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Invited Paper

Atom Trapping Atomic Absorption Spectrometric Determination of Some Trace Elements in Soils, Natural Waters, Seawater, and Bovine Liver

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The operational conditions for the determination of Ag, As, Au, Bi, Cd, Cu, Mn, Pb, Sb, Se, Tl, and Zn by atom trapping atomic absorption spectrometry are summarised. With this technique some of these trace elements can be determined in soils, natural waters, seawater and bovine liver at concentrations that are not possible by the conventional technique of flame AAS. For example, seawater is diluted ten-fold with distilled water to overcome nebulisation problems due to salt concentrations and the trace elements are collected for 2 min in situ in the air-acetylene flame before release and measurement. The attack of sodium on the hot silica atom trap tube in the flame gases is prevented by pre-aspiration of aluminium chloride into the flame, thus depositing a protective film of Al_2O_3. X-Ray diffraction, infrared spectroscopy, scanning electron microscopy, and spark source mass spectrometry are used to show that the protective alumina film consists of mainly σ alumina with a small amount of θ alumina spheroids of varying sizes <1 μm diameter and is highly pure. The nature of a similarly deposited Fe_2O_3 film is shown to be a more closely packed and irregular form of hematite with a small content of metallic iron. The results obtained by this simple new technique compare well with those obtained by spark source mass spectrometry and electrothermal AAS with a graphite furnace.

The development of atom trapping atomic absorption spectrometry[1)] as a potential analytical technique for ultratrace element determination has been described in previous papers.[2–7)] The surface of a water-cooled 4 mm o.d. silica tube traps and preconcentrates atomic species, or their precursors, within the body of an air-acetylene flame. When a sufficient amount has been collected (e.g. after 30 s—5 min) the trapped species are released into the flame subsequently by ejecting the water with a blast of air. The skin temperature of the silica tube attains that of the flame gases within 5—10 seconds. The trapped analyte is then atomised normally as a transient cloud of atoms within the flame. The tube is mounted permanently in the flame. Because of the uniquely low coefficient of thermal expansion of silica, the tube withstands the repeated thermal shocks produced by switching cold water back through the hot silica tube for the next trapping cycle for at least one hundred experiments before the surface becomes seriously etched. The atom trapping technique preserves the inherent simplicity, element-specificity and reliability of conventional flame AAS, as well as its ease of operation. In addition, it offers considerably higher sensitivity than the conventional technique whilst preserving most of its relative freedom from matrix interference when compared to other analytical methods of similar capacity. Hence we found it possible directly to determine selenium in plants,[4)] and also lead and cadmium[5)] in soils which would have been impossible by conventional flame AAS because of the low levels involved. This paper further explores the analytical applications of atom trapping AAS for the determination of some trace elements in fresh water, seawater, liver and soil samples, with particular attention to those containing very low analyte element concentrations. It also collates and summarises operational conditions for atom trapping AAS of Ag, As, Au, Bi, Cd, Cu, Mn, Pb, Sb, Se, Tl, and Zn.

Experimental

Equipment: The atom trapping AAS measurements were made with a Varian Techtron Model AA6 atomic absorption spectrophotometer equipped with background correction as described previously.[6)] Instrumental parameters for each of the elements were optimised using standard solutions; these are summarised in Table 1. The possibility of background absorption and scattering effects occurring during atomic absorption measurements was examined in each case; only for elements with resonance lines below 240 nm was background correction necessary.

An Instrumental Laboratories Model 751 atomic absorption spectrophotometer fitted with a Model 555 controlled-temperature graphite furnace was used for electrothermal AAS determinations of some fresh water samples for the purposes of comparison.

Sample Preparation: Six Scottish top-soils (1 g samples) were digested with three 10 ml aliquots of aqua regia and taken to dryness each time on a steam bath, as previously described.[5)] The final solutions were made up to 25 ml in 0.5 M nitric acid (1 M=1 mol dm^{-3}) and the arsenic concentrations in these solutions were measured by atom trapping AAS.

