Trace element measurements of environmental water samples using inductively coupled plasma optical emission spectrometry

J M COOK
British Geological Survey, Hydrogeology Research Group, Wallingford

1 Introduction

One of the advantages of inductively coupled plasma optical emission spectrometry (ICP-OES) as an analytical technique is that major, minor and trace element determinations can be performed simultaneously, thus minimizing sample handling and reducing sample contamination. However, for dilute waters, detection limits obtained by ICP-OES are not always sufficiently sensitive to allow the direct determination of some important trace elements. Sample pre-concentration is often required and any procedure which is used must therefore be applicable to a wide range of elements, in order to utilize the multi-element capability of the ICP. Thus, a simple method of evaporation under ultra-clean conditions was developed at BGS Wallingford, initially for the purpose of determining trace element concentrations in groundwaters, where many determinands were found to be present in unpolluted sources at very low levels.

Subsequently, the procedure has proved to be very robust when applied to rain and surface waters in studies of acidic deposition.

Underlying the methodology described here is the broader philosophy of trace element measurement. This paper reviews some of the precautions which need to be taken at each stage, from sample collection to data interpretation, and discusses them in relation to the determination of trace elements in natural waters by ICP-OES.

2 Sample handling strategy

To obtain reliable environmental data it is important to make a critical assessment of the procedures adopted at each of the 4 interdependent stages of sample collection, sample storage, laboratory analysis and data interpretation. Each stage will influence the accuracy and precision of the final result. Miles and Cook (1981) have outlined the problems of collecting data on the inorganic chemical composition of groundwaters.

At all stages of handling the samples, the overall objective should be to minimize:

i. contamination of the sample,
ii. loss of analyte by adsorption on to surfaces, and
iii. modification of the chemical form of the analyte.

For example, during sample collection and storage, attention should be focused on the materials used in the construction of the collection apparatus and the sample containers themselves. Pre-treatment of apparatus and containers is often necessary, particularly to reduce contamination.

The overall aims of a project may well dictate whether filtered or unfiltered samples are collected. A common practice is to use a filter with a nominal pore size of 0.45 μm as an arbitrary division between 'dissolved' and 'particulate' material. This distinction may be inadequate, especially for samples containing colloidal material (Danielsson 1982). A study of the particle size distribution of iron and manganese species in fresh waters by Laxen and Chandler (1983) showed that it was essential to filter on-site, as changes in the size distribution occurred within several hours. Filtration introduces the possibility of contamination from the apparatus and loss of analyte by adsorption (Gardner & Hunt 1981).

Consideration should be given to the stability of the analyte during storage. Sorption losses on to container surfaces have been demonstrated by Massee *et al.* (1981) for a number of trace elements, and Batley and Gardner (1977) have reviewed published data on storage experiments for various analytes.

Altogether there is a wealth of literature which addresses the problems associated with the sampling and storage of natural waters. In the end, whatever the procedure adopted, the essential prerequisite is that it be thoroughly evaluated, prior to its application to a particular project.

Once a sample reaches the laboratory, anything that comes in contact with it is a potential source of contamination. A direct consequence of this is a requirement for (i) a very clean working environment, and (ii) a source of high-purity water.

At BGS Wallingford this requirement is achieved in the following manner.

i. Air is filtered before it enters the trace element laboratory, and a positive pressure is maintained in the room, relative to the external atmosphere. Laminar flow hoods are used to

