

# Observations on the Limitation Imposed by Interferences in Flame Atomic-absorption Spectrometry at High Analyte Concentrations

M. S. Cresser and D. A. MacLeod

*Soil Science Department, University of Aberdeen, Aberdeen, AB9 2UE*

When burner rotation or an absorption line of poorer sensitivity is used in flame atomic-absorption spectrometric analysis, care must be taken to establish the absence of fresh or increased interferences at higher concentrations of the analyte element. At high concentrations, sulphate was found to cause severe depressions in the determinations of magnesium, cobalt and nickel, although under normal conditions the interference is negligible. The risk of substantial error can be reduced either by dilution of samples and standards, or by taking measurements by using the upper part of a fuel-lean flame that is burning on a slot burner with a triangular cross-section, or by adding a suitable releasing agent.

An inherent limitation of atomic-absorption spectrometry is the incidence of curvature of calibration graphs at high concentrations of analyte elements. In practice, the useful working range of the technique is often extended by the use of an alternative absorption wavelength, or, when flame atomisation is employed, by rotating the burner to give a shorter absorption path length. We have recently found in our laboratory, however, that when magnesium is determined over the range 0-15  $\mu\text{g ml}^{-1}$ , using burner rotation to attain higher (poorer) sensitivity, very substantial interference was encountered from sulphate, although under normal working conditions, over the concentration range 0-2  $\mu\text{g ml}^{-1}$ , the interference from this anion was negligible in the air-acetylene flame. The depression of calcium absorbance by phosphorus is known to decrease with decreasing calcium concentration, a fact which leads to increased curvature of calibration graphs in the presence of phosphate.<sup>1</sup> Very little work has been carried out on the effect of the concentration of the analyte element on the incidence and extent of interferences for other elements, however.

According to Aldous and Reynolds,<sup>2</sup> the sensitivity of the determination of magnesium is slightly diminished when sulphate, rather than chloride or nitrate, is used to prepare magnesium standards for atomic-absorption analysis; most books on atomic absorption do not mention this possible interference. As we observed a very substantial depression at higher magnesium concentrations, it was decided to investigate this interference further, and to search for further instances of enhanced or fresh interferences occurring at high analyte concentrations.

## Experimental

### Apparatus

*Atomic-absorption spectrophotometers.* The instruments used were: an EEL, Model 240, equipped with either a conventional 100-mm air-acetylene burner or a laboratory-built 50-mm brass slot burner with a triangular cross-section, constructed as shown in Fig. 1, and a Shandon Southern Instruments A3400 with a standard air-acetylene burner.

### Standard Solutions

Solutions containing 1000  $\mu\text{g ml}^{-1}$  of magnesium, nickel and cobalt were prepared from the analytical-reagent grade chlorides and sulphates. The magnesium solutions were standardised by complexometric analysis before further dilution. The magnitude of the effects observed was so substantial that standardisation of the other stock solutions was unnecessary.

## Results and Discussion

For the EEL, Model 240, instrument, the effects of burner type, fuel flow-rate (at a constant air flow-rate for both burners) and height of measurement on the change in magnesium absorbance at 285.2 nm caused by nebulising 10  $\mu\text{g ml}^{-1}$  of magnesium, as the sulphate

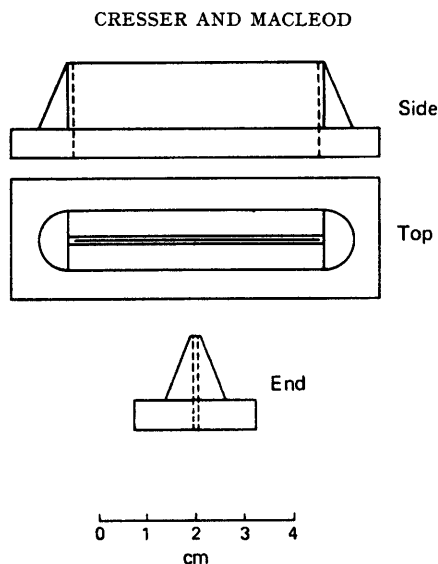


Fig. 1. Design of burner with triangular cross-section.

rather than the chloride, are shown in Fig. 2. Both burners were rotated through an angle of  $90^\circ$  in order to increase the sensitivity for 1 per cent. absorption. The interference became greater for both burners as the ratio of fuel to oxidant was increased, or as measurements were made at lower heights in the flame. The interference was significantly reduced when the burner with a triangular cross-section was used, and with this burner could be eradicated completely over a wide range of burner heights and fuel to oxidant ratios.

