Investigation of spectral interferences in the determination of trace elements in water by ICP-OES

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1 Introduction

Inductively coupled plasma optical emission spectrometry (ICP-OES) is an established technique for the inorganic analysis of waters for major, minor and trace elements. At the British Geological Survey's (BGS) laboratories at Wallingford, an Applied Research Laboratories 34000C ICP is at present calibrated for the simultaneous determination of 28 elements in groundwaters; it operates under compromise conditions given in Table 1.

Table 1. Compromise ICP operating parameters for the ARL 34000C

Spectrometer	ARL 34000C Quantovac; 1-m Paschen-Runge mounting; grating ruled 1080 lines mm^{-1} Primary slit width 20 µm Secondary slit width range 37.5–75 µm
Frequency	27.12 MHz
Forward power	1080 W
Reflected power	0–5 W
Observation height	17 mm above load coil
Argon flow rates	Coolant 11 l min^{-1}, plasma 1.2 l min^{-1}, carrier 1 l min^{-1}
Sample uptake rate	2.5 ml min^{-1}
Sample acidity	1% v/v HCl
Nebulizer	Concentric glass, J E Meinhard model TR-30-A3
Read-out	Digital read-out of mean signal from 3 10-second integrations

The Hydrogeochemistry Section of BGS Wallingford has a particular interest in the occurrence and behaviour of trace elements in groundwaters and surface waters vulnerable to acidic deposition, funded by a major commissioned research contract from the Department of the Environment (DoE) and various science budget projects. Because the natural levels of many elements in these waters are extremely low, a pre-concentration procedure, based on evaporation under infra-red lamps in ultra-clean conditions, has been developed. However, this method of pre-concentration is non-selective and the resulting high concentrations of alkaline-earth elements give rise to spectral interferences. These have been thoroughly investigated and appropriate inter-element corrections entered into the instrument's data processing software to minimize their effect. Normally, the levels of iron in natural waters are low and do not cause any problems. Recently, some iron-rich groundwaters were collected and pre-concentrated. The enhanced iron concentration in this particular set of samples, combined with the fact that iron has a very line-rich emission spectrum, made it necessary to investigate its potential spectral interference in the determination of other trace elements.

2 Investigations into spectral interferences caused by high concentrations of iron

Iron solutions of 200 mg l^{-1} Fe were prepared by dilution from 2 different stock solutions:

i. 1000 mg l^{-1} Fe AAS standard (Spectrosol, BDH Chemicals)

ii. 1000 mg l^{-1} Fe, prepared by dissolution of Fe powder (Specpure, Johnson Matthey Chemicals) in Aristar grade HCl.

Scans over small wavelength regions around the spectral lines of interest were obtained by displacing the primary slit in precise increments under computer control.

Wavelength scans of the 2 different Fe solutions were obtained for each of the trace element wavelengths listed in Table 2, and plotted against an appropriate blank. With the BDH solution, peaks were observed at the Sr, Cr and Co lines, whereas the corresponding scans of the Specpure solution were indistinguishable from those of the blank. Figure 1 illustrates the response obtained at the 407.77 nm Sr line for both Fe solutions and shows that significant amounts of Sr are present as impurities in the BDH AAS Fe solution. Similar results were

Table 2. Trace elements routinely determined by ICP-OES at Wallingford

Element	Wavelength (nm)	Element	Wavelength (nm)
Sc	361.38	Cr	267.72
Sr	407.77	Ni	231.60
Y	371.03	Mo	202.03
Ba	455.40	Al	308.21
Mn	257.61	Pb	220.35
Be	313.04	Co	228.62
Cu	324.75	Zn	202.55
V	311.07	Ce	380.15
Cd	226.50	La	398.85
Zr	343.82	B	249.68
		Li	670.78

obtained for Co and Cr.

