The application of inductively coupled plasmas to the analysis of natural waters and acidic deposition

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1 Introduction

High-power, electrodeless, plasma discharges were first sustained in air at atmospheric pressure by Babat (1947), working at the Svetlana plant in Leningrad during World War II. His research ceased when the entire power system of that blockaded city failed and several of his colleagues perished in the hostilities. Almost 20 years later, Reed (1961) described the formation and stabilization of an inductively coupled argon plasma which he used as a very high temperature torch in research on the growth of single crystals of refractory oxides.

The analytical potential of Reed's inductively coupled plasma (ICP) as a spectroscopic source was recognized independently in the UK by Greenfield *et al.* (1964) and in the USA by Wendt and Fassel (1965). Since the mid-1960s, and particularly during the last 10 years, when various types of commercial spectrometer using ICP sources have been available, there has been an enormous increase in the use of ICP spectrometric techniques in many fields of analysis. This paper seeks to review briefly those techniques relevant specifically to the analysis of natural waters.

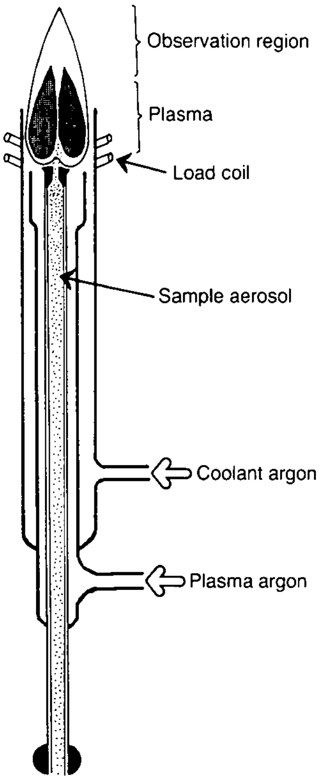


Figure 1. ICP torch

2 The ICP source

A conventional ICP torch typically consists of 3 accurately aligned, concentric silica tubes (Figure 1). The longest, outermost tube is surrounded at its tip by a 2- or 3-turn, water-cooled induction coil, connected to a radio-frequency generator operating usually at 27.12 or 40—50 MHz. Argon flows at carefully controlled rates through the 2 annular spaces formed between the tubes. The normally non-conducting argon is partially ionized initially by a spark from a Tesla coil and a toroidal plasma is sustained by inductive coupling between the coil and the ionized gas. Temperatures of 6000—9000°K result from Ohmic heating, and one of the functions of the high argon flow rate (10—20 l min^{-1}) between the outer and middle tubes is to cool and protect the torch tip from the intense heat. Sample aerosol is injected into the axial channel of the plasma via a stream of argon flowing up the central quartz tube.

3 Inductively coupled plasma-optical emission spectrometry (ICP-OES)

3.1 Instrumentation

By far the largest number of ICP spectrometric systems in use at the present time involve the detection of the photon emission from the ICP by means of some form of spectrometer having conventional optics consisting of lenses, primary entrance slit, diffraction grating, and one or more exit slits and detectors. Two types of spectrometer are commonly employed: polychromators having the Paschen-Runge mounting with a fixed concave grating and typically 20—60 fixed exit slits on the Rowland circle, each with its own detector (Figure 2); and monochromators with a movable flat grating in a Czerny-Turner mounting (Figure 3). Polychromators permit the simultaneous determination of many elements at pre-determined wavelengths, whereas in monochromators the grating is turned, usually under computer control, so that spectral lines chosen at the start of each analytical programme are monitored sequentially. One manufacturer has recently produced a novel sequential system based on a Paschen-Runge mounting, in which small displacements of the primary slit are used to image the chosen spectral line on one of 200 exit slits equally spaced around the Rowland circle, where it is monitored with a movable detector. Simultaneous and sequential systems each have their strengths and weaknesses. An ideal system

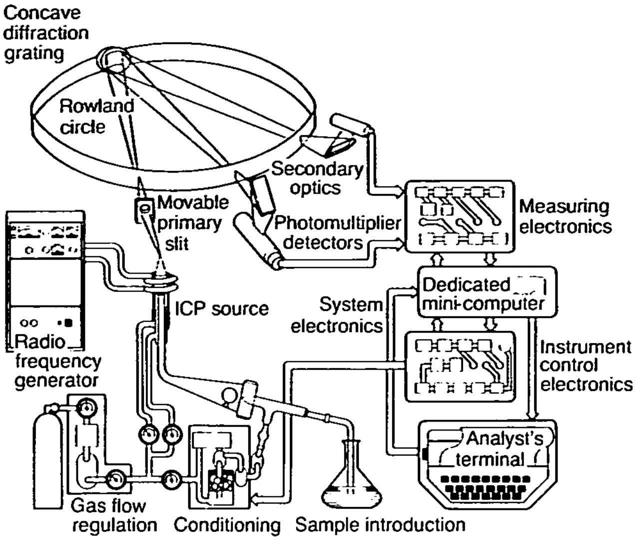


Figure 2. Schematic diagram of an ICP polychromator

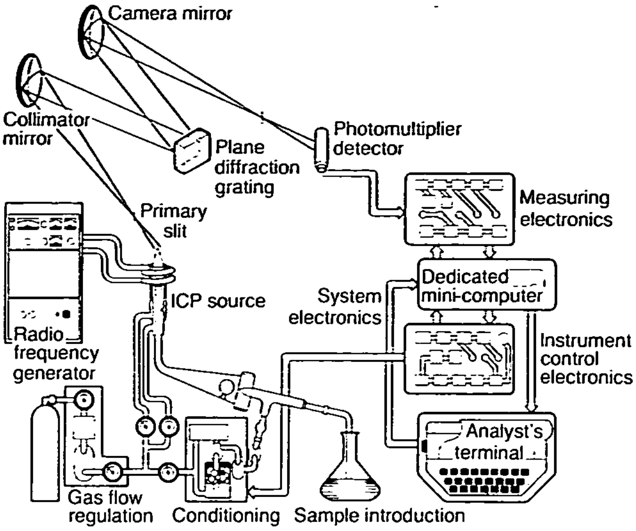


Figure 3. Schematic diagram of a scanning ICP monochromator

would combine the high data rate and good stability of a polychromator with the flexibility of a monochromator. This combination can be achieved by viewing the plasma with both types of spectrometer at the same time, as is done in some systems.