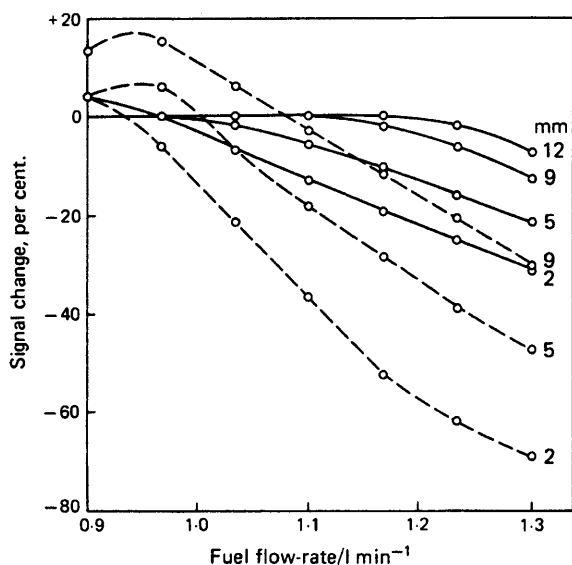


Fig. 2. Effect of fuel flow-rate on the change in magnesium absorbance caused by using sulphate in place of chloride at various heights above a flat-topped, 100-mm burner (broken lines) and a triangular cross-section, 50-mm burner (solid lines), with burners rotated through an angle of  $90^\circ$ . Air flow-rate,  $6.5 \text{ l min}^{-1}$  for both burners.

The extent of the interference varied significantly with magnesium concentration: it was negligible at  $2 \mu\text{g ml}^{-1}$  of magnesium, but rose to a 30 per cent. depression for  $15 \mu\text{g ml}^{-1}$  of magnesium under the routine operating conditions used in our laboratory (*i.e.*, wavelength, 285.2 nm; air flow-rate,  $6.5 \text{ l min}^{-1}$ ; acetylene flow-rate, about  $1 \text{ l min}^{-1}$ ; and burner height about 4 mm).

The atomisation of magnesium sulphate proceeds, at least in part, via the formation of magnesium oxide. Magnesium sulphate decomposes at 1397 K, whereas the oxide melts and boils at 3073 and 3873 K, respectively. The chloride, on the other hand, boils at 1685 K, so that while the chloride is readily volatilised, and hence atomised, the sulphate tends to form stable oxide particles, the size of which depends primarily upon the droplet size distribution produced by the nebuliser, and the magnesium concentration in solution. Larger particles, which secure the magnesium atoms more efficiently, are formed as the magnesium concentration is increased. It should be emphasised that as the droplet size distribution varies between instruments and between nebulisers, the precise analyte concentration at which such an interference becomes significant will also vary between instruments.

The effect and trends described above were still observed when an A3400 atomic-absorption spectrophotometer was used in place of the EEL, Model 240, instrument, for example, but the extent of the effect was much smaller. Even when measurements were made at a low height in a fuel-rich flame, the use of magnesium sulphate instead of the chloride reduced the absorbance by only about 20 per cent. If, however, the impact bead was displaced from its normal, optimised position, the effect became more pronounced, which indicates that a finer mist is normally produced by the A3400 nebuliser, although the higher oxidant and fuel flow-rates used with this instrument may also contribute to the improvement in selectivity.

Magnesium calibration graphs for the concentration ranges 0–15 and 0–25  $\mu\text{g ml}^{-1}$  exhibited far greater curvature when sulphate rather than chloride solutions were employed, as would be expected under these conditions. Typical curves for the EEL, Model 240, instrument, are shown in Fig. 3.

