Atomic Absorption Spectrophotometry 1979 version

An Essay Review

Methods for the Examination of Waters and Associated Materials

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An Essay Review
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Methods for the Examination of Waters and Associated Materials

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Warning to users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary. Local Safety Regulations must be observed. Laboratory procedures should be carried out only in a properly equipped laboratory. Field operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried. Care should be taken against creating hazards for others. Lone working, whether in the laboratory or field, should be discouraged. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specification. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

There are numerous handbooks on first aid and laboratory safety. One such publication is 'Code of Practice for Chemical Laboratories' issued by the Royal Institute of Chemistry, London. Another such publication, which includes biological hazards, is 'Safety in Biological Laboratories' (editors E Hartree and V Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London.

Where the committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. It cannot be too strongly emphasized that prompt first aid, decontamination, or administration of the correct antidote can save life, but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radiochemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of the correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first aid, fire-fighting, and rescue equipment. If in doubt it is safer to assume that a hazard may exist and take reasonable precautions rather, than to assume that no hazards exists until proved otherwise.

About this series

This booklet is one of a series intended to provide recommended methods for the determination of water quality. In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, has issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as individual methods, thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods being issued when necessary. The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users – the senior analytical chemist, biologist, bacteriologist etc, to decide which of these methods to use for the determination in hand. Whilst attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is one of the joint technical committees of the Department of the Environment and the National Water Council. It has nine Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

1.0 General principles of sampling and accuracy of results
2.0 Instrumentation and on-line analysis
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General non-metallic substances
6.0 Organic impurities
7.0 Biological methods
8.0 Sludge and other solids analysis
9.0 Radiochemical methods

The actual methods etc are produced by smaller panels of experts in the appropriate field, under the overall supervision of the appropriate working group and the main committee. The names of those associated with this method are listed inside the back cover.

Publication of new or revised methods will be notified to the technical press, whilst a list of Methods in Print is given in the current HMSO Sectional Publication List No 5, and the current status of publication and revision will be given in the biennial reports of the Standing Committee of Analysts.

TA DICK
Chairman

LR PITTWELL
Secretary

20 July 1977

Preface

This essay review is intended as an introduction to the application of atomic absorption spectrophotometry (AAS) in general water analysis. Atomic absorption spectrophotometry does not require elaborate sample preparation procedures and is a relatively rapid, interference free technique that is ideally suited to the analysis of waters, sewage effluents, sewage sludges and trade wastes for a wide range of elements.

This review outlines theoretical aspects of AAS, basic instrumentation, safety considerations, performance and operating characteristics of the technique, interference effects, applications in the water industry, pre-concentration techniques and complementary AAS techniques.

Eighty references, which include the full title of the paper, are cited in order to allow the interested reader to pursue specific applications or techniques. Over 700 scientific papers are published each year on the uses and applications of atomic absorption techniques and this gives some indication of the importance of atomic absorption spectrophotometry in chemical analysis.

It should be noted that this essay review only describes techniques that can be performed using commercially available atomic absorption instrumentation. Radio-frequency induction coupled plasmas are not discussed.

Atomic Absorption Spectrophotometry 1979 version

1 Introduction

Atomic absorption can be defined as the absorption of photons by an atomic vapour. When an atom absorbs a photon of visible or ultraviolet light, one of the outer electrons of the atom is transferred to an excited energy level. The wavelength at which absorption occurs is characteristic of the element, and the degree of absorption is a function of the concentration of atoms in the vapour. The absorption lines of most elements lie between 190 and 850 nm.

The basic principles underlying atomic absorption spectroscopy were established by Kirchhoff[1] in 1860, when he used the dark lines in the Fraunhofer spectrum to deduce the presence of certain elements in the cooler, outer-solar atmosphere. Although a great deal of theoretical work by physicists and astrophysicists has been published over the last fifty years[2], it was not until 1953 that Sir Alan Walsh[3] and later in 1955 Alkemade and Milatz[4] realized the analytical potential of the technique and demonstrated its superiority to flame emission spectroscopy.

Atomic absorption spectrophotometry (AAS) is an analytical technique that can be used to determine over sixty elements provided that they are in a homogeneous solution, and is very well suited to water analysis. The technique has very good specificity, consequently sample preparation is relatively simple and handling errors are minimal. Analyses can be performed far more rapidly than by procedures requiring more elaborate preparative steps.

Interelement effects in water analysis are not very pronounced and can readily be minimized. Detection limits of less than $0 \cdot 1$ mg/litre are readily obtainable for the most commonly determined elements in water analysis and recent adaptions have resulted in even lower detection limits of $0 \cdot 001 - 0 \cdot 005$ mg/litre for a number of elements (see 8). It must be stressed that these adaptions are more time-consuming and suffer from significantly more matrix interference effects than conventional atomic absorption using direct nebulization into flames.

2 Theory

2.1 Absorption Line Profiles

Figure 1 depicts a typical absorption line profile of an atomic vapour in a conventional flame, and a typical profile of a molecular electronic absorption band in solution. The ordinate represents the absorption coefficient (K) and the half-width is the width across the profile where the absorption coefficient is half its maximum value. The large half-widths of molecular electronic absorption bands in solution (10–50 nm) arise from vibrational and rotational fine structure of the electronic energy levels and also from solvent-solute interaction in the condensed phase. Spectral interference due to overlap of absorption line profiles is very common in solution spectrophotometry. However it can readily be seen that spectral overlap of atomic line profiles will be a rare occurrence in AAS, viz:

Wavelength range for both techniques 660 nm (190–850 nm)
Typical half-width of an absorption line profile $\quad 5 \times 10^{-3}$ nm
Typical half-width of a molecular absorption band 25 nm
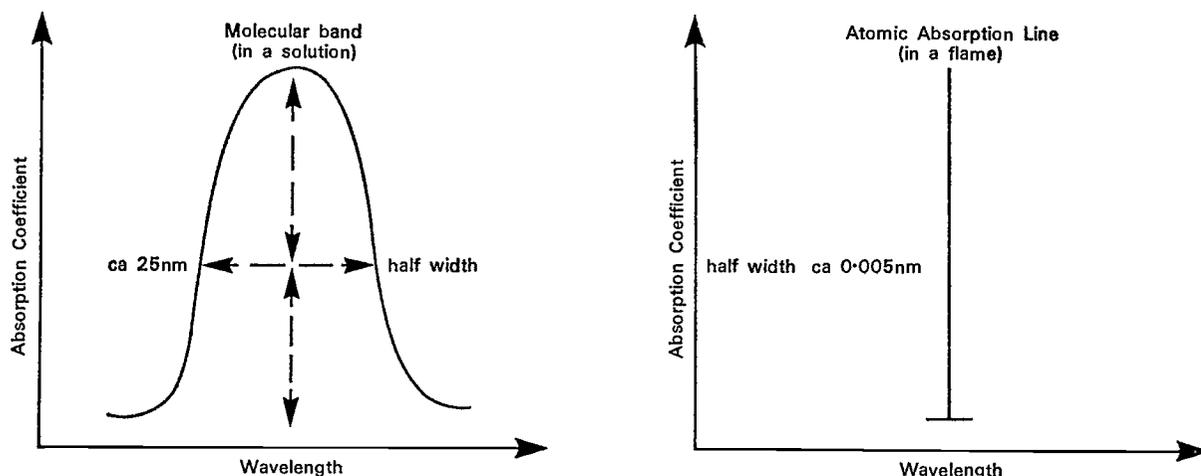
Figure 1   Typical molecular band (in solution) and atomic absorption line (gas phase)

Atomic absorption is a 'lock and key' technique whereby a given element will only absorb radiation specific to that element. Spectral interference caused by overlap of atomic line absorption profiles is insignificant except for a few rare instances mainly involving little used less sensitive absorption lines[5]. If a solution containing a given element is nebulized into a suitable flame an atomic vapour of the element will normally be formed. Some of the atoms may be raised to an excited energy level and emit characteristic radiation of that metal, a phenomenon that is exploited in flame emission spectroscopy. However the overwhelming majority, more than 99·9%, of the element atoms will remain in the non-emitting ground state (see 2.3). If these ground state atoms are irradiated with light of a wavelength (and frequency) corresponding to an absorption line, the atoms will absorb some of the radiation. The amount of light absorbed will be a function of the concentration of the ground state atoms in the flame.

The small half-widths of atomic absorption lines (Figure 1) means that if a continuous source is used to measure the absorption (as in solution spectrophotometry), a very expensive high resolution monochromator must be used in order to obtain any appreciable atomic absorption signal. Walsh[3] overcame this problem by using a hollow-cathode lamp atomic line source (see 3.1.1). These lamps emit the atomic line spectrum of the element to be determined. The half-widths of the atomic lines emitted by these lamps are somewhat less than the corresponding absorption lines of atomic vapours in conventional flames since the lamps operate at low pressures and temperatures. Absorption lines are commonly referred to as resonance lines. An inexpensive, relatively low resolution monochromator can now be used to isolate the desired resonance emission line emitted by the hollow-cathode lamp from any unwanted non-resonance (non-absorbing) emission lines (Figure 2).
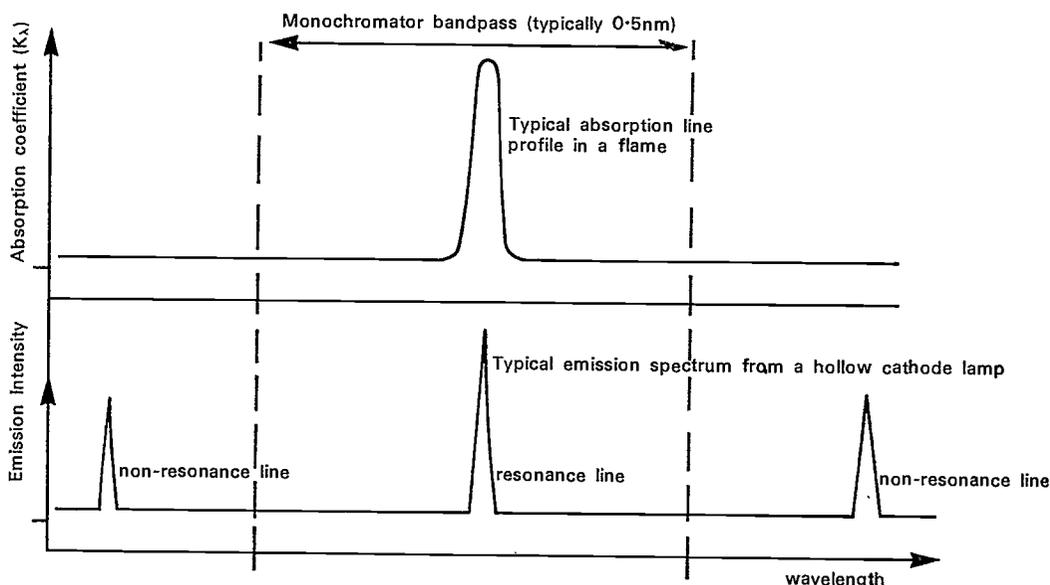
Figure 2   Spectral effect of the combination of a hollow-cathode lamp and a relatively low resolution monochromator

The combination of a hollow-cathode lamp and a low resolution monochromator is equivalent to a continuous source and a very high resolution monochromator.

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2.2 Shape of Calibration Graphs

Figure 3 gives a pictorial representation of atomic absorption. If I_o is the *intensity* of a resonance emission line reaching the detector in the absence of any atomic vapour, and I_t is the intensity of radiation reaching the detector after absorption by an atomic vapour then, from the Beer-Lambert law:

$$A = \log_{10}\frac{I_o}{I_t} = kcl$$

where A = Absorbance (or optical density)
  k = Constant
  c = Concentration of ground state atoms per unit volume
  l = Path length of absorbing atomic vapour

(uniform density of atomic vapour)
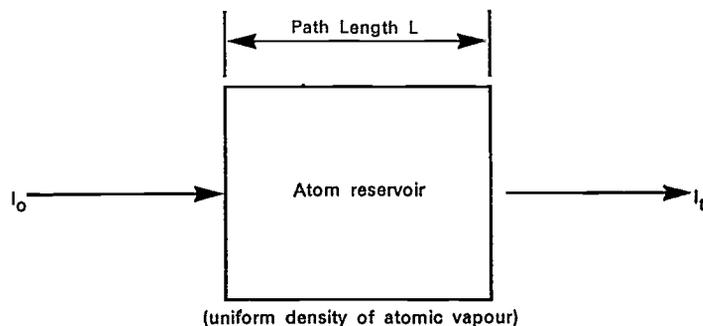
Figure 3 Pictorial representation of atomic absorption

This derivation assumes that the resonance emission line is resolved from all other emission lines and that the resonance emission line width from the hollow-cathode lamp is considerably less than the corresponding resonance absorption line width of the atomic vapour in a high temperature flame. Unfortunately this latter assumption is not strictly true and, although a linear concentration-absorbance relationship is usually followed for absorbances of less than $0 \cdot 3$ to $0 \cdot 4$, for absorbance values above this, the calibration graph becomes increasingly non-linear. This effect of more pronounced for low boiling point elements such as arsenic, cadmium, selenium, tellurium and zinc because of self-absorption effects (see 3.1.1). Figure 4 illustrates a typical calibration graph.
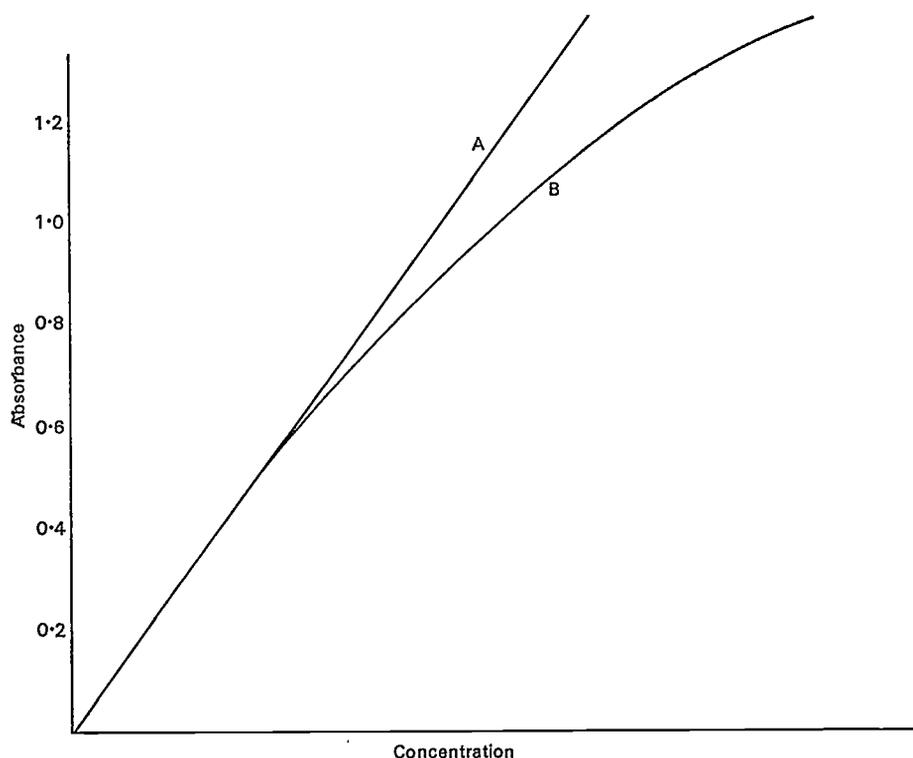
Figure 4 Calibration graph shape
A. As predicted by equation 1
B. Typical observed calibration graph

All modern AAS instruments have electronic facilities for converting the absorbance values obtained from a small number (3–5) of standard solutions into a linear calibration graph, and giving direct concentration read-outs calculated from this graph. However, this device should be used with caution because, if significant deviation from Beer's Law is present, the analytical results will be of poor precision – see also Section 3.5.3. In any case, it is not good practice to work with absorbance values greater than about $0 \cdot 8$ as this will usually lead to reduced precision.

2.3 Comparison with Flame Emission Spectroscopy

Absorption measurements are confined to atoms in the ground state. Atoms in excited states do not contribute to the atomic absorption signal.

The number of atoms (N_1) that are in an excited state compared to the number (N_0) in the ground state (for a system in effective thermal equilibrium) is given by the Boltzmann equation:

$$N_1 = N_0 \frac{g_1}{g_0} e^{-\frac{E_1}{kT}}$$

Where E_1 is the energy of the excited state above the ground state:

g_1, g_0 are the statistical weights of the excited and ground states respectively
k is the Boltzmann constant
T is the absolute temperature

The calculated values of N_1/N_0 for some resonance lines at different temperatures are given in Table 1, which shows that this ratio (N_1/N_0) rapidly decreases with decreasing wavelength (increasing E_1). This means that flame emission methods are not very sensitive for elements with resonance lines below 270nm, such as (arsenic, antimony. bismuth, cadmium, mercury, selenium, tellurium and zinc, etc) whereas the sensitivity of atomic absorption is only dependent on the ground state atom population and not on the wavelength of the resonance line. Also, since the number of excited atoms varies exponentially with temperature (Table 1) whilst the number of ground state atoms remains essentially constant, any slight temperature fluctuation in an atomic vapour will have a much more pronounced effect on the excited state atom population utilized in flame emission than on the ground state atom population utilized in atomic absorption.