3.2 Sample introduction

The most commonly used method of sample introduction in ICP-OES is as an aerosol generated by pneumatic nebulization of a liquid into a spray chamber, and thence to the torch. Natural waters are thus in an ideal form for direct analysis, requiring the minimum of pre-treatment. Concentric glass Meinhard nebulizers (Figure 4) have proved very popular and will run consistently for long periods, provided that no suspended matter is present in the test solutions (Baginski & Meinhard 1984); membrane filtration of water samples is recommended if blockage is to be avoided.

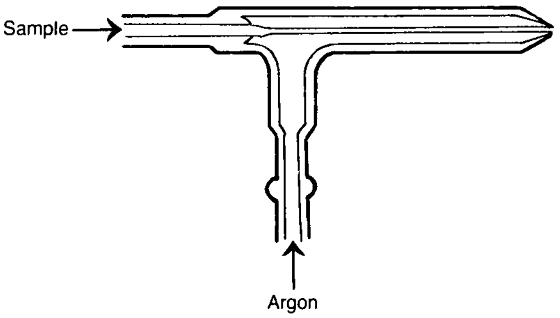


Figure 4. Concentric glass Meinhard nebulizer

Sample uptake rate is usually 1–2 ml min^{-1} which, combined with the simultaneous, multi-element capability of ICP-OES, enables large amounts of analytical data to be acquired from relatively small volumes of solution. In studies of acidic deposition, this feature is particularly helpful when sample volume is very limited, for example during investigations of solute mobilization and transport in soil and unsaturated zone pore waters extracted by centrifugation (Kinniburgh & Miles 1983).

Despite the relatively low sample consumption rate, the transport efficiency of the combination of aerosol-producing nebulizers such as the Meinhard and a conventional spray chamber is very poor, with only about 2% of the aspirated sample reaching the plasma and the remainder draining to waste. A novel approach to improving the overall efficiency of the sample nebulization and transport system, by ensuring that a much higher proportion of the liquid aspirated is ultimately injected into the ICP, has been described by Hulmston (1983) in the form of a recirculating nebulizer (Figure 5). A normal Meinhard nebulizer is mounted vertically in a specially designed spray chamber such that aerosol droplets impacting on the chamber walls drain down to the inlet of the nebulizer and the solution is recirculated. Approximately 2 ml of sample are required for 20 minutes of continuous operation, and sensitivity, precision and stability are reported to be comparable to those obtained with a conventional nebulizer system (Hulmston & McKillop 1985). However, wash-out times could be expected to be long with such a system, if sample carry-over is to be avoided. Alternative pneumatic nebulizers include the cross-flow (Kniseley *et al.* 1974) and Babington types, of which the latter is particularly suitable for nebulizing solutions containing high concentrations (>5%) of dissolved salts or those containing suspended particles (Ebdon & Cave 1982). The conespray nebulizer, recently developed by Sharp and co-workers (British Technology Group 1984), was designed to combine the merits of both the cross-flow and Babington V-groove nebulizers.

Ultrasonic nebulization followed by desolvation has been used to improve detection limits significantly by increasing the amount of solute entering the ICP in unit time (Taylor & Floyd 1981). Although, in principle, it is an inherently attractive technique, it has not been widely used in routine analysis, possibly because of the operational reliability of such nebulizers in terms of stability and memory effects. A commercial ultrasonic nebulizer and desolvation system has recently been produced by the Baird Corporation, and it will be interesting to see if it gains acceptance.

Direct nebulization of aqueous samples does not provide sufficient sensitivity to enable several important trace elements to be determined by ICP-OES at the concentrations at which they typically occur in natural waters. For those elements such as germanium, tin, lead, arsenic, antimony, bismuth, selenium and tellurium, which form gaseous hydrides at ambient temperatures, vapour phase sample introduction may be used to obtain considerably enhanced sensitivity and lower limits of detection. Thompson and co-workers (1978a, b, 1979, 1981) described a continuous-flow hydride generation system which they used for the simultaneous determination of As, Sb, Bi, Se and Te in waters; pre-concentration by collection on freshly precipitated lanthanum nitrate lowered detection limits further to about 50 ng l^{-1}.

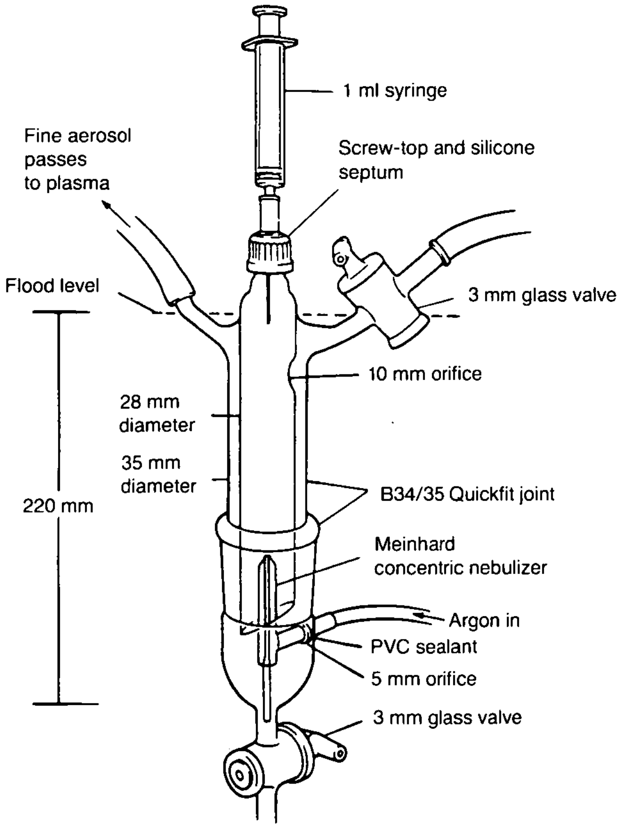


Figure 5. Recirculating nebulizer. (Redrawn from Hulmston 1983. Copyright: Royal Society of Chemistry)

3.3 Wavelength selection

The wide calibration ranges spanning 4–6 orders of magnitude, which are characteristic of ICP-OES, mean that most elements can be determined in natural water samples by choosing a single, appropriate wavelength. Occasionally, to maintain good precision, and to avoid saturation of the detector or the need to dilute samples, it may be helpful to use an alternative spectral line of considerably different intensity for those few elements which may be encountered at extreme concentrations, eg calcium in rainwater or geothermal brines.

