

Information on Concentration and Determination Procedures in Atomic Spectrophotometry 1992

Methods for the Examination of Waters and Associated Materials

This document
contains **31** pages

© Crown Copyright 1992

Applications for reproduction should be made to HMSO

First Published 1992

ISBN 0 11 752375 5

Within the Methods for the Examination of Waters and Associated Materials series are four-ring binders suitable for use in storing reports. These are available from HMSO Price £4 (ISBN 0 11 7514373).

HMSO

Standing order service

Placing a standing order with HMSO BOOKS enables a customer to receive other titles in this series automatically as published.

This saves the time, trouble and expense of placing individual orders and avoids the problem of knowing when to do so.

For details please write to HMSO BOOKS (PC 11C), Publications Centre, PO Box 276, London SW8 5DT quoting reference X22.04.22.

The standing order service also enables customers to receive automatically as published all material of their choice which additionally saves extensive catalogue research. The scope and selectivity of the service has been extended by new techniques, and there are more than 3,500 classifications to choose from. A special leaflet describing the service in detail may be obtained on request.

Contents

About this series	4
Warning to users	5
About this booklet	6
Introduction	8
Atomic spectrophotometric interference effects	10
Atomic absorption	10
Emission	14
References	16
Useful wavelengths for flame, AAS, AFS, EAAAS and ICPS (with sources and interference data)	17
Concentration techniques	32
Membership assisting with this booklet	37
Address for correspondence	38

Abbreviations used:

AAS	Atomic absorption spectrometry
AFS	Atomic fluorescence spectrometry
EAAAS	Electrothermal atomization atomic absorption spectrometry
ICPS	Inductively coupled plasma spectrometry

About This Series

This booklet is part of a series intended to provide recommended methods for determining the quality of water and associated materials. In addition, short reviews of the more important analytical techniques of interest to the water and sewage industries are included.

In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, have 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 is published as a series of booklets on single or related topics; 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.

Although ideally, all methods published should be fully tested, this is not often possible without delay in publication. Furthermore, the limit of detection, range, precision and interference effects applying to instrumental methods can be dependent on the actual instrument used, as well as on sample type, reagent purity and operator skill, etc. Even methods tested in many laboratories have been known to acquire problems, for example when new domestic products appear (introducing new substances into effluents), when changes in production methods affect reagent quality, or when methods are used to analyse new types of samples (despite apparent similarity to samples already evaluated). As a guide, the following categories have been given to methods:

- (i) tested, usually in five or more laboratories
— no grade indicated;
- (ii) tested in one to three or four laboratories
— Tentative;
- (iii) evaluated, but not fully tested, but publication is urgently required
— Note;
- (iv) tested and found to be satisfactory by several laboratories, but in the opinion of experts requires a high degree of skill or has some other difficulty such that the method would be replaced if a better method were discovered
— Provisional.

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

United 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 and senior technical staff, to decide which method to use for the determination in hand. Whilst the attention of users 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 a committee of the Department of the Environment set up in 1972. Currently 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 Microbiological methods
- 3.0 Empirical and physical methods
- 4.0 Metals and metalloids
- 5.0 General nonmetallic substances
- 6.0 Organic impurities
- 7.0 Biological methods
- 8.0 Sewage works control methods
- 9.0 Radiochemical methods.

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, in co-operation with the working group and the main committee. The names of those members associated with this booklet are listed at the back of the book.

Publication of new or revised methods will be notified to the technical press. A current list of publications may be obtained from the Secretary.

Every effort is made to prevent errors from occurring in the published text. Correction notes and minor additions to published booklets not warranting a new booklet in this series will be issued periodically. However, should any errors be found, please notify the Secretary.

Dr D WESTWOOD
Secretary

11 June 1992

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 and COSHH Regulations must be observed.

Laboratory procedures should be carried out only in properly equipped laboratories.

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 one's self, one's colleagues, those outside the laboratory or workplace, or subsequently for maintenance or waste disposal workers. 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. Reagents of adequate purity must be used along with properly maintained apparatus and equipment of correct specifications. 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.

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 to be often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of 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. Hazardous reagents and solutions should always be stored in plain sight and below face level. Attention should also be given to potential vapour and fire risks. If in doubt, it is safer to assume that the hazard may exist and take reasonable precautions, rather than to assume that no hazard exists until proved otherwise.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Safe Prac-

tices in Chemical Laboratories' and 'Hazards in the Chemical Laboratory', issued by the Royal Society of Chemistry, London: 'Safety in Biological Laboratories' (Editors Hartree and Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London, which includes biological hazards; and 'The Prevention of Laboratory Acquired Infection', Public Health Laboratory Services Monograph 6, HMSO, London.

It cannot be too strongly emphasised 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. If an ambulance is called or a hospital notified of an incoming patient, give information on the type of injury, especially if poisoning is suspected, as the patient may be taken directly to a specialized hospital.

Safety while Sampling

Prior consideration must be given, especially when sampling in confined spaces or where access is difficult, to guard against suffocation, drowning, falls, and poisoning or infection by ingestion, inhalation, or skin contact.

Good Laboratory Practice

The Department of Health issue a booklet entitled: Good Laboratory Practice; the United Kingdom Compliance Programme, 1989. This can be obtained by writing to that Department in London. It deals chiefly with toxicity studies, but much can be applied to analytical chemistry.

About this booklet

There are occasions when it would be useful to modify or to extend methods already published in this series, but when publication of a separate new booklet would be unwarranted. The information given here should be read in conjunction with the following booklets in this series:

Lead and Cadmium in Fresh Waters by Atomic Absorption Spectrophotometry. (2nd edition). A General Introduction to Electrothermal Atomization Atomic Absorption Spectrophotometry 1986.

Lead in potable waters by atomic absorption spectrophotometry 1976 (for 2nd edition see above).

Cadmium in potable waters by atomic absorption spectrophotometry 1976 (for 2nd edition see above).

Lithium, Magnesium, Calcium, Strontium and Barium in Waters and Sewage Effluents by AAS 1987.

Magnesium in waters and sewage effluents by atomic absorption spectrophotometry 1977 (for 2nd edition see above).

Calcium in water and sewage effluents by atomic absorption spectrophotometry 1977 (for 2nd edition see above).

Dissolved Sodium in Raw and Potable Waters 1980.

Dissolved Potassium in Raw and Potable Waters 1980.

Copper in Potable Waters by Atomic Absorption Spectrophotometry 1980.

Zinc in Potable Waters by Atomic Absorption Spectrophotometry 1980.

Cobalt in Potable Waters 1981.

Nickel in Potable Waters 1981.

Chromium in Raw and Potable Waters and Sewage Effluents 1980.

Mercury in Waters, Effluents and Sludges by Flameless Atomic Absorption Spectrophotometry 1978.

Mercury in Waters, Effluent, Soils and Sediments etc (additional methods) 1985.

Silver in Waters, Sewages and Effluents by AAS 1982.

Iron and Manganese in Waters by AAS 1983.

Molybdenum (especially in sewage sludges and soils) by Spectrophotometry 1982.

Arsenic in potable waters by Atomic Absorption Spectrophotometry, Semi Automatic Method 1982.

Selenium in Waters 1984

Arsenic and Selenium in Sludges and Soils and related materials 1985.

A note on the Use of Hydride Generator Kits 1987.

(There have been developments which have improved the reliability of Hydride Generator Kits since this note was written. A revision is contemplated. In the meantime users should thoroughly evaluate kits on their own equipment.)

Antimony, Arsenic, Beryllium, Chromium, Cobalt, Copper, Gallium, Germanium, Indium, Nickel, Selenium, Silver, Thallium, Vanadium, and Zinc by Electrothermal AAAS 1988.

The Determination of Twelve Trace Metals in Marine and other Waters by Voltammetry or AAS 1987

especially the following methods therein:

I. Determination of Dissolved Cadmium, Copper, Lead, Nickel and Zinc in saline Waters by mixed dithiocarbamate extraction, nitric acid back extraction AAS; with notes on the determination of Cobalt, Iron and Manganese and the analysis of particulate matter.

J. Determination of Dissolved Cadmium, Copper, Lead and Nickel in Saline Waters by pyrrolidine dithiocarbamate extraction AAS (Semi micro scale method).

K. Determination of Dissolved Chromium in River, Estuarine, and Coastal Waters by Iron Collection—EAAAS.

L. Determination of Total Particulate Chromium in River, Estuarine and Coastal Waters.

Cadmium, Chromium, Copper, Lead, Nickel and Zinc in Sewage Sludges by Nitric Acid/Atomic Absorption Spectrophotometry 1981.

Extractable Metals (cadmium, copper, lead, manganese, nickel and zinc) in Soil, Sewage Sludge and Sewage Sludge treated Soils 1982.

Methods for the determination of metals in Soils, Sediments and Sewage Sludge, by hydrochloric-nitric acid digestion, with a note on the determination of insoluble metal contents 1986.

The Determination of Organic, Inorganic, Total and Specific Tin Compounds in Water, Sediments and Biota 1992.

Atomic Absorption Spectrophotometry, An Essay Review 1979.

Emission Spectrophotometric Multielement Methods of Analysis for Waters, Sediments and other materials of interest to the Water Industry 1980.

Inductively Coupled Plasma Spectrometry of Water Samples, in preparation.

Introduction

A few of the methods used in this series do not specify the wavelength used when taking measurements. For some elements there are alternative wavelengths to those which have been given in the aforementioned booklets that are useful either to change the range of the method or to avoid interference effects. It is also useful to know which types of source unit have been used successfully to excite the sought element. In addition there are a number of elements on which information is available, but which are so rarely determined that they do not warrant a specific booklet of their own. Very few metals require so specialist a treatment as tin, but even here, once the required forms of tin have been brought into solution, the final quantification procedures possible are similar to those for other metals.

There are only about six or seven basic commonly used preconcentration procedures of which the most important are:

- evaporation
- solvent extraction (often as a complex),
- volatilization (as hydride, element, chloride etc),
- ion exchange,
- precipitation (often on a carrier) and
- electrodeposition

Similarly, for quantification, there are the various forms of atomic emission, absorption and fluorescence which can be combined with these different methods of concentration. Atomic emission analysis is now usually either carried out using an inductively coupled plasma source, or with the much cooler air-acetylene flame or the intermediate temperature nitrous oxide-acetylene flame. Various sources such as nitrous oxide-cyanogen, AC spark and 10 amp (or higher) DC arc are occasionally used for special purposes. Atomic absorption analysis uses three basic absorption media, a flame (either air-acetylene or nitrous oxide-acetylene), a carbon or similar electrically heated furnace, and relatively cold vapour in a tube. Atomic fluorescence relies on the fluorescence excited by illumination of such an absorption media, but measurement is at right angles to the exciting light. For more information see the various reviews in the booklets listed earlier. Which combination is best, depends on the determinand and on the sample itself. The tables given in this booklet are intended to extend the usefulness of the existing publications in this series by giving other proven wavelengths, sources and methods of concentration or separation. As many elements as possible have been included in this survey, including ones for which no specific booklet has previously been issued. It must be remembered that performance characteristics, such as limit of detection, useful analytical concentration range, and interference, can be instrument dependent and may vary with sample type.

