# Emission Spectrophotometric Multielement 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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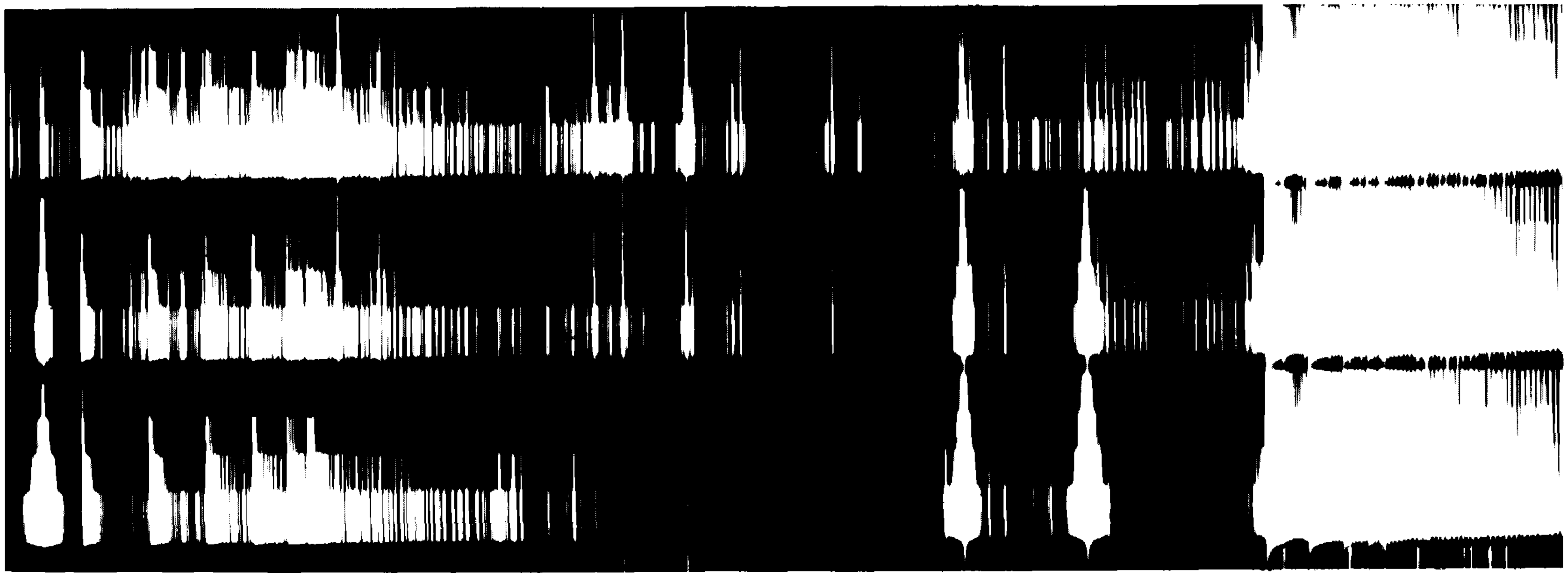
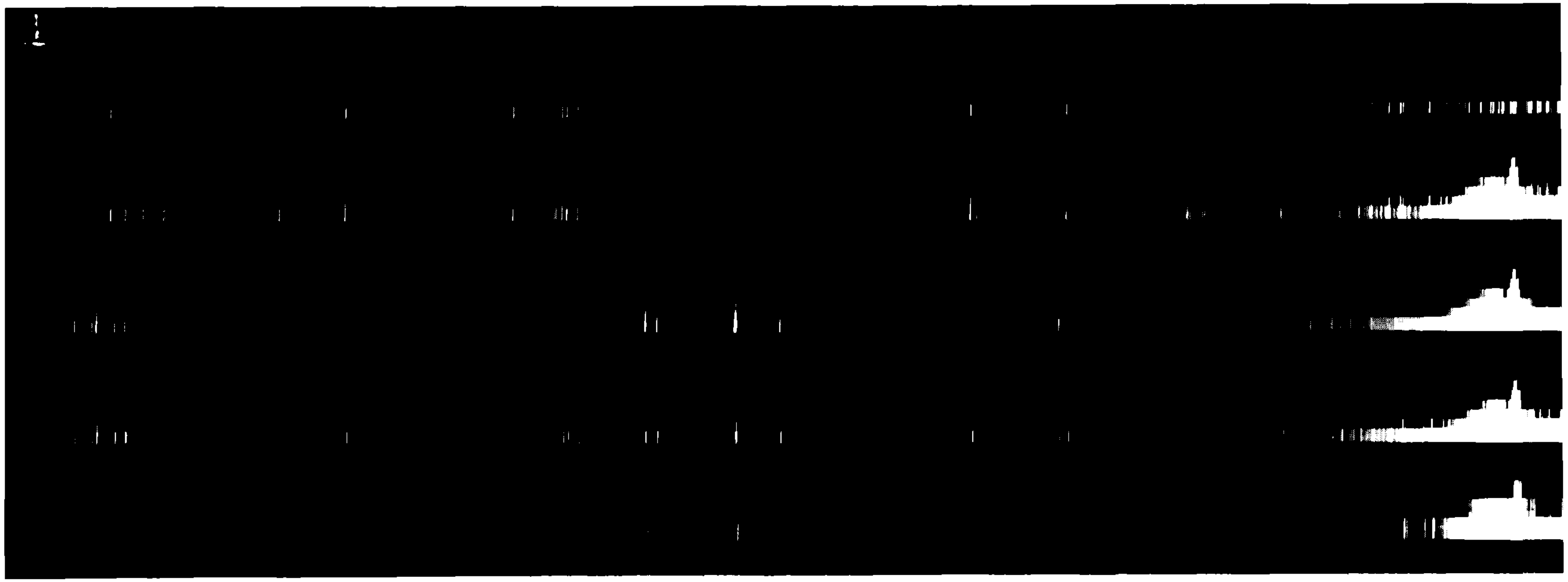
Figures 1a and b Portions of photographic spectrum records. The single narrow spectrum at the top of each photograph is an iron arc used for reference. Ordinary exposures are typically of this size. The other three spectra are taken with 4 and 7 step rotating sectors respectively (as in Fig 7). Note the line broadening effect apparent at high concentration, which at higher exposures tends to obscure adjacent lines due to complete exhaustion of the film. Note also the band spectrum with overlapping lines showing through, note how this band spectrum tends to tail off in intensity until only the full exposure sufficiently sensitizes the film enough to leave a record, and eventually even this disappears. The bands due to cyanogen formation in the carbon arc in air have a sharp edge.



1. a



1. b

(ii)

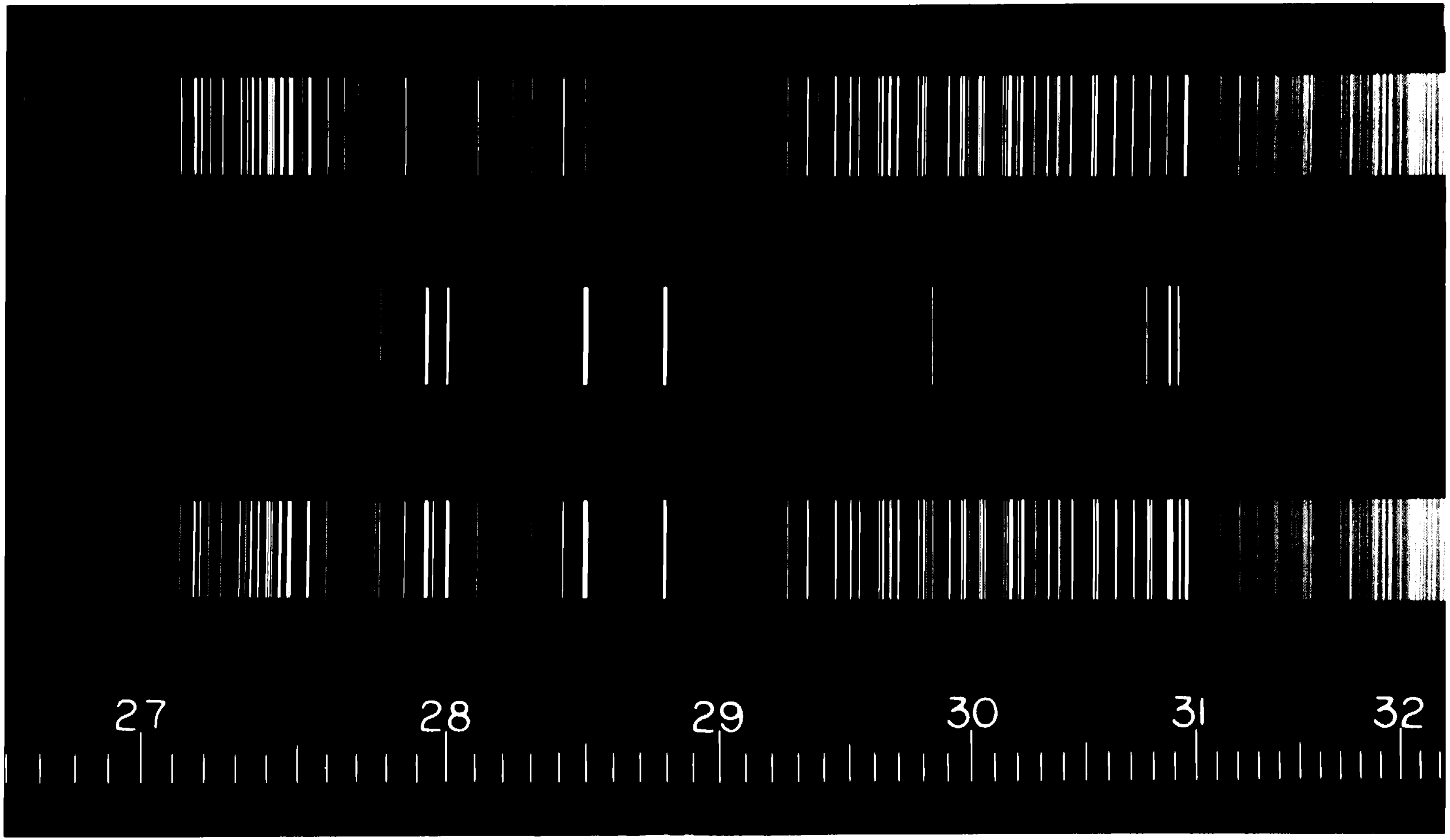


Figure 2 A repeat analysis of the same samples as in Fig 1b but without the step sector, but a smaller wavelength range has been shown at higher magnification of the negative. The magnesium quintet is plainly visible in the middle spectrum.

# Emission Spectrophotometric Multielement Methods of Analysis for Waters, Sediments and other Materials of Interest to the Water Industry 1980

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# About this series

This booklet is part 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 analyticals techniques of interest to the water and sewage industries. 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 nonmetallic 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.