Spectral interference is often observed in flame emission spectrometry owing to the relatively large number of atomic lines and broad molecular bands that can be observed. In atomic absorption spectrophotometry the primary radiation source is modulated either electronically or mechanically and a suitable amplifier, tuned or phase locked to the modulation frequency, is connected to the detector. This ensures that any emission from the flame is not detected by the measuring system (see 3.1). It should be pointed out that weak non-specific absorption, mainly caused by undissociated matrix molecules in the flame, is sometimes observed in atomic absorption spectrophotometry. However this effect can easily be corrected (see 3.6 and 6.3).

Table 1   The Ratio of the Number of Atoms in the Excited State (N_1) to the Number in the Ground State (N_0) at Various Temperatures

Resonance Wavelength (nm)	Ratio N_1/N_0		
	T = 2000°K	T = 3000°K	T = 5000°K
Cs 852·1	$4 \cdot 44 \times 10^{-4}$	$7 \cdot 24 \times 10^{-3}$	$6 \cdot 82 \times 10^{-2}$
Na 589·0	$9 \cdot 86 \times 10^{-6}$	$5 \cdot 88 \times 10^{-4}$	$1 \cdot 51 \times 10^{-2}$
Ca 422·7	$1 \cdot 21 \times 10^{-7}$	$3 \cdot 69 \times 10^{-5}$	$3 \cdot 33 \times 10^{-3}$
Mg 285·2	$4 \cdot 05 \times 10^{-11}$	$1 \cdot 68 \times 10^{-7}$	$1 \cdot 34 \times 10^{-4}$
Zn 213·9	$7 \cdot 29 \times 10^{-15}$	$5 \cdot 58 \times 10^{-10}$	$4 \cdot 32 \times 10^{-6}$

3 Instrumentation

Figure 5 illustrates the main components of a typical atomic absorption spectrophotometer.
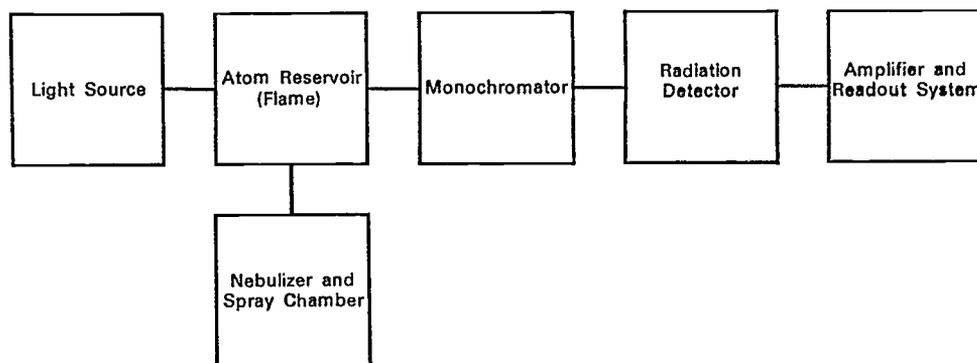
Figure 5   Main components of a typical atomic absorption spectrophotometer

3.1   Radiation Source

By far the most commonly used radiation source is the hollow-cathode lamp, but other sources are occasionally used, and these as well as hollow-cathode lamps are described below.

In order to ensure that the system only responds to radiation from the source and not from the atom reservoir (the flame), the light output from the radiation source is modulated. This can be achieved either using a mechanical chopping device or alternatively the current to the source can be modulated. The output from the detector is normally passed through an amplifier tuned to modulation frequency or passed through a phase sensitive amplifier. Thus any radiation emanating from the atom reservoir will not be detected.

3.1.1   *Hollow-cathode Lamps*

All commercial instruments are fitted with hollow-cathode lamp power supplies. Figure 6A depicts a typical hollow-cathode lamp which consists of a borosilicate cylindrical glass envelope with a silica end window, which will transmit radiation of wavelength greater than 180nm.
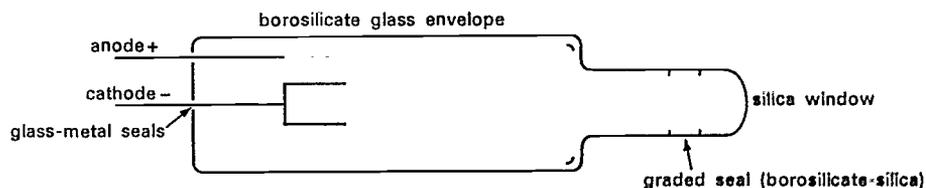
Figure 6A   Typical hollow-cathode lamp

Certain lamps, such as calcium, chromium and copper often have a less expensive borosilicate glass window as the main resonance lines of these elements lie at wavelengths greater than 320nm. A hollow cathode is situated in the centre of the lamp; this cathode is fabricated from either the pure form of the element or from a suitable alloy if the pure element is very volatile and/or non-conducting. The anode is usually a tungsten rod.

The lamp is filled with an inert gas (normally neon or, sometimes, argon) at a low pressure (4–10 Torr). Most lamps use a standardized octal base plug which is in electrical contact with the anode and cathode of the lamp. These octal based hollow-cathode lamps fit the majority of commercial instruments. Typically, currents of 2–15mA are passed through the lamps from a current stabilized power supply and a stable discharge is formed inside the cathode. Adjustments are provided for accurately aligning the lamp along the optical axis of the instrument. Most modern hollow-cathode lamps have operating lives well in excess of 5000mA hours. The lamps with the shortest lives are those constructed from alloys of volatile elements such as arsenic or selenium.

All lamps have a maximum operating current which should not be exceeded. As the lamp current is increased the emission intensity of a given resonance line increases but the analytical sensitivity tends to decease because of line broadening and self-absorption.

The line broadening is caused by an increase in the cathode operating temperature whilst the self-absorption is caused by absorption of the emitted radiation by unexcited ground state atoms in front of the cathode. Self-absorption is equivalent to an increase in the emission line width and is particularly noticeable for the volatile elements arsenic, cadmium, selenium, zinc etc. The selected lamp operating current should give adequate intensity with minimum line broadening.

Many multielement lamps are now commercially available. These have the advantage that one lamp can be used to determine a number (2 to 6) of elements. They have the disadvantages that their output intensity is somewhat less than the equivalent single element lamp, their emission spectrum is more complex, the selection of an optimum operating current is more difficult and the useful operating lifetime is in most cases somewhat less than most equivalent single element lamps. The main advantage of these lamps is in their use with instruments which only have facilities for powering a single hollow-cathode lamp. They have little advantage in instruments fitted with multi-lamp turrets. Calcium-magnesium and copper-zinc hollow-cathode lamps are however very good dual element lamps which have been successfully used over a long period of time.

3.1.2 *Radio Frequency Excited Electrodeless Discharge Lamps*

The lamps consist of a silica bulb containing a small amount of a given element or a suitable compound of that element filled with argon or neon at a low pressure (see Figure 6B). The lamp is excited by a low power (5–20 watts) radio frequency (27MHz) field generated in a radio frequency (RF) coil surrounding the lamp. Some commercially available lamps are constructed with their own matched RF coils permanently attached to the lamp[6]. These lamps are more intense (5–10 times) than hollow-cathode lamps and also exhibit narrow line widths. This can result in a slightly improved sensitivity and a longer linear range of calibration graph for very volatile elements such as arsenic and selenium than can be obtained with the equivalent hollow-cathode lamps[6]. Their main advantage is for elements such as arsenic and selenium where the main resonance
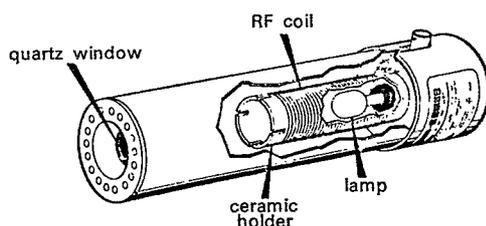
Figure 6B Typical radio frequency excited electrodeless discharge lamp
(*Reproduced with permission from ref 6*)

lines lie in the extreme ultra-violet region of the spectrum below 200nm where the poor lamp intensity from hollow-cathode lamps can limit the usefulness of these latter lamps with some atomic absorption instruments (see 3.7). The main disadvantages of these lamps is that at present they are only commercially available for a limited number of elements (volatile elements or elements that form relatively volatile halides), they are more expensive than equivalent hollow-cathode lamps and, in addition, require a separate power supply.

3.1.3 *Other Potential Light Sources*

Microwave excited electrodeless discharge lamps have been employed as light sources in AAS[7]. These are similar to the radiofrequency excited lamps previously described, but are excited by a relatively high power (30–100 watts) microwave (2450MHz) field. These lamps are 100–500 times more intense than hollow-cathode lamps, but considerably less stable. In addition, the high cost of a microwave power supply precludes their general use in AAS. It should be stressed that increasing the intensity does not increase the analytical sensitivity (see Equation 1).

Vapour discharge lamps have been used in the past but these are only available for a very limited number of elements (cadmium, caesium, gallium, indium, rubidium, sodium, potassium and zinc). They tend to give poorer analytical sensitivity due to the high operating temperature and pressure of these lamps compared to hollow-cathode lamps.

Continuum sources such as xenon arc lamps or deuterium arc lamps have been used in conjunction with very high resolution monochromators by research workers[8] but to date no instrument company has commercially developed such an instrument for general sale. The main problem is the high cost of the monochromator and developing a suitable intense wide range continuum source.

A tuneable dye laser in conjunction with a frequency doubler would appear to be an ideal single AAS source, but to date little work has been reported using such a source for AAS work[9].

3.2 Atom Reservoir

The vast majority of routine atomic absorption work is carried out using direct pneumatic nebulization of homogenous solutions into flames. Alternative methods of atomization are considered in section 8.

3.2.1 *Nebulizers*

Figure 7 depicts a typical pneumatic nebulizer. The sample is drawn up the nebulizer capillary and on reaching the end of the capillary is reduced to a mist or aerosol of tiny droplets by the supersonic gas flow (air or nitrous oxide) that emerges from the annulus around the end of the capillary.
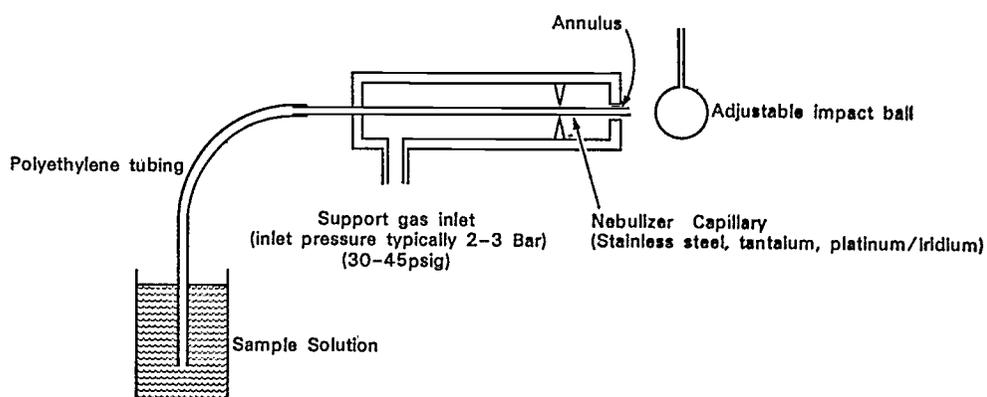
Figure 7   Typical pneumatic nebulizer

The aerosol is then passed into a spray chamber where the larger droplets precipitate and run to waste. The remaining tiny droplets are carried by the oxidant and fuel gases, with which they are thoroughly mixed, into the flame. Figure 8 depicts the processes occurring during nebulization and atomization of a sample.
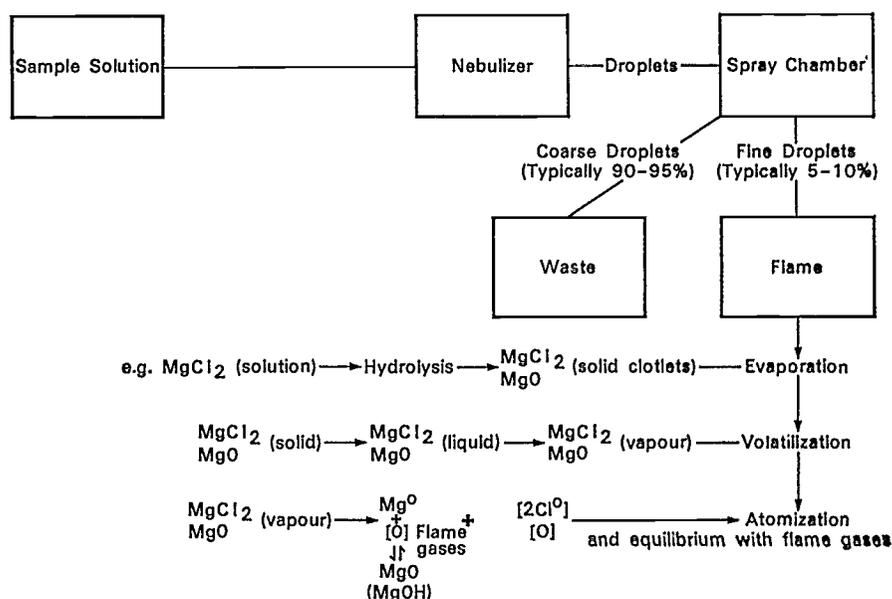
Figure 8   Idealized depiction of nebulization and atomization

The efficiency of this system can be increased by using a spray disperser or impact ball (fitted as standard to many modern atomic absorption spectrophotometers). This consists of an inert spherical bead situated in front of the nebulizer outlet onto which the spray impinges; this device causes an increase in the number of droplets small enough to reach the flame and therefore results in an increase in the analytical sensitivity. The analytical sensitivity is very dependent on the position of the impact ball and instruments fitted with these devices usually have some external means of adjusting the position of the impact ball. It is important to optimise this each time the nebulizer is removed or changed. This can conveniently be achieved whilst nebulizing a 5mg/litre copper solution when an absorbance signal of greater than 0·5 should be obtained on most modern instruments.

3.2.2 *Flames*

The two most commonly used flames in AAS are the air-acetylene and the nitrous oxide-acetylene flames, which exhibit maximum temperatures of about 2200°C and 2750°C respectively. A 100 or 120mm path/length laminar flow slot burner is normally used to support the air-acetylene flame whilst for the nitrous oxide the optimum slot length is 50–60mm. The hotter nitrous oxide-acetylene flame is used to determine elements that are poorly atomized in the cooler air-acetylene flame. In general it can be stated that elements such as aluminium, silicon, titanium, vanadium and zirconium which form stable refractory oxides cannot be determined in the air-acetylene flame whilst elements such as cadmium, copper, lead, nickel, silver and zinc that do not form highly stable oxide species can satisfactorily be determined in this flame. Elements such as chromium and molybdenum can be determined in either flame but interelement effects are significantly less in the hotter nitrous oxide-acetylene flame. Appendix A lists the optimum flame for each element. It should be stressed that the nitrous oxide-acetylene flame could be used to determine all the elements listed in Appendix A, but that for elements that do not form refractory oxides the analytical sensitivity is 5–10 times lower than the air-acetylene flame.

It is important never to attempt to ignite or maintain a nitrous oxide-acetylene flame on an air-acetylene burner. The very fast burning velocity of a nitrous oxide-acetylene mixture will result in a violent explosive flashback that could damage the spray chamber and will certainly temporarily deafen the operator. Most modern instruments have an interlock system to prevent such a flashback occurring (see also 4.3).

Many atomic absorption instruments are now fitted with an automatic gas control unit that will automatically sense that the correct burner is fitted, ignite the flame and continually monitor for the presence of the flame. Similarly it can automatically shut the flame down. If a fault such as power failure, air compressor failure, exhaustion of a gas supply were to develop during flame operation the unit will switch off the flame gases and safely extinguish the flame.

Clogging of the burner slot is not normally encountered unless solutions containing more than about 2%m/V of dissolved solids are nebulized for prolonged periods; this does not represent a significant problem in non-saline water analysis.