Interference effects are not only sample, determinand and method dependent, but also instrument dependent. Thus, if the light detector is relatively insensitive at the wavelength used, it may be necessary to use a wider entrance slit on the spectrometer (or monochromator), which will give poorer resolution and so allow light from adjacent spectral lines to overlap the chosen line of the determinand thus causing interference. Some substances alter the volatility or ionizability of the determinand in the source. In general, the hotter the source the less likely the volatility effect is to cause problems, but the more likely it is that atoms in the ground state, such as for instance those which, with sodium, emit the yellow doublet (589.592 and 588.995 nm) will be excited to a higher energy level, in the case of sodium, enhancing the far violet doublet (330.299 and 330.232 nm). Increase in power may also cause increase in interference by increasing the intensity of adjacent lines of other elements more than those of the determinand, so causing new problems. This sometimes happens with DC arc and ICP emission spectroscopy. It is often possible to change the range of the method by changing the

spectral line used. Thus, the yellow lines of sodium mentioned above are usually measurable at lower concentrations than the violet lines, but the latter may be more useful at higher concentration, thus avoiding having to dilute the sample. Many examples of the use of wavelength or source change to alter the range determined, or to avoid interference are given in the table which follows.

Elements with low excitation potentials (ie easily excited) such as the alkali metals and some lanthanides often cause problems by reducing the concentration of other determinand atoms in the emitting or absorbing states. Other elements and ions can have a similar effect by increasing or decreasing the excitable concentration of the determinand in the source. These problems are at their worst when the interfering elements are among the major ones present, but their concentrations may vary over a range of samples. Historically, three solutions have been adopted. All three are equally effective. The first method, which is the simplest, seeks to make the effect uniform by addition of a large excess of a salt of an easily excited element such as potassium, caesium or lanthanum, or for the volatility effect by adding ammonium chloride. Ionization suppression unfortunately does have the effect of reducing the sensitivity at low determinand concentrations. The second method is to change the matrix. In its chemical versions the technique can be used for concentration of the determinand. Examples are given in the appropriate section. The third method requires much preliminary investigation, but is useful if a large number of relatively similar samples are examined routinely. The various interference effects are determined quantitatively, the interferent concentrations are recorded simultaneously with the determinand signal and the true determinand value calculated. A few computerised instruments have a facility for this incorporated, but a small second computer, programmed specially to make the correction when given the interferent concentrations and the apparent determinand value, has also been used. As most of the literature on this topic is in North American journals and the booklet in this series explaining the technique is out of print, a summary is included at the end of this booklet.

Most of the preconcentration techniques are broad spectrum methods concentrating several elements, sometimes many; but it is sometimes possible to make the method concentrate only one or two determinands. The most important of these is chromatography using an ion exchange resin (see the section on concentration techniques). However, by use of selective complexation, solvent extraction can occasionally be made specific. Thus if a solution is treated with citrate, EDTA, and diethyldithiocarbamate salts, and the pH adjusted to 7.5–8.5, only copper, silver and bismuth are extracted by chloroform. It is possible to remove the silver and bismuth with chloride and so be left with just the copper. Such specific separations are not common.

Finally, whilst this booklet gives advice on the determination of all metals, metalloids and some non metals, there are other useful techniques at percentage range concentrations. Thus X-ray fluorescence is useful at higher concentrations, while at very low concentrations anodic and cathodic stripping voltametry are very useful. Polarography is useful at inbetween concentrations. Methods for these techniques are given in several other booklets in this series.

Because concentration techniques are important when determining traces, a general summary of these procedures, by element, is also included.

Atomic Spectrophotometric Interference Effects

Atomic Absorption

A brief survey of the literature could easily lead the newcomer to atomic absorption spectrophotometry into believing that he has been misled when informed that this analytical technique is free from interferences. This impression unfortunately arises from early work in atomic absorption spectroscopy when, of course, only a few applications had been studied. With the increase of interest, a wider range of applications has been studied and consequently many more problems have been encountered.

However, the interferences encountered in atomic absorption spectrophotometry are now extremely well documented and some which were reported early in the literature, were found to be due to instrumental imperfections (eg the apparent increase in zinc sensitivity with acid concentration was caused by a prototype brass burner head). 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:

1 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 demodulator (caused by intense emission from the flame spectrum and/or sample matrix emission)
- g) Ionisation
- h) Background non-specific absorption (or light scatter by the sample matrix)

2 Chemical Interferences

- a) Stable compound or solute vaporisation interferences

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

Physical Interferences

Spectral overlap of atomic line profiles

It can safely be said that this form of interference is of no practical significance in atomic absorption spectrometry. The typical absorption line half width is approximately 0.003 nm, with a 650 nm spectral range for this technique from 193.7 nm (arsenic) to 852.1 nm (caesium). Thus, there is little likelihood of spectral overlap of atomic line profiles.

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.

Viscosity or bulk matrix variations

This effect is caused by variation in the rate of nebulisation with increasing viscosity (ie increasing matrix concentration). Thus, the sensitivity for a given element in distilled water (eg lead) will decrease in the presence of a large (eg 10,000 $\mu\text{g mL}^{-1}$) level of another element (eg zinc). For most water industry analyses this effect is not very significant. It can be observed with sea and other saline waters and possibly if the concentration by evaporation technique is used. It can be overcome by using matching standards, calibration by the standard addition technique or by solvent extraction of the cation(s) to be determined from the interfering matrix. If this type of interference is observed, a check should be made for background (non-specific) absorption.

Solution temperature variations

The dependence of the response on solution temperature for most elements is not too critical (eg typically a 50–100% 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 $\pm 3^\circ\text{C}$ for most applications. However if sample pre-treatment requires boiling the solution it must be allowed to cool prior to measurement.

Variation in the composition of the solvent

This will cause an effect not only because of surface tension and viscosity changes (see b and c) which result in a change in 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 vaporisation. The droplets produced by the nebuliser will tend to evaporate more on their journey from the nebuliser to the flame and a greater proportion of these small droplets will reach the flame. Thus, the enhancement in the signal when organic solvents are used is caused by the increased sample uptake rate and the larger proportion of small droplets that reach the flame.

Overload of the demodulator

All modern atomic absorption instruments have phase sensitive detection systems and in theory 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 309.2 nm (this being a wavelength region of very intense flame background emission) with a low lamp current (eg 3 mA) and a large spectral bandpass (eg 1.0 nm). 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 553.6 nm barium resonance line wavelength will overload the demodulator even for calcium levels of approximately 1000 $\mu\text{g mL}^{-1}$ and result in very noisy erratic signals.

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

Ionisation

Ionisation occurs in high temperature flames such as the nitrous oxide-acetylene flame, and affects elements with relatively low ionisation potentials (eg Cs, Rb, K, Na, Li, Ba, Sr and Ca). Ionisation is only appreciable for Cs, Rb, K, Na and Li in the air-acetylene flame. The higher the flame temperature the more the equilibrium existing between free atoms and ions is shifted towards the ionic states.



The effect is characterised by the calibration curve bending away from the concentration axis (Figure 1). 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. (NB. The resonance radiation will only be absorbed by ground state atoms and *not* by ions). The interference is overcome by the addition of an ionisation buffer to the sample solution which is

another easily ionisable metal and one that will ionise preferentially to the one being determined. Na and K (as chlorides) in concentrations of $1000 \mu\text{g mL}^{-1}$ are commonly used.

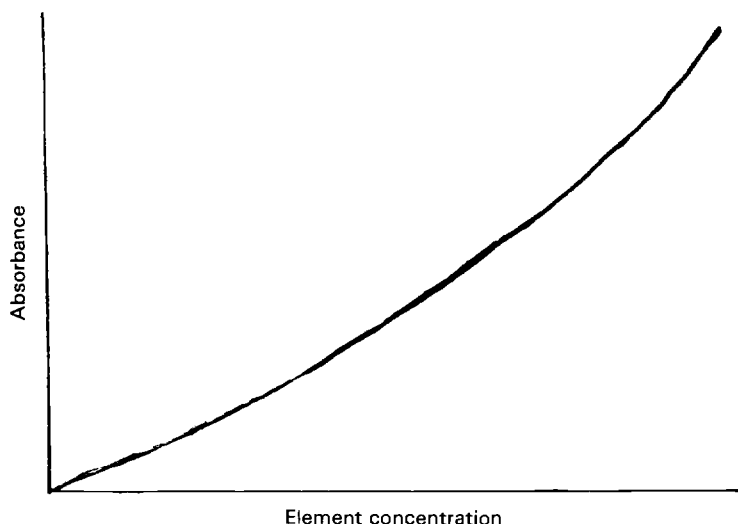


FIGURE 1 Calibration curve showing the effect of ionization.

Background (non-specific) absorption

Background absorption, often called 'scatter' or molecular absorption, is an interference phenomenon caused by solid particles or molecular species in the flame.

These can cause a physical scattering, or more probably, a molecular absorption of the resonance line before it is received by the detector. It is therefore possible for an apparent (but spurious) absorption signal to appear on the readout system. This interference is analogous to turbidity in molecular spectrometry and although it is more pronounced at low wavelengths, commonly below about 350 nm, it can be observed at all wavelengths. The effect also increases proportionally to an increase of a given matrix species in the flame.

In a cool flame, the scattered radiation or molecular absorption tends to be more pronounced than with a hot flame, eg the nitrous oxide-acetylene flame will more completely vaporise the solid particles and dissociate molecular species present in the flame than the cooler air-acetylene flame.

Methods of overcoming background absorption

a) Chemical

The simplest 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 absolute purity of matrix reagents.* An alternative would be to use the hotter nitrous oxide-acetylene flame, but this in turn may introduce other interferences such as ionisation as well as markedly degrading the analytical sensitivity.