Four main factors govern wavelength selection in ICP-OES: analyte concentration, overall sample composition, potential spectral interferences, and the spectral range of the instrument. In the case of natural waters, the major analytes are Na, K, Ca, Mg, Si and total S, and their concentrations typically range from 0.1 to 10^4 mg l^{-1}. With the possible exception of the determination of potassium in very dilute waters, appropriate spectral lines can be selected which will allow all these constituents to be determined directly in most samples, without the need for dilution or pre-concentration. In the case of Ca and Mg, it is necessary to avoid their most sensitive lines in order to achieve calibration ranges which can be extended to high enough concentrations. For minor and trace elements, present at concentrations ranging from <1 to 10^3 μg l^{-1}, the most sensitive emission lines are usually chosen, subject always to any constraints imposed by spectral interferences from major components of the sample. Several elements, including Sr, Ba, Li, B, Fe and Mn, can be determined directly in natural waters at typical environmental concentrations. However, the limits of detection attainable in ICP-OES are insufficient to allow many important transition and rare earth elements to be determined without pre-concentration. Nevertheless, direct measurement may still be used to screen large numbers of samples rapidly for anomalously high concentrations of a wide range of geochemically significant or potentially toxic elements. Numerous pre-concentration procedures have been reported in the literature (Sturgeon *et al.* 1980, 1982; Thompson *et al.* 1982; Long & Snook 1983; Vos *et al.* 1984), and an example of this application of ICP-OES to the analysis of natural waters is discussed elsewhere in this volume by Cook (1987).

Several compilations of ICP spectral lines have been published recently (Parsons *et al.* 1980; Michaud & Mermet 1982; Anderson *et al.* 1982; Boumans 1984; Brenner & Eldad 1984; Anderson & Parsons 1984; Winge *et al.* 1985; Forster *et al.* 1982; Wohlers 1985). These compilations may be used in the initial selection of analytical wavelengths, but it is vital that the suitability of individual lines be fully evaluated in relation to the spectroscopic characteristics of the instrumental system employed and the composition of the waters under investigation. Modern computer-controlled data acquisition and display facilities make this a relatively rapid and straightforward operation.

The most intense and sometimes the only analytically useful ICP emission lines of several elements lie in the ultra-violet region of the spectrum below 200 nm and may be utilized with the vacuum spectrometer systems which are now widely available. Sulphur emission at 180.7 nm has been used as the basis of a rapid means of determining sulphate simultaneously with major and trace metals in oxygenated waters (Miles & Cook 1982). Total phosphorus may be determined down to c 0.1 mg l^{-1} using the 178.29 nm line (Cook & Miles 1985). Of particular relevance to the application of ICP-OES to studies of acidic deposition is the recent investigation of the vacuum ultra-violet region by Uehiro *et al.* (1984), which revealed that the aluminium 167.1 nm line provides much greater sensitivity than the 308.2 nm line commonly used (Figure 6). A 3σ detection limit of 0.5 $\mu g\ l^{-1}$ was reported, enabling Al to be directly determined in lake waters; slight interference from a nearby iron line was recorded.

A typical wavelength programme that is routinely used for the determination of major, minor and trace elements in rain, surface and groundwaters is given in Table 1. Examples of calibration graphs are shown in Figure 7.

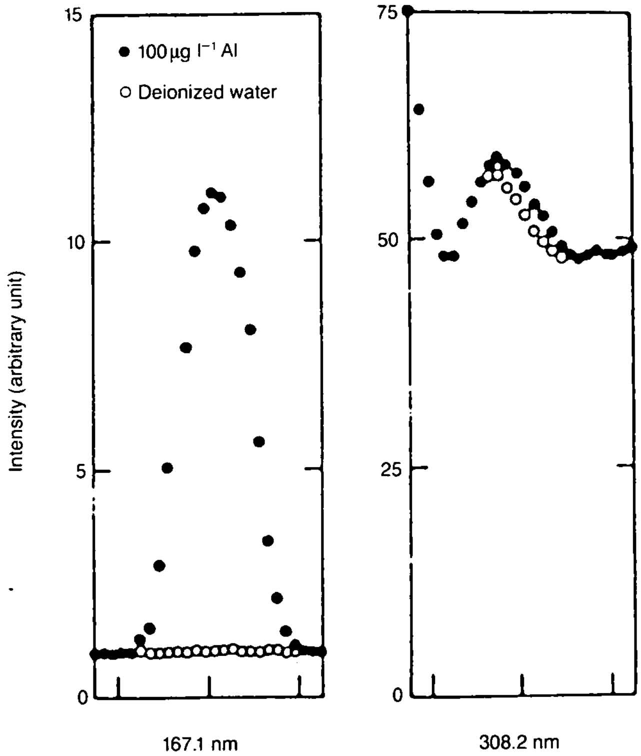


Figure 6. Spectra in the vicinity of the 167.1 nm and 308.2 nm lines of aluminium showing the enhanced sensitivity obtained with the vacuum ultra-violet line. (Redrawn from Uehiro et al. 1984. Copyright: American Chemical Society)

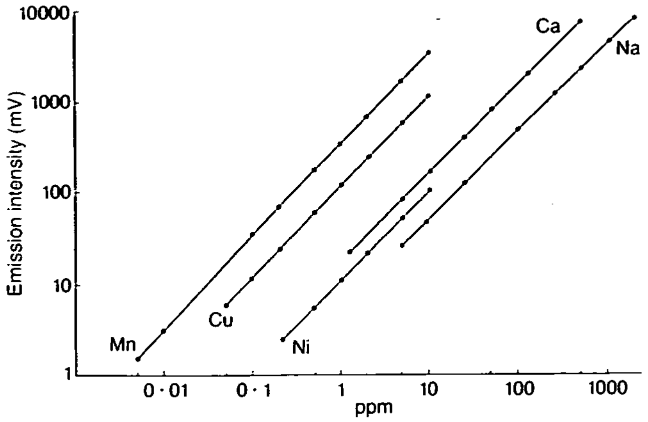


Figure 7. Typical ICP-OES calibration graphs for Na, Ca, Cu, Mn and Ni

Table 1. Typical ICP-OES wavelength programme for the determination of major, minor and trace elements in natural waters

