

ATOMIC SPECTROMETRY UPDATE—ENVIRONMENTAL ANALYSIS

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This review describes developments in atomic spectrometry relevant to environmental analysis reported in *Atomic Spectrometry Updates References* in *JAAS*, Volume 1 (other than in the initial supplement). Thus it follows the review published last year (86/1814) and is also concerned with the analysis of the atmosphere, waters, effluents, soils, plants, fertilisers and related materials. The full references, names and address of authors can be readily found from the *Atomic Spectrometry Updates References* in *JAAS*, Volume 1, however, as an additional service to readers an abbreviated form of each literature reference quoted (except for those to Conference Proceedings) is given at the end of the review. This innovation is in response to the suggestions of readers, and other comments as to possible improvements in future reviews are always welcome. It is hoped that succeeding reviews in this series will be extended to include X-ray spectrometry although this current review is principally concerned with the applications of AAS, AFS and AES (with arcs, sparks, plasmas, flames, furnaces and lasers) as well as ICP-MS. The format of the tables is as last year, in addition to the abbreviations listed elsewhere, Hy is used to show where hydride generation was used and S, L and G in the "Analyte form" column signify solid, liquid or gaseous sample introduction, respectively.

It can be seen that the application of atomic spectrometry to environmental samples has remained a lively if mature area of scientific endeavour. Interest continues to grow in rapid multi-element approaches, particularly those which can readily be automated. All of which suggests that the demand for trace element information on environmental samples continues to grow but that tight financial constraints on environmental monitoring are now ubiquitous.

1. AIR ANALYSIS

The use of atomic spectrometry for the monitoring of trace elements in atmospheres and airborne particulates is now well established and widely practised. The literature in this area has thus reached a maturity in which dramatic developments are rare and most papers are devoted to methods that will

improve the efficiency of monitoring programmes. Prominent amongst such developments are simultaneous multi-element determination and direct analyses which minimise sample preparation. Table 1 summarises the papers concerning air analysis reported in *Atomic Spectrometry Updates References* in *JAAS*, Volume 1. Some papers deal with the direct determination of gases and vapours, including mercury, but the majority are concerned with the measurement of trace metals in airborne particulates.

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Table 1. SUMMARY OF ANALYSES OF AIR AND PARTICULATES

Element	λ/nm	Matrix	Concentration	Technique; atomisation; analyte form	Sample treatment/comments	Reference
As	—	Workplace air	From $0.3 \mu\text{g m}^{-3}$	AA; ETA; L	Collect on AgNO_3 impregnated 37-mm backup pad and 37-mm 0.8- μm cellulose acetate filter impregnated with Na_2CO_3 , glycerol solution. Wet ash pads in concentrated HNO_3 (150 °C, 2 h) using $\text{Mg}(\text{NO}_3)_2$ (5%) as ashing aid. Use Ag matrix modifier in ETA-AAS	86/C454
As	—	Atmospheric samples	—	AA; ETA; G	Separate As compounds on 0.5-m GC column packed with Tenax	86/C927
Be	313	Airborne dust	From 3.6 ng	AE; laser spark; S	Dust collected on filter subjected to direct laser spark	86/213
C	193.1	Nitrogen gas	—	AE; MIP; G	Mix sample gas with He and introduce into the MIP. Quantify by standard additions	86/C870
Cd	—	Air particulates	—	AA; ETA; S	Use a porous graphite probe both as a filter and atomisation substrate for ETA-AAS	86/C928
Cd	—	Laboratory air	3 ng m^{-3}	AA; ETA; S	Use of an impaction ETA-AAS system for direct and nearly real-time measurement	86/1067
Cd	—	Particulates	pg	AA; ETA; S	Collect on 0.45- μm filter for direct Zeeman-effect AAS using a graphite boat	86/1925
Co	—	Furnace dust	—	AA; —; L	Remove Pb by PbCl_2 precipitation and Zn and Fe by HCl - triisooctylamine - IBMK extraction	86/1740
Co	—	Metallurgical dusts	—	AA; —; L	Remove Cu, Fe, Pb and Zn in two-stage separation, by IBMK from 6 M HCl and 0.1 M tetrahexylammonium iodide in IBMK from 3 M HCl as ion pairs	86/1951
Cr	—	Furnace dust	—	AA; —; L	See Co, ref. 86/1740	86/1740
Cr	—	Welding fumes	From 5 ng	AA; —; L	Water soluble Cr^{III} and Cr^{VI} separated by anion exchange HPLC using 0.03 M Na_2CO_3 (pH 11) eluent	86/1768
Cr	—	Airborne particulates	—	AE; ICP; S	Collect on glass-fibre filter, place in a microboat, dissolve in 2% HF , electrothermally vaporise residue into ICP	86/1805
Cr	—	Metallurgical dusts	—	AA; —; L	See Co, ref. 86/1951	86/1951
Cu	—	Air particulates	—	AA; ETA; S	See Cd, ref. 86/C928	86/C928
Cu	—	Laboratory air	100 ng m^{-3}	AA; ETA; S	See Cd, ref. 86/1067	86/1067
Cu	—	Soldering fumes	< 1 p.p.m.	AA; —; —	Pre-concentration on Dowex A-I and semi-automatic FI	86/1316
Cu	—	Particulates	pg	AA; ETA; S	See Cd, ref. 86/1925	86/1925
Dy	—	ICP exhaust gases	—	AE; ICP; L	Particulate matter in ICP exhaust gases collected in a cascade impactor using Dy as an inactive species to give information on particle size distribution	86/1634
Ga	294.4	Flue dust	$50\text{--}830 \mu\text{g g}^{-1}$	AA; ETA; L	Heat 0.5-g sample in PTFE beaker with 30 ml H_2O - HNO_3 - HF (5 + 1 + 1) to dryness (1–1.5 h). Cool add 20 ml H_2O + 5 ml HNO_3 , re-heat 5–10 min and filter. Make up to 100 ml in 1% HNO_3 . Use $\text{Mg}(\text{NO}_3)_2$ matrix modifier	86/1631
H	656.3	Nitrogen gas	—	AE; MIP; G	Mix sample gas with He and introduce into He MIP. Quantify by standard additions	86/C870
Hg	253.7	Air	From 0.01 ng	AE; MIP; G	Filtered air passed into reducing solution (CdCl_2 + SnCl_2 in 1 M NaOH) and then over Au wire. Wire heated to release Hg into surfatron discharge	86/6
Hg	—	Airborne particulates	$0.018\text{--}0.93 \text{ ng m}^{-3}$	AA; CV; —	Collect on quartz-fibre filter with high-volume sampler. Determine by CV-AAS via Au wire trapping - heat vaporisation pre-concentration	86/235
Hg	—	Air	From 0.1 μg	AE; arc; S	Precipitate PbS from Pb acetate with Na_2S in aqueous solution, adjust to pH 1. Collect Hg in PbS and pack into hollow Fe electrode for d.c. arc determination	86/748
Hg	—	Atmospheric samples	—	AA; ETA; G	Separate Hg compounds on 0.5-m GC column packed with Tenax	86/C927
Hg	253.7	Air	—	AA; CV; G	Comparison of collectors. Gold coated sand recommended, desorbed at 800 °C, to second collector and thence for direct AAS	86/964
Hg	—	Air and workplace	$0.08\text{--}16.7 \mu\text{g m}^{-3}$	AA; —; —	Sample pre-concentration with Richter's absorption device	86/965
Hg	—	Air	0.4 ng m^{-3}	AA; —; G	Long-path (km) atmospheric monitoring by high-resolution differential absorption	86/1659

Table 1. SUMMARY OF ANALYSES OF AIR AND PARTICULATES—*continued*

Element	λ/nm	Matrix	Concentration	Technique; atomisation; analyte form	Sample treatment/comments	Reference
Hg	—	Air	—	AF; CV; G	Hg, HgCl_2 , MeHgCl and Me_2Hg sequentially collected on Chromosorb W treated with HCl gas, Tenax GC, Carbosieve B and Au wire. Pyrolysis used to produce elemental Hg	86/1769
Hg	—	Air	$0.2 \mu\text{g m}^{-3}$	AA; CV; G	Prepare pure MnO_2 from KMnO_4 - MnSO_4 , pack into glass column and pass through 50–500 l of air. Reduce collected Hg with H_2SO_4 (1 M) - SnCl_2 (5%) - $\text{NH}_2\text{OH} \cdot \text{HCl}$ (5%)	86/1770
Hg	—	Particulates	pg	AA; ETA; S	See Cd, ref. 86/1925	86/1925
Hg	—	Particulates	—	—	Filter snow, use GC-AAS to speciate Hg compounds	86/1940
Mn	—	Laboratory air	30 ng m^{-3}	AA; ETA; S	See Cd, ref. 86/1067	86/1067
Mn	—	Soldering fumes	$<1 \text{ p.p.m.}$	AA; —; —	See Cu, ref. 86/1316	86/1316
Mn	—	Furnace dust	—	AA; —; L	See Co, ref. 86/1740	86/1740
Mn	—	Metallurgical dusts	—	AA; —; L	See Co, ref. 86/1951	86/1951
N (as N_2)	299.3, 297.7, 298.3, 298.9	Gases from micro-Dumas combustion <i>e.g.</i> , of phytoplankton	$1\text{--}110 \mu\text{g}$	AES; MIP; G	Oven dry sample overnight at 25°C . CaO (15 mg) + CuO - Cu (15 mg) added. After evacuation to $<2 \times 10^{-4}$ Torr, sealed tubes combusted at 500°C for 6 h. Tubes inserted directly into r.f. cavity and excited at 27.5 MHz at up to 20 W. ^{15}N abundance calculated from emission peaks for $^{28}\text{N}_2$, $^{29}\text{N}_2$ and $^{30}\text{N}_2$	86/1632
Ni	—	Air particulates	—	AA; ETA; S	See Cd, ref. 86/C928	86/C928
Ni	—	Furnace dust	—	AA; —; L	See Co, ref. 86/1740	86/1740
Ni	—	Metallurgical dusts	—	AA; —; L	See Co, ref. 86/1951	86/1951
O	777.2	Nitrogen gas	—	AE; MIP; G	Mix sample gas with He and introduce into He MIP. Quantify by standard additions	86/C870
O	144.1, 148.6	Gas phase	—	—	Use of O_2 absorption of H emission lines by metastable O_2 ($a'\Delta_g$) produced by reacting alkaline H_2O_2 with Cl_2	86/1837
P	213.6	Airborne particulates	$38\text{--}146 \text{ ng m}^{-3}$	AE; ICP; S	Collect on glass- or quartz-fibre filters with high-volume sampler. Extract with water ($>24 \text{ h}$), heat for $>3 \text{ h}$ with 5 ml of HNO_3 + 0.5 ml of HClO_4 . Filter and make up to 30 ml	86/1690
Pb	283.3	Atmospheric aerosols	$0.3\text{--}0.6 \text{ ng}$	AA; ETA; S	Collect on cellulose filters (1.2- μm pore size) with a low volume collector. Cut out 2 mm diameter discs, place on pyrolytic graphite microboats for direct ETA-AAS	86/C459
Pb	—	Air particulates	—	AA; ETA; S	See Cd, ref. 86/C928	86/C928
Pb	—	Air	—	AA; F, air - H_2 ; G	Two-stage thermal desorption for organolead compounds collected on polymeric absorbents prior to GC-AAS	86/1082
Pb	—	Air	$0.06\text{--}205 \text{ ng m}^{-3}$	AA; F, air - H_2 ; G	Directly coupled GC-AAS compared with ICI wet-chemical method for alkylleads	86/1096
Pb	—	Soldering fumes	$<1 \text{ p.p.m.}$	AA; —; —	See Cu, ref. 86/1316	86/1316
Pb	—	Air	—	AA; F, air - H_2 ; G	Propylate ionic alkyllead species and determine these with tetraalkyllead species by GC-AAS	86/1629
Sb	—	Airborne particulates	—	AA; Hy; L	Digest with HF - HNO_3 - H_2SO_4 - KMnO_4 or HF - HNO_3 - H_2SO_4 , add KI to reduce interferences	86/1673
Tl	276.8	Incinerator ash	$2.8 \mu\text{g g}^{-1}$	AA; ETA; L	To 600 mg add 1 ml of H_2O and 1 ml of H_2SO_4 (concentrated), evaporate to dryness. Cool add 1.3 g of LiBO_2 , muffle at 400°C , then at 950°C for 15 min. Dissolve melt in 50 ml of 10% HNO_3 at 100°C . Use Zeeman-effect background correction	86/1620
Various (9)	—	Sintering furnace dusts	—	AE; ICP; —	—	86/61
Various	—	Pyrolysis products	—	AE; ICP; G	GC-ICP analysis of combustion and pyrolysis products	86/68
Various (15)	—	Airborne particulates	—	AA; F; L	Collect on high-volume polystyrene filters, separate into four fractions by sedimentation, Na_2CO_3 - $\text{Na}_2\text{B}_4\text{O}_7$ fusion, acid dissolution	86/315
Various	—	Airborne particulates	—	AE; ICP; —	Review (12 refs.)	86/326

Table 1. SUMMARY OF ANALYSES OF AIR AND PARTICULATES—*continued*

Element	λ/nm	Matrix	Concentration	Technique; atomisation; analyte form	Sample treatment/comments	Reference
Various	—	Airborne particulates	—	AE; ICP; G	Decompose by fluorination with XeF_4 in an autoclave. Sweep volatile products to an Ar ICP	86/341
Various (10)	—	Human lungs	0.002– 2500 $\mu\text{g g}^{-1}$	AA; —; —	—	86/420
Various (11)	—	Trimethyl- and triethyl-arsine	5×10^{-8} – $5 \times 10^{-5}\%$	AE; arc; —	Pre-concentrate by matrix removal with CCl_4 in presence of 0.1 M HCl	86/743
Various	—	Air filters	—	AF; ICP; —	Prepare according to NIOSH PC and M method No. 173	86/C830
Various	—	Air particulates	—	—	Comparison of FAAS, ETA-AAS, ICP-AES and ion chromatography	86/C911
Various	—	Respiratory gases	—	—	New gas analyser based on measurement of light emitted by excited atoms or ions in a GDL, <i>e.g.</i> , O, N, CO_2 , He and N_2O determined	86/1333
Various	—	Particulates	—	AE; —; S	Particulates collected directly on to an Ag coated polycarbonate filter that is vaporised by a d.c. plasma discharge	86/1397
Various (5)	—	Incinerator ash	From 11 pg l^{-1}	AE; ICP; L	Ash dissolved in HNO_3 - HClO_4 for Cd, Cu, Ni and Zn but $\text{Li}_2\text{B}_4\text{O}_7$ fusion preferred for Cr	86/1466
Various	—	Fly ash	—	AE; ICP; L	Use of air-cooled low flow ICP and method of standard additions	86/1605
Various (9)	—	Urban aerosols	—	AE; ICP; —	—	86/1806
Various (14)	—	Particulates	—	AE; ICP; L AA; ETA; L	Soluble fractions of snow analysed	86/1940
Various (8)	—	Air particulates	—	AA; ETA; S	Collect on a porous graphite probe used direct as atomiser probe in graphite furnace	86/C1978

1.1. Determination of Gases

Plasma emission spectrometry is well suited to the direct determination of gases. Hanamura *et al.* (86/C870) have demonstrated the use of a single-electrode atmospheric-pressure He microwave plasma to determine trace O, H and C in "pure" nitrogen gas. The sample was mixed with He and introduced directly to the plasma. A higher flow-rate of plasma gas (He , 5 l min^{-1}) was used than is usual to minimise permeation of analyte species from the surrounding air. For the same reason thick-walled polythene tubing had to be used to connect the plasma to the gas cylinder. Standard additions, of O_2 , H_2 and CCl_4 vapour, were used to quantify the method. In an elegant approach to the determination of ^{15}N abundance, Timperley and Priscu (86/1632) used micro-Dumas combustion in a tube that was directly inserted into a specially designed microwave cavity. Using an inexpensive generator (27.5 MHz, 20 W) and an AA spectrometer to monitor the N spectra, they needed only 30 s to record a three-peak spectrum. Those considering the use of ICP-AES for molecular gas determination will find the report of Goldfarb and Goldfarb (86/68) useful. They studied the influence of H_2 , O_2 , N_2 , H_2O , hydrocarbons and carbon oxides on an Ar ICP. Molecular gases at concentrations above 0.1% influenced the plasma properties, and these effects required further investigation, but the potential for GC-ICP to obtain molecular composition, *e.g.*, for combustion and pyrolysis products, was demonstrated.

Research into the utility of *other excitation techniques* for gas analysis, including metastable transfer emission spectrometry (MTES), continues. The technique has been used to monitor the purity of nitrogen (86/1835). Hood and Niemczyk (86/1389) used MTES to determine molecules containing S and P based on the emissions of NS and PN from the active nitrogen flow. A new spectrometer for respiratory gas analysis based on AE from a d.c. glow discharge has been described by Fraser and Turney (86/1333). Simultaneous measurement of O, N, CO_2 , He and N_2O was possible in 100 ms at a sampling

rate of less than 20 ml min^{-1} . Good agreement was found in the clinical setting between results from the new spectrometer and from a mass spectrometer. A novel laser intracavity photothermal detector has also been described (86/1663). The sample absorbed the pump laser power within the cavity of a He - Ne laser causing modulation in the gain and hence output power. This new technique appears to offer a dynamic sensitivity range, linear response and stability which make it attractive for quantitative trace analysis of gases and potentially as a GC detector.

1.2. Determination of Mercury

The importance of environmental monitoring for Hg continues to inspire novel and often highly sensitive new technologies. Only one new *direct method* was proposed (86/1659). This involved a high-resolution differential absorption spectrometer with a long path length especially designed for pollution monitoring. The source was a broad-band lamp and the detector, a dispersive, fast-scanning optical receiver, was a few kilometres away from the source. The system appeared to have several advantages over the more established laser band systems, both in terms of cost and sensitivity.