*It is sometimes difficult to determine very low levels of vital impurities in standard materials. A procedure, which is basically a standard multiple addition procedure, originally developed for pure emission methods is described in Nachtrieb (1950).

b) Instrumental

These are all based on the fact that background absorption and in some instances emission 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. It is therefore possible to measure the degree of interference at nearby non-absorbing

wavelengths, preferably by taking the mean of readings just adjacent to each side of the absorption wavelength, and subtracting it from the value obtained at the resonance wavelength. However, this technique can lead to errors because since the degree of interference changes with wavelength, unless the non-absorbing wavelength is very close to the absorbing wavelength, the degree of interference will be different. A more accurate method for wavelengths below 350 nm is to use a deuterium lamp to measure the background effect at the same wavelength as the resonance line occurs.

Since the emission profile of a resonance line emitted by a hollow cathode lamp represents only a very small proportion of the spectral band-width of a spectrophotometer, being of the order of 0.001 nm compared with about 0.6 nm for a typical instrument bandwidth, when atomic absorption occurs, the energy seen by the instrument from the hollow cathode lamp is reduced in proportion to the absorption of the element line. Whereas the amount of energy removed from the deuterium source represents only a very small proportion of the energy seen by the instrument. Figure 2 shows this diagrammatically.

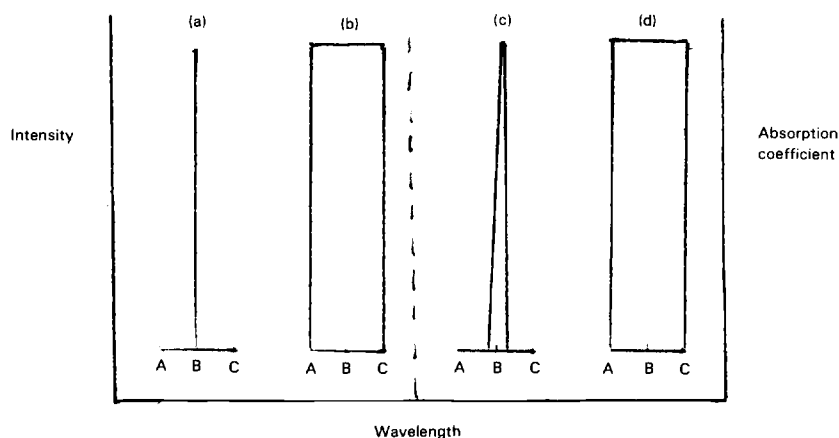


Figure 2

Diagrammatic representation showing how absorption line half-widths of hollow-cathode lamps and flames are small compared with instrument bandpass and molecular absorption bandwidth.

- (a) Line width of hollow cathode lamp (approx. 0.001 nm)
- (b) Effective 'line' half-width of deuterium source, typically 0.6 nm
- (c) Absorption line half-width of the atoms in the flame, approximately 0.003 nm
- (d) Effective molecular absorption bandwidth of molecules in the flame, typically 0.6 nm. (Spectral Bandpass of Monochromator)

Care is also needed with molecular (band) spectral background, which has a comb like intensity profile (See under Emission below).

2 Chemical Interferences

These are often referred to as stable compound or solute vaporisation interferences and are by far the most frequently encountered interferences in atomic absorption spectrometry. Basically, a chemical interference can be defined as anything that prevents 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, barium and many other metals. This is due to the formation of low volatility aluminates, silicates and phosphates, which are only poorly atomised to the ground state in the analytical flame being used.

In order to overcome this type of interference, two techniques may be emphasised, both of which release the element under investigation. The first relies upon the application of chemistry. Sometimes a compound can be added which will release the element of interest by the formation of a preferential complex. Thus a chelate, such as EDTA, can be added to complex the cation thus preventing its association with an anion that could lead to the formation of a refractory involatile compound. 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 phosphate anions. The calcium is 'released' due to the preferential formation of lanthanum phosphate. It is possible to use strontium in place of lanthanum.

Alternatively, virtually all chemical interferences may be overcome by using the nitrous oxide-acetylene flame, but for many elements (eg Cd, Cu, Ni, Pb, Zn etc.) this results in a large unacceptable drop in sensitivity (5–10 times).

Emission

The interference effects listed above also occur with the various types of direct emission, whether gas flame, D C arc, spark or ICP. However their importance varies greatly with instrument design and source parameters, especially source and sometimes sample type.

Spectral line overlap (see page 10) is often more important in emission methods, and for instruments with grating spectrometers can include strong lines in other orders (where $n_1\lambda_1 = n_2\lambda_2$). Factors influencing the flow of sample to the source can also have an effect. If solid samples are used, electrode design can greatly affect volatility. In all cases standardization of source parameters is the cure. For advice on solid electrode design see a specialized text such as that issued by the American Society for Testing Materials.

A new problem presents itself in emission. Just as unwanted emission in the source by the determinand can reduce atomic absorption, so atomic absorption along the optical path, called self reversal, can create problems with emission analyses. In fact, the emission curve for readings at the line centre can, at high concentrations turn right round and virtually become an atomic absorption analytical curve. Ionization and background effects are similar to those with atomic absorption, the former changing the concentration of the emitting species, the latter adding a spurious signal, often related to sample content. The band spectral problem can be a nuisance.

The chemical effect of the other ions present can also affect the determinand concentration in the source, by increasing or reducing the volatility. Thus chlorides often increase the determinand concentration, while phosphates, silicates, and aluminates (the latter from aluminium ions) often reduce it. The solutions are similar to those given above for Atomic Absorption.

Background Correction

In emission, background can arise from the measuring electronics or similar equipment (as in many other instrumental methods), but in spectrometry it is usually the spectral background which causes the main interference. This is due either to stray light (which should be preventable), or to continuum or band (molecular) emission in the source itself. If the background is due to a continuum, correction is relatively easy; measure its intensity at wavelengths free of other spectral lines close to the determinand line and on each side of it. If the background is due to a band or molecular spectra, the problem is more complicated and is very dependent on the breadth of spectrum examined by the instrument optics. Band spectra are series of closely spaced spectral lines (much like teeth in a comb), they are occasionally used analytically (oxide bands for calcium, strontium and barium, or calcium fluoride bands for fluoride) measurement being made at the band head (most intense line). Correction can be made only if very precise measurements and calculations are made (using a scanning instrument) to determine the interference due to the band lines involved and precise determination of this from readings of other band component lines. Such corrections are rarely made, and then only by well equipped experts.

Computer Correction

Use of most of the above methods for suppressing interference effects, except those which include trace element pre-concentration, tend to reduce the sensitivity of the determination of trace elements. However these effects fall into three basic types

(i) Firstly, there are those effects in which there is an increase in light from the source obeying either the Malpika equation $I = aC^n$ or the Beer-Lambert Absorption Law, which in this case becomes $I = aC^n b^{1/c}$ for simple self absorption (self reversal).

In the case of overlapping spectral lines from other elements, $I_{\text{total}} = I_1 + I_2$ etc where I_1 , I_2 etc are related to the determinand and interferent element concentrations by terms such as those above. Background is usually in this class too. The curves are the well known stretched reversed S shape.

(ii) Secondly, there are effects where chemical reactions reduce or increase the concentration of the excited state in the source. These all obey the mass law, which is applicable for any form of equilibrium, including the dynamic equilibrium usually found in spectroscopic sources. In which case a term such as $I = a(f_1 C_1 \times f_2 C_2)^n$ is used. Instances are known where such mass law effects apply to the interfering overlapping spectral line, and sometimes to both determinand and overlapping lines. In these cases, C in the above equations is replaced by mass law and correction terms of the above type. A family of parallel curves results.

(iii) Finally, there are cases of interference where the interferent and determinand form two different compounds (of different volatility and emissivity). For these it is necessary to calculate the relative concentration of determinand in each compound in the source and sum these (with their separate emissivity factors) as above. Such analytical curves are basically two curves joined by a dog-legged section in between, at concentrations where neither compound predominates.

In the above expression

I terms are light intensities

C terms are concentrations

a and n are emissivity constants

b is the absorption coefficient

and f terms are mass law effect constants.

The above procedures seem complicated; but if large numbers of similar samples, but with variable amounts of interferent are examined regularly, it may be worth while investigating the types of interference, then using spiked and standard samples and graphical methods to programme a computer to correct results given determinand and interferent element signal outputs.

Quite complex multielement effects with several types of interference occurring simultaneously have been accurately corrected for in routine analysis. (See Pittwell 1962 and 1966. Most of the examples given are for solid samples using internal standards; but the principles are the same).

References

Atomic absorption instrument training seminar notes, Instrumentation Laboratory (UK) Ltd, 1979.

Borowiec J A, Boorn A W, Dillard J H, Cresser M S, Browner R F, and Matteson M J, *Anal Chem* 52, 1054-9 1980.

Ebdon L, *An introduction to Atomic Absorption Spectroscopy*, Heyden & Son Ltd, 1982.

Elwell W T and Gidley J A F, *Atomic Absorption Spectrophotometry*, Pergamon Press, 1966.

Nachtrieb N H, *Principles and Practice of Spectrochemical Analysis*. McGraw, New York 1950.

Pickett E E, Afreshaidat M, Broadway S, and Koirtyohann S R, *Spectrochimica Acta*. 44B. 1273-1284 1989.

Pittwell L R, *Applied Spectroscopy* 16. 77-86 1962.

Pittwell L R, *Canadian Spectroscopy* 131, 132, 136. 1966.

Rothery E, *Analytical Methods for Graphite Tube Atomisers*, Varian, 1988.

Thomerson D R and Thompson K C, *An introduction to the Principles and Applications of Atomic Absorption Spectroscopy*, Shandon Southern Instruments Ltd, 1975.

Thompson K C, *Analyst* 103. 1258-1262. 1978.

Thompson K C and Wagstaff K, *Analyst* 105. 641-650 1980.

Thompson M and Walsh J N, *A Handbook of Inductively Coupled Plasma Spectrometry*, Blackie and Son Ltd, 1983.

Useful Wavelengths for Flame, AAS, AFS, EAAAS and ICPS (with sources and interference data)

It must be noted that range and interference effects are highly instrument and sample dependent. The ranges quoted are typical ones reported by committee members. Users should check with their own instruments and samples, as a listing here does not necessarily mean that their instrument will be similar. With grating spectrometer instruments it must be remembered that lines in a different order can occasionally overlap the determinand line in use.