3.3 Monochromator

The monochromator isolates the required spectral resonance line emitted by the radiation source and also minimizes the effect of background radiation emanating from the flame or the nebulized sample or both. Silica prism monochromators used to be popular but have the disadvantage that the optical dispersion of a prism varies with wavelength, so that resolution for a fixed slit width setting decreases markedly with increasing wavelength. Thus a prism will have good resolution at wavelengths below 250nm but relatively poor resolution for wavelengths above about 400nm. Diffraction grating monochromators are universally used in modern instruments and have the advantage that the optical dispersion of a grating is virtually independent of the wavelength, thus resulting in a linear wavelength readout. The resolution is essentially constant throughout the spectrum for a given slit width setting. Modern blazed diffraction gratings, where the reflecting surface of each groove on the grating lies at a fixed angle to the grating surface, concentrate about 60–80% of the incident light energy into the first order spectrum. One grating, normally blazed at about 300nm, can satisfactorily be used to cover the wavelength range 190–850nm. However some higher priced instruments are fitted with two gratings; one is blazed at about 250nm for use in the ultraviolet region of the spectrum, whilst the other is blazed at about 500nm for use in the visible and near infra-red region of the spectrum. The gratings are automatically interchanged at a wavelength of about 400nm.

Adjustable slit widths are situated along the optical path of the monochromator so that the optimum compromise may be made between spectral purity and energy reaching the photodetector. In practice spectral bandpasses of $0 \cdot 2$–$1 \cdot 0$ nm are normally used for the vast majority of atomic absorption analyses.

3.4 Radiation Detector

Photomultipliers are universally used, the main requirements being an adequate response over the spectral range 190–780 nm and low dark current. If caesium, with its main resonance line at $852 \cdot 1$ nm, is to be determined, a wide range photomultiplier is essential. Most modern instruments are now fitted with these wide range photomultipliers.

3.5 Amplifier and Readout System

3.5.1 *General Considerations*

The modulated light signal from the hollow-cathode lamp (see 3.1.1) is detected by the photomultiplier and selectively amplified whilst any continuous radiation emanating from the flame is effectively rejected. The output from the photomultiplier is directly proportional to the incident light intensity; however the concentration of the analyte is related to the measured absorbance (see equation 1), thus a logarithmic conversion of the signal must be performed. The final output is then displayed either on a meter or a digital display device, the latter readout being used on almost all modern instruments. Facilities to monitor simultaneously the output on a potentiometric recorder are standard.

3.5.2 *Signal Integration*

If readings are taken directly from a meter or a digital display errors in visual averaging of the output signal can often occur. For this reason all modern instruments allow the signal to be integrated for a fixed period of time and the resulting steady integrated signal displayed. Integration times of 1 to 10 seconds are normally used.

3.5.3 *Curve correction*

It has already been shown that the calibration graphs are only linear at low absolute absorbance values (Figure 4). Thus if direct concentration readout is to be employed some automatic method of linearizing the calibration graph is essential. All modern instruments have this capability. A simple correction system will require two standard solutions and a blank for setting up. One standard solution must give an absorption which lies on the linear part of the calibration graph (typically an absolute absorbance of $0 \cdot 1$–$0 \cdot 2$) and this solution is nebulized whilst setting the scale expansion control. The other standard solution should be the highest concentration to be determined, and is nebulized whilst setting the curve correction control. It is wise to prepare other standard concentrations to check the applicability of the calibration graph. If a poor fit is observed the concentration of the top standard solution should be reduced.

It is very important to ensure optimum alignment of the light source and the burner and that the lamp is operating correctly prior to applying any form of curve correction. Although many modern instruments are capable of linearizing a grossly non-linear calibration curve caused by incorrect optical alignment or excessive lamp current this will lead to a significant loss of precision.

A more elaborate correction system can be achieved using a microprocessor controlled instrument (see 3.5.5). In this case three to five standards are commonly used and the microprocessor will automatically apply a suitable curve fitting routine. The routines used vary from instrument to instrument. However, these devices are not infallible – see Appendix B, Section B9.

3.5.4 *Automatic Zero and Automatic Calibration Facilities*

Many modern instruments are fitted with automatic zero and automatic calibration facilities. The former device will set the output to zero absorbance when the appropriate control is operated, and is utilized whilst nebulizing the blank solution. The automatic calibration facility is used to maintain a constant response to a given standard and should not be activated before setting the output to zero absorbance with the blank solution being nebulized. It allows a constant preselected reading to be obtained during the nebulization of a given standard. This reading is usually selected so that direct concentration readout is obtained. Both these devices can be remotely activated when using an automatic sampler so that a stable baseline and a constant sensitivity can be maintained during prolonged operation.

3.5.5 *Microprocessors*

Microprocessors are now incorporated into the majority of modern atomic absorption units. These devices process the output data upon instructions from a keyboard fitted to the instrument. For instance, the blank and standards can be nebulized sequentially whilst the concentration level of each standard is keyed into the unit. The unit will then automatically compute a suitable calibration graph so that the final displayed read out is in the desired concentration units. Once the calibration graph has been determined it can be updated by simply nebulizing one standard and depressing the appropriate keys.

The microprocessor can also be used to control the operation of an automatic gas control unit (see 3.2.2) and the operation of an automatic background correction system (see 3.6 and 6.3).

A word of warning is essential: many users of atomic absorption instruments will increasingly regard microprocessor controlled instruments as black boxes into which the sample is introduced at one end whilst the correct result mysteriously appears at the other end. Even with this labour-saving device fitted, it is just as essential to clean out the burner and spray chamber regularly, check for a partial blockage of the nebulizer, carefully align the burner with respect to the light beam, and select the appropriate burner height and gas flow settings. It is often assumed that with a completely automated system these time-consuming procedures are not so important. This is incorrect. Although a microprocessor can effectively linearize a grossly non-linear calibration graph caused by incorrect selection of spectral bandpass or poor burner alignment, the precision of the results will suffer unless the unit is carefully optimized prior to each new determination.

3.6 Background Correction Systems

Although atomic absorption does not suffer from spectral interference caused by the overlap of atomic line profiles, weak non-specific background absorption by undissociated matrix molecules in the flame is significant in certain analyses. This non-specific background absorption has also been attributed to physical scattering of the radiation by unvaporized solid particles in the flame. However it is now generally accepted that molecular absorption by undissociated matrix molecules in the flame is mainly responsible for this absorption[10, 11].

Non-specific background absorption for a given matrix occurs over a much wider wavelength range than typical atomic line profile widths (see Figure 9). A hydrogen or deuterium hollow-cathode lamp, which emits a continuous spectrum from 190 to 350nm, can be used to monitor this background absorption. With a typical spectral bandpass of 0·5nm and a typical absorption line half width of analyte atoms in the flame of 0·005nm, the energy absorbed by the analyte atoms from a continuum source represents only a negligibly small proportion of the energy as seen by the detector. Figure 9 shows this diagrammatically. Thus if a measurement is performed with the analyte element
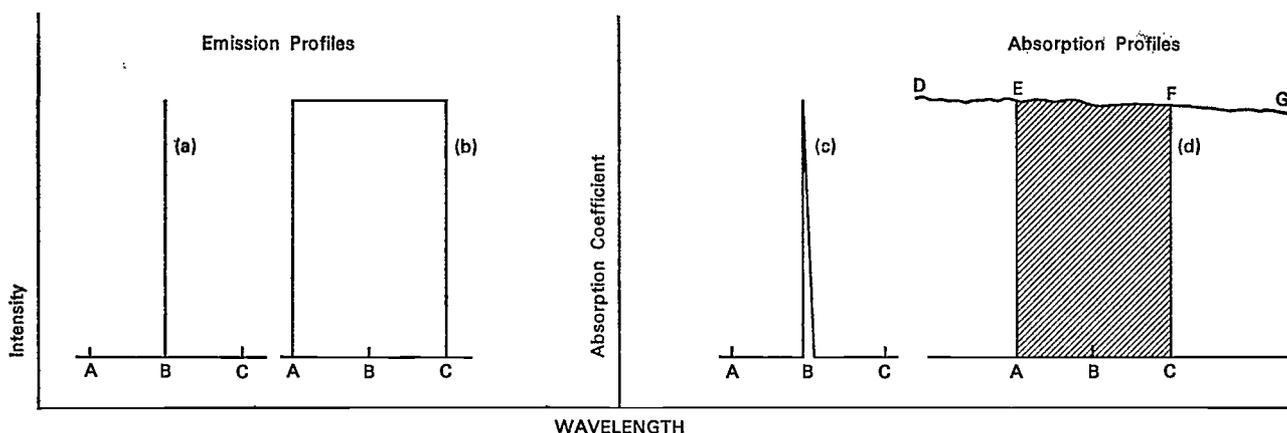
Figure 9   Diagrammatic representation showing how absorption line half-widths of hollow-cathode lamps and atoms in flames are small compared with monochromator spectral bandpass and molecular absorption bandwidths

(a)   Line half-width of hollow-cathode lamp. Typically 0 ·001 nm

(b)   Effective 'line' half-width of hydrogen or deuterium lamp source. Typically 0 ·6 nm, equivalent to monochromator spectral bandpass

(c)   Absorption line half-width of atoms in the flame. Typically 0 ·003 nm

(d)   Effective molecular absorption band width of molecules in the flame (shaded area) Typically 0 ·6 nm equivalent to monochromator spectral bandpass.

Note: Distance AC represents monochromator spectral bandpass
DEFG represents molecular absorption spectrum of a typical matrix over a small wavelength interval (1 -2 nm)

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lamp the absorbance signal will be proportional to both the analyte concentration and the matrix concentration. If a subsequent measurement, with otherwise identical operating conditions, is now taken with a hydrogen (or deuterium) lamp at the same wavelength the absorbance signal will simply be proportional to the matrix concentration. By subtracting the latter signal from the former, a signal that is only dependent upon the analyte concentration is obtained. Many modern instruments have facilities for automatically correcting for any background absorption. The light beam from a hydrogen (or deuterium) lamp and the analyte lamp are combined using a semi-silvered mirror and passed through the flame (or other atom reservoir). By alternately passing current pulses through each lamp and automatically subtracting the two absorbance signals, automatic background correction can be achieved. This is illustrated in Figure 10.
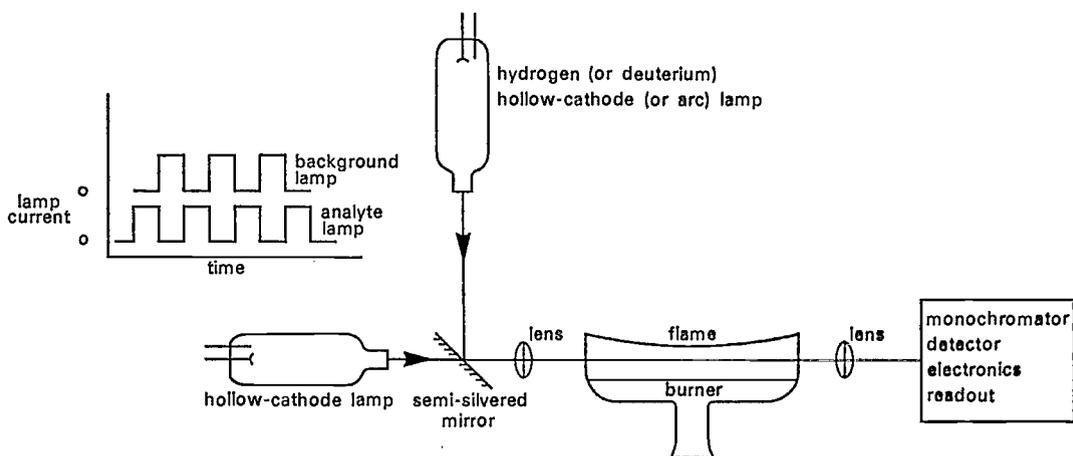
Figure 10   Diagrammatic representation of an automatic background correction system (single beam instrument)

It is also possible to correct manually for background absorption using a non-resonance line emitted by a suitable element hollow-cathode lamp. The absorbance signal observed with the non-resonance line is subtracted from the absorbance signal observed using the analyte resonance line.

The chosen line should lie within 2nm of the resonance line wavelength because the background absorption does vary with wavelength. The analytical significance of background absorption is discussed in Section 6.3.

3.7   Single and Double Beam Instruments

The difference between a single and a double beam instrument is that any variation in the source intensity during measurement will have no effect on the output signal level in a double beam instrument, but will have an effect proportional to the variation in intensity in a single beam instrument.

Figure 11 illustrates the optical layout for the two types of instrument. In the double beam instrument the light beam is split into two; one beam passes through the flame whilst the other passes around the flame, and the two beams are recombined prior to
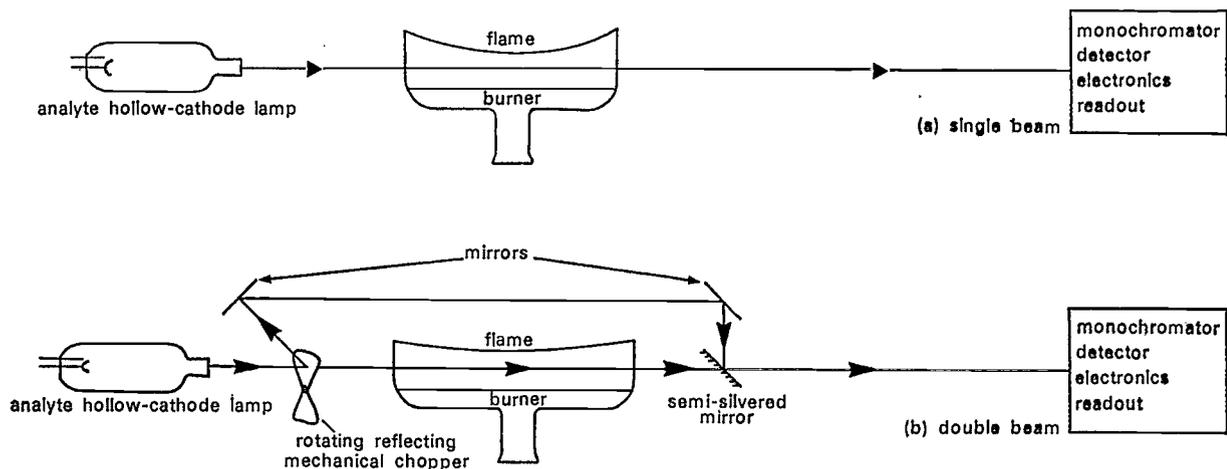
Figure 11   Diagrammatic representation of single and double beam atomic absorption spectrophotometer

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entering the monochromator. A mechanical chopping device allows the amplifier to resolve the two beams. The ratio of the intensities of the two beams is taken and this will be independent of any variations in light intensity. The advantages and disadvantages of single and double beam operation are summarized in Table 2. It should be stressed that although in theory a lamp warm-up period (that is, the time taken for the output intensity to stabilize) is not required for a double beam instrument, the analytical sensitivity can markedly change as the cathode warms up: this is especially true for volatile elements such as arsenic, cadmium, selenium and zinc.

Table 2   Comparison of Single and Double Beam Operation

Single Beam Instrument

Advantages

1. Simple, usually only two lenses (and a half silvered mirror if a background corrector fitted). Can be readily cleaned and realigned.
2. Less expensive than a comparable double beam instrument.
3. High luminous throughput.

Disadvantages

1. Longer lamp warm-up time and a multi-lamp turret is required.
2. Poor detection limit observed for lamps with unstable output.

Double Beam Instrument

Advantages

1. Short warm-up time.
2. Lamp stability not critical.
3. No significant baseline drift.

Disadvantages

1. More optical components, especially when automatic background correction is employed.
2. More expensive than a comparable single beam instrument.
3. Luminous throughput poorer than equivalent single beam instrument. This is especially noticeable in the far ultraviolet region of the spectrum (eg arsenic, $193 \cdot 7$nm; selenium, $196 \cdot 0$nm; and lead $217 \cdot 0$nm).

Modern hollow-cathode lamps have a very stable output and in the author's experience there is little difference in detection limits betewen the two types of instrument. Noise originating in the nebulization flame system is the limiting factor in many instances. The double beam instrument will probably show some advantage if prolonged unattended automatic operation is envisaged.

Although double beam instruments can be operated in a single beam mode, the disadvantages given above will still apply.

3.8   Automatic Operation

Most instruments are capable of automatic operation but care should be exercised in the choice of the sampler. Ideally the sampler should have a variable sampling and wash time and the sample cups should hold sufficient sample for the proposed analyses. Some samplers do not have a wash facility but simply directly transfer the inlet probe from one sample to the next. This is satisfactory if all the samples contain similar concentrations of the various analytes, but if large concentration differences between subsequent samples are likely to occur, then sample carry-over might be a problem and the use of alternate blank solutions should then be considered. The normal operating sequence is that the sampling arm transfers from the wash solution to the sample and after a fixed period (3–6 seconds), the signal is integrated for a fixed period (5–10 seconds). The sampling arm then transfers to the wash solution for a fixed period (3–10 seconds) and the next sample is moved to the sampling position. Automatic zero and automatic calibration facilities (see Section 3.5.4) simplify automatic operation. The appropriate blanks and standards are marked with a suitable identification tag that triggers the appropriate control.