Element	Wavelength (nm)	3σ Detection limits (mg l^{-1})
Na	589.0	0.02
K	766.5	0.15
Ca	315.9	0.006
Mg	279.1	0.03
Si	288.2	0.015
S	180.7	0.1
B	249.7	0.007
Li	670.8	0.002
Sr	407.8	0.0005
Ba	455.4	0.0005
Fe	259.9	0.002
Mn	257.6	0.0006
Cu	324.8	0.002
Zn	213.9	0.002
Cr	267.7	0.006
Ni	231.6	0.02
Al	308.2	0.02
Cd	226.5	0.005
Sc	361.4	0.0005
Y	371.0	0.0005
Be	313.0	0.0005

3.4 Spectral interferences

Two types of spectral interference are recognized in ICP-OES: spectral line coincidence or overlap, and enhanced spectral background caused by recombination continuum radiation or stray light from intense emission lines, typically those of alkaline earth elements. In addition, instrument-specific stray light interferences may arise because of, for example, incomplete optical isolation of adjacent detectors in a multi-channel spectrometer. These interferences must be avoided or quantified and compensated for, if accurate data are to be obtained during the analysis of natural waters.

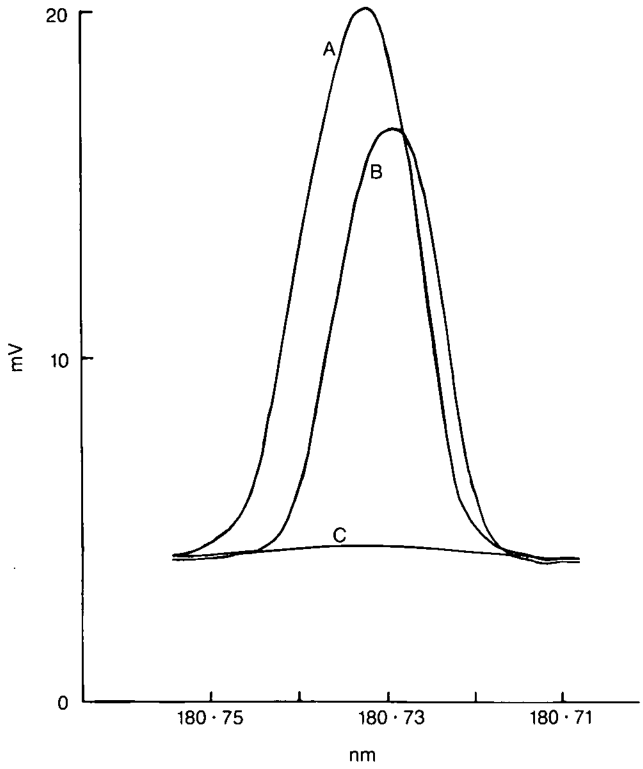


Figure 8. Spectra in the vicinity of 180.73 nm during the aspiration of (A) 8 mg l^{-1} sulphur, (B) 1000 mg l^{-1} calcium, and (C) deionized water, showing almost complete line overlap interference

An example of interference caused by almost complete spectral line overlap is shown in Figure 8. A weak calcium line virtually coincides with the most sensitive sulphur line at 180.73 nm. However, the difference in intensity of the 2 lines is such that a 1000 mg l^{-1} Ca solution produces a signal corresponding to an apparent sulphur concentration of only c 8 mg l^{-1}. Because of the very different relative intensities of the 2 lines, and the fact that these 2 elements occur at similar order of magnitude concentrations in water, correction for this slight interference effect is easily achieved by establishing the relationship between calcium concentration and apparent sulphur signal, and inserting this information in the controlling software. The effect of calcium is thereby automatically subtracted during the analysis of samples.

Interference caused by the partial overlap of the wing of one spectral line on another is illustrated in Figure 9. The wing of the 202.58 nm Mg line overlaps the nearby 202.55 nm Zn line to an extent that, although automatic correction is possible at low Mg concentrations, above c 500 mg l^{-1} Mg it would be wise to choose an alternative Zn line, such as the slightly less intense 213.86 nm line.

Small but significant shifts in spectral background intensity are observed when high concentrations of certain elements are nebulized into the ICP. Radiation is emitted between 190 nm and 220 nm when large amounts of aluminium are present, because of the recombination in the plasma of aluminium ions with free electrons having a continuous energy distribution. This interference can be a serious problem in the analysis of many geological samples, where aluminium is a major constituent, but is insignificant as far as most natural waters are concerned because Al is present only at trace concentrations. Much more important are the enhanced background signals which are observed at certain wavelengths in the presence of calcium and magnesium at concentrations typical of some moderately saline waters. An example of the interference caused by calcium at the 371.03 nm yttrium line is given by Cook (1987).

The magnitude of this type of spectral interference is both analyte and interferent specific (Table 2), and probably also varies between instruments because of differences in optical configuration. While the so-called 'on-peak' mode of correction outlined for the Ca/S interference may be used to minimize the errors caused by background shifts, an alternative 'off-peak' correction procedure may also be used, particularly where the background in the vicinity of the analyte line is relatively flat and unstructured. In addition to making the usual intensity measurement at the correct wavelength (ie on-peak), intensity measurements are made at pre-determined positions on either side of the line by displacing the entrance slit or grating under computer control. A mean background level is then interpolated for each sample and subtracted from the total intensity.