Element	Notes	Wavelength nm	Source type	Range, or for ICPS only, typical limit of detection ^(13,14)	Interference ⁽¹³⁾	Modifier or repressant
Actinium	1	591.1 450.7	direct air-C ₂ H ₂ flame			
Aluminium		309.3 396.2 237.5 257.4	N ₂ O-C ₂ H ₂ AAS	0.2-200 mgL ⁻¹ 0.3-250 mgL ⁻¹ 1-1,000 mgL ⁻¹ 2-2,000 mgL ⁻¹	Fe, SO ₄	
		309.3 396.2 396.4	EAAAS ⁽¹⁵⁾	0.005-0.25 mgL ⁻¹	ClO ₄ ⁻ , N ₂ , carbide formation.	
		167.08 308.215 309.3 394.4 396.152	ICPS	5-100 µgL ⁻¹ 8-150 µgL ⁻¹	Mn, V Mg, V	
				30 µgL ⁻¹	V, Ca	
Antimony		217.6 206.8 231.2 212.7	air-C ₂ H ₂ AAS	0.1-60 mgL ⁻¹ 0.2-150 mgL ⁻¹ 0.3-150 mgL ⁻¹ 1-250 mgL ⁻¹		
		217.6	EAAAS ⁽¹⁵⁾	0.1 mgL ⁻¹	Cu, Pb plus many more	add Ca ²⁺ and use a platform
		217.6	Hydride AAS	5-25 µgL ⁻¹	Fe,Au,Cu,Ni,Pt, Pd, Co. Sb(III) more sensitive than Sb(V)	
		206.833	ICPS	40-200 µgL ⁻¹	Al,Cr,Fe,Ni,Ti, V, Ge, Sn, W, Ir, Mo, Co, Al,Fe,Ni	
			217.58 231.147 252.8 231.147 259.80		70+ µgL ⁻¹	
	12					

Element	Notes	Wavelength nm	Source type	Range, or for ICPS only, typical limit of detection ^(13,14)	Interference ^(11,13)	Modifier or repressant
Arsenic		193.7	Hydride AAS	0.2–50 mgL ⁻¹ (0.03) mgL ⁻¹	Au,Cu,Ni,Pt,Pd, Fe,Co. As (III) more sensitive than As (V)	
		197.2 189.0		0.4–100 mgL ⁻¹		
		189.0 193.7	EAAAS ⁽¹⁵⁾			
		193.7	air-C ₂ H ₂ AAS	1–100 mgL ⁻¹	much interference.	
		193.7	N ₂ O-C ₂ H ₂ AAS	–50 mgL ⁻¹	less interference.	
	12	189.0 193.696 193.759 197.3 228.81 233.527 278.0	ICPS	–200 μgL ⁻¹ 30 μgL ⁻¹ 10–125 μgL ⁻¹ 200 μgL ⁻¹ 30–100 μgL ⁻¹ 50–700 μgL ⁻¹	Cr,Fe,Mg,Mn,V Fe,Ca Al,Fe,V Al,V Cd Fe,V,Ni	
	Barium	2	553.6 455.4 350.1	N ₂ O-C ₂ H ₂ AAS	0.2–60 mgL ⁻¹ 0.2–60 mgL ⁻¹ high concn	ionization.
3		614.2 553.6 455.4	direct air-C ₂ H ₂ flame			
		553.6	EAAAS ⁽¹⁵⁾	0.5 mgL ⁻¹	carbide formation affects emission.	add molybdate (use pyrographite)
		553.6 233.527 455.403 493.409	air-C ₂ H ₂ AAS ICPS	100–500 mgL ⁻¹ 3–10 μgL ⁻¹ 2–5 μgL ⁻¹ 3 μgL ⁻¹	many interferences. Fe,V,Ni Cr,Ni,Ti Fe	
Beryllium			234.9	N ₂ O-C ₂ H ₂ AAS	0.1–4 μgL ⁻¹	acids (nitric sulphuric, etc) enhance reponse, Si,Mg,As depress response.
		234.9	EAAAS ⁽¹⁵⁾		HClO ₄ and other acids enhance response.	measure in ammoniacal solution.
		234.86 313.04 313.107	ICPS	0.6–2 μgL ⁻¹ 0.1–2 μgL ⁻¹ 2 μgL ⁻¹	Fe,Ti V,Ti Ti	
	Bismuth	223.1 222.8 306.8 227.7	air-C ₂ H ₂ AAS	0.2–50 mgL ⁻¹ 1–200 μgL ⁻¹ 1–200 μgL ⁻¹ high concn.		

Element	Notes	Wavelength nm	Source type	Range, or for ICPS only, typical limit of detection ^(13,14)	Interference ^(11,13)	Modifier or repressant
Bismuth contd		223.1	EAAAS ⁽¹⁵⁾	10–50 μgL^{-1}	Au,Cu,Al,Pt, Ag,Co,Se,Te	addition of Ni(II) overcomes interference effects by allowing use of higher ash temperatures.
		223.1	Hydride AAS	5–25 μgL^{-1}	Au,Cu,Ni,Al,Pt, Ag,Co,Se,Te	
	12	223.1 306.77	ICPS	10–200 μgL^{-1} 10–500 μgL^{-1}	Cu,Ti Fe,V	
Boron	4	249.7 208.9	N ₂ O-C ₂ N ₂ AAS	3–1,500 mgL^{-1} 10–4,000 mgL^{-1}		
		249.7	direct air-C ₂ H ₂ flame			
		249.7	EAAAS ⁽¹⁵⁾	0.5–2.5 μgL^{-1}	chlorides, sulphates, Mg, Ca Fe,Cu in excess.	
		208.959 249.678	ICPS	50 μgL^{-1} 5–100 μgL^{-1}	Al,Fe Co,Fe (less than 249.773)	
		249.773		0.6–30 μgL^{-1}	Fe	
Cadmium		228.8 326.1	air-C ₂ H ₂ AAS	0.3–5 mgL^{-1} high concn		
		228.8 326.1	EAAAS ⁽¹⁵⁾	0.001–0.01 mgL^{-1} higher concn	chlorides, sulphates, Mg, Ca Fe, Cu in excess.	with La(III) or NH ₄ ,H ₂ PO ₄ added.
		214.44 226.502 228.802	ICPS	20 μgL^{-1} 2–20 μgL^{-1} 3–20 μgL^{-1}	Al,Fe Fe,Ni As,Al,Fe,Ni	add Mg(NO ₃) ₂ or NH ₄ ⁺
Caesium	2	852.1 894.4 455.5	air-C ₂ H ₂ AAS	0.03–10 mgL^{-1} 0.1–20 mgL^{-1} 2–50 mgL^{-1}	ionization.	Add 3% m/v K ⁺
		894.3	direct air-C ₂ H ₂ flame			
		852.1	EAAAS ⁽¹⁵⁾	0.005–0.025 mgL^{-1}	Fe, Co	
Calcium		422.7 239.9	air-C ₂ H ₂ AAS	0.006–90 mgL^{-1} high concn	P, Al, Si	
	3	854.2 422.7 396.8 393.4	direct air-C ₂ H ₂ flame		P, Al, Si	
	2	239.9		0–100 mgL^{-1}		

Element	Notes	Wavelength nm	Source type	Range, or for ICPS only, typical limit of detection ^(13,14)	Interference ^(11,13)	Modifier or repressant
Calcium contd		422.7 430.2	N ₂ O-C ₂ H ₂ AAS	0.008-5 mgL ⁻¹		K ⁺ or La ³⁺ added
		422.7	EAAAS ⁽¹⁵⁾	1-5 µgL ⁻¹	carbide formation, emission effects, contamination.	
		181.45 315.889 317.933 393.366 396.8 445.478	ICPS	100 µgL ⁻¹ 1-50 µgL ⁻¹ 0.2 µgL ⁻¹ 5 µgL ⁻¹ 400 µgL ⁻¹	Co,Cr,Fe Fe,Cr,V Fe,V	
Carbon	8	193.09 247.86	ICPS	500 µgL ⁻¹ 1,000 µgL ⁻¹	Al,Mn,Ti Fe,Cr,Ti,V	
Cerium		413.77	ICPS	150 µgL ⁻¹	Ca,Fe,Ti	
Chromium		357.9 306.5 359.4 425.4 429.0	air-C ₂ H ₂ AAS	0.02-15 mgL ⁻¹ 0.03-20 mgL ⁻¹ 0.05-50 mgL ⁻¹ 0.2-150 mgL ⁻¹	Fe,Ni,Cu,Co,SO ₄ all PO ₄	NH ₄ Cl added
		357.9 359.4 306.5 429.0 425.4	EAAAS ⁽¹⁵⁾	0.015 mgL ⁻¹		Mg ²⁺ or Ca ²⁺ added
		357.9	N ₂ O-C ₂ H ₂ AAS	0.02-25 mgL ⁻¹		K ⁺ or Cs ⁺ added
		205.552 267.716 283.563 284.325 425.43	ICPS	4-30 µgL ⁻¹ 5-30 µgL ⁻¹ 5 µgL ⁻¹ 10 µgL ⁻¹	Fe,Mo,Al,Cu,Ni Mn,V,Fe,Ti Fe,Mo,Mg,V	
Cobalt		240.7 252.1 352.7 346.6 228.6	air-C ₂ H ₂ AAS	0.02-20 mgL ⁻¹ 0.05-60 mgL ⁻¹ 0.5-300 mgL ⁻¹ high Conc.	Fe,Cu,Ti, Ni	
		240.7	EAAAS ⁽¹⁵⁾			
		228.616 238.89 343.35	ICPS	3-20 µgL ⁻¹ 10 µgL ⁻¹	Cr,Fe,Ni,Ti Fe,V	

Element	Notes	Wavelength nm	Source type	Range, or for ICPS only, typical limit of detection ^(13,14)	Interference ^(11,13)	Modifier or repressant		
Copper		324.8	air-C ₂ H ₂ AAS	0.01–10 mgL ⁻¹				
		327.4		0.02–20 mgL ⁻¹				
		217.9		0.1–100 mgL ⁻¹				
		222.6		0.3–300 mgL ⁻¹				
		249.2		high concn				
		216.6						
		244.2	high concn					
		324.8	EAAAS ⁽¹⁵⁾	0.002–0.1 mgL ⁻¹	Na,K,Mg,Cl			
		327.4						
		578.2	direct air-C ₂ H ₂ flame					
	327.4							
	324.8							
	224.7	ICPS		20 µgL ⁻¹	Fe			
	296.12							
	324.754			0.3–10 µgL ⁻¹			Ca,Cr,Fe,Ti	
	327.396			10 µgL ⁻¹				Ca,Fe,Ni,Ti,V
	510.55							
Dysprosium		421.2	N ₂ O-C ₂ H ₂ AAS	5–25 mgL ⁻¹	ionization.	add 0.2% m/v K ⁺		
		416.8	(10× less sensitive)					
		404.6	(1.2× less sensitive)					
Erbium		400.8	N ₂ O-C ₂ H ₂ AAS	5–25 mgL ⁻¹	ionization.	add 0.2% m/v K ⁺		
		386.3		(1.5× less sensitive)				
		389.3		(4.0× less sensitive)				
		380.5		(18× less sensitive)				
Europium		576.5	direct air-C ₂ H ₂ flame					
		459.4	N ₂ O-C ₂ H ₂ AAS		Al,Si	K ⁺ added		
		462.7						
		466.2						
		397.2						
		393.0						
		390.7						
Fluoride		Fluoride has been determined in the presence of excess calcium ion using a CaF bandhead, see note 3 for wavelength reference.						
Gadolinium		432.7	direct air-C ₂ H ₂ flame					
		432.5						
		407.9	N ₂ O-C ₂ H ₂ AAS	300–1,500 mgL ⁻¹		K ⁺ added		
Gallium		287.4	air-C ₂ H ₂ AAS	0.1–250 mgL ⁻¹				
		294.4		0.2–250 mgL ⁻¹				
		417.2		0.2–500 mgL ⁻¹				
		403.3		0.3–500 mgL ⁻¹				