If appreciable amounts of air are passed through the nebulizer during the time that sampling probe transfers from sample to sample, significant changes in the baseline level can be observed at wavelengths below 250nm. This can be overcome by using the automatic background mode (if fitted), or devising a system that avoids passing excessive amounts of air through the nebulizer.

Checks should always be made for non-specific background absorption when performing trace analysis. This can be achieved by either repeating the run with a hydrogen or deuterium hollow-cathode lamp or by using the automatic background correction mode, assuming this is available (see Sections 3.6 and 6.3).

4 Safety Considerations

The instrument manufacturer's handbook should be read carefully and any safety procedures given should be adhered to strictly.

4.1 Compressed Gases

Acetylene cylinders contain acetone and therefore should always be stored and used in an upright position. Ideally they should be placed in a cool adequately ventilated and fire resistant store well away from oxidant gases (eg nitrous oxide). All gas cylinders should be securely fastened to a wall or a suitable bulkhead. Free standing gas cylinders represent a very serious hazard should they topple over.

A flashback arrestor should be fitted close to the acetylene cylinder and a shut-off valve should be positioned close to the atomic absorption instrument. It is important that copper tubing or certain types of brass are not used to convey acetylene as explosive copper acetylide can be formed. The acetylene manufacturer or a safety officer acquainted with the appropriate legislation should always be consulted before undertaking the construction of an acetylene store or the selection and installation of pipework, flashback arrestors and shut-off valves between an acetylene store and the atomic absorption instrument. The acetylene pressure should not exceed 62kN/m² (9 psig) unless approval is obtained from the Health and Safety Executive[12].

Regular tests for leaks using soap solutions should be made. The acetylene and the nitrous oxide should be turned off at the cylinders when the equipment is not in use.

Acetylene is supplied dissolved in acetone and as the cylinder pressure decreases the proportion of acetone in the acetylene gas increases. This can cause an increase noise level as well as drift in sensitivity especially for certain elements such as calcium, chromium and molybdenum in the air-acetylene flame. To avoid this problem the acetylene cylinder should be replaced when the pressure falls to 520kN/m² (75 psig).

4.2 Fume Extraction

It is essential that an efficient corrosion resistant fume extraction system is used to vent the flame exhaust gases. The instrument handbook normally gives guidance on the selection and installation of a suitable extraction system. If possible the extractor fan should automatically be turned on when the atomic absorption instrument is switched on. The exhaust gases from a nitrous oxide-acetylene flame contain significant quantities of toxic nitrogen oxides and it is imperative that the extractor is switched on when operating this flame even if deionized water is being nebulized.

When purchasing a new AAS unit adequate allowance should be made for the purchase and installation of a suitable fume extraction system. In some situations, the cost of this item can be substantial.

4.3 Flames

The manufacturer's operating instructions should always be rigorously adhered to when igniting the flame. Ensure that the correct burner is fitted (see 3.2.2). Always check that the water trap is full and that it does not contain large amounts of precipitated solids. The waste reservoir should be a plastic bucket placed in a well ventilated area, so that the risk of accumulation of explosive mixtures is minimized. Extra care, because of the fire risk, should be exercised when nebulizing organic solvents and the waste reservoir must be emptied at the end of each run. If chlorinated solvents are nebulized the exhaust gases will contain appreciable quantities of phosgene.

4.4 Light Sources

The nitrous oxide-acetylene flame emits strongly in the ultraviolet region of the spectrum and should not be viewed directly with the naked eye. Flames should only be viewed through the protective screen fitted by the manufacturer.

Hollow-cathode lamps and especially microwave or radiofrequency electrodeless discharge lamps emit ultraviolet radiation and should not be directly viewed. Ordinary Crown glass spectacles do not give full protection against near ultraviolet radiation, suitably tinted glasses are required.

Electrothermal flameless atomizers (see 8.3) emit large amounts of infra red radiation during the atomization stage and repeated exposure can result in cataracts.

5 Performance and Operating Characteristics

This section gives an indication of the analytical performance data, a general description of the main operating parameters and their optimization.

5.1 Sensitivity for 1% Absorption (also known as characteristic concentration)

This is defined as the concentration of analyte in a solution that results in an absorbance of $0 \cdot 0044$. This is equivalent to a 1% decrease in the transmitted radiation. It can be readily calculated by determining the concentration of the analyte that will give an absorbance value of $0 \cdot 1$ and dividing that concentration by 22.7. This figure corresponds to the analytical sensitivity but it does not directly relate to the detection limit as it can give no indication of the signal to noise ratio.

Note. It is possible to reduce the sensitivity by rotation of the burner in order to reduce the length of the light path through the flame; this is sometimes useful for calcium and magnesium.

5.2 Detection Limit

A detection limit quoted by an instrument manufacturer is usually defined as that concentration of the analyte that gives an absorption signal equivalent to twice the within batch standard deviation of the noise fluctations of the blank (deionized water) signal (σ_w). The detection limit, unlike the sensitivity for 1% absorption, is very dependent on the instrumental stability. In practice a more realistic definition of detection limit, (as recommended by the Standing Committee of Analysts) where a single sample reading is compared with a single blank reading, is given by $4 \cdot 65 \, \sigma_w$[13]. This detection limit corresponds to that analyte concentration for which there is only a 5% probability that the result will be less than half of this detection limit value. It is important to stress that even then the detection limit refers to a pure aqueous solution of the analyte; if the samples contain appreciable quantities of matrix elements (eg estuary samples), the detection limit can be significantly degraded. If the samples require background correction (whether automatically or manually performed) this can result in a degradation in detection limit when compared to the non-background corrected value. In fact for routine analyses of typical non-saline waters by inexperienced staff the above points should be carefully considered when assessing realistic working detection limits. They should also be borne in mind when purchasing a new instrument, and any $2\sigma_w$ quoted detection limit values should be multiplied by a suitable factor.

5.3 Precision of Measurement (Repeatability)

This is usually defined as the standard within batch relative standard deviation when a given sample or standard solution is nebulized a number of times (10 or more). For concentrations greater than 20 times the $(4 \cdot 65\sigma_w)$ detection limit, the repeatability is usually between $0 \cdot 5$ and 2%.

5.4 Selections of Operating Parameters

5.4.1 *Hollow Cathode Lamp Current*

All lamps have a recommended maximum operating current which should never be exceeded. For routine flame work, lamp currents of 30–60% of the maximum current rating are typically used. For volatile elements such as arsenic, cadmium, selenium and zinc the sensitivity and linearity of the calibration graph can be markedly dependent

upon the lamp current, both parameters exhibiting marked degradation at high lamp currents (see 3.1.1). Most lamp manufacturers give both a recommended operating current as well as a maximum operating current and operating at this former value will usually give satisfactory results.

5.4.2 *Monochromator Spectral Bandpass*

The monochromator spectral bandpass is normally selected so that the desired resonance line is resolved from all other adjacent lines. Thus it would appear that a single small spectral bandpass of about 0·2nm would be ideal for all elements. However the intensity of some element lines is relatively low so that if a narrow slit width was always employed the detection limit for some lines would be degraded because of the high noise level associated with the low intensity of the radiation reaching the photomultiplier. This is particularly noticeable in the far ultraviolet region of the spectrum below 220nm. Most instrument handbooks recommend suitable spectral bandpasses for the lines listed in Appendix A.

5.4.3 *Choice of Flame Conditions*

The optimum support gas (air or nitrous oxide) flow rate is normally specified by the manufacturer and always set to this value. Thus the flame conditions are varied by changing the acetylene flow rate. For the majority of elements that are routinely determined in the air-acetylene flame the response is not very dependent upon the acetylene flow rate and this is adjusted to give a stoichiometric flame. This can be achieved by turning the acetylene flow down until the flame starts to lift off the burner and then increasing the acetylene flow by 10–30%. For elements with lines below 240nm a better approach is to adjust the acetylene flow for maximum transmission of light (minimum absorbance) whilst nebulizing deionized water.

Elements that form refractory oxides require fuel rich, for calcium, or even luminous, for chromium and molybdenum, air-acetylene flames in order to achieve maximum sensitivity. Under these conditions severe calibration problems can be experienced with chromium (see Appendix B, Section B9).

The acetylene flow rate has a far more critical effect on the response of elements normally determined in the nitrous oxide-acetylene flame. It is essential to optimize carefully the acetylene flow rate whilst nebulizing a suitable solution of the analyte. For elements that require very fuel rich flames, such as silicon and titanium, it is often better to set the acetylene flow rate slightly below the optimum response setting. Although this will result in a small reduction in sensitivity the rate at which carbon forms along the burner slot will be considerably reduced. If appreciable carbonization of the burner slot occurs the flame should be shut down and the burner slot gently scraped clean.

5.4.4 *Burner Height Setting*

For most elements routinely determined in the air-acetylene flame the response is not very dependent upon the burner height setting. The burner height is normally set so that without a flame the burner grid just begins to intercept the light beam. This can be achieved by fully lowering the burner and then slowly raising it until an absolute absorbance reading of 0·01 is obtained. For elements that form refractory oxides, such as calcium, chromium and molybdenum, a lower setting is better. The author has found that a more stable response and a more nearly linear calibration graph is observed for iron if the burner is lowered slightly from the grazing incidence position and a fuel lean flame is used*: With the nitrous oxide-acetylene flame the burner height setting is more critical and this should be optimized whilst nebulizing a solution of the analyte. It is important to appreciate that the optimum acetylene flow often is markedly dependent upon the burner height setting.

5.4.5 *Construction of Calibration Graph*

When setting up a new method it is good practice to run a range of standard solutions. Although many instruments only require three or even two standards in order to set up a linear calibration graph (see 3.5.5) this should be checked using a range (at least five) standard solutions (see Appendix B, Section B9).

Once the calibration graph has been established recalibration during a run can be achieved by simply nebulizing the top standard solution.

* See Appendix B, section B10.

Whenever a new method is adopted it is a wise precaution to analyse a number of typical samples using the standard addition technique[9, 14] and compare the results with those obtained using a calibration graph. If significant differences are observed the method is prone to interelement effects and requires further investigation before it is suitable for routine analysis. It should be noted that even if the standard addition technique and calibration graph results agree this does not indicate that all the naturally occurring analyte contained in the original sample has been recovered (see 7.4.2 and 7.4.3).

5.5 Routine Maintenance

Atomic absorption instruments require little user maintenance. The most important task is to clean out the burner head and spray chamber at the end of each day (or even each run if the samples contain large quantities of dissolved solids). It is also advisable to nebulize deionized water for 5–10 minutes prior to shutting down the flame in order to wash the nebulizer and impact ball. The burner head should be washed out with hot water, then with deionized water and finally rinsed with acetone to remove water from the slot. Any carbonisation of the nitrous oxide-acetylene burner slot should be removed by gentle scraping using a suitable feeler gauge. The spray chamber can usually be cleaned using deionized water from a wash bottle. For stubborn deposits or encrustations the burner and spray chamber can be immersed in a hot solution of laboratory detergent for a few hours. It is essential to rinse thoroughly both items prior to re-assembly otherwise reduced surface tension could result in erroneous results (see 6.2.2).

Always ensure that the water trap (connected to the drain tube of the spray chamber is filled and is not clogged with precipitated solids. It is also worthwhile checking that the spray chamber can freely drain and that there are no obstructions or kinks in the tube connecting the spray chamber to the waste trap. If poor drainage occurs a gurgling sound can be heard from the spray chamber. The plastic waste collection vessel should be regularly emptied. Accessible lenses and the end windows of hollow-cathode lamps should be occasionally cleaned using lens cleaning tissues. Some instruments are fitted with front surfaced aluminized mirrors and these must not be cleaned unless they have been specially coated and the manufacturer gives specific directions for this operation. The cleaning of monochromator optics (if required) should be left to the manufacturer.

Regular checks for gas leaks at all joints should be made using soap solution.

5.6 Fault Finding

Some commom symptons and possible causes are given below.

Symptom	Possible Causes
Lamp will not light	Burnt out lamp Electronic fault
Lamp working but no read out	Obstruction in light path Lamp incorrectly aligned Incorrect operating mode Wavelength incorrectly selected
Noisy signal with no flame	Unstable lamp output Wrong lamp current or spectral bandpass Lamp incorrectly aligned Dirty optics (especially noticeable at wavelengths below 220nm)
Noisy signal with flame alight and nebulizing deionized water	Burner and/or spray chamber contaminated with analyte
Noisy signal when nebulizing standards	Burner incorrectly aligned Impact bead badly aligned Nebulizer partially blocked Badly fitting plastic capillary uptake tubing to nebulizer Faulty nebulizer Unstable support gas supply pressure Liquid build up in spray chamber resulting in poor drainage (Check for obstruction)

Symptom	Possible Causes
Low sensitivity	Impact lead badly aligned Variable nebulizer set to non-optimized uptake rate Partially blocked nebulizer Burner incorrectly aligned Incorrect burner height Incorrect gas flow rates Spectral bandpass too large Lamp current too high Wrong wavelength setting (less sensitive line being used) Contaminated blank solution
Ragged irregular flame	Burner slot partially blocked
Slow change in sensitivity	Acetone carry over from acetylene cylinder operating at a cylinder pressure below 520kPa (75 psig) Slight changes in gas flow rates Encrustation forming around end of nebulizer from solutions with high dissolved solids Slow blockage building up in nebulizer capillary Nitrous oxide cylinder head icing up Encrustations forming in burner slot Carbonization of nitrous oxide acetylene burner
Excessive baseline drift	Monochromator wavelength setting drifting as unit warms up. This can be a problem with very small (ie near minimum) spectral bandpass settings Unstable lamp output Slow change in gas flow rates (eg cylinder nearing exhaustion)

6 Interference Effects in Atomic Absorption Spectrophotometry

6.1 General

A brief survey of the early literature could easily lead the newcomer to atomic absorption spectrophotometry into believing that this analytical technique is almost free from interference effects. With the increase of interest, a wider range of applications was studied and consequently many more interference problems were encountered. However most interferences, especially in water analysis, can be overcome by the use of simple techniques.

Interferences encountered in atomic absorption spectroscopy can be placed in one of the following categories:

A. Physical Interferences

    a. Spectral overlap of atomic line profiles

    b. Surface tension variations

    c. Viscosity or bulk matrix variations

    d. Solution temperature variations

    e. Variation in the composition of the solvent

    f. Overload of the phase sensitive amplifier caused by intense emission from the flame spectrum and/or sample matrix emission

    g. Ionization

B. Non-specific Background Absorption

C. Chemical Interferences (Stable compound or solute vaporization interferences)

The majority of difficulties that the water analyst can expect to encounter using flame analysis arise from background (non-specific) absorption, ionization, viscosity and chemical interferences.

6.2 Physical Interferences

6.2.1 *Spectral Overlap of Atomic Line Profiles*

It can safely be said that this form of interference is no practical significance in atomic absorption spectroscopy[5].

6.2.2 *Surface Tension Variations*

This effect should not be significant in most water industry analyses. If sample beakers are washed with detergent, then they should be thoroughly rinsed prior to drying.

6.2.3 *Viscosity or Bulk Matrix Variations*

This effect is caused by variation in the rate of nebulization with change in viscosity with increasing matrix concentration. Thus the sensitivity for a given element in distilled water will often be found to decrease in the presence of a significant amount of a mineral acid. For most applications in the water industry this effect is not very significant, but it can be observed with seawater or estuary analyses and possibly if the concentration by evaporation technique is used. It is important that any reagents used in the sample preparation stage, such as mineral acids, lanthanum chloride or potassium chloride, must be present in the standards at the same concentration as in the samples. It can be overcome by using matching standards, calibration by the standard addition technique or solvent extraction of the cation(s) to be determined from the interfering matrix (see 7.4). If this type of interference is observed, a check should be made for non-specific background absorption.

6.2.4 *Solution Temperature Variation*

The dependence of the response versus temperature for most elements is not too critical (eg typically a 25–50% increase in sensitivity is observed if the temperature is increased from 20–90°C). The variation is thought to be insignificant for temperature changes of ±3°C for most applications. However if sample pre-treatment requires boiling the solution it must be allowed to cool prior to measurement.

6.2.5 *Variation in the Composition of the Solvent*

This will cause an effect not only because of surface tension and viscosity changes (see above) which result in a changed sample uptake rate but also will affect the distribution of the droplets within the spray chamber. Most organic solvents are more volatile than water, and have a lower latent heat of vaporization. The droplets produced by the nebulizer will tend to evaporate more on their journey from the nebulizer to the flame and a greater proportion of these small droplets will reach the flame. Thus the enchancement in the signal when organic solvents are nebulized is caused by the increased sample uptake rate and a larger proportion of small droplets that reach the flame.