Whilst an effort is made to prevent errors from occurring in the published text, a few errors have been found in booklets in this series. Correction notes for booklets in this series are given in the Reports of The Standing Committee of Analysts, published by the Department of the Environment but sold by the National Water Council, 1 Queen Anne's Gate, London SW1H 9BT. Should an error be found affecting the operation of a method, the true sense not being obvious, or an error in the printed text be discovered prior to sale, a separate correction note will be issued for inclusion in the booklet.

TA DICK
*Chairman*

LR PITTWELL
*Secretary*

*4 December 1980*

# 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 specifications. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Code of Practice 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 radiochemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of 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 book

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. Some of these techniques 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.

The purpose of this booklet is threefold, to provide sufficient information for those who want to use the more common of these methods to be able to do so, to provide information to enable laboratories starting in this field to purchase the right instrument for their needs and to provide a short summary of other techniques so that readers can assess whether the technique may be helpful in solving their problem and then seek specialist advice.

Most of the methods described are highly dependent on the instrument used, only outline methods can therefore be supplied and preliminary development work is essential.

# Specific references to methods of determination

Although this whole booklet is about multielement analysis and tables 1, 2 and 3 list elements determinable by methods described here, specific references, often with enough detail for a method to be worked out are given for a few elements. Specific methods for some of these elements are given in other booklets in this series, but for other elements no such booklet exists. The following list is a guide to information in this booklet useful when read in conjunction with the booklet as a whole, for the specific determination of a variety of elements. References in brackets are to less important methods.

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# Emission Spectrophotometric Multielement Methods of Analysis for Waters, Sediments and other Materials of Interest to the Water Industry (1980)

## 1 Introduction

This Review is intended as an introduction and guide to this field of analysis, rather than as a set of detailed instructions on how to carry out such analyses. Usually such 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. Quantitative results are obtained by comparison with standard samples. Full details are not given as these are often dependent on the make of instrument used, and in some cases the number of instruments available to the water industry is very small. For some techniques, where there are a variety of versions, more information has been given so that potential users may know which version to use. Test data has been omitted as this too is highly dependent not only on the equipment but often on laboratory conditions and the type of technician used. For routine analysis of large numbers of samples, better quality control can often be obtained by using production line techniques rather than a normal laboratory routine.

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 few, if any, 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.

This group of methods includes some of the most important in water analysis. 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. In some cases, if proper care is taken, it is possible subsequently to re-examine the record of a qualitative analysis and obtain either a quantitative or order of magnitude determination of the elements present in the sample.

To understand how 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 spectrophotometry. Flame photometry gives only relatively low energy spectrum lines from the source, electrical emission can give higher energy ultra violet spectrum lines as well, and under special conditions the X-rays used in the X-ray methods. If the energy is absorbed as light, this forms the basis of atomic absorption (which is the subject of a companion booklet to this one) and atomic fluorescence depending on whether the initial absorption or subsequent re-emission is measured. When the light energy absorbed and re-emitted as fluorescence is in the form of X-rays, this is the basis for the X-ray fluorescence technique which is very useful for solids. Gamma radiation which originates in transitions in the nucleus of the atom can 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 be used for analysis.

Of all the known terrestially 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 these methods were originally developed for use directly on solid samples, but techniques have subsequently been 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.

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 and 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 co-operation 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 investigation of deposits, material failures, evaluation of reagent purity, analytical interferences and the like, or other special routine analyses requiring this equipment.

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 spectrograph 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 with recording read-out. Such scans take time and may be unreliable due to volatility differences because emission varies with time unless a flame constantly fed with a uniform sample is used. There have been problems in the supply and cost of photographic film made specially for spectrography, partly due to this change to photoelectric instruments, partly due to the rise in price of silver and partly to a world shortage of suitable base "gelatine"; but reliable imported film is now readily available. 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 sub units and that the older technical literature contains much useful information even on such things as ways of changing the sensitivity of photographic film to make it respond to light of different wavelengths. Secondhand equipment is available. Furthermore, instrument design is always changing, thus scanning and film loading plasma emission instruments have recently come on the market.

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. See also References 1-7, 14 and 38.

## 1.1 Chemical Pretreatments

Chemical Pretreatments are used for three purposes, to get the sample into a form suitable for the technique, to separate the determinands from interferents and to concentrate the determinands. Often all objectives are combined in one process.

Most pretreatments are well described in the literature, but, though much of it has not been specifically developed for the water industry, a trained analyst should have no difficulty in adapting other methods to the samples in hand. Much depends on the final form in which the sample is required for the analysis (liquid or solid), the nature of the determinand (how easy it is to extract or precipitate, and how easy it is to lose or pick up accidentally) and the interferents present in the initial sample.

The usual methods of evaporation of solutions to give solid residues or solution of solids to obtain solutions can contain hidden snags and care is needed. If in doubt, investigate using synthetic samples before carrying out analyses with real samples. On evaporation, solutions may deposit different solid phases in succession which can result in inhomogeneous samples. Some solutions are notorious for bumping and spitting and may require overhead surface infra-red evaporation. For accurate repeatable results, some methods require not only homogenous samples, but uniform samples if good quality quantitative analyses are required. 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 and tin chlorides have volatilized from aqueous solutions. During the drying and ignition of precipitates and residues, care must likewise be taken not to lose determinand by volatilization. Some methods can form volatile carbonyls or hydrides. 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 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, whilst proving the method, collect any gases and vapours given off and analyse them for determinand.

Concentration of traces, or separation from interferents may be achieved by formation of a complex soluble in a separable solvent, or by direct precipitation or by coprecipitation with a carrier precipitate. Soluble extracts may be used as such, or even further concentrated or separated by back extraction into an aqueous medium, or evaporated and used as solids. As solvent extraction is based on partition of a substance between two solvents, care is needed if reproducible results are to be obtained, and some degree of standardization, whether it be by volumes used and number of extracts made, or by degree of extraction, is essential. Precipitation, can lead to inhomogeneity, due to partial sequential precipitation of different substances or formation of a soluble complex with excess reagent. The slow addition of ammonia solution to a mixture of iron, aluminium, lanthanum, magnesium, calcium and copper salts in acid solution is a good example, the first four metals tend to precipitate in the order given, but with no clean separation, calcium is not precipitated but may be absorbed, whilst copper is precipitated but redissolves later. Due to the problems of local high concentrations when two solutions are mixed, the most homogeneous precipitate is often obtained by adding sample to excess of precipitant, provided always that none of the determinands are soluble in excess reagent. Precipitations, where there is a risk of formation of such soluble compounds, should be avoided and never used analytically without thorough prior testing for reproducibility.

The following techniques are well documentated in the literature:

i. Solvent extraction of dithizonates, 8-quinolinolates, diethyldithiocarbamates (and other dithiocarbamates), cupferronates etc into chloroform, carbon tetrachloride or other organic solvent. Chlorides and some other inorganic salts are soluble in organic solvents such as diethyl ether. Reference 72F gives an example of dithiocarbonate extraction into chloroform for the determination of some trace metals in sea water by Inductively Coupled Plasma Emission.

ii. Precipitation and coprecipitation with a carrier element (often also used as an internal standard) of metals as oxides or hydroxides, fluorides, sulphides, 8-quinolinolates, mandelates, oxalates, tannates, thionalides, phenyl- thiohydantoates etc with or without complexation of other metals by reagents such as tartrate or ammonia in order to keep them in solution.

iii. Selective absorption and elution on to ion exchange resins or other absorbants such as active carbon, alumina etc.

iv. Electroplating concentration techniques are rarely used for metals of interest in the water industry.

v. Freeze drying is used occasionally.

In general, reagents that separate a group of elements are preferred to specific reagents for one element, unless that element is an interferent which it is desired to remove. For further ideas consult texts on general analytical separation techniques and treatises on organic reagents for metals. Table 6 summarizes much of this information for chloride extraction into diethylether, and dithizone, 8-quinolinol and dithiocarbamate extraction into chloroform or carbon tetrachloride. Table 7 summarizes typical carriers also used as internal standards with analytical lines suitable for many analyses. See also Refs 4, 9-12, 51, 52 and 77-80.

The use of liquid sample plasma sources necessitates the solution of solid samples. Samples high in organic matter, such as sewage sludge, should not be ashed to remove organic matter and redissolved. Volatile elements can be lost whilst others such as molybdenum and aluminium may form highly insoluble carbides or silicates. Wet oxidation with, nitric acid alone or nitric and perchloric acids, or with hydrogen peroxide as detailed in some of the specific methods for determinands in sludge published in this series should be used. Even so, there is a slight risk of volatilizing a few metals. If this is suspected, collect all fumes evolved in water and analyse these scrubbings separately. Solution of rocks and sediments is a more specialist technique, for detailed information two well tested systems are described in refs 10 and 11.

### 1.1.1 Samples Predominantly of Organic Matter

The analysis of the inorganic constituents of predominantly organic materials is dependent on whether the organic matter interferes with the excitation of the sample, and whether the inorganic constituents are volatile on ignition. If removal of the organic matter is desirable, techniques used include:

i. simple ignition in air in a muffle furnace;

ii. Schoniger oxygen flask decomposition, see below and reference 12;
Small amounts of organic material are readily decomposed by ignition in a flask filled with oxygen using techniques developed by Schoniger (reference 12) and others from work done at the end of last century. In the basic procedure, up to 50 mg of sample is wrapped in ashless filter paper, shaped so that a tail protrudes to act as a fuse, and placed in a platinum gauze clip mounted on a stout platinum wire fused into a B24 ground glass male stopper. A small volume of water, usually less than 10 ml is placed in a 500-ml conical flask fitted with a B24 female ground glass joint. The flask is flushed with oxygen until completely filled with oxygen, then without delay the paper tail is lit and the stopper assembly inserted firmly in the neck of the flask. The flask is held upside down in a stand behind a safety screen, to protect the operator, whilst the sample is allowed to burn. When combustion is complete, the flask is allowed to stand with intermittent shaking until all fumes appear to be absorbed, usually within about 20 minutes. Non volatile liquids may be absorbed onto filter paper for combustion, but liquids are best handled using methyl-cellulose capsules that are inserted into the platinum clip together with a paper fuse. Remote ignition of samples can be carried out using electrically fired devices. For some determinands such as metals, the water in the flask may be acidified. The technique is suitable for elemental analysis for nitrogen, sulphur, phosphorus, halogens, and metals. A wide variety of organic materials can be handled such as solvents, oils, plastic materials, grasses, leaves, cereals and other natural vegetation.

iii. Wet ashing with, sulphuric, nitric and perchloric acids, or with strong solutions of hydrogen peroxide. Unless it is absolutely certain that the sample will not react violently when heated with acids, always start with a digestion with concentrated sulphuric acid, followed by gradual increase in the concentration first of nitric acid and then of perchloric acid. Such treatments should always be carried out behind safety screens and the oxidation potential of the oxidant only raised gradually until a clear solution is obtained. How this solution is treated depends on the final sample form required.