Element	Notes	Wavelength nm	Source type	Range, or for ICPS only, typical limit of detection ^(13,14)	Interference ^(11,13)	Modifier or repressant
Gallium contd		417.2	direct air-C ₂ H ₂ flame			
		403.3				
		294.4 287.4	EAAAS ⁽¹⁵⁾	25-125 mgL ⁻¹	HClO ₄ , alkali & alkaline earth metals, halides.	
		287.4	N ₂ O-C ₂ H ₂ AAS	10-50 mgL ⁻¹	ionization.	add 0.2% m/v K ⁺
		294.364	ICPS	100 + μgL ⁻¹		
Germanium		265.2 269.1 303.9	N ₂ O-C ₂ H ₂ AAS	0.4-200 mgL ⁻¹ 2-1,000 mgL ⁻¹ high concn	chloride.	
		265.2	Hydride AAS			
		209.42	ICPS	1,000 + μgL ⁻¹		
Gold		242.8	air-C ₂ H ₂ AAS	0.05-20 mgL ⁻¹	cyanide, Pt,Pd,Ru, Ir,Cu,Ni,Fe	
		267.6		0.2-100 mgL ⁻¹		
		242.8	EAAAS ⁽¹⁵⁾	5-25 μgL ⁻¹	Cu,Re,K,Na,Ca	
		242.78 267.58	ICPS	50 μgL ⁻¹ 50 μgL ⁻¹		
Hafnium		307.3	N ₂ O-C ₂ H ₂ AAS	4-2,000 mgL ⁻¹	oxidising acids, Fe	add ammonium fluoride
Indium		303.9 410.5 271.0	air-C ₂ H ₂ AAS	0.2-100 μgL ⁻¹ 0.5-300 μgL ⁻¹ 4-2,000 μgL ⁻¹	Al,Cu,Mg,Zn,Pb	
		451.1 410.2	direct air-C ₂ H ₂ flame			
		303.9	EAAAS ⁽¹⁵⁾	0.03-1.5 μgL ⁻¹	chloride.	
		230.61 303.9	ICPS	250 μgL ⁻¹ 250 μgL ⁻¹	Fe,Mn,Ni,Ti Cr,Fe,Mn,V	
Iridium		208.9 264.0 285.0 254.4 292.5	air-C ₂ H ₂ AAS	0.6-200 mgL ⁻¹ 2-5000 mgL ⁻¹ 3-1,000 mgL ⁻¹ 3-1,000 mgL ⁻¹		
		208.9	N ₂ O-C ₂ H ₂ AAS	3-1,500 mgL ⁻¹		
		208.9	EAAAS ⁽¹⁵⁾	0.25-1.25 mgL ⁻¹	Cu,Fe,Ni	
		264.0		1-4 mgL ⁻¹		

Element	Notes	Wavelength nm	Source type	Range, or for ICPS only, typical limit of detection ^(13,14)	Interference ^(11,13)	Modifier or repressant		
Iron		248.3 252.3 271.9	air-C ₂ H ₂ AAS	0.02–20 mgL ⁻¹ 0.05–50 mgL ⁻¹ 0.1–100 mgL ⁻¹	Cu,Co,Ni,Mn			
		372.0 344.1 392.0		0.2–200 mgL ⁻¹ 1–500 mgL ⁻¹ high concn				
	7	271.9	EAAAS ⁽¹⁵⁾	0.002–0.01 mgL ⁻¹				
		248.3 372.0		0–0.002 mgL ⁻¹				
		233.38 238.207 239.56 249.33 259.940	ICPS	6–40 µgL ⁻¹ 5–20 µgL ⁻¹	Cr,V			
	Lanthanum		550.1 418.7 365.0	N ₂ O-C ₂ H ₂ AAS	500–2,500 mgL ⁻¹ (1.5 × less sensitive) (7.0 × less sensitive)	ionization.	add 0.2% m/v K ⁺	
			379.5 398.8 408.67	ICPS	20 µgL ⁻¹ 6–20 µgL ⁻¹ 20 µgL ⁻¹	Ca,Fe,V Ca,Cr,Fe		
		Lead		217.0 283.3	air-C ₂ H ₂ AAS	0.05–25 mgL ⁻¹ 0.1–50 mgL ⁻¹	Al,Si,Ca,Mg,La	
				261.4 405.7		high concn very high concn.		
		283.3 217.0	EAAAS ⁽¹⁵⁾	0.002–0.01 mgL ⁻¹ –0.1 mgL ⁻¹	chloride(17).	La(III) added or Mg ₃ (PO ₄) ₂		
	205.3 261.4							
	220.351 280.2 283.31 405.78	ICPS	30–100 µgL ⁻¹ 30–200 µgL ⁻¹ 200 µgL ⁻¹ 7–300 µgL ⁻¹	Al,Cr,Fe Fe,Cr,Mg				
Lithium		670.8 323.3	air-C ₂ H ₂ AAS	0.005–4 mgL ⁻¹ high concn		Sr ²⁺ or K ⁺ added		
		670.8	direct air-C ₂ H ₂ flame					
		670.784	ICPS	3–15 µgL ⁻¹	V,Ti			
Lutetium		336.0	N ₂ O-C ₂ H ₂ AAS	100–500 mgL ⁻¹	ionization.	add 0.2% m/v K ⁺		

Element	Notes	Wavelength nm	Source type	Range, or for ICPS only, typical limit of detection ^(13,14)	Interference ^(11,13)	Modifier or repressant
Magnesium		285.2 202.5	air-C ₂ H ₂ AAS	0.001–9 µg L ⁻¹ 0.05–30 µg L ⁻¹	P,Al,Si	La(III) added
		285.2	N ₂ O-C ₂ H ₂ AAS	0.2–1 µg L ⁻¹		K ⁺ or La(III) added
		285.2	direct air-C ₂ H ₂ flame			
		279.079 279.553 280.27 285.213 518.36	ICPS	30 µg L ⁻¹ 0.5 µg L ⁻¹ 1 µg L ⁻¹ 3–10 µg L ⁻¹	Cr,Fe,Mn,Ti Fe,Mn Cr,Mn,V Fe,Cr,V	
Manganese		279.5 279.8 280.1 403.1	air-C ₂ H ₂ AAS	0.01–5 mg L ⁻¹ 0.02–6 mg L ⁻¹ 0.02–10 mg L ⁻¹ 0.01–60 mg L ⁻¹	Si,Mo,W	Mg ²⁺ added
		279.5 280.1 403.1	EAAAS ⁽¹⁵⁾	0.001–0.005 mg L ⁻¹ 0.002–0.01 mg L ⁻¹ 0.02–0.1 mg L ⁻¹	Chloride	
		257.610 263.82 293.306	ICPS	0.4–5 µg L ⁻¹ 20 µg L ⁻¹	Fe,Al,Cr	
Mercury		253.7	air-C ₂ H ₂ AAS	0.5–500 mg L ⁻¹		
		253.7	EAAAS ⁽¹⁵⁾	60–300 mg L ⁻¹		matrix modifier essential.
		184.9	cold vapour	0.5–2 µg L ⁻¹	Cu,Ni,Bi,Fe,Se,Au Ag	
		253.7	AAS	5–20 µg L ⁻¹		
		253.7	AFS	0.1 to 10 µg L ⁻¹		
	12	184.950 194.23 253.65	ICPS	50 µg L ⁻¹ 100 µg L ⁻¹	Al,V Fe,Mn,Ti	
Molybdenum		313.3 317.0 386.4 320.9	air-C ₂ H ₂ AAS	0.2–200 mg L ⁻¹ 0.3–300 mg L ⁻¹ 0.4–400 mg L ⁻¹ 2–1,500 mg L ⁻¹	many metals.	
		313.3	N ₂ O-C ₂ H ₂ AAS	0.2–100 mg L ⁻¹		K ⁺ added
	7	313.3	EAAAS ⁽¹⁵⁾			
		202.032 281.6 317.03 379.82 386.4	ICPS	9–30 µg L ⁻¹ 20 µg L ⁻¹ 1 µg L ⁻¹ 0.6–30 µg L ⁻¹	Al,Fe Cr,Fe,Mg,Mn,Ti	