6.2.6 *Overload of the Phase Sensitive Amplifier*

All atomic absorption instruments have detection systems that, in principle, will not respond to emission from the flame or sample matrix. However if a low intensity source is used in a region of high flame background, the intense emission will result in an increased noise level and in extreme cases can cause erroneous signals. A good example of this can be demonstrated by trying to determine aluminium using the nitrous oxide-acetylene flame at 309·2nm (this being a wavelength region of very intense flame background emission) with a low lamp current (for example, 3mA) and a large spectral bandpass (for example, 1·0nm). The effect is negligible for most elements if the manufacturer's operating instructions are followed. If this form of interference is suspected the lamp current should be increased and the spectral bandpass decreased. The only common example of this form of interference using flame techniques is the determination of barium in the presence of calcium using the nitrous oxide-acetylene flame. The intense thermal emission from CaOH species at the 553·6nm barium resonance line wavelength can overload the phase sensitive amplifier for calcium levels above 500–1000mg/litre and result in very noisy erratic signals. (Appendix B, Section B4).

It should be stressed that this form of interference can be observed in electrothermal flameless atomization (see 8.3) when measuring at wavelengths above 320nm. It is caused by the intense black body emission from the graphite tube or rod. It is essential therefore to optimise carefully the tube or rod position so that the detector does not directly view the graphite surface.

6.2.7 Ionization

Ionization occurs in high temperature flames such as the air-acetylene and nitrous oxide-acetylene flames, and affects elements with relatively low ionization potentials; such elements include barium, caesium, calcium, lithium, rubidium, sodium and strontium. However, in the hotter nitrous oxide-acetylene flame it is significant for a number of other elements as well[15], aluminium, chromium, magnesium, titanium and vanadium. The higher the flame temperature the more the equilibrium existing between free atoms and ions is shifted towards the ionic states.

$$M \rightleftharpoons M^+ + e$$

The effect is characterized by the calibration curve bending away from the concentration axis (Figure 12). This is because as the concentration of the metal to be determined increases, the ratio of ground state atoms to ions also increases (Law of Mass Action) until at higher concentrations the effect becomes less noticeable. (Note, the resonance radiation will only be absorbed by ground state atoms and not by ions). The interference is overcome by the addition of an ionization buffer to the sample solution. This buffer is another easily ionizable metal and one that will ionize preferentially to the one being determined. Na and K (as chlorides) in concentrations of 1000–2000mg/litre are commonly used.
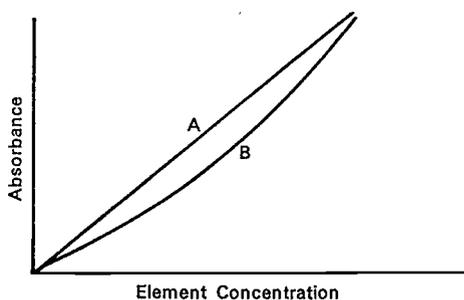
Figure 12   Calibration graph showing the effect of ionization
A. In the presence of an ionization suppressant
B. In the absence of an ionization suppressant

6.3 Non-Specific Background Absorption

Background absorption, often called scatter or molecular absorption, is an interference phenomenon caused by absorbance of the resonance line by molecular species formed in the flame from the sample matrix[10, 11]. This interference is analogous to turbidity in molecular spectroscopy and although it is more pronounced at low wavelengths, commonly below about 350nm, it can be observed at all wavelengths. The background absorbance also increases proportionally to an increase in the concentration of a given matrix in the sample solution. Whenever a new type of analysis is to be performed a check for background absorption should be made.

In a cool flame, molecular absorption tends to be more pronounced than with a hot flame; the nitrous oxide-acetylene flame will more completely vaporize the solid particles and dissociate molecular species present in the flame than the cooler air-acetylene flame. The background absorption signal from a given matrix is independent of the analyte concentration and thus the relative error from non-correction of background absorption increases as the analyte concentration decreases.

6.3.1 Methods of Overcoming Background Absorption

6.3.1 (a) *Chemical*

A simple method is to prepare a blank solution containing the same matrix as present in the samples, so producing the same amount of background absorption which can readily be measured and subtracted from the sample values. However for this to work, one must first know accurately the matrix composition and ensure purity of matrix reagents. An alternative would be to use the hotter nitrous oxide-acetylene flame in place of the air-acetylene flame, but this in turn may introduce other interferences such as ionization as well as markedly degrading the analytical sensitivity.

(b) *Instrumental*

These methods are all based on the fact that background absorption occurs over a wider wavelength range than that used for atomic absorption, and will equally affect the radiation from any source at the particular wavelength (see 3.6). It is therefore possible to measure the degree of interference at a nearby non-absorbing wavelength, and subtract it from the value obtained at the resonance wavelength. However this technique can lead to errors. Since the degree of interference changes with wavelength, unless the non-absorbing wavelength is very close ($\pm$ 2nm) to the absorbing wavelength, the degree of interference can be different. A more accurate method for wavelengths below 350nm is to use a deuterium or hydrogen hollow-cathode lamp to measure the background absorption at the same wavelength setting as the resonance line. Many instruments will perform this operation automatically (see 3.6).

At wavelengths above 350nm the relatively low light intensity obtained from most hydrogen or deuterium lamps results in a signal with a high noise level when automatic background correction is employed. In these cases non-automatic (sequential) correction using nearby non-absorbing lines is recommended[14].

When performing any trace level analysis, a check for non-specific background absorption should always be made. This is especially important if the concentration by evaporation technique is used (see 7.4). The main elements in non-saline water analysis responsible for this background absorption are calcium, magnesium and sodium. Normally, any sample that gives a significant background absorption signal will result in an intense visible coloration of the flame from the sodium and calcium present. In order to give the reader some indication of typical levels of background absorption, some values that were obtained on two different manufacturers' instruments are given in Table 3; they were measured at the lead (217·0nm), the cobalt (240·7nm) and the copper (324·7nm) wavelengths using a deuterium hollow-cathode lamp. All values are expressed as mg/litre of the appropriate element with both instruments optimized for measurement of each element. The background absorption for a given matrix varies with wavelength and in general is less significant at wavelengths above 300nm.

Table 3   Typical Background Absorption Signals

Element*	Concentration of element mg/litre	Background absorption signal expressed as analyte concentration** (mg/litre)							
		Pb 217·0nm		Co 240·7nm		Pb 283·3nm		Cu 324·7nm	
Instrument		1	2	1	2	1	2	1	2
Ca	20,000	1·60	2·10	0·70	0·95	1·30	1·20	0·14	0·11
Mg	20,000	0·48	1·20	0·25	0·40	1·85	1·85	0·09	0·12
Na	20,000	0·32	0·61	0·48	1·0	0·51	1·35	0·08	0·12

*   Present as chlorides
** Measured with a deuterium hollow-cathode lamp

The background absorption signal (expressed as an analyte concentration) is directly proportional to the matrix concentration. Table 3 shows that for typical non-saline water samples the characteristic background absorption signals are likely to be very small, but that for samples that are concentrated by evaporation they will almost certainly be significant. It can be seen that the relative background absorption signals do vary from instrument to instrument and this is probably due to differing light beam geometries through the flame as well as slight differences in flame conditions.

It should also be noted that high concentrations (greater than 1M) of nitric acid and especially sulphuric acid can result in significantly raised background absorption signals at wavelengths below 250nm[14]. This effect is not observed with hydrochloric acid even at the 5M level.

6.4 Chemical Interferences (also referred to as Solute Vaporization Interferences)

These are by far the most frequently encountered interferences in atomic absorption spectroscopy. Basically, a chemical interference effect is observed when a matrix constituent enhances or suppresses the formation of ground state atoms in the flame. A common example is the interference produced by aluminium, silicates and phosphates in the determination of magnesium, calcium, strontium, and many other metals in the air-acetylene flame. This is due to the formation of low volatility aluminates, silicates and phosphates which, in many instances, are only poorly atomized in the flame (see Figure 8). In order to overcome this type of interference, two techniques are used, both of which release the element under investigation. The first, seldom used now, relies upon the formation of a complex compound of the analyte that will lead to the release of the analyte element by the preferential formation of an easily atomized complex. Thus a chelate such as EDTA can be added to complex the analyte thus preventing its association with an anion that could lead to the formation of a refractory involatile compound in the flame. Alternatively, a reagent can be added that will preferentially form a compound with the interfering anion again leading to the release of the cation, eg the addition of an excess of lanthanum chloride to solutions of calcium containing the phosphate anion. The calcium is 'released' due to the preferential formation of lanthanum phosphate. This latter technique is the most commonly employed technique used to minimize chemical interferences. Alternatively, most common chemical interference effects may be overcome by using the nitrous oxide-acetylene flame, but for many elements (eg Cr) this results in a significant deterioration in the detection limit.

The most common chemical interference effects in the air-acetylene flame that the water analyst will have to deal with are:

1. Depression of the signal by phosphate, silicate, sulphate and aluminium in the determination of calcium and, to a much lesser extent, magnesium.

2. The effect of various substances on chromium absorption and the effect of the chromium valence state.

The first effect can be overcome by the addition of 1,000–2,000 mg/litre of lanthanum (as chloride) to all solutions, standards and blanks. The second effects may be minimized by working with a just non-luminous flame rather than a highly luminous flame (however this reduces the analytical sensitivity about 2·5 times) and the incorporation of 2% m/V ammonium chloride[18] or ammonium perchlorate[17] into the final solution.

The following elements are subject to minimal chemical interference effects in the air-acetylene flame when present in nitrate or chloride media:

Bismuth, cadmium, cobalt, copper, lead, lithium, nickel, silver, sodium and zinc.

7 Applications in the Water Industry

7.1 Storage and Preservation of the Sample

The sample should be stored in a suitable polyethylene or polypropylene container fitted with polyethylene or polypropylene screw caps. These caps should not contain cardboard liners. Some thermosetting plastic screw caps contain substantial quantities of zinc and significant levels of some other metals and should be avoided. Ideally the containers should always be rinsed out with dilute acid (HNO_3 or HCl) prior to sample collection. If a filtered sample is required this should be filtered using a standard membrane filter with a known pore size either at the time of sampling or as soon as possible after taking the sample. It is a good idea to prewash the membrane filters with 1M nitric acid[18]. The samples should be acidified with nitric or hydrochloric acid either at the time of sampling or as soon as possible after sampling. A final concentration of 0·2–1% V/V is suitable.

For ultra trace level work (at concentrations below 10μg/litre) polyethylene, polypropylene or polytetrafluoroethylene containers that have been soaked in 5–10% V/V acid should always be used. These containers should be reserved solely for this type of work.

Special precautions are required for the preservation of trace levels of mercury (see 8.1).

7.2 Sample Pretreatment Techniques

7.2.1 *Natural Waters, Supply Waters, Sewage, Final Effluent Samples and Some Trade Wastes*

It is common practice simply to acidify an aliquot of the sample with nitric or hydrochloric acid so that the final acid concentration is about 1% V/V (1ml of the concentrated acid per 100ml sample). The acidified sample is gently boiled for 3 – 5 minutes, cooled and made up to the original volume with deionized water. Standards are prepared in 1 % V/V of the appropriate acid.

Note. Care should be exercised when acidifying unknown trade wastes as these can contain appreciable quantities of sulphide or cyanide.

7.2.2 *Sludge Analysis*

Numerous digestion techniques involving a wide range of reagents have been recommended for this analysis,[19] − [23] the author and co-worker[23] have found that a simple 15 minute nitric acid digestion in a 50ml calibrated test tube gives effectively full recovery of Cd, Cu, Cr, Ni, Pb and Zn in a wide range of sewage sludges when compared to a standard nitric-perchloric acid digestion technique. However the latter digestion technique gave somewhat higher values for barium and iron. Rees and Hilton[21] have recommended digestion with hydrochloric acid and 30 %m/m hydrogen peroxide and found good agreement with conventional wet digestion methods.

Although in principle the highly sensitive technique of flameless electrothermal atomization might appear attractive (see Appendix D) in practice the relatively high concentrations of metals of interest makes this procedure inconvenient and time consuming when compared to conventional flame analysis.

7.2.3 *Miscellaneous Samples* (Animal tissue, plant tissue and sediment analysis)

The previous technique[23] where the dried homogenized sample is digested with nitric acid in a 50ml calibrated tube has been found eminently suitable for these analyses using $0 \cdot 5$–$2 \cdot 5$g of the well homogenized sample dried to constant weight at 105°C. Any floating fat residues from tissue samples can be removed by shaking the final diluted extract with 3–5ml of chloroform and nebulizing the upper aqueous layer.

Alternatively, conventional digestion techniques using nitric-perchloric acid,[24, 25] nitric-sulphuric acid,[24] nitric acid-hydrogen peroxide[26] or sulphuric acid-hydrogen peroxide[27] can be used. It should be stressed that the use of sulphuric acid can result in low lead recoveries and increased chemical interference effects (see 6.4). For samples containing a siliceous matrix the above digestion techniques will not release all the naturally occurring elements firmly bound within the siliceous matrix. If a true total result is required alternative dissolution techniques are required to dissolve the siliceous matrix. A common technique involves the use of nitric-perchloric-hydrofluoric acids[9, 14, 23, 28]. However it should be stressed that elements firmly bound in a siliceous matrix are not normally of physiological significance.

7.3 Measurement Techniques

Measurements can either be taken in the direct readout mode on a meter, digital display or a chart recorder, and then visually averaged by the operator. For this procedure the output should have some degree of electronic damping applied; a time constant of $0 \cdot 3$–$0 \cdot 6$s is normally satisfactory. This technique can lead to operator errors especially when working at high levels of scale expansion because of errors in averaging the noise level associated with the signal. A much better technique is to integrate the signal for a fixed period (typically 3–5s) and then a steady signal is obtained at the end of the integration period. For automatic operation (see 3.8) this technique should always be used because it greatly aids subsequent data handling.

Appendix A gives the wavelength, the flame system, an indication of the characteristic concentration (sensitivity for 1% absorption) and the expected detection limit range for the more commonly determined elements.

Appendix B contains some additional analytical information for certain elements where problems can often be encountered.

Appendix C lists some approved DOE methods for water analysis which have been published so far together with a brief description of each method, an indication of the expected detection limit and the range of applicability of the method.

7.4 Preconcentration Techniques

Often the limit of detection using conventional flame atomic absorption techniques is not adequate to determine accurately elements at concentrations around the levels of interest in drinking waters. Thus, if flame techniques are to be used, some form of preconcentration is required. The main preconcentration techniques are summarized below.

7.4.1 *Concentration by Evaporation*

A suitable volume (typically 200ml) of the sample is acidified with nitric or hydrochloric acid so that the final acid concentration is 1% V/V with respect to the concentrated acid. The sample is then evaporated to a volume 10–15ml and quantitatively transferred to a 20ml graduated flask. Standards are prepared in 10% V/V of the appropriate acid; this should minimize any variation in surface tension and/or viscosity of the evaporated samples. It is essential to use background correction because of the increased matrix concentration in the final nebulized solution. Severe absorption losses can occur if the beakers boil dry during the evaporation step. The absorbed material (especially iron) is very difficult to de-sorb and even prolonged simmering with nitric acid (70% m/m) does not always remove all the absorbed material from the beaker. Chemical interference effects for cadmium, cobalt, copper, iron, lead, nickel and zinc were found by the author not to be very significant for most natural water samples but the addition of ammonium perchlorate (2% m/V) was required to overcome the severe chemical interference effects observed with chromium[17].

The main advantages of the concentration by evaporation technique are that it is relatively simple, it requires the minimum of reagents which consequently results in negligible blank levels, it gives a 5–10 fold improvement in detection limit, and it is applicable to all elements that can be determined by atomic absorption. Its main disadvantages are that background correction must always be used, and the technique cannot be applied to seawater or estuary samples because of the very high dissolved solids content of the final solution. The original sample should have an electrical conductivity below about $2000\,\mu S\,cm^{-1}$.

7.4.2 *Solvent Extraction*

A suitable metal complex forming reagent is added to the sample and the resulting metal complex is extracted into a small volume of organic solvent. Typically extraction volume ratios (sample volume to organic solvent volume) of 10–20 are used. The sensitivity is increased not only by the extraction volume ratio but also by the enhanced rate of nebulization of the organic solvent (typically 2–3 times).

