

# **A Survey of Multielement and Related Methods of Analysis for Waters, Sediments and Other Materials of Interest to the Water Industry 1980**

**Methods for the Examination of Waters and Associated Materials**

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### Contents

Warning to Users	2	7. Neutron Activation Analysis	32
About this series	3	8. Chromatography and Electrophoresis	33
Introduction	4	8.1 Liquid Adsorption Chromatography	33
1.1 General Information	7	8.2 Ion-exchange Chromatography	33
1.1 Summary	7	8.3 Gas Chromatography	33
1.2 Examination of an Unknown Material	9	8.4 Electrophoresis	34
1.3 Chemical Pretreatments	10	9. Multiple Channel Automatic Analysers	35
1.4 Instrumental Drift	11	10. Thermogravimetry and Differential Thermal Analysis	36
1.5 Hazards	11	11. References	37
1.6 Recovery of Spent Development Solution	11	12. Determinand Index	43
2. Electrochemical Methods	12	<b>Tables</b>	
2.1 Polarography	12	1 A selection of typical Polarographic Half Wave Potentials in various solutions.	13
2.2 Anodic Stripping Voltametry	15	2 Ion Selective and related Electrodes for Water and Effluent Analysis	17
2.3 Potentiometric Stripping Analysis	17	3 Elements determined by Atomic Absorption Spectrophotometry, with their usual wavelengths	20
2.4 Ion Selective Electrodes	17	4 Elements readily determined by Flame Photometry with their usual wavelengths	23
3. Spectrophotometric Methods	20	5 Elements determined by Ultra Violet-Visible Emission Spectroscopy	23
3.1 Atomic Absorption Spectrophotometry	20	<b>Figures</b>	
3.2 Atomic Fluorescence Spectrophotometry	21	1 A simple polarograph circuit diagram	14
3.3 Ultra Violet and Visible Region Emission Spectrography including Flame Photometry and Plasma Emission	22	2 Typical anode stripping voltametry Read-out Charts	16
3.4 X-Ray Fluorescence Spectrophotometry	22	3 Typical X-ray Diffractometer diagrams	28-29
3.5 Electron Microprobe X-ray Spectrometry, Auger Electron Spectrometry, and X-ray Photoelectron Spectrometry	25	Address for Correspondence	45
3.6 Gamma Ray Spectrometry (and related radiochemical methods)	25	Responsibility for this method	45-46
4. X-Ray Diffraction	26		
5. Reflectance, Ultra Violet and Infra Red Absorption Spectrophotometry	30		
6. Spark Source Ion Mass Spectrometry	31		

# 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 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. 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. Among such publications are: 'Code of Practise for Chemical Laboratories' and 'Hazards in the Chemical Laboratory' issued by the Royal Society of Chemistry, London; and 'Safety in Biological Laboratories (Editors Hartree and Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London, which includes biological hazards.

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

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 radio chemical 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 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 the hazard may exist and take reasonable precautions, rather than to assume that no hazard 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 addition, the series contains short reviews of the more important analytical techniques of interest to the water and sewage industries. This booklet is one such review. 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*

*4 December 1980*

# A Survey of Multielement and Related Methods of Analysis for Waters, Sediments and Other Materials of Interest to the Water Industry, 1980

## Introduction

The majority of booklets in this series contain tested and recommended methods for the analysis of waters, effluents and related solids for one or more determinands. Other booklets in the series supply additional information on techniques used by many laboratories in the water industry and are intended to help users derive the fullest benefit from the available equipment. A few booklets, this being one of them, are intended to provide information on techniques which have been well tried and tested in other branches of industry, which may also be useful for certain analytical problems in the water industry. Many of these techniques are almost unknown to the water industry. Some of them are applicable in all laboratories, others are more suited to a central service laboratory, whilst for some of them, it is suggested that such determinations might best be contracted out to specialists. Even so, it is useful to know that such techniques exist, against the day when a problem requiring such an analysis arises.

Whilst the bulk of the analysis carried out by the water industry is concerned with waters, sewage and effluents, there are occasions when other materials such as pipes, concrete, soil etc have to be examined. Brief information on some of the more useful methods for the examination of such samples has been also included.

This booklet has three main objectives,

- (i) to provide a short summary and comparison of various methods for multi-determinand analysis.
- (ii) to provide sufficient information to enable the commoner of these methods, for which separate reviews or detailed methods have not been included in this series, to be used once the usual preliminary development work on the specific determination has been carried out.
- (iii) to provide a short summary and comparison of methods used to identify compounds or phases.

Where the method is the subject of a separate review booklet, which is part of this series, a brief description has been included for purposes of comparison, with reference being made to the other booklet where information, in greater detail, may be found. The information herein is intended as an introduction and guide, rather than as a set of detailed instructions on how to carry out such analyses. For many methods such as are described here, detailed instructions are supplied, at least in part, by the instrument manufacturers, and carrying out an analysis consists chiefly in converting a sample to a convenient form, inserting it into the apparatus and following the makers instructions. Analytical results are obtained by comparison with results from standard samples which have been submitted to an identical procedure.

How this booklet is used, depends on the analytical problem in hand. Basically, there are two kinds of chemical analytical operations, those to determine whether certain substance is. Even in this latter instance, there is usually a sample history, sample appearance and ancillary local information which reduce the number of possibilities. Users who are interested in finding a suitable method for a specific determinand are referred to the determinand index at the back of this booklet. Users who require to analyse small inclusions, or thin films are referred to section 3.5. Users who wish to identify specific phases of a compound are referred to sections 4, 5, 8.1 and 10. Users who wish to find out what the sample is, are referred first to section 1.2 and then to sections such as 3, 4, 5 and 8. However it should not be assumed that the above advice exhausts all the possibilities, sections 6 and 7 have not been mentioned but can be useful when equipment is available.

There are two good reasons for multielement analysis for trace elements. Firstly, although the initial cost may be high, it is often cheaper to carry out a number of determinations either simultaneously, or in quick succession on the same sample than to perform each determination separately. This advantage increases as the number of such samples analysed per day increases. Secondly, there are times when it is useful to know what elements are present in a sample, in order to know, either which are worthy of

accurate determination, or whether any elements likely to interfere with a specific determination are present in significant amounts.

There are no absolutely universal methods which will accurately determine every known element. Some methods are satisfactory for a very large number of elements, others for only a few; but sometimes it may be easier to obtain accurate results with the latter methods than with the more universal methods, or the apparatus may cost less or be more readily available. Some methods supply additional information on valence state, or compounds present. Analytical problems vary. There are times when a complete scan for as many elements as possible may be advisable, whilst at other times it may only be necessary to check for a few elements. This review therefore describes methods suitable for identifying and, or, determining several elements in the same sample. Some methods described can determine a very large number of elements indeed. Most of these methods are capable of giving accurate quantitative as well as qualitative results, provided enough attention is given to detail; many can also give a permanent record which can be kept and re-examined later if further information or a check on the analysis is required.

Of all the known terrestrially occurring natural elements, almost all have been detected in at least one natural water sample. Effluents may contain almost every element, dependent on source. Some of the methods described were originally developed for handling liquid samples, or for converting liquid samples to an acceptable solid form. For many of these methods solvent extraction, carrier precipitation, or similar concentration techniques have been developed which can significantly change the range of the method. The sensitivity of each method varies from element to element, and interference effects need to be considered; but these can often be overcome by the use of appropriate preliminary concentration or separative procedures.

Sometimes, it is useful to know not only the elements present, but also the actual compounds present and for solid samples the phase. Techniques have been devised for such determinations which are also included.

Few laboratories can afford more than one or two of the instruments described in this booklet; but, with the grouping together of laboratories belonging to Water Authorities, Regional Councils and so on, consideration might be given for the siting of special equipment in certain laboratories which would be available to the whole organization for joint inter-authority cooperation and for occasional assistance agreements. Even so, consideration should be given not only to the suitability of equipment for a specific problem, but also to its general usefulness. Thus whilst an emission or X-ray fluorescence spectrograph might primarily be used for the analysis of sewage sludge, it could also be available for investigation for unknown impurities, and special investigations of deposits, material failures, evaluation of reagent purity, analytical interferences and the like; in addition, there are other special routine analyses requiring such equipment.

In this field change and reverse change is often the order of the day. In recent years some instrument makers have tended to concentrate on highly automated equipment to the exclusion of some of the simpler models. This may confer some advantages, but it also has its disadvantages. Thus a photoelectric direct reading UV emission spectrometer is quicker and cheaper to operate for a large sample throughput than a photographic model, and often gives more precise results (accuracy may be partly dependent on choice of analytical wavelength, knowledge of and ability to correct for interference effects, and such variables as electric power supply and film quality); but it cannot detect elements for which it has no phototube, nor can it be used for those elements for which the phototube is overloaded by a strong matrix, background or interferent emission. Many photographic instruments can cope with such problems because a large range of spectrum is used, which allows a general scan to be made, or an alternative line to be used for the analysis. Similarly unforeseen hazards such as a change in background or interferences can be more readily noticed by skilled observers when using photographic instruments. A phototube instrument of corresponding versatility capable of a qualitative - semiquantitative analysis of an unknown material would require many hundred analytical channels unless fitted with a moving scanning phototube. Scans take time and may be unreliable due to volatility differences; emission varies with time unless a constantly fed flame such as is found in plasma emission spectrometer is used. For some purposes X-ray fluorescence can be used instead. It should not be forgotten that, given good workshop facilities and determination, some quite sophisticated instruments can be made or built up from commercially available parts, and that the older technical literature contains much useful information. Secondhand equipment is available, as are also parts for assemble-yourself instruments. Instrument design is always changing, thus scanning and film loading plasma emission instruments have recently come on the market, but the price of film has risen. When a new technique is first developed, its advantages are more apparent than its disadvantages. It usually takes several years for

interference effects and other problems to become apparent. Investigation of new ideas needs therefore to be as thorough as possible before adoption for routine use.

The following sections describe the principles of the more important major methods, give some information on relative costs and ease of construction, discuss the various advantages and disadvantages including sensitivity and interferences, suitability for various types of sample, and ways in which apparent limitations have been overcome. No overall comparison has been attempted. Some of the methods mentioned below are also the subject of other specialist reviews published in this series, or are the basis of specific methods for individual elements. In the United States of America, many such methods have official status see Refs 11 and 12. References which are collected together at the end are subdivided by method. Where a reference covers more than one technique, it is given under the first section to be listed. Additional bibliography has also been included grouped by technique. For general comparative references see Refs 1-9. A few journals regularly carry useful review articles on analytical chemistry. These are listed after the last reference.

# 1 General Information

In addition to summarized information on the actual methods of analysis, which, for convenience, is grouped by type of method, some more general information applicable to many types of instrumental methods has been collected in this section.

## 1.1 Summary

The following is a brief summary of the various methods described in this booklet with some evaluation of their uses and usefulness.

**Electrochemical Methods** – all are useful for special applications.

**Polarography** (Refs 13, 14) – the sample must be capable of being brought into solution – a true multielement method but the number of suitable elements is severely restricted. Prior concentration techniques can be added.

**Anodic Stripping Voltammetry** (Refs 15–25) – as polarography but more sensitive, can sometimes differentiate between complexes of the same element, but is subject to interference effects.

**Potentiometric Stripping Analysis** (Ref 26) – as polarography.

**Ion Selective Electrodes** (Refs 27–45) – a series of simultaneous single analyses can be devised. Useful for remote monitoring; but very subject to interference effects. Only a very few electrodes are reliable enough for routine use, and of these, several only give an accurate order of magnitude figure.

### **Spectrophotometric Methods**

**Atomic Absorption Spectrophotometry** (Refs 46–53) – one of the most widely used techniques in the water industry and the subject of a separate booklet in this series. It is really a series of successive single element determinations using one instrument. The sample must be capable of being brought into solution. The determinand must have a Ground State Spectral line within the range of the instrument (usually 190–800 nm). Prior concentration techniques can be added. For optimum operation samples are pretreated together and then all are analysed in succession for one element, then all for the next and so on. For a list of elements determinable see table 3. In the long term there may be cheaper methods if many regular analyses for a large number of determinands are required.

**Atomic Fluorescence Spectrophotometry** (Refs 46, 54–58) – similar to Atomic Absorption Spectrophotometry, but far less widely used. Most instruments have been home made. It is said to be superior to AAS for the determination of certain elements. It is mentioned in the booklet on Atomic Absorption Spectrophotometry.

**Ultra-Violet – Visible Emission Spectrophotometry** (Refs 10, 46, 59–80) – often regarded as three separate techniques:

- Flame Emission Spectrophotometry,
- DC Arc or Spark Emission Spectrophotometry, and
- Plasma Emission Spectrophotometry.

All are true multielement methods of analysis, and can use either solid or liquid samples. Whilst basically the same technique with different types of sample excitation, Flame and Plasma Emission can be used directly on water samples provided the concentration of determinand is high enough, which, for the elements usually determined by flame emission spectrophotometry, is often the case. DC Arc or Spark Emission can be used with liquid samples, but is best suited to solid samples such as soils and dried sludges, but,



if concentration techniques are used, solid samples are not difficult to prepare on a routine basis. It is ideal for those very refractory substances such as molybdenum carbide (formed by ignition of many molybdenum containing samples). Only the alkali and alkaline metals, and about a dozen other elements give reliable flame emission spectra. With the DC Arc or Spark and Plasma Emission, most but not all elements give good excitation (about 12 are almost impossible to analyse for, about 5 more including mercury may not be very sensitive unless special techniques are used), some substances are difficult to volatilize as solids but can be determined if brought into solution. More elements are determinable using Plasma Emission, than Arc, and least with Spark Emission. For details see tables 4 and 5. Flame Emission Spectrophotometry is also mentioned in the booklet on Atomic Absorption Spectrophotometry. Interferences occur but can be corrected for exactly. The degree of interference encountered is instrument dependent.

As both multipurpose and single purpose machines are available for the various different techniques the following specialized information is of use:

Plasma Emission – uses liquid samples or dissolved solids, will determine almost all elements except halides and noble gases, though concentration levels determinable depend on the spectrometer used, and the type of read out employed.