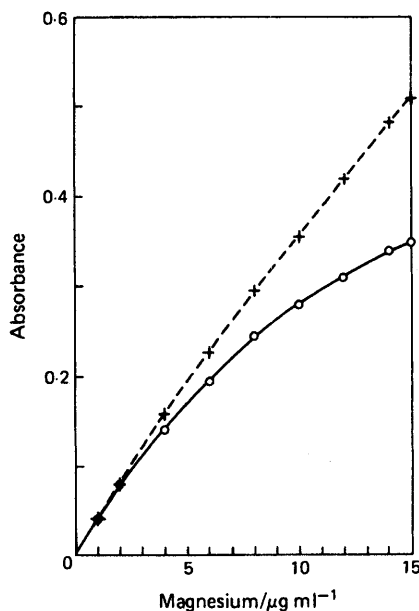


Fig. 3. Magnesium calibration graphs at 202.5 nm: broken line,  $\text{MgCl}_2$ ; and solid line,  $\text{MgSO}_4$ .

The advantages of the burner with a triangular cross-section must arise from the fact that burners of this design give a stiffer, narrower flame, because of the different pattern of air entrainment. The burner with a triangular cross-section required a slightly higher acetylene

flow-rate in order to give a luminous flame, which indicates that more air is entrained by the stiffer flame. This effect would make the flame leaner and hotter, and could result in the observed decrease in the extent of the interference when this burner was used. The increase in the extent of the interference with burner rotation is probably attributable to the effects of lateral diffusion interference,<sup>3-5</sup> which might be expected to occur under these conditions, although they are not normally observed in air-acetylene flames. A brief investigation of the absorption profiles showed a small but significant effect in this instance, but it would be difficult to relate it quantitatively to the increase in interference when burner rotation is used.

It was found that the interference effect of sulphate on the absorbance of magnesium could readily be overcome by the addition of a suitable excess of one of the commonly used releasing agents, such as lanthanum chloride or strontium chloride. The main risk of unsuspected error arising at higher concentrations of the analyte element will therefore be in analyses in which the addition of a releasing agent is not normally regarded as essential. However, in view of the extent of the effect in the determination of magnesium, it is surprising that a more widespread occurrence of sulphate interference has not been reported. Nickel chloride, for example, sublimes<sup>6</sup> at 1246 K, whereas the sulphate decomposes at 1121 K, and the oxide melts at 2263 K, so that the effect should be observed, particularly at a low height in the flame, for nickel. Cobalt chloride melts and boils at 997 and 1322 K, respectively, while the sulphate decomposes at 1008 K, and the oxide only melts at 2208 K.

It has been stated in the literature,<sup>2</sup> however, that nickel chloride and sulphate and cobalt chloride and sulphate will give the same responses. It was found in practice, however, that considerable depressions could be observed when sulphates were used to prepare standard solutions at higher concentrations than those normally employed under the most sensitive conditions for the determinations of these two elements. The extents of the effects for 50  $\mu\text{g ml}^{-1}$  solutions of cobalt and nickel are shown in Fig. 4 for various observation heights as functions of the fuel flow-rate. The same trends were observed as for magnesium: the degree of interference became greater at lower heights in the flame, and as the fuel flow-rate

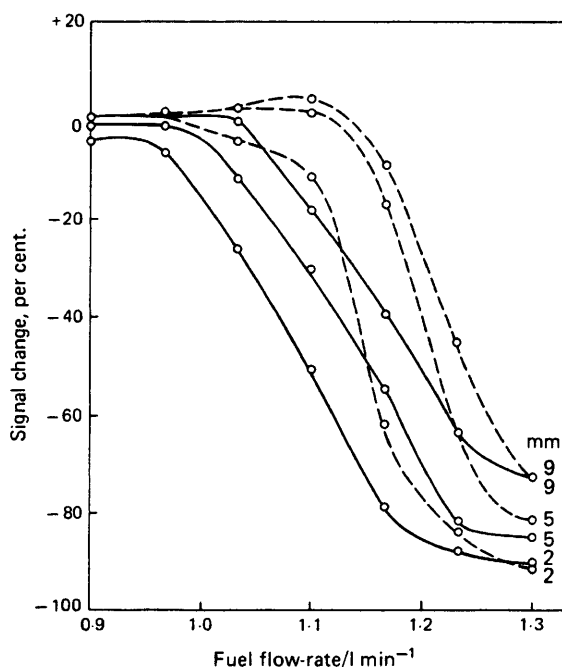


Fig. 4. Effect of fuel flow-rate on the change in cobalt absorbance at 341.3 nm (broken lines) and nickel absorbance at 234.8 nm (solid lines) caused by using sulphate in place of chloride, at various heights above a 100-mm, flat-topped burner in line with the optical axis.

was increased. The effects were slightly less pronounced when the burner with a triangular cross-section was used, but became more pronounced when either burner was rotated, and as the concentrations of the analyte element increased.