The most commonly used complex forming reagent is ammonium pyrrolidine dithiocarbamate (APDC) whilst the most commonly used extraction solvent is 4 – methylpentan-2-one (also known as methylisobutylketone, MIBK)[9, 14], [29–31]. The following metals can be quantitatively extracted Ag, Cd, Co, Cr^{VI}, Cu, Mn, Ni, Pb and Zn under optimized conditions. The Department of the Environment have published recommended methods for cadmium[29] and lead[30] using this technique. For a detailed appraisal of the uses of solvent extraction in atomic absorption the reader is referred to the treatise by Cresser[31]. An important point that is often overlooked is that the blank nebulized solvent should always be saturated with water. This will ensure that at wavelengths below 250nm no significant difference in the baseline level between a true blank solution taken through the extraction procedure and the nebulized solvent will be observed. This difference will not be observed if automatic background correction is employed. Direct extraction of the trace metals present in river waters and sewage final effluents often gives poor recoveries because of the interaction, (such as complex formation or absorption), between the trace metals and natural constituents of the sample so that the predigestion by boiling with acid is essential. The main advantages of the solvent extraction techniques are that for carefully selected extraction conditions it can be applied to a number of elements, it is applicable to seawater and estuary samples and background correction is not essential. The main disadvantages are that it is relatively time consuming, especially if predigestion and accurate control of the pH is required, that blanks can be significant and variable, and interelement effects can result in a significantly reduced efficiency of extraction of the analyte from the sample solution into the organic solvent. A good example of this latter effect is the marked reduction in the extraction efficiency of trace levels of nickel using APDC/MIBK at copper levels above 1mg/litre in the analyte solution[32].

7.4.3 *Ion Exchange*

Chelating resins have been used to concentrate a range of elements from natural water samples[33-35]. The samples are normally predigested to release the metals from naturally occurring substances (see 7.4.2) and then the buffered digested sample is passed through a column of the resin and subsequently eluted using a small volume of a suitable acidic solution.

The main advantages of the ion exchange technique are that large concentration factors (up to about 100 times) can be obtained and it is directly applicable to seawater and estuary samples. The main disadvantages are that it is relatively time consuming compared to the concentration by evaporation or solvent extraction techniques, blanks can be significant and variable, especially if predigestion is required, and that chromium cannot readily be determined simultaneously with the other routinely determined toxic metals[36].

8 Complementary Atomic Absorption Techniques

Although preconcentration techniques can be used to improve the sensitivity for a large number of elements (see 7.4), these techniques have several drawbacks; they can be time-consuming; they can cause variable blanks; and they are not readily applicable to some elements (eg arsenic, mercury and selenium). There are now commercially available accessories for atomic absorption instruments that allow many elements to be determined without preconcentration at low levels using complementary atomic absorption techniques.

8.1 The Mercury Cold Vapour Technique

Mercury is rarely determined using direct nebulization into the air-acetylene flame because of the poor detection limit (0·4–1mg/litre). Fortunately, elemental mercury has an appreciable vapour pressure at room temperature and exists as a monatomic vapour. Thus if a solution containing trace levels of ionic mercury is reduced to elemental mercury using stannous chloride and air or nitrogen bubbled through the solution the mercury will be rapidly volatilized in the gas stream. Then by passing the gas stream containing the mercury vapour through an absorption cell and monitoring the absorption at 253·7nm, low levels of mercury can be determined[37]. The typical instrumental set-up is depicted in Figure 13. The light bulb placed above the absorption cell prevents
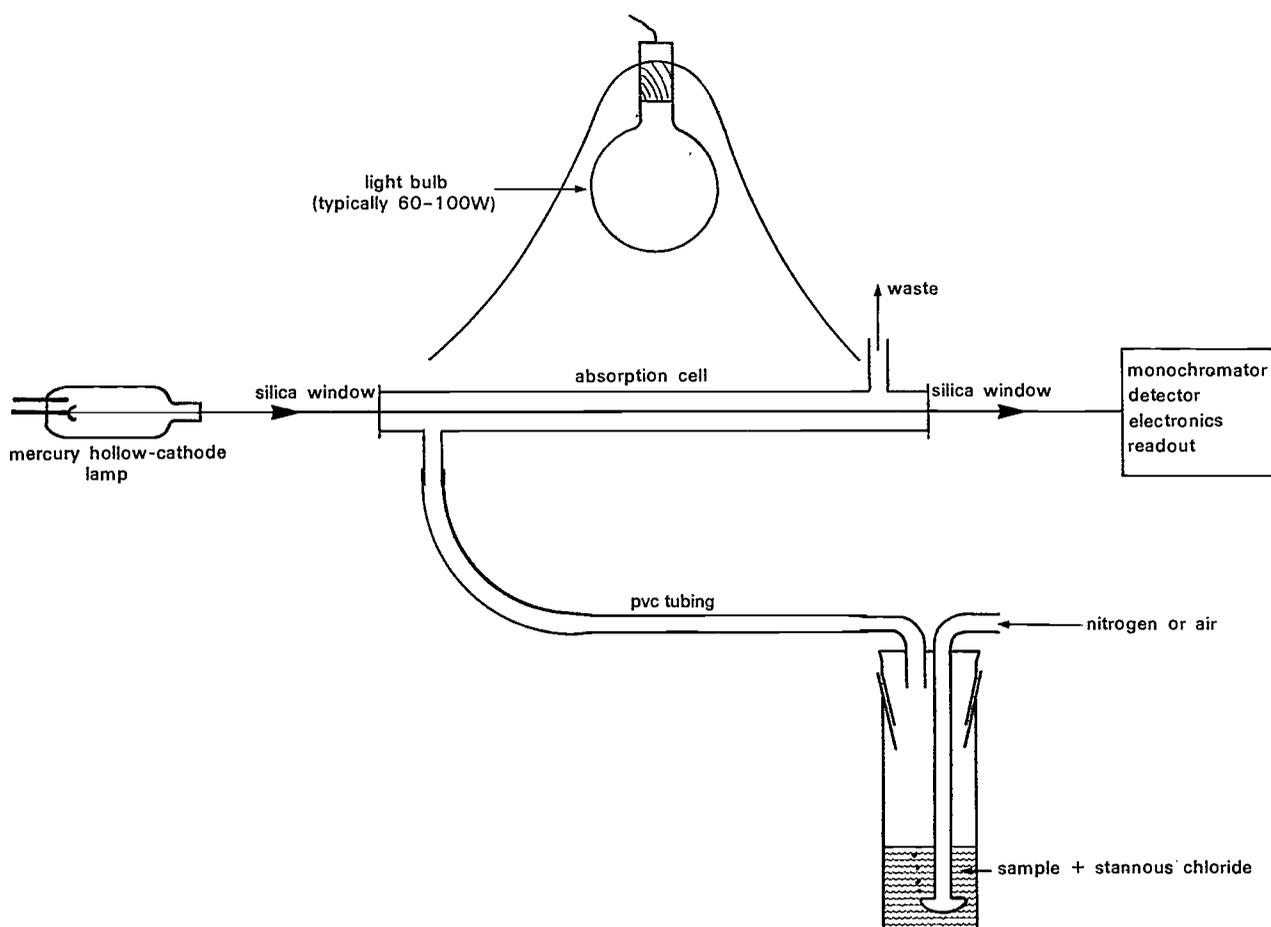
Figure 13   Diagrammatic representation of the mercury cold vapour technique

condensation on the cell windows. A typical 4.65σ detection limit is 2–10ng mercury which for a typical 50ml sample volume corresponds to a mercury concentration of 0.04–$0.2\mu g$/litre in the original sample solution. For very low mercury levels the cold vapour atomic fluorescence technique can be used and gives an improvement in detection limit of about ten times[38]. A problem in the determination of mercury is that organomercurial compounds (eg methyl mercuric chloride, phenyl mercuric acetate etc) are not reduced by stannous chloride and consequently require more vigorous digestion to produce ionic mercury prior to the stannous chloride reduction step. Various digestion reagents have been recommended, including prolonged digestion with potassium permanganate[39], prolonged digestion with potassium permanganate-potassium persulphate[40], digestion for ten minutes with bromine[41] (generated by the addition of potassium bromide and potassium bromate to the acidified sample). The DOE has published a recommended method for determining total mercury in non-saline waters and effluents where the acidified sample is digested with potassium permanganate at 70°C for seven hours prior to the stannous chloride reduction[42] (see Appendix C).

Sample preservation is a very important consideration and trace levels of mercury can be lost from acidic solutions. Various sample preservatives (which maintain oxidizing conditions) have been recommended, namely potassium dichromate[42, 43], bromine[41] and frequent aeration of the sample[44]. Glass bottles are to be preferred to plastic bottles for this analysis[42].

8.2 Hydride Generation Techniques

A number of elements, arsenic, antimony, bismuth, germanium, selenium, tellurium and tin, form volatile hydrides when an acidic solution of the element reacts with a solution of sodium borohydride. The liberated hydride is carried by a stream of nitrogen either into a nitrogen-hydrogen-entrained air flame[45] or preferably into a flame heated[46] or electrically heated silica tube[47]. The technique is depicted in Figure 14. The basic operating procedure is that some sodium borohydride solution is added to the glass cell and an aliquot of the suitably acidified sample is rapidly injected through the side arm, the hydride is instantly formed and is carried by the carrier gas to the heated silica tube.
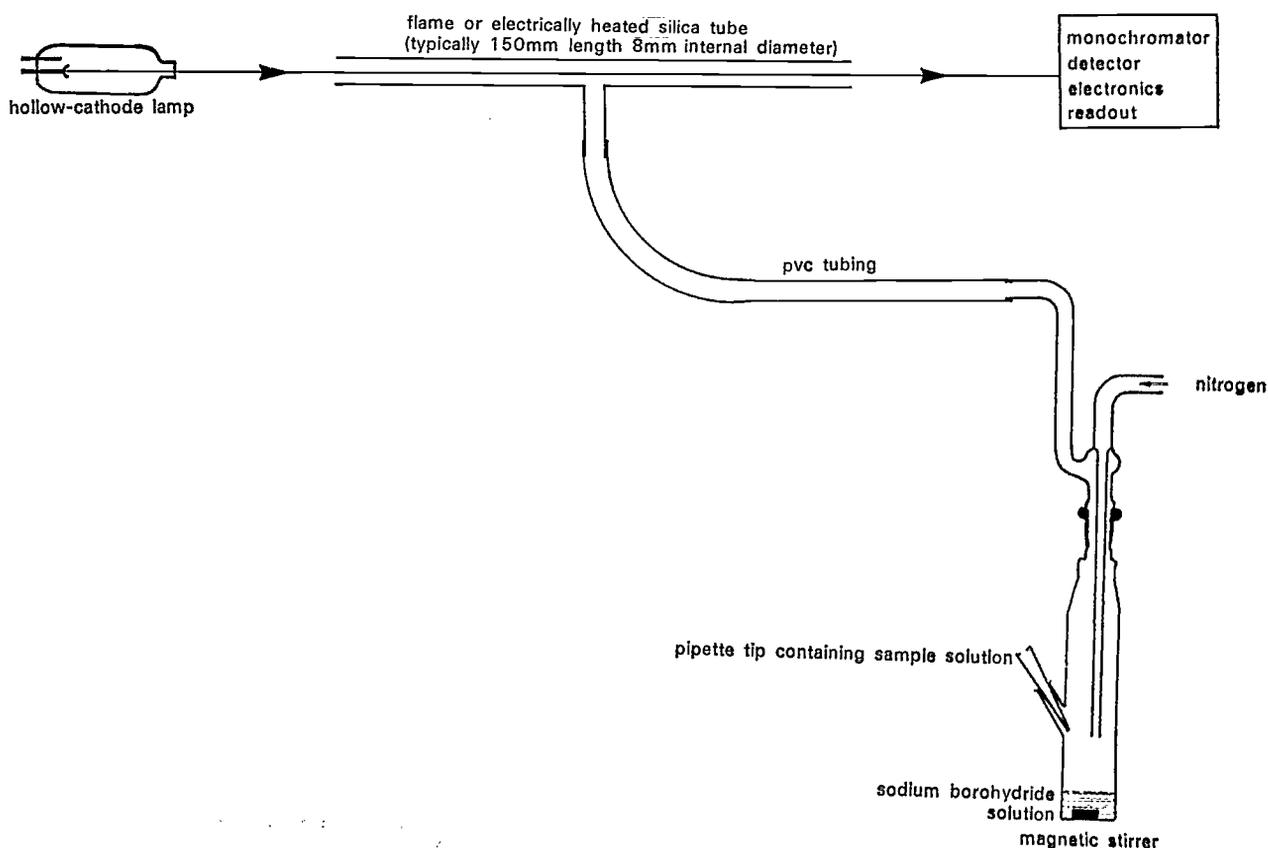
Figure 14   Diagrammatic representation of hydride generation technique using a heated silica tube to atomize the hydride

The technique is very sensitive; typical (4·65σ) detection limits in pure solution of 0·001–0·005mg/litre are readily obtained for As, Bi, Sb, Se, Sn and Te. The main disadvantage of the technique is that interelement effects can be very severe[48] and consequently calibration by standard addition is often necessary. Significant amounts of elements such as copper, silver, gold etc which are easily reduced by sodium borohydride are particularly prone to cause interference. Another important point is that the response is dependent upon the analyte oxidation state. Arsenic and antimony should be in the (III) state[46, 47, 49] whilst it is essential that selenium and tellurium must be in the (IV) state prior to the sodium borohydride reduction step[14, 46, 48]. An automatic method for the direct determination of lead in natural waters with a 4·65σ detection limit of 0·25µg/litre has been reported.[50] It was found that for efficient formation of lead hydride, the hydrogen peroxide had to be added to the analyte solution prior to the sodium borohydride reduction step. The reagents concentrations were very critical and interelement effects were minimized (but not completely eliminated) by the addition of a solution containing citric acid and potassium cyanide[50].

8.3 Flameless Electrothermal Atomization

The sensitivity of conventional flame techniques is limited by the fact that only 5–15% of the nebulized sample reaches the flame whereupon it immediately undergoes considerable dilution by the flame gases. For example, a typical nebulizer may have a sample uptake rate of 4ml/min of which 0·4ml/min will reach the flame. A typical air-acetylene flame will consume about 10 litres/min of flame gases. Thus the sample is effectively diluted about 25,000 times. If an aliquot of the analyte solution were evaporated to dryness and the residue were to be rapidly vaporized and atomized a large increase in sensitivity would be expected. This can be achieved by adding a small volume (typically 2–50µl) of the sample to a graphite tube or rod maintained in an inert atmosphere. A small controlled current is passed through the device to evaporate the solvent, followed by a larger current to dry ash the sample without loss of analyte and finally a much larger current heats the device to a suitable temperature to atomize and vaporize the analyte. During this latter stage the transient atomic absorption signal is monitored. Common forms of this type of device are depicted in Figure 15. This technique results in a significant improvement in detection limit for a large number of elements[51]; however, interelement effects can be very severe and are very difficult to predict. It is important to appreciate also that interelement effects can depend upon both the age and the sample history of the graphite heating element[14, 52, 53, 54]. A good example of this has been observed in the determination of lead and cadmium in natural waters where calibration by the standard addition technique was considered essential[55, 56] although, in fairness, it should be pointed out that methods for overcoming these effects and allowing direct calibration have been reported[57–59].
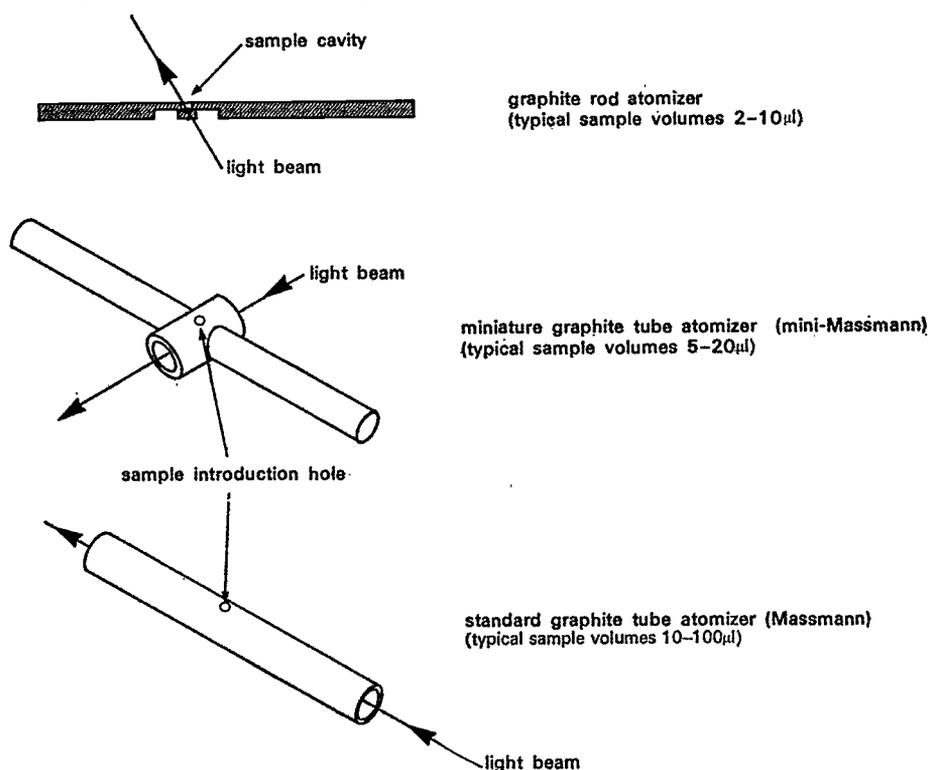
Figure 15 Diagrammatic representation of various types of graphite based flameless electrothermal atomization devices

For most elements it is advisable to use automatic background correction (see 3.6 and 6.3) because non-specific background absorption is much more significant in flameless electrothermal atomization than in flame atomization. Calibration by standard addition is often essential and this can be very time consuming.