DC Arc Emission – uses solid samples, or solidified extracts, precipitates, or evaporites from liquid and will determine most elements. Also used for a special lubricating oil maintenance checking procedure.

AC Arc and Spark Emission – at present only used for analysis of certain solid metal samples.

Flame Emission – only used for alkali, alkaline earth and a few other metal determinands on liquid samples or dissolved solids.

Fixed Photomultipliers – readily available, but, unless coupled with an alternative system of measurement, cut out the ability to scan for unexpected impurities.

Scanning Photomultiplier – enables scanning for unexpected impurities, can also be used alone for single element determinations, but should be used with a continuously fed source such as plasma emission for reliable results to be obtained. The addition of fixed photomultipliers is also worthwhile.

Film Read-out – complicated, the equipment is usually cheap and very versatile. Given skilled routine technicians and attention to detail this technique can be made as accurate as photomultipliers; some photomultiplier instruments can be fitted with an additional film holder to provide scanning for unexpected impurities. The operating cost is dependent on the price of photographic film. Gives a permanent record, and wider choice of analytical lines than fixed photomultipliers do.

Vacuum Path Instruments – only worthwhile if carbon, nitrogen, phosphorus, sulphur, mercury and a few other elements are analysed for routinely in quantity along with the normal spectrographically determined elements, in which case, it is worth considering.

Prism Dispersion – is non uniform, but has best resolution in the far ultra violet, which region contains many useful spectrum lines, especially if carbon is present in the sample and liable to cause band spectra.

Grating Dispersion – is uniform for curved gratings which also focus lines without the use of a lens. The spectral dispersion is not uniform for plane gratings.

The choice of dispersion is usually a question of maker, elements determined and price. Both types are good.

**X-Ray Fluorescence Spectrophotometry (Refs 80–84)** – a true multielement method of analysis, best done with solid samples, though liquids are not impossible. The first ten elements in the periodic table are impossible to analyse for, about ten more present problems which can be overcome. Much used for solid analysis outside the water industry.

**Electron Microprobe X-ray Spectrometry** – not a routine method, but ideal for special problems involving small inclusions in other material, a true multielement method of analysis. Needs solid samples. Not suitable for the first ten elements in the periodic table, sensitivity improving with increase in atomic number.

**Auger- and Photo- Electron Spectrometry** – not routine methods, very similar to Electron Microprobe X-ray Spectrometry in use and technique, but can determine all elements except hydrogen and helium, with a preference for those of low to medium atomic number. Very few instruments are available, but these are often available as part of an analytical service.

**X-Ray Diffraction Crystallography, Reflectance and Infra Red Absorption Spectrophotometry** (Refs 10 and 76-79) – three methods for identifying and analysing for compounds rather than analysing for elements. All need solid samples, preferably in powdered form.

**Ultra Violet and Infra Red Absorption Spectrophotometry** (Refs 89-91) – well known techniques for the identification of organic compounds which can also be used for some inorganic materials. Reflectance is used for some opaque materials.

**Spark Source Ion Mass Spectrometry (Refs 92-95), Gamma Ray Spectrometry and Neutron Activation** (Refs 96-105) – specialized methods ideal for some types of trace element analysis or if isotopic abundance is important. Need solid samples. Neutron Activation techniques are the subject of a specialist review booklet in this series.

**Chromatography** (The major chromatographic techniques are the subjects of several booklets in this series).

**Liquid Adsorption Chromatography** (Refs 106 and 107) – usually only used as a pretreatment, samples must be brought into solution.

**Ion-exchange Chromatography** (Refs 110 and 111) – useful for mixtures of cations or anions. Samples must be brought in aqueous solution.

**Gas Chromatography** (Refs 108 and 109) – rarely used for metals but sometimes useful if volatile derivatives can be safely handled, especially useful for organometallic and organometalloid analysis. Samples must be volatile.

**Electrophoresis** (Ref 112) – very similar to simple and ion-exchange chromatography.

**Multiple Channel Automatic Analysis** – a series of simultaneous single element analyses on liquid samples.

**Thermogravimetric and Differential Thermal Analysis** (Refs 113 and 114) – techniques useful for identifying compounds that decompose on heating.

## **1.2 Examination of an Unknown Material**

There is no single ideal scheme for the examination of an unknown material, but the following advice may be helpful. No sample is completely unknown. Some information is always available to guide the analyst. Usually, enough is known to decide whether the sample is organic or inorganic; though instances are known where this information was misleading; for example, a river sediment which contained crystals of explosive, a blue powder found in a drain which turned out to be distemper, or a slab, thought to be brass, which was, instead, pyrite. The first step with most unknown samples should be careful physical inspection, tests such as heating, and the effect of water being cautiously carried out on very small samples. Examination by eye with a hand lens or low power microscope can be useful.

The identification of organic substances is not dealt with in this booklet. However, it is often necessary to identify the inorganic constituents of a substantially organic material. If only an elemental analysis is necessary and the sample can be safely burnt, the Schoniger-oxygen flask method of ashing (Ref 115) may be suitable; otherwise oxidation with a series of progressively more powerful oxidants such as sulphuric, nitric and perchloric acids, using binary mixtures as intermediate reagents may be required. If in doubt, always carry out a pilot test on a very small quantity of sample before treating a larger amount. For the identification of the elements present in unknown inorganic solids or evaporated residues, either emission spectroscopy, or X-ray fluorescence spectrophotometry (XRF) methods are usually used.

Some laboratories carry out examination by X-ray diffraction (XRD) and infra-red absorption spectrophotometry (IR) at an early stage in the proceedings. The XRF, XRD and IR techniques have the advantage that usually the sample is not decomposed during the analysis. Further analysis is dependent on the sample and the degree of identification necessary. Emission spectroscopy will not detect every element, nor will X-ray fluorescence spectrophotometry, though there are very few elements that cannot be determined by a combination of the two. On the other hand, anions usually have to be

detected individually. Examination with various microscopy techniques is also of use for some samples and should not be forgotten (Ref 117).

### 1.3 Chemical Pretreatments

Chemical Pretreatments are used for three purposes, to get the sample into a form suitable for the main quantifying technique, to separate or concentrate the determinands and to remove interferences. Often all these objectives are combined.

The techniques used are common to most methods of analysis, solvent extraction of the determinand or interferent, precipitation or coprecipitation of the determinand, volatilization and recovery of the determinand or interferent. To the latter category can also be added simple concentration by evaporation. Absorption-desorption, especially by ion exchange and elution is also used, as is the electrodeposition onto cathode or anode. Complexants are also used in conjunction with the above methods to hold other substances in aqueous solution. Ref 6 lists some techniques commonly used for water, but many other schemes can be worked out by adaptation after consulting general works on analysis. Typical examples are:

Concentration of elements for determination by Atomic Absorption Spectrophotometry by use of organodithiocarbonates and organic solvents,

Concentration and separation of metals with overlapping polarographic waves by extraction and back-extraction with dithizone as the main reagent at controlled pH in the presence of other ligands,

Removal of zirconium and similar metals prior to the determination of traces of calcium etc by extraction as cupferronates (this extraction of cupferronates should always be made at  $<5^{\circ}\text{C}$  as some cupferronates decompose rapidly at  $>15^{\circ}\text{C}$ ),

Separation of major anions and cations from trace elements by precipitation or solvent extraction of the latter using a mixture of organic reagents,

Coprecipitation of trace elements with a carrier-internal standard for examination by emission spectroscopy,

Concentration or removal of arsenic, antimony, germanium, tin, selenium and tellurium as volatile hydrides or chlorides,

Separation of borate, fluoride and fluoroborate, or of the lanthanides, prior to quantification by other techniques, using ion exchange resins,

Removal of excessive amounts of lead by deposition at an anode, or concentration of trace metals by deposition at a mercury cathode, often subsequently made an anode for recovery by redissolving once again in a new electrolyte.

The analytical hazards for the above operations are loss or conversion of the determinands into an unreactive form and pick-up of determinand or of a new interferent during the pretreatment. In addition to the usual attention to purity of reagents and to the prevention of mechanical losses due to poor separation or leaving some precipitate on filters, losses due to bumping and spitting during evaporation to dryness, losses due to solids back absorbed or plated by hydrolysis onto glass are common sources of error.

Care is also necessary to avoid loss of determinand as a volatile derivative such as hydride, chloride etc during solution. Under certain conditions, even substances such as copper nitrate and nitrite have volatilized from aqueous solutions. During the drying and ignition of precipitates and residues, care must be taken not to lose a determinand such as molybdenum by volatilization. In some methods volatile carbonyls or hydrides can form. The presence of water vapour, ammonia, and hydrochloric acid etc can lower the temperature at which a substance volatilizes. Many substances have an appreciable vapour pressure well below their boiling point and such loss of vapour can be significant. Some salts decompose on heating giving off volatile components. Hence, during an initial study of a method, attention should be given to losses by volatilization and absorption. If necessary collect and analyse the gases and vapours for determinand.

In the analysis of sludge care must be taken, if samples are ashed, not to volatilize sought elements nor to turn them into unreactive carbides. Few methods given here will analyse carbides. Molybdenum is especially susceptible, being readily lost as the volatile trioxide, or converted to a very unreactive carbide.

If time permits, thorough examination of all aspects of an analysis in addition to the usual recovery precision and interference tests is often worthwhile. Instances of compensating errors which are only truly compensating over a limited range of concentrations or conditions are not unknown.

#### **1.4 Instrumental Drift**

All these methods have an instrumental basis, and so are often liable to instrumental drift. This can cause a steadily increasing bias, which during the sequential analysis of a series of samples may give the impression of a false apparent trend; hence for many of these methods, randomization of sample order, inclusion of standards and control samples spaced regularly throughout the analytical samples, with random order of determinand concentration, or the regular repetition of the same control standard is essential for analytical quality control. The latter technique is to be preferred when it is possible to recognize and correct such a drift before all the batch of samples has been analysed. This is only possible for some instrumental techniques, not all of them.

#### **1.5 Hazards**

Special hazards can occur with some of these methods: high voltage, high current, and radio-frequency electric supplies and condenser charges, X-rays, UV and microwave radiation. Mercury vapour and many reagents are harmful. Bumping solutions can produce bad scalds. Black-hot materials can give bad thermal burns. Most fumes are harmful and many are highly toxic. Proper ducting and ventilation is therefore essential. A few compounds such as certain metal cupferronates have unexpected explosive properties. Strong perchloric acid should not be brought into contact with readily oxidizable or combustable materials. Bottles of it should be stored in stainless steel trays. See also Ref 10.

#### **1.6 Recovery of Spent Development Solution**

Some of the techniques described in Sections 3.3 and 4 involve development of photographic film. Silver is worth recovering. Precious metal dealers will accept waste silver in relatively small amounts. For information on the best way to process spent developer solution for return to the trade, contact a suitable dealer. Dealers are listed in trade directories such as the latest edition of Kompass (Ref 116).

## 2 Electrochemical Methods

Generally electrochemical methods are best suited to the rapid successive determination of a small group of elements on the same sample rather than a general element scan. Quantitative as well as qualitative results can be obtained. In some cases a few substances other than metals can also be determined, or distinctions made between valence states.

It is sometimes possible to determine two elements simultaneously by simple electrodeposition, one on the anode of the other on the cathode – the determination of lead and copper in effluent is a case in point. It may occasionally be possible to determine two or three metals sequentially on the same electrode from the same solution by intermediate drying and weighing with change of plating conditions between, but these are special cases and will not be discussed further. For details consult text books on metallurgical analysis.

Electrophoresis is really an electrochemical method but is better described under chromatography, which see.

### 2.1 Polarography

In Simple Polarography, a solution containing an electroactive species is subjected to a linear potential increase from about +0.1 volts to -1.5 volts between, usually, a dropping mercury cathode and a suitable reference electrode as anode, a graph of the current against the potential being made either automatically or manually. The potential at which a sudden increase in current occurs is characteristic of the ionic species discharging at that potential, and the magnitude of this current rise is directly proportional to the concentration of the species. The commonest anodes are calomel and silver – silver chloride. For a few special analyses a rapidly rotating platinum electrode is used as cathode. Occasionally for substances reacting at the anode, the electrodes are reversed.

The half wave potential, which is the way these increases in current are identified, varies, not only with the ion and its oxidation state, but also with the composition of the electrolyte. Values are listed in many specialized texts and in most chemical data books and hand books. A selection is given in table 1. Analyses are made by comparison of current increase given by the sample at the appropriate potential with that given by standard solutions of the sought metal at the same potential.

It is possible to make your own equipment, but excellent recording instruments are available commercially. Although the capital outlay for a home-made instrument is not great, samples can only be analysed by laborious manual graph plotting for each metal in turn unless a recorder is incorporated; but with recording instruments up to about five or six metals can be determined in succession in one potential sweep which only takes a few minutes. The method requires more skilful technicians than do many other instrumental methods. A diagram of the basic circuit is given in Fig 1.

Although about thirty metals can be determined directly, concentration either by evaporation, or by solvent extraction and recovery, usually using dithizone, or similar organic reagent with reconversion to the aqueous state is necessary for many water samples. Polarography is often used as a finish to a method based on solvent extraction by a broad spectrum organic reagent such as dithizone, as a better alternative to selective extraction followed by colorimetry, several related metals such as lead, cadmium, zinc, cobalt and manganese being measured in succession on the same solution. Analyses can only be made for metals with half wave potentials sufficiently far enough apart for the current increase to be measured accurately. A separation of 0.15 volts is usually just sufficient but far larger separations are necessary if the waves are not sharp. There should be sufficient plateau between each wave for the wave heights to be measured without any doubt. The increases must not merge into each other, which they will do if the half wave potentials are too close. Although nonaqueous solvents can be used, the decomposition potential for water practically prevents the determination of the alkali and alkaline earth

Table 1 A Selection of Typical Polarographic Half Wave Potentials in various solutions (in volts relative to a saturated calomel electrode\*\*).