The past year saw considerable interest in different approaches for the *collection and pre-concentration* of mercury vapour, *e.g.*, established sorption tubes (86/965) and novel collectors such as manganese dioxide (86/1770) or lead sulphide (86/748). It is not clear whether any of these possess unique advantages. Dumarey *et al.* (86/964) compared the collection and thermal desorption efficiency of activated charcoal, silver and gold. Activated charcoal and silver-coated sand were found not to give quantitative recovery. Gold-coated sand showed quantitative collection at sampling flow-rates up to 5 l min^{-1} , although the sorption capacity was limited to 10–30 ng cm^{-2} . Thermal release of Hg at 800°C was rapid, complete and reproducible from the gold substrate. Thermally activated gold wire was the favoured collector when Hg was determined using a surfatron (Hubert, J.,

Moisan, M., and Ricard, A., *Spectrochim. Acta, Part B*, 1979, **34**, 1) (86/6). Air was first passed via a filter into a reducing solution and then the Hg vapour was captured on the gold wire in a glass tube. The Hg was released into the MIP (2450 MHz, 50 W) by heating to 500 °C in a stream of Ar.

Methods for the speciation of mercury are described in section 1.4.

1.3. Determination of Airborne Particulates

The *direct collection* of airborne particulates on an atomiser substrate for subsequent solid sample analysis not only offers advantages of speed of analysis but, in minimising sample pre-treatment, reduces the possibility of contamination. One approach is to insert directly the filter used to collect the particulates into a graphite furnace for ETA-AAS. In such a case Zeeman-effect background correction has been advocated to reduce high backgrounds (86/1925). In a comparison of wet ashed and directly inserted filters, Moura *et al.* (86/C459) showed good correlation between the methods, with similar standard deviations. They noted a need to reduce the N₂ flow in the graphite furnace to about 28 m³ h⁻¹ during the drying stage to prevent dragging of the cut filter discs along the furnace. Sugimae and Barnes (86/1805) placed glass-fibre filters in a microboat for electrothermal vaporisation into an ICP. They found that treatment *in situ* with 2% HF prevented glass formation, which otherwise limited the sensitivity. Some workers now collect the sample directly in the atomiser or, in the case of Chakrabarti *et al.* (86/C928, 86/C1978), on to an atomiser probe. A detachable porous graphite probe was installed in an air filtration unit to collect atmospheric particulates. The probe head was then inserted into a modified graphite furnace for probe atomisation ETA-AAS.

Sneddon (86/1067) has further described his *direct impaction* ETA-AAS system (see *J. Anal. At. Spectrom.*, 1986, **1**, 2R) for nearly real-time laboratory air monitoring. A connecting faceplate has now been added to the impactor to facilitate more convenient standardisation. Similarly, Marinescu (86/673) has extended his alternative electrostatic precipitation approach (see *J. Anal. At. Spectrom.*, 1986, **1**, 2R) by proposing alternative graphite furnace designs utilising either a circular or boat-type L'vov platform or a coaxial tube insert for delayed atomisation of the sample. In each case the electrostatic sampling takes place *in situ*. A study of the collection mechanism of an electrostatic accumulation furnace for ETA-AAS showed the filter operated in the Trichel pulses region, and most of the captured species were in a region 4 mm wide around the tip of the active electrode (86/2017). The use of a silver-coated polyethylene filter to collect particulates has again been reported (86/1397, see also *J. Anal. At. Spectrom.*, 1986, **1**, 2R). The sample was then vaporised in a discharge between two electrodes placed diametrically opposite. This arrangement was useful for exciting particulate material, though generally it was not superior to the original arrangement using an annular anode and a cathode concentrically beneath the filter.

More conventional *electrothermal atomisation* AAS procedures are still popular. Original reports were largely confined to unusual elements, *e.g.*, the determination of Tl in city waste incineration fly ash (86/1820) where an acid pre-treatment, LiBO₂ fusion, followed by ETA-AAS with Zeeman-effect background correction, was reported to give excellent recovery. A similar furnace system was used by others to determine Ga in phosphorus flue dust, stainless-steel flue dust and coal fly ash (86/1631). The use of the 294.4-nm wavelength and Mg(NO₃)₂ matrix modifier gave good agreement with NAA results. Hydride generation techniques have been less popular in air analysis, largely because of the limited sample size available and interference problems. A comparison of wet digestion methods for Sb in ambient particulates was largely directed to reducing interferences in the subsequent hydride

generation stage (86/1673). While As, Bi and Se all interfered, the addition of KI (50 000 fold excess) was reported to eliminate Ni interference.

The attractions of *inductively coupled plasma* spectrometry are largely the capability for multi-element analysis and relative freedom from interference. This area was reviewed by Miyazaki (86/326). The convenience and accuracy of ICP-AES has been demonstrated on CRMs, *e.g.*, by Taylor *et al.* (86/1466) on the European Community Bureau for Reference Materials (sample BCR No. 176) city waste incinerator ash and by Marquat *et al.* (86/1806) on IAEA reference atmospheric aerosol materials. The running cost of an ICP is often cited as a disadvantage of the technique and there is thus interest in torches that operate at low Ar flows. de Galan and his colleagues (86/1605) have demonstrated such a torch using 1 l min⁻¹ of Ar and air cooling. Fly ash was amongst the reference materials used to demonstrate the practical utility of this torch. Another problem with ICP-AES may be spectral interferences and ICP-AFS has been advocated as a way of overcoming these in industrial hygiene air-filter analysis (86/C830). For some elements ICP-AES offers the most viable atomic spectrometric technique, *e.g.*, for P, and Dokiya *et al.* (86/1690) have compared ICP-AES, ion chromatography and solution spectrophotometry for the determination of P in airborne particles. The latter technique gave consistent results with ICP-AES when a K₂S₂O₈ decomposition procedure was employed. Ion chromatography was used to determine PO₄³⁻ in an aqueous extract. In atmospheric particulate matter, 10–20% of the P was water soluble, 90–95% of this being PO₄³⁻.

Truly *novel methods* are less frequently applied in air analysis. Cremers and Radziemski (86/213) reported a method to determine Be on 0.8-µm pore-size filters using a laser spark. The spark was formed on the filter by a cylindrical lens. Although the spot was only 0.1 mm wide and 4–8 mm long, a larger area could be sampled by rotating the filter. The sparks were generated at 10 Hz using a pulsed and Q-switched Nd:YAG laser, usually at 125 mJ per pulse. This represents a power density of 10⁹ W cm⁻². The emission of the Be II doublet at 313 nm was measured by a PMT, and the signal time resolved and averaged. While a detection limit of 3.6 ng of Be on a 32 mm diameter filter was obtained, particle size effects may limit the method to rapid, semi-quantitative screening. Rigin (86/341) has developed an elegant sample decomposition procedure by fluorination with XeF₄ in an autoclave. The gases were then atomised in an Ar ICP and monitored by AFS with a non-dispersive polychromator. The method was applied to dust analysis and compared with more tedious alternatives such as organic extraction (APDC - IBMK) and GC using volatile trifluoro-derivatives.

To assess the nature of any hazard from airborne dusts *particle size information* is essential. Assessment of the trace metal burden in the respirable range by lung analysis is generally regarded as rather posthumous. Normal ranges from autopsy samples of 125 human lungs have been determined (86/420). In eight samples some of the trace metal levels were above the normal levels, indicating occupational exposure. Cadmium concentrations in non-smokers were 0.1–0.2 µg g⁻¹ but in smokers were 2–3 µg g⁻¹, correlating with daily tobacco consumption. These levels fell to the normal range for non-smokers after about 10 years abstinence from tobacco. Kapeller *et al.* (86/315) separated airborne particulates into four size fractions by sedimentation and then analysed these by Na₂CO₃ - Na₂B₄O₇ fusion, followed by FAAS. Oishi (86/61), however, characterised sintering furnace dusts in the iron industry by ICP-AES, ion microanalysis and total secondary ion monitoring. High concentrations of Al, Ca, Co, K, Na and Si were detected on the surface of a particle and volatile elements such as Cd, Cu and Pb showed higher relative concentrations in the smaller particles. In a study of interest to ICP-AES users, particularly those who may have to

analyse toxic or radioactive samples, Davies and Jefferies (86/1634) examined the size of particulate matter in an ICP exhaust. The objective was to define the filtration requirement for glove-box installation and Dy was used as the tracer element with a five-stage cascade impactor for collection. The majority of the particulates were of sub-micrometre size with a median diameter of 0.1–0.2 μm , which was unaffected by concomitant elements.

1.4. Speciation Studies

As noted last year (*J. Anal. At. Spectrom.*, 1986, 1, 2R) interest in speciation of the forms of trace metals in the air continues to grow. For many elements toxicity and availability are critically dependent on chemical form. The development of GC-AAS instrumentation for this purpose has again been the subject of review (86/1082). Both flame and electrothermal atomisers were detailed for elements such as As, Pb and Sn. Particular attention was paid to the determination of organolead species by a coupled GC-AAS system (reviewed last year, *J. Anal. At. Spectrom.*, 1986, 1, 2R) interfaced with a two-stage thermal desorption system. Procedures for the separation and determination of dimethylmercury, methylmercury, ethylmercury, dimethylarsenic and methylarsenic (as their bromides) in atmospheric samples using a Tenax column and AAS have been discussed (86/C927).

The speciation of *mercury compounds* is still popular. Schroeder and Jackson (86/1769) have reported their methodology by which Hg, HgCl_2 , MeHgCl and Me_2Hg were sequentially collected from air samples, desorbed by pyrolysis and then detected by resonance AFS. Chromosorb W treated with HCl vapour, Tenax GC, Carbosieve B and gold wire were the favoured absorbents. Organomercury compounds were speciated in filtered snow by GC-AAS (86/1940). It was considered that snow was a useful indicator of atmospheric pollution in winter-time Toronto. The ratio of Hg in particulates to free Hg in the air is a valuable measurement and has

been made by Nakagawa (86/235). In Chiba, Japan, the ratio of Hg in particulates to total Hg was 0.07–10.2% with an average value of 2%. Particulate Hg tended to be higher in winter and this increased the above ratio by about a factor of five. This appeared to be due to the presence of more fine particles in winter.

Advances in *alkyllead measurements* continued to be reported by Harrison and his very active group. Simultaneous determination in the gas and aerosol phase of tetraalkyllead by GC-AAS and of total organolead by the wet chemical ICI method, showed differences suggesting the presence of tri- (and or di-) alkyllead in both rural and urban air (86/1096). These ionic alkyllead species can be determined by derivatisation to tetraalkyllead forms followed by GC-AAS. The same group have now proposed a propylation technique for this purpose (86/1629). Some advantages over the established butylation procedure were suggested.

The importance of *arsenic speciation* is well known. Pederson (86/C454) has proposed a sampling method using a silver nitrate impregnated filter and a sodium carbonate-glycerol impregnated filter. The latter collected arsenic trioxide vapour and particulate As and the former, used as a back-up pad, collected arsine. The device was successfully evaluated in a lead-acid battery manufacturing plant using ETA-AAS to complete the analysis.

Part of the hazard of welding fumes comes from the emission of chromium in the hexavalent state. Suzuki and Serita (86/1768) have proposed a method for speciating Cr^{III} and Cr^{VI} in simulated welding fumes. The species were separated by anion-exchange HPLC equipped with both UV absorption and AA detection. The eluent was 0.03 M Na_2CO_3 (pH 11) at a flow of 2 ml min^{-1} , Cr^{III} having been converted into the EDTA chelate prior to the chromatography. Excellent recoveries and nanogram level detection limits were reported. It can only be expected that interest in such speciation studies will grow in air analysis as in other branches of trace metal analysis.

2. WATER ANALYSIS

The number of publications in the water analysis field remains high and inspection of the published literature (summarised in Table 2) reveals an extensive and diverse level of activity. Undoubtedly high sensitivity has been a priority and much effort has been given to the development of enrichment/separation schemes which extend the detection performance of plasma and furnace techniques to the ng l^{-1} level. The interest in automated pre-concentration which was reported in last year's review (86/1814) has, unexpectedly, not been maintained. Developments of practical significance include the increased use of certified reference waters for validation of methodology and the use of quality control measures in routine analysis. Several reviews on trace element analysis of natural waters with special reference to ICP-AES have been published (86/326, 86/358, 86/396).

2.1. Sample Preparation

A wide range of pre-concentration techniques have been used to enhance the performance of atomic spectrometric procedures and critical reviews on the subject have been presented (86/C447, 86/C997). There has been considerable activity in the development of *new resin systems*. More recently the use of a chelate-forming cellulose (iminodiacetic acid-ethylcellulose) for the collection of trace metals (including U) from waters and ammonium citrate and acetate solutions has been reported (86/1302, 86/1446). Methodology was devised for ICP-AES and ETA-AAS and for the latter technique detection capabilities in drinking water for Cd and Pb of 0.1 and 1 $\mu\text{g l}^{-1}$, respectively, were reported. More recently the same

group reported on the use of a polyurea polyaminoacetic-polyiminodiacetic acid (PPA) chelating resin for the pre-concentration of heavy metals and REEs (86/C868, 86/2018). Resin uptake from synthetic solutions and natural waters was quantitative and analyte recoveries, after elution with strong acid, were ca. 100%. The PPA resin was suitable for repeated column use and, in contrast to that for Chelex 100, undesirable swelling did not occur when the ionic form was altered. A polyacrylic ester resin, XAD-7, has been applied to the pre-concentration of Cd, Cr, Cu and Pb in drinking water samples prior to determination by ETA-AAS (86/C163, 86/361). A two-column procedure was devised to account for complexation by humic substances. A macroporous weak-base anion exchanger, diethylaminoethyl-Sephadex A-25 has been used to separate trace metals (Cd, Cu and Pb) complexed with humic and fulvic acids from the simple cationic species in fresh water samples (86/1098). The sorbed metal complexes were quantitatively desorbed with 4 M HNO_3 prior to determination by ETA-AAS. A sensitive procedure for the determination of Co in fresh waters was based on pre-concentration on an anion-exchange resin (Dowex 1-X8 converted into the nitroso-R salt form) and determination by AAS after elution with strongly acidic titanium chloride solution (86/320). The procedure yielded a pre-concentration factor of 100 and was applicable to Co concentrations in the range 0.01–1 $\mu\text{g l}^{-1}$. Complex formation of Al^{III} with 1,2-dihydroxybenzene-3,5-disulphonic acid and retention on a macroporous anion-exchange resin provides an important route for enrichment of trace Al in water samples (86/338). Application to river waters and haemodialysis fluids gave

Table 2. SUMMARY OF ANALYSES OF WATERS AND EFFLUENTS

Element	λ/nm	Matrix	Concentration	Technique; atomisation; analyte form	Sample treatment/comments	Reference
Ag	—	Waters	—	AA; F; L	See Cr, ref. 86/C842	86/C842
Ag	—	Natural waters	—	AA; ETA; L	Studies on sample preservation and pre-treatment	86/968
Ag	—	Water	—	AA; F; L	Atom-trapping technique for 100-fold sensitivity improvement	86/1304
Ag	328.0	Water	—	AA; ETA; L	Sample (50 ml), after adjustment to pH 3.3, passed through ion-exchange filter-paper	86/1367
Ag	—	Natural waters	—	AA; ETA; L	Chelation - solvent extraction with dithizone and IBMK	86/1774
Ag	—	Drinking water	—	AE; ICP; L	Direct determination and comparison with ETA-AAS after solvent extraction. Reference water analysed	86/1907
Al	396.15	Water	—	AE; ICP; L	Direct analysis with automatic background correction	86/47
Al	396.15	River water	—	AE; DCP; L	Complex formation with 1,2-dihydroxy-benzene-3,5-disulphonic acid and retention on macroporous anion-exchange resin	86/338
Al	—	Natural waters	—	AA; ETA; L	Use of H_3PO_4 as matrix modifier	86/1628
As	—	Waters	—	AA; F; G	HPLC and hydride generation used for determination of inorganic and organic As species	86/14
As	—	River water, waste water	—	AF; F; G	Procedures for determination of main oxidation states using hydride generation	86/321
As	—	River water	—	AA; ETA; G	Collection of hydrides at pressures up to 0.4 atm	86/381
As	—	Water	—	AA; ETA; L	Conversion into hydride in graphite furnace	86/400
As	193.77, 197.20	Sea water, brine	—	AE; ICP; G	Hydride generation study on responses of oxidation states in presence of KBr, KI and HCl	86/C596
As	—	Natural waters	—	AA; ETA; G	Speciation procedure based on GC and subsequent pyrolysis in quartz atomiser	86/C927
As	—	Waters	—	AA; ETA; L	Evaluation of several matrix modifiers (Ni, Pd and Pt). Analysis of reference water	86/1037
As	—	Synthetic waters	—	AE; ICP; G	Simplex optimisation of conditions for hydride generation	86/1839
As	—	Sea water	—	AA; F; G	Digestion with $\text{K}_2\text{S}_2\text{O}_8$ and hydride generation for As speciation. Data reported for Japan Sea and Pacific Ocean samples	86/1859
Au	—	Natural waters	—	AA; ETA; L	Evaporation, digestion in aqua regia and extraction into IBMK	86/94
Au	—	Natural waters	—	AA; ETA; L	See Ag, ref. 86/1774	86/1774
Au	—	Natural waters	—	AA; ETA; L	Pre-concentration by anion-exchange batch extraction	86/2004
B	518.0	Brine	$0.95\text{--}28\text{ g l}^{-1}$	AA; F; L	Sample, after dilution and acidification, was passed through ion-exchange (strongly acidic) column	86/1958
Be	—	Natural waters	—	AA; ETA; L	Extraction of acetylacetonate complexes into toluene	86/407
Be	—	Surface waters	—	AA; ETA; L	Assessment of interferences using ordinary and Ta-coated graphite tubes	86/C592
Bi	—	Waters	—	AA; F; L	Pre-concentration with 2,5-dimercapto-1,3,4-thiotriazole bonded on silica gel	86/1858
Bi	223.06	Waste water	—	AE; ICP; G	Hydride generation	86/C1127
C	247.9	Water	—	AE; ICP; G	Dissolved organic carbon converted into CO_2 after passage through heated quartz tube filled with Cu oxide	86/C644, 86/1675
Non-ionic surfactants	—	River water	—	AA; F; L	Indirect method based on complex formation with potassium zinc tetrathiocyanate	86/1433
Phenol	—	Water	$6 \times 10^{-7}\text{--}0.9 \times 10^{-5}\text{ M}$	AA; F; L	Indirect method based on bromination and complex formation between Cd^{2+} and I^-	86/12
Ca	422.7	Mineral waters	—	AA; F; L	Use of $\text{N}_2\text{O} - \text{C}_2\text{H}_2$ to eliminate chemical interferences	86/C590
Ca	393.37	Brine	—	AE; ICP; L	Comparison of ICP-AES and ETA-AAS	86/1417
Cd	—	Sea water	—	AA; ETA; L	Chelation - solvent extraction based on mixed dithiocarbamate - Freon TF system	86/13
Cd	—	Waters	—	AA; F; L	Comparison of FAAS, spectrophotometry with dithizone and emission spectrometry	86/64
Cd	—	Drinking waters	—	AA; F; L	Comparison with isotope dilution mass spectrometry	86/1348