If organic samples such as sewage sludge are ignited in a furnace, care must be taken to avoid loss of volatiles. Some metals may form carbides or nitrides which are not easily dissolved or volatilized except at high temperatures, and so not be analysed.

Molybdenum is particularly susceptible to loss by these means due to volatile trioxide, and oxychlorides, and refractory carbides and nitrides.

## 1.2 Instrumental Drift

All these methods have an instrumental basis, and so are often liable to instrumental drift. This can cause a false apparent trend if samples are analysed sequentially; hence for many of these methods, randomization of sample order, inclusion of standards and control samples spaced regularly throughout the analytical samples, but in random order of determinand concentration, or the regular repetition of the same control standard is essential for analytical quality control.

## 1.3 Hazards

Special hazards can occur with some pretreatment methods.
Perchloric acid, especially solutions over 60%, can cause fires and explosions if mishandled in the presence of organic matter. Wash away all spillage, only add this reagent to samples previously oxidized with nitric acid, and then initially only when diluted with nitric acid. Special fume hoods, ducting and fans, made entirely of non inflammable materials resistant to strong acids are needed.

Strong hydrogen peroxide solutions cause skin irritation (with white discoloration) which is best treated by thorough rinsing with water.

Hydrofluoric acid should never ever be allowed to come in contact with any part of the body. Care is essential, as initially a burn from this acid can numb the skin, pain only developing later. If in doubt, wash immediately. If contamination is certain, or painful symptons subsequently develop, get expert medical advice without delay.

Bumping solutions can produce bad scalds. Black-hot materials can give bad thermal burns.

Most fumes are harmful, many are highly toxic, proper ducting and ventilation is therefore essential. The volatility of some three valent thallium salts in steam is a typical unexpected hazard. A few compounds such as certain metal cupferronates have unexpected explosive properties.

Ultra-violet, and X-radiation are hazardous, as are also electron and ion beams, but good laboratory and instrument design and good laboratory discipline can prevent accidents happening with these sources. Appropriate screening and avoidance of scatter is essential. The radiation ceases once the equipment is switched off. Some instruments build up high electrical charges on some of their internal parts, some generate radio-frequency electric currents which require special wiring and special grounding, but this should be covered by makers instructions. Do not open equipment whilst in operation and thoroughly ground all metal parts before touching them (a clean dry wooden handle steel headed hammer fitted with an insulated ground wire is useful for this).

Most, but not all, spectrographs give off fumes. These not only contain products from the vaporization of the sample, but may include gases such as carbon monoxide, cyanogen, oxides of nitrogen and so on. These should be ducted away. Occasionally, dependent on the sample being analysed, such fumes may need treatment before being vented to atmosphere, but this is not the normal rule (see also Ref 8).

## 1.4 Recovery of Silver from Spent Development Solutions

Some of the techniques described in this booklet involve development of photographic film. Precious metal dealers will accept waste silver for recovery even in relatively small amounts. For information on the best way to process spent developer solutions for return to the trade, contact a suitable dealer. Dealers are listed in trade directories such as the latest edition of Kompass (Ref 86).

## 1.5 General Advice on Choosing a New Instrument

Analytical techniques are often common to many kinds of analysis including that of samples of types far removed from those encountered in water industry. Hence before purchasing a new instrument of an unfamiliar type it is best to find out as much as possible about the technique by which it operates. Find out the variables and criteria affecting performance. Consult existing users, even ones outside the water industry, for their opinion, and if possible inspect equipment and have your own test samples examined. Sometimes instruments basically consist of several units joined together. Atomic Absorption Spectrophotometry and all forms of Emission Spectroscopy including plasma are examples. In such cases even a hybrid instrument may be considered. Sometimes good appraisals already exist, for example ref 72E on plasma emission spectroscopy.

As so much of this booklet is concerned with the various forms of emission spectroscopy, choice of an emission spectrograph will be used as an example, but the same approach can be made to the purchase of most other instruments described here. In fact, the first question that ought to be asked is not which ICP instrument do we buy or even which type of emission instrument, but which technique do I use.

First consider all the techniques used for the determinations you are wanting to make. Then consider whether such equipment might enable you to do other analyses which you make from time to time. Decide whether the instrument is for use by one laboratory or whether it should analyse other samples as well from elsewhere. Then consider which techniques look the most promising from the standpoint of purchase price, operating costs and overall usefulness. This will narrow the field, but several techniques may still remain. Thus for some types of sample (such as soils, sludges and evaporated liquids) XRF (Chapter 4) might be an alternative worthy of comparison with emission.

During the preceding initial consideration, it will have been decided what sample types and which determinands are to be analysed now, and a list of possible future extensions also made. In preparing such lists take into account the versatility of the technique. Using various pretreatments, most of the techniques mentioned in this booklet can be adapted to the analysis of waters of all types, sewage sludges, soils, treatment and reagent chemicals, maintenance control samples, and many general investigations.

If considering the purchase of an emission spectrograph, first consider the source unit, or source units. It is sometimes possible to increase the versatility of a spectrometer by having interchangeable source units for different sample types or even different determinands. Some makers may prefer to sell a separate spectrometer for each source, but the possibility of interchange should be borne in mind. Decide on the possible sample forms to be used for the analysis, taking into account sample pretreatments and their effects on accuracy and precision, and the ability of the pretreatment to be done on a production line basis in the laboratory concerned. Samples might even be pretreated before shipment from one laboratory to another.

The type of source will determine the spectral lines emitted for each determinand. At this stage, and before finally deciding on the source, consider the sensitivity of the lines available, is the limit of detection low enough, what is the coefficient of variation at your sample concentration range? Then consider whether the lines need special instruments such as vacuum spectrometers, or gas shielded sources to suppress cyanogen bands. Consider also the degree of resolution required to separate lines and reduce overlapping line interference. Note also that choice of source and sample type determine the various chemical types of interference that can occur. If a variety of different sample compositions are to be analysed it is sometimes advisable to use different wavelengths for a single determinand dependent on sample composition. Interference and analytical concentration range are deciding factors here. All this will begin to outline the choices of source and spectrometer. The choice of spectrometer is dependent on the dispersion required for good resolution of the lines emitted by the source (the minimum of overlap; remember that lines have width in addition to the width due to the entrance slit, the overall line intensity resembling a probability distribution curve; see figure 9, emission lines have a similar shape.

The choice of light measurement equipment may be restricted by what the makers have available, but consider fixed and scanning phototubes, whether it is possible to add extra phototubes later, whether a combination of fixed and scanning tubes is possible, can film also be loaded, and so on. Adding extra phototubes later probably entails addition of extra switching and extra computer channels.

Before making the final choice consult other users of similar equipment within and outside the water industry. Attempt to have some of your own samples examined. Consult reviews and surveys, there may already be a critical survey published.

## 2. Atomic Fluorescence Spectrophotometry

This technique is similar to Atomic Absorption Spectrophotometry except that the fluorescence caused by the excited atoms reverting to the ground state is measured. A passing reference to this technique and to flame emission (discussed as part of the next section) occurs in the Atomic Absorption Spectrophotometry booklet in this series (Ref 19).

Apparatus is often home-made from commercially available parts, but good commercial instruments are available. 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 resulting fluorescence measured using a spectrophotometer or spectrograph placed at right angles to the line of the two source units. 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; otherwise analysis is for single elements in succession, as in atomic absorption spectrophotometry. For some elements greater sensitivity can be obtained than from 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. Table 1 lists the elements usually determined by Atomic Absorption Spectrophotometry. The normally used resonant wavelengths are given in Reference 19 Appendix A. Resonant lines are usually indicated in wavelength tables by an R. (Refs 23, 24, 25, 26 and 27, see also Refs 7 and 13-19).

## 3. Ultra Violet and Visible Region Emission Spectrography including Flame Photometry and Plasma Emission Techniques

### 3.0 Introduction

This section covers a number of important techniques which are 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, which can be used for 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 the determinand is high enough, which, for the elements usually determined by flame emission spectrophotometry, is often the case. Dissolved solids such as sludges are also determinable by plasma emission. Flame emission is usually used in the same way as atomic absorption spectrophotometry for the sequential determination of specific readily excited elements in a series of samples. DC Arc and Spark Emission can be used with liquid samples, but these sources are best suited to solid samples such as soils and dried sludges; but, if concentration techniques are used, solid samples are not difficult to prepare from liquid samples on a routine basis. The DC Arc source 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 are not very sensitive unless special techniques are used, though commercial plasma emission instruments with good sensitivity for mercury, phosphorus and several more of these elements are now available. Some substances are difficult to volatilize as solids but can be determined if brought into solution. More elements are determinable using Plasma Emissions than with DC Arc, and least with Spark Emission. For details see tables 2, 3 and 5. Flame Emission Spectrophotometry is also mentioned in the booklet on Atomic Absorption Spectrophotometry (Ref 19). 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 summarized information is of use:

Plasma Emission, which uses liquid samples or dissolved solids, will determine almost all elements except halides and rare gases, though concentration level depends on the spectrometer used. There are several types of plasma source varying from an almost pure plasma torch to sources approximating to the hottest DC arc sources.

DC Arc Emission, which uses solid samples, or solid extracts, precipitates or evaporites from liquid will determine most elements. It is also used for a special lubricating oil maintenance checking procedure.

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

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

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

A Scanning Photomultiplier enables scanning for unexpected impurities, can also be used alone for single element determinations, but should be used in conjunction with plasma emission to ensure a constant source and fixed photomultipliers for routine determinations to be worthwhile.

Film Read-out is complicated, but usually cheap and very versatile, given skilled routine technicians and attention to detail it can be made as accurate as photomultipliers; it can be fitted to some photomultiplier instruments to provide scanning for unexpected impurities.

Vacuum Path Instruments are 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. Use of gas purged instruments are an alternative (see table 5).

Prism Dispersion is non uniform but has its best resolution in the far ultra violet. Grating Dispersion is uniform for curved gratings which also focus lines without the use of a lens. The choice of dispersion method is usually a question of maker, elements determined and price. Both types are good. Plane gratings do not give uniform dispersion.