Metal and Valence	Supporting Electrolyte (deoxygenated plus added gelatine)						
	0.1M N(CH <sub>3</sub> ) <sub>4</sub> Cl	M HCl	0.1-1M KCl	M KCNS	M NH <sub>3</sub> plus M NH <sub>4</sub> Cl	2M Pyridine plus M HCl	0.5M Tartrate at pH9
As <sup>3</sup>		-0.43			-1.7*		
*Ba <sup>2</sup>	-1.94						
Bi <sup>3</sup>		-0.09					-1.0
†Cd <sup>2</sup>			-0.60	-0.65	-0.81	-0.60	
				-1.27			
Co <sup>2</sup>			-1.20	-1.05	-1.29	-1.06	
Co <sup>3</sup>			-0.26		-0.3		
*Cr <sup>3</sup>			-0.61	-1.05	-1.43	-0.95	
			-0.85				
			-1.47				
*Cr <sup>6</sup>			-0.3		-0.2		
			-1.0				
			-1.55				
Cu <sup>1</sup>					-0.50		
Cu <sup>2</sup>		+0.04	+0.04	-0.54	-0.24	+0.05	-0.30
		-0.22	-0.22		-0.51	-0.25	
Fe <sup>2</sup>			-1.3	-1.52	-1.49		
Fe <sup>3</sup>							-1.20
*H			-1.58				
Mn <sup>2</sup>			-1.51	-1.54	-1.66		
Ni <sup>2</sup>			-1.1	-0.68	-1.10	-0.78	
†Oxygen‡			-0.05				
			-0.9				
Pb <sup>2</sup>		-0.44	-0.40	-0.44		-0.35	-0.75
Sb <sup>3</sup>		-0.15					-1.32
Sn <sup>2</sup>		-0.47		-0.46			-0.92
†Sn <sup>4</sup>		-0.1		-0.50			
		-0.47					
Ti <sup>4</sup>		-0.8		-0.5			
Tl <sup>1</sup>		-0.48	-0.48	-0.52	-0.48		
				-1.07			
†U <sup>6</sup>		-0.20		-0.26	-0.8	-1.1	
		-0.9		-1.32	-1.4		
Zn <sup>2</sup>			-1.00	-1.05	-1.33	-1.02	-1.15

Notes

\* Ammonium, Alkali and Alkaline Earth Metals and several other ions discharge at potentials beyond that for the hydrogen ion. Measurements at such potentials are very difficult to make and are usually impossible in aqueous solution.

† Some ions have more than one electron transfer reaction at the electrode and so give more than one wave. Usually either may be used for analytical purposes. Where such a second half wave potential is beyond the capability of ordinary instruments it has been omitted from the table.

‡ Unless oxygen is removed by chemical or physical means these waves cause interference.

\*\* There are many other supporting electrolytes listed in the literature, also there are minor discrepancies for a few of the values given. Absence of a value often means that the method will not work for that metal/electrolyte combination, but it may mean that the system has not been investigated. If sulphite is used as a deoxygenator it may cause slight shifts in some potentials. The analyst is advised to check out his procedure with synthetic solutions first.

metals etc. Test solutions can be quite complex due to the need to prevent spurious peaks in the current due to the diffusion effects around the moving or electrically pulsating electrode, gelatine and some nonionic detergents are commonly used ingredients for this purpose. Interference produced by large amounts of other reducing species can be minimized either by careful selection of the supporting electrolyte or by initial separative procedures such as carrier precipitation and resolution, or by solvent extraction. Separation of metals can sometimes be achieved by changing the complexation of the ions in aqueous solution by addition of ammonia, pyridine, chloride, thiocyanate etc (see Table 1). Removal of interferences from trace determinands by precipitation of the interferent is not recommended. It is also necessary to destroy many organic substances

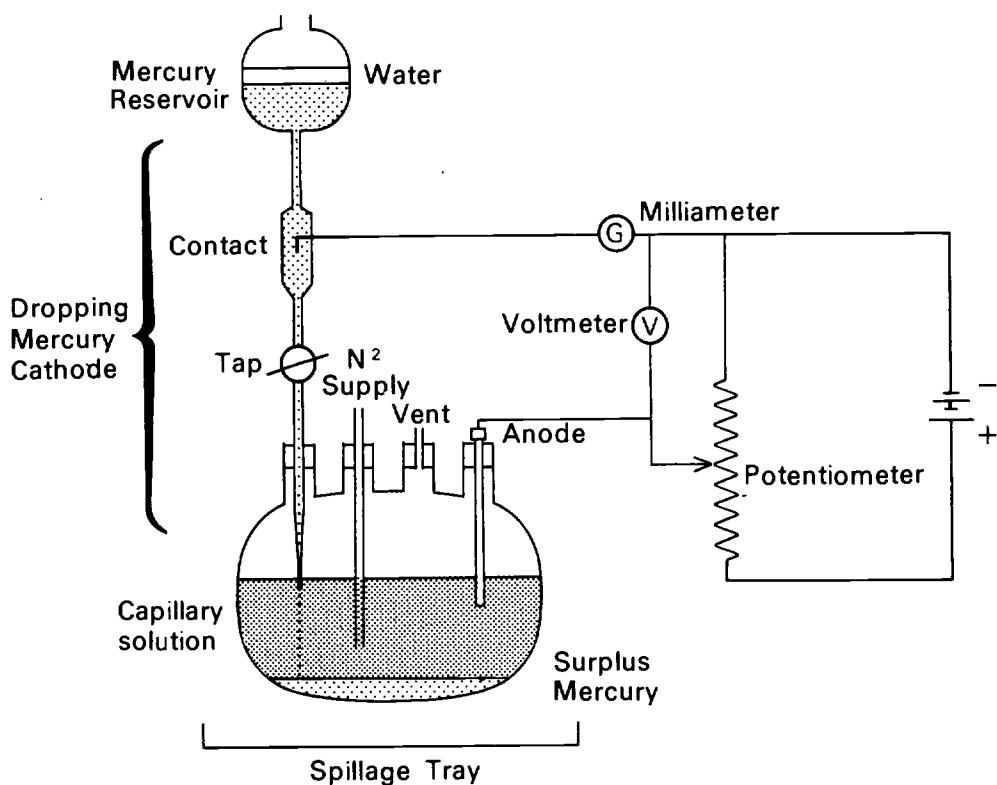


Fig 1. A SIMPLE POLAROGRAPH CIRCUIT DIAGRAM  
(The nitrogen bubbles system is not always necessary)

and to deoxygenate the sample thoroughly, which increases overall analytical time, but if a large number of samples is being analysed, an echelon like procedure may be used with each sample being ready for polarography just as the polarogram of the preceding sample is completed, thus saving on total batch time.

In addition to simple analysis, polarography is often capable of producing information about metal complexes, and oxidation states, though care is essential when interpreting the results. The complex present in a solution may not be directly related to the corresponding ion stabilizing it in solution. Thus  $\text{Cu}(\text{HCO}_3)_4^-$  has been postulated as being present when  $\text{Cu}(\text{CO}_3)_2^-$  was the ion probably formed in an alkaline bicarbonate solution

Some soluble organic compounds can also be determined by anodic oxidation or by cathodic reduction. The technique has been used to measure dissolved oxygen.

Samples are usually aqueous solutions, and should preferably be free of suspended solids otherwise recovery of spent mercury becomes a problem. It is possible to carry out polarography in nonaqueous solvents, in which case analysis for alkali metals becomes possible. But this is a rarely used specialist technique. Methods for cleaning up samples or bringing them into solution depend on the sample type, analytical problem and whether any chemical concentration or separation technique is intended. The used mercury can be cleaned and used again. It may be filtered using chamois leather filters and then cleaned by allowing it to drop in fine drops down a long column of approximately 0.5M nitric acid. A burette makes a suitable apparatus.\* Occasionally purification by distillation is desirable, but a special vacuum still is essential\*\*.

\* Mercury residues are toxic and must not be disposed to land or water without permission. Methods of recovery are given in the methods for Chemical Oxygen Demand (Dichromate Value) and for Chloride also published in this series.

\*\*Mercury vapour is highly toxic. Boiling mercury is exceedingly prone to very heavy bumping, and the boiling point at atmospheric pressure is about 356°C. Distillation is made in a very good fume cupboard with ample safety trays to catch any spillage, and screens to protect the operator. The distillation is made under vacuum, usually with a glass bodied water pump as mercury is absorbed by many metals. There should be a trap in the waste water lines to prevent mercury entrainment and all controls should be outside the fume cupboard. Not only is mercury vapour toxic, it can damage many items of expensive electronic equipment by forming an amalgam with different electrical properties. Careful handling and good housekeeping are essential.

Use of vibrators to ensure smaller mercury drops than are obtainable with gravity alone, rotating platinum electrodes, and pulsed, alternating sine or square wave currents, and differential plotting of the polarogram (current-potential graph) all extend the range and accuracy of the method, but at increased instrument cost. If purchasing or making recording equipment, it is recommended that it be fitted with a circuit for shifting the zero of the plot. This will enable accurate measurements to be made for metals with half wave potentials beyond those of ones present in such concentration that their waves almost take up the full chart scale. Reference should be made to specialist journals and monographs for details.

## 2.2 Anodic Stripping Voltammetry

There are several anodic stripping techniques in use, but in each the determinands are first deposited onto a mercury cathode, and then determined. In its earliest form this was merely a method of separation for determination by other methods (Ref 15) and the metals were recovered either by distilling off the mercury, which is a hazardous process requiring special apparatus and skill,\*\* or by making the dilute amalgam the anode and stripping the metals back into a smaller volume of solution from that originally used. Subsequently controlled potential techniques, often called anodic stripping polarography, were introduced.

This technique, which is similar to polarography, involves two steps. In the first, the metals are plated from the solution onto a mercury cathode, usually a mercury coated graphite electrode, but a hanging mercury drop can be used, by means of a predetermined controlled potential for an accurately timed period, usually of between 15 to 30 minutes, but sometimes less. If some loss of precision can be tolerated, a shorter time may be used. In the second step the electrode is made the anode and the metals are stripped sequentially from it by application of a potential sweep (preferably pulsed). The pulsed technique offers higher sensitivities and can reduce the total analytical time. The metals are stripped at potentials which are characteristic of them, and the currents which flow are proportional to the concentration of the particular elements of the original solution. Provided care is taken in their preparation, mercury coated graphite electrodes are more stable and give more reproducible results than hanging mercury drops.

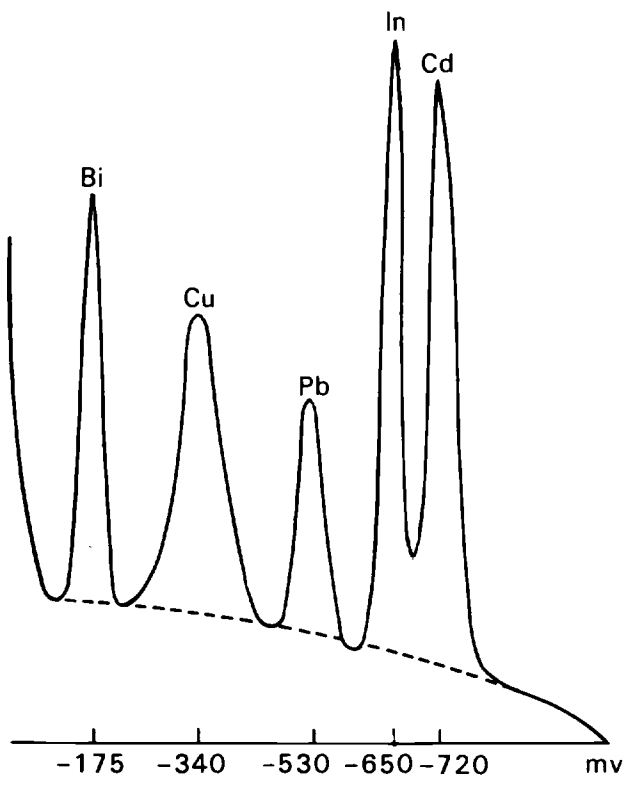
Anodic stripping voltammetry is only applicable to a restricted range of metals (Fe, Cu, Ni, Pb, Cd, Zn, Tl and Bi) but for these metals it is extremely sensitive and concentrations down to below the micrograms per litre range can readily be determined. (Note, the above reference to Lundell and Hoffman (Ref 15) lists more elements that can be collected at a mercury electrode). This technique can also be used for the separate determination of complexed or bound metals existing in aqueous substrates, but sample pre-treatment becomes essential when total metal concentration is required. Nanogram per litre quantities have been determined for a few metals with exceptional sensitivity using total stripping total recovery coulometric techniques on large samples, and using Faraday's Laws to calculate the quantity of metal stripped (1 coulomb is required per electrochemical equivalent of metal). As with polarography, interferences due to overlapping of plating potentials and changes of potential due to complexation are not unknown, but can be overcome. The presence of unknown unexpected complexation can prove a hazard to the unwary but can sometimes be used to achieve separation of metals with otherwise overlapping potentials (Ref 24). Tests should be made before introducing the technique.

