	5	4.99	99.8	0.92
30	10	10.26	102.6	0.86
90	50	50.14	100.3	0.92

**Table 2: Data for calcium measurements in samples ranging from 5–50 mg/mL at burner angles of 30 and 90 degrees**

The optimum working range\* for copper is generally 1 to 5 µg/mL. There are four resonance lines available for copper which would allow extension of the working range. To use them, however, would require four separate applications, rather than one using automatic burner rotation. Copper was measured up to a concentration of 125 µg/mL by rotating the burner. Calibration curves at 0, 20 and 90 degrees rotation (Figure 2) each showed minor curvature indicating that the upper measurement range is about 250 µg/mL.



**Figure 2: Calibration curves for copper measurement in samples at concentrations ranging from 1–125 µg/mL at burner angles of 0, 20 and 90 degrees**

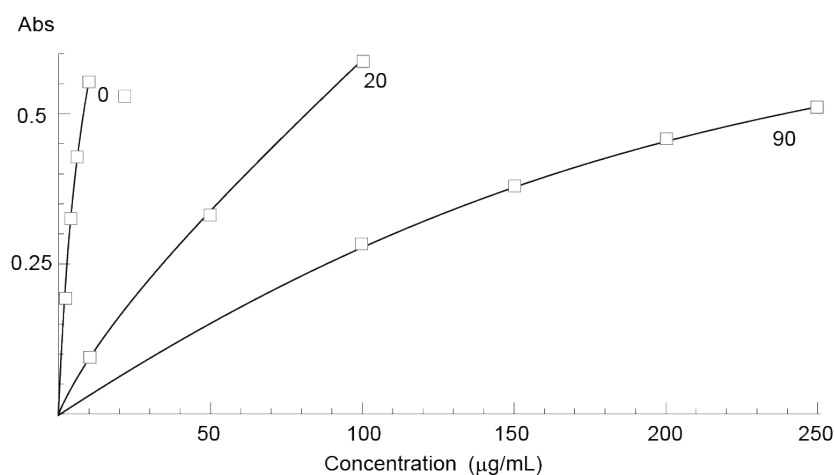
Table 3 lists copper data for accuracy, with percent recovery ranging from 98.2 to 99.9. Once more the recoveries were excellent and independent of burner angle. The corresponding average precision (% RSD) throughout the run was about 0.4%, compared to the between-run precision which was only marginally higher at 1.01%. Both parameters show excellent results up to the maximum concentration measured.

\* “Optimum Working Range” is that concentration range which produces an absorbance range from 0.2 to 0.8. Within this range the relative error in concentration measurement is minimum. The burner angle of rotation is set to zero.

Burner Angle	Expected Conc. (µg/mL)	Actual Conc. (µg/mL)	% Recovery	% RSD
20	8	7.99	99.9	0.46
20	10	9.97	99.7	0.47
20	25	24.65	98.6	0.15
20	50	49.32	98.6	0.30
90	75	74.89	99.9	0.53
90	100	99.77	99.8	0.69
90	125	122.7	98.2	0.27

**Table 3: Data for copper measurement in samples ranging from 8–125 mg/mL at burner angles of 20 and 90 degrees**

The usual upper concentration measurable for Iron at the primary wavelength of 248.3 nm is 10 µg/mL. To analyse iron above the optimum working range, two resonance lines, 372.0 and 386.0 nm are available. This latter wavelength only allows a concentration range of up to 150 µg/mL. The use of ABR extended the range to beyond 250 µg/mL at the 248.3 nm primary line. The calibration curves (Figure 3.) at each angle illustrated curvature which is normal for iron analysis. However, accuracy and precision were excellent in all cases (Table 4.) and independent of burner angle.



**Figure 3: Calibration curves for iron measurement in samples at concentrations ranging from 1–250 µg/mL at burner angles of 0, 20 and 90 degrees**

Burner Angle	Expected Conc. (µg/mL)	Actual Conc. (µg/mL)	% Recovery	% RSD
20	16	16.19	101.2	0.58
20	20	20.34	101.7	0.66
20	50	49.49	99.0	0.83
20	100	99.77	99.8	0.43
90	150	148.2	98.8	0.78
90	200	198.3	99.2	0.70
90	250	251.9	100.8	0.48

**Table 4: Data for iron measurements in samples ranging from 16–250 µg/mL at burner angles of 20 and 90 degrees**

To demonstrate the ability of the ABR to handle real-life samples, Al and Cd were analysed in fertiliser and Si was analysed in a 10% sodium chloride matrix. In all cases the results were exceptional with errors of less than  $\pm 2\%$ . The results are detailed in Table 5.