provide an extra clean working area within the laboratory. The effectiveness of these measures can be judged from Figure 1, which compares the levels of iron, lead and zinc in the ambient air outside with those of the filtered air inside the laboratory and that produced by the laminar flow hoods. Even coarse filtration reduces the levels significantly, and the metal concentrations in the air in the laminar flow hoods are a fraction of those of the ambient air.
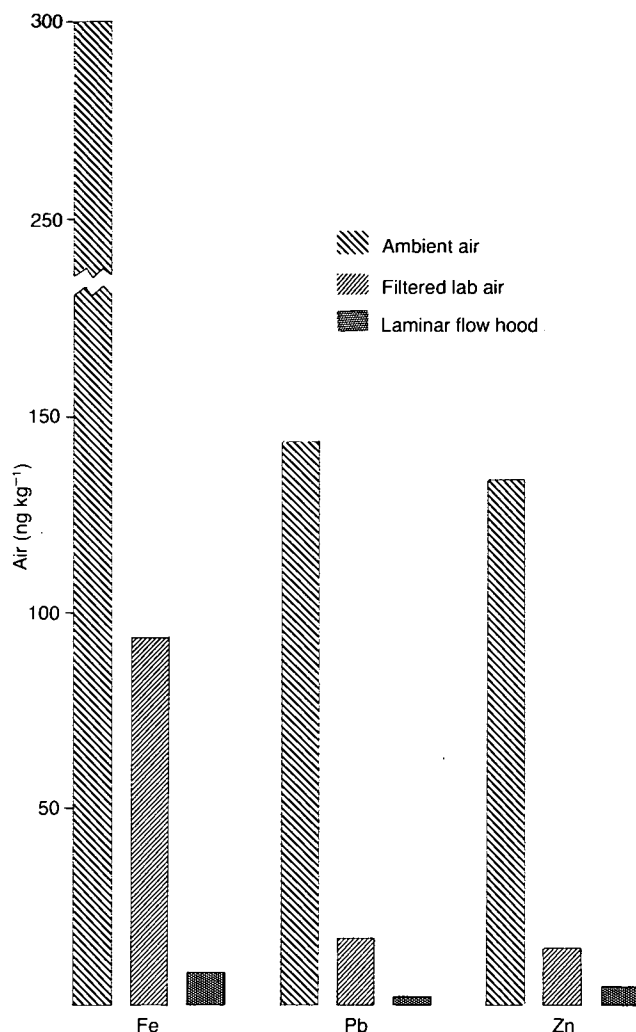

Figure 1. Concentrations of particulate iron, lead and zinc in the filtered laboratory air and laminar flow hoods, compared with those of the unfiltered atmosphere

ii. Water from a reverse osmosis plant is supplied to a *Millipore* system containing a pre-filter, 2 mixed-bed ion exchange columns, one column of activated carbon and a final filter of pore size 0.22 μm. The final water produced has a resistivity of up to 18 Megohms cm^{-1} and will be referred to as MilliQ water in this paper.

3 Collection and storage of trace element samples
One litre polyethylene bottles were soaked in 50% v/v Analar HCl for 24 hours, rinsed with high-purity water (MilliQ), soaked in 10% v/v high-purity Aristar HCl for another 24 hours, and copiously rinsed and stored full of MilliQ water. Just before transport to the field, the bottles were rinsed a further 3 times in MilliQ water and packed into plastic bags.

All plastic tubing and filtration equipment with which the water comes in contact was also acid-washed, rinsed with MilliQ water and rinsed thoroughly with the sample before its final collection.

High-purity Aristar HCl was added to the samples to give a final concentration of 1% v/v, lowering the pH to approximately pH 1—2 to stabilize the trace elements in solution and discourage adsorption on to the container walls. A blank of MilliQ water was also acidified in an identical manner in the field, to check on contamination from the bottles and the acid. Samples were stored at 4°C in the dark until required.

4 Pre-concentration by evaporation
PTFE beakers, of 500 ml capacity, were thoroughly soaked in 50% v/v Aristar HCl overnight and copiously rinsed with MilliQ water. Four hundred millilitres of sample were poured into each beaker and placed under an infra-red lamp in a laminar flow hood. After 6—7 hours, the approximately 5 ml of solution that remained was decanted into an acid-washed 20 ml volumetric flask. The PTFE beaker was rinsed with 0.2 ml Aristar HCl and several aliquots of MilliQ water, and all the washings were decanted into the flask and made up to volume; this procedure resulted in a 20-fold concentration of the sample.

Blanks of 1% v/v Aristar HCl in MilliQ water were also carried through the whole analytical procedure with each set of evaporations to monitor contamination levels.