A nitric acid–hydrogen peroxide dissolution method was applied to the liver sample. In this method, a 1 g sample of the freeze-dried, powdered liver was digested with 10 ml of concentrated nitric acid on a steam bath and another 10 ml portion of the acid was added before the mixture was evaporated to less than 5 ml. The procedure was repeated with two 10 ml portions of 20 vol.(6%) hydrogen peroxide. The final mixture was filtered on Whatman No. 542 filter paper and the filtrate made up to 10 ml with 0.5 M nitric

Table 1. Instrumental Parameters for Atom Trapping AAS Determination of Twelve Elements

Working condition	Element											
	Ag	As	Au	Bi	Cd	Cu	Mn	Pb	Sb	Se	Tl	Zn
H. C. lamp current/mA	1	4	4	3	2	3	5	3	4	7	6	2
Band width/nm	0.2	1.00	0.2	0.2	0.5	0.5	0.2	1.00	0.2	1.00	0.5	0.5
Wavelength/nm	328.1	193.6	242.8	223.1	228.8	324.8	279.5	217.0	217.6	196.0	276.8	213.9
Distance between collector tube (base) and the burner head/mm	5	21	7	5	7	5	9	5	5	10	6	12
% obscuration of optical path by tube/%[a)]	50	35—40	25	10—15	50	50	35—40	50	35—40	25	35—40	50
Flame mixture[b)]	A-A	A-B	A-A	A-A	A-A	A-A	A-A	A-A	A-A	A-A	A-A	A-A
Flame condition[c)]	R	O	O	R	O	O	S	R	R	O	R	O
Background correction	No	Yes	No	Yes	Yes	No	No	Yes	Yes	Yes	No	Yes

a) % obscuration figures are approximate. b) A-A=Air-acetylene. A-B=Air-butane. c) Flame Condition: R=reducing, O=oxidizing, S=stoichiometric.

acid.

Fresh water samples were collected and stored in polypropylene bottles and were acidified with 1% nitric acid prior to use. The samples were stored in a cold room (4 °C) and warmed up to room temperature for an hour before analysis.

The sea water was first filtered through a 50 μm sintered glass filter to remove suspended material and acidified with 1% hydrochloric acid before storing in a polypropylene bottle.

Standard Solutions: Stock solutions for the analyte elements were prepared from analytical reagent grade chemicals. Standard solutions with concentrations appropriate to the analysis were diluted from the stock solutions immediately before use. These standard solutions were prepared with an acid strength and matrix similar to the samples so that any interference effects of matrix elements on nebulisation of the solution or the trapping or release of the analyte could be minimised.

Preparation of Coated Tubes: The pre-deposited alumina and iron oxide coatings on the silica atom trap tubes were prepared by aspirating a 5000 μg ml^{-1} solution of aluminium (5 min) or iron(III) chloride (30 s) into the flame, and collecting the oxide formed on the surface of the water-cooled silica atom trap tube.

Procedure for Measurement. Arsenic in Aqua Regia Digests of Soils: Standard arsenic solutions were prepared in the range 0.1 to 0.5 μg ml^{-1} As and were made up in 0.5 M nitric acid with 200 μg ml^{-1} each of sodium and iron added to the solutions to match the approximate content of soil digests. Both the sample digests and standard solutions were collected for four minutes on an iron oxide-on-alumina-coated tube prior to atomic absorption measurement. The standard solutions were measured before and after the sample to ensure no change in sensitivity as a result of tube surface alteration. The concentrations of arsenic in the digests found from the standard calibration curve were checked by a standard addition method. Arsenic, 25 μg equivalent to 1.0 μg ml^{-1} arsenic in the digest, was added to the sample soils before the digestion procedure. The amount of arsenic recovered from the digest was measured as above.

Zinc in Seawater: Standard zinc solutions (0.8—8 ng ml^{-1} Zn^{2+}) were prepared by diluting from a zinc stock solution. The solutions were made up in 0.05 M hydrochloric acid and with the addition of 1000 μg ml^{-1} NaCl to simulate the main matrix constituent of seawater. The seawater sample was diluted ten times with double distilled water. The zinc in this diluted sample and the standard solutions were collected on an alumina coated tube for a period of 1 minute prior to atomic absorption measurement. The accuracy of the measurement was checked by testing the recovery of added zinc (2, 4, and 6 ng) to aliquots of the diluted seawater sample.