A simple apparatus is relatively inexpensive, can be home-made, and requires little ancillary equipment, but the analytical time with such equipment is rather long. With such equipment, only a few samples can be analysed per eight hour working day; but if more expensive commercially available multi-cell units are used, up to 100 samples can each be analysed for five metals in eight hours. Careful planning including deoxygenation of the next sample whilst a sample is being run can halve the analytical time. The method is more of use for determining the few suitable metals than as a general multielement

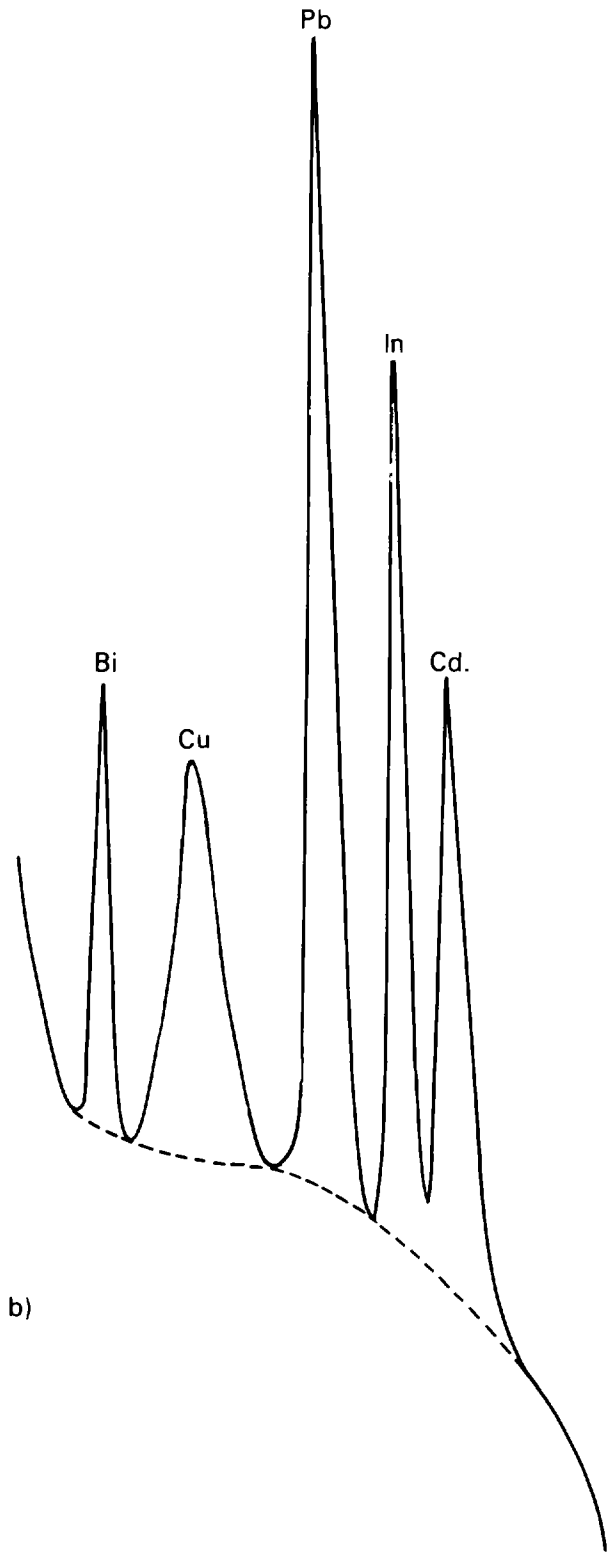
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\*\*Mercury vapour is highly toxic. Boiling mercury is exceedingly prone to very heavy bumping, and the boiling point at atmospheric pressure is about 356°C. Distillation is made in a very good fume cupboard with ample safety trays to catch any spillage, and screens to protect the operator. The distillation is made under vacuum, usually with a glass bodied water pump as mercury is absorbed by many metals. There should be a trap in the waste water lines to prevent mercury entrainment and all controls should be outside the fume cupboard. Not only is mercury vapour toxic, it can damage many items of expensive electronic equipment by forming an amalgam with different electrical properties. Careful handling and good housekeeping are essential.

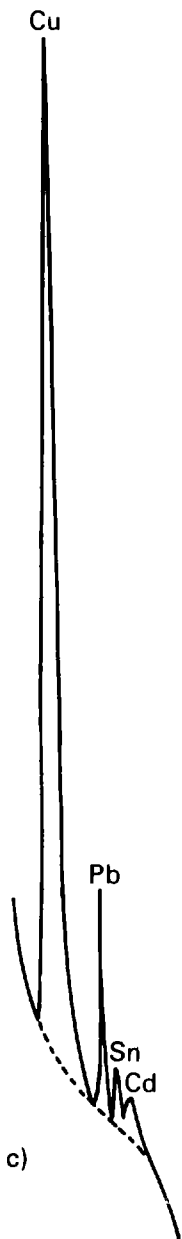




a)



b)



c)

Fig 2. TYPICAL ANODE-STRIPPING  
VOLTMETER READ-OUT CHARTS

method. Circuit diagrams are given in the literature. Fig 2 gives examples of typical analytical read outs.

Two of the main problems with the method are reproducibility of the electrodes, either in uniformity of drop size used or uniformity of plating of the carbon by mercury, and purification of the electrolyte to a sufficient degree to get a blank comparable with the full sensitivity of the instrument.

Some authors claim that Anodic Stripping Voltammetry can sometimes be used to differentiate between different ionic complexes of a metal in solution due to the changes in plating potential that occur with complexation. (For further information see Ref 16). The same is true of polarography; but, as with that technique, great care must be taken when allocating structures to the species found.

### 2.3 Potentiometric Stripping Analysis

This technique is similar to anodic stripping and determines the same elements. Initially, the metals are plated onto a special carbon electrode from a solution containing mercury II ions. They are then stripped back into solution by oxidation in succession, each element being oxidized as the appropriate redox potential is reached, which potential serves to identify the element. Concentrations are determined by the length of time each oxidation step takes before the potential rises for the oxidation of the next element. Some interferences are known, which are due to formation of intermetallic compounds other than amalgams at the electrode, some can be overcome (see Ref 26). Commercial instruments are available.

### 2.4 Ion Selective and other Electrodes

Although not normally used, it is possible to arrange a series of ion selective electrodes for the simultaneous monitoring of flowing water for a number of metal and other ions and a few compounds. Refs 40 and 41 mention probes that can be combined in such multi sensors whilst Ref 42 describes a network which could be used to feed such measurements to a central point. It must be remembered however that there are interelement and pH effects that affect the accuracy of these electrodes, and that some of them at least, can be inactivated permanently by organic matter. Some electrodes are also slightly light sensitive and should be used under constant (optimum) illumination or completely shielded from light if an accurate analysis rather than an order figure is required. A list of suitable electrodes with relevant information is given in Table 2. However, due to the

Table 2 Ion-selective and related Electrodes for Water and Effluent Analysis

Electrode/ Determinand	Concentration Range for reliable measurements	Comments
Ag <sup>+</sup>	sat. sol. - 2 × 10 <sup>-6</sup> M	No interferences except Hg <sup>2+</sup>
Br <sup>-</sup>	1 - 1 × 10 <sup>-5</sup> M	I <sup>-</sup> and S <sup>2-</sup>
Ca <sup>2+</sup>	1 - 1 × 10 <sup>-5</sup> M	Electrodes are available based on two groups of active material with different performance characteristics, particularly in respect of the selectivity ranking of Mg <sup>2+</sup> , Sr <sup>2+</sup> , Ba <sup>2+</sup> , and H <sup>+</sup> . Choose the most suitable electrode for the application. Li <sup>+</sup> may interfere.
Cl <sup>-</sup>	1 - 1 × 10 <sup>-4</sup> M	Br <sup>-</sup> , I <sup>-</sup> , S <sup>2-</sup> , CN <sup>-</sup> interfere
CN <sup>-</sup>	1 × 10 <sup>-2</sup> - 1 × 10 <sup>-5</sup> M	I <sup>-</sup> , S <sup>2-</sup> interfere. Sample pH must lie between 11 and 13.
F <sup>-</sup>	sat. sol. - 2 × 10 <sup>-6</sup> M	Sample pH must lie between 5 and 8. Interferences from iron (III) and aluminium need removal for total fluoride measurements. A specific fluoride method is given in another booklet in this series.
I <sup>-</sup>	2 × 10 <sup>-1</sup> - 2 × 10 <sup>-6</sup> M	CN <sup>-</sup> , S <sup>2-</sup> interfere
K <sup>+</sup>	1 - 1 × 10 <sup>-5</sup> M	NH <sub>4</sub> <sup>+</sup> , Cs <sup>-</sup> , Rb <sup>-</sup> interfere
Na <sup>+</sup>	1 - 5 × 10 <sup>-8</sup> M	Sample pH must be > pNa + 3 (for example if pNa is 3 the pH value must be > 6). Ag <sup>+</sup> interferes
NH <sub>3</sub>	1 - 1 × 10 <sup>-6</sup> M	Gas-sensing probe. Only volatile bases and strong surfactants interfere. A specific ammonia method is given in another booklet in this series.
NO <sub>3</sub> <sup>-</sup>	1 - 1 × 10 <sup>-5</sup> M	ClO <sub>4</sub> <sup>-</sup> , I <sup>-</sup> interfere strongly. Cl <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , Br <sup>-</sup> , CN <sup>-</sup> , anionic surfactants interfere and need removal. Electrodes are available based on two groups of active material with partially different performance characteristics, particularly in respect of response range and selectivity.
S <sup>2-</sup>	sat. sol. - 1 × 10 <sup>-6</sup> M	Thiols interfere. Sample pH must be >13.
O <sub>2</sub>	saturated - 8 × 10 <sup>-6</sup> M	See Ref 34 part B.

multiplicity of substances present in most waters and the above problems, only a few electrodes are at present used and these only for special applications. These are:

Fluoride\* (needs addition of a buffer to decompose fluoro-complexes if total fluoride is to be measured),

Chloride (in a few special analyses where the effect of other halides is negligible),\*

Nitrate\* (for control and order of concentration analysis in some clean waters),

Cyanide

Ammonia\* (for control and order of concentration analysis of some waters and effluents),

Oxygen\* (for BOD measurements and for dissolved oxygen measurement in some waters),

Hydrogen\* (pH),

Sodium and calcium (if other metal concentrations are negligible and the water is relatively clean).

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\*These electrodes are used in determinations given in other booklets in this series.

Although the sulphide electrode can give reliable results (Ref 41), for reliable performance it requires solutions which are so alkaline that it is unsuitable for most water and sewage analyses. Samples must be brought to a pH value greater than 13 prior to measurement.

Electrode systems can also be used for the measurement of Eh (the reduction-oxidation potential). Reduction-Oxidation potentials are occasionally useful for monitoring purposes when the concentration of an oxidizing or reducing agent is liable to change, and can also be used for the detection of end points in titrations. Thus, if when titrating with ferrocyanide as one of the reactants, ferricyanide is added to the sample, the appearance of excess ferrocyanide, or conversely the disappearance of ferrocyanide can be determined by such an electrode. For more information on Eh measurement and also on pH measurement see Ref 31.

Ion selective electrodes usually have an almost linear logarithmic response to concentration, the potential observed usually being related to the concentration by equations of the type:

$$E = E^{\circ} - \frac{RT}{nF} \ln [aC]$$

Where E is the potential observed,  $E^{\circ}$  is the characteristic potential for the cell, T is the absolute temperature, R and F are constants (Ridberg's and Faraday's respectively), n is the ionic charge involved, a is the activity coefficient of the determinand and C is the concentration of the determinand. Some cells derive their potential from complex reactions; in which case the [aC] term is replaced by a fraction, the numerator being the product of the terms for one side of the chemical reaction equation, and the denominator being the similar product for the other side of the reaction equation. This is especially true for reduction-oxidation cells.

It must be emphasized that the concentration referred to above is the actual concentration of the species taking part in the electrode reaction, and not the total concentration of a determinand in all the forms present in the system. An example is the fluoride electrode, where the response is due to the free fluoride ion concentration not the concentration of complex ions such as fluoroaluminates, fluorosilicates, fluoroferrates etc which may be in equilibrium with it in the sample. Of course, if fortuitously, or by the use of competing complexants or buffers the concentration of these other complexed forms of the determinand can be kept constant or minimized, the electrode response can be made proportional to the total determinand concentration (see Ref 32).

On the other hand, the electrode system will also respond to other possible chemical reactions which may go on in such a cell system, and will also respond to subsidiary concentration change cells which may be set up in side the overall system by the use of salt bridges. Salt bridges are tubes containing an electrolyte not otherwise part of the cell which are used when it is necessary to separate an electrode from the sample to prevent damage to the electrode. Typical examples of this type of interference are the metal ion electrodes which may also respond to a lesser degree to metals with similar chemistry, the chloride electrode which responds somewhat to bromide and also to some other anions

(depending on the cell construction, see Ref 33), or the nitrate electrode which responds slightly to chloride etc (see Ref 34). These effects can be corrected for mathematically, provided the concentrations and effects of all the various interferences are known, by the introduction of terms into the basic equation, relating interferent ion concentration to its contribution to the cell potential. Similar terms can be used for junction potentials at salt bridges but this complicates the system and constant conditions plus calibration are preferred. An alternative method of arriving at the concentration of the determinand is the standard addition method. For further information see reference 34.

Interference can also be caused by mechanical blocking of the electrode surface, as for instance formation of a more stable insoluble compound on the electrode surface or by physically coating it with an impermeable film. Thus tannins can ruin fluoride electrodes in one reading. Such interference permanently damages the electrode unless it can be cleaned. This depends on the electrode make and the nature of the damage; dilute acid dips and gentle abrasion as with cigarette ash are typical treatments, but manufacturers advice is essential. Salt bridges (mentioned above) are sometimes used to protect electrodes from samples. The salt solution used in the bridge depends on the electrode and the sample, but should react with neither.

The conditions essential for reliable electrode operation are constant temperature, constant ionic strength, relatively constant pH, constant illumination or shielding from light and suppression or correction for interference effects. It must always be remembered that an electrode is not used in isolation. It takes two electrodes to form a cell, and the performance of the reference electrode is as important as the determinand electrode. The usual reference electrodes are various types of mercury - mercurous chloride calomel, or silver - silver chloride, or platinum electrodes. Recently, determinand electrodes with complex assemblies making use of diffusion, or bound enzyme systems have appeared on the market. For further information on all points see Refs 27-30 and 43-45.

### 3 Spectrophotometric Methods

This group of methods includes some of the most important in water analysis. Some are not truly multielement methods in that with some instrument designs it is customary to analyse a series of samples for one element, then switch to another element, reanalyse and so on. However, one sample often suffices for all determinations, and instruments have been designed which change determinand and analyse one sample completely before passing to the next. All can be used for single substance analysis, and a few related special single determinand analyses are also mentioned as they use the same techniques.

To understand how some of these methods work, it is necessary to know a little about how atoms emit light – the theory behind such tests as the flame test used in qualitative analysis. Atoms and ions consist of a nucleus and orbiting electrons. It is possible for these electrons to change orbits provided the necessary amount of energy is absorbed, or in the case of a change in the opposite direction, is taken away. When energy is lost, it is usually emitted as light of a wavelength characteristic of that particular electron change.