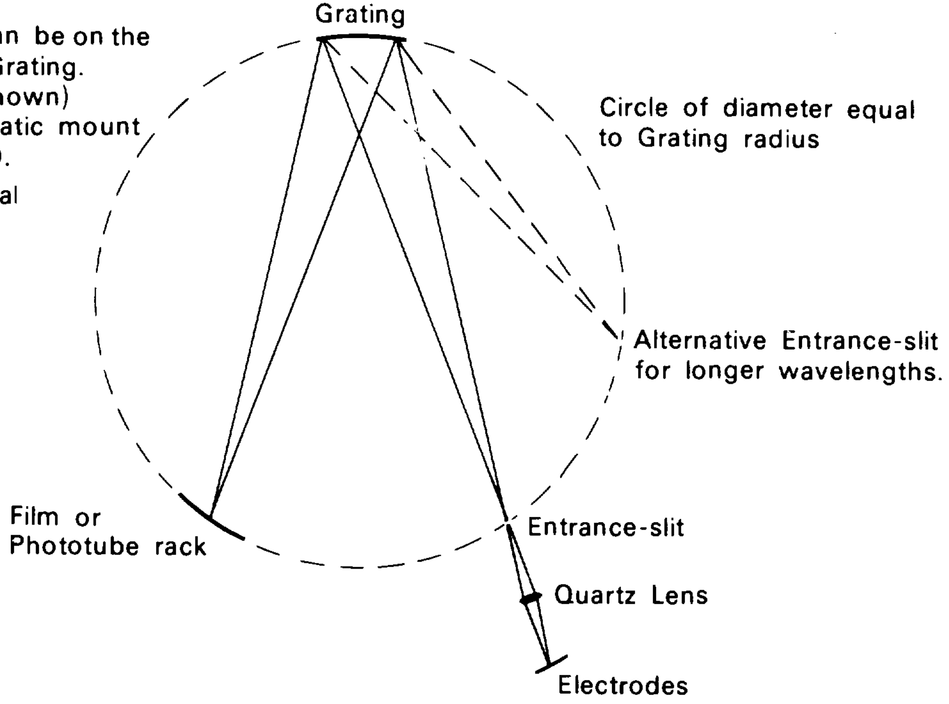
Although usually bought as complete instrumental packages, some users do build up their own instrumentation from parts, and the basic principles of all three are the same - a source, a spectrometer to split up the light by wavelength, and either a photometer or a camera device to record and measure the 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. This section will therefore be more detailed than the others, as much of the information is not readily available, especially to those unfamiliar with the specialty. 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. Equipment of this type is usually custom made. 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 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.

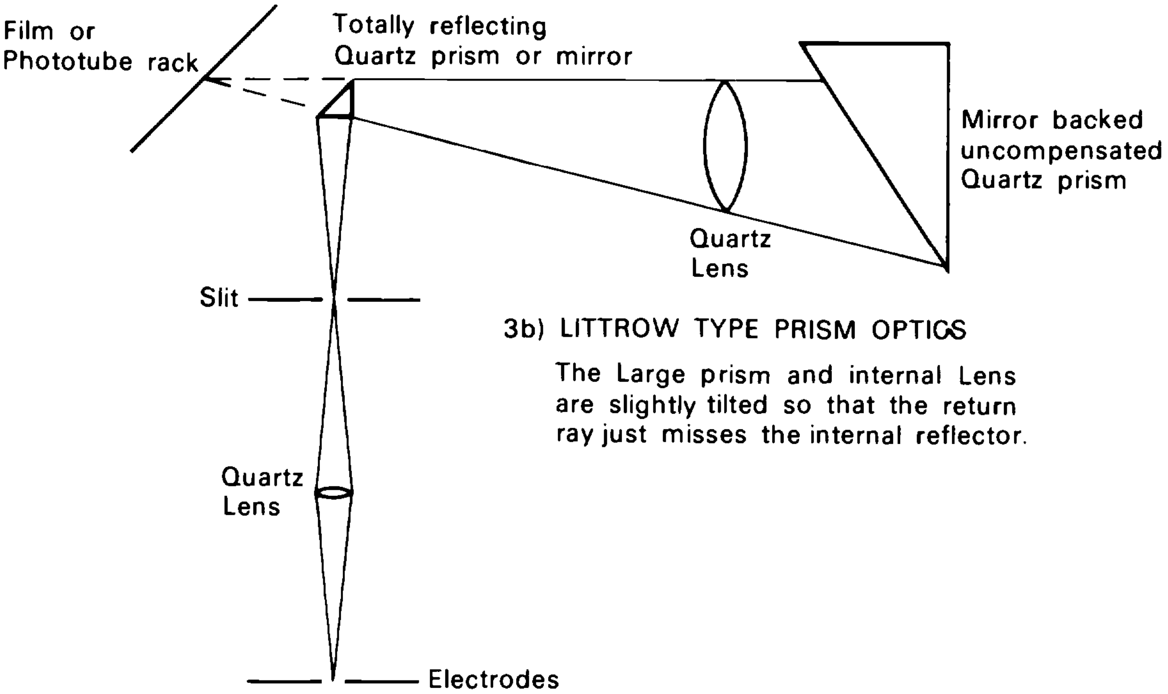
Apparatus cost varies enormously from exceedingly expensive to relatively cheap. It is possible, given enough time and workshop skill, to get good results from homemade equipment. The method requires technicians with a penchant for routine work rather

Fig 3. TYPICAL SPECTROGRAPH OPTICAL ARRANGEMENTS

3a) TYPICAL ROWLAND CIRCLE
FOR A CURVED GRATING-ASTIGMATIC

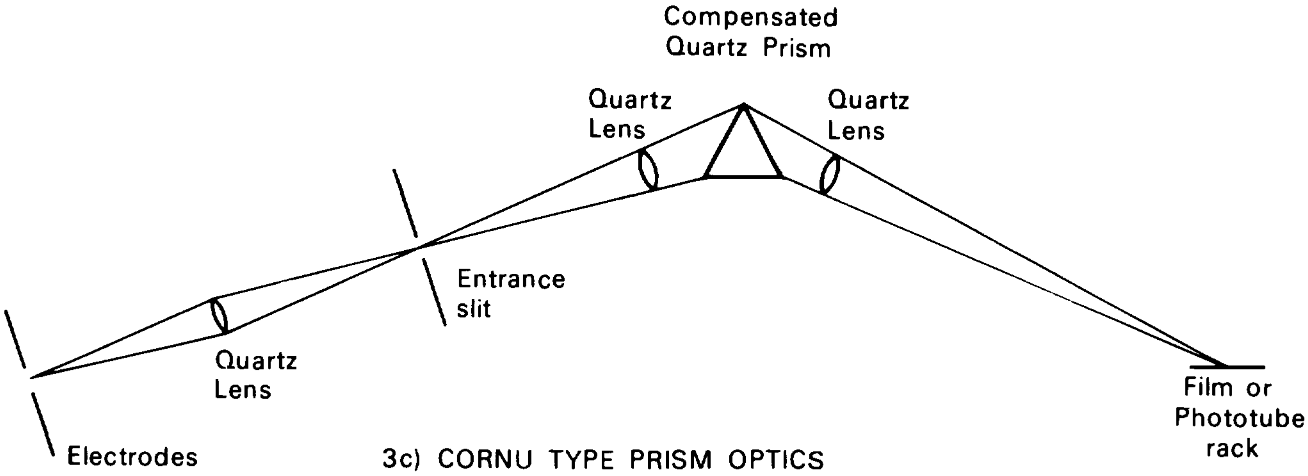
The slit and film can be on the same side of the Grating. (Eagle mount not shown) Normal for a stigmatic mount see Wadsworth FLO. Astrophysical Journal 1896.3.54





3b) LITTROW TYPE PRISM OPTICS

The Large prism and internal Lens are slightly tilted so that the return ray just misses the internal reflector.



3c) CORNU TYPE PRISM OPTICS

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 to four if everything is done manually, including calculations, to fifty or more samples for up to over thirty elements if automated equipment is used to its fullest capability.

The basic requirements of all instruments are therefore the same, a source unit, a device for separating the light, and a means of measuring the amount of light emitted at the wavelength of interest. This is regardless of whether the instrument is flame, arc or plasma. As commercial instruments vary in these component parts, each stage will be discussed separately.

## 3.1 General Description

Basically, emission spectroscopy is an improved version of the flame test. The sample is excited to emit light characteristic of the elements it contains. This light is dispersed, either by diffraction using a grating, or refraction using a prism; important spectral lines of the sought elements are identified, and their intensity estimated. This can be done photographically. Unfortunately, many but not all instrument manufacturers now manufacture only phototube instruments, but photographic instruments, are still in production or available second hand; furthermore, they are not very difficult to make from readily available parts.

In most advanced instruments, the intensity is measured photoelectrically, often with computerized calculation of the analytical results.

Flame photometry is a type of Emission Spectroscopy. In some of the cheaper instruments used for this method, wavelength selection is made using narrow band (usually interference) filters. Such instruments usually use simple photocells for measuring the emitted light. More sophisticated instruments use prisms or gratings, often with simple photocell read out; but integrating and photographic instruments have been made. The technique is one of the preferred methods for lithium, sodium, potassium, rubidium, caesium and some lanthanides.

As mentioned above, Emission Spectroscopy is often thought of as a qualitative or semiquantitative analytical method giving at best the order of magnitude, if enough attention is paid to detail, for routine analysis, a relative standard deviation of at least 10%, usually better, is attainable. Even 1% and less is not impossible if great attention is paid to every detail. For some elements such as beryllium and certain lanthanides, especially at trace levels, emission spectroscopy is the preferred method.

A good spectrographic laboratory is an expensive capital item, but they are relatively cheap to operate. It is possible, given a good workshop, to assemble your own spectrograph, using a replica grating or quartz prism, and quartz lenses. Many of the more complicated parts such as slits and electrode stands are available commercially. If a photographic model is built, provision should be made for reducing the amount of light reaching the film either by being able to mount filters or screens, and or by ability to mask part of the grating if used, in order to vary the light intensity by known amounts when calibrating the film, a rotating step sector in the optical path is also desirable. Sectors with a very large number of steps in binary logarithmic order are often used for this purpose. Sectors with steps obscuring in the ratio 1, 2, 4, 8 and so on (as in Fig 7 and Fig 1) are often used for semiquantitative analysis. Smooth logarithmically or exponentially curved sectors have also been made which are used for some semiquantitative analysis. Stepped filters are also available for similar purposes but are not suitable for calibrating film due to variation in absorbancy with wavelength.

Quartz is birefringent, in such cases compensatory design is essential. Usually prisms and lenses are made in two halves, one half compensating for the birefringence of the other whilst contributing normally to the ordinary optical properties. If quartz lenses are not available, face silvered mirrors are often used; but require a modified optical path.

Spectrographic methods are most economic when there are a large number of samples for the determination of several suitable elements at once. Once set up and calibrated, one large photomultiplier spectrograph is capable of analysing solid sludge, soil and sediment samples for thirty or more elements at a rate of better than one every ten minutes. At the other end of the scale, times for water samples analysed on photographic spectrographs will be longer than this depending on the degree of sample preparation required, and the number of elements determined per sample, but with proper organisation for routine use, rates of several samples an hour can be achieved for five or more elements even, for skilled operators, up to the full list in table 3.