Trace Elements in a Bovine Liver Sample: Ag. Bi, Cd, and Pb were determined in nitric acid-hydrogen peroxide digests of freeze-dried bovine liver. Standard solutions of these elements were prepared to contain 500 μg ml^{-1} Fe, and 200 μg ml^{-1} each of Ca, K, and Na approximately to match the matrix of the sample digests. The sample and standard solutions were collected for a period of 2 min (except for Cd which required only 30 s) on an iron oxide-on-alumina-coated silica atom trap before atomic absorption measurements were made. The accuracy of the method was checked by calculating the % recovery of lead added to the liver sample solution, and also by comparing the values with previous spark source mass spectrometry results.

Trace Elements in Fresh Water Samples: Several elements (Ag, Cd, Cu, Mn, Pb, Tl, and Zn) were analysed in water samples. The standard solutions were prepared by freshly diluting from stock solutions and making up in 0.05 M nitric acid. Both the standard and sample solutions were collected on alumina coated tubes, usually with a four or five min. collection time, depending on the concentration of the elements in the samples, except for zinc where the concentration was adequate for conventional flame AAS. The accuracy of the method was checked by graphite furnace atomic absorption spectrometry in some cases.

Results and Discussion

The twelve elements (Ag, As, Au, Bi, Cd, Cu, Mn, Pb, Sb, Se, Tl, and Zn) were first determined by atom trapping AAS using a silica atom trap tube according to the instrumental conditions outlined in Table 1.

Table 2. Comparisons of Characteristic Concentration[a)] and Detection Limits[b)] of Twelve Elements Determined by Conventional Flame AAS and Atom Trapping AAS

		Ag	As	Au	Bi	Cd	Cu	Mn	Pb	Sb	Se	Tl	Zn
Conventional Flame AAS													
Characteristic concentration[a)] /μg ml^{-1}		0.036	0.92	0.22	0.25	0.012	0.088	0.037	0.12	0.44	0.38	0.28	0.01
Detection limit[b)]/μg ml^{-1}		0.025	0.85	0.018	0.05	0.004	0.044	0.011	0.04	0.65	0.4	0.15	0.005
Relative standard deviation (%) (12 results)		1.5	7	4	5	3	5	2.5	3.5	5.5	8	4	5
Atom Trapping AAS (Silica Atom Trap)													
Characteristic Concentration[a)]/μg ml^{-1}	30 s collection	0.003	0.087	0.049	0.022	0.0013	0.015	0.010	0.010	0.038	0.050	0.043	0.002
	1 min collection	0.0016	0.045	0.037	0.012	0.0007	0.0075	0.005	0.0057	0.021	0.028	0.022	0.001
	2 min collection	0.0009	0.024	0.028	0.006	0.00046	0.004	0.003	0.0029	0.011	0.015	0.015	0.0005
	3 min collection	0.0006	0.019	0.022	0.004	0.00037	0.0028	0.002	0.0020	0.007	0.0088	0.012	0.00036
Detection limit[b)]/μg ml^{-1} (2 min collection)		0.0005	0.05	0.020	0.010	0.0001	0.004	0.002	0.005	0.036	0.030	0.009	0.001
Relative standard deviation/% (12 results)		2.9	10	8.7	8	7.4	5	4.2	6.8	8.3	14	5	6.3

a) Sometimes called sensitivity (μg ml^{-1} required for 1% absorption). b) Signal/Noise ratio 2/1.

Table 3. Characteristic Concentration and Detection Limits of the Twelve Elements Determined by Atom Trapping AAS Using Alumina and Iron Oxide Coated Tubes

	Ag	As	Au	Bi	Cd	Cu	Mn	Pb	Sb	Se	Tl	Zn
Alumina Coated Tube (2 min collection)												
Characteristic concentration /μg ml^{-1}	0.0015	0.072	0.039	0.010	0.0005	0.008	0.008	0.0026	0.044	0.023	0.024	0.0005
Detection limit/μg ml^{-1}	0.0008	0.15	0.035	0.030	0.0003	0.019	0.010	0.0011	0.048	0.05	0.011	0.0017
Relative standard deviation/% (12 results)	4	10	9	10	8	7	7	7.5	12	12	6	4
Iron Oxide Coated Tube (2 min collection)												
Characteristic concentration /μg ml^{-1}	0.0022	0.095	Not applicable	0.012	0.0002	Not applicable	Not applicable	0.003	0.090	0.022	0.027	0.0002
Detection limit/μg ml^{-1}	0.001	0.19		0.040	0.0001			0.015	0.10	0.045	0.012	0.0005
Relative standard deviation/% (12 results)	6	11		10	8			7	11	13	5	5