If the energy supplied to move the electrons to the higher energy levels is in the form of heat, this forms the basis of flame photometry. If it is supplied as a combination of electric and magnetic energy, this is the basis of emission spectrography or emission spectrophotometry. Thermal emission as in flame photometry gives only relatively low energy spectrum lines from the subsequent emission, electrical sparks, arc or plasma emission can give higher energy ultra violet spectrum lines as well, which can be used for analysis. Under special high energy conditions X-rays can be emitted which are characteristic of the elements present. If the energy is supplied as light which is absorbed, this forms the basis of atomic absorption and atomic fluorescence methods depending on whether the initial absorption or subsequent re-emission is measured. Absorption of X-rays can give rise to X-ray fluorescence which is another useful method for the analysis of solid samples. Gamma radiation, which originates in transitions in the nucleus of the atom, can likewise be used for determination of elements emitting such radiation.

Molecular vibrational changes can also result in light emission and absorption in the ultra-violet and visible region, but chiefly in the infra-red. On the other hand due to the multiplicity of energy states in molecular bonding, molecular spectra consist of a series of closely spaced lines called band spectra which can also be used for analysis; but chiefly for the identification of compounds or radicals though a few emission methods for elements are based on band spectra of simple compounds.

#### 3.1 Atomic Absorption Spectrophotometry

There is a specialist essay review on this topic available in this series (Ref 48), and several specific methods use this technique, with or without some form of prior concentration. For more detailed information see this booklet. Table 3 lists typical elements that can be determined without prior concentration. Usually this technique is preferable to emission (plasma) methods if less than 4 to 6 elements are being determined per sample.

Table 3 Elements determinable directly by Atomic Absorption Spectrophotometry

Li	Be	B													
Na	Mg	Al	Si												
K	Ca		Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga		As	Se
Rb	Sr		Hf		Mo					Ag	Cd	In	Sn	Sb	Te
Cs	Ba		Zr							Au	Hg	Tl	Pb	Bi	

Sensitivity varies widely and can be changed by solvent extraction. Several additional elements such as sulphur may be determined differentially by precipitation of ions of one of the elements above.

The sample is either converted into a gaseous state such as hydride, a vapour state by means of a furnace, or fed in liquid form, though not necessarily as an aqueous solution into a flame as in flame photometry. A beam of light from a source generating mainly resonant (otherwise called self-absorbing) lines of the sought element (usually an electronic ground state line) is passed through this vapour or flame to a photometer. The light from the resonant lines is absorbed by atoms of the sought element in the ground state (the commonest state in the sample under the conditions normally found in the apparatus) exciting them to higher energy levels. This absorption is measured and is proportional to the sought element concentration. Readout is almost always digital, or by recorder, and instruments are calibrated with standard samples. Single and double beam instruments are available. Separate source lamps are usually needed for each element determined. The commonest sources of incident light are hollow cathode lamps and electrodeless discharge lamps. The latter are best used for the more volatile elements such as arsenic, selenium, tin, cadmium and phosphorous. Multielement source lamps have been made for a few metals, some of which are very successful (the iron, chromium, nickel, cobalt, copper lamp is a good example).

Use of a pure white light is impracticable due to the background effects. Such lights would create too bright a background on either side of the absorption line, which would make measurement of the absorption too difficult. Complete package installations are commercially available. Other users prefer to build up apparatus from commercially available modules, or add to their basic instrument.

The most economic use of an instrument is achieved with analysis of large numbers of samples for up to four to six determinands. It is advisable to determine all samples for one element, then change element, though it is possible with some instruments to determine all elements sequentially on one sample. The method is relatively rapid for single determinand analyses of large numbers of samples.

Although initially claimed to be free from all interference effects, and probably free from the overlapping line effects that plague direct emission methods of analysis, Atomic Absorption Spectrophotometry is susceptible to those types of interference that affect volatility and the concentration of the determinand in the ground state in the absorption unit. Thus the major ions present in sea water cause significant variations in the absorption by trace metals (Ref 49). For further information see the section on interference effects in the Review on Emission Spectrophotometric Multielement Methods of Analysis also published in this series (Ref 80). Phosphate and silicate are typical such interferants, but variations in the relationship between absorption and determinand concentration can also be caused by variations in the concentration of ions such as hydroxide and chloride in the sample solution. Variations in vapourization techniques in the absorption unit can also affect the absorption and interference effects. Thus air-acetylene flames will not detect barium present as sulphate, whereas hotter flames such as those using nitrous oxide will. This fact is utilized in one of the methods for sulphate given in the booklet on Sulphate in Waters, Effluents and Solids in this series (Ref 52). Likewise, the usable concentration range of a method is dependent on the type of vapourizer or flame used as absorption unit. The commonest such units are long narrow flame emission burners, cold vapour absorption cells (for elements obtainable in gaseous form), and various types of high temperature furnace. Some flames mentioned in the literature can be unstable and cause explosions; nitrous oxide-acetylene has a bad reputation and requires special precautions. Fumes from these units are toxic and must be ducted away with due regard also to the safety of occupants of neighbouring buildings.

As with all spectrographic methods, correction is often necessary for background light. The nature and intensity of such light is dependent on instrument design and location, source used and the nature of the sample. Method A in Chromium in Raw and Potable Waters and Sewage Effluents, a method published in this series is typical of methods with correction for background light (Ref 51).

### **3.2 Atomic Fluorescence Spectrophotometry**

This technique is similar to Atomic Absorption Spectrophotometry except that the fluorescence caused by the excited atoms, mentioned above, reverting to the ground state once again is measured. A passing reference to this technique and to flame emission (discussed in the next section) occurs in the Atomic Absorption Spectrophotometry booklet mentioned above.

Apparatus is commercially available, some atomic absorption instruments can be adapted for this technique, instruments can also be made from commercially available components. A source flame or vapourizer similar to that in flame photometry is irradiated by an intense source of resonant light from the determinand, and the fluorescence measured using a spectrophotometer or spectrograph placed at right angles

to the line of the two source units. In theory, it is possible to measure several elements simultaneously by mounting several source units around the sample atomizer or flame, mutually at right angles to the axis of the measuring apparatus; however, this has not been attempted in practice, workers preferring to analyse for single elements in succession, as in atomic absorption spectrophotometry. For some elements, greater sensitivity can be obtained than with Atomic Absorption, the interference effects being similar. Source units are often DC arcs or discharge lamps. To date, the most popular analyses are for magnesium, zinc and mercury in waters and solutions at the microgram per litre level.

### **3.3 Ultra Violet and Visible Region Emission Spectrophotometry including Flame Photometry**

There is a specialist essay review on these methods issued in this series, which see for detailed information. (Ref 80) There are three important related ultra-violet visible region emission techniques: plasma, DC arc, and flame spectrophotometry. Plasma emission is suitable for liquid samples and dissolved solids. DC arc emission is suitable for the direct analysis of solids, it is used for the analysis of some sludges and the monitoring of equipment maintenance by the analysis of used lubricating oil. Dissolved sludges are also analysed by plasma emission. Flame emission is sometimes used in the same way as atomic absorption spectrophotometry for the sequential determination of specific readily excited elements.

Emission Spectrography is the multielement method of choice for many applications, and (though in Britain it is often regarded as at best a semiquantitative method with relative standard deviations of only 50%) may be capable of relative standard deviations of under 10%, and even of as low as 1%, for many determinations provided sufficient attention is paid to detail. Furthermore, there are an exceptionally large number of important instrumental variations in the technique. There are also numerous important single element determinations that are usually made by one or other of the variations of this technique, some of which can be carried out simultaneously.

Tables 4 and 5 summarize the elements that can be determined by flame photometry and by emission spectrophotometry. Sample Pretreatments can greatly extend the versatility of the methods to lower concentrations and to both liquid and solid samples. Some of the techniques are also useful for quality control of the ancillary equipment and materials used by the water industry, whilst routine analysis of lubricating oils has been used to determine when certain types of expensive equipment such as diesel engines require maintenance. Interference and background effects occur, but once known, can be corrected for by well established techniques. Calculations are now facilitated by the use of small computers.

The method requires technicians with a penchant for routine work rather than academic skill; though the more experienced the supervisors are in the technique, the better the quality of results and the more likely anomalies are to be detected and their cause found. The number of samples handled in one day varies with the method and apparatus, from three or four samples for a few elements, to fifty or more samples for up to over thirty elements on each sample.

Although usually bought as a complete instrumental packages, some users do build up their own instrumentation from parts, and the basic principles of all three are the same – a source, a spectrometer to split up the light by wavelength, and either a photometer or a camera device to record and measure the light emitted. Furthermore, not only is it possible to vary the combinations obtainable in an instrument, but it is possible to buy, make, or adapt instruments with interchangeable source units and recording systems. Whilst this type of equipment can be very expensive, choice of the right instrument can save considerably on operating costs. Equipment of this type is usually custom made. Second hand equipment often capable of adaptation is also available. Hence, when buying or building such expensive equipment it is advisable to know what can be obtained and will best suit present and future needs rather than accept a first offered package.

### **3.4 X-Ray Fluorescence Spectrophotometry**

This technique is very useful for solid samples especially if the main constituents (matrix) are made of low atomic weight elements and the sought impurities or constituents are of relatively higher atomic weight. It has occasionally been adapted for the direct analysis of liquid samples but care must be taken not to spill liquid inside the instrument. Precipitative concentration solidification techniques are sometimes used. For instance

Table 4 Elements readily determinable by Flame Photometry with their usual wavelengths (4)

Element	Wavelength in nm	Typical limit of detection in mg/l metal ion (as chloride)
Actinium (1)	591.1 and 450.7	
Aluminium (2)	396.1 and 394.4	
Barium (3)	614.2, 553.6 and 455.4	1 (for 553.6)
Boron (3)	548, 521 and 495	
Calcium (3)	854.2, 422.7, 396.8 and 393.4	0.2 (for 422.7)
Cesium	894.3 and 852.1	0.1 (for 852.1)
Chromium (2)	425.4	
Copper	578.2, 327.4, 324.8	
Europium	397.2, 393.0 and 390.7	
Gadolinium	432.7 and 432.5	
Gallium	417.2 and 403.3	
Indium	451.1 and 410.2	
Iron (2)	386.0 and 372.0	
Lithium	670.8	0.02
Magnesium	285.2	1
Molybdenum (2)	390.3 and 386.4	—
Potassium	769.9, 766.5 and 404.4	0.05 (for 766.5)
Radium (1)	714.1	—
Rubidium	794.8 and 780.0	1 (for 780.0)
Sodium	589.6 and 589.0	0.001
Strontium (3)	460.7	0.1
Thallium	535.0 and 377.6	0.5 (for 377.6)
Ytterbium	555.6	—

Notes

- (1) Though determinable by this method these elements are too hazardous to determine by this technique without very special safety precautions.
- (2) Volatility problems often prevent the determination of these elements by this technique.
- (3) Oxide or similar band spectra may also be used for these elements.
- (4) Many other elements may be determined by this technique provided the concentration is high enough. Lead and most of the other lanthanides are examples. Many other elements are reported as determinable by this technique, but are seldom, if ever, so determined, due either to complex interference/volatility problems or the need for special flames for their excitation.

For the elements given, limits of detection in the solution aspirated to the flame vary from one or two parts per million down to several orders of magnitude lower still. To some extent this is dependent on anion present and flame used.

Table 5 Elements determined by Ultra Violet-Visible Emission Spectroscopy

Li	Be	B																	{C}**	{N}*	{O}	{F}	(He)
Na	Mg	Al																	Si	{P}*	{S}*	{Cl}	(Ne)
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	[As]	[Se]								(Ar)
Rb	Sr	Y	Zr	Nb	Mo	[Tc]	Ru	Rh	Pd	Ag	Cd	In	Sn	[Sb]	Te								(Kr)
Cs	Ba	RE	Hf	Ta	[W]	Re	Os	Ir	Pt	Au	[Hg]	Tl	Pb	Bi	[Po]								(Xe)
[Fr]	[Ra]	AC																					(Rn)

RE = La Ce Pr Nd [Pm] Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

AC = [Ac] Th [Pa] U [Np Pu and somewhat higher]

( ) free element in gases determined by discharge tube techniques

[ ] usually analysed for by some other method, but can be analysed for routinely by special techniques such as vacuum spectrometers and/or plasma emission sources, or using special hygiene precautions for highly radioactive elements.

{ } can be analysed for by band spectral emission techniques.

\* can also be determined using vacuum-ultra violet range instruments.

\*\* occasionally determined using ultra violet emission.



silver is sometimes determined in effluents by coprecipitation with a known amount of mercury as sulphide at the moment of sampling followed by subsequent determination of the silver-mercury ratio. Other similar techniques useful in water analysis are described in the literature. Instruments are constantly being improved, but there are problems with analyses for elements below sulphur in atomic weight and analyses for elements below sodium are not attempted. Equipment is expensive, but operational costs can be relatively low, and if sample preparation can be kept simple, the number of samples analysed per day can be large. Because of the hazard from stray radiation, the need for vacuum seals due to the absorption of X-rays by air, and due to the complexity of the instrumentation, potential users are recommended not to attempt to build their own equipment. Furthermore the instrument manufacturers are usually willing to collaborate in the development of individual instruments. Most instruments are fitted with rotating sample loading and unloading devices and chart or other automated read out for almost continuous operation. Some also include visual display on a cathode ray tube. They are therefore most economic at high utilisation. Samples are irradiated with high energy radiation, usually X-rays, to produce secondary X-rays which are characteristic of the individual elements present with intensities proportional to their concentration in the sample (for wavelengths see Ref 82). There are two types of instrument in production, those in which the emitted radiation is separated by wavelength using crystals as gratings, and those in which the radiation is not separated but identified by energy dispersive electronic techniques using solid state detectors and multi-channel analysers. Instruments with X-ray spectrometers use special curved crystal gratings which either focus the various secondary X-rays onto fixed detectors set for the sought element wavelengths, or the spectrum is scanned by a rotating head containing a detector which plots a trace of intensity against angle (a function of wavelength). Crystal gratings made of different materials may be needed for different wavelength regions. Energy dispersive instruments rely on solid state energy detectors coupled to energy discriminating circuitry to distinguish the radiation by its energy level and measure the amount at each level.