The two big advantages with the photographic method are the ability to return to an exposure later and analyse for additional elements coupled with the ability to preserve the essential record of the analysis for later checking and the ability to check for unusual or unexpected elements and make qualitative-semiquantitative analyses. Some photomultiplier spectrographs with chart readout also have this ability of preserving results; but unless they are scanning units (see below) photomultiplier spectrographs are not capable of providing analyses for elements other than those for which they are set up. The disadvantages of the photographic method are cost of film and the time and labour involved in developing and reading the films or plates.

## 3.2 Types of Sample

### 3.2.1 Liquids and Dissolved Solids

Direct analysis of liquid samples by sucking or spraying them into the analytical flame is normally used for flame photometers and plasma source spectrophotometers. DC arc analysis of liquids is also possible using special sprays. Flame photometer type gas burners have been used as sources for photographic type spectrographs for trace level alkali and alkaline earth metal and similar determinations of those metals with low excitation potentials. Variations in viscosity, surface tension, and density can alter the amount of sample arriving at the source. The acidity of a sample and the acid anions present in it can affect line intensity and also the spectral background both for flame and plasma sources. Samples and standards should therefore be as similar as possible.

Special hollow graphite and porous carbon electrodes are available for liquid samples used with spark and similar sources, but usually these are only suitable for analyses for major metallic ions in concentrates. Either the sample is placed in a hollow cup which is part of or attached to the lower electrode, the liquid continually wetting a central rod in the electrode, or the upper electrode consists of a hollow tube with a porous bottom through which the sample soaks into the source itself. Both techniques have relatively poor precision and are falling into disuse. A few laboratories have used inert gas atomizer sprays similar to plasma source units for DC arc spectroscopy etc. A method using a rotating disc lower electrode dipping into a trough filled with sample has been suggested by ASTM (ref 20) for use with water samples. Liquid samples may also be converted to solids and analysed as solids, see below.

### 3.2.2 Solids

Dried sludges, sediments, soils, and rocks, often preignited to prevent the sample being blown out of the flame prematurely by gas evolution, are usually mixed with high purity graphite in weighed amounts, loaded into hollow graphite electrodes for use with DC arc and similar sources. Complete fine grinding is essential prior to mixing. For some analyses, samples may also be mixed with fluxes or spectroscopic buffers which control the volatilization and excitation of the sample. When determining elements present in the sample as very volatile compounds which volatilize early in the discharge, some analysts use porous graphite caps to cover the charge and only measure that portion of the discharge known to contain the sought element. The optimum time for measurement is determined during the preliminary investigations, by making a series of measurements for the sought element at regular intervals throughout the total burn. How this is done depends on the type of instrument used. For phototube instruments the phototube output or condenser charge may be monitored against burn time. For photographic instruments either a series of identical samples are exposed for increasing times to complete sample burn, or the film is moved at regular intervals during one or two sample burns. Typical limits of detection can be estimated using table 4.

Alternatively solid samples may be dissolved and analysed as liquids chiefly by plasma emission. Limits of detection are dependent on instrument type, exposure time and spectrum line used, but typical values are given in table 5.

Large volume water samples can be evaporated to dryness for analysis as solid samples, the final stage being done in a preweighed platinum or similar dish from which the evaporite can be easily removed after first being weighed, then homogenized and used as a solid sample, or the sample may be evaporated under an infra red lamp into a graphite cup electrode. If this latter technique is used greater care is needed to ensure symmetrical evaporation, as asymmetric samples are a cause of analytical error due to the consequent poor alignment of the discharge with the optical path; it is not recommended for accurate work. For water samples, chemical concentration techniques are more usual.

Extraction of chlorides into ether, or of dithizonates, 8 quinolinolates, and diethyldithiocarbamates into chloroform are the most commonly used methods (see Ref 51, 52 and table 6). Such extracts are evaporated, converted into a convenient form, often by ignition, the solid weighed and made up into electrodes in the same way as solid samples. Precipitation as hydroxide, or more usually as insoluble organic complexes such as diethyldithiocarbamates, tannates, 8-quinolinolates, thionalides and similar salts, which are then subsequently converted to oxide, forms the basis of several very accurate methods for trace impurities such as silver, molybdenum, beryllium, hafnium, and the lanthanides. These precipitates are ignited at temperatures low enough to avoid volatilization of the sought elements in the most volatile form that is likely to be formed, and are then analysed as solid samples.

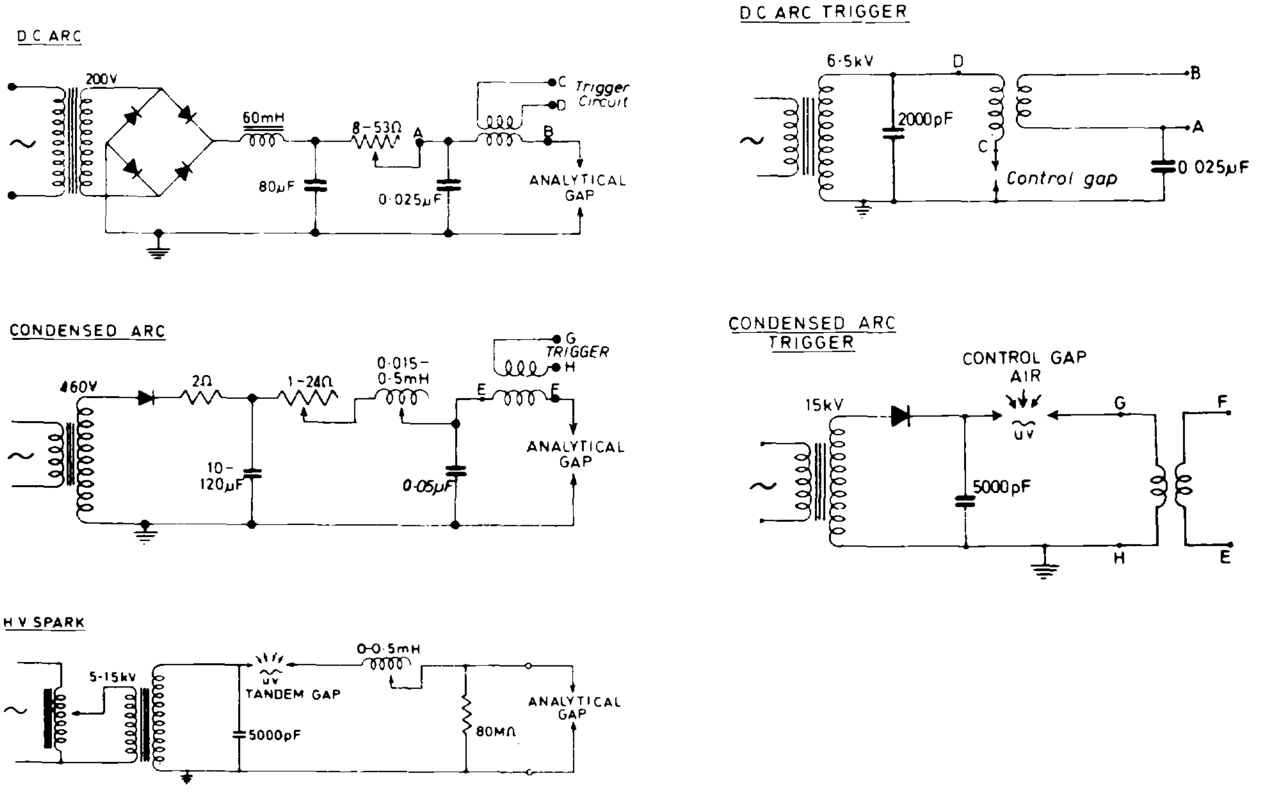


Figure 4 Typical DC ARC, AC ARC and HV spark source unit diagrams (Courtesy of Rank Precision Industries)

Carrier concentration coupled with the internal standard technique, in which the internal standard used is also the carrier can also be used to provide solid samples and often greatly improve the accuracy and precision in the analysis of liquid or dissolved samples. After concentration, by evaporation if necessary, a known amount of a salt of a carrier metal, which can also act as an internal standard (see below) and is also neither likely to be present in the sample nor a determinand, is added to the sample solution and precipitated with a reagent that also precipitates the sought elements. The sought trace determinands are coprecipitated along with the carrier metal, and then determined as if they were an impurity in that matrix, calculation being via the weight of added carrier and volume of sample taken. In some cases special ignition control is necessary to ensure reproducible results. Thus with an aluminium carrier, provided the determinand is not volatilized, ignition is best carried out at 1400°C or higher as this improves reproducibility of the reference aluminium signal. See References 40-47, which give details for the determination of traces of: aluminium, beryllium, chromium, hafnium, molybdenum, nickel, silver, tin, titanium, vanadium, zirconium, yttrium, scandium, lanthanum and all the lanthanides (except promethium) in solid samples by solution in acid, and addition of the carrier etc. If a water sample is acidified, the carrier added and the method then followed, it is equally possible to determine the above elements in a water sample. (See Table 7.) A similar concentration step followed by resolution could be used with plasma sources.