Table 2. SUMMARY OF ANALYSES OF WATERS AND EFFLUENTS—*continued*

Element	λ/nm	Matrix	Concentration	Technique; atomisation; analyte form	Sample treatment/comments	Reference
Cd	—	Sea water	—	AA; ETA; L	Intercomparison of ASV with ETA-AAS after pre-concentration (either chelation - extraction with dithiocarbamate and organic solvent or use of Chelex 100 column)	86/1695
Cd	—	Sea water	—	AA; F; L	Pre-concentration with sulphhydryl cotton	86/1857
Ce	—	Radioactive wastes	—	AE; ICP; L	Specification of instrumentation for remote analysis of highly active wastes	86/C505
Cl	—	Brines	—	—; —; —	Molecular absorption spectrophotometry (using AA instrumentation and flow-through absorption cell) in gas phase after oxidation of sample	86/1284
CN	—	Waters	—	AA; F; L	Indirect method based on formation of cuprocyanide in FI system	86/1284
Co	—	Fresh water	0.01–1 $\mu\text{g l}^{-1}$	AA; F; L	Pre-concentration on anion-exchange resin, Dowex 1-X8 (converted into the nitroso-R salt) and elution with strongly acidic TiCl_3	86/320
Co	—	Water	—	AA; ETA; L	Coprecipitation - flotation using hydrated ZrO and sodium oleate	86/C483
Co	—	Natural waters	—	AA; ETA; L	Micro-solvent extraction with Capriquat and <i>o</i> -dichlorobenzene	86/1943
Cr	—	Waters	—	AA; F; L	Chelation - solvent extraction with APDC and IBMK for determination of Cr^{III} and Cr^{VI}	86/63
Cr	—	River water	—	AA; F; L	Coprecipitation techniques for speciation of Cr. Concentration of organic Cr^{III} used to determine status of effluent discharge	86/398
Cr	—	Waters	1–200 $\mu\text{g l}^{-1}$	AA; F; L	Use of Ce^{IV} for oxidation of Cr species prior to chelation - extraction with APDC - IBMK	86/C842, 86/C1481
Cr	—	Natural water	—	AA; F; L	Methodology for dissolved and particulate Cr using a coprecipitation technique	86/1097
Cr	—	Surface water	—	AA; ETA; L	Direct determination	86/1414
Cr	—	Water	—	AA; ETA; L	Reaction of Cr^{III} with trifluoroacetylacetone in graphite furnace	86/1449
Cr	—	Waters	—	AE; ICP; L	On-line HPLC technique for fractional determination of Cr^{III} and Cr^{VI}	86/1949
Cu	324.7	Water	—	AA; F; L	Determination of free and EDTA-complexed Cu^{2+} using FI system with ion-exchange column	86/37
Cu	—	Water	—	AA; ETA; L	See Co, ref. 86/C483	86/C483
Cu	—	River water	—	AA; F; L	Selective adsorption of Cu at pH 3.5 on keratin gel	86/1010
Cu	—	Sea water	—	AA; F; G	Use of high temperature ($>1500\text{ K}$) GC system	86/1068
Cu	—	River water	—	AA; F; L	Chelation - solvent extraction with capric acid - benzylamine and <i>n</i> -heptane	86/1303
Cu	—	Sea water	—	AA; ETA; L	See Cd, ref. 86/1695	86/1695
Cu	—	Sea water	—	AA; F; L	See Cd, ref. 86/1857	86/1857
Cu	—	Sea water	—	AA; F; L	Chelation - extraction with 5-chlorosalicylaldehyde and CHCl_3	86/1948
F	—	Water	—	AE; ICP; L	Indirect method based on measurement of La emission. Lanthanum - alizarin - fluoride complex extracted into organic solvent after addition of lanthanum alizarin complexone to water sample (50 ml)	86/C1269
Fe	—	Pore water	—	AA; ETA; L	Operational characteristics of portable sampling system	86/11
Fe	—	Sea water	—	AA; F; L	Distribution of total and particulate Fe in Atlantic Ocean samples	86/1300
Fe	—	Sea water	—	AA; F; L	See Cu, ref. 86/1948	86/1948
Hg	—	Sea water	—	AA; cold vap.; G	Distribution of dissolved and particulate Hg in the 0–100 m layer in Atlantic and Mediterranean Sea	86/8
Hg	253.65	Drinking water	—	AE; ICP; G	Electrothermal vaporisation and use of $(\text{NH}_4)_2\text{S}$ as matrix modifier	86/221
Hg	253.65	Sea water	—	AE; ring discharge plasma; G	Amalgamation - reduction	86/C473
Hg	—	Water	—	AA; ETA; G	Electrochemical pre-concentration on to Pt wire cathode and subsequent atomisation in graphite cup	86/693
Hg	—	Water	—	AA; F; G	See As, ref. 86/C927	86/C927
Hg	—	Drinking water	—	AA; ETA; L	Thermal pre-treatment of platform with Pd	86/1040
Hg	253.7	Lake water	—	AE; MIP; G	Cold-vapour generation and collection with Au amalgamation technique	86/1624
Hg	—	Natural water	—	AE; MIP; G	Reduction - amalgamation on Au wool using FI system	86/1692

Table 2. SUMMARY OF ANALYSES OF WATERS AND EFFLUENTS—*continued*

Element	λ/nm	Matrix	Concentration	Technique; atomisation; analyte form	Sample treatment/comments	Reference
Hg	253.7	Natural water	—	AA; cold vap.; G	Cold-vapour technique	86/1957
I	178.28, 206.16	Waters	—	AE; ICP; L	Sample (500 ml) treated with NaNO_2 and H_2SO_4 and evolved I_2 extracted into xylene (5 ml) for iodide determination. A pre-reduction with ascorbic acid for iodate determination	86/C1269
Ir	—	Sea water	—	AA; ETA; L	Isolation of the anionic form on ion-exchange resins	86/1625
Mg	285.2	Mineral water	—	AA; F; L	See Ca, ref. 86/C590	86/C590
Mg	279.55	Brine	—	AE; ICP; L	See Ca, ref. 86/1417	86/1417
Mn	—	Pore waters	—	AA; ETA; L	See Fe, ref. 86/11	86/11
Mn	—	Sea water	—	AA; ETA; L	See Cd, ref. 86/13	86/13
Mn	—	Drinking water	—	AA; F; L	Complexation - solvent extraction with capric acid - <i>o</i> -phenanthroline and heptane	86/248
Mn	—	Waters	—	AA; F; L	Extraction of the ion pair formed between benzohydroxamic acid - Mn complex and trioctylmethylammonium	86/1693
Mn	—	Sea water	—	AA; F; L	Chelation - solvent extraction using 2-hydroxy-1-naphthaldehyde and CHCl_3	86/1874
N ¹⁵	—	Water	—	AE; ICP; G	Measurement of ¹⁵ N percentage abundance using AA spectrometer and inexpensive r.f. generator	86/1632
N	—	Waters	—	AA; F; L	Indirect determination of NO_3^- and NO_2^- using continuous ligand - ligand extraction in a FI system. The ion-pair complex (Cu - neocuproine - NOX) extracted into IBMK	86/1950
Ni	—	Water	—	AA; ETA; L	See Co, ref. 86/483	86/483
Ni	—	Sea water	—	AA; F; L	See Mn, ref. 86/1874	86/1874
P	—	Natural waters	—	AA; ETA; L	Coprecipitation using $\text{Zr}(\text{OH})_2$. Use of cation-exchange column to remove Al, Ca, Fe and Si	86/1941
Pb	—	Sea water	—	AA; ETA; L	Determination of Pb (dissolved and particulate) in 105 samples from North Sea and NE Atlantic Ocean. Comparison data by ASV	86/318
Pb	—	Waters	—	AA; F; L	See Cr, ref. 86/C842	86/C842
Pb	—	Waste water	—	AA; ETA; L	Tetraalkyl Pb compounds extracted into hexane, converted into water-soluble halides and re-extracted into dilute HNO_3	86/969
Pb	—	Drinking waters	—	AA; F; L	See Cd, ref. 86/1348	86/1348
Pb	—	Water	—	AA; F; L	Speciation of Pb based on <i>in situ</i> ethylation with sodium tetraethylborate, trapping of alkyllead molecules and thermal desorption into quartz furnace	86/1390
Pb	—	Water	—	AA; F; G	Derivatisation with propyl MgCl for determination of tetraalkyllead and ionic alkyllead species	86/1629
Pb	—	Sea water	—	AA; ETA; L	See Cd, ref. 86/1695	86/1695
Pt	—	Sea water	—	AA; ETA; L	See Ir, ref. 86/1625	86/1625
S	—	Snow	—	AE; ICP; L	See Various, ref. 86/357	86/357
S	180.73	Natural waters	0.1–100 $\mu\text{g l}^{-1}$	AE; ICP; G	Addition of HCl (1%) for evolution of H_2S	86/C595
Sb	—	River water, waste water	—	AF; F; G	See As, ref. 86/321	86/321
Sb	206.83	Sea water, brine	—	AE; ICP; G	See As, ref. 86/C596	86/C596
Sb	—	Sea water	—	AA; ETA; G	Generation of SbH_3 and trapping in graphite furnace at 460 K	86/720
Sb	—	Waste water	—	AE; ICP; G	Generation of hydride in presence of malic or tartaric acid for determination of Sb^{III} and Sb^{V}	86/1365
Sb	—	Synthetic water	—	AE; ICP; G	See As, ref. 86/1839	86/1839
Sb	—	Natural waters	70–460 ng l^{-1}	AA; F; G	Hydride generation and collection in cold trap. Differential determination of main oxidation states	86/1942
Se	—	Waste water	—	AA; ETA; G	Hydride generation and use of radiotracer to identify sources of error	86/62
Se	—	River water, waste water	—	AF; F; G	See As, ref. 86/321	86/321
Se	—	Drinking water	—	AA; F; G	Methods for Se^{IV} and total Se	86/319
Se	—	River water	—	AA; ETA; G	See As, ref. 86/381	86/381
Se	—	Waters	—	AA; ETA; G	Hydride generation, pre-concentration on Chromosorb W and thermal desorption into quartz furnace. Radioisotope used for optimisation of the individual steps	86/389

Table 2. SUMMARY OF ANALYSES OF WATERS AND EFFLUENTS—*continued*

Element	λ/nm	Matrix	Concentration	Technique; atomisation; analyte form	Sample treatment/comments	Reference
Se	196.03	Sea water, brine	—	AE; ICP; G	See As, ref. 86/C596	86/C596
Se	—	Sea water	—	AA; ETA; L	Direct determination using Zeeman-effect AAS	86/C832
Se	—	Sea water	—	AA; ETA; L	Evaluation of matrix modifiers	86/C837
Se	—	Natural water	—	AA; F; G	Addition of sulphanilamide to prevent interferences in hydride generation	86/1437
Se	—	Synthetic water	—	AE; ICP; G	See AS, ref. 86/1839	86/1839
Se	—	Sea water	—	AA; ETA; G	Hydride generation and trapping in graphite furnace at 600 °C. Reference waters analysed	86/1922
Se	—	Natural waters	—	AA; F; G	See Sb, ref. 86/1942	86/1942
Sn	—	Natural waters	—	AA; F; L	Evaluation of sample introduction techniques for speciation of organotin using HPLC - FAAS	86/C142, S/919
Sn	—	Sea water	—	AA; ETA; L	Extraction of Bu_3Sn^+ into toluene and use of either $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ as matrix modifier or L'vov platforms for enhanced sensitivity	86/684
Sn	—	Water	—	AA; F; L	Use of ion exchange and extraction with tropolone - toluene for pre-concentration. Comparison with ASV	86/1375
Sn	—	Natural waters	—	AA; ETA; G	Speciation procedure based on hydride generation, chromatographic separation and atomisation in quartz furnace	86/1807
Sn	—	Natural waters	—	AA; F; L	Speciation procedures based on ion-exchange chromatography and hydride generation. Survey analyses of estuaries	86/C2038
Sr	460.8	Sea water	—	AE; F; L	Dilution	86/401
Tc	—	Radioactive waste leachates	—	AA; ETA; L	Use of glovebox-adapted AAS facility for analysis of highly active waste. Comparison with ICP-AES data	86/C523
Te	—	Sea water	—	AA; ETA; L	Coprecipitation with $\text{Mg}(\text{OH})_2$, injection of NaBH_4 and trapping of hydride in graphite furnace. Pre-reduction used to differentiate between Te^{IV} and Te^{VI} . Data reported for North Atlantic Ocean	86/1772
Tl	—	Drinking water	—	AA; F; L	See Cd, ref. 86/1348	86/1348
U	—	Radioactive waste	—	AE; ICP; L	See Ce, ref. 86/C505	86/C505
U	—	Groundwater, mine waters	2–300 mg l^{-1}	AE; DCP; L	Matrix-matched standards containing sodium acetate used to compensate for severe enhancements	86/671
U	—	Effluent	—	AE; ICP; L	Direct determination and comparison with radiochemical and fluorimetric methods	86/C1268
U	—	Sea water	—	AA; ETA; L	See Various, ref. 86/1302	86/1302
U	409.01	Sea water	—	AE; ICP; L	Amidoxime resin used for extraction of U. Comparison made with spectrophotometry and fluorimetry	86/1877
W	—	Brines	—	AE; ICP; L	Matrix matching and internal standardisation techniques utilised	86/343
Zn	—	Sea water	—	AA; F; L	See Mn, ref. 86/1874	86/1874
Various (11)	—	Drinking water	—	AA; ETA; L	Procedures for determination of trace elements	86/10
Various (26)	—	Natural waters	—	AE; ICP; L	Routine determination by sequential ICP-AES	86/9
Various (6)	—	River water	—	AA; F; L	Preparation and characterisation of a chelating resin coated with 1-(2-pyridylazo)-2-naphthol (Cd, Cu, Fe, Ni, Pb and Zn)	86/C128
Various	—	Rain water	—	MS; ICP; L	Direct determination (Al, Fe, Mn and Zn)	86/C152
Various	—	Water	—	AE; ICP; L	On-line pre-treatment using column packed with an amidoxime resin	86/C158
Various	—	Waters	—	AE; ICP; S	Electrochemical pre-concentration in conjunction with a direct insertion technique	86/C161, 86/374
Various (4)	—	Drinking water	—	AA; ETA; L	Pre-concentration with a polyacrylic ester resin, XAD-7. Reference water analysed (Cd, Cr, Cu and Pb)	86/C163, 86/361
Various	—	Natural waters	—	AE; ICP; L	Comparison of ICP-AES with ion chromatography	86/C174
Various	—	Sea water	—	MS; ICP; L	Pre-concentration and matrix isolation by adsorption on silica - oxine	86/C164, 86/2039
Various	—	Natural waters	—	AA; ETA; L AE; ICP; L	Comparison of ICP-AES and ETA-AAS	86/C180
Various	—	Natural waters	—	MS; ICP; L	Assessment of ICP-MS for routine analysis	86/C182

Table 2. SUMMARY OF ANALYSES OF WATERS AND EFFLUENTS—*continued*

Element	λ/nm	Matrix	Concentration	Technique; atomisation; analyte form	Sample treatment/comments	Reference
Various	—	Water, effluents	—	AE; ICP; G	Electrothermal vaporisation for sample introduction	86/C187
Various	—	Water	—	AA; F; L	Method development using FI techniques	86/200
Various (17)	—	Natural waters	—	AE; ICP; L	Inter-laboratory comparison of FAAS,	86/219
Various (15)	—	Sea water, estuaries	—	AA; F; L	ICP-AES and molecular spectrophotometry	86/237, 86/238
Various	—	Water	—	AA; ETA; L	Survey of metal concentrations in estuaries	86/249
Various (21)	—	Water	—	AA; F, ETA; L	Chelation - solvent extraction of rare earths using $\text{C}_{18}\text{H}_{37}\text{NH}_2$ and CHCl_3 - ethanol	86/C271
Various	—	Natural waters	—	AE; ICP; L	Use of ICP-AES and AAS for water analysis	86/C278
Various (7)	—	Natural waters	—	AA; ETA; L	Use of stabilised temperature platform and Zeeman-effect AAS for direct analysis	86/322
Various	—	Sea water	—	AE; ICP; L	Pre-concentration on sulphhydryl cotton in the presence of tartaric acid (Ag, Cd, Cu, Hg, Pb and Zn)	86/324
Various (4)	—	Natural waters	—	AA; F; L	Coprecipitation with $\text{Fe}(\text{OH})_2$ (REEs and Th)	86/325
Various	—	Natural waters	—	AE; ICP; L	Pre-concentration with 2-mercaptobenzothiazole loaded on glass beads (Cd, Co, Pb and Zn)	86/326
Various (5)	—	Brines	—	AE; ICP; L	Review on ICP-AES	86/343
Various	—	Snow	—	AE; ICP; L	See W, ref. 86/343	86/357
Various	—	Waters	—	AE; ICP; L	Direct analysis of melted snow samples with emphasis on determination of Ca, Mg, P, S and heavy metals. Reference water analysed	86/358
Various (6)	—	Sea water	—	AE; ICP; L	Review	86/360
Various	—	Waters	—	AE; ICP; L	B, Ca, Mg, Na, S and Sr determined after 10-fold sample dilution. Reduction in interelement interferences and improved nebuliser stability	86/396
Various	—	Natural waters	—	AA; F; L	Pre-concentration on to metal hydroxide [$\text{Fe}(\text{OH})_3$] coated cellulose	86/397
Various	—	Natural waters	—	AE; ICP; L	Review of pre-concentration techniques	86/C447
Various	—	Sea water	—	—; —; —	Assessment of interferences in the determination of REEs	86/C457
Various (4)	—	Water	—	AA; ETA; L	Analytical conditions for analysis with the FANES system (Al, Cu, Fe and Ni)	86/C507
Various	—	Natural water	—	AE; DCP; S	Use of evaporation, electrochemical pre-concentration and sorption for enhanced sensitivity	86/C591
Various	—	Spring water	—	AE; hollow cathode; S	Evaporation to dry residue	86/C593
Various	—	Natural waters	—	AE; ICP; S	Pre-concentration on to silica immobilised oxine for XRF determination	86/C600
Various (10)	—	Water	—	AE; ICP; L	HPLC (cation-exchange column) technique used for speciation of polyvalent cations	86/C643
Various (6)	—	Sea water	—	AA; ETA; L	Chelation - extraction with <i>m</i> -tetra-(<i>p</i> -sulphonatophenyl)porphine and IBMK (Cd, Co, Cu, Mn, Ni and Pb)	86/687
Various (20)	—	Natural waters	—	AA; F, ETA; L	Size fractionation techniques for determination of elements associated with particulate and colloidal matter	86/688
Various	—	Natural waters	—	AE; ICP; L	Application of ICP-MS to hydrogeochemical research. Use of isotope dilution techniques	86/C754
Various	—	Natural waters	—	MS; ICP; L	Assessment of instrumental techniques for use in water quality programmes	86/C757
Various (9)	—	Water	—	—; —; —	Electrochemical pre-concentration on to hanging Hg drop with subsequent vaporisation in graphite furnace	86/C867
Various	—	Water	—	AE; ICP; G	Electrothermal vaporisation for sample introduction	86/C894
Various	—	Waste water	—	AE; MIP; G	Electrothermal vaporisation for sample introduction	86/C895
Various (4)	—	Water	—	AE; ICP; G	Comparison of FAAS, ETA-AAS and ion chromatography (Al, Cd, Mn and Pb)	86/C911
Various (17)	—	Sea water	—	AA; F, ETA; L	Zr coprecipitation procedure with pre-concentration factor of 20	86/967
Various	—	Reference waters	—	AE; ICP; L	Analysis of "interference" quality control samples	86/C992
Various	—	Natural waters	—	AE; ICP; L	Review of enrichment techniques	86/997