Element	Notes	Wavelength nm	Source type	Range, or for ICPS only, typical limit of detection ^(13,14)	Interference ^(11,13)	Modifier or repressant
Neodymium		492.5	N ₂ O-C ₂ H ₂ AAS	100–500 mgL ⁻¹	ionization.	add 0.2% m/v K ⁺
Nickel		232.0	air-C ₂ H ₂ AAS	0.02–15 mgL ⁻¹	Fe	
		231.1		0.04–30 mgL ⁻¹		
		234.6		0.1–60 mgL ⁻¹		
		341.5		0.1–80 mgL ⁻¹		
		352.5		0.15–100 mgL ⁻¹		
		351.5		0.25–200 mgL ⁻¹		
		247.7		high concn		
		362.5		high concn		
		232.0	EAAAS ⁽¹⁵⁾	0.1 mgL ⁻¹		
		341.5				
	303.8					
	323.3					
	225.39	ICPS	50 μgL ⁻¹	Co,Fe		
	231.604		9–20 μgL ⁻¹			
	341.48		80 μgL ⁻¹			
Nitrogen	9	174.3 174.5	ICPS			
Niobium		334.9	N ₂ O-C ₂ H ₂ AAS	50–4,000 mgL ⁻¹	Fe,F enhance.	
		316.34 319.5	ICPS	60 μgL ⁻¹ 100 μgL ⁻¹	Ca,Cr,Fe	
Osmium		290.9	N ₂ O-C ₂ H ₂ AAS	0.5–250 mgL ⁻¹		
Palladium		247.6	air-C ₂ H ₂ AAS	0.1–40 mgL ⁻¹	Rh,Ru,Ir,Au,Ag,Fe Co,Cu,Ni,Pt	
		244.8		0.1–40 mgL ⁻¹		
		276.3		0.3–100 mgL ⁻¹		
		340.5		0.5–200 mgL ⁻¹		
		247.6	N ₂ O-C ₂ H ₂ AAS	1–200 mgL ⁻¹		
		247.6	EAAAS ⁽¹⁵⁾	0.01–0.05	oxidants.	
	340.46	ICPS	70 μgL ⁻¹	Fe,Ti,V		
Phosphorus		213.6	N ₂ O-C ₂ H ₂ AAS	30–150 gL ⁻¹		
		177.50	ICPS		Cu,Al,Cr,Fe,Ti Cu,Al Cr,Fe,Mn,Ti	
		178.287		20 μgL ⁻¹		
		213.62		20–100 μgL ⁻¹		
		214.9		50–150 μgL ⁻¹		
		253.57		20–200 μgL ⁻¹		
	265.9	air-C ₂ H ₂ AAS		0.3–300 mgL ⁻¹		Fe,Co,Cu,Ni,Pd,Rh Ir,Au,Ag
	299.8		2–1,500 mgL ⁻¹			
	264.7		2–1,500 mgL ⁻¹			
	265.9	N ₂ O-C ₂ H ₂ AAS	3–2,000 mgL ⁻¹			

Element	Notes	Wavelength nm	Source type	Range, or for ICPS only, typical limit of detection ^(13,14)	Interference ^(11,13)	Modifier or repressant
Platinum contd		265.9	EAAAS ⁽¹⁵⁾	0.06–0.3 mgL ⁻¹	oxidants.	
		214.4 265.9	ICPS	30 µgL ⁻¹ 80 µgL ⁻¹	Al,Fe Fe,Mg,Cr,V,Mn	
Potassium	5	766.5	air-C ₂ H ₂ AAS	0.01–9 mgL ⁻¹	ionization.	Cs ⁺ added
		769.9		0.02–8 mgL ⁻¹	ionization.	Cs ⁺ added
		404.4		high concn		
		766.5 769.9 404.4	direct air-C ₂ H ₂ flame	0.08–10 mgL ⁻¹ 0.1–10 mgL ⁻¹		
		404.72 766.490	ICPS	40 mgL ⁻¹ 0.1–3 mgL ⁻¹	Ca,Fe,V (Mg in 2nd order) Ti	
		769.90		0.4 mgL ⁻¹	Cr,Ti	
Praseodymium		495.1	N ₂ O-C ₂ H ₂ AAS	500–2,500 mgL ⁻¹	ionization.	add 0.2% m/v K
Radium	1	714.1	direct air-C ₂ H ₂ flame			
Rhenium		346.1	N ₂ O-C ₂ H ₂ AAS	3–1,500 mgL ⁻¹	Al,Ca,Fe,Pb,Mn	K ⁺ added
Rhodium		343.5	air-C ₂ H ₂ AAS	0.1–100 mgL ⁻¹	Co,Cu,Ni,Fe,Pt,Pd Ru,Ir,Ag,Au	
		369.2		0.3–300 mgL ⁻¹		
		365.8		0.5–500 mgL ⁻¹		
		370.1		1.0–800 mgL ⁻¹		
		328.1		high concn		
		343.5	N ₂ O-C ₂ H ₂ AAS	0.2–100 mgL ⁻¹		
	343.5	EAAAS ⁽¹⁵⁾	0.02–0.1 mgL ⁻¹	oxidants.		
	343.46	ICPS	60 µgL ⁻¹			
Rubidium	2	780.0	air-C ₂ H ₂ AAS	0.03–10 mgL ⁻¹	Al	K ⁺ added
		794.8		0.05–20 mgL ⁻¹		
		420.2		high concn		
		794.8 780.0	direct air-C ₂ H ₂ flame			
		780.0	EAAAS ⁽¹⁵⁾	1–5 µgL ⁻¹		
	780.0	ICPS	200 µgL ⁻¹	Ti		
Ruthenium		349.9	air-C ₂ H ₂ AAS	0.3–150 mgL ⁻¹	Pd,Rh,Ir,Au,Ag,Cu Ni,Fe,Co,W,Pt	
		392.6		3–1,200 mgL ⁻¹		
		349.9	EAAAS	0.025–0.125 mgL ⁻¹	oxidants	

Element	Notes	Wavelength nm	Source type	Range, or for ICPS only, typical limit of detection ^(13,14)	Interference ^(11,13)	Modifier or repressant
Samarium		429.7	N ₂ O-C ₂ H ₂ AAS	50–250 mgL ⁻¹	ionization.	add 0.2% m/v K ⁺
Scandium		391.2	air-C ₂ H ₂ AAS	3–15 mgL ⁻¹	F ⁻ , oxidants.	K ⁺ added
		361.364	ICPS	0.05–2 µgL ⁻¹	Cr,Cu,Fe,Ti	
Selenium		196.0	hydride AAS	0.2–20 mgL ⁻¹	Hg	
		196.0 204.0	air-C ₂ H ₂ AAS	2–50 mgL ⁻¹		
		196.0	N ₂ O-C ₂ H ₂ AAS	high concn.		
		196.0	EAAAS ⁽¹⁵⁾	0.01–0.05 mgL ⁻¹		Ni(II) to suppress interferences.
	12	196.090 204.0	ICPS	20–100 µgL ⁻¹ 120 µgL ⁻¹	Al,Fe Al,Cr,Fe,Mn	
Silicon		251.6 250.7 288.2	N ₂ O-C ₂ H ₂ AAS	1–400 mgL ⁻¹ 3–1,200 mgL ⁻¹ high concn.		K ⁺ added
		250.690 251.61 288.158 390.55	ICPS	40 mgL ⁻¹ 5–120 mgL ⁻¹ 20–150 mgL ⁻¹	Cr,Fe,Mn,V Cr,Fe,Mg,V	
		328.1 338.3	air-C ₂ H ₂ AAS	0.005–10 mgL ⁻¹ 0.01–20 mgL ⁻¹	Al,Th,MnO ₄ ⁻ , IO ₄ ⁻ ,WO ₄ ⁻	
		328.1 338.3	EAAAS ⁽¹⁵⁾	0.001–0.2 mgL ⁻¹ higher	chloride.	
Silver		328.07 338.29 320.068	ICPS	5–10 µgL ⁻¹ 20 µgL ⁻¹ 20 µgL ⁻¹	Fe,Mn,V Cr,Ti	
		589.0 589.6 330.3	air-C ₂ H ₂ AAS	0.004–30 mgL ⁻¹ 0.01–4 mgL ⁻¹ high concn	ionization.	Cs ⁺ added Cs ⁺ added
		589.0 589.6	direct air-C ₂ H ₂ flame			
		330.23 588.995 589.592	ICPS	10,000 µgL ⁻¹ 20–150 µgL ⁻¹ 6–200 µgL ⁻¹	Cr,Fe,Ti Ti Fe,Ti,V	
Strontium	2	460.7 293.2 689.3	N ₂ O-C ₂ H ₂ AAS	0.02–20 mgL ⁻¹	ionization.	K ⁺ or Cs ⁺ added
	3	460.7	direct air-C ₂ H ₂ flame			

Element	Notes	Wavelength nm	Source type	Range, or for ICPS only, typical limit of detection ^(13,14)	Interference ^(11,13)	Modifier or repressant	
Strontium contd		407.771	ICPS	0.2–2 μgL^{-1} 10 μgL^{-1} 70 μgL^{-1}	Cr,Fe,Ti		
		421.552					
		460.733					
Sulphur	10	180.73	ICPS	80 μgL^{-1} 200 μgL^{-1} 5,000 μgL^{-1}	two working curves, one for volatile, one for non-volatile.		
						182.036	
						469.4	
Tantalum		271.5	N ₂ O-C ₂ H ₂ AAS	4–2,000 mgL^{-1}	Fe, Hf enhance.		
		226.23	ICPS	40 μgL^{-1}	Al,Fe		
Tellurium		214.3	air-C ₂ H ₂ AAS	0.2–80 mgL^{-1} 3–1,500 mgL^{-1} 4–1,500 mgL^{-1}	Ca,Cu,Si,Na,Zn, Zr		
		225.9					
		238.6					
			214.3	Hydride AAS	0.01–0.05 mgL^{-1}	Fe,Cu,Ni,Pt,Pd, Co	
	12	214.2	ICPS	20–50 μgL^{-1}	Al,Fe,Ti,V		
Terbium		432.7	N ₂ O-C ₂ H ₂ AAS	150–650 mgL^{-1}	ionization.	add 0.2% m/v K ⁺	
Thallium		276.8	air-C ₂ H ₂ AAS	0.05–80 mgL^{-1}			
		535.0	direct air-C ₂ H ₂ flame				
		377.6		0.15–1 mgL^{-1}			
		276.8	EAAAS ⁽¹⁵⁾	0.015–0.08 mgL^{-1}	chloride.		
		190.86	ICPS	50 μgL^{-1}	Al,Ti		
Thulium		371.8 nm	N ₂ O-C ₂ H ₂ AAS	3–15 mgL^{-1}	ionization.	add 0.25% m/v K ⁺	
Tin		224.6	air-C ₂ H ₂ AAS	0.1–125 mgL^{-1} 0.2–100 mgL^{-1} 0.2–100 mgL^{-1} 0.5–300 mgL^{-1} 0.2–100 mgL^{-1}	Fe,Co,Cu,Th,Cr, Ti,V		
		235.5					
		254.7					
		266.1					
		286.3					
			286.3	air-C ₂ H ₂ AAS	0.2–100 mgL^{-1}	Fe,Co,Cu,Mn,Cu, Ti,V	K ⁺ added
			224.6	N ₂ O-C ₂ H ₂ AAS	0.05–300 mgL^{-1} 50 mgL^{-1} 1 –600 mgL^{-1}		
			235.5				
			286.3				
			235.5	EAAAS ⁽¹⁵⁾	0.04–0.2 mgL^{-1} 0.02–0.1 mgL^{-1}	PO ₄ ³⁻ , SO ₄ ²⁻ , ClO ₄ ⁻ , Cl ⁻	
		224.6					