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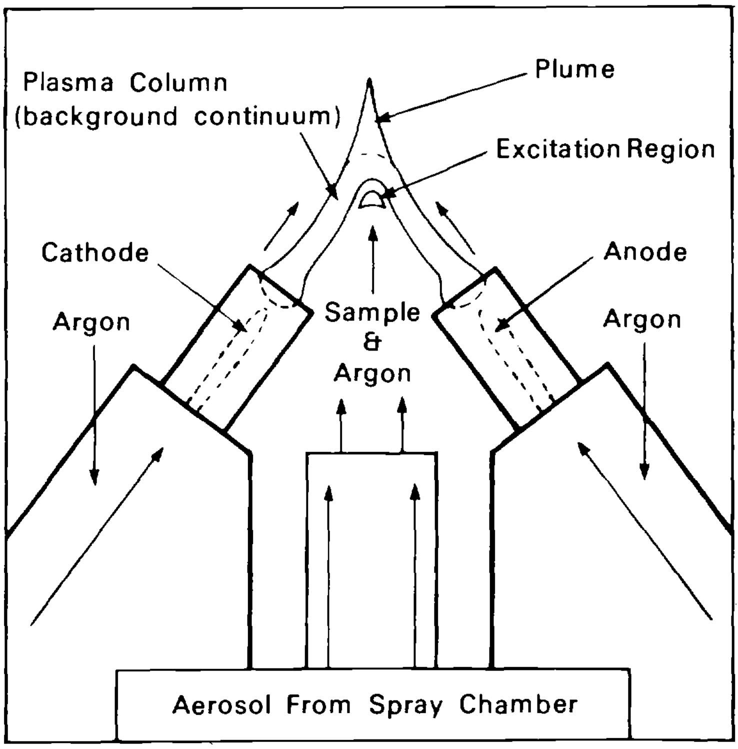


Figure 4a Schematic arrangement of a D.C. Plasma Jet

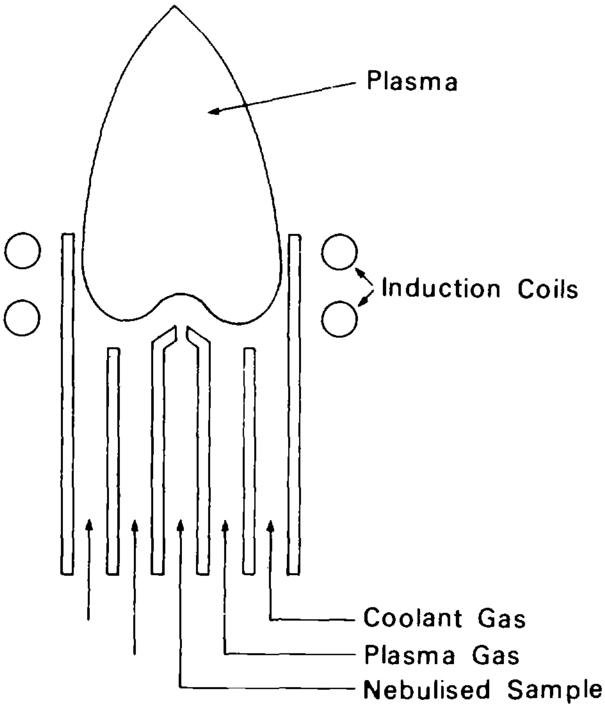


Figure 4b Schematic arrangement of an inductively-coupled Plasma torch

## 3.3 Types of Source

The simplest though least used source unit is a small gas burner with aspiration of a liquid sample. There are several types of commercially available burner, designed for various gas mixtures. Although a large number of elements can be determined using such sources, they are normally only used for those elements with strong spectrum lines with excitation potentials of about 4 electron volts or less (see Table 2).

### 3.3.1 Flame Sources

Because of the relatively low temperature of most flames, the volatility of the sample is very important and can affect the observed result. The anions present in the sample can greatly affect volatility and so affect the analysis; conversion to a single reproducible anion such as chloride or perchlorate is therefore desirable. Ion exchange is often suitable for this. Even so, interelement effects such as those between sodium, potassium and calcium can occur in the flame; but corrections can be made for this (see on). The commonest flames used are air/acetylene, oxygen/acetylene, nitrous oxide/acetylene and oxygen/propane or butane, but some very peculiar mixtures including cyanogen-oxygen have been described in the literature. Only the more readily available flames are recommended, electric sources are safer and more controllable than the bizarre flames. Always use the gas mixture for which the burner was designed. If in doubt consult the makers. Use of wrong mixtures has caused explosions. See Refs 53-61.

### 3.3.2 Plasma Sources

For solutions, either the Inductively Coupled or the DC Plasma Jet which are really extensions of the DC arc are most frequently used sources. These sources combine the ease of sample introduction of flame sources with the high excitation temperature of electric discharges. They are characterised as being flame-like in that they are extended from the point at which power is applied. This allows the sample to be atomised and excited in different spatial regions of the plasma so that the spectrum emitted may be observed at a point remote from the core of the discharge where there is comparatively low intensity of background radiation. They have the advantage that the sample remains homogeneous throughout the exposure and hence they can also be used for both qualitative and quantitative analyses using phototubes. To carry out a complete qualitative analysis for all elements excitable within the capability of the instrument, the instrument is equipped with a scanning phototube moving slowly along the Rowland circle or focal plane of the prism optical system. Output from such a phototube is recorded on a chart recorder against position of the phototube inside the spectrograph. Line identification is made in a similar way to photographically recorded spectra. For quantitative measurements, for which there is no permanent fixed phototube, the scanning tube is stopped so as to record the intensity of the required line. Liquid sources should always be cleaned or washed thoroughly between samples to avoid cross-contamination.

Recent developments in plasma emission spectroscopy have occurred in three main areas: –

i. d.c. plasma jet
ii. microwave plasma
iii. radio frequency inductively-coupled plasma.

#### *i. DC Plasma jet*

Many designs of dc plasma jet have been described (ref 64). One system which has been used is shown schematically in Fig 4a. The source consists of a dc arc which is extended by streams of argon which surround the electrodes and by a stream of argon which carries the nebulised aqueous sample. The excitation region is separate from the plasma core and is reported to be at a temperature of around 6000° K. The dc plasma jet has been successfully used for simultaenous multi-element analysis for a wide variety of samples, and systems using this type of plasma are commercially available.

#### *ii. Microwave Plasma*

The microwave-induced plasma draws its energy from a high frequency (usually 2.45 GHz) electromagnetic wave resonating in a specially tuned cavity. It has been reported that the introduction of even small quantities of water into the argon which supports the plasma causes it to be extinguished (ref 65). Desolvation of aqueous samples may be used (ref 65) but this, in itself, may lead to matrix interferences (ref 66). As a result of these limitations the microwave-induced plasma has not found extensive application in analytical spectroscopy. Another microwave plasma, the capacitatively-coupled plasma in which microwave energy produces a discharge in a suitable gas at the tip of an electrode, is not of great analytical importance.

The technique has been used for the determination of traces of ammonia and nitrite in water. Ammonia is reacted with hypochlorite, nitrite is reacted with sulphanilamide forming nitrogen which is purged out by helium into the plasma. Nitrate can be prior reduced to nitrite (ref 72H).

*iii. Radio Frequency Inductively-Coupled Plasma*

This type of plasma is shown schematically in Fig 4b. It is sustained by an oscillating magnetic field produced by a coil through which a radio frequency alternating current is passed. Free electrons in the plasma gas (usually produced by initial "seeding" with a Tesla coil) are caused to flow in circular paths by the oscillating magnetic fields. The resistance to this current causes ohmic heating of the gas producing a plasma discharge at a temperature of 6000-10000° K.

The three gas flows in the plasma torch result in a stable annular plasma into the central channel of which the nebulised sample is injected. The emission spectrum is viewed at a point above the plasma core where the background emission is low.

Inductively-coupled plasmas have been used extensively for simultaneous multi-element analysis of aqueous solutions. The features which make the inductively-coupled plasma particularly suitable as an analytical source are:—

i. A range of linear calibration which may be up to five orders of magnitude.

ii. Limits of detection for many elements which are comparable or superior to flame atomic absorption spectrophotometry. They are reported to be similar to the limits for the most sensitive DC arc solid sources.

iii. An extensive range of elements which may be determined.

iv. Interference effects can be made small by correct choice of analytical line and design of equipment. However, hydroxyl band spectra and emission lines from the plasmagas (agron, nitrogen, helium) can cause overlapping line interference. Some transition elements have complex spectra, other elements such as calcium and magnesium can cause background. These interference effects are similar to DC arc emission and can be corrected for similarly (Sections 3.10 and 3.11) Blank samples cannot be used for correction (Refs 66 and 72A). See also Refs 5, 39, 59, 62 and 67.

See also Refs 7 and 62-72G.

All liquid sources require as clear solutions as possible to avoid blocking the nebulizer tube. As with the DC arc described below, there are optimum viewing heights above the electrodes for the plasma emission.

### 3.3.3 Direct Current Arc Sources

The commonest source used for the analysis of solid samples and evaporated residues is DC arc. There are numerous designs of electrodes, which can be made of either graphite or carbon. These electrodes give rise to cyanogen and carbon monoxide band spectra (see section 3.8). Only the former are a great nuisance. They can be masked by surrounding the source with an atmosphere such as 80% argon 20% oxygen. If with DC sources, the sample is made the cathode, positively charged ions are held in the flame rather than repelled from it, and the sensitivity for trace elements is increased, DC arc sources are hotter than the spark and AC arc sources and so are more suitable for trace element analysis and refractory samples such as sand and alumina. Early workers found them suitable only for semiquantitative analyses, but later workers have developed reliable quantitative DC arc techniques whilst the development of the plasma source has improved the reliability of analysis for liquid samples.

In general, the hotter the source the less likely it is to suffer from interference effects. Hence the advantage of the inductively coupled plasma emission source, though even here interference effects are known. However interference corrections are possible (see section 3.11). Other sources are known, such as combinations of DC arc and laser heating, argon jacketed DC arcs, and arcs fitted with concentric sprays.

In the DC arc method, a known amount of solid sample, mixed with graphite and carbon to make it conducting (unless it already contains sufficient carbon already) is loaded into a graphite or carbon cup lower electrode which, for low concentration analysis is normally made the cathode of the arc. If the sample electrode is made the anode positive ions are repelled and attracted to the cathode so that residence time in the plasma is short. Making the sample cathodic and the counter electrode the anode tends to increase residence time in the plasma and so enhances the emission of many lines. A round tipped graphite or carbon rod is usually used as the upper electrode (usually the anode). For samples likely to contain refractory substances such as silica and alumina, the cup in the lower electrode is usually undercut by a groove to limit heat loss down the electrode. The more volatile substances tend to vapourize first, and the most refractory substances last or hardly at all, though concentration and solubility in the molten bead that often forms in the sample electrode cup also affect the vapour pressure. In consequence the composition of the plasma between the electrodes will vary with time throughout the burn. Occasionally, where there is a marked difference in volatility between two substances this can be used to enhance the spectrum of one relative to the other. A time study is made in which the film is exposed or the intensity is measured only for a known time during the burn, a series of such exposures being made for overlapping time intervals. From these it can be determined whether it is desirable to omit some of the early or late part of the burn. In the former case, the part of the total burn which is disregarded is sometimes known as preburn.

Table 3 lists elements determinable by routine emission spectrographic methods. Typical source units are illustrated in Fig 4. Table 5 lists some typical Plasma Emission spectrum lines.

Arc sources are usually started with a spark igniter, though other devices have been used in the past. Spark sources are interrupted either with an air jet device as shown in Fig 4, often with ultra violet light ionization of the gap, or by a rotating commutator device with gaps so that contact is made and broken again continually. Such sources are used with all types of read out; although usually used with phototubes, plasma and flame sources can be used with film.

## 3.4 Spectrometers and Spectrographs

Resolution of spectrum lines is essential if interference effects due to overlapping lines of other elements are to be avoided. For the relatively simple spectra given by flame sources, high resolution is usually not required, but for the hotter high energy sources, good resolution is essential. For the hottest plasma torch sources the best resolution obtainable is essential; even so background correction and overlapping line interference correction may be needed (see the appropriate sections below).

