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SOME RECENT STUDIES IN OPTICAL EMISSION AND ABSORPTION SPECTROSCOPY FOR TRACE ANALYSIS

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ABSTRACT

The applications of atomic absorption spectroscopy to small samples of a biological nature, particularly related to the determination of trace elements in standard reference materials, are reviewed. Atomic emission spectroscopy using the inductively coupled plasma source is considered for a variety of metallurgical and other analyses. Some considerations are made of the manner in which dedicated atomic fluorescence systems can be employed; these are illustrated by reference to the determination of arsenic and selenium in soil digests.

INTRODUCTION

During the past two decades, two major new techniques of analytical atomic spectroscopy suitable for trace and major element analysis of solution samples have emerged. These are, respectively, atomic absorption spectroscopy (AAS) and optical emission spectroscopy using plasma sources. Atomic absorption spectroscopy, in particular, has become one of the techniques most extensively employed for the determination of trace element composition of a wide variety of materials. The principal attraction of AAS for these purposes is the high attainable sensitivity for a wide range of elements and high selectivity for the element sought. Instrumentation for AAS is relatively inexpensive and suitable for routine operation in most laboratories by operators who have undertaken only a small amount of basic training. Relatively few problems are encountered in the determination by AAS of trace concentrations of elements in dilute aqueous solutions. It is the intention of this lecture to review some recent studies undertaken at Imperial College, London and UMIST, Manchester concerned with practical problems in atomic absorption spectroscopy.

The second technique which has emerged as a powerful method of analysis for solution samples is concerned with optical emission spectroscopy and employs a high-frequency inductively coupled argon plasma as a spectrochemical source. This provides effective excitation suitable for simultaneous multi-element determination of metals and metalloids over a wide concentration range in solutions. The ICP source can allow detection limits in the parts per billion level for many metals, linear dynamic concentration ranges typically 5 orders of magnitude and freedom from chemical, condensed phase and vapour phase interferences. This lecture will outline some experiments concerned with methods of sample introduction to the plasma, both by pneumatic nebulisation and by discrete sample introduction.

Atomic fluorescence spectroscopy has not developed in the manner which its original multi-channel function was envisaged. Dedicated analytical instrumentation, however, based on the principle of atomic fluorescence spectroscopy has been developed. Again this employs discrete sample introduction and a simple instrumentation for selected applications of clinical and/or environmental and agricultural interest will be described in this paper.

Thus it is hoped to present an overview of the current state of analytical atomic spectroscopy using emission, absorption and fluorescence modes of operation.

ATOMIC ABSORPTION SPECTROSCOPY

Some comments on the manner of operation of the technique, the main types of atom cell and other instrumental systems most frequently encountered in AAS are pertinent. These can then be illustrated by the application of the technique to the examination of

biological materials. Specific consideration will be given to the applicability of the technique to the determination of toxic and essential trace elements in selected matrices. Figures 1 and 2 review the fundamental basis of observation of the phenomenon of atomic absorption for atomic species in the vapour state. The essential selectivity of the process can be envisaged from the narrow atomic line profile of the analyte in the sample vapour and the narrow emission line profile from the source employed (the hollow cathode discharge lamp). Figures 3 and 4 illustrate the manner in which this phenomenon can be exploited experimentally. Figures 5 and 6 show somewhat more sophisticated systems in which double beam operation of an AAS system or, single beam operation with background correction, can be effected. These principles are well known and need no further elaboration.

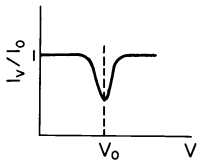

Fig. 1. Variation of transmitted intensity with frequency for absorption of monochromatic radiation of frequency ν by a dilute absorbing atomic vapour

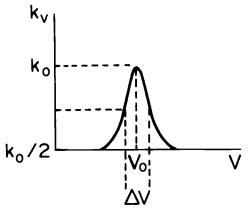

Fig. 2. Variation of absorption coefficient $k\gamma$ with frequency for absorbing atomic vapour

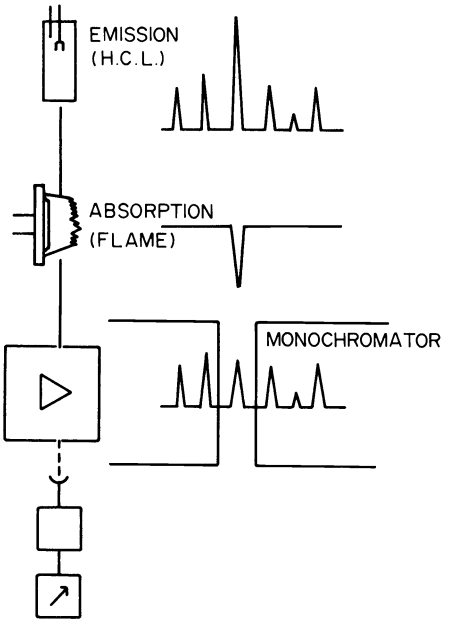

Fig. 3. Schematic representation of principle of operation of atomic absorption spectroscopy

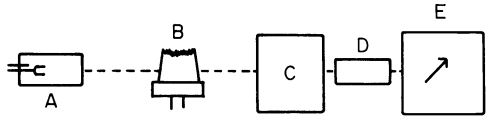

Fig. 4. Single-beam atomic absorption spectrometer

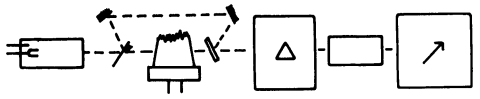

Fig. 5. Double-beam atomic absorption spectrometer

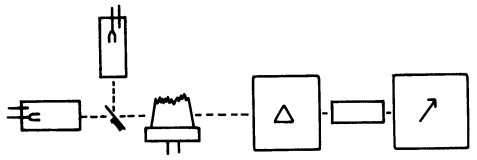

Fig. 6. Single-beam atomic absorption spectrometer with background correction using a deuterium hollow cathode lamp

ATOM CELLS FOR AAS

The two principal types of atom cell employed in AAS to provide thermal energy for sample vaporisation and atomisation are the premixed flame and the electrothermal atomiser. The atom cell chosen for a particular determination will depend on consideration of the required sensitivity and determination limit - occurrence of interference effects from the matrix elements, extent of sample preparation required, speed, precision and available sample mass or volume. We can consider a review of sample introduction techniques and atom cells specifically illustrated from the viewpoint of use of AAS for the examination of biological materials.

SAMPLE INTRODUCTION FOR AAS WITH PREMIXED FLAMES

There are four principal ways in which AAS with flame atom cells may be utilised with liquid samples:

(a) With direct nebulisation of aqueous samples using a pneumatic nebuliser/ spray chamber system;

(b) With direct pneumatic nebulisation of samples after pre-concentration of the analyte element by solvent extraction;

(c) With the "boat-in-flame" or Delves cup technique;

(d) With generation of the gaseous hydride of the analyte element (s) and introduction of this into a hydrogen-based diffusion flame.

The preferred technique of sample introduction will usually depend primarily upon the concentration of the analyte in the prepared sample solution (digest) and the sample volume available. It is proposed to review sample introduction into flame atom cells by reference to the use of AAS in the examination of biological materials. The matrices which will be considered are animal muscle (H4), Bowen's kale, NBS bovine liver and human blood serum.

(a) Direct pneumatic nebulisation of aqueous solutions

Direct aspiration of prepared sample solutions by the air for oxidant gas supply to the flame using the type of pneumatic nebuliser and spray chamber assembly routinely employed in all commercially available AAS systems is probably the simplest technique in flame AAS and is still in widespread usage. The advantages and disadvantages of this type of flame/sample introduction system are reviewed for biological samples in Table I. Flame AAS may be employed successfully for the direct determination of the most commonly encountered major elements in biological materials (Ca, Mg, Na and K) and can be used in some cases also for the determination of some trace elements for which the technique exhibits sensitivity (e.g. zinc). For solution samples of low dissolve solid content, direct flame AAS with pneumatic nebulisation is capable of good precision (1-2% or better), and allows relative freedom from matrix effects. The minimum sample volume required per analysis is usually 3 ml.