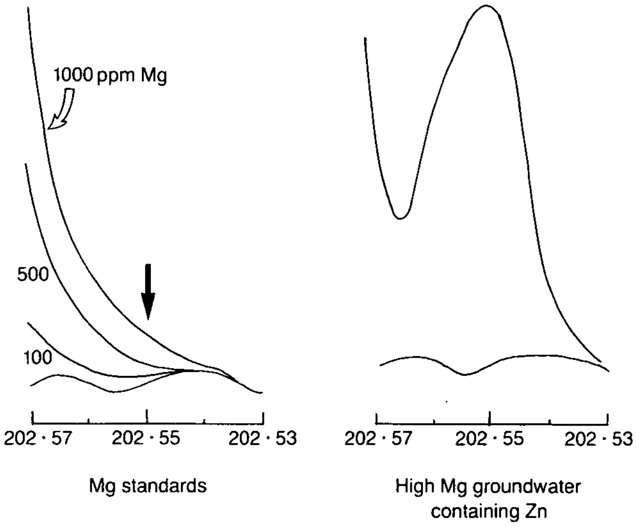


Figure 9. Spectra in the vicinity of the 202.55 nm line of zinc showing interference from the wing of the 202.58 nm line of magnesium at high concentrations

Table 2. Apparent analyte concentrations, in µg l^{-1}, arising from background shifts in ICP-OES when calcium and magnesium solutions are nebulized

Interferent	Cr 267.7	Fe 259.9	La 398.8	Mn 257.6	Si 288.16	Ti 337.3	Y 371.0
	Analyte element and wavelength (nm)						
1000 mg l^{-1} Ca	—	—	200	—	●	130	4
1000 mg l^{-1} Mg	48	25	—	5	350	—	—

● Line overlap interference from a weak Ca line at approximately 288.17 mm

Compared with some types of sample, eg geological and biological materials, natural waters tend to present fewer spectral interference problems. Elements such as aluminium with its recombination continuum and iron with its very line-rich spectrum are typically present as trace constituents rather than major components, and so exert little influence. Precipitation samples and upland surface waters of the type frequently examined in studies of acidic deposition are usually so dilute that interferences from major cations on minor and trace element measurements are minimal. However, all spectral interferences become proportionately more important as the true analyte signal decreases and the detection limit is approached, and thus must be carefully evaluated when reliable trace element data are being sought. Trafford (1987) has described how additional problems of reagent purity have to be taken into account when examining spectral interferences.

3.5 Advantages and limitations

Within the specific context of the analysis of natural waters, as opposed to, say, geological materials or metals, some of the main advantages and limitations of ICP-OES may be summarized as follows.

3.5.1 Advantages

i. Samples are in an ideal form for presentation.

ii. Calibration ranges covering 4–5 orders of magnitude allow samples of widely varying composition, eg rainwater and moderately saline groundwater, to be analysed without further treatment using a single spectral line and calibration function.

iii. Good sensitivity for some minor and trace elements, eg Sr, Fe and Mn, permits their direct determination at environmental concentrations, simultaneously with the major constituents. Samples may be screened for several other trace metals, eg Co, Cu and Zn, at potentially toxic or legislatively undesirable levels.

iv. Elements such as Fe and Al, which can give rise to spectroscopic problems if present at high concentrations, as for example in metallurgical analysis, occur mainly at trace levels in natural waters.

v. The high temperature of the ICP minimizes chemical interferences.

vi. The multi-element capability of the technique, whether simultaneous or rapid sequential, considerably reduces sample handling and the attendant risk of contamination.

vii. Elements such as B and Ba, which for various reasons are difficult or tedious to determine by other techniques, can be determined rapidly by ICP-OES with adequate sensitivity.

3.5.2 Limitations

i. Suspended material may block certain nebulizers.

ii. High concentrations of certain major constituents, particularly calcium and magnesium, give rise to spectral interferences in the determination of trace elements.

iii. The sensitivity of ICP-OES is inadequate to permit the direct determination of many trace elements at the very low concentrations at which they typically occur in natural waters.

iv. Emission intensities relate to total elemental concentration; information on the chemical speciation of the analyte cannot be obtained without additional treatment, eg by HPLC. Data on isotopic composition are not recoverable.

4 Inductively coupled plasma-fourier transform spectrometry (ICP-FTS)

Fourier transform spectrometry (FTS) is a very widely used technique in infra-red spectroscopy, where it has virtually replaced conventional dispersive-based measurement, but its application to the visible and UV regions has been much more limited, partly because of the more demanding mechanical and optical tolerance dictated by the shorter wavelengths. However, in recent years, various workers have been actively exploring the coupling of Fourier transform spectrometers to ICP sources, both for plasma diagnostic studies and as the basis of potentially powerful analytical systems (Faires 1986).

In FTS, a Michelson interferometer replaces the conventional grating spectrometer. Collimated light from the ICP is divided by a beam splitter and reflected from one fixed and one moving mirror before being recombined and reflected to the detector (Figure 10). Differences in path length caused by the moving mirror result in an interference pattern which is related to wavelength and the position of the mirror. The original spectrum is recovered from the interferogram by Fourier transformation of the digitized wave form.

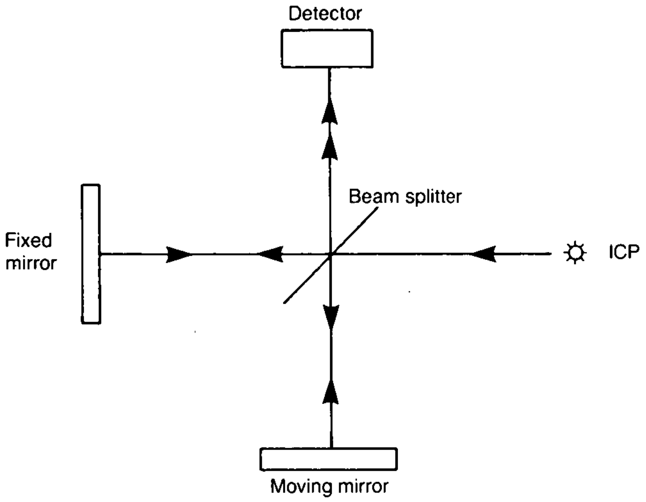


Figure 10. Schematic diagram of an ICP Fourier transform spectrometer

The inherent attractions of FTS are considerable. Spectral information is gathered simultaneously over the entire region of interest, rather than at specific wavelengths corresponding to pre-selected lines. High resolution is attainable and excellent wavelength accuracy is provided by the laser-referenced interferometer. Execution of the Fourier transformation requires significant computing capacity, but the power and speed of modern, small computers allows this to be accomplished relatively rapidly.