Table 2. SUMMARY OF ANALYSES OF WATERS AND EFFLUENTS—*continued*

Element	λ/nm	Matrix	Concentration	Technique; atomisation; analyte form	Sample treatment/comments	Reference
Various (6)	—	Natural waters, drinking water	—	AA; F; L	Pre-concentration with 2,2'-dipyridyl-4-amino-3-hydrazo-5-mercapto-1,2,4-trizolehydrazone supported on silica gel (Cd, Co, Cu, Ni, Pb and Zn)	86/1026
Various	—	Sea water	—	AA; F; L	Pre-concentration using SRAFIION NMRR ion exchanger. U extracted from acidic eluent with TOPO - cyclohexane	86/1069
Various (3)	—	Water	—	AA; ETA; L	Separation of metals complexed with humic substances by sorption on a weak-base anion exchanger (diethylaminoethyl-Sephadex A25) (Cd, Cu and Pb)	86/1098
Various (14)	—	Sea water	—	AA; ETA; L	Comparison of solvent extraction - ETA-AAS, Zeeman-effect ETA-AAS (matrix modification) and ASV	86/1099
Various (8)	—	Reference waters	—	MS; ICP; L	Assessment of accuracy and precision of ICP-MS procedures	86/C1108
Various	—	Waters	—	—; —; —	Review of FI techniques	86/C1142
Various (13)	—	Synthetic water	—	AE; ICP; L	FI system with activated alumina for pre-concentration of metal ions	86/C1144
Various	—	Waste water	—	AE; ICP; L	Quality control considerations	86/C1197
Various (20)	—	Waste waters	—	AE; ICP; L	Inter-laboratory comparison. Reference waters analysed	86/C1199
Various (17)	—	Rain, runoff water	—	AE; ICP; L	Dedicated instrumentation for analysis of samples from coal-fired power station. Automated recalibration and correction techniques utilised	86/C1201
Various (4)	—	Sea water	—	AA; ETA; L	Use of ascorbic acid for matrix modification (Mn, Mo, Pb and V)	86/1216
Various (25)	—	Rain	—	AE; ICP; L	Survey analyses (3500 samples) to identify sources of acid precipitation	86/C1234
Various (12)	—	Natural waters	—	AE; ICP; L	Coprecipitation with Co and APDC for 100-fold pre-concentration	86/1263
Various (5)	—	Natural waters, reference waters	—	AE; ICP; L	Quality control measures specified (Ca, Fe, Mg, Mn and Na)	86/C1270
Various (14)	—	Effluents	—	AE; DCP; L	Treatment of samples with mixed buffer solution and internal standardisation	86/C1271
Various (11)	—	Lake water	—	AE; ICP; L	Pre-concentration by chelation with oxine followed by adsorption on a Sep-Pak C ₁₈ cartridge	86/1301
Various (3)	—	Sea water, drinking water	—	AA; ETA; L	Pre-concentration with chelating resin, iminodiacetic acid ethylcellulose (Cd, Pb and U)	86/1302
Various (13)	—	Water	—	AE; F; L	Laser enhanced ionisation	86/1315
Various (7)	—	Waste water	—	AA; F; L	Samples treated with HNO ₃ and evaporated to dryness. Residue dissolved in buffer solution (pH ca. 4) and extracted into IBMK	86/1347
Various	—	Sea water	—	AA; ETA; L	Slow-flow column extraction using Chelex 100	86/1386
Various (9)	—	Sea water, waste water	—	AE; ICP; L	Chelation - solvent extraction with mixed carbamate and diisobutyl ketone. Ultrasonic nebulisation of extract. Reference water analysed	86/1413
Various	—	Waste water	—	AE; ICP; L	Influent samples of treatment plant treated with HNO ₃ - H ₂ O ₂ , followed by centrifugation - filtration. XRF used for analysis of solid phases	86/1434
Various (9)	—	Waste water	—	AE; ICP; L	Complexation of trace elements with APDC and filtration with activated carbon-lined filter (Bi, Cd, Cu, Cs, In, Ni, Pb, Tl and Zn)	86/1435
Various	—	Water	—	AE; ICP; L	Pre-concentration with chelating resin, iminoacetic acid ethylcellulose	86/1446
Various (13)	—	Sea water	—	AE; ICP; L	Pre-concentration (200-fold) using Chelex 100 resin column	86/1467
Various	—	Natural waters	—	MS; ICP; L	Optimisation and performance characteristics of ICP-MS. Reference waters analysed	86/C1474
Various (7)	—	Water	—	AA; F; L	See Cr, ref. 86/C1481	86/C1481
Various (4)	—	Rain	—	AE; ICP; L	Monthly deposition data reported (Ba, Ca, Mg and Sr)	86/C1530
Various	—	Water	—	AA; F; L	FI system with semi-micro ion-exchange column for separation of free and complexed metal ions	86/C1549
Various	—	Reference water	—	AE; ICP; L	Fourier transform spectrometer	86/C1552

Table 2. SUMMARY OF ANALYSES OF WATERS AND EFFLUENTS—*continued*

Element	λ/nm	Matrix	Concentration	Technique; atomisation; analyte form	Sample treatment/comments	Reference
Various (4)	—	Water	—	AA; ETA; L	Comparison between Zeeman-effect and deuterium arc background correction techniques	86/C1594
Various (12)	—	Sea water	—	AE; ICP; L	Coprecipitation with $\text{Ga}(\text{OH})_3$ for >200-fold pre-concentration	86/1618
Various (11)	—	Drinking water, rain	—	AE; ICP; L	FI system with Chelex 100 mini-column for on-line pre-concentration	86/1671
Various	—	Waste water	—	AE; ICP; L	Evaluation of operational parameters; use of peristaltic pump, sample dilution and internal standardisation to obtain reliable data	86/1674
Various	—	Waters	—	AA; F; L	Review of FI	86/1680
Various (6)	—	Sea water	$0.2\text{--}200\ \mu\text{g l}^{-1}$	AE; ICP; L	Pre-concentration with column containing chelating resin (D401) (Co, Cu, Fe, Ni, Pb and Zn)	86/1691
Various (24)	—	Rain, snow	—	AE; ICP; L	Evaporation of 1-l sample using a rotary evaporator incorporating PTFE vessel	86/1694
Various	—	Waters	—	AA; ETA; L	Review of Zeeman-effect AAS	86/1724
Various (4)	—	Sea water	—	AA; ETA; L	Chelation - solvent extraction with APDC and diisobutyl ketone	86/1773
Various (18)	—	Sea water	—	AE; ICP; L	Pre-concentration on silica gel supported oxine resin	86/1808
Various (13)	—	Waste water	—	AE; ICP; L	Low-flow, low-power sample introduction - excitation system evaluated. Internal standardisation and matrix matching investigated. Reference waters analysed	86/1809
Various	—	Waters	—	—	Review	86/1814
Various (8)	—	Waters	—	AA; F; L	Sorption pre-concentration with NaDDC	86/1827
Various	—	Simulated water	—	AA; ETA; L	Direct determination using delayed atomisation cuvette and aerosol sampling device	86/1920
Various	—	Lake water	—	AA; ETA; L	Collection of suspended matter on Millipore filter ($0.45\ \mu\text{m}$) and direct analysis using graphite boat technique	86/1925
Various (7)	—	Reference waters	—	AA; F; L AE; ICP; L	Pre-concentration on to oxine - cellulose column. Reference waters analysed (Cd, Co, Cu, Fe, Mn, Ni and Zn)	86/1946
Various	—	Marine samples	—	MS; ICP; L	Assessment of calibration procedures	86/C1971
Various (9)	—	Mine waters, reference waters	—	AF; ICP; L	Direct analysis for Cd, Cu, Fe, K, Li and Zn; 100-fold dilution for Ca, Mg and Na	86/1983
Various	—	Waters	—	AE; ICP; L	Enrichment of trace metals with a polyurea polyaminoacetic - polyiminodiacetic acid chelating resin (Ag, Cd, Co, Cu, La, Mn, Pb Zn and REEs)	86/C868, 86/2018
Various (7)	—	Water	—	AE; ICP; L	FI system with activated alumina for enrichment of oxyanions	86/2019
Various (13)	—	Brines	—	AE; arc; L	Electrochemical pre-concentration on to hanging Hg drop	86/2022
Various (10)	—	Saline solutions	—	AA; F; L	Chelation - extraction using APDC and IBMK	86/2025

recoveries of *ca.* 100% at the $1\ \mu\text{g l}^{-1}$ level. A separation and enrichment procedure for trace elements in water samples (drinking water, mineral water and sea water) based on complexation with APDC and filtration with an activated carbon-lined filter was reported (86/1435). Sample volumes of 100 ml–10 l were processed and over-all precision for FAAS and ICP-AES measurements was 4% RSD at the $\mu\text{g l}^{-1}$ level. An ion-exchange filter-paper has been used for the trace enrichment of Ag (86/1367). Sample volumes of typically 50 ml were passed through the filter and after the paper had dried a disc was punched out and subjected to AAS measurement in an electrothermal atomiser.

The development of schemes based on the use of *complexing agents immobilised on suitable substrates* has continued to receive attention. Silica gel supported oxine remains a popular system (86/C600, 86/1808, 86/1858) but new approaches

include oxine-cellulose (86/1946) and metal hydroxide-cellulose (86/397). For the latter, iron(III) or indium hydroxide fixed on cellulose was used to retain trace elements at the ng l^{-1} level. The element distribution coefficients between the adsorbent and strongly saline solutions were of the order $10^4\text{--}10^5$ and dissolved organic complexing matter did not interfere. The method, applicable to sea water, surface and mineral waters, yielded detection limits of $0.1\ \mu\text{g l}^{-1}$ and RSDs of 3–5% when used in conjunction with FAAS and ICP-AES. Immobilisation of complexing reagents on silica (86/1026) and glass beads (86/1325) has also yielded favourable results.

Coprecipitation remains a popular route for achieving high pre-concentration factors although it must be realised that such approaches are generally time consuming. In two separate papers, Akagi *et al.* (86/967, 86/1618) described the

use of gallium and zirconium hydroxides for coprecipitation of trace metals in sea water prior to multi-element determination by ICP-AES. Whereas the technique using gallium afforded a concentration factor of 200, the zirconium procedure provided only a 20-fold improvement and, in addition, was limited by zirconium spectral interferences. An additional advantage cited by the authors for the gallium hydroxide procedure was that it was less prone to contamination on account of the availability of gallium of high purity. The gallium hydroxide method proved effective for coastal and open-ocean waters but was not applicable to fresh waters because precipitation at pH 9 required the presence of Mg at concentrations $>500 \text{ mg l}^{-1}$. Coprecipitation with APDC and Co has been utilised in hydrogeochemical survey analyses because it provided a convenient method for trace metal pre-concentration at the sampling site (86/C1263). The results for groundwaters and meltwaters analysed directly by ETA-AAS, and by ICP-AES after coprecipitation, were in good agreement although the latter approach was considered more efficient. The determination of REEs in sea water by ICP-AES after coprecipitation with iron(III) hydroxide has been reported (86/324). Limits of detection were $0.1\text{--}50 \text{ ng l}^{-1}$, but in view of earlier remarks concerning spectral interferences an alternative precipitating agent might be more appropriate. A sensitive procedure for the determination of P in natural waters, based on coprecipitation with zirconium hydroxide and ETA-AAS, has been proposed (86/1941). Chemical interferences, however, resulted from coprecipitants Al, Ca, Fe and Si and further sample manipulation to avoid the interferences makes the method time consuming and complicated.

Electrochemical pre-concentration has been exploited. Xu *et al.* (86/693) utilised electrolytic deposition on a platinum-wire cathode in conjunction with ETA-AAS for the determination of sub- $\mu\text{g l}^{-1}$ levels of Ag in natural waters. The limit of detection for a deposition time of 5 min was $0.04 \mu\text{g l}^{-1}$ and the RSD at $0.4 \mu\text{g l}^{-1}$ was 7%. Matusiewicz (86/2022) described the use of hanging mercury drop (HMD) electrodeposition with emission spectrography. Later, together with Fricke (86/C867) he combined the same approach with electrothermal vaporisation and ICP-AES. Using the HMD technique effectively eliminated the matrix interferences associated with high concentrations of Ca, K, Mg, Na and P and substantial improvements in sensitivity were realised. Controlled potential electrodeposition on both graphite electrodes and on a HMD were used in conjunction with ICP-AES and a direct insertion device (86/374). The determination of Cu ($63 \mu\text{g l}^{-1}$) in artificial sea water was demonstrated but, generally, limits of detection (e.g., Cu, $2.4 \mu\text{g l}^{-1}$ for 5 min deposition) were substantially poorer than the competing technique of anodic stripping voltammetry. The technique was subsequently modified to use reticulated vitreous carbon as the electrode material (86/C161).

In contrast with the previous year, rapid growth in *on-line pre-concentration techniques* for FAAS and ICP-AES has not been maintained. Hartenstein *et al.* (86/1671) have extended an on-line FI system with a miniature Chelex 100 column and ICP-AES for the determination of trace metals at the sub- $\mu\text{g l}^{-1}$ level in drinking waters and rain run-off. A FI manifold with a microcolumn of activated alumina (acid form) provided a novel route for the pre-concentration of oxyanion species including arsenate, borate, chromate, molybdate, selenate and vanadate (86/2019). Activated alumina (basic form) has been used in the same manner for the pre-concentration of cations prior to determination by ICP-AES (86/C1144). Limits of detection in pure aqueous solution for representative elements (Cd, Cr, Cu, Mn, Pb and Zn) were $0.03\text{--}3 \mu\text{g l}^{-1}$.

2.2. Developments in Atomic Absorption Spectrometry

The *minimisation of matrix interferences in electrothermal atomisation AAS* remains an important objective as evidenced

by the number of reports in this area. Analyte separation, instrumental correction techniques and use of matrix modifiers have been frequently utilised for this purpose. Craney *et al.* (86/1628) proposed that the addition of phosphoric acid to natural waters (e.g., molten glacier ice) compensated for matrix effects observed in the determination of Al and resulted in improved sensitivity (characteristic concentration, 8 pg). In the determination of trace elements in sea water, ascorbic acid was effective in suppressing interferences for Mn, Mo, Pb and V but not for Co and Cu (S/1216). Detection performance was sufficient to allow quantification at the $\mu\text{g l}^{-1}$ level and hence the methodology would be most appropriate for analysis of relatively polluted inshore waters. Other studies advocating matrix modification include the use of Pt and Pd for the determination of As (86/1037) and Se (86/C832, 86/C837), respectively.

Zeeman-effect AAS procedures are now being widely employed. Palladium was added to a graphite platform for a thermal pre-treatment stage prior to measurement of Hg by Zeeman-effect AAS (86/1045). The approach was successfully applied to the analysis of drinking water. Zeeman-effect AAS was also combined with the graphite boat technique for the determination of trace elements in suspended matter in lake water. The particulate matter, collected on organic filter material, was analysed directly for Cd, Cu and Hg. Relatively good precision and low blank values were claimed to be the main advantages of the method. Despite the availability of new furnace designs with improved analytical performance (86/1920) sample pre-treatments such as solvent extraction and ion exchange remain in wide use as evidenced in Table 2.

Sun *et al.* (86/1304) employed a stainless-steel *atom trap* in an air- C_2H_2 flame for the determination of Ag in water samples. Sensitivity was improved 100-fold relative to conventional FAAS with a 10-min collection time.

Vapour generation techniques continue to be utilised in the determination of hydride-forming elements and the following studies reflect present trends. Pre-concentration of H_2Se on Chromosorb W at -150°C was incorporated into a hydride generation AAS procedure for the determination of Se at the ng g^{-1} to pg g^{-1} level (86/389). Individual steps in the procedure such as reduction of Se^{VI} to Se^{IV} , hydride generation, pre-concentration and atomisation of H_2Se were optimised with the aid of a radiotracer. Another significant study utilised a radiotracer technique to identify sources of systematic error in the determination of Se in wastewaters (86/62). The procedure involved sample decomposition with sulphuric acid - hydrochloric acid and pre-reduction of Se^{VI} to Se^{IV} with hot hydrochloric acid (5 M). Time-dependent back-oxidation of Se^{IV} to Se^{VI} by residual chlorine was identified as a potentially serious source of error and removal of chlorine was necessary if hydration did not immediately follow the reduction step. For the same analysis, Sinemus and Maier (86/1437) reported that the presence of organic matter in water samples promoted the back reaction of Se^{IV} to Se^{VI} . The authors recommended addition of sulphanilamide or amidosulphuric acid to stabilise the Se^{IV} species. A novel method for the determination of Se in sea water was based on hydride generation using NaBH_4 and subsequent trapping of H_2Se in a graphite furnace at 600°C (86/1922). Accuracy of the method was demonstrated by analysis of an open-ocean sea water CRM (NASS-1, Se^{IV} concentration $0.02 \mu\text{g l}^{-1}$). More recently the same approach has been adapted for the determination of Sb in sea water (86/720). A hydride trapping procedure was developed for the determination of Te^{IV} and Te^{VI} in sea water by ETA-AAS (86/1772). The procedure for Te^{IV} involved coprecipitation with $\text{Mg}(\text{OH})_2$, injection of NaBH_4 and trapping of TeH_4 in a graphite furnace at 300°C . The detection limit for the method was 0.5 pmol l^{-1} and precision at the 0.05 nmol l^{-1} level was 10%. Total Te was determined after a pre-reduction stage to permit calculation of the Te^{VI} content by difference.