(b) Direct pneumatic nebulisation after pre-concentration by solvent extraction

This procedure has been widely used in flame AAS of biological materials (particularly urine and tissue digests). In a typical procedure, the analyte element to be determined is extracted in the form of its chelate complex with a suitable organic chelating agent into the organic solvent (such as ethyl acetate or methyl iso-butyl ketone).

Pretreatment of samples by this type of procedure can result in increased sensitivity and selectivity. By extraction from a relatively large volume of aqueous sample solution into a smaller volume of organic solvent a preconcentration of the analyte(s) is achieved; in addition the nebulisation efficiency for organic solvents with conventional pneumatic nebuliser-spray chamber assemblies may be substantially greater than for aqueous solutions. Thus, preliminary solvent extraction of the analyte(s) can allow the determination of elements which are present in the original solution at concentrations too low for direct determination by flame AAS. Additionally, greater freedom from condensed phase and vapour phase interferences caused by matrix elements may be obtained in procedures where the analyte is separated at the solvent extraction step from bulk components such as Ca, Na, Cl^-, PO_4^{3-} and organic matter. The most widely employed chelating reagents for these extractions applied to biological materials are sodium diethyldithiocarbamate (NaDDTC) and ammonium pyrrolidine dithiocarbamate (APDC); methyl iso-butyl ketone is extensively employed as an appropriate organic solvent. Table 1B illustrates the application of preconcentration and separation techniques

to some biological materials.

TABLE I APPLICATION OF ATOMIC ABSORPTION SPECTROSCOPY TO DETERMINATION OF ELEMENTS OF INTEREST IN BIOLOGICAL MATERIALS

A. Flame Atomization – Direct Nebulization of Aqueous Sample Solutions

ELEMENT	Bowen's kale	NBS Bovine Liver SRM 1577	Animal Muscle H-4	Blood Serum
As	-	-	-	-
Be	-	-	-	-
Ca	+ + +	+ + +	+ + +	+ + +
Cd	+	?	-	-
Cl	-	-	-	-
Co	-	-	-	-
Cr	+ +	+ +	+ +	+ +
Cu	+ +	+ +	+ +	+ +
F	-	-	-	-
Fe	+ +	+ +	+ +	+ +
Hg	-	-	-	-
I	-	-	-	-
K	+ + +	+ + +	+ + +	+ + +
Mg	+ + +	+ + +	+ + +	+ + +
Mn	+ +	+ +	+ +	+ +
Mo	-	-	-	-
Na	+ + +	+ + +	+ + +	+ + +
Ni	-	-	-	-
P	?	?	?	?
Pb	?	-	-	-
Sb	-	-	-	-
Se	-	?	-	?
Si	+ +	?	+ +	+
Sn	-	-	-	-
Tl	-	-	-	-
U	-	-	-	-
V	-	-	-	-
Zn	+ + +	+ + +	+ + +	+ + +

+++ determinable to a high precision (~ 1% rel.)
++ determinable to a medium precision (~ 10% rel.)
+ determinable, but only to a poor precision (~ 20 – 40% rel.)
? borderline (~ 50 – 100% rel.)
– not determinable

(c) Boat-in-flame or Delves cup technique

These techniques employ devices which permit the efficient introduction of small liquid samples (10-100µl) into the flame used for atomisation. The liquid sample is placed in a cup or 'boat' (nickel, stainless steel, tantalum or molybdenum), dried in the edge of a premixed flame (usually air-acetylene) and then inserted into the hot interzonal part of the flame. The sample is vaporised and the analyte atomic absorption recorded during the time that the sample takes to vaporise completely. A transient absorption signal is thus obtained whose peak height (and/or area) is proportional to the mass of analyte element introduced in the sample cup. In the Delves cup technique, the analyte and sample vapour leave the cup and enter a cylindrical cell, fabricated of ceramic or silica, also placed higher in the flame. The radiation from the hollow cathode lamp source passes along the axis of this tube. These devices permit high sensitivity to be obtained using only small samples by increased sample transfer efficiency to the flame compared with pneumatic nebulisation; in addition, in the Delves cup technique the greater residence time of the analyte atoms in the long cylindrical cell yields additional signal enhancement.

1B. Flame Atomization – Special Sample Introduction Techniques, or after Preconcentration and Separation

ELEMENT	Bowen's kale		NBS Bovine Liver, SRM 1577		Animal Muscle H-4		Blood Serum	
		NOTE		NOTE		NOTE		NOTE
As	+ +	a	+ +	a	+ +	a	+ +	a
Be	+	b.1	-	-	-	-		-
Ca	+ +	2A	+ +	2A	+ +	2A	+ +	2A
Cd	+ +	b.2	+ +	b.2	+ +	b.2	+ +	b.2 (c)
Cl	-	-	-	-	-	-	-	-
Co	+ +	b.2	+ +	b.2	+ +	b.2	+ +	b.2
Cr	+ +	b.3	+ +	b.3	+ +	b.3	?	b.3
Cu	+ +	b.2	+ +	b.2	+ +	b.2	+ +	b.2
F	-	-	-	-	-	-	-	-
Fe	+ +	b.2(2A)	+ +	b.2(2A)	+ +	b.2(2A)	+ +	b.2(2A)
Hg	+ +	b.2(d)	+ +	b.2(d)	+ +	b.2(d)	+ +	b.2(d)
I	-	-	-	-	-	-	-	-
K	-	2A	-	2A	-	2A	-	2A
Mg	-	2A	-	2A	-	2A	-	2A
Mn	+ +	b.2	+ +	b.2	+ +	b.2	+ +	b.2
Mo	+ +	b.2	+ +	b.2	+ +	b.2(?)	+ +	b.2
Na	-	2A	-	2A	-	2A	-	2A
Ni	+ +	b.2	+ +	b.2	+ +	b.2	+ +	b.2
P	+ +	e	+ +	e	+ +	e	+ +	e
Pb	+ +	b.2(c)	+ +	b.2(c)	+ +	b.2(c)	+ +	b.2(c)
Sb	+ +	a	+ +	a	+ +	a	+ +	a
Se	+ +	a	+ +	a	+ +	a	+ +	a
Si	+ +	e	+ +	e	+ +	e	+ +	e
Sn	+ +	a	+ +	a	+ +	a	+ +	a
Tl	+ +	b.2	+ +	b.2	+ +	b.2	+ +	b.2(c)
U	-	-	-	-	-	-	-	-
V	+ +	b.4	-	-	-	-	?	-
Zn	+ +	b.2	+ +	b.2	+ +	b.2	+ +	b.2

2A Special sample introduction not necessary, see Table IIA.
a Hydride generation technique.
b After preconcentration by suitable ashing procedure and extraction with (1) acetylacetone (2) APDC/MIBK (3) tributyl phosphate/MIBK (4) cupferron/MIBK.
c Delves cup technique possible.
d Mercury cold vapour technique preferred.
e Indirectly by determination of Mo associated with heteropoly phosphomolybdic acid (for P) or silicomolybdic acid (for Si) after solvent extraction.

These techniques are most effective for the determination of elements such as Ag, As, Cd, Hg, In, Pb, Se and Tl which are relatively volatile and easily vaporised at the temperatures achieved in the cup (somewhat less than the flame temperature). The entire sample atomisation process is usually complete within only a few seconds after insertion of the boat into the flame and the amplification and recorder system employed in the AAS system must, therefore, have a fast response time (<1 s). Interference effects may be more pronounced with these devices than in a flame with pneumatic nebulisation. The Delves cup technique has found widespread application for the determination of Pb in blood.