5 Analysis by ICP-OES
All measurements were carried out using an Applied Research Laboratories (ARL) 34000C inductively coupled plasma optical emission spectrometer, with a 44-channel vacuum polychromator, operated under the compromise conditions given in Trafford (1987). A typical analytical programme determines 28 elements simultaneously, using conventional pneumatic nebulization, with an uptake rate of just over 2 ml min^{-1}.

The ARL 34000C is fitted with a scanning accessory for multi-element analysis (SAMI), which is linked to the primary slit of the polychromator. Under computer control, the SAMI displaces the primary slit in precise increments, causing the spectrum to move across the secondary slits. In this way, detailed information

on the spectral structure in the region of each analyte wavelength can be obtained.

In trace element analysis, particular care has to be taken in the interpretation of small signals, and scans obtained with the SAMI are an invaluable aid in this process. The power of the scanning facility is demonstrated for an evaporated acidic surface water which has been scanned around the Be 313.04 nm line (Figures 2a & 2b). At this wavelength, the background has some structure (Figure 2a) and it is not easy to quantify the amount of Be in the sample. However, if the computer is used to subtract the background signal from the sample signal, the difference scan in Figure 2b is produced, showing a clean beryllium peak of about 2 μg l^{-1}, which represents a concentration of 0.1 μg l^{-1} in the original sample.