The characteristic concentration (μg ml^{-1} for 1% absorption) and detection limit for each element obtained by atom trapping AAS are compared with those of conventional flame AAS in Table 2. For all of these elements, even for Mn which has a relatively high melting point of 1244 °C, the atom trapping technique increased the sensitivity (characteristic concentration) considerably when ca. 2 min trapping periods were used. However, the loss of hollow cathode lamp signal due to partial obscuration of the optical path by the silica tube and light scattering noise on the tube surface, led to a somewhat poorer relative standard deviation. It will be seen that for elements with resonance lines below 200 nm, e.g. As and Se, this factor resulted in % relative standard deviations >10%. All the elements were determined using an air-acetylene flame except for arsenic which required the cooler air-butane flame to minimise volatilization losses of arsenic during the trapping cycle.

In order to minimise interference arising from the co-deposition of major matrix or chemically active species on the silica tube during the trapping of analyte species, alumina or iron oxide was pre-deposited on the silica tube before the sample solutions were analysed.[5] The determination of these elements by atom trapping AAS was, therefore, also made on alumina and iron oxide coated silica atom trap tubes. Table 3 summarises the results. Most elements were less sensitive when collected on these surfaces except for Cd, Pb, and Zn. The signals for Au, Cu, and Mn were depressed on the alumina coated tube and no signals were obtained from an iron oxide coated tube.

Nature and Structure of Alumina and Iron(III) Oxide Coating Materials: Investigations were made to identify the nature and structure of the alumina and iron oxide coatings, formed by rapid condensation of the vaporized products from an aluminium or iron(III) chloride solution on the ca. 200 °C silica

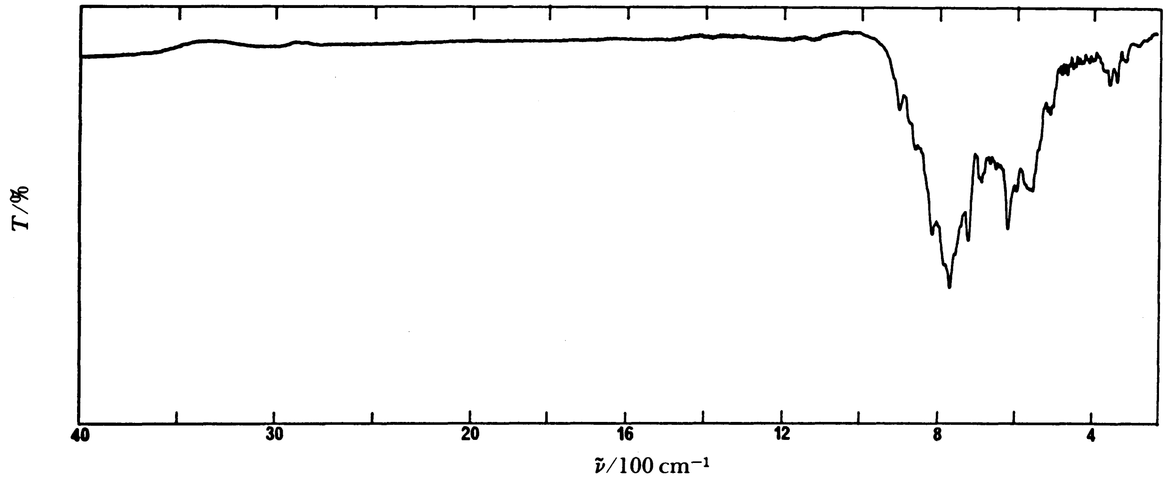

Fig. 1. Infrared absorption spectrum of alumina deposited on 'cold' surface of silica atom trap in air-acetylene flame. The Al_2O_3 is mainly δ but with a small amount of θ alumina.