(d) Gaseous hydride generation technique

In this technique aqueous sample solutions are treated with a reducing agent (usually sodium borohydride) after acidification to generate the volatile covalent hydride of the analyte element(s). The hydrides are swept out of the hydride generation cell on a stream of inert gas (usually argon) into an argon-hydrogen diffusion flame or an electrically heated silica tube for the atomisation and determination by AAS of the element concerned. The technique is most commonly used for the determination of As and Se but may also be applied in the determination of Sb, Bi, Ge, Sn and Te. High sensitivity may be achieved

by this technique as high transient concentration of hydride per unit volume of the flame gas may be achieved during the generation process provided that this is rapid and efficient. This technique also may achieve a separation of the analyte from the matrix elements and allow greater freedom from interference effects caused by non-specific background absorption. Certain elements, however, may cause interference by reduction of the efficiency of hydride liberation; the presence of copper, for example, results in serious interference in the determination of Se due to formation of copper selenide in the reduction process on addition of the sodium borohydride reagent.

A similar technique, although not involving the generation of hydride, is found in the determination of mercury by the 'cold-vapour technique'. The unique properties of mercury, the only metal exhibiting appreciable vapour pressure at room temperature, has a monatomic vapour and that it does not react readily with atmospheric oxygen, facilitate its determination by AAS without recourse to flame or other heated atom cell techniques. Stannous chloride may be added to sample solutions to reduce mercury to elemental form; air is then passed through the solution to sweep the vapour into a silica absorption cell for AAS. Organic material may be destroyed by oxidation (usually with $KMnO_4$) before reduction of mercury for absorption measurement. Digestion with $KMnO_4/H_2SO_4$ may release both inorganic and organically bound mercury. This type of method has found widespread application to the determination of mercury in biological samples; simple accessory equipment for the technique is available from all AAS instrument companies.

ELECTROTHERMAL ATOMISATION

This technique has achieved great impact on trace analysis by AAS. Small liquid samples (5 - 10µl) are transferred directly to an electrically heated graphite (or tantalum) rod, ribbon or tube. The solvent is removed by heating at a low temperature (ca. 100°C), the organic matter is destroyed by ashing at a preselected elevated temperature (ca. 400-900°C) and the residual material containing the analyte element is vaporised (atomised) at high temperature (up to 3000°C) and the absorption measured at the analyte wavelength. Most commercially available AAS systems now offer some form of graphite tube device. The applications of this type of system to biological materials have continued to attract attention at an increasing rate.

Advantages of the use of electrothermal AAS include:

(a) Small sample size (5-10µl);

(b) High sensitivity (usually 10^2 or better in concentration terms than flame methods, i.e. ng or pg absolute weight sensitivity);

(c) ease of operation, safety.

Disadvantages include:

(a) Matrix effects more prevalent than with flames;

(b) Simultaneous multi-element analysis not possible;

(c) Analysis time per sample slower than flame methods.

The single most attractive feature of the technique is the high absolute (weight) and relative (concentration) sensitivity which may be attained. The sensitivity is great enough for many elements to allow their direct determination in biological samples (blood, urine, tissue digests). The single biggest difficulty is concerned with the occurrence of matrix effects and their recognition, control or suppression. For real samples, particularly where complex matrices are present, automatic background correction (D_2 corrector) is an essential requirement. Suitable in-situ sample pretreatment by controlled ashing of organic matter is also essential. Electrothermal atomisers have also been employed using direct sampling of solids rather than solution samples. Table 1C reviews the applicability of electrothermal atomisation to determination of trace elements in selected biological materials.

SENSITIVITY AND DETECTION LIMITS IN AAS

The sensitivity attainable for the determination of an element by AAS with given instrumentation is defined as the concentration of the element (usually in ppm, $\mu g.ml^{-1}$ or $mg.l^{-1}$ in aqueous solution) which produces a 1% absorption signal (0.0044 absorbance) under optimal experimental conditions. This sensitivity defines the slope of a linear calibration graph of absorption against concentration and hence it is frequently used when a knowledge of the required analyte concentration range in sample and standard solutions is needed. The achievable 1% absorption sensitivities for particular elements remain fairly constant between well-designed instruments of the same type. For

1C. Electrothermal Atomization – Graphite Furnace System

ELEMENT	Bowen's kale	NBS Bovine Liver SRM 1577	Animal Muscle	Blood Serum
As	?	?	?	?
Be	+ +	-	-	-
Ca	2A[1]	2A[1]	2A[1]	2A[1]
Cd	+	+	+	+
Cl	-	-	-	-
Co	?	?	?	?
Cr	+ +	+ +	+ +	+ +
Cu	+ +	+ +	+ +	+ +
F	-	-	-	-
Fe	+ +	+ +	+ +	+ +
Hg	+[2](2B)	+[2](2B)	+[2](2B)	+[2](2B)
I	-	-	-	-
K	2A	2A	2A	2A
Mg	2A	2A	2A	2A
Mn	+ +	+ +	+ +	+ +
Mo	+ +[1]	+ +[1]	+ +[1]	+ +[1]
Na	2A	2A	2A	2A
Ni	+ +	+ +	+ +	+ +
P	+[3]	+[3]	+[3]	+[3]
Pb	+ +[2]	+ +[2]	+ +[2]	+ +[2]
Sb	?	?	?	?
Se	+ +[2]	+ +[2]	+ +[2]	+ +[2]
Si	+ +	+ +	+ +	+ +
Sn	+ +	?	?	+ +
Tl	?	-	-	-
U	-	-	-	-
V	?[1]	-	-	?[1]
Zn	+ +[2]	+ +[2]	+ +[2]	+ +[2]

2A Flame preferred to electrothermal atomization, see Table IIA.
2B Cold vapour technique preferred, see Table IIB.
1 Subject to carbide formation in furnace.
2 Volatile analyte may require matrix stabilization.
3 Using PO_x absorption at Pb ion line at 220.3 nm.

analytical work a disadvantage of using the 1% absorption sensitivity is that it yields no information about the achievable precision or the minimum concentration that may be determined or detected.

Adequate analytical precision may be obtained with modern AAS instruments for many elements at solution concentrations that produce less than 1% absorption. The detection limit defines the lowest detectable concentration of the analyte in the sample solution. This may be defined as that concentration of the element that produces an absorption signal equivalent to twice the standard deviation in the noise fluctuation of the background (zero absorption) signal under the experimental conditions employed. Some workers also use a definition of the detection limit based on the analyte concentration required to produce an absorption signal-to-background noise ratio of 2.

PRECISION AND ACCURACY

The reproducibility of analytical absorption signals in flame AAS for repetitive introduction of liquid samples can frequently be better than 1%, i.e. a relative standard deviation of 0.01. For electrothermal atomisation, even with simple aqueous or organic solvents manually introduced repetitively into graphite tube furnaces, it is usually difficult for a skilled operator to achieve better than 3% reproducibility, i.e. a relative standard deviation of 0.03. With automated sampling systems recently introduced for AAS with electrothermal atomisation, however, this may be improved considerably (to relative standard deviation values as low as 0.005).

It is important, however, to consider the reproducibility of the complete analytical

procedure, i.e. to include random errors associated with the sampling process, sample preparation, pretreatment and AAS determination. Under these conditions the attainable reproducibility in both flame and electrothermal AAS may vary widely depending upon the element(s) determined and the sample type. For major element determinations (e.g. Na, Ca) the required relative standard deviation (RSD) of the complete analytical procedure is usually low and their precise determination is frequently important; fortunately in flame AAS with careful sample preparation RSD values of not greater than 0.01 - 0.02 are realisable for these elements. For trace element determinations it is usually possible to relax the requirements of high precision and RSD values of 0.1 are frequently acceptable. Again, fortunately, provided care is taken to minimise random losses or contamination of samples during sample preparation, RSD values of this order may be attainable for trace element determinations using flame AAS and, with careful operation, by electrothermal atomisation for some elements.