In contrast to IR-FTS, where noise is detector-limited, noise in ICP-FTS is source-limited. Consequently, because of the multiplex nature of the technique, noise from the more intense spectral lines is distributed into the spectral baseline. In addition to this so-called multiplex disadvantage, intense emission at certain wavelengths also poses problems through the dynamic range limitations of the detector. Comparisons conducted so far (Stubley & Horlick 1985a) indicate that ICP-FTS detection limits are 1—2 orders of magnitude poorer than those attainable by ICP-OES using a modern polychromator. Stubley and Horlick (1985b) have recently demonstrated that the interposition of a medium resolution monochromator between the ICP and the interferometer, to provide an adjustable optical filter with a bandpass of c 4 nm, can very largely overcome both dynamic range and signal-to-noise limitations. Improvements in detection limits of about one order of magnitude were reported. As a novel departure from the use of the fast Fourier transform algorithm to recover the original spectrum, Ng and Horlick (1985a) have also used cross-correlation techniques to process the interferogram directly. Square-wave, digital, cross-correlation masks of any number of spectral lines of interest can be stored compactly in the computer, and the advent of powerful electronic multiplier chips opens up the possibility of real-time correlation-based data processing and rapid, automatic qualitative analysis by ICP-FTS (Ng & Horlick 1985b).

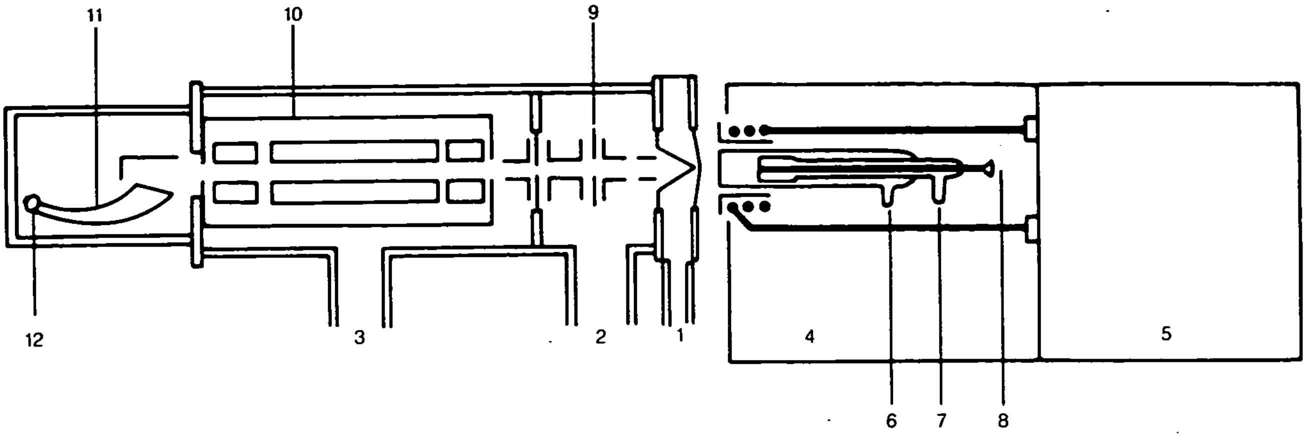
At present, no complete ICP-FTS system is commercially available and studies of the technique are confined to a small number of research laboratories. However, it is understood that at least one major ICP equipment manufacturer will shortly be marketing an ICP-FTS system.

5 Inductively coupled plasma-mass spectrometry (ICP-MS)

The principle of using an atmospheric pressure plasma as an ion source for atomic mass spectrometry was first demonstrated in the early 1970s by Gray (1974, 1975a, b), initially using a DC capillary arc plasma. Because of the severe inter-element and matrix effects experienced with this type of plasma, an ICP source was later substituted (Houk *et al.* 1980; Date & Gray 1981).

A schematic diagram of a typical ICP-MS system is shown in Figure 11. A conventional ICP source is positioned horizontally so that the plasma tail flame plays on a water-cooled, metal cone having a small (0.5—1.1 mm diameter) hole at its tip through which a portion of the ionized gas passes into the vacuum system of a quadrupole mass spectrometer. Considerable research effort continues to be concentrated on elucidating the processes controlling ion transport and recombination which occur in and around this interface between the very hot, atmospheric pressure plasma and the ambient temperature, high-vacuum environment of the mass spectrometer. A major step forward in the development of ICP-MS was the achievement of continuum flow sampling of ions from the bulk plasma, rather than from the cool boundary layer (Gray & Date 1983), and this form of ion extraction is embodied in the 2 commercial ICP-MS systems which have recently become available.

Liquid sample introduction in ICP-MS is fundamentally identical to that in optical ICP spectrometry, and is thus considerably more direct and rapid than that involved in thermal ionization mass spectrometry. Even for complex natural samples, the mass spectra obtained are relatively simple compared with corresponding optical emission spectra, and inherent in the



Arrangement of plasma and mass analyser. 1, 2, 3, Successive vacuum stages; 4, torch housing; 5, radiofrequency matching unit; 6, 7, coolant and plasma gas inlet; 8, sample (injector) gas flow; 9, ion lens; 10, quadrupole analyser; 11, ion detector; and 12, signal output

Figure 11. Schematic diagram of an ICP-MS system. (Redrawn from Gray & Date 1983. Copyright: Royal Society of Chemistry)

technique is the provision of information on the isotopic as well as total elemental composition of samples. This latter feature opens up the possibilities of the wider use of stable isotopic tracers in studies of hydrologic systems and of the use of stable isotope dilution techniques in accurate and precise, low-level, analytical methods.