With nickel, it is perhaps worth mentioning here that although under normal working conditions the effect of using sulphate rather than chloride to prepare standard solutions was negligible for 1 and 5  $\mu\text{g ml}^{-1}$  concentrations, and only an 8 per cent. depression occurred for 50  $\mu\text{g ml}^{-1}$  concentration, if measurements were made at a low height in a fuel-rich flame depressions of 48, 72 and 90 per cent., respectively, could be observed for these three concentrations.

There can be little doubt that many other instances will be found when the incidence and extent of interferences increases at higher concentrations of the analyte element. The effect is not confined to sulphate, and may be observed for other oxy-anions. Thus, for example, the depression of the absorbance of magnesium by the addition of different excess amounts of phosphate was found to vary with magnesium concentration (see Table I).

TABLE I  
EFFECT OF PHOSPHATE ON MAGNESIUM ABSORBANCE AT A LOW HEIGHT  
IN A FUEL-RICH FLAME

Magnesium (as $\text{MgCl}_2$ )/ $\text{mg ml}^{-1}$	Change in absorbance, per cent., with phosphate ( $\text{PO}_4^{3-}$ ) concentrations of—		
	2 $\mu\text{g ml}^{-1}$	20 $\mu\text{g ml}^{-1}$	200 $\mu\text{g ml}^{-1}$
0.5*	0	0	0
5.0†	4	9	10
50.0‡	12	29	46

\* 285.2 nm, burner aligned.

† 285.2 nm, burner rotated through an angle of  $90^\circ$ .

‡ 202.5 nm, burner rotated through a small angle.

When possible cationic interferences are being investigated, care must be taken to ensure that the associated anion does not cause a variation in the incidence or extent of apparently simple cationic interferences. Thus, for example, 50  $\mu\text{g ml}^{-1}$  of magnesium (as sulphate) interfered considerably in the determination of 2  $\mu\text{g ml}^{-1}$  of cobalt or nickel, whereas the same concentration of magnesium as the chloride caused no interference.

It can be concluded that care should be taken to establish the absence of additional or increased interferences from concomitant elements and ions when employing burner rotation or an absorption line of poorer sensitivity for analysis at high concentrations of the analyte element. The risk of increased interference can be reduced by making measurements by using the upper part of a fuel-lean flame, particularly if a burner with a triangular cross-section is used.

Although the results obtained with one particular instrument provide an indication of interference trends, significant variation can be expected to occur between different instruments and even between different nebulisers, so that it is essential to check for interferences on the instrument to be used for the analysis.

The authors are indebted to Messrs. G. Wilson and D. Strath, for the construction of the burner with a triangular cross-section, and to Mrs. S. Reid, for assistance with some of the experimental work.

### References

1. Kirkbright, G. F., and Sargent, M., "Atomic Absorption and Fluorescence Spectroscopy," Academic Press, London, New York and San Francisco, 1974.
2. Aldous, K., and Reynolds, R. J., "Atomic Absorption Spectroscopy," Charles Griffin & Co. Ltd., London, 1970.
3. Koirtiyohann, S. R., and Pickett, E. E., *Analyt. Chem.*, 1968, **40**, 2068.
4. West, A. C., Fassel, V. A., and Kniseley, R. N., *Analyt. Chem.*, 1973, **45**, 1586.
5. West, A. C., Fassel, V. A., and Kniseley, R. N., *Analyt. Chem.*, 1973, **45**, 2420.
6. "Handbook of Chemistry and Physics," 53rd Edition, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1972-1973.

Received August 8th, 1975

Accepted October 6th, 1975