INTERFERENCES

The occurrence of specific interferences in AAS, where a particular atomic species present in a sample together with the analyte element causes interference, is very rare owing to the high spectral line selectivity of the technique. Non-specific effects, however, are commonly encountered. These arise most frequently from the formation of molecular species of elements present in the matrix which absorb radiation at the wavelength of determination of the analyte element or as a result of chemical interference effects in which the concomitant materials present in the sample affect either the rate of efficiency of analyte atom formation, or both, in the flame or atom cell employed. After it is recognised, the former effect of non-specific molecular absorption can usually be minimised or eliminated by the use of a continuum source background corrector. The latter effect of chemical interference, however, is usually more troublesome. The occurrence of chemical interference effects gives rise to change in slope sensitivity of the analytical calibration function. Depending upon the origin and nature of these interferences a number of techniques may often be employed for their elimination or minimisation. These include, for example, the use of matrix modification procedures, ionisation suppression and releasing and protective agents. It is sometimes preferable to resort to extensive separation of the analyte element(s) from the matrix by solvent extraction, ion-exchange or coprecipitation before the flame or electrothermal AAS when severe matrix effects would otherwise be obtained. When these effects cannot be easily eliminated or minimised, it is usual to employ the techniques of standard additions to provide for their compensation.

MULTI-ELEMENT ANALYSIS AND AUTOMATION

AAS is primarily a single-element technique in which the spectrometer is operated at any time using the hollow cathode lamp source appropriate to the element being determined at the wavelength of one of its resonance lines. Although spectrometers capable of simultaneous multi-element analysis have been designed and employed in a research environment to permit the determination of perhaps 6-8 elements in a particular matrix, this approach has not been taken in commercially available AAS instruments. Although at least one two-channel (dual element) AAS spectrometer is commercially available, systems capable of multi-channel operation have not become of widespread commercial availability. The principal reason for this is the restricted analytical dynamic concentration range of the technique (usually not more than 2 orders) which conspires against the ability of a multi-channel fixed wavelength system to effect simultaneous analysis for a large number of elements unless only a limited restricted range of concentration ratios of one analyte element to another is expected. For some applications, however, where this is the case, for example in the routine analysis of serum for major and minor components, this may not be a serious limitation because of the relatively constant composition expected and if sufficient demand is created for AAS systems for these purposes it will no doubt be fulfilled by the instrument manufacturers.

Modern AAS spectrometers are now equipped with facilities which make their operation routine and trouble-free through the use of microprocessor control. Thus wavelength control, slit programming, calibration, curve correction, integration, etc. may be undertaken with high precision by only a semi-skilled operator. Automated sample introduction systems are routinely available for most commercial instruments to permit unattended analysis of large numbers of liquid samples. It has recently been demonstrated that the use of an automatic sampler to deliver repetitively small volumes of samples to electrothermal atomisers can result in significant improvement in attainable precision compared with manual sample introduction.

OPTICAL EMISSION SPECTROSCOPY WITH RADIO FREQUENCY PLASMA SOURCES

The development of the inductively-coupled plasma operating at radio frequencies on

Argon and its use as an emission source for optical emission spectroscopy has resulted in transformation of trace analytical techniques. A schematic of the manner in which such plasma sources can be operated for analytical purposes is shown in Figure 7.

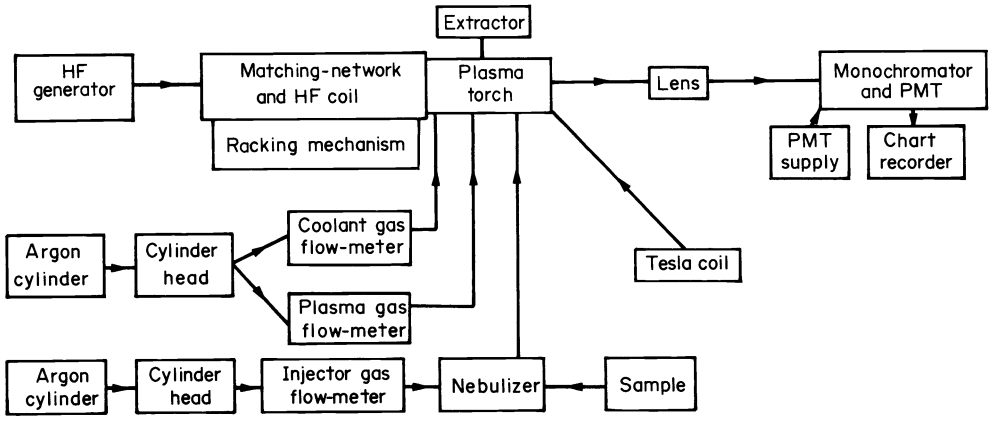

Fig. 7. Schematic diagram of an ICP system with single channel detection.

In its most common form a torch which provides for central injection of analyte material from a pneumatic nebuliser through an anular fireball created, most commonly, at 27 Mhz at powers between 1 and 10 kilowatts is mounted within a coil provided with the radio frequency energy. This type of arrangement, used in conjunction with either single-channel or multi-channel direct reading optical spectrometers has been used to undertake trace analysis with detection limits which are found to be considerably superior for a wide range of elements to those attainable for atomic absorption techniques. Typical detection limits for ICP-OES are shown in Table 2. The three principal advantages of this type of optical emission spectroscopy which are clear are;

(a) High sensitivity for a wide range of elements,

(b) Freedom for interelement effects due to the high temperature (4-6000 K) available to the analyte during its passage into the tail flame where conventionally the emission from the sample would be viewed, and

(c) The long linear dynamic range available (4-6 orders of magnitude). This results from the optically thin nature of the source at the viewing point and freedom from self-absorption effects.

Traditionally, samples would be introduced into the plasma by pneumatic nebulisation. Recent work in our laboratories, however, has been directed towards discrete sample introduction using both the volatile hydride technique and electrothermal atomisation of particulate material produced from a graphite rod atomiser. Studies of this type have been applied for both the analysis of biological materials and semi-conductor materials and uranium and other samples of industrial interest. Some examples of the results obtained in these studies are shown in Figures 8, 9 and 10. In particular, and of value in analysis of soils, soil waters and digests from biological materials after Kjeldahl digestion, is the possibility of the determination of nitrogen by optical emission spectroscopy rapidly using the ICP. Examples of the technique for the determination of nitrogen in this type of sample are given in Figures 11 and 12.

The volatile hydride generation technique applied to the determination of arsenic, selenium, tellurium, antimony and tin has been exploited successfully in examination of the digests of plant samples in our laboratories in the past years. A continuous system whereby a pump is used to mix the sample solution at the correct acidity with the sodium borohydride reagent solution, a separator where solution sample is rejected, and a system whereby the hydride generated is delivered to the plasma has been developed successfully. Some results obtained with this type of system are shown in Table 3. Analysis for all of the elements investigated was conducted simultaneously with a 27 MHz plasma used with a multi-channel direct reading spectrometer.

TABLE 2.

LOWEST REPORTED DETECTION LIMITS FOR ICP-OES (1978)

Element & line (nm)		Detection limit (ng ml^{-1})	Element & line (nm)		Detection limit (ng ml^{-1})
AgI	328.1	2	NaI	589.0	0.02
AlI	396.1	0.2	NbII	309.4	0.1
AsI	228.8	2	NdII	401.2	0.3
AuI	267.6	0.9	NiI	352.5	0.2
BI	249.8	0.1	OsI	290.9	6
BaI	455.4	0.01	PI	253.6	15
BeI	234.9	0.003	PbII	220.3	1
BiI	289.8	10	PdI	360.9	2
CII	193.0	100	PrII	422.5	10
CaII	393.4	0.0001	PtI	265.9	0.9
CdII	226.5	0.07	Rh*		3
CeII	418.7	0.4	RuI	349.9	90
CoII	238.9	0.1	SI	182.0	30
CrII	267.7	0.08	SbI	217.5	15
CuI	327.4	0.06	ScII	361.3	0.4
DyII	353.2	2	SeI	196.0	1
Er*		1	Si*		10
EuII	382.0	0.06	SmII	359.3	0.5
FeII	259.9	0.09	SnI	303.4	3
GaII	417.2	0.6	SrII	407.8	0.003
GdII	342.3	0.4	TaII	296.5	5
GeI	265.1	0.5	TbII	350.9	0.1
HfII	339.9	10	TeI	238.6	15
HgI	253.6	1	ThII	401.9	3
HoII	345.6	3	TiII	334.9	0.03
II	206.2	10	Ti*		200
In*		30	TmII	346.2	0.15
IrI	322.1	90	UII	386.0	1.5
KI	766.5	30	VII	309.3	0.06
LaII	408.7	0.1	WII	276.4	0.8
LiI	670.8	0.02	YII	371.0	0.04
Lu*		8	YbII	369.4	0.02
MgII	279.5	0.003	ZnI	213.8	0.1
MnII	257.6	0.01	ZrII	343.8	0.06
MoI	379.8	0.2			

* Spectral lines used were not quoted in reference 160.