Spectral interferences in ICP-MS arise from a variety of sources, including plasma gases, solvent, isobaric singly charged analyte ions, doubly charged ions, oxide and other molecular ions. Thus, background spectra show strong peaks at 40 and 41 m/z corresponding to $^{40}Ar^+$ and $^{40}ArH^+$ respectively, which preclude the detection of $^{40}Ca^+$ and $^{41}K^+$. Similarly, peaks corresponding to ions of H, C, N and O, singly or in combination, occur at various m/z values below 81. The significance of these interferences depends upon the relative intensity of the corresponding analyte peak. For example, $^{40}Ar^{14}N^+$ and $^{40}Ar^{16}O^+$ peaks degrade the detection limits for $^{54}Fe^+$ and $^{56}Fe^+$, but do not totally preclude the determination of these isotopes. Interference from ions of even a minor isotope of a major constituent can swamp the signal derived from a trace element in the same sample, eg $^{48}Ca^+/^{48}Ti^+$. In such cases, it is often possible to choose an alternative, interference-free isotope by which to determine the trace element, but some sensitivity may be sacrificed because of its lower abundance.

Careful choice of sample pre-treatment can substantially reduce some molecular ion interferences. McLaren *et al.* (1985) have shown that acidification with HNO_3 rather than HCl is to be preferred in order to avoid interference from chlorine-containing molecular species, such as that of $^{35}Cl^{16}O^+$ on $^{51}V^+$ and $^{40}Ar^{35}Cl^+$ on $^{75}As^+$. Interferences from metal-oxide species (MO^+) have been widely reported, but their origin, magnitude and control are disputed. However, available evidence points to their being produced in the region of the ion extraction zone. In addition, Olivares and Houk (1985) have recently demonstrated that MO^+/M^+ ratios can be related to plasma operating conditions, such as nebulizer gas flow rate and forward power.

Current ICP-MS detection limits under realistic multi-element operating conditions are typically of the order of 0.1 $\mu g\ l^{-1}$ for a wide range of elements. They are characteristically more uniform than those attainable by ICP-OES, to which they are generally superior by 1—2 orders of magnitude.

6 Conclusion

In the 20 years since its initial recognition as a potential spectroscopic source, the ICP has proved to be a stable and powerful vaporization, atomization, excitation and ionization cell. It has been successfully combined with several different modes of spectrometric detection, including direct and Fourier transform optical emission spectrometry, atomic fluorescence spectrometry and mass spectrometry. Used in appropriate combination, these techniques provide the bases of analytical methods by which natural waters may be characterized almost completely for their total elemental and isotopic composition. However, much remains to be achieved in extending the sensitivity of the overall analytical procedures to enable many trace elements to be detected reliably at the sub-ppb concentrations at which they typically occur in the environment.

7 Summary

Traditionally, molecular and atomic absorption spectrometry has been widely used in the analysis of natural waters, with the latter being especially popular for the determination of alkali, alkaline earth and some transition metals. In recent years, the development of the inductively coupled plasma (ICP) as a spectroscopic source has provided the basis of sensitive atomic emission spectrometric techniques utilizing both optical and mass spectrometric detection. The advantages and disadvantages of plasma emission spectrometry for the analysis of natural waters and acidic deposition are reviewed, including instrumentation, sensitivity, sample treatment and interference effects. Utilization of emission in the UV region for the determination of non-metals such as sulphur and phosphorus are discussed.

8 References

Anderson, T.A. & Parsons, M.L. 1984. ICP emission spectra: III. The spectra of the group IIIA elements and spectral interferences due to group IIA and IIIA elements. *Appl. Spectrosc.*, **38,** 625–634.

Anderson, T.A., Forster, A.R. & Parsons, M.L. 1982. ICP emission spectra: II. Alkaline earth elements. *Appl. Spectrosc.*, **36,** 504–509.

Babat, G.I. 1947. Electrodeless discharges and some allied problems. *J. Instn elect. Engrs,* **94,** 27–37.

Baginski, B.R. & Meinhard, J.E. 1984. Some effects of high-solids matrices on the sample delivery system and the Meinhard concentric nebulizer during ICP emission analyses. *Appl. Spectrosc.*, **38,** 568–572.

Boumans, P.W.J.M. 1984. *Line coincidence tables for inductively coupled plasma atomic emission spectrometry.* 2nd ed. Oxford: Pergamon.

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.

British Technology Group. 1984. *Method of and apparatus for the nebulization of liquids and liquid suspensions.* UK Patent Appl. no. 8432338.

Cook, J.M. 1987. Trace element measurements of environmental samples using inductively coupled plasma optical emission spectrometry. In: *Chemical analysis in environmental research,* edited by A.P. Rowland, 50–55. (ITE symposium no. 18.) Abbots Ripton: Institute of Terrestrial Ecology.

Cook, J.M. & Miles, D.L. 1985. Utilisation of emission in the ultra-violet region for the determination of phosphate in geochemical samples by inductively coupled plasma optical emission spectrometry. *Analyst, Lond.*, **110,** 547–549.

Date, A.R. & Gray, A.L. 1981. Plasma source mass spectrometry using an inductively coupled plasma and a high resolution quadrupole mass filter. *Analyst, Lond.*, **106,** 1255–1267.

Ebdon, L. & Cave, M.R. 1982. A study of pneumatic nebulization systems for inductively coupled plasma emission spectrometry. *Analyst, Lond.*, **107,** 172–178.

Faires, L.M. 1986. Fourier transforms for analytical atomic spectroscopy. *Analyt. Chem.*, **58,** 1023A–1034A.

Forster, A.R., Anderson, T.A. & Parson, M.L. 1982. ICP spectra: I. Background emission. *Appl. Spectrosc.*, **36,** 499–503.

Gray, A.L. 1974. A plasma source for mass analysis. *Proc. Soc. anal. Chem.*, **11,** 182–183.

Gray, A.L. 1975a. Mass-spectrometric analysis of solutions using an atmospheric pressure ion source. *Analyst, Lond.*, **100,** 289–299.

Gray, A.L. 1975b. Plasma sampling mass spectrometry for trace analysis of solutions. *Analyt. Chem.*, **47,** 600–601.

Gray, A.L. & Date, A.R. 1983. Inductively coupled plasma source mass spectrometry using continuum flow ion extraction. *Analyst, Lond.*, **108,** 1033–1050.