However, for both Fe solutions, peaks of similar intensity were observed near the Zn, Zr, V and Cd wavelengths, as illustrated by a comparison of the 2 scans at the 266.50 nm Cd line in Figure 2. A search of various line tables (Brenner & Eldad 1984; Parsons *et al.* 1980; Michaud & Mermet 1982) revealed Fe lines close to, or coincident with, the Zn, Zr, V and Cd lines, as shown in Table 3.

Once the existence of spectral interferences from weak Fe lines at these analyte wavelengths had been established, it was relatively straightforward to calculate apparent concentrations for Zn, Zr, V and Cd caused by the iron present in the samples (Table 4) and to use these to automatically correct any trace element signals recorded.

Table 3. Wavelengths of interfering Fe lines listed in spectral line atlases

Element	Wavelength (nm)	Fe line (nm)	Reference
Zr	343.82	343.83	1,2
Cd	226.50	226.50	1
V	311.07	311.07	1
Zn	202.55	202.55	3

1 Brenner & Eldad (1984)
2 Parsons *et al.* (1980)
3 Michaud & Mermet (1982)

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SCAN OF SPECTROSOL FERRIC NITRATE STANDARD AROUND SR 407.77nm


                                  INC.=   0.20     F.S.= 11.9mV
 NM.
      I....I....I....I....I....I....I....I....I....I....I....I....I
407.82                          B*
407.81                          B *
407.81                          B   *
407.80                          B      *
407.79                          B           *
407.79                          B                 *
407.78                          B                       *
407.77                          B                              *
407.76                          B                                 *
407.76                          B                                *
407.75                          B                          *
407.74                           B                  *
407.74                           B           *
407.73                            B    *
407.72                            B *
407.72                            B *
      I....I....I....I....I....I....I....I....I....I....I....I....I


     B = 1% HCL BLANK
     * = 200 PPM FE
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SCAN OF STANDARD PREPARED FROM SPECPURE IRON POWDER
AROUND SR 407.77nm

                                  INC.=   0.10     F.S.=  6.0mV
 NM.
      I....I....I....I....I....I....I....I....I....I....I....I....I
407.82                                                        *
407.81                                                       B*
407.80                                                       *
407.80                                                      *B
407.79                                                      *B
407.78                                                      *B
407.78                                                      *B
407.77                                                       *
407.76                                                       *B
407.76                                                       *
407.75                                                       *B
407.74                                                        *
407.74                                                         *B
407.73                                                          *
407.72                                                           *B
407.72                                                            *
      I....I....I....I....I....I....I....I....I....I....I....I....I


     B = 1% HCL BLANK
     * = 200 PPM FE
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Figure 1. Scans around the 407.77 nm Sr line of a BDH iron solution and a standard prepared from Specpure iron powder reveal that there is a significant strontium impurity in the BDH solution

Table 4. Apparent analyte concentration caused by the presence of 200 mg l^{-1} Fe

Element	Apparent concentration mg l^{-1}
Zr	0.025
Cd	0.054
V	0.023
Zn	0.023

3 Conclusions

3.1 Comparison of 2 iron standards showed the need for careful selection of contamination-free stock solutions in multi-element analysis.

3.2 Good line atlases are invaluable as an aid to identifying interfering lines when augmented by spectral scans.

3.3 The effect of sample pre-treatment must be taken into account. Spectral interferences not normally encountered in water analysis by ICP-OES become significant following sample concentration by evaporation.

4 References

Brenner, I.B. & Eldad, H. 1984. A spectral line atlas for multitrace and minor element analysis of geological and ore mineral samples by ICP-AES. *ICP Inf. Newsl.*, **10,** 451–508.

Michaud, E. & Mermet, J.M. 1982. Iron spectrum in the 200-300 nm range emitted by an inductively coupled argon plasma. *Spectrochim. Acta,* **37B,** 145–164.

Parsons, M.L., Forster, A. & Anderson, D. 1980. *An atlas of spectral interferences in ICP spectroscopy.* New York: Plenum.