The detection limits shown are the lowest reported for sample introduction by pneumatic or ultrasonic nebulization. For certain elements lower detection limits than those shown may be obtained using alternative sample introduction techniques such as electrothermal vaporization or hydride generation.

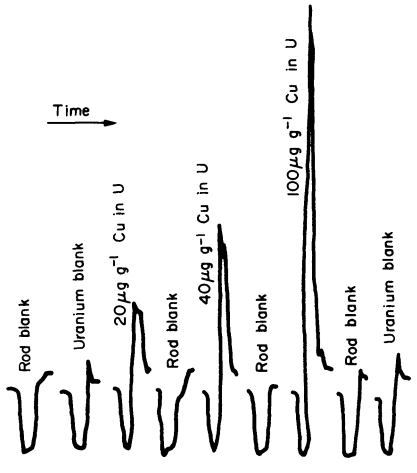

Fig. 8. Signals obtained at 324.7nm for the determination of Cu in 10 µl samples containing 1000 µg ml^{-1} U

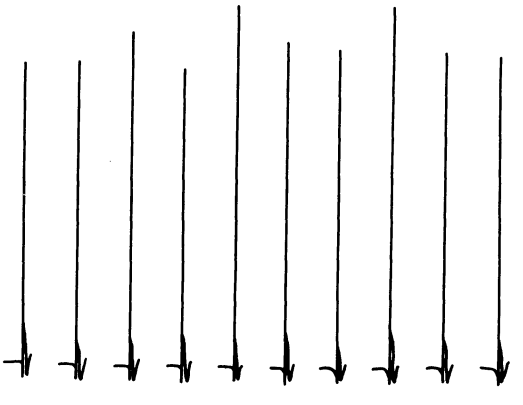

Fig. 9. Reproducibility of signals obtained for Ga from 10µl aliquots of a 0.2µg ml^{-1} Ga solution

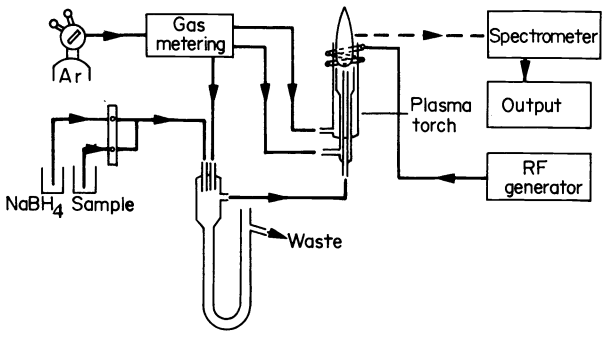

Fig. 10a. Schematic diagram of the hydride reduction-ICP spectrometry system

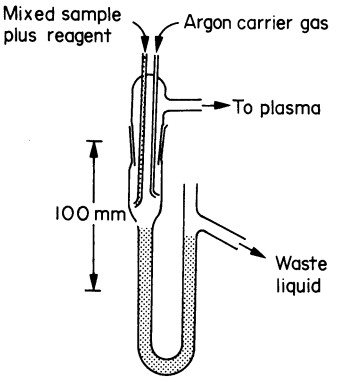

Fig. 10b. Hydride generation cell

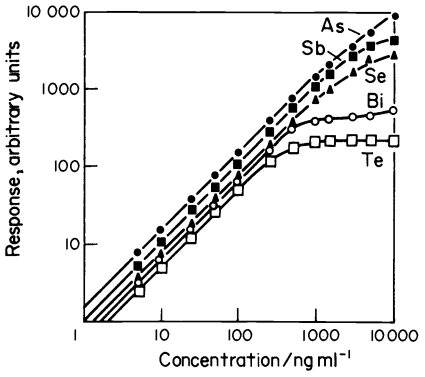

Fig. 10c. Calibration graphs obtained under the experimentally selected operating conditions

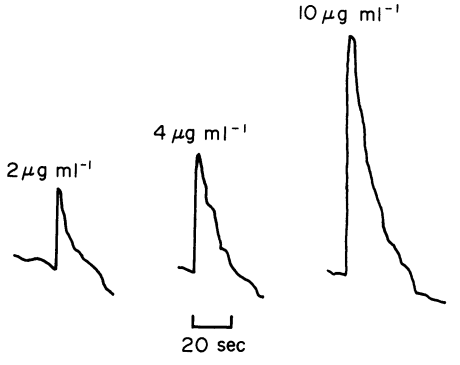

Fig. 11. Typical signals obtained at 336.0nm at different concentrations of ammonium ion (expressed as μg ml^{-1} N)

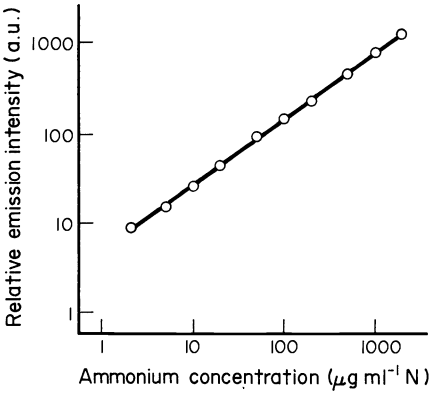

Fig. 12. Calibration graph for determination of ammonium ion by hypobromite oxidation method

An indication of the long linear dynamic range attainable with the inductively coupled plasma source is shown in Table 4. In this example the analysis of minor elements in aluminium alloys was investigated. It will be noted that by flame emission or absorption spectroscopy it was necessary to conduct serial dilutions of the sample in order to ensure that the analyte concentrations were on the linear range for determination. In contrast, however, all of the results obtained by optical emission spectroscopy using the ICP source were obtained at the same dilution. This is a direct result of the fact that in emission (using a flame) or absorption spectroscopy a linear range of only 1-2 orders of magnitude can be obtained compared to the 416 orders of magnitude obtainable using the ICP source and employing optical emission spectroscopy.

ELECTROTHERMAL VAPORISATION INTO THE INDUCTIVELY COUPLED PLASMA SOURCE

The most commonly used technique for the introduction of sample solutions into the ICP is based on the injection of a liquid aerosol generated by either a pneumatic or an ultrasonic nebuliser. Desolvation of the sample aerosol prior to its injection has also been employed. The major advantages of the ultrasonic nebuliser are the substantial

TABLE 3

LINEAR RANGES OF CALIBRATION OBTAINED BY USE OF AN ICP AND BY USE OF ATOMIC-ABSORPTION SPECTROPHOTOMETRY (AAS)

	ICP		AAS	
Element	Detection limit/ ng ml^{-1}	Limit of linearity/ ng ml^{-1}	Detection limit/ ng ml^{-1}	Limit of linearity/ ng ml^{-1}
As	0.8	800	0.8	20
Sb	1.0	1500	0.5	50
Bi	0.8	500	0.2	50
Se	0.8	800	2.0	200
Te	1.0	250	2.0	200