The technique suffers from matrix, back scatter and secondary fluorescence effects. These can be compensated for by using a standard matrix (this is no problem if all the samples are similar in basic composition), having the samples of similar particle size and thickness, or by use of the La Chance correcting equations (Ref 81). Some instruments rotate the sample during exposure to compensate for any inhomogeneity or lack of symmetry in the sample. Typically, instruments will determine elements from percent down to parts per million levels in the solid sample. The technique is non destructive. Water samples are usually converted to a solid prior to analysis, though if great care is taken to avoid corrosion problems and vaporization of the sample, liquid samples can be analysed. Most analyses are made with the sample in vacuum as X-rays are absorbed rapidly by air. A few heavy metal analyses can be carried out in air. Water samples must either be sealed to prevent evaporation, or analysed in a helium atmosphere. If only a few matrix types are analysed, different calibration curves may be used. However for laboratories analysing a wide variety of substances, matrix conversion is sometimes used. Fusion to a glass with borax, or a lithium tetraborate/fluoride flux is the commonest of these, but has the disadvantage of diluting the sample, hence it is mainly used for major element analyses of rocks and sediments. Some work has been done on the analysis of dried sewage by this method.

As the method is non destructive, provided samples do not have to be damaged to get them into the instrument, they are available for re-analysis. The method may be used for qualitative analysis including many elements not detectable by ordinary emission spectroscopy. However, like all methods it has its limitations. For elements with atomic numbers below that of sodium, sample excitation becomes almost impossible; above about lanthanum, the energy input required to excite the K series lines becomes impossibly high, though readily excitable L series lines are available right into the actinides. The spectra are far simpler than those obtained in ordinary emission spectroscopy, which is both an advantage and a disadvantage. There are a few instances of elements for which overlapping lines makes high resolution and curve analysis necessary to detect low concentrations of one element of a pair in the presence of high concentrations of the other, and trace analysis for that element becomes virtually impossible. Such pairs are lead and arsenic, chlorine and rhodium, and molybdenum and sulphur. However as lines are symmetrical, curve analysis and background correction often enables accurate measurements to be made. In some instances filters can be used to obscure one line and leave the other relatively unabsorbed. Wavelength dispersive instruments tend to be most accurate and precise for trace element determinations. Energy dispersive instruments tend to lose precision for traces of light elements in heavy

element matrixes unless longer counting times are used. With short counting times, for instance, the coefficient of variation for a minor constituent element determination by an energy dispersive instrument should be better than 10%, but for a light trace element it may only be 50%. The advantage of the energy dispersive instrument is that it can be so made that almost all the radiation emitted hits the detector. Qualitative analysis is made by comparison with standard samples of known composition using total line energy. This is given by total detector output for the line, or line peak area depending on method of read-out used.

### **3.5 Electron Microprobe X-ray Emission Spectrometry, Auger Electron Spectrometry and X-ray Photoelectron Spectrometry**

These are very much specialized instruments, but are very useful for the identification of small inclusions in solids.

#### **3.5.1 Electron Microprobe X-ray Emission Spectrometry**

The basic instrument is an electron microscope, but all or part of the electron beam can be focussed onto any desired part of the sample causing it to emit X-rays characteristic of that material. These are then collimated and analysed as in the conventional x-ray fluorescence spectrograph, thus giving at least a partial ratio analysis of that part of the sample. As with X-ray fluorescence spectrophotometry the technique becomes more difficult at lower atomic numbers and impracticable for elements with atomic numbers lower than that of sodium. These instruments are expensive and are not often used for routine analysis unless the samples are too small for more conventional methods; but are very useful for the identification of small problem areas in solid materials, such as faults in a weld, inclusions in a casting, grains in concrete or rock, or foreign bodies in plant and animal tissue.

#### **3.5.2 Auger Electron Spectrometry and X-ray Photo-electron Spectrometry**

These are even more sophisticated techniques than the Electron Microprobe, but like it are useful for the analysis of small inclusions. They are especially useful for studying small surface inclusions and films, especially corrosion problems as oxygen is detectable even in quite thin atomic layers. Unlike the electron microprobe, they are most suitable for the determination of lighter elements with atomic numbers down to 3 (lithium). Under certain kinds of excitation by electron beams or X-rays of elements such as aluminium or magnesium (for AES and XPS respectively), these lighter elements will emit electrons with energies characteristic of the element. These electrons can be analysed by energy and rate of emission, thus allowing identification and determination to be made. Such equipment is suitable only for highly specialised laboratories such as those at Harwell, but arrangements can be made for analyses to be carried out.

### **3.6 Gamma Ray Spectrometry**

(and related radiochemical methods)

Analyses for radioactive isotopes can often be made using a gamma ray spectrometer. Energy dispersive techniques are usually used, coupled with pulse height analysers in a similar manner to that used for the X-ray techniques mentioned earlier. Concentration and, or partial separation may be used as a preliminary step. Beta-particle analysis has also been used, as has alpha-particle analysis, but due to the larger size, alpha-particles are more susceptible to absorption by the sample with consequent reduction in sensitivity. It must be remembered that these methods measure specific isotopes of an element and not total element. Hence, if the element is subject to isotopic variation in nature, and most radioactive elements are, or if the element occurs several times in its own natural decay series, gross errors can occur in total element (all isotope) analyses based on single radiation measurements. This is especially true if the natural decay series has been interrupted by chemical or metallurgical processes in the past.

## 4 X-ray Diffraction

Strictly, this is not a multielement method as it determines crystalline compounds not elements. Instruments range from the simple to the elaborate and expensive. The latter are the quickest and cheapest to operate if technician time is taken into account.

The principle of X-ray diffraction is quite different from that of the preceding techniques. Light is diffracted if it passes through gaps of comparable size with its own wavelength. The wavelengths of X-rays are comparable with the interatomic distances found in atoms, hence if suitably arranged, diffraction patterns characteristic of the substance under examination can be obtained.

A beam of X-rays is focussed onto the sample, usually in the form of a fine powder, which acts as a grating, producing a diffraction pattern related to the inter-atomic distances occurring in the crystal lattice. In one way, this is complicated by the random arrangement of the crystallites, but in another way this randomness is a simplification, as it eliminates the need for accurate alignment of the sample with respect to its crystal axes.

The diffraction pattern can be measured in either of two ways. By photography using a strip of film arranged in a circular holder, or by an electronic detector rotated around the sample in a goniometer, a graph being made of detector output against angle of rotation. From this data and a knowledge of the wavelength of x-radiation used,  $d/n$  values are calculated for the various diffractions. The diffraction equation is  $n\lambda = 2d \sin \theta$  where  $\lambda$  is the wavelength used,  $d$  the lattice spacing,  $2\theta$  is the angle through which the beam is diffracted and  $n$  is the order (for explanation of order see the companion booklet in this series on Emission Spectrophotometric Methods of Analysis for Wastes etc (Ref 80). Hence:

$$\frac{d}{n} = \frac{\lambda}{2 \sin \theta}$$

This use of  $2\theta$  is a catch to the unwary. For the reason why half the angle of diffraction is used in this equation see a textbook on theoretical optics.

These  $d/n$  values have been tabulated for a very large number of substances (see Refs 85–87). Hence, by starting with the strongest diffraction peaks, and confirming by subsidiary peaks, the main constituents in the sample can be identified. This enables other peaks to be eliminated as due to the same substance, and so impurity peaks can be detected, confirmed in the same way, and so on. By using standard samples, it is sometimes possible to work out the concentration ratios of substances from peak intensities much as in polarography or emission spectroscopy. Background correction is necessary.

Unfortunately X-ray sources rarely emit monochromatic radiation but a series of lines (described in section 3.4) and a low level of continuous (usually called white) X-radiation. The latter being continuous is no problem, however if strong enough the other lines of the target element can cause confusion by producing secondary series of diffraction patterns. Fortunately it is possible to filter out the most troublesome with special metal filters. For more details see Ref 88.

Amorphous substances do not give sharp diffraction patterns; however, if an amorphous solid starts to crystallize, a faint fuzzy diffraction peak starts to form, sharpening as crystallization proceeds. Lattice defects can cause peak broadening or slight shifts in the  $d/n$  value.

Interference due to the masking of diffractogram peaks due to minor constituents by diffraction from other substances present in the sample is not unknown. If the masked constituent is important, even though at low concentration, for instance harmful minerals in a dust, the consequences can be serious. Attempts are sometimes made to separate the components by chemical or mechanical means for subsequent identification, but care must be taken in so doing not to manufacture the substance sought. An interesting problem of this type is discussed in Ref 88A.

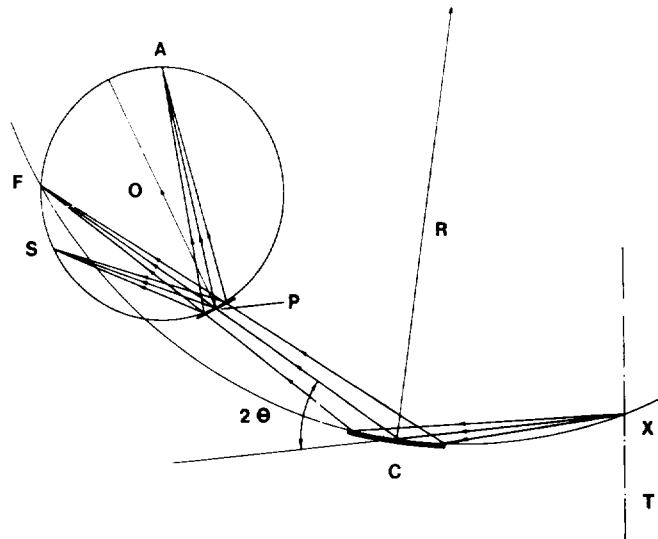
If a powder diffraction camera is home-made, it is essential to remember to include markers at known angles to the incident beam from which measurements can be made. Small vee-shaped metal points are used in commercial instruments.

Unless the instrument is equipped with a remote control sample changing device and is regularly checked for the absence of radiation leaks, it is essential that X-ray diffraction equipment be kept in a separate room, which has been shielded all round, including the floor, ceiling, doors and windows, and that the door be fitted with a safety lock such that instruments will not operate if anyone is in the room. Lead metal, lead compounds and barium sulphate plaster are used to absorb radiation. Doors can be shielded by use of baffle walls. Even when instruments are self shielded it is recommended that these precautions be taken and instruments be operated by remote control. If an accident happens, it can be nasty. X-ray tubes come in several types. Care must be taken to use a tube of the correct rating for diffraction, giving a known wavelength radiation with a minimum of X-ray continuous (sometimes called white X-radiation). Additional safety advice is given in Ref 88. Figs 3a-e illustrate typical instruments and their read-out methods.

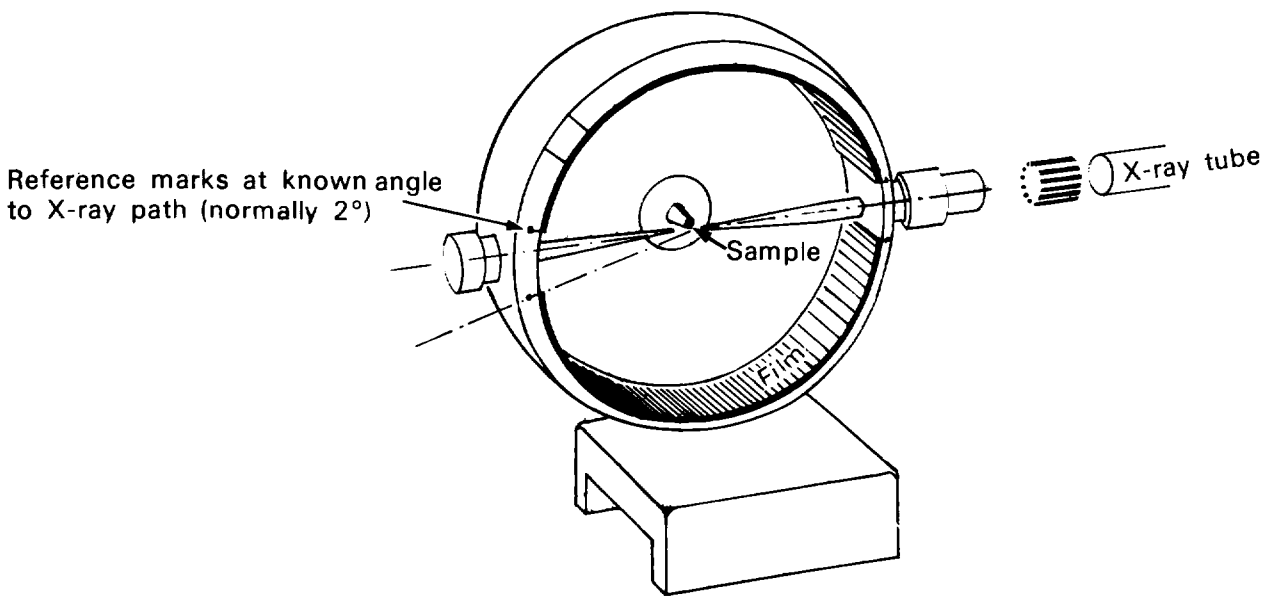
Fig.3 . X-RAY DIFFRACTION ANALYSIS

3a THE PRINCIPLE OF THE GUINIER METHOD

- X Line focus of X-ray tube
- T Axis of X-ray tube
- C Centre (axis of rotation of monochromator crystal)
- R Radius of monochromator focussing circle
- O Centre of film cylinder in holder
- P Centre of powder specimen
- F Focal line
- A & S Examples of diffraction lines in the case of "addition" and "subtraction" respectively
- $2\theta$  Angle of deviation at the monochromator = angle between reflected beam CF and primary beam XC

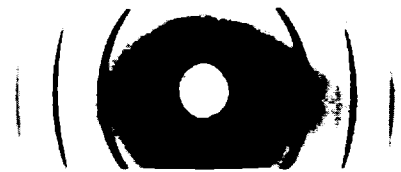


3b. THE PRINCIPLE OF THE DEBYE-SCHERRER POWDER CAMERA



3c. TYPICAL DEBYE-SCHERRER FILM ILLUSTRATING HOW IT CAN BE USED TO IDENTIFY MIXTURES OF MATERIALS.

i) Diffraction pattern obtained from NaF.



ii) Diffraction pattern obtained from NaF + LiF (CuK $\alpha$ -radiation)

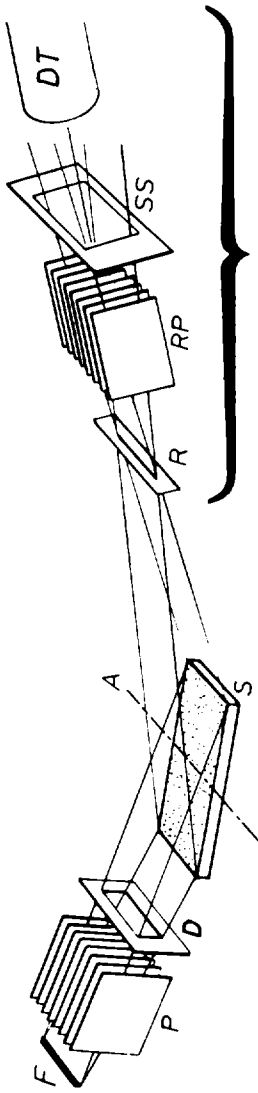


iii) Diffraction pattern obtained from LiF.