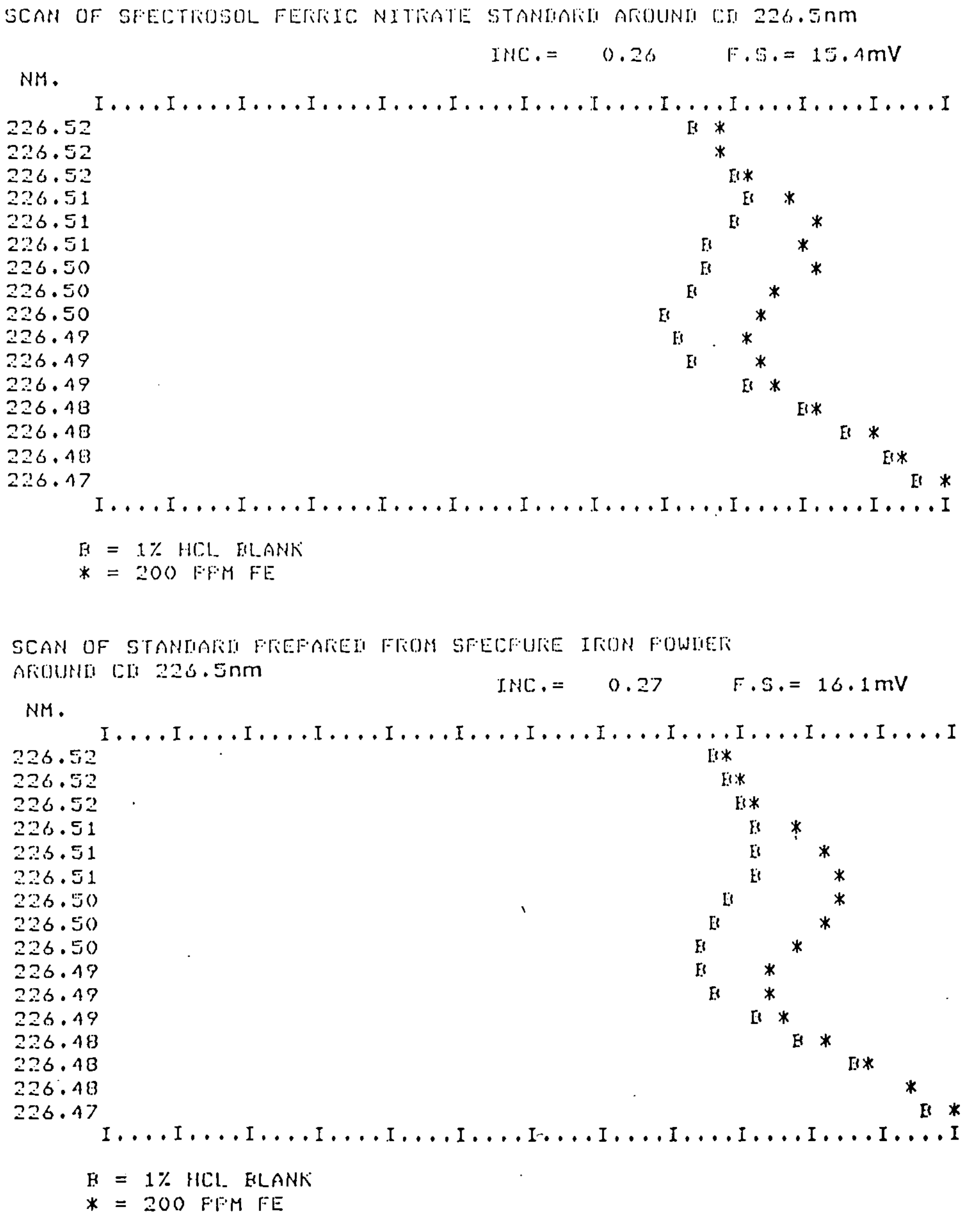

Figure 2. Scans around the 226.50 nm Cd line of a BDH iron solution and a standard prepared from Specpure iron powder give very similar responses. This is due to the presence of a weak iron line also at 226.50 nm