Table 4. Analysis of aluminium alloys by plasma and flame emission

Element	Certificate value	Content, % Plasma	Content, % Flame	
		B.C.S. 181/1		
Cu	3·99 ± 0·02	3·97 ± 0·08	3·8 ± 0·4	[a]
Fe	0·36 ± 0·01	0·36 ± 0·01	0·34 ± 0·04	
Mg	1·42 ± 0·03	1·41 ± 0·04	1·4 ± 0·1	[b]
Mn	0·10 ± 0·01	0·10 ± 0·01	0·09 ± 0·01	
Ti	0·14 ± 0·01	0·14 ± 0·01	0·18 ± 0·04	
Zn	0·02 ± 0·01	0·02 ± 0·01	[c]	
		B.C.S. 216/2		
Cu	4·56 ± 0·01	4·54 ± 0·10	4·3 ± 0·3	[a]
Fe	0·28 ± 0·01	0·28 ± 0·01	0·27 ± 0·03	
Mg	0·75 ± 0·01	0·75 ± 0·03	0·90 ± 0·04	[b]
Mn	0·71 ± 0·01	0·70 ± 0·01	0·71 ± 0·04	
Ti	0·037 ± 0·001	0·037 ± 0·003	0·04 ± 0·02	
Zn	0·20 ± 0·01	0·20 ± 0·02	[c]	
		B.C.S. 263/1		
Cu	0·09 ± 0·01	0·10 ± 0·01	0·10 ± 0·02	
Fe	0·35 ± 0·01	0·33 ± 0·02	0·34 ± 0·03	
Mg	4·92 ± 0·05	4·94 ± 0·11	4·6 ± 0·3	[b]
Mn	0·36 ± 0·01	0·36 ± 0·01	0·35 ± 0·05	
Ti	0·038 ± 0·001	0·037 ± 0·004	0·04 ± 0·02	
Zn	0·05 ± 0·01	0·05 ± 0·01	[c]	
		B.C.S. 300		
Cu	1·28 ± 0·02	1·27 ± 0·04	1·4 ± 0·1	[a]
Fe	0·30 ± 0·01	0·30 ± 0·01	0·29 ± 0·02	
Mg	2·76 ± 0·03	2·78 ± 0·09	2·9 ± 0·1	[b]
Mn	0·41 ± 0·01	0·41 ± 0·01	0·41 ± 0·02	
Ti	0·15 ± 0·01	0·16 ± 0·01	0·18 ± 0·06	
Zn	5·98 ± 0·04	5·94 ± 0·15	[d]	

All analyses were performed on a solution containing 1 g of alloy in 100 ml of solution, by plasma-emission spectrometry. These solutions were also used for flame-emission spectrometry except as indicated by:
[a] 0·1 g of alloy per 100 ml of solution.
[b] 0·01 g of alloy per 100 ml of solution.
[c] Not detected.
[d] Not determined.

improvement in the detection limits obtained, this improvement being typically a factor of 10 or greater, the greater freedom of choice of sample injection rate and the need for only small sample volumes. Coupled with these very significant advantages are a number of disadvantages, for example, the use of high injection rates may necessitate desolvation of the aerosol prior to its passage into the plasma, which is inconvenient and may give rise to so-called "desolvation interference", and the magnitude of any matrix effect may then increase correspondingly. These disadvantages, and the high cost and possibly less convenient operation of the ultrasonic nebuliser, tend to mitigate against the advantages so that pneumatic nebulisation may frequently be preferable for rapid routine analysis.

Direct vaporisation of samples into a low-power ICP source from a graphite disk support mounted directly within the body of the plasma torch has been reported. The use of a tantalum filament electrothermal vaporisation (TVF) apparatus as a sample introduction device for the inductively coupled plasma has been described and detection limits for 16 elements have been reported in the range between nanograms and micrograms per litre for 100 ml. samples have been obtained. Nixon et al have pointed out that this system gave an improvement in detection limits of 1-2 orders of magnitude, comparing these results with those obtained using pneumatic nebulisation of solutions into the ICP. The reason for this significant improvement in detection power has been attributed to the result of the increased concentration of the analyte, already desolvated and vaporised by the tantalum filament, passing as a pulsed sample through the axial channel of the plasma and giving rise to a transient analytical atomic-emission signal. In our laboratories we have made application of a graphite filament electrothermal vaporisation apparatus as a sample introduction system for optical emission spectrometry using the ICP as a source. Detection limits obtained with this system for 10 ml.aqueous sample solutions are encouraging. The apparatus employed is illustrated in Figure 13.

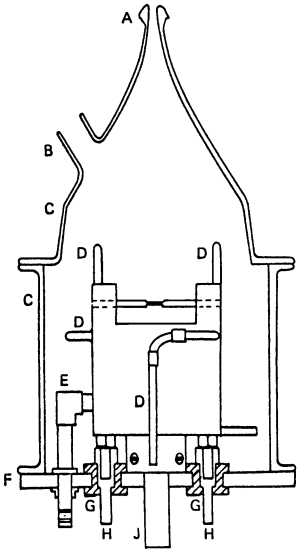

Figure 13. Graphite rod vaporisation apparatus: A, ball joint to plasma torch sample inlet; B, sample delivery port; C, cylindrical glass manifold; D, water cooling link; E, argon sample transport gas inlet; F, circular brass base; G, Tufnol insulating blocks; H, electrode terminals; and J, mounting pillar.

A graphite rod (about 70 mm in length and 3 mm in diameter) is positioned between the terminals of the power supply in a shielded chamber (in the position of the dotted lines); the terminals are cooled with water. The unit is contained within a cylindrical glass manifold (100 mm diameter, to 10 mm long) of the shape shown in Figure 13. The total volume of the manifold is approximately 1 litre and the distance from the top manifold to the plasma is about 0.5 metre. The enclosure is fitted with a conical top containing 2 ports. Port A is fitted with a ground glass ball joint allowing the argon sweep gas carrying the vaporised sample to be transported to the injector tube of the ICP source and Port B is fitted with a polypropylene stopper and is positioned to allow delivery by a micro pipette of sample solution to the depression on the graphite rod. The filament is heated by a low-voltage, high-current power supply fitted with a programmer allowing variation of the power and time during desolvation, ashing and vaporisation procedures (A 3370 electrothermal atomiser, Shandon Southern Instruments Limited). Other experimental facilities and operating conditions are shown in Table 5.

TABLE 5

EXPERIMENTAL FACILITIES AND OPERATING CONDITIONS

Plasma power supply	International Plasma Corp., Model 120-27; operating frequency 27.12 MHz; power output 0-2 kW, continuously variable. Work coil, 1½ turns, 6 mm o.d. copper tubing.
Spectrometer	Hilger Monospek 1000; Czerny-Turner scanning monochromator with grating 1 200 lines mm^{-1}) blazed for 300 nm; reciprocal linear dispersion, 0.8 nm mm^{-1}.
Optics	Plasma imaged in 1:1 ratio on to entrance slit with two 7.5 cm focal length, 5 cm diameter fused silica lenses.
Readout	Signal from EMI 6256B photomultiplier tube displayed on Servoscribe chart recorder.
Plasma torch	Demountable fused silica fitting into brass base. Coolant gas tubing, 21 mm o.d.; plasma gas tubing, 17 mm o.d.; injector tubing, 6 mm o.d., 1.5 mm i.d.
Filament power supply	Shandon Southern Instruments, Model A3370, electrothermal atomiser; the temperature and times of desolvation and vaporisation were set at 100°C for 30 s and 2400°C for 1.5 s, respectively.
Filament	Single-depression graphite rods were constructed to be of 70 mm length and 3 mm diameter; the depression for the sample was a channel length of 8 mm and depth 1.0 mm; maximum sample volume, 20µl.
Gas flow rates	Argon flow-rates of 1l, 1.0 and 0.81 min^{-1} were used for the coolant, plasma and injector tubing, respectively.
Sample introduction	A 10µl Eppendorf micropipette with a disposable polypropylene tip was used to introduce 10µl volumes of sample solution on to the graphite rod.
Standard solutions	All stock solutions were prepared by dissolving analytical-reagent grade salts in dilute mineral acid or distilled water. Working solutions were prepared daily from these stock solutions.