Scans in the neighbourhood of analyte lines are also useful when investigating possible spectral interferences (Miles 1987). Stray light from a strong emitter such as calcium can cause a shift in the background signal, as shown in the scan around the yttrium 371.03 nm line in Figure 3. The sample is a shallow groundwater which contained about 20 mg l^{-1} calcium before pre-concentration. The evaporated sample does contain a measurable amount of yttrium, but about one third of the total signal is due to the background shift produced by the 400 mg l^{-1} calcium present in solution after pre-concentration. The background can be subtracted manually or by computer, leaving a signal of 8 μg l^{-1} yttrium, which represents a concentration of 0.4 μg l^{-1} yttrium in the original solution.


```
                                          F.S.= 26.0 mV
   NM.
        I....I....I....I....I....I....I....I....I....I....I....I....I....I....I
   313.06
   313.06
   313.06
   313.05
   313.05
   313.05
   313.04
   313.04
   313.04
   313.03
   313.03
   313.03
   313.02
   313.02
   313.02
        I....I....I....I....I....I....I....I....I....I....I....I....I....I....I

   B = 1% HCL BLANK
   2 = 1% HCL PRECONCENTRATED X20
   * = SAMPLE PRECONCENTRATED X20
```
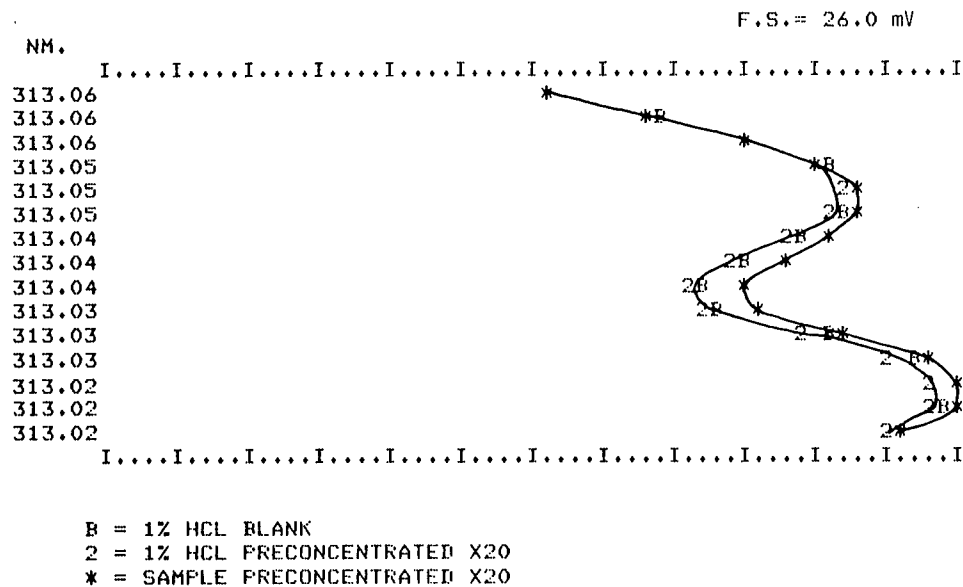
Figure 2a. Scans around the 313.04 nm beryllium line obtained while aspirating a pre-concentrated acidic surface water and blanks, indicating a small quantity of beryllium present in the pre-concentrated sample


```
                                          F.S.= 1.7 mV
   NM.
        I....I....I....I....I....I....I....I....I....I....I....I....I....I....I
   313.06
   313.06!
   313.06!
   313.05!
   313.05!
   313.05!
   313.04!
   313.04!
   313.04!
   313.03!
   313.03!
   313.03!
   313.02!
   313.02!
   313.02!
        I....I....I....I....I....I....I....I....I....I....I....I....I....I....I

   * = SAMPLE PRECONCENTRATED X20
   ! = MV BASELINE
```
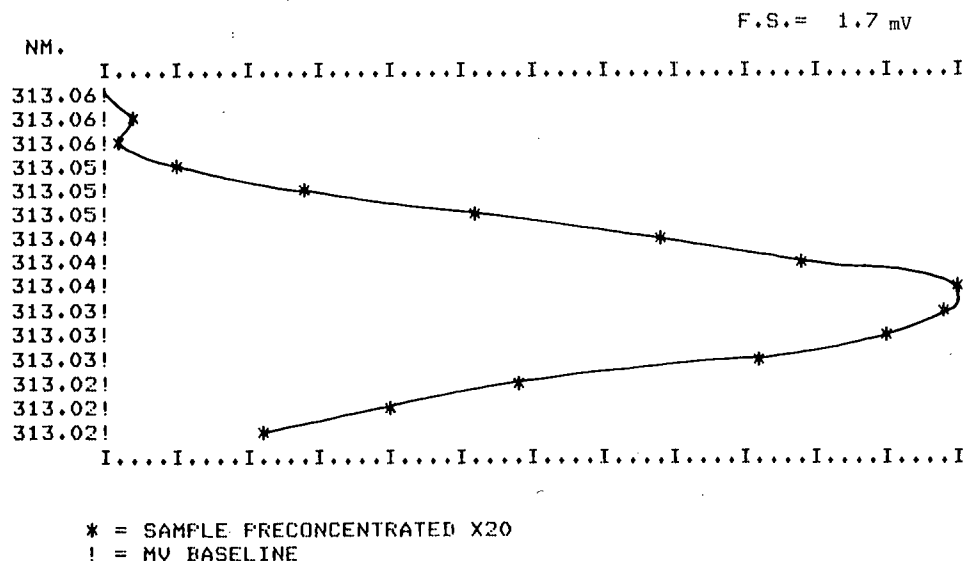
Figure 2b. Scan data in Figure 2a displayed in an alternative format by subtracting the blank from the pre-concentrated sample signal to reveal a sharp beryllium peak of about 2 μg l^{-1}

6 Data evaluation

The blanks which are carried through the pre-concentration step are normally low and reproducible but, in spite of all the precautions taken, they always contain small amounts of boron, barium, iron and zinc. A typical iron blank is about 30 µg l^{-1} Fe and is significant when compared with the iron signal from the pre-concentrated sample of rainwater (Figure 4). Such a blank will degrade the ultimate detection limit obtainable, but in practice this is very seldom a limiting factor for most of the waters under investigation.

To assess the recovery of the pre-concentration procedure, a standard solution was analysed before and after pre-concentration. Table 1 shows

that the recovery is better than 95% for a wide range of elements. Typical recoveries are also illustrated by results from surface waters from Loch Fleet, which is situated in a granitic upland catchment in SW Scotland, and is the subject of a multidisciplinary project on acidic deposition and the effect of liming a catchment. Data from this project are shown in Table 2 for elements sensitive enough to be detected both before and after evaporation. The agreement is good and, after pre-concentration, extra confidence can be placed in the second significant figure.