RECORDING DIFFRACTOMETRY

- Receiving slit R
- Soller slit between specimen and scatter slit RP
- Scatter slit SS
- Detector DT
- Line source F
- Soller slit between focus and specimen P
- Divergence slit D
- Specimen S



Vertical Goniometer unit.

FIG 3d. INSTRUMENT OPTICS DIAGRAM

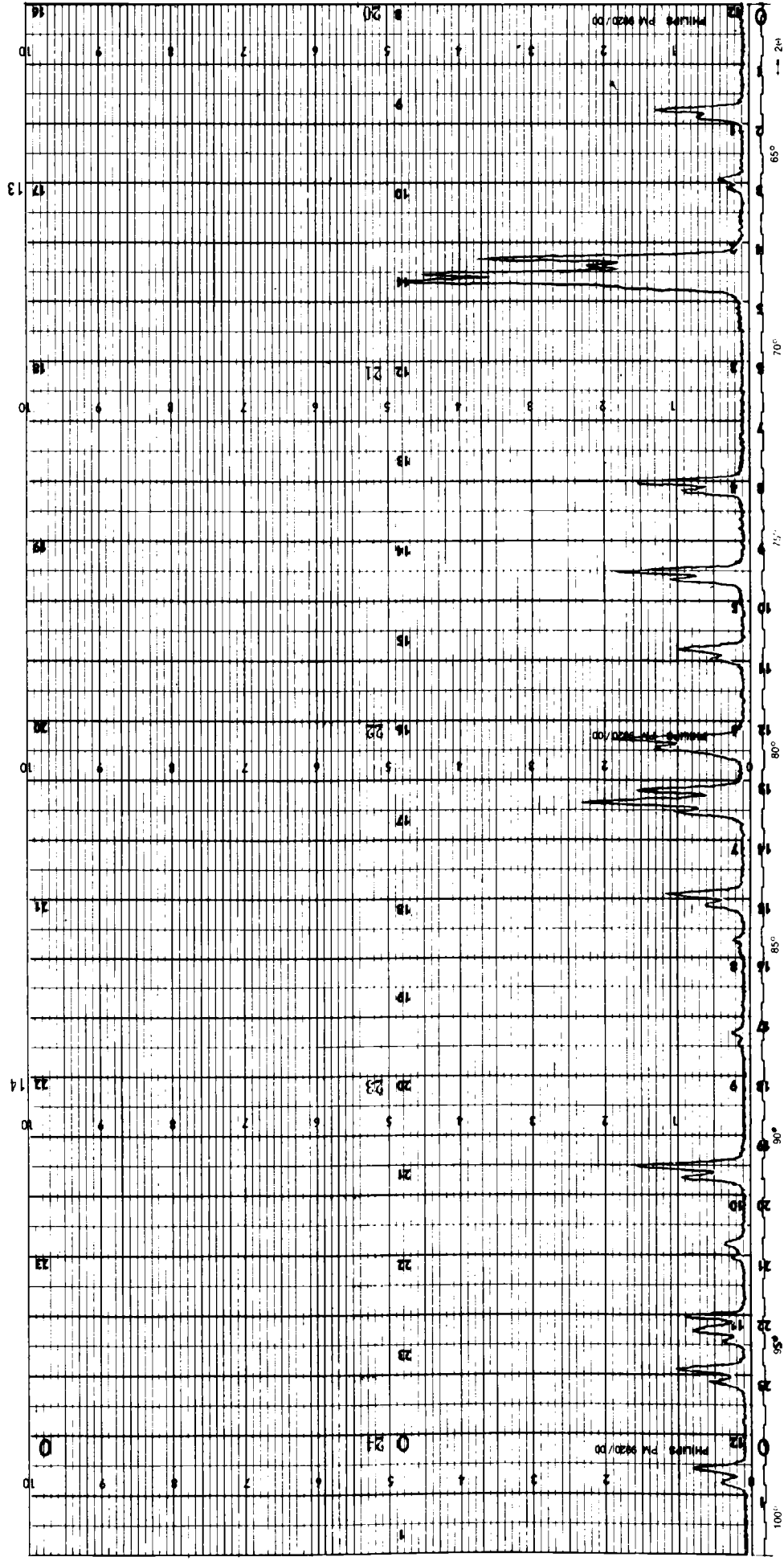


FIG 3e. A TYPICAL CHART RECORDED DIFFRACTOGRAM

## **5 Reflectance, Ultra Violet and Infra Red Absorption Spectrophotometry**

Reflectance Spectrophotometry is a little used technique except in the dyestuff industry, however it can be used for the comparison of solids. It is basically similar to conventional colorimetry.

Ultra Violet and Infra red absorption spectrophotometric techniques are used chiefly for the identification of solid samples such as sediments and plastics though the latter can be used for a limited range of aqueous sample analyses such as for carbonate and bicarbonate ions separately, and also for other inorganic substances after extraction into a nonaqueous solvent. However, the equipment is often available in water industry laboratories and attention is therefore drawn to these unusual uses.

A few spectrophotometers are so designed that, besides being able to measure light absorption by transmission through the sample, they can also do this by reflectance. This may be done by moving the photocell unit to a new position, and replacing the sample cell holder by a plate mounted to reflect the light beam from the spectrometer onto the cell. Alternatively replace the cell holder by a series of mirrors set to divert the light beam from the spectrometer onto the sample, to collect the light reflected back from the sample and to focus it on the photocell. Measurements are usually made in the infra red region, but visible and ultra violet range instruments are available and used. The reflectance spectrum of a solid may not necessarily be the same as its transmittance spectrum. The classic example of this is gold, which transmits a green wavelength if in thin enough section. However, reflectance spectra are useful for identifying some solid substances, provided comparison samples are available. Usually the substance is powdered and dusted onto adhesive tape which is mounted in the sample holder, and the reflectance spectrum is plotted in exactly the same way as a transmittance or conventional absorption spectra (except for the different optical arrangements). Infra Red region Reflectance Spectra have been especially used for the identification of plastics. This latter version is usually called Attenuated Total Reflectance IR Spectrophotometry.

Although infra red absorption spectrophotometry is usually associated with organic chemical analysis, it can be used for the identification of inorganic compounds, mainly by the potassium bromide disc and related techniques. The attenuated total reflectance method is also sometimes used. Occasionally aqueous solutions can be used, the copper tetragonal stretching frequency is just on the limit of a few visible region spectrophotometers which go a little way into the near infra-red, whilst the interesting interactions that occur between carbonate and bicarbonate ion in water are just at wavelengths where water transmits infra red light. For more information see Refs 89-90. Ref 90 also includes data on Nuclear Magnetic Resonance Spectra, which is useful for identifying some organic and fluoride compounds. Ultra violet absorption spectrophotometry can be used in a similar manner, see Ref 91. These three techniques are described in Refs 1 and 8 but there are also many other specialized texts available on these topics.

## 6 Spark Source Ion Mass Spectrometry

This technique is well known for the analysis of organic substances, but it was originally developed for inorganic substances. The method is sometimes used for confirmatory determinations, or when isotope ratios are important for identification of the source of material. The technique can also be used, after preliminary solvent extraction and recovery, for the determination of organometallic derivatives of mercury, arsenic, and so on. Equipment is expensive and is usually custom built, or specially modified either by the maker or the user. Virtually all elements can be determined. A charged beam of sample particles is produced, which are deflected by electric and magnetic fields according to the mass/charge ratio, to give a kind of spectrum from which it is possible to deduce the nature of the sample.

The technique involves the production of gaseous ions derived from the atoms of the sample. These are then dispersed according to their mass-to-charge ratios by application of magnetic or electric fields to produce a mass spectrum. Several designs are possible. The mass-to-charge ratios indicate which ions are present and the ion currents indicate the amounts of the ions which are present.

Mass spectrometry is a potentially attractive multielement technique, not only because of its specificity and sensitivity, but also because it can give information about isotopic abundances. One of the major drawbacks to the technique is that considerable practical difficulties arise in the introduction of the sample. A common approach has been to volatilize the solid sample by means of a spark (spark source mass spectrometry). Although almost all elements may be determined simultaneously, it is only possible to exploit the full sensitivity of the technique (approximately  $0.05 \mu\text{g/g}$ ) by monitoring the total ion current for specific elements and this adds considerably to the analytical time. The recent application of the plasma source to sample introduction appears to offer the following advantages:

- (a) Ionization at atmospheric pressure in a plasma contained within an inert gas such as argon achieves a core temperature of thousands of degrees.
- (b) The sample is presented to the plasma in aerosol form by means of a pneumatic nebulizer and therefore solutions can readily be analysed without pretreatment.
- (c) The technique requires the use of a relatively inexpensive quadrupole mass spectrometer.

Conventional organic chemical mass spectroscopy sometimes coupled with gas chromatography is used for the determination of specific organometallics (eg of mercury or arsenic) after extraction from water or sediment. Both organomercury and organoarsenic compounds have been found in rivers; the latter are formed by microorganisms growing in the presence of arsenical pyrites and so on. Formation of volatile metal derivatives such as tetraberyllium oxyhexacetate, and metal acetylacetonates has also been used.



## **7 Neutron Activation Analysis**

This technique is usually used for confirmatory analysis of special samples and carried out under contract by Harwell and similar laboratories.

In this technique the sample is irradiated usually with thermal neutrons to produce radionuclides, though occasionally non-thermal neutrons are used for some elements. After a cooling period, which may be 1 to 2 weeks, the activities of the radionuclides are determined, usually by gamma-ray spectrometry using a lithium drifted germanium detector and a multi-channel analyser. The amount of an element present in the sample is obtained by comparing its activity with that induced in a known amount of that element irradiated under identical conditions.

Neutron activation procedures have been extensively used for multielement analysis of natural waters. It is one of the most sensitive methods for many trace elements, but two of the metals of interest to the water analyst, namely lead and nickel, have poor sensitivities. Interference effects can occur and, if fissionable elements are present, the analysis may be complicated and confused by traces of fission products and their resultant radiation.

The elaborate equipment required is expensive and the technique is often time consuming. Chemical treatment is sometimes required to remove interfering elements which have high neutron capture cross-sections such as sodium and chlorine, but techniques are known which can handle samples containing even these elements. An advantage of the technique is that contamination of the sample occurring after irradiation produces no error.

As the technique is described more fully in a specialist booklet in this series, no further information will be given here.

## **8 Chromatography and Electro-phoresis**

All kinds of chromatography have been used for the separation of metal ions and anions with varying degrees of success. Several of these techniques are described in separate reviews in this series so the basic principals will not be given here. A few special applications are worthy of note. Electrophoresis is related and is included here instead of in chapter one.

Specialist reviews on Ion-Exchange, Gas and High Pressure Liquid Chromatography are available in this series.

### **8.1 Liquid Adsorption Chromatography**

This technique is used for laboratory analysis, especially of organic compounds, and on an industrial scale for certain special separations both organic and inorganic. Many inorganic analytical separations are also given in the literature. Success depends on there being a large enough difference in the  $R_f$  values between the substances being separated to make the method practicable. Choice of absorbant, complexant, solvent and elutant affect this. This variant is more usually used as an initial separation prior to determination of the individual ions by some other method.

Occasionally, instead of the separated material being eluted and collected in separate fractions, the strip or column may be streaked along an edge or side with an indicating reagent, made to fluoresce, or the fractions identified in some other way and then mechanically divided. For some analyses colours can be developed in the chromatogram itself and the colour density measured by reflectance (see Section 5 above), and hence a measure of concentration obtained by use of standard samples treated in the same way.

### **8.2 Ion-Exchange Chromatography**

This technique is virtually identical with the preceding one but is applicable only to ions.

It has however been developed further by the addition of pumps and programmers to control the instrument and of recording eluent detectors so that in a way the technique has become a true multi-ion analytical method. By using different resins, analyses have been made for mixtures such as chloride, bromide, phosphate and sulphate, mixtures of organic acids with up to about six carbon atoms and some substitution, mixtures including nitrate, and fluoride, mixtures of amines and ammonia, alkali and alkaline earth metals, and so on, but not large anions or transition metals. The detector used in commercially available instruments is based on a conductivity meter with the inclusion of a separate column to convert the eluate into a relatively non conducting species and increase the conductivity of the determinand; but other forms of detector such as refractive index, and light absorption have been mentioned in the literature.

Analysis time is about half an hour per sample. Detection limits depend on the sensitivity of the detector used. For samples where there is evidence of unidentified species, or one ion in a mixture has poor sensitivity, the appropriate element fraction may be collected and analysed by other means. Mixtures of fluoride, fluoroborate and borate are of this type. Fluoride and fluoroborate give sharp conductivity peaks, whilst borate gives only a poor hump due to its low specific conductivity. Care must be taken not to poison columns or to form insoluble compounds by ion exchange and thus ruin columns. For further information see the specific review in this series mentioned above.