RESULTS AND DISCUSSION

The mode of operation of the graphite rod electrothermal vaporisation device for introduction of the sample into the ICP is different from that required in the use of this type of device in AAS. In the latter technique, the graphite rod (or tube) device is required both to release the analyte from the surface of the graphite (vaporisation) and also to effect atomisation of the analyte so that free atomic species are available above the graphite surface for measurement by AAS. In the use of the graphite rod as described here for the introduction of discrete samples into the ICP source, however, the atomisation requirement is not necessary. The electrothermal device is required only to release a discrete pulse of analyte material from the sample transferred to it; this may be released alone or together with the component of the sample matrix and may also be released bound in molecular form, as finely divided particulate material or as free atoms. Atomisation (and excitation for optical emission spectrometry) is then provided

subsequently by passage of the analyte through the axial channel of the core of the ICP source. Provided, therefore, that no problems arise from premature loss of analyte during the desolvation and/or ashing stages of the temperature cycle employed with the graphite rod device, the requirement for close control of the final temperature of vaporisation used to remove different analyte elements from the graphite rod is not as critical as is encountered in AAS. It is necessary only to provide a sufficiently high heating rate to the rod to ensure a rapid rate of removal of analyte from the surface and a discrete pulse of sample material above the surface of the rod for transport to the plasma source for excitation. For the elements studied in our work a satisfactory compromise vaporisation temperature for the graphite rod was found to be 2400°C. More important for the purposes of attaining high sensitivity and precision in the technique employed is careful optimisation of the parameters controlling sample transport to the ICP.

The principal parameters governing the rate and efficiency of sample transport from the graphite rod manifold to the ICP source are the length of the polythene connecting tubing between the two units and the flow-rate of the argon injector gas used to sweep the analyte from the manifold into the source. The effects of these parameters on the analytical performance of the system have been studied using silver as the test element and monitoring the transient atomic-emission signal at 328.1 nm produced on vaporisation of 400 picograms amounts of silver from the graphite rod at 2400°C after desolvation of 10µl aliquots of an aqueous 0.04 ppm silver solution. Figure 14 shows the effect on the analytical signals obtained for silver of variation of the length of the tubing connecting the graphite rod manifold to the plasma torch injector gas inlet; the injector gas flow-rate was maintained constant for this experiment. It is apparent that the vaporised analyte can be transported effectively over a considerable distance to the plasma (even utilising the 20 metre length of connecting tubing a useful analytical signal is recorded for silver) and that, as expected, the appearance of the signal is delayed after the start on the vaporisation cycle for a period proportional to the distance over which it must be transported to the plasma source. In addition, as the length of the connecting tubing is increased, the analytical peak height decreases and the duration of the signal increases; this effect is attributed to progressive mixing and dilution of the analyte particles with the argon injector gas to cause "tailing". Some analyte is undoubtedly lost by deposition onto the walls of the manifold cover and the part of the connecting tubing nearest to the manifold as the vaporised material cools and aggregates; after this has occurred as the primary process that lowers the sample transport efficiency, however, little further loss of analyte material by deposition occurs. At the initiation of the vaporisation step a decrease in plasma background intensity is observed. This is caused by the pressure pulse that occurs as the argon carrier gas in the sample manifold is heated by its passage over the hot graphite rod and gives rise to an instantaneous temporary increase in the injector gas flow-rate at the plasma via a "piston effect"; for short tubing lengths this occurs just before the analyte material arrives at the plasma and for longer tubing this event is well separated in time from the analyte signal.

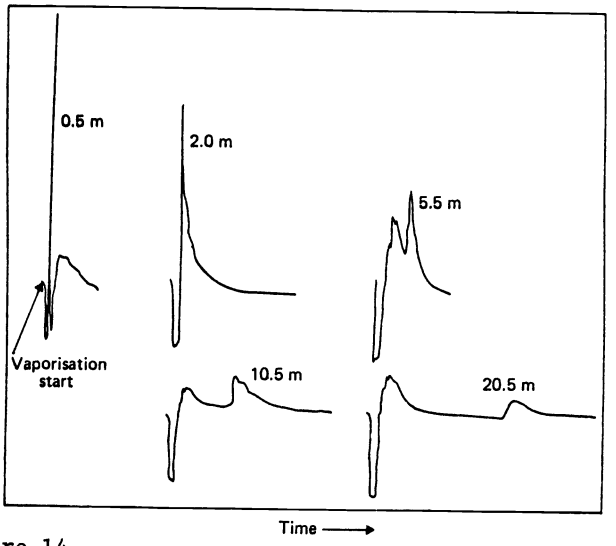

Figure 14. Effect of variation of the length of connecting tubing on the analytical signal at 328.1 nm obtained from 400 pg of silver. Aliquots of 10 µl of 0.04 µg ml^{-1} silver solution. Injector gas flow-rate, 1.3 l min^{-1}.

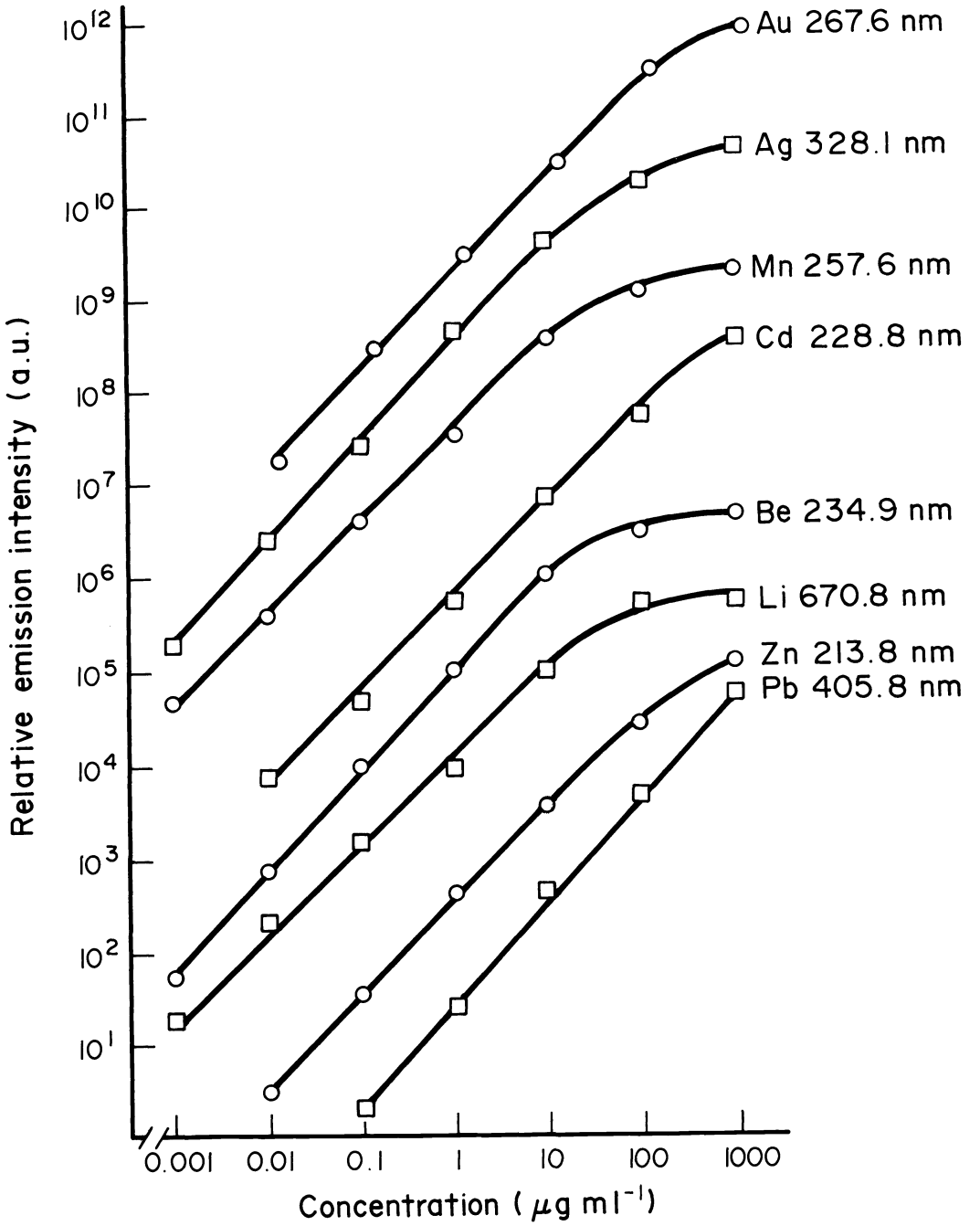

Figure 15. Calibration curves for 8 elements obtained for 10µl aqueous sample solutions by graphite rod - ICP-OES technique.