Greenfield, S., Jones, I.L. & Berry, C.T. 1964. High-pressure plasmas as spectroscopic emission sources. *Analyst, Lond.*, **89,** 713–720.

Houk, R.S., Fassel, V.A., Flesch, G.D., Svec, H.J., Gray, A.L. & Taylor, C.E. 1980. Inductively coupled argon plasma as an ion source for mass spectrometric determination of trace elements. *Analyt. Chem.*, **52,** 2283–2289.

Hulmston, P. 1983. A pneumatic recirculating nebulizer system for small sample volumes. *Analyst, Lond.*, **108,** 166–170.

Hulmston, P. & McKillop, S. 1985. Nebulization characteristics of a microprocessor-controlled recirculating nebulizer for inductively coupled plasma atomic-emission spectrometric analysis of small sample volumes. *Analyst, Lond.*, **110,** 559–562.

Kinniburgh, D.G. & Miles, D.L. 1983. Extraction and chemical analysis of interstitial water from soils and rocks. *Environ. Sci. Technol.*, **17,** 362–368.

Kniseley, R.N., Amenson, H., Butler, C.C. & Fassel, V.A. 1974. An improved pneumatic nebulizer for use at low nebulizing gas flows. *Appl. Spectrosc.*, **28,** 285–286.

Long, S.E. & Snook, R.D. 1983. Electrochemical pre-concentration technique for use with inductively coupled plasma atomic-emission spectrometry. *Analyst, Lond.*, **108,** 1331–1338.

McLaren, J.W., Mykytiuk, A.P. & Berman, S.S. 1985. Applications of inductively coupled plasma mass spectrometry in marine analytical chemistry. *Colloq. Spectrosc. int., 24th, 1985,* 395–396.

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.

Miles, D.L. & Cook, J.M. 1982. The determination of sulphate in natural waters by inductively-coupled plasma emission spectrometry. *Analytica chim. Acta,* **141,** 207–212.

Ng, R.C.L. & Horlick, G. 1985a. A real-time correlation-based data processing system for interferometric signals. *Appl. Spectrosc.*, **39,** 841–847.

Ng, R.C.L. & Horlick, G. 1985b. Correlation-based data processing for an inductively coupled plasma/Fourier transform spectrometer system. *Appl. Spectrosc.*, **39,** 834–840.

Olivares, J.A. & Houk, R.S. 1985. Ion sampling for inductively coupled plasma mass spectrometry. *Analyt. Chem.*, **57,** 2674–2697.

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

Reed, T.B. 1961. Induction-coupled plasma torch. *J. appl. Phys.*, **32,** 821–824.

Stubley, E.A. & Horlick, G. 1985a. Measurement of inductively coupled plasma emission spectra using a Fourier transform spectrometer. *Appl. Spectrosc.*, **39,** 805–810.

Stubley, E.A. & Horlick, G. 1985b. A windowed slew-scanning Fourier transform spectrometer for inductively coupled plasma emission spectrometry. *Appl. Spectrosc.*, **39,** 811–817.

Sturgeon, R.E., Berman, S.S., Desaulniers, A. & Russell, D.S. 1980. Pre-concentration of trace metals from sea-water for determination by graphite-furnace atomic-absorption spectrometry. *Talanta*, **27,** 85–94.

Sturgeon, R.E., Berman, S.S. & Willie, S.N. 1982. Concentration of trace metals from sea-water by complexation with 8-hydroxy-quinoline and adsorption on C_{18}- bonded silica gel. *Talanta*, **29,** 167–171.

Taylor, C.E. & Floyd, T.L. 1981. Inductively coupled plasma-atomic emission spectrometric analysis of environmental samples using ultrasonic nebulization. *Appl. Spectrosc.*, **35,** 408–413.

Thompson, M. & Pahlavanpour, B. 1979. Reduction of tin and germanium to hydrides for determination by inductively-coupled plasma atomic emission spectrometry. *Analytica chim. Acta*, **109,** 251–258.

Thompson, M., Pahlavanpour, B., Walton, S.J. & Kirkbright, G.F. 1978a. Simultaneous determination of trace concentrations of arsenic, antimony, bismuth, selenium and tellurium in aqueous solution by introduction of the gaseous hydrides into an inductively coupled plasma source for emission spectrometry. Part I. Preliminary studies. *Analyst, Lond.*, **103,** 568–579.

Thompson, M., Pahlavanpour, B., Walton, S.J. & Kirkbright, G.F. 1978b. Simultaneous determination of trace concentrations of arsenic, antimony, bismuth, selenium and tellurium in aqueous solution by introduction of the gaseous hydrides into an inductively coupled plasma source for emission spectrometry. Part II. Interference studies. *Analyst, Lond.*, **103,** 705–713.

Thompson, M., Pahlavanpour, B. & Thorne, L.T. 1981. The simultaneous determination of arsenic, antimony, bismuth, selenium and tellurium in waters by an inductively coupled plasma/volatile hydride method. *Wat. Res.*, **15,** 407–411.

Thompson, M., Ramsey, M.H. & Pahlavanpour, B. 1982. Water analysis by inductively coupled plasma atomic emission spectrometry after a rapid preconcentration. *Analyst, Lond.*, **107,** 1330–1334.

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.

Uehiro, T., Morita, M. & Fuwa, K. 1984. Vacuum ultraviolet emission line for determination of aluminium by inductively coupled plasma atomic emission spectrometry. *Analyt. Chem.*, **56,** 2020–2024.

Vos, G., van Dordrecht, P. & ten Bras, P.W. 1984. Preconcentration of trace metals for their determination with ICP-AES. *Fortschr. atomspektrom. Spurenanal.*, **1,** 491–499.

Wendt, R.A. & Fassel, V.A. 1965. Induction coupled plasma spectrometric excitation source. *Analyt. Chem.*, **37,** 920–922.

Winge, R.K., Fassel, V.A., Peterson, V.J. & Floyd, M.A. 1985. *Inductively coupled plasma-atomic emission spectroscopy. An atlas of spectral information.* (Physical sciences data, vol. 20.) Amsterdam: Elsevier.

Wohlers, C.C. 1985. Experimentally obtained wavelength tables for the ICP. *ICP Inf. Newsl.*, **10,** 593–688.