The simplest flame photometers use narrow transmission range interference filters to isolate the sought element wavelength. For more complex emissions, spectra are produced either by refraction with a quartz prism (most optical glass absorbs ultra violet light and the majority of reliable analytical emission spectrum lines are in the ultra violet), or with a reflection grating which also focuses the light on to the film or photocell. All other factors being equal, and if air absorption is not important, which it can be, the longer the spectrograph path, the better the resolution; but other factors are also important. Prisms have non linear resolution, the resolution being better the further into the ultra violet they are used. Gratings have constant resolving power which makes initial wavelength calibration much easier. The more closely a grating is ruled (the more lines it has per unit length) the better the resolution, but the higher the cost. On the other hand they produce a series of spectra (called first order, second order, third order and so on) which overlap each other such that the wavelength multiplied by the order number is constant. However this is rarely a problem. Most of the regularly used spectrum lines are in the region of 210nm to 400nm with a few lines sometimes used up to 700nm, hence the overlaps are as follows:

| | | | | | |
|---|---|---|---|---|---|
| 1st order | 210 | - | 400 | - | 700nm |
| 2nd order | 420 | - | 800 | - | 1400nm |
| 3rd order | 630 | - | 1200 | - | 2100nm |
| 4th order | 820 | - | 1600 | - | 2800nm |

Usually most light is in the zero order ray, a lesser amount is in the first order, the intensity falling off rapidly with higher orders. Additional stacking of spectra can be obtained by using crossed gratings (two gratings, one transmission, one reflecting, mounted with their rulings at right angles) or a prism and a grating, a device occasionally used when order overlap causes confusion between lines with wavelengths an exact whole number multiple apart. (Both these effects are noticeable when car headlights are viewed through very fine net curtains). It is possible to "blaze" a grating so that it focuses the majority of its light into two selected groups of orders. This is done by making the rulings vee shaped. If the two sides of the vee are at different angles there will be two selected groups of orders, one lighter than the other. These gratings tend to be more expensive than ordinary ones but are sometimes used when higher order spectra are necessary to improve resolution of lines not overlapping due to broadening. Holographic gratings are sometimes used to minimize stray light. Good quality replica gratings are available. These are not ruled themselves but cast using a ruled grating as a mould. They are much cheaper than ruled gratings.

As good a quality grating as possible should be chosen. It should be free from ghosts. Ghosts are spurious spectral lines, or misplaced lines due to faults in the ruling of the grating. Gratings are also known which have gaps in their spectra. Always check a grating for such faults before accepting it. Never touch the face of a grating, and keep it in an absolutely clean condition. Prevention is better than cure. Whether a dirty grating can be cleaned or not depends on the grating itself and the dirt. Dust will ruin the performance and be a cause of error.

Whilst increasing dispersion by increasing the number of rulings per unit width of the grating, increasing the refraction of the prism system, increasing the length of the spectrograph, and reducing the entrance slit width will improve the resolution of a spectrum, there is a natural limit to the extent to which two adjacent (or overlapping) lines can be resolved. This is due to the finite widths of the spectral lines. Figure 9 shows an example taken from an X-ray fluorescence spectrum where resolution may just be possible. If the lines were a little closer together only one large broad line might be visible and the lines might not be resolvable.

Slit width is another criterion for the determination of elements. The narrower the entrance slit, the better the resolution, but the less light is passed for the detector system (phototube or film) to measure. A compromise is necessary. With phototube measurement of light intensity, exit slits are also used. Such slits should admit as much light from the determinand line as possible, but exclude as much other light as possible. In some circumstances compromise is again necessary.

Prism and plane grating spectrographs need ancillary optics, usually quartz lenses or face silvered mirrors to focus the image of the entrace slit on to the photographic plate or phototubes; but concave gratings are available that, which if suitably used, dispense with all ancillary optics; except perhaps for a quartz lens to focus the arc or spark onto the entrance slit. Most grating spectrographs use reflectance gratings (gratings which are also mirrors) for simplicity of design. If a concave grating is used, the optics can be greatly simplified as entrance slit, grating and final spectrum all lie on a circle of radius equal to half the radius of curvature of the grating. This circle is called the Rowland circle. Typical spectrographs are illustrated in Fig 3.

Sometimes it is not possible to bring the whole of the desired spectral range on to the film or phototube bank due to lack of space. The simplest solution to this problem for a grating spectrograph is to have multiple entrance slits and optical benches. If this is done, the entrance slits not in use must be completely capped over to prevent unnecessary light entering the instrument. In a few instruments the zero order undiffracted ray from the main grating is taken to a second grating inside the same case which produces another set of spectra. With proper design the wavelength range available in given dimensions can be extended by such means. For prism spectrographs the more usual technique for extending the spectrum is to rotate the prism, but the locks should be firm if reproducibility is desired. Hence there should only be a few preset positions in which the prism unit can be set. With phototube instruments care will have to be taken to ensure that the correct tubes are used with each prism setting. The insides of spectrographs are usually fitted with light baffles and are covered with light absorbent paint or material which will absorb the zero order ray from the grating or other scattered light. In addition, phototubes are shielded except over their light entrance.

Quartz lenses and prisms are usually amenable to careful cleaning provided there is no risk of scratching or etching the surface, but face silvered mirrors are, like gratings, exceedingly difficult to clean. If in doubt, seek expert advice.

In simple flame photometers and some scanning instruments the prism or grating is rotated to bring the desired wavelength on to the phototube. In most spectrographs, film or phototubes are arranged on a rigid holder at the focal plane of the optical system. Various arrangements are available commercially, designed to suit the constraints of manageable shape and good resolution at the most useful wavelengths. This latter is determined by the spectra of the elements sought, and the type of source used.

If photomultiplier tubes are used, accurately adjusted exit slits may be used to cut out interference from adjacent lines of other elements. If the analytical spectrum lines are located too close together in one region of the spectrum for all the phototubes to be mounted, small face silvered mirrors are sometimes used to reflect the desired lines on to phototubes mounted in more convenient places. With such sophisticated designs, accurate optical alignment is essential. Many commercial phototube instruments are fitted with self monitoring devices to maintain alignment. Vibration proof mounting for the instrument and very good temperature control also help. Visible region lines are often used for initial alignment and clips are provided for film to be mounted both in front of and behind the exit slits for use when making fine adjustments. Unfortunately, the size of the slit and its mount precludes the use of two spectrum lines closer than 2nm apart. For this reason some instrument makers may measure the stronger of a pair of close lines, whether due to real relative line intensity or to concentration, using the second order spectrum to get better resolution even at the expense of loss of sensitivity. With grating instruments, a few makers mount the entrance slit exactly opposite the grating across the Rowland circle thus giving two first order spectra, but this enlarges the instrument considerably.

Other devices have been considered such as special exit optics, extra gratings, prisms and so on. All are dependent on very firm mounting to the spectrograph frame, good housing conditions and very skilled adjustment.

Air absorbs ultra violet light of shorter wavelengths, but the effect does not start to become appreciable until well below 250 nm. By 230 nm it is quite marked, for 3m spectrographs and below 207 nm observation in air is impossible even with 1.5m instruments. Fortunately spectral lines are usually widely spaced in this region especially if quartz prism instruments are used. However, in addition to very sensitive lines such as Zn 213.8 nm, Cd 228.8 nm and Te 214.3 nm, there are some very useful spectrum lines below 210 nm, especially for mercury and the non metallic elements. Recourse is made to an evacuated spectrometer case and argon jacketing of the external optical path. Argon filled spectrometers fitted with a purging device have also been used successfully by Severn-Trent Water Authority down to 196nm. Most instruments are fixed photomultiplier types, but gadgets to enable film to be loaded and unloaded have been devised, using small entry locks with rapid pump down systems such as are used for X-ray fluorescence samples.

## 3.5 Measurement of the Spectrum

Two measurements are essential, the wavelength of the spectral line, and its intensity. Most fixed photomultiplier tube instruments have the exit slit phototube assemblies checked on delivery by the makers who will usually also service the instrument subsequently if it goes out of adjustment. Checks on slit location can often be made using film carriers provided in the instrument. For scanning phototube instruments, the problem of line identification is similar to that for film except that calculations are made by direct measurement of distance travelled from known lines rather than measurement of projected images. With gratings, wavelength can be calculated, but, for later use, films should have a recognisable reference mark on them from which calculations and alignments are made. For prisms, wavelength can also be calculated, and calibrated scales are often fitted to commercial instruments; but, if as may happen, it becomes necessary to check the dispersion of an instrument, a photograph is made of a suitable spectrum and calculations made from that. Iron and copper are the most frequently used calibration spectra; but aluminium, magnesium, silver and tungsten are other favourites. The chief requirements are that the element used be available in a reasonable degree of purity, have a few very readily identifiable spectrum lines (either by strength or by pattern), which act as a starting point of known wavelength, and a series of sufficiently strong lines spaced fairly regularly across the wavelength region to be checked. With instruments that are normally photographically recording, it is not so much the location of the lines in the spectrograph itself that matters, as their location on the magnified image given on the film comparator or densitometer screen. This will be subject to the magnification system incorporated in this latter instrument. In which case, for reliable work, it may be advisable to run control measurements periodically, checking the dispersion of a convenient easily identifiable multiplet such as the copper doublet (324.759 and 327.396nm), the magnesium quintet (277.669, 277.829, 277.938, 278.142 and 278.297nm) (see Fig 2), or the silica series (250.690, 251.433, 251.612, 251.921, 252.412 and 252.852nm) or one of the several convenient series of iron lines. Atlases of spectral lines exist (Refs 23-27); but it should be remembered that for some of the rarer elements these are not complete. Reference may need to be made to current journals etc. Even common elements may have unrecorded faint lines which can be the cause of interference effects. These too are listed in the journals and trade bulletins as they are discovered. A few otherwise unlisted lines for rare elements at shorter wavelengths are listed in Table 4. Recently two tables specially for plasma sources, which are intermediate between arc and spark line atlases, have been issued (refs 27A and 27B). This intermediate nature is due to the combination of high temperature and the oscillating nature of the discharge. Portions of typical spectra are illustrated in Figs 1 and 2.