For those elements which cannot be determined directly by ICP-OES, pre-concentration by a factor of 20 permits measurements of several elements well below 1 µg l^{-1} (Table 3). The figures for lead

F.S.= 13.6 mV

NM.

```
371.06
371.05
371.05
371.05
371.04
371.04
371.04
371.03
371.03
371.03
371.02
371.02
371.02
371.01
371.01
371.01
```

B = 1% HCL BLANK
2 = 1% HCL BLANK PRECONCENTRATED X20
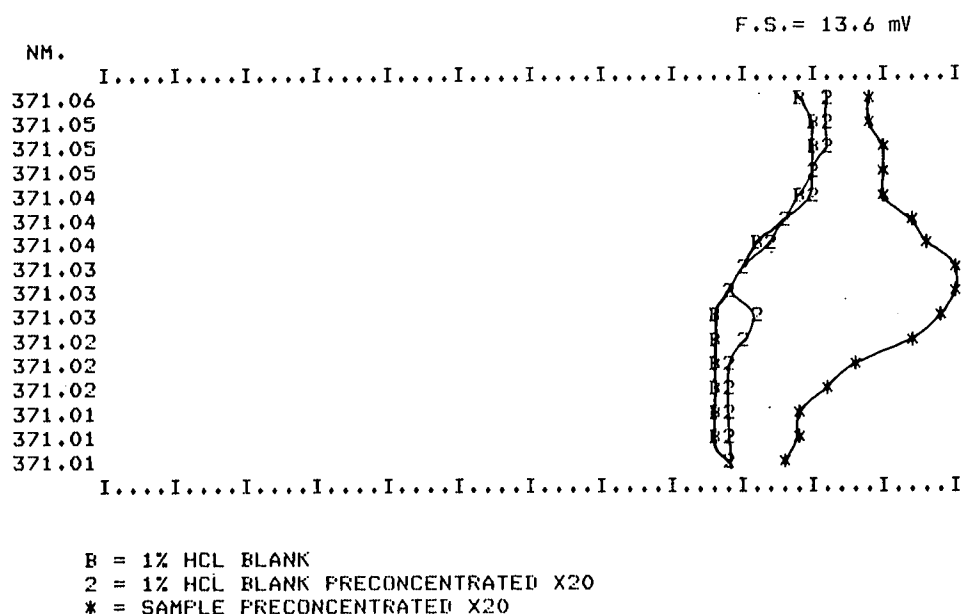* = SAMPLE PRECONCENTRATED X20

Figure 3. Scan around the 371.03 nm yttrium line obtained by aspirating a pre-concentrated shallow groundwater, showing the background shift caused by 400 mg l^{-1} Ca present in the pre-concentrated sample