Several indirect determinations by FAAS have been described. Amin *et al.* (86/1382) have developed a novel FI procedure for the determination of cyanide. Aqueous cyanide samples were injected into an on-line copper sulphide-packed column with potassium hydroxide as carrier solution. The eluent containing copper cyanide complex was directly introduced to the AA spectrometer for measurement of Cu. The limit of detection was 1 mg l^{-1} and the RSD at 26 mg l^{-1} was 2%. A sampling rate of 40–50 samples per hour was achieved. A FI system coupled on-line with a continuous liquid-liquid extractor was used for the rapid determination of nitrate and nitrite. The procedure, based on ion-pair formation between the anions and Cu^{I} -neocuproine, was suitable for determinations at the mg l^{-1} level with a sampling rate of 35 per hour. Indirect methods have also been published for determining trace phenols (86/12) and non-ionic surfactants in waters (86/1433).

2.3. Developments in Atomic Emission and Fluorescence Spectrometry

Inductively coupled plasma atomic emission spectrometry retains a dominant position in water analysis and complementary techniques such as ICP-AES and ICP-MS have yet to make a significant impact. *Gaseous evolution* forms the basis for a number of new methodologies. Dissolved organic carbon (DOC) was determined after conversion into CO_2 in a heated quartz tube filled with copper oxide (86/C644). The combustion gases (water vapour removed) were flushed into the ICP with argon for measurement of C emission at 247.9 nm. The method appeared to be rapid (2 samples min^{-1}), sensitive, reproducible, amenable to automation and was considered by the authors to overcome response differences when standard solutions of different organic compounds were analysed by conventional ICP-AES. The generation of H_2S has been exploited for the determination of sulphide in natural waters by ICP-AES (86/C595). Linear calibration was established up to $100 \text{ } \mu\text{g l}^{-1}$ and the limit of detection was $0.3 \text{ } \mu\text{g l}^{-1}$. Of potential interferences investigated (Al, Ca, Cu, Fe, SO_4^{2-} and Zn), only signal suppression associated with the formation of insoluble CuS was significant.

A re-evaluation of *hydride generation* with ICP-AES for the determination of As, Sb and Se in sea water has been undertaken (86/C596). The importance of the pre-reduction stage for the higher oxidation states was confirmed, but in conflict with other studies (Thompson, M., Pahlavanpour, B., and Thorne, L. T., *Water Res.*, 1981, **15**, 407), potassium bromide was shown to be an ineffective pre-reductant for As^{V} and Sb^{V} . Plasma instability due to hydrogen entrainment was minimal with a Mermet - Trassy demountable torch. Pyen *et al.* (86/1834) utilised a fixed-size simplex procedure to establish the optimum conditions for the simultaneous determination of As, Sb and Se by hydride generation ICP-AES. The detection limit for Se ($0.3 \text{ } \mu\text{g l}^{-1}$) was comparable to the pre-optimised value but two-fold and four-fold improvements were realised for As ($0.3 \text{ } \mu\text{g l}^{-1}$) and Sb ($0.8 \text{ } \mu\text{g l}^{-1}$), respectively. A hydride generation procedure that permits the differential determination of Sb^{III} and Sb^{V} in waste waters has been developed by Nakahara and Kikui (86/1365). The procedure exploited the fact that stibene was effectively produced from reduction of Sb^{III} using NaBH_4 in the presence of either malic acid (1 M) or tartaric acid (0.5 M) whereas no response was observed for Sb^{V} . Thiourea was an effective pre-reducing agent and was also used to overcome inter-element interferences. The limit of detection using ICP-AES detection was $0.2 \text{ } \mu\text{g l}^{-1}$ and RSDs at 1 and $100 \text{ } \mu\text{g l}^{-1}$ were 3.8 and 2.1%, respectively. The same group has recently reported a sensitive hydride generation procedure for Bi (86/C1127).

The *determination of mercury* at the ng l^{-1} level has been the subject of a number of investigations. Nojiri *et al.* (86/1624) have used cold vapour generation and a gold

amalgamation technique in conjunction with MIP-AES for ultratrace analysis of lake-water samples. The limit of detection was 0.01 ng l^{-1} and the inorganic Hg concentration in unpolluted lake water was 0.3 ng l^{-1} . A FI approach based on amalgamation-reduction, evaporation and MIP-AES detection was employed for the determination of total, inorganic and organic Hg in natural waters (86/1692). The detection capability was similar to that in the previous study. The gold amalgamation technique has been used with a ring discharge plasma for the determination of Hg (86/C473). The limit of detection in pure water was 0.05 ng l^{-1} and in sea water was 0.3 ng l^{-1} . Mercury concentrations reported for Baltic sea water samples (total Hg 20–50 ng l^{-1} ; dissolved Hg 5–12 ng l^{-1}) were consistent with literature values. Electrothermal vaporisation has been combined with ICP-AES for the determination of Hg in drinking water (86/221). Ammonium sulphide was used to control the vaporisation rate. The limit of detection for a 5- μl sample injection was $0.8 \text{ } \mu\text{g l}^{-1}$.

Miyazaki and Bansho (86/C1269) have devised novel procedures for the *determination of halogens* in waters at the $\mu\text{g l}^{-1}$ level. For the determination of iodide the sample (500 ml) was treated with sodium nitrite and sulphuric acid and evolved iodine was extracted into a small amount of xylene before introduction to the ICP. Limits of detection were 8.3 and $21 \text{ } \mu\text{g l}^{-1}$ at 178.28 and 206.16 nm, respectively. For iodate determination a pre-reduction stage with ascorbic acid was first performed. Results for geothermal brines and coastal sea water were in agreement with data by colorimetry. An indirect method for fluoride was based on the formation of the ternary complex, lanthanum - alizarin - fluoride and measurement of La emission at 333.75 nm. The detection limit was $0.6 \text{ } \mu\text{g l}^{-1}$ and data presented for drinking water and sea water were in agreement with that from a standard colorimetric procedure.

Several reports have been published on the *determination of uranium* by plasma emission spectrometry. Uranium was extracted from sea water with an amidoxime resin and subsequently determined by ICP-AES (86/1877). The limit of detection was 0.02 mg l^{-1} and linear calibration up to 30 mg l^{-1} was realised. McClure (86/C1268) employed a rapid ICP-AES method for the determination of U in industrial effluents and performance was judged to be comparable to approved radiochemical and fluorimetric procedures. The direct determination of U in groundwaters ($5\text{--}16 \text{ mg l}^{-1}$) and mine waters ($2\text{--}300 \text{ mg l}^{-1}$) by DCP-AES was subject to enhancements by naturally occurring salts (86/671). Matrix effects were compensated for by the addition of 0.05 M sodium acetate solution to the calibration standards.

Methodology for multi-element analysis of acid mine waters and CRMs by *inductively coupled plasma atomic fluorescence spectrometry* has been published (86/1983). Elements were determined in two groups based on compatibility of operating conditions and consideration of element abundance levels. For example, Ca, Mg and Na were determined for one set of operating conditions and after 100-fold sample dilution, whilst Cd, Cu, Fe, K, Li and Zn were determined directly but under different operating conditions. Limits of detection were in the range $1\text{--}15 \text{ } \mu\text{g l}^{-1}$.

Progress in *inductively coupled plasma mass spectrometry* continues to be reported but few comprehensive studies have been published. Trace elements in sea water were pre-concentrated 50-fold by adsorption on silica-immobilised 8-hydroxyquinoline prior to determination by ICP-MS (86/C164, 86/2039). Standard additions calibration and isotope dilution were used for accurate determinations of Co, Cu, Mn, Ni and Zn and Cd, Cr, Cu, Ni and Zn, respectively, in a coastal sea water CRM (CASS-1). Limits of detection were in the range $0.2\text{--}2 \text{ ng l}^{-1}$. Calibration techniques for ICP-MS (including isotope dilution) have been critically assessed by McLaren *et al.* (86/C1475). External calibration was judged to be the most convenient, from the point of view of achieving high sample throughput, but was most prone to inaccuracy

because of susceptibility to interferences and instrumental drift, especially when standards were not matrix-matched to samples. Taylor and Garbarino (86/C182, 86/C754, 86/C1108, 86/C1474), in a series of investigations, have evaluated the utility of ICP-MS for routine determinations of trace metals in natural waters. The performance studies have addressed a number of topics including simplex optimisation of analyte response, detection limits, short and long-term drift, background spectra, interferences, accuracy and precision.

2.4. Coupled Chromatographic Techniques and Speciation

Progress has continued in the specialised area of trace element speciation where studies have focused principally on As, Cr, Pb and Sn. Tye *et al.* (86/14) described the use of HPLC in combination with hydride generation AAS for the determination of inorganic and organic *arsenic* in soil waters. Sample pre-concentration was achieved with a pellicular anion-exchange column and detection limits were 2 ng for arsenate, arsenite and monomethyl arsinic acid and 1 ng for dimethyl arsinic acid.

On-line ion chromatography - ICP-AES was used for fractional determinations of *chromium* in waste waters (86/1949). Improved sensitivity and shortened retention time for Cr^{VI} were obtained by formation of the tetrathiocyanatochromate(III) anion and the use of a pre-column packed with a polyacrylate anion-exchange resin. Limits of detection for Cr^{III} and Cr^{VI} were 75 and 220 µg l⁻¹, respectively. The reaction of Cr^{III} with trifluoroacetylacetone inside a graphite furnace was used as the basis for differential determination of the main chromium oxidation states (86/1449). A procedure for the determination of total Cr and Cr^{VI} (Cr^{III} by difference) in waters was based on APDC extraction with IBMK and then FAAS (86/63). For samples spiked with 8 µg of Cr^{III} and Cr^{VI}, recoveries were ca. 100% and RSDs were 5.1–6.4% and 1.8–4.1%, respectively. In a similar study involving APDC extraction, Ce^{IV} has been recommended for the oxidation of all chromium species to Cr^{VI} (86/C842). In addition to a considerable time saving relative to the conventional permanganate procedure, consistently more reliable data were obtained for certified reference waters (concentration range 4–28 µg l⁻¹) using the Ce oxidation method. Coprecipitation with hydrous iron(II) oxide followed by FAAS was used by Harper and Riley (86/1097) to determine dissolved and particulate Cr in natural waters. Sample pre-treatment procedures included the use of HNO₃ - HF to dissolve suspended particulate matter and UV photolysis to break down organic complexes of Cr. Samples for total Cr determination were stable for up to three weeks at pH 2 in contrast to those for Cr^{III} where determinations must be performed immediately.

A sensitive procedure for the determination of *lead* and methyllead ions in waters was based on *in situ* ethylation, collection of the alkyllead species on a Chromosorb W AW trap, and subsequent desorption into a quartz furnace for AAS (86/1390). The limit of detection of Pb for a 50-ml sample was ca. 10 pg. The avoidance of solvent extraction and sample transfers (all steps performed in closed apparatus) were cited as major advantages of the approach. A propylation technique in conjunction with GC-AAS has been recommended for the simultaneous determination of tetramethyllead and ionic alkyllead species (86/1629). Advantages claimed over a previously published butylation procedure (Harrison, R. M., and Radojevic, M., *Environ. Tech. Lett.*, 1985, 6, 129) included shorter analysis time, increased recoveries and improved detection limits for the ionic alkyllead species. Trace tetraalkyllead compounds were determined in refinery waste waters after hexane extraction, conversion into water-soluble iodides and re-extraction into dilute HNO₃ before

determination by ETA-AAS (86/969). The method yielded a 50–250-fold enrichment and a mean Pb recovery of 95%.

A procedure for the determination of *tributyltin* compounds in sea water (concentrations 1 µg l⁻¹) using toluene extraction has been developed by Parks *et al.* (86/684). For ETA the use of ammonium dichromate as matrix modifier or L'vov platforms was reported to improve sensitivity. The authors cautioned on the need for careful washing of the extract with distilled water otherwise carry-over of sea-water salts would result in interference. Inorganic Sn species and methyl- and n-butyl-tin compounds in water samples were determined by AAS after volatilisation by hydride generation, separation on a chromatographic column and atomisation in an electrically heated quartz furnace (86/1807). Limits of detection for most alkyltin compounds were 20–50 pg and the precision for 15 ng of Sn was 15%. Ebdon *et al.* (86/C2038) recently reported procedures for the speciation of Sn compounds based on a combination of HPLC and hydride generation FAAS. The methodology provided a detection capability in the ng l⁻¹ level and was used for survey analysis of estuarine waters, sediments and oyster tissue. Attempts have been made to characterise the association of elements with particulate and colloidal matter in natural fresh waters (86/688). *In situ* filtration, centrifugation and dialysis were used in combination with FAAS, ETA-AAS, ICP-AES and instrumental NAA. Three laboratories participated in this important study and data were presented for 20 elements.

2.5. Comparative Studies

Water quality laboratories are under increasing pressure to provide data of high quality and in quantity, and it is considered timely that *quality control measures* have been a feature of several reports. Zaykowski (86/C1270) has described details of procedures used at the US Geological Survey, in Denver, where there is a requirement for the analysis of ca. 30 000 samples per year by ICP-AES. Typical control measures included (1) detection limit verification every 7 days, (2) high and low concentration quality control samples, (3) spike recoveries and (4) duplicate analyses for each set of samples. An indication of performance over an eight-day period was presented for the determination of Ca, Fe, Mg and Mn in several hundred samples. Under the auspices of the US Environmental Protection Agency an inter-comparison study of elemental analyses in hazardous wastes by ICP-AES was undertaken (86/C1199). Extensive quality control measures were implemented and were designed to produce "not only data of known quality with precision and accuracy statements but also a complete documented 'data' package containing all instrumental parameters and raw data to permit an independent review of the laboratories' results." It was concluded that ICP-AES can be used successfully for multi-element analyses of diverse environmental samples. In an inter-laboratory study the performance of ICP-AES was compared with FAAS and molecular absorption spectrophotometry for the determination of 17 major and trace elements in 100 filtered natural water samples (86/219). Recovery experiments indicated that the accuracy of the ICP determinations was ±2–10%, while precision for the technique was equal to or better than the alternative methods. Other inter-comparison studies include the following: analysis of sea water for dissolved Cd, Cu and Pb (86/1695); determination of Cd, Pb and Tl in water samples at p.p.b. and p.p.t. levels by isotope dilution mass spectrometry (86/1348); determination of heavy metals in the Dead Sea (86/1099); determination of ultratrace Cd and Mg in brine (86/1417); and ICP-AES determination of Ag in tap water (86/1907).

3. SOILS, PLANTS AND FERTILISERS

There has been wider acceptance of some of the more significant developments in analytical atomic spectrometry by environmental scientists concerned with soils, plants and waters since the publication last year of the first Update in this series (86/1814). Most notable is the increase in papers concerned with the direct analysis of solid samples in either flames or plasmas, a trend clearly discernible in both Table 3, which summarises the applications in this area over the past year, and in the following text.

While most attention has been focused upon the analysis of soils and plants to assess nutrient status, pollutant levels, or simply soil-parent material effects, there have been a few interesting analyses of *unusual sample types*. Jeffrey and Lyons (86/C600), for example, raised *Heliothis* moths on a rubidium-rich nutrient medium, and were then able to determine the Rb by ICP-AES or, for moths with $>15 \mu\text{g}$ of Rb, by AAS. The moths were for use in entomological marking experiments. It has been suggested that application of pattern recognition techniques to data from multi-element ICP-AES analysis of boll weevils might prove useful for monitoring weevil migrations (86/717). Trace inorganics in caterpillar metabolites, again determined by multi-element ICP-AES, might also be useful in this respect (86/C849). While not exactly plant samples, it seems appropriate to include these illustrations here as being indicative of the broad scope for applying analytical atomic spectrometry in soil and plant science. Such studies are, as yet, less widespread than the more common use of tree-ring analysis as a tool in studying possible causes of forest die back (86/C1232, 86/C1233), and analysis of other vegetation types for assessing heavy-metal pollution from local or distant sources (86/C126, 86/C453, 86/1058).

3.1. Sample Preparation

The search for simpler and/or safer and/or less expensive methods for sample dissolution has continued unabated over the past 12 months. Numerous examples of minor modifications have been included in Table 3, but some points are worth highlighting here.

Various attempts have been made over the past decade to eliminate the need for ignition or strong acid digestion of plant materials. Usually these involve grinding or agitation with much milder *extractants such as dilute acids* ($<2 \text{ M}$). Procedures have been published for extraction of K from finely ground seeds or aerial parts of plants by 5-min agitation with 0.5 M HCl (86/354), for removal of Fe from peach leaves by soaking in 1 M HCl at room temperature for 8–24 h (86/1055) and for extraction of Ca, Cu, Fe, K, Mg, Mn and Zn from plants by subjecting suspensions of the plant material in 1.5 M HCl to ultrasound at 44 kHz for 4 min (86/959). In the last instance, it was necessary to repeat the procedure three times to obtain good recovery for Fe.

Among the “streamlined” procedures for extraction of soils or sediments, five are worth noting. Gregoire (86/1885) has described a system for extraction of organically bound Au based upon a mild oxidation with $5\% \text{ NaOCl}$ solution. Recovery was almost quantitative for lake and stream sediments high in organic matter, but as low as 70% for more mineral samples. Sodium hydroxide treatment has been used to extract SeO_4^{2-} and SeO_3^{2-} from biogenic particles and sediments in a speciation study (86/1286). Total Se was determined after $\text{HNO}_3 - \text{HClO}_4$ digestion. Aqua regia has been suggested for extraction of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn from soils and sewage sludges (86/1430). Recoveries averaged 88% of reported values for CRMs. A fusion method from China has been described for total element analysis of soils based upon formation of a flux at 900°C with $\text{Li}_2\text{CO}_3 - \text{H}_3\text{BO}_3$ in a cavity formed in a layer of graphite powder in a porcelain crucible (86/1093). The flux

was dissolved in $4\% \text{ HNO}_3$ and treated with Li at 5 mg ml^{-1} prior to analysis by DCP-AES. Finally Mayer *et al.* (86/1041) have described a method for the determination of Cr in geochemical samples by AAS following homogenisation with $85\% \text{ H}_3\text{PO}_4$ in a screw-cap tube and heating for 6 h on a hot-plate.