To further establish that the burner angle was not contributing to errors, a study was conducted comparing the results for iron using automatic burner rotation with those achievable using manual sample dilution. Iron was chosen due to the calibration curvature which would be most likely to emphasise any errors in the analysis. The results are summarised in Table 6. These clearly show that the results are better for ABR than for manual dilution and superior to those achievable using an automated dilution system based on a peristaltic pump, where dilution errors are over 6%.

Matrix	Element	Actual Conc. (µg/mL)	Measured Conc. (µg/mL)	% Recovery
Fertiliser	Al	550	550.3	100
Fertiliser	Al	550	536.7	97.6
Fertiliser	Cd	40.07	39.05	97.5
Fertiliser	Cd	40.07	39.29	98.1
10% NaCl	Si	890	889.3	99.9
10% NaCl	Si	890	889.3	99.9

**Table 5: Results for fertiliser and brine samples using automatic burner rotation**

Expected Conc. (µg/mL)	Actual using ABR	% Recovery using ABR	Actual using manual dilution	% Recovery using manual dilution
10.00	10.01	100.1	10.01	100.1
10.00	9.99	99.9	10.17	101.7
200	200.2	100.1	198.3	99.2
200	200.4	100.2	197.6	98.8
200	200.9	100.5	198.1	99.1

**Table 6: Data for iron measurements comparing automatic burner accuracy with manual dilution accuracy**

## Conclusion

The automatic burner rotation accessory greatly simplifies the operation of the atomic absorption spectrometer, expanding the dynamic range by up to two orders of magnitude. Using the primary resonance line allows the measurement of overrange samples without intervention by the analyst, thus greatly increasing sample throughput and saving time. This feature provides major advantages for applications in mining, minerals processing, metallurgy, industrial waste, the environment, agriculture and many other areas. Automatic burner rotation has also been shown to be more accurate than other dilution techniques including manual dilution and on-line dilution with peristaltic pumps.

The benefits of automatic burner rotation are:

1. Over-range samples can be run without sample dilution or selection of an alternative resonance line.
2. Accurate and precise results are obtained automatically without operator intervention.
3. Accurate and precise results are obtained for samples at concentrations up to 50 times higher for some elements than the optimum (zero-rotation) working range.
4. Up to five separate calibrations can be run with automated dynamic range-switching.
5. No alteration of the sample matrix is required, as would have occurred with sample dilution, therefore the analytical result is inherently more accurate than the dilution method.
6. There is no need to purchase an expensive sample dilution device.
7. Valuable bench space is preserved.
8. High sample throughput is assured.

## References

1. Flame Methods Manual for Atomic Absorption, GBC Scientific Equipment.
2. The use of Automatic Burner Rotation to expand the working range in flame AAS.

Cu Program No. 1		1:22:57 pm				
Calibration Mode Conc. Least squares				Measurement Mode Integration		
Starting Recal Cu Autorotate Burner				Rotation = 0.0		
Sample Type	Conc µg/mL	%RSD	Mean Abs.	Replicates		
Blank	0.000	—	-0.001	-0.001	0.001	-0.001
Standard 1	1.000	0.09	0.232	0.232	0.232	0.232
Standard 2	2.000	0.29	0.456	0.456	0.456	0.454
Standard 3	3.000	0.12	0.669	0.669	0.670	0.668
Standard 4	5.000	0.27	1.104	1.012	1.013	1.017
Cu 1	0.980	0.69	0.230	0.232	0.229	0.230
Cu 2	Error	0.18	1.400	1.402	1.397	1.401
Cu 3	Error	0.61	2.118	2.133	2.112	2.109
Cu 4	1.984	0.43	0.450	0.452	0.448	0.450
Cu 5	Error	1.03	2.055	2.047	2.039	2.079
Cu Recal Autorotate Burner				Rotation = 20.0		
Sample Type	Conc µg/mL	%RSD	Mean Abs.	Replicates		
Blank	0.000	—	-0.002	-0.002	-0.001	-0.002
Standard 1	5.000	0.49	0.122	0.123	0.122	0.122
Standard 2	10.000	0.49	0.232	0.231	0.233	0.233
Standard 3	25.000	0.53	0.559	0.556	0.561	0.561
Standard 4	50.000	0.61	1.018	1.011	1.022	1.022
Cu 2	7.992	0.46	0.190	0.190	0.191	0.190
Cu 3	49.118	0.30	1.003	1.000	1.006	1.004
Cu 5	24.647	0.15	0.550	0.550	0.549	0.551

**Figure 4: Typical results printout for copper**