F.S.= 29.3 mV

NM.

```
259.96
259.96
259.96
259.95
259.95
259.95
259.94
259.94
259.94
259.93
259.93
259.93
259.92
259.92
259.92
```

B = 1% HCL BLANK
2 = 1% HCL BLANK PRECONCENTRATED X20
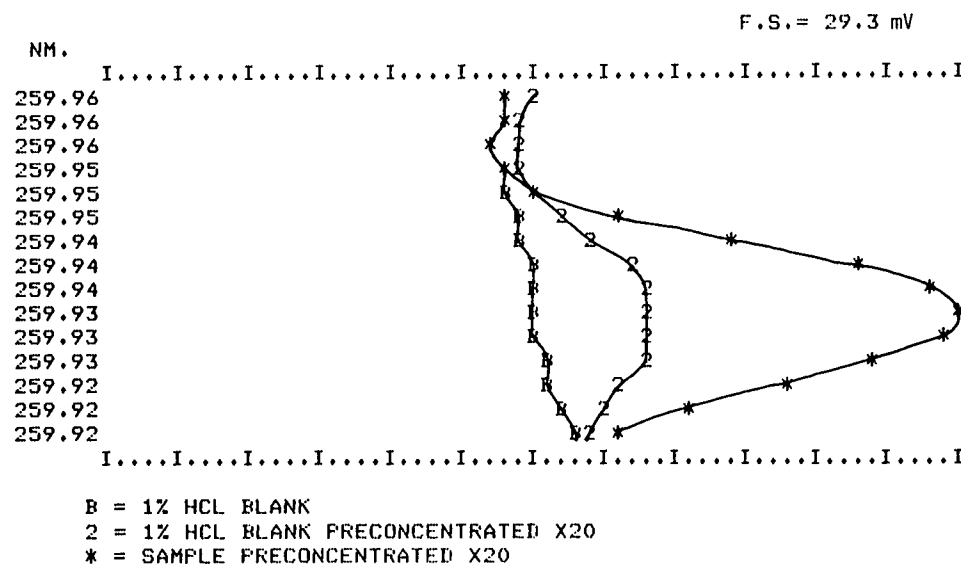* = SAMPLE PRECONCENTRATED X20

Figure 4. Scan around 259.94 nm iron line illustrating that a typical pre-concentrated iron blank contains a significant amount of iron compared with a pre-concentrated sample of rainwater

indicate that the improvement in detection limit is greater than a factor of 20; this is a result of the extra work involved in interpreting the small signals above background, using the scans, which would not be done normally in routine analysis.

Table 1. Recoveries obtained by evaporation of a standard solution. Concentrations in $\mu g \ l^{-1}$

Element	Before evaporation	After evaporation ×20	% recovery*
Y	44	846	98
Ba	48	942	98
Mn	44	863	98
Cu	46	873	94
Fe	44	896	100
V	47	900	96
Cd	20	397	99
Co	40	811	101
Zn	38	765	99
Ni	154	3060	99
Mo	154	3010	97
Al	178	3380	93
Pb	163	3330	102

*All recoveries calculated after blank correction

Table 2. Comparison of major and minor element determinations on samples from Loch Fleet outflow (30.8.85) before and after pre-concentration

Element	Original measurement (mg l^{-1})	After pre-concentration (mg l^{-1})
Na	4.0	4.0
K	<0.5	0.22
Ca	0.82	0.86
Mg	0.52	0.56
SO$_4$	4.4	4.5
Sr	0.005	0.0052
Ba	0.039	0.042
Mn	0.17	0.17
Fe	0.13	0.13
Zn	0.032	0.035
Al	0.18	0.18

Table 3. Comparison of trace element determinations on samples from Loch Fleet outflow (30.8.85) before and after pre-concentration

Element	Original measurement ($\mu g \ l^{-1}$)	After pre-concentration ($\mu g \ l^{-1}$)
B	<35	12
Li	<10	0.9
Be	<1	0.10
Y	<2	0.08
V	<20	0.3
Cu	<10	1.6
Ni	<100	4
Pb	<200	13

Table 4. Chemical data for Loch Fleet inflow and outflow (30.8.85) compared with bulked rain for August 1985

Element	August rain	Inflow	Outflow
	mg l^{-1}		
Na	1.3	2.5	4.0
Mg	0.13	0.32	0.56
SO$_4$	1.4	2.6	4.5
	$\mu g \ l^{-1}$		
Al	<5	300	180
Fe	2.6	120	130
Mn	1.3	23	170
Sr	1.6	3.2	5.2
Cu	1.5	1.2	1.6
Y	<0.05	0.21	0.08
Be	<0.05	0.06	0.10
Ni	<1	<1	4

7 Results

Representative trace element data obtained using the technique of pre-concentration by evaporation and measurement by ICP-OES from the Loch Fleet catchment are shown in Table 4, as an example of the precision and sensitivity of the method. A selection of the data for the outflow and major inflow to Loch Fleet are compared with those for the bulked rainfall for the same month. Some of the main features of the data generally are the following.

i. Sodium, magnesium and sulphate show a similar proportional increase in concentration between the rain, the major inflow and the outflow.