Semu *et al.* (Fresenius. Z. Anal. Chem., 1985, 322, 440–442) found that drying of lettuce, wheat or ryegrass at 105°C resulted in *loss of mercury*, whereas drying at 50°C did not. Milling did not result in any loss. Digestion with $\text{HNO}_3 - \text{KBrO}_3$ gave 90–100% recovery of Hg added to various plant species.

Microwave ovens appear to be gaining favour as an aid to sample dissolution or at least element extraction from plant samples. Procedures based upon HNO_3 (86/1472) or $\text{HNO}_3 - \text{H}_2\text{O}_2$ (86/715, 86/C812) digestion have been recommended. In the former instance, prior 2-h soaking in $1 \text{ M HNO}_3 - 1 \text{ M HCl}$ was necessary. Subsequent “cooking” times in the oven are only a few minutes. Smith *et al.* (86/1619) have suggested acid dissolution of sulphide mineral samples with potassium chlorate - concentrated $\text{HNO}_3 - \text{HF}$ in sealed PTFE vessels in a microwave oven. Heating for only 3 min was necessary at 477 W.

Another domestic appliance, a *pressure cooker*, has once again been recommended for speeding up digestion of soil and sediment samples (86/432). The optimum conditions, compared with results obtained by $\text{HNO}_3 - \text{HClO}_4$ digestion, were found to be treatment of 1-g samples with 20 ml of $1 + 1 \text{ H}_2\text{O} + \text{HNO}_3$ at 2.2 atm for 4 h.

Other aids to fusion, ashing or digestion are not as widely used as they might be, even though some are commercially available. Dalton (86/C1555) has described a fusion procedure based upon lithium tetraborate that used a Claisse Fluxer VI. The fluxes were dissolved in dilute HNO_3 prior to analysis by ICP-AES. A novel publication from Japan discussed the use of a photoelectric sensor for monitoring the combustion of organic materials during low-temperature ashing (86/1047). Whilst such a device would be valuable during the optimisation of ashing of a new sample type, it is hard to envisage its use on a routine basis.

Comparisons of dissolution techniques, if carefully conducted, may be of great value. Van der Veen *et al.* (86/88) contrasted the merits of ten procedures for monitoring As in soils by hydride generation AAS. The methods studied included dry ashing, several acid leaching procedures and digestions in pressure decomposition vessels or Kjeldahl apparatus. An $\text{HNO}_3 - \text{H}_2\text{SO}_4$ based procedure was most satisfactory. Papp and Harms (86/55) evaluated several digestion methods for peat analysis. They favoured dry ashing followed by HF treatment, or digestion with an $\text{HNO}_3 - \text{HClO}_4 - \text{HF}$ mixture, the latter approach allowing determination of at least 11 elements. Treatment with H_2O_2 could be used to separate organic and inorganic components. Stoeppler (86/1682) has reviewed methods for the determination of Cd in biological and environmental samples. Comparisons of sample preparation techniques have sometimes also formed the basis of conference presentations (86/C1493, 86/C1537).

In spite of the high selectivity of atomic spectrometric methods of analysis, separation techniques are still sometimes a necessary pre-requisite to successful determination. Usually this is because of a need for separation from matrix components and sometimes to achieve a useful degree of concentration of one or more determinands. Jones and O'Haver (86/112) published an account of an investigation of the effect of pH and digestion conditions upon the separation of trace elements from plant tissue digests with Chelex 100. A pH of 4.7–5.5 was best suited to a range of elements from acid digests. Below pH 4.7 elution losses occurred for some elements, whereas above pH 5.5 precipitation of hydrous

Table 3. SUMMARY OF ANALYSES OF SOILS, PLANTS, FERTILISERS AND RELATED MATERIALS

Element	λ/nm	Matrix	Concentration	Technique; atomisation; analyte form	Sample treatment/comments	Reference
Ag	—	Soil	$0.04 \mu\text{g ml}^{-1}$	AA; F; L	Discrete sample nebulisation	86/339
Ag	328.1	Soil	$0.2 \mu\text{g g}^{-1}$	AA; ETA; S	Direct atomisation of powdered sample	86/C455
Ag	—	Plants (lichens, bryophytes)	$0.1\text{--}1.0 \mu\text{g g}^{-1}$	AA; ETA; L	Samples digested with acid	86/747
Ag	328.07	Kale	$>0.02 \mu\text{g g}^{-1}$	AE; ICP; L	1.5-g sample mixed with 30 ml 5 + 1 $\text{HNO}_3 + \text{HClO}_4$; left overnight; boiled to half volume; 10 ml of HNO_3 added; heated to fumes with HNO_3 addition to prevent charring; electrothermal vaporisation used	86/971
Al	—	Soils	—	AA; —; L	CuCl_2 extraction	86/309
Al	—	Soils	—	AA; —; L	Hydroxylamine or ammonium oxalate extraction	86/355
Al	—	Soils	—	AA; —; L	Extracted with 1 M KCl with and without 0.01 M Triton B	86/356
Al	—	Plants	—	AA; ETA; L AE; DCP; L	Extracted with hot, 12 M HCl	86/1059
Al	—	Soil extracts	—	AA; —; L	Extracted with 0.3 M BaCl_2	86/1855
Al	—	Soil	$0.02\text{--}20 \mu\text{g ml}^{-1}$	AE; arc; S	Co-precipitated with iron; ignited precipitate analysed in cathode-layer arc; for 0.5 M acetic acid or 1 M ammonium acetate, Al precipitated with 8-hydroxyquinoline	86/1887
As	193.7	Soils	$3\text{--}100 \text{ mg kg}^{-1}$	AA; Hy; L	Comparison of ten digestion procedures, including Kjeldahl, dry ashing, acid leaching and pressure vessels; acid digestion with $\text{HNO}_3 - \text{H}_2\text{SO}_4$ preferred	86/88
As	197.2	Soil	$94 \mu\text{g g}^{-1}$	AA; ETA; S	Solid samples analysed by cup-in-tube ETA technique	86/192
As	—	Sediments	—	AA; ETA; L	Use of Pt as matrix modifier	86/1037
As	—	Plant leaves	—	AA; Hy; L	Digested with $\text{H}_2\text{SO}_4 - \text{HNO}_3 - \text{HClO}_4$	86/1331
As	—	Geochemical samples	—	AA; Hy; L	Description of automated hydride generation system	86/C1581
As	189.05	Soils	$7 \mu\text{g g}^{-1}$	AE; ICP; L	As NaPDC complex extracted into CHCl_3 ; back-extracted into 25% HNO_3 ; for total As, As^{V} is reduced with $\text{Na}_2\text{S}_2\text{O}_3$ first	86/1905
Au	—	Plants	$>0.2 \text{ ng g}^{-1}$	AA; ETA; L	Digested with fuming HNO_3 ; HCl added, and chloro complex extracted into IBMK. Iron removed by back-extraction with water	86/423
Au	—	Soils, rocks	—	AA; F; L	Digested with HF - aqua regia - HBr - Br; extracted from 0.1 M HBr into IBMK	86/862
Au	Non- dispersive	Geochemical samples	$>1 \text{ ng ml}^{-1}$	AF; F, N-separated air - C_2H_2 ; L	30 g slurried with water and digested for 1 h with 60 ml of concentrated HCl + 25 ml of concentrated HNO_3 ; diluted to 300 ml; separated if necessary by extraction with 2 ml 1% <i>m/V</i> Aliquat 336 in diisobutyl ketone	86/1368
Au	—	Soils, sediments	—	AA; —; L	Organically bound Au extracted with NaOCl (5%); recovery down to 70% for low organic matter soils	86/1885
Au	—	Algae	$>1 \mu\text{g g}^{-1}$	AE; DCP, ETA; S	Au from solid cells volatilised from graphite boat into DCP	86/1903
B	249.7	Plants	$70\text{--}250 \mu\text{g g}^{-1}$	AA; cold vap.; L	Sample solution reacted with methanol in concentrated H_2SO_4 to produce volatile methyl borate	86/1470
Be	—	Soils	$>5 \times 10^{-11} \text{ g}$	AA; ETA; L	Dissolution, followed by solvent extraction of acetylacetonato complex from neutral solution containing complexon III into toluene	86/407
Bi	223.1	Soil	$0.5 \mu\text{g g}^{-1}$	AA; ETA; S	Direct atomisation of powdered sample	86/C455
Ca	422.76	Plants	—	AA, AE; F; L	H_2SO_4 -based acid digestion; Mg at 2.5 mg l^{-1} used to overcome Al interference	86/4
Ca	422.6	Soils	—	AE; ICP; L	Aqueous or ethanolic NH_4Cl extraction	86/232
Ca	—	Soils	—	AA; —; L	Extracted with 1 M KCl with and without 0.01 M Triton B	86/356
Ca	—	Soils	—	AE; F; L	Soil extracts analysed by automated system	86/393
Ca	—	Rice grain surface	$18\text{--}800 \text{ mg kg}^{-1}$	AA; F, air - C_2H_2 ; L	Extract CaCO_3 from surface with 0.1 M HCl	86/1089
Cd	228.8	Hay	$0.31 \mu\text{g g}^{-1}$	AA; ETA; S	Powdered and homogenised hay analysed by cup-in-tube ETA technique	86/192
Cd	228.8	Plants	$>0.02 \text{ mg kg}^{-1}$	AA; ETA; L	Ashed at 450°C , digested and extracted into CCl_4 as the dithizonate	86/422
Cd	—	Rocks	—	AA; ETA; L	Iron used as matrix modifier	86/434

Table 3. SUMMARY OF ANALYSES OF SOILS, PLANTS, FERTILISERS AND RELATED MATERIALS—*continued*

Element	λ/nm	Matrix	Concentration	Technique; atomisation; analyte form	Sample treatment/comments	Reference
Cd	228.8	Soils	$0.1 \mu\text{g g}^{-1}$	AA; ETA; S	Direct atomisation of powdered sample	86/C455
Cd	228.8	Soils	—	AA; ETA; S	Finely ground sample converted into slurry for direct ETA	86/C514
Cd	228.8	Soils	$0.8 \mu\text{g g}^{-1}$	AA; ETA; S AA; F; L	Finely ground sample converted into slurry for platform ETA; good agreement between the two techniques	86/659
Cd	228.8	Soils	—	AA; ETA; S	H_3PO_4 added to prevent Cd and Pb losses during charring	86/741
Cd	228.80	Kale	$>0.15 \mu\text{g g}^{-1}$	AE; ICP; L	See Ag, ref. 86/971	86/971
Cd	214.44	Biological samples	$>0.4 \text{ ng ml}^{-1}$	AE; ICP; L	Sample digested at 90°C under pressure with HNO_3 for 2 h, then at 140°C for 4 h; HNO_3 evaporated and residue fumed with HClO_4 ; H_2SO_4 - HNO_3 added and evaporated to near dryness; diluted with water. DDTC complex extracted into CCl_4	86/1023
Cd	—	Soil extracts	$\text{ca. } 0.34 \text{ pg}$	AA; ETA; L	—	86/1712
Cd	—	Soils	$0.003\text{--}0.029 \text{ mg l}^{-1}$	AA; F; L	Extracted with CaCl_2 ; atom trapping used for pre-concentration	86/1854
Cd	—	Soils	$0.1\text{--}1 \mu\text{g g}^{-1}$	AA; ETA; S AA; F; nickelcup AA; ETA; L AA; F; L	Slurry atomisation and acid digestion - solution atomisation compared	86/C1964
Cd	—	Plants	—	AA; ETA; S	Slurry in HNO_3 (5%); gave satisfactory results for CRMs	86/C1974
Cd	—	Pepperbush standard	$\text{ca. } 30 \mu\text{g kg}^{-1}$	AA, FI; F; L	Sample solution adjusted to pH 7 with $\text{CH}_3\text{CO}_2\text{NH}_4$; Cd concentrated on mini ion-exchange column; eluted with 2 M HNO_3 to nebuliser	86/2024
Co	—	Soils, plants	—	AA; ETA; L AE; ICP; L	Comparison of digestion procedures and analytical techniques	86/231
Co	—	Soils	—	AA; —; L	Digested with HCl - HNO_3 - HClO_4 ; dried and residue dissolved in 1 M HCl ; filtered; filtrate diluted with 1 M HCl , treated with NH_4F , sodium citrate and NaDDC prior to extraction into IBMK	86/1094
Cr	—	Plants	$>0.02 \mu\text{g g}^{-1}$	AA; ETA; L	HNO_3 - H_2SO_4 - HClO_4 digestion; Cr reduced by NaSO_3 then co-precipitated with $\text{Fe}(\text{OH})_3$; Fe removed by dissolution and extraction; silica residue dissolved in HF	86/48
Cr	360.5	Hay	$2.2 \mu\text{g g}^{-1}$	AA; ETA; S	Powdered and homogenised samples analysed by cup-in-tube ETA technique	86/192
Cr	429.0	Soil	$29 \mu\text{g g}^{-1}$	AA; ETA; S	Comparison of digestion procedures and analytical techniques	86/231
Cr	—	Plants, soils	—	AA; ETA; L AE; ICP; L	0.2 g homogenised with 1 ml of H_3PO_4 in a sealed tube and heated for 6 h; diluted to 10 ml	86/1041
Cr	357.9	Geochemical samples	$12\text{--}95 \text{ mg kg}^{-1}$	AA; F; N_2O - C_2H_2 ; L	Digested with H_2SO_4 ; ashed at 500°C for 3 h; digested with HNO_3 ; redissolved in HCl ; filtered	86/1343
Cr	—	Tea leaves	$>0.03 \mu\text{g ml}^{-1}$	AE; —; L	Acid extracts of soils and plants	S/1210
Cu	—	Plants, soils	—	AA or AE; —; —	Powdered and homogenised samples analysed by cup-in-tube ETA technique	86/192
Cu	327.4	Hay	$4.3 \mu\text{g g}^{-1}$	AA; ETA; S	Comparison of digestion procedures and analytical techniques	86/231
Cu	249.2	Soil	$77 \mu\text{g g}^{-1}$	AA; ETA; L AE; ICP; L	Extracted with 1 M KCl with and without 0.01 M Triton B	86/356
Cu	—	Plants, soils	—	AA; —; L	1 g of soil digested with 20 ml 1 + 1 HNO_3 for 4 h at 2.2 atm in a pressure cooker	86/432
Cu	—	Soils	—	AA; —; L	0.5 M HNO_3 , 1 M NH_4HCO_3 -0.005 M DTPA, 0.5 M $\text{CH}_3\text{CO}_2\text{H}$ -0.5 M $\text{CH}_3\text{CO}_2\text{NH}_4$ -0.02 M EDTA, 0.8 M $\text{CH}_3\text{CO}_2\text{Na}$ -0.5 M $\text{CH}_3\text{CO}_2\text{H}$ -0.0001 M DTPA, 0.1 M KCl -0.05 M EDTA and distilled water were compared as extractants	86/C598
Cu	—	Soils	—	AE; ICP; L AA; F; L	1–10 mg sample digested with 200 μl HNO_3 + HCl + HClO_4 (10 + 1 + 1) in PTFE snap-cap vessel; placed in bomb; heated at 90°C for 2 h and 140°C for 2 h; evaporated almost to dryness; diluted to $<1 \text{ ml}$ with 0.1 M HClO_4 ; nebulised entire sample for absolute analysis	86/666
Cu	—	Plants	$3\text{--}12 \mu\text{g g}^{-1}$	AA; F; L		