A typical electrothermal device can make 20–30 firings per hour and each analytical measurement is normally made at least twice as rogue results are much more likely to occur when using these devices than when using flames. For standard addition measurements each sample is spiked with at least two different analyte concentrations, and thus each analytical result requires duplicate firings from three samples (that is, the sample and the two spiked samples) and this takes about 12 to 15 minutes.

Pure solution detection limits should be viewed with caution as the sample matrix may result in a significant degradation in the observed detection limits. This is especially true for saline water analysis[64-67] where the matrix results in a severe degradation of the pure solution detection limit for a number of elements (especially cadmium and lead). Some realistic detection limits for non-saline waters are given in Appendix D.

The number of operating parameters in electrothermal atomization is significantly greater than in flame atomization (viz solent, dry ashing and atomization temperatures and time settings, rate of heating during the atomization stage, nature and flow rate(s) of the purge gas(es) etc). The reproducibility of manually adding small volumes (2–50μl) of the samples and standards to the graphite heating element can significantly vary from operator to operator. However, the use of automatic sampling devices can effectively overcome this problem. With care it is possible to obtain accurate and reproducible results for a number of elements using this technique, but considerably more operator skill is required in setting up the instrumental conditions than for conventional flame analysis. The technique has been applied to the direct analysis of both non-saline [55-63] and saline water samples[64-67]. For further literature references the reader is specifically referred to References[14, 51, 68].

It is to be hoped that ultimately flameless electrothermal atomization will be further developed and refined so that it can be used on a routine basis for the determination of a number of elements in natural water samples.

8.4 Wavelength Scanning Flame Emission Spectroscopy

Flame emission spectroscopy where the monochromator is set to the analyte emission wavelength is often used to determine sodium, potassium and other alkali metals in natural waters, using standard atomic absorption instruments and an air-acetylene flame. In fact sodium and potassium can even be satisfactorily determined using a simple filter flame photometer and an air-natural gas flame. The sodium and potassium signals from natural waters are normally significantly greater than the flame background signal and few spectral interferences are likely to be observed. Unfortunately this is not the case with other elements in natural waters where the hotter nitrous oxide-acetylene flame is required to excite a sufficient number of the analyte atoms to the excited state (see 2.3). At analyte levels around the pure solution detection limit the emission signal from the analyte is only about 0·2–5% of the intensity of the flame background emission signal. This flame background signal is very dependent on the sample or blank solution uptake rate; if this uptake rate increases very slightly the flame temperature will drop and the flame background will increase significantly. Thus if a sample solution has a slightly different viscosity or surface tension compared to the blank solution, a significant change in the flame background signal will be observed and this change will be attributed to a change in the analyte concentration with respect to the blank. Another problem is that there are a number of broad molecular bands emitted by matrix elements, particularly calcium and magnesium, that can easily be mistaken for the analyte.

This problem can be minimized by the use of the wavelength scanning technique. The wavelength is set slightly below the analyte emission line wavelength and is then slowly scanned through the analyte emission wavelength using a synchronous electric motor to rotate the wavelength drive mechanism while at the same time spraying the sample. The maximum scan speed, time constant of the readout system and spectral bandpass are linked by the following equation[14]:

$$\text{Maximum scan speed (nm/min)} = 60 \times \frac{\text{spectral bandpass (nm)}}{4 \times \left(\begin{array}{c} \text{time constant of the} \\ \text{readout system(s)} \end{array} \right)}$$

For trace level determination of elements in natural waters the conventional 50mm path length nitrous oxide-acetylene burner is used. Normally the minimum spectral bandpass is selected. In order to obtain realistic detection limits a spectral bandpass of less than 0·3nm must be used because the flame background signal (which usually determines the detection limit) is proportional to the square of the spectral bandpass whilst the analyte signal is directly proportional to the spectral bandpass. The burner height should be adjusted so that the detector does not view the very intense primary reaction zone situated immediately above the burner slot and for most elements the acetylene flow rate should be adjusted so that the flame background emission signal is minimized.

The author has found that a spectral bandpass of 0·1nm, a scan speed of 1nm/min and a time constant of the readout system of 1·5s are suitable for this type of analysis and Figure 16 shows some typical traces for aluminium and thallium. Appendix E lists
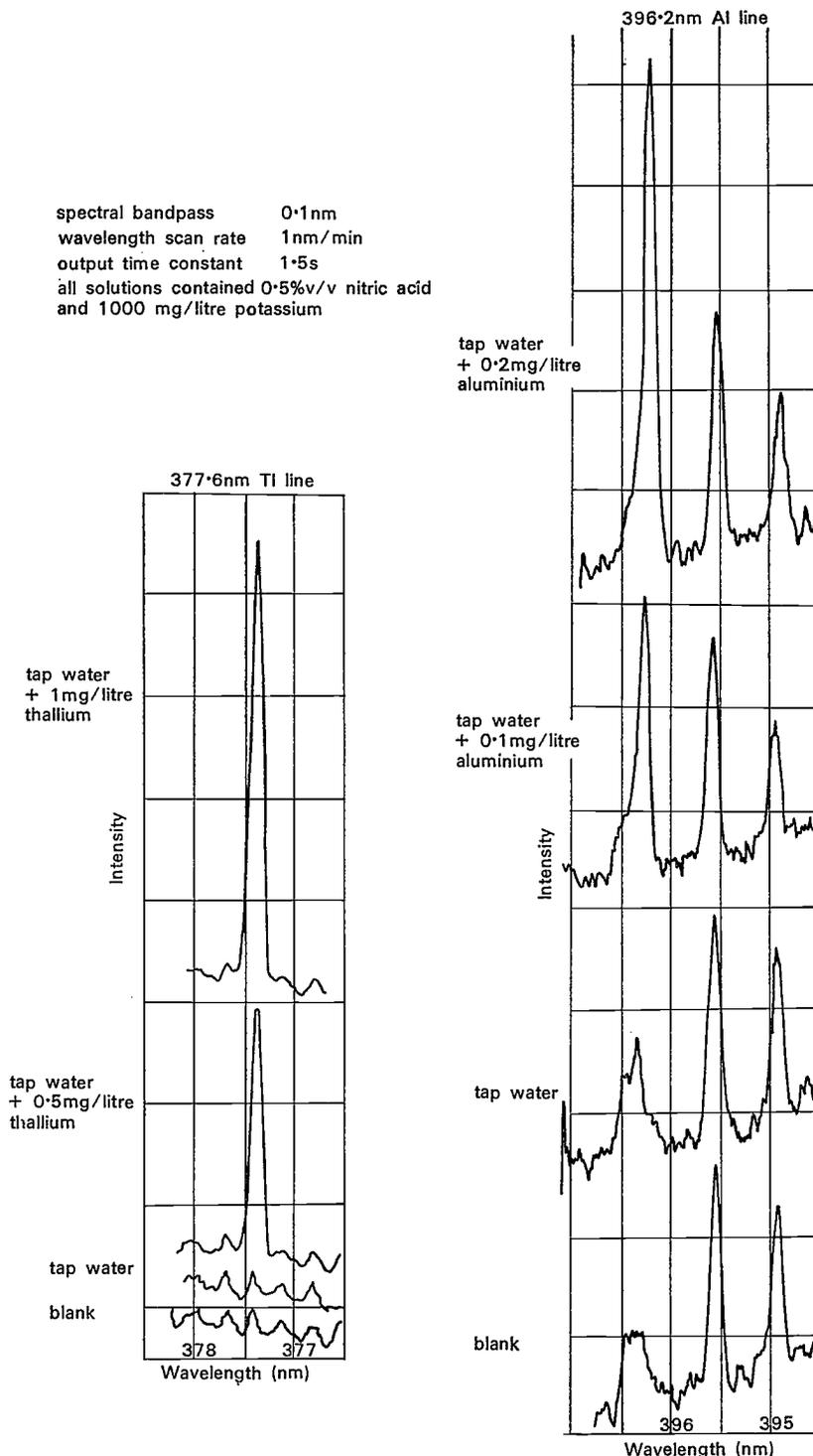
Figure 16   Typical scanning wavelength flame emission traces

spectral bandpass   0·1 nm
wavelength scan rate   1 nm/min
output time constant   1·5 s
all solutions contained 0·5%v/v nitric acid and 1000 mg/litre potassium

33

some flame emission wavelengths and gives an indication of the detection limits obtainable. However it should be stressed that flame emission detection limits are very dependent of the resolution, stray light characteristics and light throughput of the monochromator as well as the stability of the flow control of the flame gases. (The stability of the flame background signal is dependent upon the stability of the flame gas flow rates). Thus considerable detection limit variations can be observed between different instruments. These variations are not so pronounced in atomic absorption where the detection limit is usually determined by the stability of the light source and fluctuations in the transmission properties of the flame.

Interelement effects are similar to those observed in atomic absorption (see 6) but spectral interferences are more likely to occur (see 2.3). Flame emission is not suitable for trace detection of elements such as antimony, arsenic, cadmium, lead, mercury, selenium, tellurium and zinc with emission lines below about 300nm, because the temperature of the nitrous oxide-acetylene flame is not high enough to excite a sufficient number of the analyte atoms. (see 2.3).

9 Some Potential Future Developments

A brief indication of some potential future developments in atomic absorption and related techniques is now given.

9.1 Multielement Atomic Absorption

Simultaneous multielement atomic absorption would appear to be an attractive technique, but there are various problems associated with it, viz:

a. It is difficult to accurately align more than two or three hollow-cathode lamps so that their radiation passes along the flame axis coincident with the radiation from the hydrogen lamp required for automatic background correction. Although multielement lamps can be used, this increases the complexity of the spectral radiation reaching the detectors and can result in increased non-linearity of calibration graphs.

b. Compromise flame conditions and burner height settings have to be used. For example chromium, iron and lead require different flame conditions and burner height settings for optimum performance.

c. The limited range of the calibration graph in atomic absorption would not allow simultaneous determinations in natural waters of the macro-level elements calcium, magnesium and sodium with the trace level elements such as cadmium, nickel and lead.

Thus it would appear that simultaneous multielement atomic absorption is unlikely to be commercially developed. To the best of the author's knowledge there is no commercial instrumentation for multielement (four or more elements) atomic absorption. There are a few dual element instruments that have two monochromators and allow simultaneous determination of two elements.

An alternative approach that utilizes rapid sequential measurement of a range of elements has recently been developed and uses a microprocessor controlled completely automated atomic absorption instrument[69]. This unit will select the appropriate hollow-cathode lamp, select a chosen spectral bandpass, accurately set the wavelength, and flame conditions, analyse a set of samples contained in a specially designed autosampler and then select another lamp and repeat the procedure. Up to six elements can be sequentially determined in a set of 50 samples in a period of one hour.

9.2 Multielement Atomic Fluorescence

Atomic fluorescence is a technique where the detector does not directly view the source but monitors the fluorescence signal that results from the absorption of resonance radiation from the source[70]. The fluorescence signal is directly proportional to the exciting resonance radiation intensity when non-laser sources are used. Conventional flame atomic fluorescence using microwave sources (see 3.1.1) has a number of drawbacks[14] and is seldom used in routine analysis. However now that scanning dye lasers[9, 70, 71] and frequency doublers are commercially available this technique would
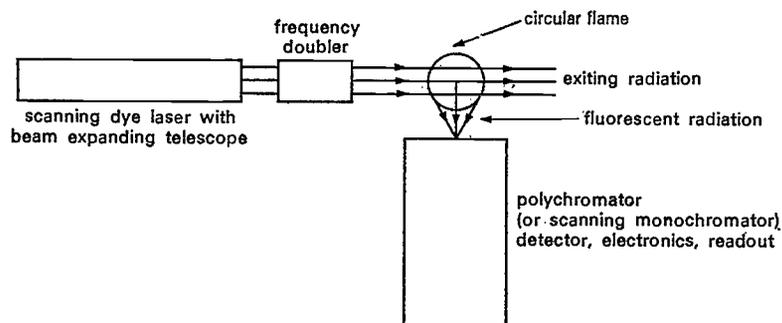
Figure 17 Diagrammatic representation of a multi-element atomic fluorescence spectrophotometer

appear to have considerable potential and is depicted in Figure 17. A single source can be used to excite a large number of elements and a polychromator, or a synchronously scanning monochromator with its wavelength drive coupled to the dye laser wavelength control, can be used to detect the resulting fluorescence signals.

Calibration graphs are linear over a wide concentration range.

9.3 Heated Spray Chamber

Only 5–15% of nebulized sample actually reaches the flame; the remainder simply drains to waste from the spray chamber. Thus an obvious method of increasing the atomic absorption sensitivity is to increase the amount of sample reaching the flame. If the solution uptake rate of a conventional pneumatic nebulizer is increased much above 6–8ml/min the sensitivity starts to decrease. This is due to the fact that the mean droplet size produced by the nebulizer increases at high sample uptake rates, more droplets condense out in the spray chamber and consequently less sample reaches the flame.

This situation can be improved if the spray chamber is heated so that the nebulized sample is correctly vaporized. However the increased amount of water vapour carried to the flame causes flame stability problems and can result in increased interelement effects because the flame temperature is significantly reduced. These problems can be overcome by incorporating a condenser between the heated spray chamber and the flame. This has been found to remove the vast majority of the water vapour whilst allowing almost all the analyte (and matrix) to pass into the flame. A typical heated spray chamber is depicted in Figure 18. Increases in sensitivity of 5 to 30 times have been reported [72-74] for a range of elements in the air-acetylene flame. At least two units were produced commercially but to the best of the author's knowledge they are no longer available. The disadvantages of the technique are that the spray chambers take a long time to reach thermal equilibrium, and that solutions with a high dissolved solids content cause deposits to form around the end of the nebulizer and also result in significant memory effects.
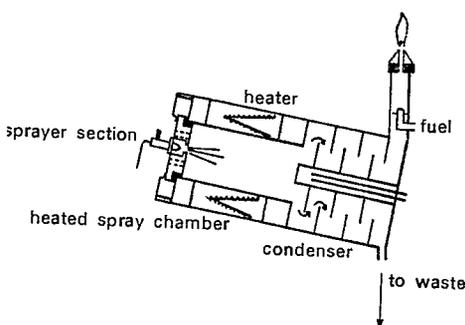
Figure 18 Diagram of the burner system with infra-red radiation heated spray chamber and condenser
(*Reproduced with permission from ref 73*)

However in the author's opinion the heated spray chamber technique in conjunction with an air-acetylene flame could be developed for the analysis of non-saline waters. It should allow reasonably accurate direct determination of a number of elements at concentrations found in drinking water.

The technique cannot be recommended for use with the nitrous oxide-acetylene flame because of the high risk of violent explosive flashback into the relatively large volume of the heated spray chamber.

10 Conclusions

It has been shown that atomic absorption spectrophotometry is a technique ideally suited to general water analysis which can be used to determine a wide range of elements with minimum sample preparation and manipulation. Rather than list the elements for which the technique is suitable, it is easier to list the common elements for which the technique cannot be used. These are bromine, carbon, chlorine, fluorine, hydrogen, iodine, nitrogen, oxygen, phosphorus and sulphur. The resonance lines of these elements lie in the vacuum ultraviolet region of the spectrum where air and conventional flames completely absorb electromagnetic radiation. The very poor detection limit for boron (Appendix A) precludes the routine use of atomic absorption for this element. However, indirect techniques[9] can be used to determine some of these elements where the analyte reacts with another added element and then the resulting product is isolated. The concentration of the reacted or unreacted element is then determined by atomic absorption. DOE has published an indirect atomic absorption method for sulphate (see Appendix C).

Colorimetry is the other trace element analysis technique that is commonly used in water analysis, but has the disadvantage that interelement effects are usually much more severe than with flame atomic absorption techniques. If the analyte concentration is below the detection limit and background correction is employed, no significant bias should be observed when using an atomic absorption technique. (This assumes that the blank solution is not contaminated with the analyte). Thus even if a sample solution exhibited a 20% suppression of signal caused by the solution matrix (a rare occurrence in water analysis) this suppression is generally independent of concentration and not very significant at levels close to or below the detection limit. However colorimetric techniques can show a bias in the presence of interfering elements when the interferant reacts with the colour forming reagent to form a measurable colour. Thus even if the analyte is present at a level below the detection limit a significant signal is then observed in the presence of the interfering element. A good example of this is the DOE recommended colorimetric method for manganese[82] where the presence of 20mg/litre of iron (III) gave an apparent manganese concentration of 0·100 and 0·600mg/litre at the 0 and 0·500mg/litre manganese levels respectively. Similarly in the presence of 2mg/litre cobalt the corresponding apparent manganese concentrations were 0·050 and 0·555mg/litre. This bias effect is not observed in atomic absorption spectrophotometry which is a significant advantage as many measurements are often carried out at analyte levels near to the detection limit.