Figure 15 shows typical calibration graphs obtained using the graphite rod vaporisation device described here for the introduction of 10µl aqueous samples into the ICP source for optical emission spectrometry. The graphs for silver and cadmium at their atomic resonance lines at 328.1 and 228.8 nm, respectively, are linear over 4 orders of magnitude of concentration range up to 10µl of an approximately 100 ppm analyte solution. The graphs shown are drawn from a factor of 10 above the detection limit for the silver and a factor of 3 above the detection limit for cadmium so that for these, and other, elements of linear dynamic concentration range of 4/5 orders of magnitude is possible with the system employed. The reproducibility of the technique

for introduction of samples into the source was evaluated using silver as the analyte element. Aliquots of 10µl of a solution containing .4 ppm of silver were introduced repetitively (15 times) onto the graphite rod for vaporisation and the peak emission intensity observed at 328.1 nm was recorded. The relative standard deviation obtained for these determinations was 0.06 (i.e. 6%). Similar relative standard deviations were observed for other elements.

ATOMIC FLUORESCENCE SPECTROSCOPY

For some years it has been apparent that the technique of atomic fluorescence spectroscopy using flame or electrothermal atomiser sources, showed promise for simultaneous multi-element analysis and could provide high sensitivity for many elements and wide linear dynamic range of calibration. In fact, the technique has not been developed in this direction but remains in favour for the development and operation of dedicated simple systems for particular analyses. We have, in our laboratories, recently developed several dedicated analysers including those for the determination of arsenic and selenium in soil digests by non-dispersive atomic fluorescence spectroscopy (AFS) using an argon-hydrogen flame and the hydride generation technique.

The type of instrumentation employed in this work was a purpose-built non-dispersive atomic fluorescence spectrometer and a simple hydride generation apparatus as illustrated in Figure 16. Details of the components of this instrumentation are listed in Table 6.

Schematic diagram of equipment employed.

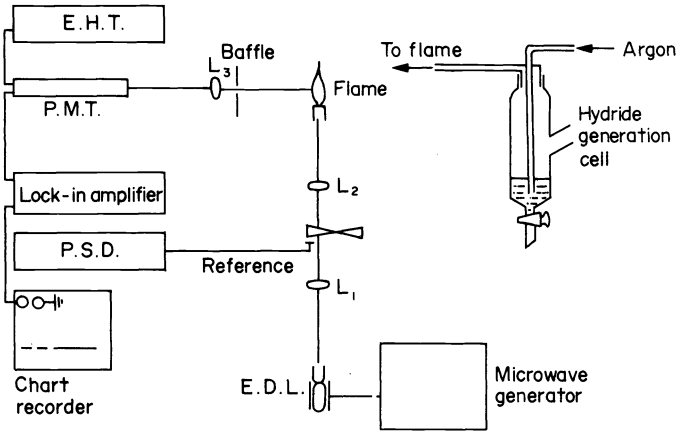

Figure 16. Non-dispersive atomic fluorescence spectrometer and hydride generation device

TABLE 6

INSTRUMENTATION EMPLOYED

Source	Selenium microwave electrodeless discharge lamp operated at 2450 MHz in a ¼-wave resonant cavity. Radiation modulated with an eight-sector mechanical chopper
Chopper..	Programmable Rofin, Model 7500, 3–800 Hz (Rofin Ltd., Egham, Surrey)
Microwave generator	Microtron 200 (EMS Ltd., Wantage, Berkshire)
Photomultiplier	Solar blind, Type R431, Hamamatsu Co., Japan
Lock-in amplifier	Brookdeal Electronics, Type 450S (Brookdeal Ltd., Bracknell, Berkshire)
Phase sensitive detector ..	Brookdeal Electronics, Type 411 (Brookdeal Ltd.)
Optics	Source focused as 1:1 image on the flame using two 7.5-cm focal length fused silica convex lenses (L_1 and L_2). Flame focused as inverted 1:1 image on PMT using 7.5-cm focal length lens (L_3)
Chart recorder	Servoscribe, Model RE 511.20 (Smiths Industries Ltd.)

Radiation from a microwave-excited selenium electrodeless discharge lamp (EDL) was focused onto a rotating sector and then refocused into the argon–hydrogen flame. The atomic fluorescence radiation stimulated from selenium atoms in the flame was then observed at 90° to the incident radiation by passage through a focusing lens to a solar blind end-window photomultiplier. The output from the photomultiplier was taken to a lock-in amplifier whose reference signal provided by the rotating sector in the incident radiation beam from the EDL source. The analytical atomic fluorescence signals for selenium observed at the output from the lock-in amplifier were displayed on the potentiometric chart recorder.

Using this type of apparatus we have determined traces of arsenic and selenium with the appropriate sources in 1 gram amounts of soil samples. The samples were weighed into a series of test tubes and digested using nitric acid at room temperature for a period of hours. A few glass beads were added to each vessel and perchloric acid was then added. The tubes then transferred into a cold aluminium digestion block, the temperature of which was increased steadily to 100°C over a period of 30 minutes. The block was maintained at this temperature for 30 minutes and then the temperature was increased to between 190° and 200°C and maintained at this temperature until digestion of the soil was complete. The test tubes were then removed from the digestion block and allowed to cool. A 2 ml volume of potassium bromide solution (2%) was added to each and the test tubes were allowed to stand in boiling water for 15 minutes to ensure complete reduction of selenium (VI) to selenium (IV). The solutions were then centrifuged and the residues rejected. The supernatant solution was taken for analysis; the solutions were then made 5 M with respect to hydrochloric acid and analysed by the hydride generation technique using the atomic fluorescence spectrometer. Typical results obtained are shown in Table 7.

TABLE 7

COMPARISON OF RESULTS FOR THE SELENIUM CONTENT OF SOIL DIGESTS

	Selenium found						
	Lanthanum nitrate method			Tellurium(IV) method			
Soil sample	Mean, p.p.m.	SD, p.p.m.	RSD, %	Mean, p.p.m.	SD, p.p.m.	RSD, %	ICP* method, p.p.m.
1	0.37	0.017	4.5	0.35	0.009	2.6	0.38
2	0.36	0.016	4.4	0.35	0.012	3.4	0.33
3	0.24	0.010	4.1	0.23	0.015	6.5	0.23
4	0.70	0.014	2.0	0.68	0.015	2.2	0.69
5	18.7	0.64	3.4	18.6	0.49	2.6	19.2
6	111	2.93	2.6	110	2.45	2.2	—
7	0.29	0.014	4.8	0.28	0.012	4.2	0.28
8	0.31	0.020	6.4	0.30	0.015	5.0	—
9	0.30	0.023	7.6	0.29	0.018	6.2	—

* ICP = optical-emission spectrometry using an inductively coupled argon plasma source.

TABLE 8

RESULTS OBTAINED FOR THE CONCENTRATION OF ARSENIC IN SOIL DIGESTS

Sample No.	Mean value/ $\mu g\ g^{-1}$	Relative standard deviation, %	ICP* result/ $\mu g\ g^{-1}$
1	2.12	8.35	1.80
2	2.43	8.04	2.50
3	2.28	7.06	2.28
4	4.50	7.04	4.46
5	17.02	4.91	—
6	50.43	8.27	—
7	8.08	9.76	7.0
8	21.42	7.56	—
9	33.55	8.73	—

* ICP = inductively coupled plasma emission spectrometry.

Similar results obtained for the determination of arsenic in soil digests are shown in Table 8. The results obtained for 9 soil digests for the determination of arsenic show good agreement with those obtained by inductively coupled plasma emission spectrometry. The use of non-dispersive atomic fluorescence spectrometry allows the sequential determination of both arsenic and selenium by simple substitution of the spectral source and no other changes of instrumental parameters.