Element	Notes	Wavelength nm	Source type	Range, or for ICPS only, typical limit of detection ^(13,14)	Interference ^(11,13)	Modifier or repressant
Tin contd		189.989	ICPS	7–150 μgL^{-1}	Al, Cr, Fe, Mg, Mn, Ti, V	
		283.999		150 μgL^{-1}		
		317.50		250 μgL^{-1}		
		333.00				
Titanium		364.3	$\text{N}_2\text{O}-\text{C}_2\text{H}_2$ AAS	0.4–400 mgL^{-1}	F, Al, Fe	K ⁺ added
		365.4		0.5–500 mgL^{-1}	F, Al, Fe	K ⁺ added
		399.0		1.0–1,000 mgL^{-1}		
		394.9		2.5–2,500 mgL^{-1}		
		334.94	ICPS	3 μgL^{-1}	Ca, Cr, Cu, V	
		336.121 (336.09)		5 μgL^{-1}		
		337.279		10 μgL^{-1}	Ni, V	
	Tungsten		255.1	$\text{N}_2\text{O}-\text{C}_2\text{H}_2$ AAS	3–1,500 mgL^{-1}	Fe
		272.4	6–3,000 mgL^{-1}			
		400.8	10–4,000 mgL^{-1}			
		407.4	high concn			
		207.91	ICPS	20–100 μgL^{-1}	Al, Cu, Ni, Ti	
		239.71		150 μgL^{-1}		
Uranium		385.5	$\text{N}_2\text{O}-\text{C}_2\text{H}_2$ AAS	80–20,000 mgL^{-1}	Fe, Co, Ni, Pb, Al	K ⁺ added
		263.55	ICPS	500 μgL^{-1}	Ca, Fe, Mg, Mn, Ti, V	
		385.96		400 μgL^{-1}	Ca, Cr, Fe	
Vanadium	6	318.4	$\text{N}_2\text{O}-\text{C}_2\text{H}_2$ AAS	0.2–150 mgL^{-1}	Al, Ti	K ⁺ added
		306.6		0.5–400 mgL^{-1}		
		439.0		2–1,200 mgL^{-1}		
		318.5				
	6, 7	318.4	EAAAS ⁽¹⁵⁾	0.025–0.125 mgL^{-1}	oxidants.	
		290.882	ICPS	10 μgL^{-1}	Fe, Mo, Mg, Cr	
		292.402		0.5–25 μgL^{-1}	Fe, Mo, Ti, Cr	
		309.31		0.3–10 μgL^{-1}	Al, Cr, Fe, Mg	
310.230	10 μgL^{-1}	Fe, Ti, Ni				
	311.071	3–20 μgL^{-1}	Fe, Mn, Ti			
Ytterbium		555.6	direct air- C_2H_2 flame			
		398.8				
		369.4				
		328.9				
	398.8	$\text{N}_2\text{O}-\text{C}_2\text{H}_2$ AAS	1–5 mgL^{-1}		K ⁺ added	
Yttrium		410.2	$\text{N}_2\text{O}-\text{C}_2\text{H}_2$ AAS	50–250 mgL^{-1}	ionization.	add 0.2% m/v K ⁺
		407.7		(1.2 × less sensitive)		
		362.1		(2.2 × less sensitive)		
Zinc		213.9	air- C_2H_2 AAS	0.003–5 mgL^{-1}	Si, Cu, Fe, Cu	(Mg ²⁺ and PO ₄ ³⁻ may be added)
		307.6		high concn		

Element	Notes	Wavelength nm	Source type	Range, or for ICPS only, typical limit of detection ^(13,14)	Interference ^(11,13)	Modifier or repressant
Zinc contd		213.9	EAAAS ⁽¹⁵⁾	0.2–1.25 μgL^{-1}		
		202.55	ICPS	2–15 μgL^{-1}	Al,Cu,Fe,Ni,Ti,V	
		206.191		10 μgL^{-1}	Al,Cr,Fe,Ni,Ti	
		213.856		5–15 μgL^{-1}	Cu,Ni,Al,Fe,Ti,V	
		239.71				
		330.25		high μgL^{-1}		
	334.50					
Zirconium		360.1	N ₂ O-C ₂ H ₂ AAS	5–2,000 mgL^{-1}	Fe,Ni,NH ₄ ,Cl ⁻ , F ⁻ ,SO ₄ ²⁻	
		339.189	ICPS	10 μgL^{-1}	Cr,Fe,Ti,V	
		343.8		20 μgL^{-1}	Ca,Cr,Fe,Mn,Ti	
		349.6		5–25 μgL^{-1}	Hf,Mn,Ni,Ti,V	

Notes

1. There are safer ways of determining this element, using radiochemical measurements.
2. With $3,000 \mu\text{g mL}^{-1} \text{K}^+$ added.
3. Oxide molecular band heads can also be used. For wavelengths see Pearce R W B and Gaydon A G. Identification of Molecular Spectra. Chapman and Hall 1950.
4. A doublet.
5. With $2,000 \mu\text{g mL}^{-1} \text{Na}^+$ added.
6. A triplet.
7. Carbide formation in the furnace should be guarded against.
8. Rarely determined by ICPS due to problems with argon purity and impurities in the air.
9. Rarely determined by ICPS due to problems with air.
10. Different analytical working curves for volatile and non-volatile substances.
11. Many users have worked out corrections for interferences. Many are negligible in effect.
12. Hydride or cold vapour generation similar to AAS can be used for these elements and greatly lowers the limit of detection.
13. May be instrument dependent.
14. May be changed by evaporation or dilution.
15. Range dependent on amount injected. Typical value given.
16. "Pyrocoated" or "total pyrolytic" cuvettes should be used.
17. Use of a L'vov or similar platform may reduce this interference.

DC Arc Sources

For information, see Emission Spectrophotometric Multielement Methods of Analysis for Waters, Sediments and other materials of interest to the Water Industry 1980. HMSO in this series, and references therein.

Concentration Techniques

Two basic techniques are listed in detail, solvent extraction and evaporation. Two others are discussed, ion exchange chromatography and carrier concentration precipitation. The latter, which can collect very low levels of many elements has been used with DC arc emission and classical chemical methods, is now also being used with AAS, ICPS etc. Full details of these two latter techniques are not given here.

It should be noted that multiple sample portions may be necessary if many different analyses are to be carried out on the same sample. Elements often coextract, so it is unwise to extract in succession at different pH or sequentially with different reagents in the hope of separating more than one set of determinands from one sample portion. There is, however, a well proven extraction technique for use with multielement methods such as ICPS and DC arc emission in which samples are chloroform extracted using a mixture of reagents, the pH being increased in steps from 0 to 12, the extracts are then bulked prior to back extraction into a suitable acid (eg nitric). The commonest such mixed reagent is a mixture of dithizone and 8-hydroxyquinoline with or without diethyldithiocarbamate. Usually the 8-hydroxyquinoline (in acetic acid) and a solution of sodium diethyl dithiocarbamate are added to the sample and dithizone is dissolved in the chloroform extractant. Any precipitates are filtered off and added to the chloroform extract for resolution. The use of cupferron has been kept to a minimum as chloroform solutions of some metal cupferronates decompose violently on warming.

Some elements are often lost during evaporative concentration. The commonest evaporative losses are:—

In the presence of chloride (or other halides):
Ge, Sn, As, Sb, Se, Te, Hg.

In the presence of oxidants:
Re, Ru, Os, Au and if halide is present Cr, Se and Te.

In the presence of acids:
boron and all volatile acids.

In the presence of alkalis:
 NH_3 , PH_3 .

In the presence of fluorides:
B, Si, As, Sb are at risk. P may be at risk if ignited under some conditions.

Some elements can be concentrated by special volatilization techniques, provided care is taken to avoid loss of the volatile phases mentioned above.

Many more may be lost if heated beyond dryness, eg Mo, Zn, Cd.

Summary of Techniques

Where not given in brackets, the optimum pH range should be ascertained and used. Extractions should be to completion. Do not try to separate elements by sequential extraction at different pH using the same reagent. For additional advice on ion exchange and carrier concentration see notes at the end of this section.

Element	Concentration method
Lithium	} Evaporation of a dilute acid solution or ion exchange.
Sodium	
Potassium	
Rubidium	
Caesium	
Francium	

Element	Concentration method
Beryllium	Extraction with 8 hydroxyquinoline into chloroform.
Magnesium	} Evaporation of a dilute acid solution or ion exchange.
Calcium	
Strontium	
Barium	
Radium	
Boron	Evaporation of an alkaline solution or distillation as trimethyl borate (see the specific booklet in this series).
Aluminium	} Extraction with 8-hydroxyquinoline into chloroform (at pH > 4) or ion exchange.
Scandium	
Yttrium	
Lanthanum	
All lanthanides	
Actinium	Evaporation of a dilute acid solution.
Thorium	Extraction with 8-hydroxyquinoline or cupferron into chloroform (Cupferron extracts must be kept at < 10°C and back extracted into acid at once. Thorium cupferronate explodes if warmed above 15°C).
Protactinium	Possibly by extraction with cupferron into chloroform—no clear information.
Uranium	Extraction with 8-hydroxyquinoline or with a disubstituted dithiocarbamate into chloroform. Keep cold and back extract at once.
Titanium	} Extraction with 8-hydroxyquinoline or cupferron into chloroform. (Cupferron extracts must not be evaporated but kept cold and back extracted into acid at once without storage.)
Zirconium	
Hafnium	
Vanadium	Extraction with 8-hydroxyquinoline or with a disubstituted dithiocarbamate into chloroform.
Niobium	} Extraction with cupferron and back extraction. Keep cold and back extract at once.
Tantalum	
Chromium	Extraction of the 3 valent state with a disubstituted dithiocarbamate into chloroform.
Molybdenum	Extraction of the ethylxanthate, a disubstituted dithiocarbamate or with 8-hydroxyquinoline (at pH 5-6) into chloroform.
Tungsten	Possibly by extraction with dithizone into chloroform—no clear information.
Manganese	Extraction with 8-hydroxyquinoline or with a disubstituted dithiocarbamate into chloroform. Extraction with dithizone has been used but tends to form emulsions.
Technetium	} Extraction with dithizone into chloroform.
Rhenium	
Iron	Extraction with dithizone (pH 7.5-8.5) (2 valent), 8-hydroxyquinoline (pH 2-3) (2 and 3 valent) or with a disubstituted dithiocarbamate (3 valent) into chloroform.
Cobalt	Extraction with dithizone (pH 7-9) (2 valent—reduce 3 first, 8-hydroxyquinoline (pH > 7) (2 valent) or with a disubstituted dithiocarbamate into chloroform (3 valent).
Nickel	Extraction with dithizone (pH 7-8), 8-hydroxyquinoline (pH > 7) or with a disubstituted dithiocarbamate into chloroform.
Ruthenium	Volatization of RuO ₄ in a closed apparatus. RuO ₄ can explode with organic matter.