### **8.3 Gas Chromatography**

Conventional gas chromatography equipment is used for these analyses.

In this technique the elements to be determined are extracted from the sample as volatile chelates such as trifluoroacetylacetonates and thenoylacetonate, which are then injected into a gas chromatograph (preferably the reagent should have a high electron

affinity, eg one containing chlorine or fluorine). After separation the chelates are detected by a flame ionisation or preferably by an electron capture detector.

The high sensitivity attainable using the electron capture detector makes gas chromatography a potentially valuable multielement technique for the water analyst. Its present use is probably limited to aluminium, chromium, copper, beryllium and selenium. For the latter two elements it is the most sensitive technique available.

The application of the technique has been delayed by the difficulty of finding reagents which form complexes with metals which are sufficiently stable at the elevated temperatures necessary in gas chromatographic separation. (Beryllium forms a series of volatile oxy-organoacid salts such as  $\text{Be}_2\text{O}(\text{O}_2\text{C}\cdot\text{CH}_3)_6$ ).

Some organometallic compounds have been analysed by this technique.

The exhaust gases are usually highly toxic and require complete destruction rather than venting.

#### **8.4 Electrophoresis**

If ions are released into an electric field in a conducting medium, they will migrate to the oppositely charged electrode at a given speed which varies with the ion and the medium. The criteria for separation are ionic charge, ionic size and absorption-desorption to the support for the conducting medium. The higher the effective charge, the faster an ion migrates, the larger the ion or the more strongly it is absorbed, the slower it migrates. Hence it is possible to separate ions which migrate at different speeds. The only exception being ions present in the conducting medium, especially solvated hydrogen and hydroxyl ions, where a kind of bond reformation mechanism results in abnormally high apparent rates of migration. Although normally used for the separation of complex organic ions such as amines and dyes, where advantage can be taken of pH variations in the conducting medium to change the charge of the ion, the technique has been used successfully for metals, including lanthanides and anions. This can be made the basis of a separative technique, or coupled with a suitable detector used as a means of analysis. The technique is very similar to chromatography except that the column or paper strip is usually horizontal, except where it dips into the electrode cells at the ends, and the column or strip must be soaked in a suitable electrolyte solution to make it conducting. Where the sample is applied depends on the ions to be separated. At the end furthest from the attracting electrode, or somewhere in the middle if both anions and cations are being separated simultaneously. The method will also separate ionic substances from nonionics which remain at the point of application.

Combinations of electrophoresis and chromatography methods can be used, especially for separating dyes for subsequent identification. Usually either electrophoresis or chromatography is carried out in one direction on a square sheet of paper, followed by the other technique at right angles, but both can be carried out simultaneously on the same sheet of paper. A large sheet of filter paper is suspended almost vertically on an insulating support, with the electrophoresis electrodes attached at the sides. The top of the paper curls over into the eluting solvent, which must be an electrical conductor. The sample is fed onto the paper continuously, almost at the top, using a capillary feeder. As ionic substances take different times to reach the bottom due to chromatographic absorption, and are therefore subject to the electrophoretic effects for different lengths of time, some separations are possible which are not achievable by either technique alone.

**9 Multiple Channel Automatic Analysers** Single determinand automatic analyses have been available for many years. By an extension of this technique, it is possible to divide the sample and carry out a number of determinations either in parallel, alternately, or in a few instances in succession, on the same sample. The technical problems are now being solved and some commercial and also some home made instruments are in use for such multideterminand analysis. Eventually, if a determinand can be determined by an automatic analyser, it ought to be determinable by this method; but whether inclusion in a multiple channel instrument or operation of several individual machines is preferred will be dependent on the local situation and economics. A few such multichannel instruments are used to maintain regular monitoring of large rivers, the results being transmitted by land line to recorders in a distant laboratory. Two systems are used for automatic analysers – air segmented continuous flow and flow injection. For further information on these techniques see references 118 and 119.

## **10 Thermogravimetry and Differential Thermal Analysis**

These two techniques are used for the identification of some types of sediments, soils, rocks and construction materials. In thermogravimetry, the samples are heated slowly with continuous weighing, weight being plotted against temperature, using a special furnace/balance. Substances are identified by comparing the plot obtained with known plots. Plots are different if gases are allowed to escape freely from samples compared with plots where the samples and evolved gases are confined, and may also differ from plots of loss on ignition at various temperatures. In Differential Thermal Analysis the sample and a control blank are placed side by side in a furnace with thermocouples in the materials and a plot made of the temperature difference as the temperature is raised and lowered. Again, identification is made by comparison with plots from known materials. The first method is suitable for substances which evolve gas or vapour on heating, the second method is suitable for substances which undergo phase changes on heating. Specialist advice is suggested if use of either of these methods is contemplated. For further information see Refs 113 and 114.

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In some instances a single reference may be referred to for several topics, in such cases no page or chapter reference is given. Consult the index of the book in question. Where a reference may exist in several editions, chapter or section titles may be given.

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Analytical Chemistry

Talanta

Atomic Absorption Reviews

J. Inst. of Water Pollution Control.

Chemical Society Annual Reports.

## 12 Determinand Index

See especially Sections listed below (notes are explained at the end of the index)

Actinides	(3.3E), (3.5), 3.4
Actinium	(3.3F & E), 3.4, 3.5X
Aluminium	3.1, 3.3(F)E (3.4), 3.5X
Ammonia	2.4, 9
Antimony	2.1*, 3.1, 3.3E, 3.4, 3.5X
Argon	(3.3E), 3.4, 3.5X
Arsenic	2.1*, 3.1, 3.3E, 3.4, 3.5X, 9
Astartine	3.4, 3.5X, (3.6)
Barium	3.1, 3.3F & E, 3.4, 3.5X
Beryllium	3.1, 3.3E, 3.5A
Bismuth	2.1*, 2.2, 2.3, 3.1, 3.3E, 3.4, 3.5X
Boron	3.1, 3.3F & E, 3.5A, 9
Bromide	2.4, 3.4, 3.5X
Cadmium	2.1*, 2.2, 2.3, 3.1, 3.3E, 3.4, 3.5X
Calcium	2.4, 3.1, 3.3F & E, 3.4, 3.5X
Cerium	2.1, 3.3E, 3.4, 3.5X
Caesium	3.1, 3.3F & E, 3.4, 3.5X
Chloride	2.4, 3.4, 3.5X, 9
Chromium	2.1*, 3.1, 3.3(F&E), 3.4, 3.5X, 9
Cobalt	2.1*, 3.1, 3.3E, 3.4, 3.5X, 9
Compounds	4,5,8,10
Copper	2.1*, 2.2, 2.3, 3.1, 3.3F & E, 3.4, 3.5X, 9
Cyanide	2.4, 9
Europium	2.1, 3.3F & E, 3.4, 3.5X
Films	3.5A
Fluoride	2.4, 3.5A, 9
Frankium	(3.3E), 3.4, 3.5X, 3.6
Gadolinium	3.3F & E, 3.4, 3.5X
Gallium	2.1, 3.1, 3.3F & E, 3.4, 3.5X
Germanium	3.3E, 3.4, 3.5X
Gold	3.1, 3.3E, 3.4, 3.5X
Hafnium	3.1, 3.3E, 3.4, 3.5X
Helium	(3.3E)
Hydrogen ion	2.4
Inclusions	3.5
Indium	2.1, 3.1, 3.3F & E, 3.4, 3.5X
Iodide	(2.1), 2.4, 3.4, 3.5X
Iridium	3.3E, 3.4, 3.5X
Iron	2.1*, 2.2, 2.3, 3.1, 3.3(F&E), 3.4, 3.5X, 9
Krypton	(3.3E), 3.4, 3.5X
Lanthanides	3.3E, 3.4, 3.5X
Lead	2.1*, 2.2, 2.3, 3.1, 3.3(F&E), 3.4, 3.5X
Lithium	3.1, 3.3F & E, 3.5A
Magnesium	3.1, 3.2, 3.3F & E, (3.4), 3.5X
Manganese	2.1*, 3.1, 3.3(F&E), 3.4, 3.5X, 9.

Mercury	3.1, 3.2, (3.3E), 3.4, 3.5X
Molybdenum	2.1, 3.1, 3.3(F&)E, 3.4, 3.5X
Neon	(3.3E), 3.5A
Nickel	2.1*, 2.2, 2.3, 3.1, 3.3E, 3.4, 3.5X, 9
Niobium	2.1, 3.3E, 3.4, 3.5X
Nitrate	2.4, 9
Nitrogen	3.5A
Organis	Introduction, 2.1, 3.3E, 3.5A, 9
Osmium	3.3E, 3.4, 3.5X
Oxides	3.5A
Oxygen	2.1*, 2.4
Palladium	2.1, 3.3E, 3.4, 3.5X
Phases	4, 10
Phosphorus	(3.3E), (3.4), 3.5X, 9
Platinum	2.1, 3.3E, 3.4, 3.5X
Polonium	(3.3E), 3.4, 3.5X, (3.6)
Potassium	2.4, 3.1, 3.3F & E, 3.4, 3.5X, 3.6
Promethium	(3.3E), 3.4, 3.5X, 3.6
Radium	(3.3F & E), 3.4, 3.5X, 3.6
Radon	(3.3E), 3.4, 3.5X, (3.6)
Rhenium	2.1, 3.3E, 3.4, 3.5X
Rhodium	2.1, 3.3E, 3.4, 3.5X
Rubidium	3.1, 3.3F & E, 3.4, 3.5X
Ruthenium	3.3E, 3.4, 3.5X
Samarium	2.1, 3.3E, 3.4, 3.5X
Scandium	3.3E, 3.4, 3.5X
Selenium	(2.1), (3.1), (3.3E), 3.4, 3.5X
Silicon	3.1, 3.3E, (3.4), 3.5X, 9
Silver	2.1, 2.4, 3.1, 3.3E, 3.4, 3.5X, 9
Sodium	2.4, 3.1, 3.3F & E, (3.4), 3.5X
Solids	1.3, 3.3E, 3.4, 3.5, 3.6, 4, 5, 6, 7, 10
Strontium	3.1, 3.3F & E, 3.4, 3.5X
Sulphide	(2.1), 2.4, (3.3E), 3.4, 3.5X, 9
Surface Films	3.5A
Tantallium	2.1, (3.3E), 3.4, 3.5X, 3.6
Tellurium	2.1, (3.1), 3.3E, 3.4, 3.5X
Thallium	2.1*, 2.2, 2.3, 3.1, 3.3F & E, 3.4, 3.5X
Thorium	3.3E, 3.4, 3.5X, (3.6)
Tin	2.1*, 3.1, 3.3E, 3.4, 3.5X
Titanium	2.1*, 3.1, 3.3E, 3.4, 3.5X, 9
Trace Elements	1.3, 2, 3, 6, 7
Tungsten	2.1, (3.3E), 3.4, 3.5X
Uranium	2.1*, 3.3E, 3.4, 3.5X, (3.6), 9
Vanadium	2.1, 3.1, 3.3E, 3.4, 3.5X, 9
Xenon	(3.3E), 3.4, 3.5X
Ytterbium	3.3F & E, 3.4, 3.5X
Yttrium	3.3E, 3.4, 3.5X
Zinc	2.1*, 2.2, 2.3, 3.1, 3.2, 3.3E, 3.4, 3.5X
Zirconium	3.1, 3.3E, 3.4, 3.5X

#### Notes

- (i) Methods 6 and 7 can be used for most elements, for details on 7 see the special essay review in this series
- (ii) 2.1\* – especially for this element
  - 3.3F– flame emission
  - 3.3E– arc or ICP emission
  - 3.5X– X-ray emission
  - 3.5A– Auger and other related emissions.
- (iii) References in brackets means that a special modification of the method is used.

## **Address for Correspondence**

However thoroughly a method may be tested, there is always the possibility of a user discovering a hitherto unknown problems. Users with information on this booklet are

The Secretary  
The Standing Committee of Analysts  
The Department of the Environment  
2 Marsham Street  
LONDON SW1P 3EB  
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## **Responsibility for this Method**

This method has had a rather unusual progress through the Committee. Credits are due as follows:

### **Original Draft:**

Mr EC Conchie	Mr JF Palframan
Mr B Gubbins (until September 1975)	Mr LR Pittwell (until January 1974)
Mr P Hewitt	Dr L Ranson (after February 1975)
Mr OD Hydes (after January 1974)	Prof JP Riley
Mr WM Lewis	Mr AL Wilson
Mr GF Lowden	

### **Second Draft: Mr LR Pittwell with assistance from**

Mr P Adams	Mr R Otter	Dr M Thompson
Dr P Bailey	Dr J Plant	Dr L Thorne
Dr ML Berrow	Dr D Purves	Dr I Thornton
Dr JM Carter	Mr PTS Sandon	Dr RC Voss (died December 1979)
Mr WM Lewis	Mr RO Scott	Mr A Westwell
Mr P Morries	Dr KC Thompson	Mr AL Wilson

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Mr J Borland from June 1975, until 1978  
Dr JM Carter from June 1975  
Dr GW Clayfield  
Mr BEP Clement from February 1978  
Dr V Collins from June 1975, until January 1977  
Dr RL Cooper from June 1975  
Dr BT Croll from June 1975  
Mr TA Dick from February 1975  
Mr JWR Dutton from July 1977  
Mr GE Eden until June 1975  
Mr GI Goodfellow from January 1980  
Mr K Goodhead from July 1978  
Mr TR Graham from April 1977  
Dr N Harkness until June 1975  
Mr I Harper from July 1978  
Mr E Hodges from June 1975  
Mr JG Holland from June 1975  
Dr AJ Howard from June 1975 until December 1976  
Dr DTE Hunt from May 1980

Mr WM Lewis until January 1980  
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Mr JC McCullins from January 1976  
Mr D Mercer until June 1974  
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Dr AT Palin until June 1975  
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Professor JP Riley from June 1975  
Mr R Sinar died, April 1979  
Mr PAH Sperring until January 1976  
Dr AM Ure from August 1979  
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