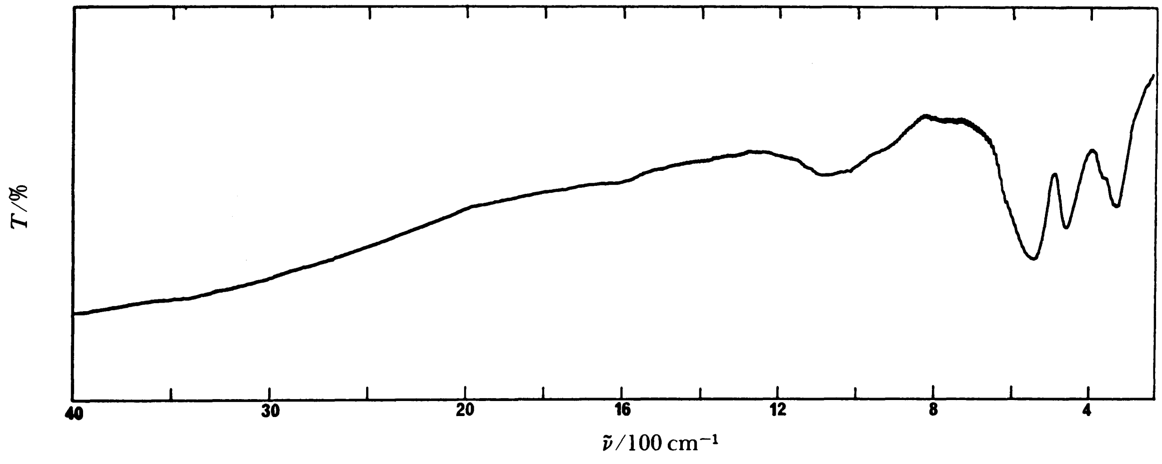

Fig. 2. Infrared absorption spectrum of iron oxide deposited on 'cold' surface of silica atom trap in air-acetylene flame. The deposit is mainly hematite with a small amount of metallic iron.

surface from flame gases ca. 3000 °C. Several techniques were employed, including infrared spectroscopy, X-ray diffraction, spark source mass spectrometry and scanning electron microscopy. The infrared spectra (Figs. 1 and 2) of the two coating materials showed that the alumina coating had a complicated absorption spectrum, but the iron oxide coating spectrum was identical to that of hematite.[8)]

The X-ray diffraction pattern showed the alumina deposit to be dominated by delta (δ) alumina with a small amount of theta (θ) alumina. The same technique confirmed that the iron oxide coating was hematite with a trace of Fe metal. The spark source mass spectrometric analysis indicated that except for Cl, P, and Si, most other elements are present at less than the $\mu g\ g^{-1}$ level in the alumina coating material. This coating can, therefore, be considered relatively free from contamination for trace element analysis.

Further studies of the coatings were made using scanning electron microscopy to examine their microstructure. Under high magnification (X10000), Figs. 3 and 4, the alumina coating is seen to consist of loosely packed spheroids. Although the spheres were of different sizes, the largest was less than 1 µm in diameter. The iron oxide coating, however, was more compact, and more irregular in size and shape. Although the pre-deposition of these coating materials on the silica atom trap surface was an efficient way of minimising interference, the sensitivity for most elements was slightly decreased relative to collection on a clean silica tube surface. Broad peak signals were also observed for some elements when collected on the coated surface. It seems probable that these coatings greatly increased the surface area whilst simultaneously allowing some of the analyte species to become sequestered in the interstitial spaces of the coating, thus protracting the release time as shown by the broader release peaks and correspondingly lower peak heights.

Effects of Extraneous Elements: Interference effects in atom trapping AAS are more complicated than in conventional flame AAS. The presence of an extraneous element in the analyte solution may influence the proportion of free analyte atoms formed in the flame as in the conventional flame technique, but additionally cause physical alteration of the tube surface or alloy formation on the trap and subsequently affect the efficiency of trapping and/or release of analyte from the collector tube.