Table 3. SUMMARY OF ANALYSES OF SOILS, PLANTS, FERTILISERS AND RELATED MATERIALS—*continued*

Element	λ/nm	Matrix	Concentration	Technique; atomisation; analyte form	Sample treatment/comments	Reference
Cu	324.75	Kale	$>0.01 \mu\text{g g}^{-1}$	AE; ICP; L	See Ag, ref. 86/971	86/971
Cu	—	Tea leaves	$>0.003 \mu\text{g ml}^{-1}$	AE; —; L	See Cr, ref. 86/1343	86/1343
Cu	—	Sediments	$\text{ca. } 50 \text{ mg kg}^{-1}$	AA; ETA; S	Direct analysis of homogenised slurry; Zeeman-effect background correction	86/1436
Cu	—	Tea	—	AA; F; air - C_2H_2 ; L	Extracted $[\text{CuI}_4]^{3-}$ from 2 M HCl solutions of tea samples with 12% KI into IBMK	86/1460
Cu	—	Sulphide minerals	—	AA; F; air - C_2H_2 ; L	Ground sample dissolved in KClO_3 in HNO_3 - HF (2 + 1) in PTFE vessel in microwave oven	86/1619
Cu	—	Plant tissues	—	AA; —; L	Digested with HNO_3 + H_2SO_4 (2 + 1), then H_2O_2	86/1801
Fe	—	Soils	—	AA; —; L	Hydroxylamine or ammonium oxalate extraction	86/355
Fe	—	Soils	—	AA; —; L	Extracted with 1 M KCl with and without 0.01 M Triton B	86/356
Fe	—	Soils	—	AA; —; L	1 g of soil digested with 20 ml of 1 + 1 HNO_3 for 4 h at 2.2 atm in a pressure cooker	86/432
Fe	—	Soils	—	AE; ICP; L AA; F; L	Six extractants were compared (see Cu, ref. 86/C598)	86/C598
Fe	—	Plants	—	AA; F; L	Dried, powdered leaves soaked in 1 M HCl for 8–24 h at 18–25 °C and solution analysed	86/1055
Fe	—	Plant tissues	—	AA; —; L	Digested with HNO_3 + H_2SO_4 (2 + 1), then H_2O_2	86/1801
Hg	253.7	Sediments	$>0.5 \mu\text{g l}^{-1}$	AA; ETA; L	0.5 g of sample digested with 2 ml of HCl + 1 ml of HNO_3 in autoclave	86/1040
Hg	253.6	Soils	Up to $0.11 \mu\text{g g}^{-1}$	AA; cold vap.; L	Range of soils digested. High Hg related to clay and organic matter	86/1060
Hg	—	Mushrooms, worms	$>1 \mu\text{g g}^{-1}$	AA; ETA; S	Solid samples analysed; Zeeman-effect background correction	86/1794
Hg	—	Soils, environmental samples	0–10 ng	AA; —; —	A dedicated Zeeman-effect Hg AA spectrometer is described and tested	86/1824
In	303.9	Minerals, sediments	$10\text{--}40 \mu\text{g g}^{-1}$	AA; ETA; L	Extract with NH_4I into IBMK; Pd used as matrix modifier in the graphite furnace; used deuterium background correction and standard additions	86/85
In	—	Soils, rocks	—	AA; F; L	Digested with HF - aqua regia - HBr - Br; extracted from 3 M HBr medium in presence of ascorbic acid (to prevent Fe extraction) into IBMK	86/682
Ir	—	Sediments	$0.5\text{--}3 \text{ ng g}^{-1}$	AA; ETA; L	Element concentrated upon a single ion-exchange resin bead	86/1625
K	—	Plant sap	$<2000 \mu\text{g ml}^{-1}$	—	Comparison of Merkoquant K test strips with conventional spectrometry	S/1029
K	766.5	Soils	—	AE; ICP; L	Aqueous or ethanolic NH_4Cl extraction	86/232
K	766.5	Plants, seeds	—	AE; F; L	500 g of plant material agitated with 40 ml 0.5 M HCl for 5 min	86/354
K	—	Soils	—	AE; F; L	Soil extracts analysed by automated flame photometry	86/393
K	—	Agricultural samples	—	AE; ICP; L	Study of plasma conditions and position effects	86/C1228
Mg	279.5	Soils	—	AE; ICP; L	Aqueous or ethanolic NH_4Cl extraction	86/232
Mg	—	Soils	—	AA; —; L	Extracted with 1 M KCl with and without 0.01 M Triton B	86/356
Mn	403.1	Hay	$58 \mu\text{g g}^{-1}$	AA; ETA; S	Powdered and homogenised samples analysed by cup-in-tube technique	86/192
Mn	—	Soils	—	AA; —; L	Extracted with 1 M KCl with and without 0.01 M Triton B	86/356
Mn	—	Soils	—	AA; —; L	1 g of soil digested with 20 ml 1 + 1 HNO_3 for 4 h at 2.2 atm in a pressure cooker	86/432
Mn	—	Soils	—	AE; ICP; L AA; F; L	Six extractants were compared (see Cu, ref. 86/C598)	86/C598
Mn	257.61	Kale	$>0.013 \mu\text{g g}^{-1}$	AE; ICP; L	See Ag, ref. 86/971	86/971
Mn	—	Soils	—	AA; —; L	See Co, ref. 86/1094	86/1094
Mn	—	Plant tissues	—	AA; —; L	Digested with HNO_3 + H_2SO_4 (2 + 1), then H_2O_2	86/1801
Mo	—	Soils, sediments, rocks	$>0.06 \mu\text{g g}^{-1}$	AE; ICP; L	Solubilised by treatment with 6 M HCl in capped tubes at 120 °C; extracted into heptan-2-one	86/72
Mo	—	Wheat	$0.44\text{--}2.2 \mu\text{g g}^{-1}$	AA; ETA; L	Digested with HNO_3 and filtered	86/352

Table 3. SUMMARY OF ANALYSES OF SOILS, PLANTS, FERTILISERS AND RELATED MATERIALS—*continued*

Element	λ/nm	Matrix	Concentration	Technique; atomisation; analyte form	Sample treatment/comments	Reference
Mo	—	Geological samples	$>0.5 \mu\text{g g}^{-1}$	AA; F; $\text{N}_2\text{O} - \text{C}_2\text{H}_2$; L	Fused with LiBO_2 ; dissolved in 50% HCl; extracted with TOPO in IBMK	86/692
Mo	—	Plants	$>0.008 \mu\text{g g}^{-1}$	AA; ETA; L	Digested with $\text{H}_2\text{SO}_4 - \text{HNO}_3 - \text{HClO}_4$; thiocyanate complex extracted into diisobutyl ketone	86/1766
Mo	—	Plants	—	AA; ETA; L	Digested with $\text{HNO}_3 + \text{H}_2\text{O}_2$	86/1848
Mo	—	Plants	—	—	Digested with $\text{HNO}_3 - \text{H}_2\text{SO}_4 - \text{HClO}_4$; Mo separated as oxine or dithiol complex into IBMK, DIBK or isoamyl alcohol	86/2030
N (NO_3^-)	—	Fertiliser	—	AA; F; L	Convert into $[\text{Ag}(\text{Phen})_2]\text{NO}_3$ by adding $[\text{Ag}(\text{Phen})_2]^+$ and determine excess of Ag ions	86/1711
Na	588.9	Soils	—	AE; ICP; L	Aqueous or ethanolic NH_4Cl extraction	86/232
Ni	—	Soils	—	AA; ETA; S	H_3PO_4 added prior to direct determination	86/741
Ni	—	Soils	—	AA; —; L	See Co, ref. 86/1094	86/1094
Ni	—	Tea leaves	$>0.03 \mu\text{g ml}^{-1}$	AE; —; L	See Cr, ref. 86/1343	86/1343
Ni	—	Sulphide minerals	—	AA; F; air - C_2H_2 ; L	See Cu, ref. 86/1619	86/1619
P	213.6	Plant	$1-2 \text{ mg ml}^{-1}$	AA; F; $\text{N}_2\text{O} - \text{C}_2\text{H}_2$; L	0.6 g of ground sample ashed at 500°C ; residue dissolved in 1.5 ml of 1 + 1 HCl and diluted to 50 ml. Alternatively 0.6 g of sample digested with 12 ml of 3 + 17 HCl + HNO_3 and diluted to 50 ml	86/C450
P	528	Plant	$10-25 \mu\text{g ml}^{-1}$	MECA; F; L	As above	86/C450
P	213.62	Plant	$1-1000 \mu\text{g ml}^{-1}$	AE; ICP; L	As above	86/C450
Pb	—	Plants, soils	—	AA or AE; —; —	Acid extracts of soils and plants	S/1210
Pb	283.3	Soil	—	AA; ETA; S	Slurry atomisation by platform in furnace ETA	86/C168
Pb	283.3	Hay	$3.6 \mu\text{g g}^{-1}$ }	AA; ETA; S	Powdered and homogenised sample analysed by cup-in-tube technique	86/192
Pb	368.3	Soil	$129 \mu\text{g g}^{-1}$ }	AA; ETA; S	Comparison of digestion procedures and analytical techniques	86/231
Pb	—	Soil, plant	—	AA; ETA; L AE; ICP; L	Ashed at 450°C , digested and extracted with dithizone into CCl_4	86/422
Pb	283.3	Plants	$>0.01 \text{ mg kg}^{-1}$	AA; ETA; L	Direct atomisation of powdered sample	86/C455
Pb	283.3	Soils	$10 \mu\text{g g}^{-1}$	AA; ETA; S	Finely ground sample converted into slurry for direct ETA	86/C514
Pb	283.3	Soils	$11 \mu\text{g g}^{-1}$	AA; ETA; S AA; F; L	Finely ground sample converted into slurry for platform ETA; good agreement between the two techniques	86/659
Pb	—	Spinach	$ca. 1.4 \mu\text{g g}^{-1}$	AA; ETA; S	Freeze-dried spinach ball-milled for 1.5 h and homogenised with water; diluted to 100 ml; deuterium background correction	86/664
Pb	—	Soils	—	AA; ETA; S	H_3PO_4 added to prevent Pb loss during charring	86/714
Pb	—	Plants	—	AA; F, micro-cup in air - C_2H_2 ; S	Pb in samples atomised from a microsampling cup	86/C761
Pb	220.35	Kale	$>0.37 \mu\text{g g}^{-1}$	AE; ICP; L	See Ag, ref. 86/971	86/971
Pb	—	Tea leaves	$>0.03 \mu\text{g g}^{-1}$	AE; —; L	See Cr, ref. 86/1343	86/1343
Pb	—	Sediments	$ca. 80 \text{ mg kg}^{-1}$	AA; ETA; S	Homogenised for slurry atomisation; Zeeman-effect background correction	86/1436
Pb	—	Plants	—	AA; ETA; S	Slurry in 5% HNO_3 ; gave satisfactory agreement for CRMs	86/C1974
Pb	—	Soils	—	AA; ETA; S	Study of matrix components effects in slurry ETA	86/C1977
Pt	—	Sediments	$1.6-20 \text{ ng g}^{-1}$	AA; ETA; L	Pt pre-concentrated on single ion-exchange resin bead	86/1625
Sb	—	Soils, rocks	$>0.21 \text{ p.p.b.}$	AA; Hy, ETA; L	Determinant converted into stibine; hydride collected in liquid N_2 trap, then displaced into graphite furnace	86/1714
Se	—	Sediments	$>10 \text{ ng g}^{-1}$	AA; Hy; L	Digested with $\text{HNO}_3 - \text{HClO}_4$ for total Se; extracted with weak NaOH for selenate and selenite	86/1286
Se	—	Plants	—	AA; ETA; L or S	Digested with HNO_3 under pressure or analysed directly with cup-in-furnace technique; Mg + Pd + HNO_3 added as matrix modifiers	86/C154
Se	—	Biological materials	—	AA; ETA, Hy; L	Development of automated reduction system for Se^{IV} and Se^{VI}	86/1718
Se	—	Sediments	—	AA; ETA, Hy; L	Se volatilised as H_2Se and trapped in a graphite furnace at 600°C	86/1922
Sn	—	Geological samples	$>1 \mu\text{g g}^{-1}$	AA; F, $\text{N}_2\text{O} -$ C_2H_2 ; L	Sample fused with LiBO_2 ; dissolved in 15% HCl; Sn extracted with 4% TOPO in IBMK	86/692

Table 3. SUMMARY OF ANALYSES OF SOILS, PLANTS, FERTILISERS AND RELATED MATERIALS—*continued*

Element	λ/nm	Matrix	Concentration	Technique; atomisation; analyte form	Sample treatment/comments	Reference
Te	—	Soils, rocks	—	AA; F; L	See In, ref. 86/682	86/682
Tl	276.8	Soils	$3 \mu\text{g g}^{-1}$	AA; ETA; S	Direct atomisation of powdered sample	86/C455
Tl	—	Soils, rocks	—	AA; F; L	See Au, ref. 86/682	86/682
Y and REEs	—	Rock powders	—	AE; ICP; L	Separation by ion-exchange chromatography using HPLC; 36-channel ICP-AE spectrometer used as detector	S/1277
Zn	—	Plants, soils	—	AA or AE; —; —	Acid extracts of soils and plants	S/1210
Zn	—	Soils	—	AA; —; L	Extracted with 1 M KCl with and without 0.01 M Triton B	86/356
Zn	—	Soils	—	AA; —; L	1 g of soil digested with 20 ml 1 + 1 HNO ₃ for 4 h at 2.2 atm in a pressure cooker	86/432
Zn	—	Soils	—	AE; ICP; L	Six extractants were compared	86/C598
Zn	—	Plant tissues	—	AA; F; L	(see Cu, ref. 86/C598)	
Zn	—	Plant tissues	—	AA; —; L	Digested with HNO ₃ + H ₂ SO ₄ (2 + 1), then H ₂ O ₂	86/1801
Various (11)	—	Plants	—	AE; ICP; L	A collaborative study based upon six plant samples and 14 laboratories	86/49
Various (16)	—	Peat	—	AA; —; —	Comparison of techniques for ten samples; dry ashing followed by HF treatment and wet digestion with HNO ₃ - HClO ₄ - HF were most satisfactory	86/55
Various (15)	—	Plants	—	AE; ICP; L	Study of pH effect on Chelex 100 separation of trace elements from various acid digests	86/112
Various (13)	—	Plant ash	—	AE; spark; L	Ashed at 500 °C for 10 h; extracted with HNO ₃ - LiNO ₃ - Bi (as internal standard); results compared well with those by AAS and ICP-AES	86/226
Various (6)	—	Aluminous earths	—	AA; ETA; S	Slurry atomisation	86/C289
Various (21)	—	Plants, soils	—	AE; ICP; L	Evaluation of techniques by analysis of CRMs	86/349
Various (18)	—	Plants	—	AA; ETA; L		
Various (11)	—	Plants	—	AE; ICP; S	Powdered plant sample in graphite cup inserted into an ICP	86/386
Various (11)	—	Red algae	—	AA; F; L	2 g of sample dried at 105 °C; 10 ml of HNO ₃ added and left for 6 h; dried in sand bath; ashed at 500 °C for 8–10 h; dissolved in 10 ml of HNO ₃ + 5 ml of HF; evaporated till almost dry; 30% perhydrol added dropwise to give clear solution; 2 ml of HCl added and mixture heated to expel nitrogen oxides; diluted to 25 ml	86/C452
Various (11)	—	Red algae	—	AE; F; L		
Various (11)	—	Red algae	—	AA; ETA; L (Co only)		
Various (6)	—	Plants	—	AA; F; L (for Cd, Pb, Zn)	Dried, homogenised samples digested with H ₂ SO ₄ + HNO ₃ + HClO ₄	86/C453
Various (6)	—	Plants	—	AA; ETA; L (for Cu, Mn, Fe)		
Various (9)	—	Soils, sediments	—	AE; ICP; L	Digested with HNO ₃ - HClO ₄ - HF in platinum crucible; HF and HClO ₄ boiled off; residue dissolved in 10% HNO ₃	86/C458
Various (11)	—	Wood	—	AE; ICP; L	Cr used as internal standard	86/C461
Various (6)	—	Animal feeds	—	AE; ICP; L	Kjeldahl digest used; 2 g of sample + 15 ml of 18 M H ₂ SO ₄ + catalyst	86/661
Various (12)	—	Flour	—	AA; ETA; L	Digested with HNO ₃ - H ₂ O ₂ ; simultaneous multi-element continuum source AA with échelle spectrometer	86/665
Various (9)	—	Plants	—	AE; ICP; L	Sample digested with HNO ₃ - H ₂ O ₂ in a microwave oven	86/715
Various (9)	—	Wood	—	MS; ICP; L	Compared H ₂ O ₂ digestion, ashing, low-pressure O ₂ ignition and O ₂ combustion methods	86/C794
Various (9)	—	Plants	—	AE; ICP; L	Sample digested with HNO ₃ - H ₂ O ₂ in a microwave oven	86/C812
Various (29)	—	Insect metabolites	—	AE; ICP; L	—	86/C849
Various (22)	—	Grapefruit peel	—	AE; ICP; L	—	86/962
Various (11)	—	Plants	—	AE; ICP; L	—	86/1058
Various (10)	—	Soils	—	AE; DCP; L	Samples fused with Li ₂ CO ₃ - H ₃ BO ₃ on a graphite powder bed at 950 °C for 20 min; dissolved in 4% HNO ₃	86/1093
Various (10)	—	Plants	—	AE; ICP; S	Direct sample insertion into ICP	86/C1136
Various	—	Sediments	—	AE; ICP; S	Direct sample insertion into ICP	86/C1138

Table 3. SUMMARY OF ANALYSES OF SOILS, PLANTS, FERTILISERS AND RELATED MATERIALS—*continued*

Element	λ/nm	Matrix	Concentration	Technique; atomisation; analyte form	Sample treatment/comments	Reference
Various (9)	—	Kaolinite, cereals	—	AE; ICP and DCP; S	Slurry nebulised into plasmas with Babington nebuliser	86/C1196
Various (25)	—	Tree rings	—	AE; ICP; L	Digested with acid - H_2O_2	86/C1232
Various (30)	—	Norway spruce	—	AE; ICP; L	—	86/C1233
Various (11)	—	Feeds	—	AE; ICP; L	Digested with 4 + 1 HNO_3 + HClO_4 , HF added if necessary; diluted with 10% HNO_3	86/C1235
Various	—	River sediments	—	AE; ICP; L	Digested with acids	86/1287
Various (48)	—	Geological materials	—	AE; ICP; L	Fused with lithium tetraborate; dissolved in glycerin - HCl	86/1288
Various (23)	—	Geochemical samples	—	AE; ICP; S	Powdered samples inserted directly into ICP	86/1297
Various	—	Plants	—	AE; ICP; L	Heated with HNO_3 to 60 °C over 30 min; heated to 90 °C for 90 min with H_2O_2 addition	86/1338
Various (6)	—	Soils	—	AA; F; L AE; F; L	Fused 200 mg of soil with 1 g of 1 + 8 boric anhydride + Li_2CO_3 ; cooled; dissolve in 15 ml of HCl	86/1366
Various	—	Leaves	—	AF; F, Ar-separated air - C_2H_2 ; L	—	86/1356
Various (9)	—	Conifer needles	—	AA; —; L	Digested with aqua regia	86/1428
Various (9)	—	Soils	—	—	Digestion with aqua regia; <i>ca.</i> 88% recovery compared with CRMs	86/1430
Various (10)	—	Sediments	—	AA; ETA; L	Digested with aqua regia; evaporated; residue dissolved in HCl + HF; evaporated; heated with HNO_3 + HClO_4 ; evaporated; dissolved in HCl	86/1450
Various	—	Leaves	—	MS; ICP; L	Digestion	86/C1476
Various	—	Soils, rocks	—	MS; ICP; L	Digested with acid mixtures; evaporated to dryness; residue dissolved in HNO_3	86/C1484
Various (23)	—	Soils	—	AE; ICP; L	Evaluation of Federal Register proposals	86/C1551
Various (10)	—	Muds, bauxites	—	AE; ICP; L	Fused with lithium tetraborate on a Claissé Fluxer VI; dissolved in HNO_3	86/C1555
Various (5)	—	Rocks	$>2\text{--}10\ \mu\text{g g}^{-1}$	XRF; —; S	Ground to 300 mesh	86/1666
Various (5)	—	Sediments	—	AA; ETA; L	Study of effects of HCl, HNO_3 , HClO_4 and HF	86/1742
Various (8)	—	Plant ash	—	AA; F, air - C_2H_2 ; L	Sorption pre-concentration on to a polymeric thioether (to concentrate trace heavy metals) in presence of NaDDC; decomposed with HNO_3 ; concentrated with HCl	86/1827
Various (27)	—	Plant	—	AE; ICP; L	Simultaneous extraction of 27 ions with APDC - hexamethylenediammonium hexamethylenedithiocarbamate into xylene	86/1880
Various (4)	—	Tomato leaves	—	AF; F; L	DCP used as excitation source for AFS	86/1888
Various (8)	—	Soils, sediments	—	AE; ICP; L	Digested with HNO_3 ; gave 82–94% recovery for heavy metals	86/1906
Various (9)	—	Geological materials	—	AA; F; L	Extracted with HCl + H_2O_2 ; extracted with 10% Aliquat 336 in IBMK from ascorbic acid + KI + 6 M HCl	86/1935
Various	—	Soils, grass	—	AE; ICP; L	ICP-AES compared with XRF	86/1953
Various (9)	—	Soils, rocks	—	AE; ICP; L AA; F; L	Fused with $\text{Li}_2\text{B}_2\text{O}_4$	86/1959
Various	—	Soils, ores	—	AA; F, air - C_2H_2 ; L	Acid digestion; coprecipitation with $\text{Fe}(\text{OH})_3$; Fe^{III} reduced with ascorbic acid; Bi, Cd, Cu, In and Sb extracted from 0.1 M KI - 2 M H_2SO_4 into IBMK; Zn back extracted; other elements back-extracted with 20% HNO_3 + 20% H_2O_2	86/2028

oxides of iron, aluminium and manganese occurred. Concentration of Ir and Pt on to a single resin bead has been used in the analysis of marine waters and sediments (86/1625). The elements were then determined by graphite furnace ETA-AAS.