The complementary atomic absorption spectrophotometry techniques of hydride generation and flameless electrothermal atomization give considerably improved detection limits when compared to conventional flame analysis and allow direct determinations at the 1–20μg/litre level for many elements. However it must be stressed that compared to conventional flame analysis interelement effects are much more significant; the sample analysis rate is considerably reduced; and more operator skill is required.

It can be safely concluded that atomic absorption and its complementary techniques are ideally suited for the analysis of a wide range of metals and metalloids in all types of water and associated samples.

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12 Acknowledgements

Appendices

Appendix A

Some Important Parameters in the Atomic Absorption Determination of the More Commonly Determined Elements

The table opposite gives the wavelength, the flame system, an indication of the characteristic concentration (sensitivity for 1% absorption) and the expected detection limit range for the more commonly determined elements in non-saline waters. The detection limit is given as a range of concentrations that the $4 \cdot 65\sigma$ detection limit may be expected to lie within for routine use of a typical atomic instrument in natural water analysis. (See 5.2).

Notes

1. Ionization suppressant required (see 6.2.7).

2A. Flame emission using air-acetylene gives a similar or better detection limit (see 8.4).

2B. Flame emission using a nitrous oxide-acetylene flame gives a similar or better detection limit (see 8.4).

3. A considerably improved detection limit can be obtained using the hydride generation technique (see 8.2).

4. Flame conditions set to verge of luminosity (see Appendix 2 section A2.9).

5. A considerably improved detection limit can be obtained using the cold vapour technique (see 8.1).

Element	Wavelength (nm)	Flame System AA = Air-Acetylene NA = Nitrous Oxide-Acetylene	Characteristic Concentration (Sensitivity for 1 % absorption) mg/litre	(4·65σ Limit of Detection) mg/litre	Notes
Aluminium	309·3	NA	1·0	0·2–0·4	1, 2B
Antimony	217·6	AA	0·4	0·1–02·	3
Arsenic	193·7	AA	0·75	1–3	3
Arsenic	193·7	NA	1·5	0·5–1	3
Barium	553·6	NA	0·3	0·1–0·4	1
Beryllium	234·9	NA	0·02	0·004–0·008	
Bismuth	223·1	AA	0·3	0·1–0·2	3
Boron	249·7	NA	12	6–12	
Cadmium	228·8	AA	0·01	0·002–0·006	
Caesium	852·1	AA	0·1	0·02–0·06	1, 2A
Calcium	422·7	AA	0·05	0·006–0·012	2B
Calcium	422·7	NA	0·02	0·004–0·01	1, 2A
Chromium	357·9	AA	0·1	0·02–0·04	4
Chromium	357·9	NA	0·15	0·05–0·10	1
Cobalt	240·7	AA	0·07	0·02–0·04	
Copper	324·7	AA	0·05	0·01–0·02	
Gallium	287·4	AA	1·0	0·1–0·2	2B
Gold	242·8	AA	0·2	0·04–0·1	
Indium	303·9	AA	0·5	0·1–0·2	2B
Iron	248·3	AA	0·07	0·01–0·02	
Lead	217·0	AA	0·15	0·04–0·08	3
Lead	283·3	AA	0·3	0·05–0·1	
Lithium	670·7	AA	0·02	0·004–0·01	1, 2A
Magnesium	285·2	AA	0·005	<0·002	
Manganese	279·5	AA	0·03	0·005–0·01	2B
Mercury	253·7	AA	4·0	0·4–1·0	5
Molybdenum	313·3	AA	1·5	0·2–0·4	
Molybdenum	313·3	NA	0·4	0·08–0·2	
Nickel	232·0	AA	0·07	0·01–0·02	
Potassium	766·5	AA	0·02	0·004–0·01	1, 2A
Rubidium	780·0	AA	0·05	0·01–0·03	1, 2A
Selenium	196·0	AA	0·5	1–3	3
Silicon	251·6	NA	2·0	0·5–1	
Silver	328·1	AA	0·05	0·007–0·02	
Sodium	589·0	AA	0·01	0·005	1, 2A
Strontium	460·7	NA	0·1	0·02–0·04	1, 2B
Tellurium	214·3	AA	0·5	0·15–0·3	3
Thallium	276·8	AA	0·4	0·08–0·2	2B
Tin	224·6	AA	3·0	1–2	3
Tin	224·6	NA	2·5	0·5–1	3
Titanium	364·3	NA	2·0	0·4–1	1
Vanadium	318·4	NA	1·0	0·2–0·5	1
Zinc	213·9	NA	0·01	0·002–0·005	
Zirconium	360·1	NA	15	3–10	1

Most of the data in this Table are reproduced by permission of the publishers, Charles Griffin and Company Limited of London and High Wycombe, from KC Thompson and RJ Reynolds, *Atomic Absorption, Fluorescence and Flame Emission Spectroscopy* 1978.

Appendix B

Additional Analytical Information for Certain Elements (see also reference 68)

B1 *Aluminium*

It is possible to sensitively determine aluminium by wavelength scanning flame emission spectroscopy using the 396·2nm line (see 8.4). 1000mg/litre potassium should be added to suppress ionization. However, there are problems in obtaining quantitative release of aluminium from samples containing aluminosilicates.

B2 *Antimony*

The flame detection limit is not adequate for general water analysis applications. Antimony can be sensitively determined using the hydride generation technique (see 8.2), after conversion of the antimony in the analyte solution to the antimony (III) state. This technique can also be used to determine arsenic, bismuth, lead, selenium, tellurium and tin. However it must be stressed that interelement effects can be severe and calibration by the standard addition technique is often essential. Typical 4·65σ detection limits are of the order of 0·001–0·005mg/litre for the seven elements given above.

B3 *Arsenic*

See antimony (B2): it is essential to convert the arsenic to the arsenic (III) state prior to the hydride reduction stage. For arsenic levels above 2mg/litre the nitrous oxide-acetylene flame should be used.

B4 *Barium*

A small spectral bandpass and a relatively high lamp current should be used to minimize the effect of calcium (see 6.2.6). The maximum calcium level that can be nebulized without a significant increase in noise level and without a significant change in signal level should be ascertained by nebulizing blanks and barium standards containing various levels of calcium and comparing the signals to those obtained with the equivalent calcium free solution[75]. The master calcium solution should be prepared from 'spectroscopically pure' calcium carbonate guaranteed to contain a negligible amount (1μg/g) of barium.

Barium cannot satisfactorily be determined by wavelength scanning flame emission spectroscopy using standard equipment because of the severe spectral interference from calcium[75].

B5 *Bismuth*

See antimony (B2).

B6 *Boron*

Flame atomic absorption cannot be recommended for the direct determination of boron in fresh waters because of the poor detection limit. At present boron cannot satisfactorily be determined using the flameless electrothermal atomization technique (see 8.3) because of severe matrix and memory effects.

B7 *Cadmium*

The DOE has published a recommended method for cadmium in potable waters[29]. (see Appendix C). Cadmium has also been directly determined in natural waters using flameless electrothermal atomization (see 8.3).

B8 *Calcium*

Calcium is subject to pronounced chemical interference effects from aluminium, phosphate and sulphate in the air-acetylene flame. Lanthanum (as chloride) is normally added to all sample, standard and blank solutions. The DOE has published a tentative method for the analysis of calcium in potable and waste waters using the air-acetylene flame. The sample is suitably diluted and lanthanum (as the chloride) is added[77] so as to give a concentration of 1000mg/litre.

B9 *Chromium*

Maximum chromium response is observed in a luminous air-acetylene flame; however under these conditions chromium (III) and (VI) exhibit different sensitivities and calibration graphs with well pronounced maxima have been observed for chromium (III)[78]. Figure 19 shows a typical calibration graph in the optimized luminous air-acetylene flame and it can be seen that certain absorbance values can correspond to three chromium (III) concentrations (the standards were prepared in 1% V/V nitric acid [70% m/m]). These strange effects could be overcome by reducing the acetylene flow so that a flame on the verge of luminosity was observed. Under these conditions chromium (III) and (VI) gave similar calibration graphs (within $\pm$ 5%) and the response
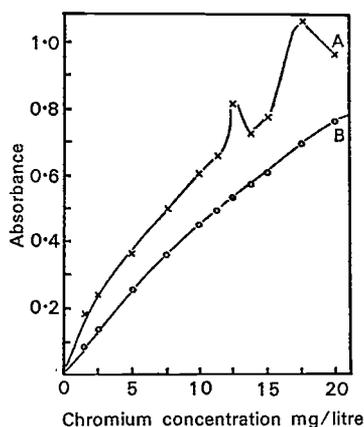
Figure 19　Chromium (III) calibration graphs
A. Luminous flame conditions (optimized whilst nebulizing 5 mg/l chromium solution)
B. Flame set to verge of luminosity
(Standards prepared in 0·5%v/v nitric acid 70% m/m)
(*Reproduced with permission from ref 78*)

was not dependent upon the age of the standards. However even with a non-luminous flame chromium is subject to pronounced chemical interference effects especially if concentration by evaporation (see 7.4.1) is used. These effects have been found to be minimized by adding ammonium perchlorate to the samples, blanks and standards so that the final solution contained 2% m/V ammonium perchlorate[17]. The acidified samples were initially heated with a small amount of hydrogen peroxide to convert all the chromium to the (III) state and the calibration standards were prepared from chromium (III) salts. Alternatively the use of the nitrous oxide-acetylene flame effectively overcomes interference effects. The samples, blanks and standards should contain 1000mg/litre potassium in order to suppress ionization.

B10 *Iron*

Chemical interference effects have been observed in sulphate media[14], but are rarely observed in chloride media especially in a fuel lean flame. A recommended procedure for the atomic absorption determination of iron has been published by the Analytical Methods Committee of the Chemical Society[79].

B11 *Lead*

Lead is normally determined using the 217·0nm resonance line although a few users still use the less sensitive but more intense 283·3nm line. The acetylene flow should be set to give maximum transmission (minimum absorption) of the light beam through the flame with the blank solution being nebulized. The Department of the Environment has published a recommended method for the determination of lead in potable waters[30] where the lead is complexed with ammonium pyrrollidine dithiocarbamate and extracted into 4-methyl pentan-2-one (see Appendix C).

Lead has also been directly determined in natural waters using both the hydride generation technique (see 8.2) and the flameless electrothermal atomization technique (see 8.3). It is to be hoped that both these techniques will ultimately be suitable for the routine determination of lead in natural waters.

B12 *Magnesium*

Magnesium is subject to slight chemical interference effects in the air-acetylene flame which can be overcome by the addition of lanthanum. DOE has published a method for the analysis of magnesium using the air-acetylene flame[80] (see Appendix C).

B13 *Mercury*

The cold vapour technique is recommended for this analysis (see 8.1). The DOE has published a method for the analysis of mercury[42] (see Appendix C).

B14 *Selenium*

See antimony (B2). The selenium must be in the Se(IV) state prior to the hydride reduction stage. Interelement effects can be severe[14].

B15 *Tellurium*

See antimony (B2). The tellurium must be in the Te(IV) state prior to the hydride reduction stage.

B16 *Thallium*

It is possible to sensitively determine thallium by wavelength scanning flame emission spectroscopy in the nitrous oxide-acetylene flame (see 8.4). 1000mg/litre potassium should be added in order to suppress ionization.

B17 *Tin*

The flame detection limit for tin is relatively poor. The hydride generation technique is applicable. See antimony (B2). The standards should be prepared from a tin(IV) standard solution as any trace levels of tin in environmental samples will almost certainly be in the tin(IV) state.

If the presence of organotin compounds (such as tributyl tin oxide used in wood preservatives) is suspected, it is essential to use a wet digestion technique (eg H_2SO_4/HNO_3) in order to destroy the organotin compound prior to the hydride generation step.

Appendix C

Department of the Environment Recommended Methods of Analysis*

Element	Range of Applicability	Brief Description of the Technique	$4 \cdot 65\sigma$ Detection Limit μg/litre	Reference Number
Ca	Natural waters and sewage effluents	Dilute sample an appropriate amount and incorporate 1000mg/litre lanthanum	400–1000	77
Cd	Potable waters	APDC/MIBK extraction. 200ml sample → 10ml MIBK	0·3	29
Hg	Saline waters, non-saline waters, effluents, sludges	Digestion with $KMnO_4$ at 70°C for 7–8 hours. Cold vapour technique	0·1–0·2 non-saline waters 0·004 saline waters	42
Mg	Natural waters and sewage effluents	Dilute sample an appropriate amount and incorporate 1000mg/litre lanthanum	60	80
Pb	Potable waters	APDC/MIBK extraction. 200ml sample → 10ml MIBK	1–6	30
Sulphate (SO_4)	Potable waters, river waters, and sewage effluents	Precipitation of $BaSO_4$, measurement of residual barium after addition of lanthanum	5000	81

* An optional pretreatment step to solubilize the analyte is given in all methods.

Appendix D

Some Typical (4.65σ) Detection Limits of Various Elements in Non-Saline Waters using Flameless Electrothermal Atomization

Element	Wavelength (nm)	4·65σ Detection Limit µg/litre (Note 1)	Comments
Al	309·3	0·5–2	
As	193·7	0·5–2	Ref 62, Notes 2 and 3
Ba	553·6	0·5–2	Note 4
Be	234·9	0·1–0·3	
Cd	228·8	0·1–0·3	Refs 56, 59
Cr	357·9	0·5–2	Ref 60
Cu	324·7	0·3–1	
Fe	248·3	1–3	Note 5
Mg	285·2	Note 6	
Mn	279·5	0·2–0·6	
Mo	313·3	2–6	
Ni	232·0	1–3	Note 5
Pb	217·0	0·5–2	Refs 53–59
Se	196·0	0·5–2	Ref 61, Note 3
Te	214·3	0·5–2	Note 3
Tl	276·8	0·5–2	
V	318·4	5–15	
Zn	213·9	Note 6	

Notes

1. These detection limits refer to typical non-saline water analysis with automatic background correction applied except for barium.

2. A severe spectral interference has been reported in the presence of a certain type of suspended particulate matter (Poldoski, JE, At. Absorpt. Newsl. 1977, *16*, 70).

3. The addition of nickel (2–10,000mg/litre) to all solutions has been recommended to decrease the volatility of these elements and hence interelement effects. (Ediger RD, At. Absorpt. Newsl. 1975, *14*, 127).

4. Manual background correction can be applied using the molybdenum 553·3nm line or the ytterbium 557·6nm line. (Thompson KC and Godden RG. Analyst 1975, 100, 198).

5. Most graphite rods and tubes contain significant amounts of iron and nickel which should be removed by repeated firings at near maximum temperature each time a new rod or tube is fitted.

6. Detection limit is normally limited by variation in the blanks and should be less than 1µg/litre.

Appendix E

Some Typical (4.65σ) Detection Limits of Various Elements in Non-Saline Waters using Wavelength Scanning Flame Emission Spectroscopy in the Nitrous Oxide-Acetylene Flame

Element	Wavelength nm	4.65σ Detection Limit mg/litre (Note 1)
Al	396·2	0·01–0·04
Ba	553·5	Note 2
Ca	422·7	Note 3
Cr	425·4	0·01–0·04
Ga	417·2	0·025–0·01
In	451·1	0·01–0·04
Sr	460·7	0·0005–0·002
Tl	377·6	0·01–0·04
V	437·9	0·1–0·4

Notes

1. Detection limits will be dependent on the instrumentation characteristics, but with a spectral bandpass of 0·1nm, a scan rate of 1nm/min. and a time constant of approximately 1·5s. the figures quoted should be obtainable with most instruments. 2000mg/litre potassium (as chloride) should be added to samples, standards and blanks to suppress ionization.

2. Barium cannot satisfactorily be determined at low levels (<0·1mg/litre) by conventional flame emission because of the intense calcium oxide band emission present at 553·5nm.

3. Detection limit is normally limited by variations in the blanks and should be less than 0·002mg/litre.

Address for Correspondence

However thoroughly a method may be tested, there is always the possibility of a us discovering a hitherto unknown problem. Users with information on this review a requested to write to:

The Secretary
The Standing Committee of Analysts
The Department of the Environment
2 Marsham Street
LONDON SW1P 3EB
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Department of the Environment/National Water Council

Standing Committee of Analysts

Membership responsible for this Method:

This essay review was written by Dr KC Thompson, under the general direction of Working Group 2 and the Main Committee.