Element	Concentration method
Rhodium	Extraction as disubstituted dithiocarbamate into chloroform.
Palladium	Extraction with dithizone (pH 0-3), 8-hydroxyquinoline or a disubstituted dithiocarbamate into chloroform.
Osmium	Volatization of OsO ₄ in a closed apparatus. (OsO ₄ vapour can blind).
Iridium	Possibly evaporation in acid solution—no clear information.
Platinum	Extraction with dithizone (pH 0-3) (2 valent) or with a disubstituted dithiocarbamate into chloroform. Oxidation state dependent.
Copper	Extraction with dithizone (pH >4), a disubstituted dithiocarbamate or 8-hydroxyquinoline (pH 3-7) into chloroform.
Silver	Extraction with dithizone (pH >1.5) or with a disubstituted dithiocarbamate into chloroform.
Gold	Extraction with dithizone (pH 3-6) or with a disubstituted dithiocarbamate into chloroform.
Zinc	Extraction with dithizone (pH 6.5-10), 8-hydroxyquinoline or with a disubstituted dithiocarbamate into chloroform.
Cadmium	Extraction with dithizone (pH >10), 8-hydroxyquinoline or with a disubstituted dithiocarbamate into chloroform.
Mercury	Reduction to metal, volatization and collection on Gold, or Extraction with dithizone (pH >2.0), 8-hydroxyquinoline or with a disubstituted dithiocarbamate into chloroform.
Gallium	Extraction with 8-hydroxyquinoline (pH >2) or with a disubstituted dithiocarbamate into chloroform.
Indium	Extraction with dithizone (pH 5-6), 8-hydroxyquinoline (pH >4) or with a disubstituted dithiocarbamate into chloroform.
Thallium	Extraction with dithizone (pH >10.7), or 8-hydroxyquinoline into chloroform.
Silicon	Evaporate in alkaline solution, or volatilize the fluoride.
Germanium	Extraction of Ge Cl ₄ into CCl ₄ from 8.5 M HCl solution, or volatilize the hydride.
Tin	Extraction with dithizone (pH 5-8), 8-hydroxyquinoline or with a disubstituted dithiocarbamate into chloroform. Oxidation state dependent. Volatilization as tetrachloride, rarely as hydride.
Lead	Extraction with dithizone (pH 8-10), 8-hydroxyquinoline or with a disubstituted dithiocarbamate into chloroform.
Arsenic	Extraction with disubstituted dithiocarbamate into chloroform, or reduce to arsine, volatize and if necessary collect with silver nitrate.
Antimony	Extract with a disubstituted dithiocarbamate or 8-hydroxyquinoline or reduce to stibine and volatilize etc.
Bismuth	Extract with dithizone (pH 2-8), a disubstituted dithiocarbamate or 8-hydroxyquinoline (pH 4-5) into chloroform.
Selenium	Distil off SeOBr ₂ from an HBr- Br ₂ mixture, or volatilize the hydride.
Tellurium	Distil off TeOBr ₂ from an HBr- Br ₂ mixture, or volatilize the hydride.
Polonium	Extraction with dithizone (pH 2-4) into chloroform.

For further information on solvent extraction see

- Pinta M Récherche et Dosage des Elements Trace. Dunod. Paris.
Detection and Determination of Trace Elements. IPTS.
Jerusalem.
- Welcher F J Organic Analytical Reagents 4 vols. Van Nostrand. New York.

Ion Exchange or Ion Exchange Chromatography

It is possible to concentrate ions (positive or negative) on an appropriate resin cartridge or column and subsequently elute them with a strong acid or strong alkali solution. It is also possible using appropriate columns and eluents to separate the ions during elution. Problems are sometimes encountered with zwitter ions or betaines (eg $(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{AsO}_3^-$), but these may sometimes be absorbed using ion pair techniques. It must also be remembered that many metals, especially transition metals and lanthanides, form complex anions (such as cyanides), metallates and thiometallates etc which are sometimes sufficiently stable to be absorbed and sequentially eluted as separate entities. Chromatography on resins, carrying chelating groups such as amines, iminodiacetic acid, or dithiocarbamates has also been used.

For further information see:

The Determination of Anions and Cations, Transition Metals. Other Complex Ions and Organic Acids and Bases in Water by Chromatography, HMSO, in this series.

Carrier Concentration Techniques

The basis of this technique is the addition to the sample of a relatively small amount (usually milligrams) of a salt of a metal which is not being determined, which is then precipitated, often by reverse precipitation (sample plus addition poured into excess precipitant). Neither the carrier metal nor the element to be concentrated should be soluble in an excess of the precipitant and, in the latest methods, the reduction potential should not be high enough to reduce the determinand to a volatile state. This latter requirement is usually achieved by control of the pH of the solutions. The carrier should precipitate in a form which either adsorbs or dissolves a compound of the element to be concentrated or is isomorphous with it so that they cocrystallize.

This accumulation of the determinand by the carrier precipitate need not be complete, but it must be easily reproducible and in an appreciable amount (analogous to solvent extraction). For application to Flame and ICPS type sources the precipitate must also be readily and completely soluble in some suitable reagent, without loss. Standards and control samples must be put through the whole procedure in the same way as samples. Reagent blanks are essential.

For methods requiring solid samples, samples are prepared by igniting the precipitate, mixing thoroughly with a standard amount of graphite, charging to an undercut graphite electrode and using as the cathode in a DC arc. For methods requiring a liquid sample, the precipitate is dissolved in a suitable acid and, made up to a standard volume.

The technique can also be used to separate a determinand from interfering substances.

Typical examples of carriers, precipitants and resolution reagents with examples of determinands so concentrated are given below.

Added carrier	Reagent for precipitation	Reagent for resolution	Typical determinand carried
Aluminium	ammonia solution	hydrochloric or nitric acid	Cr(III), Fe(III), Zr, Be, Hf, Ti, Th, U(VI), lanthanides, also SiO ₂ etc
Iron (III)	ammonia solution	hydrochloric or nitric acid	Al, Cr(III), Cd, Co, Cu, Mn(II), Ni, Pb, Zn
Lanthanum	ammonia solution plus H ₂ O ₂	hydrochloric or nitric acid	Al, Be, other lanthanides etc
Bismuth	sodium sulphide solution	nitric acid	Ag
Aluminium plus excess 8-hydroxyquinoline in acetic acid	ammonia solution	hydrochloric or acetic acid	Mo(VI), W(VI), Ca, Sr, Ba
Platinum	formic acid	aqua regia (HCl + HNO ₃)	Cu Ru, Os, Rh, Ir, Pd, Pt may also be concentrated this way if sufficiently pure Pt or Pd respectively are available.
Iron + Palladium (see Anal Chim Acta 207, 219-9, 1988)	sodium borohydride + ammonia to pH 8-9	aqua regia	Ag, As, Bi, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Se, Sn, Te, Tl, Zn, Au, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sn, Tl, V, Zn.
 (see Anal Chem 87, 2815-8, 1985)	sodium borohydride + sodium hydroxide to pH 13		Ru, Os, Rh, Ir, Pd, Pt may also be concentrated this way if sufficiently pure Pt or Pd respectively are available.

Manganese dioxide from a Mn(II) salt, plus a permanganate or chlorate has also been used as a carrier.

Manganese has also been carried on an antimony (III) salt, using sulphide as precipitant. There are many more instances of this technique in the older literature.

Department of the Environment

Standing Committee of Analysts

Members assisting with this booklet:

S Bailey	1	E J Newman	1
S Blake	1	H G M Parry	1
H B Barnhoorn	2	C J Pickford	1
F B Basketter	2	L R Pittwell	1, 2
M L Berrow	1*	L D Purdie	2
G A Best	2	G K Phillips	2
G W Bryan	1	J W Readman	1
B Buckley	2	J P Riley	1, 2
J D Burton	1	M G Rolph	1
E C Conchie	1	I R Scholes	1
P A Chave	2	B L Sharp	1
E Crowther	1	D Taylor	2
B T Croll	2	K C Thompson	1, 2
M H I Comber	1	R Toft	1
I D M Davidson	2	G Topping	1
E Dryburgh	2	C van den Berg	1
M C Finniear	2	A M Ure	2
A M Gunn	1	D Vaughan	1
J Haines	1	R J Vincent	2
D J Harper	1	P J Walker	2
M R Hurcombe	2	A Ware	2
P Jowett	1	R West	1
J G Jones	2	J G Welsh	1
R Law	2	D A Williams	2
D Lambie	1	D C Wilson	1
R H Llewellyn	1	K Wheatstone	2
D Miles	1	R Wood	2
J J Monaghan	2	M Woods	1
C J Nash	1		

1. Working group member
 2. Main committee member contributing.
- * Died whilst still a member.

Address for correspondence

However well a method is tested there is always the possibility of a user encountering a hitherto unreported problem.

Correspondence about these methods should be addressed to:—

The Secretary
The Standing Committee of Analysts
Department of the Environment (Drinking Water Inspectorate)
Romney House
43 Marsham Street
LONDON
SW1P 3PY



HMSO publications are available from:

HMSO Publications Centre

(Mail, fax and telephone orders only)

PO Box 276, London, SW8 5DT

Telephone orders 071-873 9090

General enquiries 071-873 0011

(queuing system in operation for both numbers)

Fax orders 071-873 8200

HMSO Bookshops

49 High Holborn, London, WC1V 6HB

(counter service only)

071-873 0011 Fax 071-873 8200

258 Broad Street, Birmingham, B1 2HE

021-643 3740 Fax 021-643 6510

Southey House, 33 Wine Street, Bristol, BS1 2BQ

0272 264306 Fax 0272 294515

9-21 Princess Street, Manchester, M60 8AS

061-834 7201 Fax 061-833 0634

16 Arthur Street, Belfast, BT1 4GD

0232 238451 Fax 0232 235401

71 Lothian Road, Edinburgh, EH3 9AZ

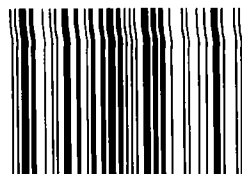
031-228 4181 Fax 031-229 2734

HMSO's Accredited Agents

(see Yellow Pages)

and through good booksellers

ISBN 0-11-752375-5



9 780117 523753