ii. The aluminium data represent the total fraction less than 0.45 μm. From several months' data it has been observed that these values for the inflow are variable and usually greater than the concentration in the outflow, whereas the aluminium level in the outflow is normally between 0.18 and 0.19 mg l^{-1}.

iii. For iron, the inflow and outflow concentrations are about the same and there is no apparent trend. In contrast, manganese displays an order of magnitude increase in the outflow over the inflow.

iv. Reliable low level data for strontium have been obtained which show that strontium behaves in a similar manner to many of the major elements.

v. There are similar levels of copper in the rain, inflow and outflow waters indicating that rain is probably the major source of copper in the catchment.

vi. Traces of yttrium and beryllium are detected, which are probably derived from the granite; there is constantly more yttrium in the inflow than the outflow.

vii. Nickel is always detected in the outflow.

8 Conclusions

To obtain reliable trace element data, it is necessary to appreciate the problems which may arise and the precautions which need to be taken all the way through sample collection, sample storage, laboratory analysis and data interpretation. A method of pre-concentrating water samples by simple evaporation prior to analysis by ICP-OES was originally developed for trace element analysis of groundwaters and has been successfully applied to rain- and surface waters.

9 Summary

Sample collection, sample storage, laboratory analysis and data interpretation are 4 interdependent stages in the measurement of any environmental sample. Each stage will influence the accuracy and precision of the final result, and this is particularly true when handling natural waters where the elements of interest may be present at well below 1 mg l^{-1}. The problems which arise and the precautions which need to be taken are discussed.

Detection limits obtained by ICP-OES are not sufficiently sensitive to determine some important trace elements directly, and pre-concentration of the sample may be necessary. However, any pre-concentration technique used must be applicable to many elements, in order to utilize the multi-element capability of the ICP. A method of pre-concentrating water samples by simple evaporation under ultra-clean conditions is discussed.

Primary spectroscopic data from a sophisticated computer-controlled instrument such as an ICP require careful interpretation, especially when deciphering small signals close to the detection limit. Typical data on trace element levels in groundwaters and dilute surface waters subject to acidic deposition are presented.

10 References

Batley, G.E. & Gardner, D. 1977. Sampling and storage of natural waters for trace metal analysis. *Wat. Res.,* **11**, 745–756.

Danielsson, L.G. 1982. On the use of filters for distinguishing between dissolved and particulate fractions in natural waters. *Wat. Res.,* **16**, 179–182.

Gardner, M.J. & Hunt, D.T.E. 1981. Adsorption of trace metals during filtration of potable water samples with particular reference to the determination of filterable lead concentration. *Analyst, Lond.,* **106**, 471–474.

Laxen, D.P.H. & Chandler, I.M. 1983. Size distribution of iron and manganese species in freshwaters. *Geochim. Cosmochim. Acta,* **47**, 731–741.

Massee, R., Maessen, F.J.M.J. & De Goeij, J.J.M. 1981. Losses of silver, arsenic, cadmium, selenium and zinc traces from distilled water and artificial sea-water by sorption on various container surfaces. *Analytica chim. Acta,* **127**, 181–193.

Miles, D.L. 1987. The application of inductively coupled plasmas to the analysis of natural waters and acidic deposition. In: *Chemical analysis in environmental research,* edited by A.P. Rowland, 40–49. (ITE symposium no. 18.) Abbots Ripton: Institute of Terrestrial Ecology.

Miles, D.L. & Cook, J.M. 1981. Chemical aspects of the collection and evaluation of data on the quality of groundwater. In: *Quality of groundwater,* edited by W. Van Duijvenbooden, P. Glasbergen & H. van Lelyveld, 725–731. (Studies in environmental science no. 17.) Amsterdam: Elsevier.

Trafford, J.M. 1987. Investigation of spectral interferences in the determination of trace elements in water by ICP-OES. In: *Chemical analysis in environmental research,* edited by A.P. Rowland, 56–58. (ITE symposium no. 18.) Abbots Ripton: Institute of Terrestrial Ecology.