More than ten extraneous elements of concentrations up to 500 $\mu g\ ml^{-1}$ were added to each of the analyte solutions and their effects on the analyte signal were determined by atom trapping AAS with an alumina coated tube. According to the effects they produced on the analyte signal, the extraneous elements could be classified into two groups. For alkali and alkaline earth metals and other volatile elements, the highest concentration added caused less than ±30% interference on the analyte signal. The presence of the alumina on the collector tube prevented chemical attack (vitrification) of the silica surface by alkali metals and the volatile nature of the

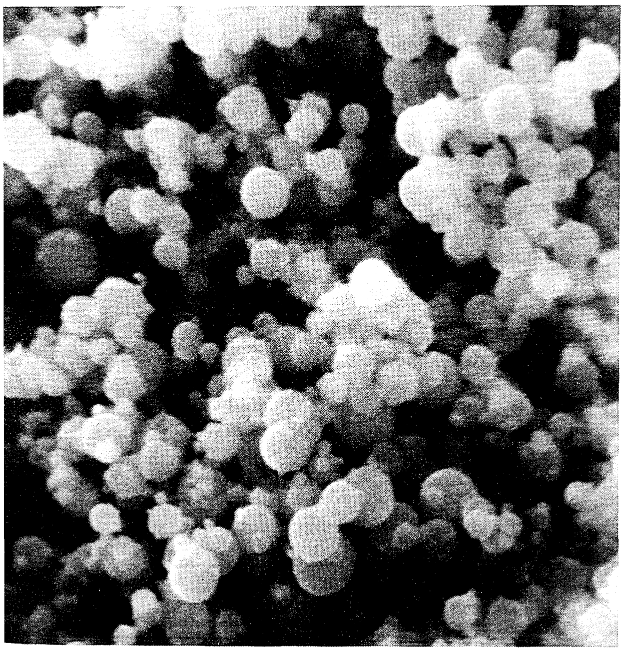

Fig. 3. Electron micrograph (X10000) of alumina deposited on 'cold' surface of silica atom trap following aspiration of $AlCl_3$ into air-acetylene flame.

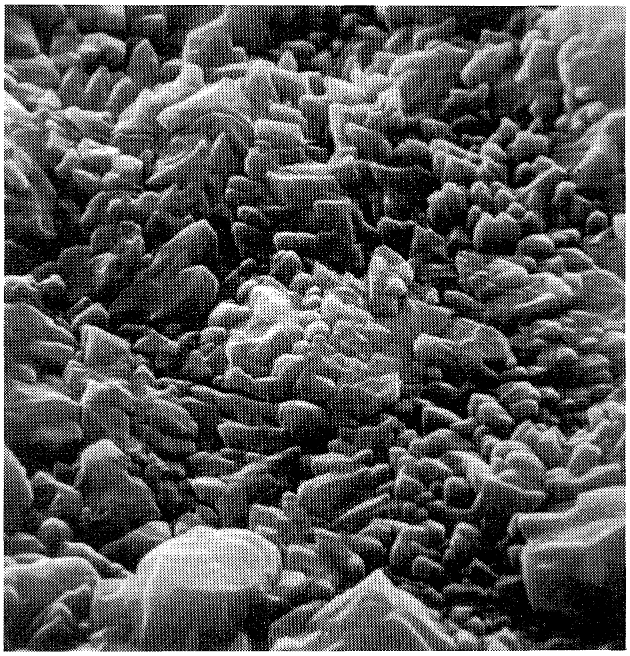

Fig. 4. Electron micrograph (X10000) of hematite deposited on 'cold' surface of silica atom trap following aspiration of $FeCl_3$ into air-acetylene flame.

metals also ensured their instant release together with the trapped analyte as the surface of the collector tube became hot without affecting the analyte signal to any marked extent. Such interference as occurred from these elements could be minimised by matrix matching and pre-conditioning of the tube with these elements before analysis.

The interference effects were more severe for involatile extraneous elements such as Fe, Co, Ni, Cu, Mn. For example, the presence of $500\ \mu g\ ml^{-1}$ Fe, $500\ \mu g\ ml^{-1}$ Co, or $500\ \mu g\ ml^{-1}$ Ni reduced the copper signal by 40, 50, and 60% respectively. The effects of these elements were mainly due to their virtually permanent deposition on the alumina surface resulting in a gradual alteration in physical structure of the surface for the trapping of the analyte species. In the case of iron, the effect could be eliminated by pre-deposition of iron oxide on top of the alumina coated tube, and then collecting the high iron-containing analyte solutions on this modified tube surface. However, for *high* concentrations of other non-volatile elements such as Co and Ni, pre-deposition of these elements or their oxides on the tube surface did not lead to elimination or compensation. Alternative methods must, therefore, be used for samples containing *high* levels of Co or Ni in their matrix.