Separation by *conversion of determinand to a volatile form* has sometimes been used with a degree of success. Willie and

co-workers (86/1922) separated Se from sediment digests as the hydride, trapping the latter in a graphite furnace at 600 °C prior to ETA-AAS determination. Boron in vegetation has been separated by volatilisation as methyl borate produced by reaction between boric acid and methanol in H_2SO_4 solution (86/1470). The methyl borate was transferred directly into the atomiser for B determination by AAS.

Numerous papers have been published in which *solvent extraction* has been used as a pre-concentration and/or separation technique. Owing to its agricultural importance, the determination of Mo has attracted particular attention in this respect (86/72, 86/692, 86/1766, 86/1935). Choice of spectroscopic finish has been fairly evenly divided between ETA-AAS, FAAS and ICP-AES. Published procedures for single elements include: As in soils (86/1905); Be in soils (86/407); Cd in biological materials (86/1023); Cu in tea (86/1460); Au in vegetation (86/423); In in sediments (86/85); and Mo in soils (86/72) and plant tissues (86/1766, 86/2030). More details of these procedures may be found in Table 3. Multi-element simultaneous extractions have also been recommended by various workers (86/422, 86/682, 86/692, 86/1094, 86/1880, 86/1935, 86/2028). One particularly interesting paper was concerned with the automated solvent extraction separation of Cd prior to determination by ICP-AES (86/1023). Automated solvent extraction is still only rarely used routinely in atomic spectrometric analysis.

Automation of sample preparation has been the subject of several other papers. Ion exchange pre-concentration becomes much more suitable for routine use if fully automated, e.g., by FI (86/2024). For plant Cd, detection limits were thus improved 15-fold at an analysis rate of 24 samples per hour. Soil As (86/C1581) and Se (86/1718) determinations by hydride generation are also much more convenient if automated. Automated FI systems offer considerable scope for facilitating soil/plant research, especially in speciation studies. Pitluck and co-workers (86/C1549), for example, used FI-AAS to fractionate and determine complexed and non-complexed trace elements. In busy routine analytical laboratories, even automation of sample presentation and data processing may offer considerable scope for time saving.

3.2. Solid Sample Analysis

Table 3 clearly shows the growth in interest in *solid analysis by atomic absorption spectrometry* with little or no sample pre-treatment. This has arisen as a consequence of the availability of platform in furnace techniques, and of improved background correction in AAS, particularly with Zeeman-based systems (86/C918, 86/1824). The technique is particularly favoured for volatile elements, especially Cd, Hg, Pb and, to a lesser extent, Cu (86/1436) and Se (86/C1542). Slavin and Carnrick (86/1471) have reviewed the applications of the stabilised temperature platform furnace. Graphite platforms are most widely used, though tantalum inserts have also been suggested (86/2027). Considerable attention has been paid to the importance of particle size in solid sample ETA. Problems generally have been related more to changes in atomisation rate rather than to pipetting errors (86/C168, 86/C514). Atomiser design is less critical for the direct determination of more volatile elements such as Ag, Bi, Cd, Pb and Tl (86/C455) than for less volatile elements. With a purpose-built cup in tube technique, however, even elements such as Cr may be determined with excellent selectivity and sensitivity (86/192). An ETA system has also been used to volatilise Au from algal cells into a DCP (86/1903).

Satake and Uehiro (86/667) have described a *carbonisation pre-treatment for biological materials* suitable for use in XRF. Heating at 300 °C for 1–2 h converted the sample materials into a form in which they could be very easily powdered with an agate mortar and pestle. This carbonisation process may be useful for slurry preparation prior to ETA or FAAS or ICP-AES analysis for some biological materials.

Nebulisation of solid samples as suspensions or slurries into flames has attracted little attention, although some success has been achieved in the determination of Pb in vegetation by *microsampling-cup* FAAS (86/C761).

Three basic techniques have been suggested for introduction of solid geological and plant samples into *plasmas* for

AES, slurry atomisation (86/C1196), direct powder introduction (86/1297) and the use of direct insertion devices (86/386, 86/C1136, 86/C1137). The last approach offers a potential advantage of being less dependent upon successful grinding of the total sample to a particle size < ca. 5 µm, a requirement for a reliable nebulisation technique. The approach has become more feasible for routine use because of the availability of inexpensive electromechanical and robotic systems well suited to automated insertion of the sample probe into the plasma (86/386, 86/C1136). All three techniques are capable of giving reliable results, but none is yet used widely on a routine basis in soil and plant analysis, although some relevant samples have been used to test the devices.

3.3. Developments in Atomic Absorption Spectrometry

Apart from the increased interest as shown in solid sample analysis by ETA-AAS, there have been a few other innovative studies worthy of specific mention. One of particular interest involved the use of discrete sample nebulisation to measure the *absolute mass* of the element of interest (Cu or Mn) (86/666). The entire digest from 1–10 mg plant samples was nebulised, and a calibration graph was obtained by nebulisation of different volumes of a single standard. Satisfactory results were obtained, but such a system depends upon linear concentration *versus* absorbance relationships and constant transport efficiency. In the strictest sense, therefore, it should not be regarded as an absolute method.

Trapping of atoms or molecular species on to cold surfaces is a useful concentration technique for some elements. West and co-workers (86/1854) have applied their atom-trapping device to the determination of Cd in CaCl₂ extracts of soil. A detection limit of 0.004 µg g⁻¹ of the soil was cited, and recovery was quantitative, except at the lowest concentration studied. Results compared favourably with those from a standard solvent extraction - back extraction FAAS procedure. Chinese scientists enhanced the detectability of Sb determination in geological materials by using a liquid-nitrogen trap to concentrate the volatilised hydride (86/1714).

The improved selectivity and excellent sensitivity of probe or platform in furnace ETA-AAS has given a new impetus to *continuum-source atomic absorption spectrometry*. When probe-ETA is coupled with the simultaneous multi-element determination capability offered by échelle spectrometers, then the potential of the technique compares favourably in many respects with that of ICP-AES. Such combinations have been tested on environmental samples with encouraging results (86/665, 86/C1975).

Interferences in AAS, particularly the effects of the various acids used in sample dissolution, have attracted the attention of several investigators. Acid effects have been examined for both FAAS (86/C586) and ETA-AAS (86/1742). Zbiral and Stana (86/4) have recommended magnesium as a releasing agent for the determination of Ca in plants, to overcome interference from aluminium. Biavati (86/1767) was unable to overcome the effect of aluminium in the determination of Ba in glasses and feldspathic sands with any of the common releasing agents.

The importance of *molybdenum* in plant and soil science has already been noted; unfortunately its determination often presents problems. It has been claimed, however, that the variability of results caused by the progressive degradation of pyrolytic graphite surfaces in ETA may be eliminated by use of integration and adequate control of base-line drift (86/1848).

Indirect determinations by AAS appear regularly in the literature, and three worth considering have been published over the past year. Malathion has been measured, following hydrolysis in methanolic 1 M KOH, by addition of Cu²⁺ and extraction of the Cu complex from weakly acidic solution with CHCl₃ (86/1458). The solvent was evaporated and the residue

dissolved with concentrated HNO_3 prior to analysis by AAS. Nicotine has been determined by precipitation with Cu, Hg, Pb or Zn and dissolution of the precipitate for subsequent metal determination (86/702). Nitrate has been measured by an indirect method based upon precipitation with silver 1,10-phenanthroline and determination of the excess of Ag by AAS in an air - C_2H_2 flame (86/1711).

3.4. Developments in Atomic Fluorescence Spectrometry

In the absence of genuinely inexpensive, high-intensity (and preferably wavelength tunable) sources, AFS remains an academic curiosity to most environmental analysts, except perhaps for the determination of low levels of Cd, Hg and Zn. This is so in spite of the instrumental cost benefits of *non-dispersive* AFS over AAS that have been stressed in a review (86/2006). With such a system, of course, some excellent detection limits are attainable, for example 1 ng ml^{-1} of Au from geochemical samples after solvent extraction (86/1368). It has also been shown that non-dispersive AFS is an excellent detector for hydride-forming elements following GC separation of the hydrides using a sub-ambient Chromosorb 102 column (86/1928).

Plants have been used as test samples in evaluations of two *novel atomic fluorescence spectrometers*. One report described the use of a DCP as an excitation source (86/1888), the other discussed an inexpensive, computer-controlled, slew-scan, AF spectrometer for multi-element determinations using a Xe arc source and a separated air - C_2H_2 flame (86/1356).

3.5. Developments in Atomic Emission Spectrometry

Whilst the use of *inductively coupled plasmas* in AES is still increasing, there is little novel to report here apart from growth in interest in the direct introduction of solid samples into plasmas discussed in section 3.2. Dean *et al.* (86/971) have described the use of graphite rod vaporisation for introduction of samples to an axially viewed ICP. Reasonable agreement with published values for Ag, Cd, Cu, Mn and Pb was obtained for Bowen's standard kale sample.

A number of authors have discussed some of the *limitations* of ICP-AES in environmental analysis. Benton Jones (86/C1229) experienced problems in the use of 0.5 N calcium lactate and BaCl_2 as soil extractants, although sodium acetate, ammonium acetate, ammonium hydrogen carbonate and Mehlich's No. 3 solution gave satisfactory results. Isaac and Johnson (86/C1228) discussed the problems of optimisation of conditions for simultaneous determination of diverse major elements in agricultural samples. Other workers have discussed the inadequacy of internal standardisation techniques for sequential ICP-AES analysis (86/C461). An appropriate internal standard could compensate for long-term drift, but introduced additional error in attempts to compensate for short-term fluctuations. Nevertheless, ICP-AES is increasingly being accepted as a reliable technique (86/C1551).

The MIP is much less widely used for AES of environmental materials. One novel application reported this year is the use of MIP-AES for *evolved gas analysis* in the speciation of carbonate minerals. Carbon emission intensity was monitored as the carbonates decomposed at different temperatures as the temperature was steadily raised (86/C1602).

Hollow cathode excitation sources have been suggested for the analysis of biological samples by some workers (86/C137, 86/C853). It is hard to see that they will ever be sufficiently convenient, however, for widespread routine use in environmental analysis. Caroli *et al.* (86/C129) have suggested that the microwave-coupled HCL is a superior source for AES, giving improved precision and line-to-background ratios.

3.6. Inductively Coupled Plasma Mass Spectrometry

The instrument manufacturers continue to report that *inductively coupled plasma mass spectrometry* is being used more

and more widely for geochemical analysis (for example, 86/C1484). True user-produced papers are still rare. Kargacin and Barnes (86/C794) gave a presentation on tree-ring wood analysis and Hausler (86/C1476) one on applications in a petroleum laboratory (where NBS orchard leaves were used as a test material). The technique is still in its infancy for routine analysis.

3.7. Other Techniques and Comparative Studies

An adequate supply of *certified reference materials* is often a problem in environmental science. MacDonald and O'Brien (86/1616) have suggested mixing CRMs to extend the range available to allow greater confidence in analytical performance. Alvarez (86/C544) has discussed the preparation, characterisation and certification of CRMs, including those for environmental science.

Numerous *comparisons of atomic absorption and plasma emission spectrometry* have been reported (86/231, 86/349, 86/C458, 86/C598, 86/1959). Results for environmental samples have generally compared favourably for the two techniques, with ICP-AES primarily being superior with respect to sample throughput (86/231, 86/1959). When $\text{Li}_2\text{B}_2\text{O}_4$ fusion was used to dissolve soils or rocks, problems were encountered when using a conventional silica torch in ICP-AES. The problem was overcome by use of a demountable, corrosion-resistant torch, in which the sample solution was supplied via a corundum tube (86/1959).

Fan and Fang (86/226) have reported the results of a *comparison of several techniques* for the determination of 13 elements in plant tissue. High voltage spark AES using rotating graphite disk electrodes with Bi as an internal standard gave similar results to AAS and ICP-AES. Graphite furnace AAS compared favourably with NAA for the determination of Ag in bryophytes, but a cyclic activation scheme to generate and detect the short-lived isotope ^{110}Ag suffered from interference from ^{76}As (86/747). In a comparison of DCP-AES, graphite furnace AAS and colorimetry for plant Al determinations, all three techniques gave comparable results (86/1059). In a study of methods for determining Al extracted from soils by BaCl_2 , AAS gave lower results than colorimetric or titrimetric methods (86/1855). Four techniques, MECA, AAS, solution spectrophotometry and ICP-AES have been compared for plant P determination (86/C450). On the basis of sensitivity, detection limit, linearity of calibration, useful concentration range, precision, accuracy, susceptibility to interferences, speed of analysis and simplicity of sample preparation, the authors suggested that ICP-AES was the method of choice. Relative costs should also perhaps be considered.

A comparison has also been made of *X-ray fluorescence* and ICP-AES for the determination of trace elements in powdered soil and grass samples (86/1953). Trace element concentrations down to between 1 and $10 \mu\text{g g}^{-1}$ could be detected by XRF using the Compton scattering peak to correct for small differences in matrix absorption between samples and standards. The precision by both methods was in the range 5–10%. The use of energy dispersive XRF for the determination of Ba, Rb, Sr, Zn and Zr in international carbonate rock standards has also been reported (86/1666).

Inter-laboratory comparisons often provide valuable information about the merits of different techniques. A recent study involving 14 laboratories showed that plant tissue analysis by ICP-AES yielded superior RSD values to those cited in an earlier study of multi-element analysis by spark emission spectrometry (86/49). Another investigation of trace elements in sediments and sewage sludges by 12 laboratories, in which three samples were analysed on ten occasions revealed three factors affecting the results (86/966). The first was an element effect, related to how difficult each element was to determine. The second was a laboratory effect, which

depended upon how well each participating laboratory could repeat its earlier results; this effect varied markedly from centre to centre. The third was a method effect, which depended upon sample dissolution procedure. Cary (86/48) has published the results of a collaborative study on the determination of plant tissue Cr by ETA-AAS. The procedure

used was based upon HNO_3 - HClO_4 - H_2SO_4 digestion, reduction with NaSO_3 and co-precipitation with $\text{Fe}(\text{OH})_3$. The iron was removed by extraction from the dissolved precipitate, silica dissolved in HF and the Cr finally determined. At Cr levels of $3 \mu\text{g g}^{-1}$, precision was good, but deteriorated dramatically at 150-times lower concentration.

4. CONCLUSION

Reference was made in the introduction to the growing maturity of atomic spectrometry applied to environmental samples and to the growing demand for more data. Frequently this is obtained by automated instrumentation, often operated unattended because of other demands upon laboratories. Clearly given these constraints and the importance of environmental monitoring, quality control is vital. Therefore the

increasing numbers of environmental CRMs are to be welcomed and fully utilised. Additionally, there would seem to be considerable scope for the development of more inter-laboratory quality control exercises. Certainly the future health of environmental analysis, as well as of the environment, will depend upon both an ability to "get it right" and to be seen to be "getting it right."

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Glossary of Abbreviations

Whenever suitable, elements may be referred to by their chemical symbols and compounds by their formulae. The following abbreviations are used extensively in the Atomic Spectrometry Updates.

a.c.	alternating current	ICP	inductively coupled plasma
AA	atomic absorption	IR	infrared
AAS	atomic absorption spectrometry	LC	liquid chromatography
AE	atomic emission	LTE	local thermal equilibrium
AES	atomic emission spectrometry	MECA	molecular emission cavity analysis
AF	atomic fluorescence	MIP	microwave-induced plasma
AFS	atomic fluorescence spectrometry	MS	mass spectrometry
APDC	ammonium pyrrolidinedithiocarbamate (ammonium tetramethylenedithio- carbamate)	NAA	neutron activation analysis
ASV	anodic-stripping voltammetry	NaDDC	sodium diethyldithiocarbamate
CMP	capacitively coupled microwave plasma	NTA	nitritotriacetic acid
CRM	certified reference material	OES	optical emission spectrometry
CW	continuous wave	PMT	photomultiplier tube
d.c.	direct current	p.p.b.	parts per billion
DCP	d.c. plasma	p.p.m.	parts per million
DMF	<i>N,N</i> -dimethylformamide	PTFE	polytetrafluoroethylene
DNA	deoxyribonucleic acid	r.f.	radiofrequency
EDL	electrodeless discharge lamp	REE	rare earth element
EDTA	ethylenediaminetetraacetic acid	RM	reference material
ETA	electrothermal atomisation	RSD	relative standard deviation
FAAS	flame AAS	SBR	signal to background ratio
FAES	flame AES	SEM	scanning electron microscopy
FAFS	flame AFS	SNR	signal to noise ratio
FI	flow injection	SSMS	spark-source mass spectrometry
GC	gas chromatography	TCA	trichloroacetic acid
GDL	glow discharge lamp	TLC	thin-layer chromatography
HCL	hollow-cathode lamp	TOPO	triocetylphosphine oxide
h.f.	high-frequency	u.h.f.	ultra-high-frequency
HPLC	high-performance liquid chromatography	UV	ultraviolet
IBMK	isobutyl methyl ketone (4-methylpentan- 2-one)	VDU	visual display unit
		VUV	vacuum ultraviolet
		XRF	X-ray fluorescence