Sample Analysis. The results reported in Tables 4—7 are those of single individual determinations.

Arsenic in Aqua Regia Digests of Soils: The presence of the extremely toxic element arsenic in the environment is mainly of geological origin, although industrial processes have also made contributions. A recent survey gave the average content of arsenic of over 1000 soils to be $11.3\ mg\ kg^{-1}$.9) A content of $>50\ mg\ kg^{-1}$ arsenic in a soil is regarded as potentially toxic to susceptible plants.10) Several acid mixtures have been used for the extraction of arsenic from soil; these include nitric and sulphuric acids,11) aqua regia,12) perchloric and nitric,13) and hydrofluoric and perchloric acids.14) Aqua regia was used in this work because it is widely used for monitoring heavy metals in polluted soils.15)

The arsenic contents of the six Scottish top-soils analysed in this study were found to range from 5—$10\ \mu g\ g^{-1}$. The % recovery of added arsenic was 100% (±10%), Table 4.

Zinc in Seawater: The direct determination of trace elements in sea water by conventional AAS is difficult because of their low concentrations and the high salt matrix. One common procedure frequently used is preconcentration/separation by solvent extraction followed by electrothermal atomization AAS for analysis,16) However, the sensitivity of the atom trapping method permits direct analysis of sea water diluted 10-fold to reduce nebulisation problems. The results of the analysis by atom trapping AAS are shown in Table 5. The concentration of zinc in the sample was found to be $9\ \mu g\ l^{-1}$ compared to a literature value of $10\ \mu g\ l^{-1}$.18) The % recovery of zinc added to the sample was also 100±10%.

Trace Elements in a Bovine Liver Sample: Flame atomic absorption spectrometry is often employed for the determination of trace elements in bovine liver tissue but, because of the high organic content in the sample, special sample treatments are required. Some

Table 4. Results of the Analysis of Arsenic in the Aqua Regia Digests of Six Scottish Top-Soils by Atom Trapping AAS, by (A) Direct Determination, and (B) Standard Addition, Reported in $\mu g\ g^{-1}$ of Soil

Sample	(A)	(B)
1	11.3	10.3
2	10.2	10.4
3	5.7	7.5
4	5.2	4.5
5	11.5	12.5
6	7.5	6.8

Table 5. Replicate Determination of Zinc in Seawater by Atom Trapping AAS

Aliquots of seawater sample (10 × dilution)	1	2	3	4
Concentration of zinc added/$\mu g\ l^{-1}$	0	2.0	4.0	6.0
Concentration of zinc found/$\mu g\ l^{-1}$	0.9	3.1	5.1	7.0
Actual concentration of zinc/$\mu g\ l^{-1}$	0.9	1.1	1.1	1.0
Concentration of zinc in undiluted seawater/$\mu g\ l^{-1}$	9	11	11	10

Table 6. The Determination of Ag, Bi, Cd, and Pb in a Bovine Liver Sample by (A) Atom Trapping AAS, Compared to (B) Spark Source Mass Spectrometry Results (Values Reported Are in $\mu g\ g^{-1}$ Freeze-Dried Liver)

Element	(A)	(B)
Ag	0.05	0.06
Bi	0.48	0.14
Cd	0.27	0.27
Pb	0.35	0.34

Table 7. The Concentration ($\mu g\ l^{-1}$) of Several Trace Elements in Three Fresh Water Samples Determined by Atom Trapping AAS, and by Electrothermal Atomization AASa) (Mn and Pb) for Comparison

Element	Sample 1	Sample 2	Sample 3
Ag	<1	<1	<1
Cd	4	<1	<1
Cu	<5	<5	<5
Mn	7; 8.3a)	<2; 0.2a)	4; 2.8a)
Pb	69; 55a)	<2; 0.4a)	23; 10a)
Tl	<5	<5	<5
Zn	500	1.5	50

of the reported methods of sample preparation suitable for analysis by flame AAS included low temperature ashing (RF-excited oxygen plasma),[19)] enzyme digestion,[20)] or wet-oxidative digestion.[21)] Amongst these, wet-oxidative digestion offers two main advantages over the other procedures. It is generally faster and, as it requires lower working temperatures (50—250 °C), the risk of losing volatile elements is reduced. The nitric acid–hydrogen peroxide procedure employed here was first tested by checking the recovery of lead added to the freeze-dried, powdered liver sample before digestion. The recovery was 100±10% of the quantity of the added lead. The concentrations of lead, cadmium, silver, and bismuth were then found by the method described, and the values were compared with those from previous spark source mass spectrometry results, Table 6. Apart from bismuth the other three elements showed consistent results by the two methods.

Trace Elements in Fresh Water Samples: Atomic absorption spectrometry is ideally suited to the analysis of fresh water for a wide range of elements. However, the extremely low levels of some elements in fresh water samples prevent their direct determination by conventional flame AAS, except for a few such as sodium, potassium, magnesium, calcium, and occasionally zinc. Several of these ultra-trace elements can, however, be determined directly by atom trapping AAS, e.g. in the three fresh water samples, featured in Table 7. Two elements (Mn and Pb) were also measured directly by electrothermal atomization AAS, which showed fair agreement with atom trapping.

Conclusion

Atom-trapping AAS can be applied to determine a wide range of elements with significant enhancement in sensitivity compared to conventional flame AAS. The successful analysis of trace elements in different types of sample showed the technique to be reliable for a range of matrices.

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References

1) C. Lau, A. Held, and R. Stephens, *Can. J. Spectroscopy,* **21**, 100 (1976).

2) J. Khalighie, A. M. Ure, and T. S. West, *Anal. Chim. Acta,* **107**, 191 (1979).

3) J. Khalighie, A. M. Ure, and T. S. West, *Anal. Chim. Acta,* **117**, 257 (1980); **134**, 271 (1982); **131**, 27 (1981).

4) C. M. Lau, A. M. Ure, and T. S. West, *Anal. Chim. Acta,* **141**, 213 (1982).

5) C. M. Lau, A. M. Ure, and T. S. West, *Anal. Chim. Acta,* **146**, 171 (1983).

6) C. M. Lau, A. M. Ure, and T. S. West, *Anal. Proc.,* **20**, 114 (1983).

7) C. Hallam and K. C. Thompson, *Analyst,* **110**, 497 (1985).

8) "The Infrared Spectra of Minerals," ed by V. C. Farmer, Mineralogical Society (1974), p. 19.

9) A. M. Ure and M. L. Berrow, "Environmental Chemistry," Vol. 2, Royal Society of Chemistry (1982), p. 189.

10) A. W. McPhee, D. Chisholm, and C. R. MacEachern, *Can. J. Soil Sci.,* **40**, 59 (1970).

11) A. J. Thompson and P. A. Thoresby, *Analyst,* **102**, 9 (1977).

12) J. Rubeska and V. Hlavinkova, *At. Absorpt. Newsl.,* **18**, 5 (1979).

13) P. N. Vijan, A. C. Rayner, D. Sturgis, and G. R. Wood, *Anal. Chim. Acta,* **82**, 329 (1976).

14) S. Bajo, *Anal. Chem.,* **50**, 649 (1978).

15) M. L. Berrow and W. M. Stein, *Analyst,* **108**, 277 (1983).

16) R. E. Sturgeon, S. S. Berman, A. Desaulniers, and D. S. Russell, *Talanta,* **27**, 85 (1980).

17) R. Guevremont, R. E. Sturgeon, and S. S. Berman, *Anal. Chim. Acta,* **115**, 163 (1980).

18) B. Mason, "Principles of Geochemistry," 3rd ed, Wiley, N. Y. (1966), p. 195.

19) J. Locke, *Anal. Chim. Acta,* **104**, 255 (1979).

20) R. C. Carpenter, *Anal. Chim. Acta,* **175**, 209 (1981).

21) J. Flanjak and H. Y. Lee, *J. Sci. Food Agric.,* **30**, 503 (1979).