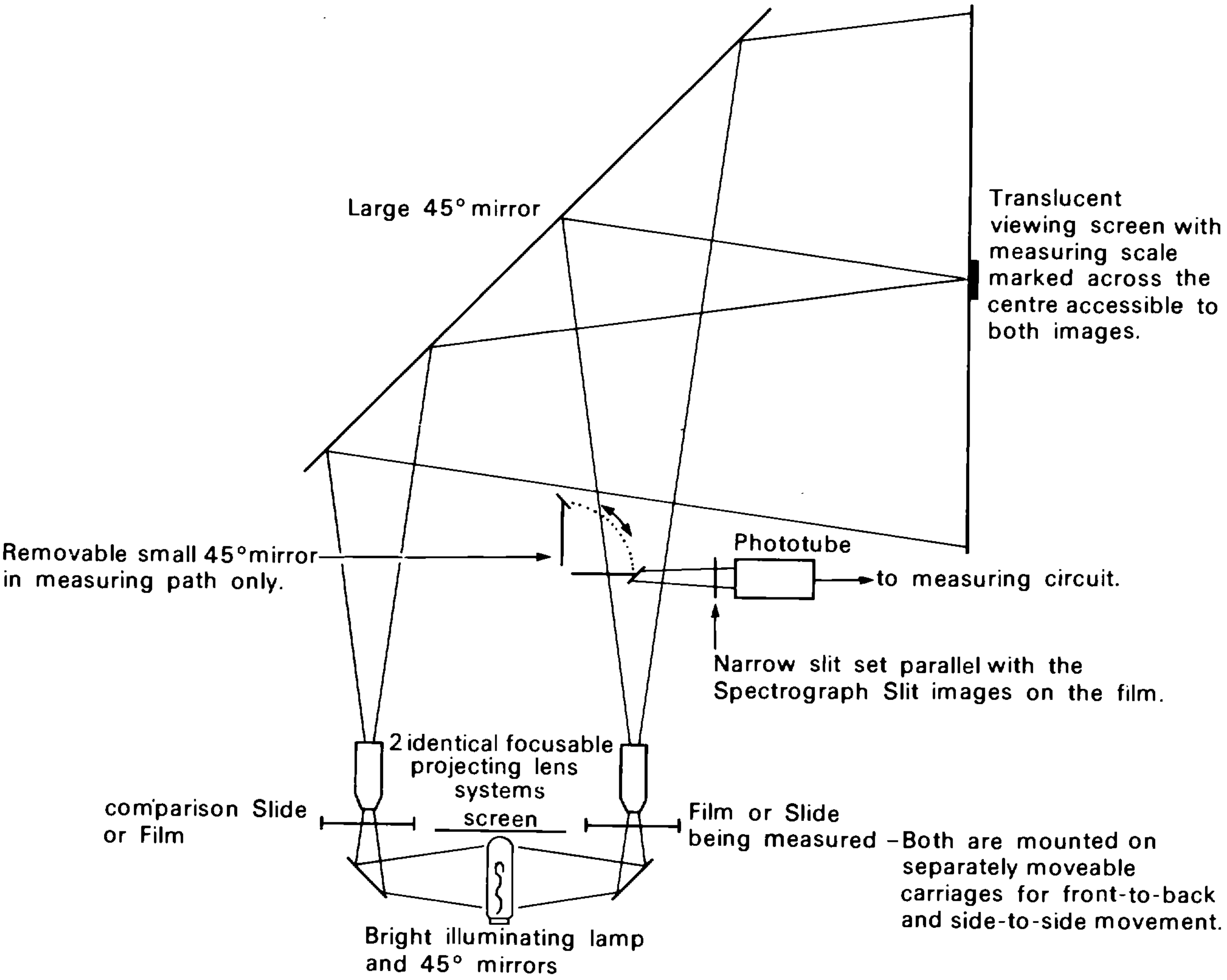


Figure 5. The principle of a slide comparator-densitometer (many other arrangements are possible).

Though satisfactory as shown, it is best if either the small moveable mirror or the slit can traverse slightly so as to be sure of reading the maximum film densities. Some instruments have only partially silvered diverting mirrors so that the line being read is still visible on the viewing screen, others have a mark on this screen corresponding to the slit position. It is possible to couple the small traverse and the phototube and put to a cathode ray oscillograph and thus obtain density profiles. Another model traverses the films and records a profile on a chart.
A similar device can be used for reading X-ray diffraction films qualitatively and quantitatively.

If wavelength calibration, especially of the image given by a densitometer or slide comparator is required, measure the distance between known spectrum lines at various parts of the analytical range using a travelling microscope mounted in front of the screen, and make a graph of dispersion against wavelength. Use this along with a reference spectrum (usually a copper or iron arc) to calculate the position of sought or unknown spectrum lines when making analyses. Check by calculating both ways from known lines above and below the wavelength of the line being sought, or the unknown line being identified. Alternatively if the instrument has a scale, note the scale readings corresponding to lines of definitely known wavelength and plot a calibration curve. Use this in a similar manner. When identifying spectra, it must also be remembered that quantized band or molecular spectra are also excitable under analytical conditions and can be mistaken for element lines. Unfortunately most spectral bands are not listed in the Tables of Line Spectra referred to above, but are published separately (Ref 28). A few of these molecular lines have been used for element detection and determination provided excess of the other unsought element in the molecule is known to be present in the sample (by addition prior to analysis if necessary). Some flame photometers use metal oxide band heads for analytical measurement and fluoride and chloride have been determined by measuring the calcium fluoride and calcium chloride band heads in the presence of excess calcium ion. Although band spectra can cause interference this can sometimes be overcome, as the line intensity varies regularly with wavelength along a band. Hence any anomalous intensity due to an overlapping line spectra can be detected and if necessary calculated. The commonest band spectra encountered are cyanogen, carbon monoxide, silicon oxide and some alkaline earth and lanthanide oxides. Calcium halides also give band spectra.

Control of spectrum line identification when using the photographic method can be made in several ways. Very experienced spectrographers may be able to recognise certain very distinctive groups of lines, though care should be exercised with unfamiliar samples. Alternatively, a substance which is not being sought and which has a useful spectrum may be added to the samples as a reference. Another alternative is to include a reference spectrum, quite often iron because of its availability and abundance of spectrum lines, on each plate as a guide. In very special cases the spectrum of the sought element may be used for comparison; if this is done, the pattern is more important than relative intensities of lines as this may vary with the compound (or free element) used to produce the reference spectrum. As there is a slight degree of play in screw threads, greater accuracy will be obtained when making measurements involving turning a worm drive (common on many instruments) if the final approach to a setting is always made in the same direction.

When using densitometers or slide comparators, it is essential to control the magnification. This can be done by matching the reference line spectra, but one rapid way is to always set the spacing of two well known moderately separated spectral lines at the same distance. Cu 324.7 and 327.4 nm are recommended for this.

For instruments using phototubes alignment is vital. Actual exit slits are usually aligned by means of photographs made with film mounted either in the front or back of the slit. Overall alignment is often checked and maintained automatically by means of special monitor slits in which the lower half of the slit is widened to one side and the top half on the opposite side, so that any displacement can be quickly spotted measured by a suitable phototube device and corrected by means of servomotors.

## 3.6 Qualitative Analysis

Qualitative analyses are most readily made using photographic techniques as described in 3.5 above. However, provided a sprayed sample is used which stays homogeneous throughout the traverse, comparable results can be obtained by a traversing phototube spectrograph. The photographic techniques are amenable to subsequent quantitative estimations if made by experienced spectroscopists. Rotating wheel electrodes and hollow cup electrodes can be used for such analyses, but it must be remembered that the less volatile substances tend to build up on such electrodes and hence no attempt should be made to use data obtained using them for semiquantitative estimates of completely unknown samples.

## 3.7 Semiquantitative Analysis

For semiquantitative analyses, a line extinction method first proposed by Kimura and Kuroda (Ref 21), but greatly extended by Harvey (Ref 22) is useful. The sample is excited in a DC arc using an undercut electrode as cathode. The light to the spectrograph is partially interrupted by a rotating step sector. The developed negative is scanned to note at which step of the sector various spectrum lines cease to be visible. Then using tables based on standard samples analysed earlier, approximate range values of sought element concentration can be calculated. A similar method using lines suitable for prism spectrographs has since been developed (see Table 4).

## 3.8 Quantitative Analysis: Choice of Spectral Lines

Provided almost perfect control of all the parameters affecting light emission and measurement can be guaranteed, so that the samples and standards are analysed under absolutely identical conditions, it is possible to make a simple plot either of phototube output, usually integrated, or of film density against concentration and make analyses directly. This is often done for flame photometry, but is very rarely used with the more complex electrical sources. The risk of variation is too great. Occasionally, with photographic recording, a separate standard exposure of a known amount of a reference substance was included on each plate or film and the ratio of signals for a suitable line of the determinand and a suitable line in the reference spectrum were plotted against determinand. This was known as the external standard method. However, experience has shown that it is rarely possible to achieve the necessary degree of uniformity of conditions between successive exposures and this technique is now rarely used. At the present time, internal standards are almost always used. With one important exception the internal standard substance should be a substance not sought in the analysis, which is also not present in the original sample in any significant amount, which can easily be uniformly incorporated into the sample at some stage in sample preparation. The two most common techniques are by direct mixing (for liquid and solid samples) or use as a carrier in the initial concentration stage when a known amount of the carrier-standard is added to a known volume of sample. The one important exception mentioned above is when a major matrix element present virtually at 100% or other already known concentration is used as the internal standard substance. This is quite common in the analysis of some metals and for some other solid samples, but will rarely occur in water analysis.

Ideally, the internal standard substance should have a spectrum line the intensity of which varies in exactly the same way with changes in the analytical source parameters as does the analytical line of the determinand so that the relationship between the intensity ratio and concentration ratio is constant. Such line pairs are called homologous lines. Truly homologous spectral line pairs are hard to find. In practice there are no perfectly homologous lines, only very close approximations, hence for good reproducibility of analytical results, it is essential to rely on good reproducibility of the source parameters - voltage, frequency cycles, amperage, fields, temperature, humidity and electrodes. Reference lines are chosen from lines of the internal standard element of convenient intensity, usually with a wavelength close to those being used for the sought elements. This latter restriction dates from the days when film was the only quantitative means of measuring light intensity and it was essential to have the same film constants for both lines. However, if background is not a problem and phototubes are used, the reference line need not be near to the sought element lines. If possible, the reference line should be a line which experience and prior testing at slightly varied source excitation conditions shows will vary similarly to the wavelengths being used for the sought elements. Comparison of line excitation potentials can be a help, but other effects such as volatility may override them.

In the choice of emission lines suitable for analysis, allowance has also to be made for the presence or absence of lines or bands of other elements or substances which may be present and cause overlapping line interference. If impossible to avoid, this interference can often be corrected for if quantified. It is useful to consult the literature to see whether line pairs used by others, even for quite different types of sample and sources, may be suitable. The relative intensities of lines of an element vary with changes of the source parameters. Most tables of spectrum lines give separate ratings for arc and spark type sources. Some also list low pressure discharge and plasma source ratings. The best advice is to consult the literature for likely lines and then try and see, with multiplicate analysis on several days, making deliberate minor variations in the source to see how much the working curve is affected.

The analytical line should preferably have a good range of variation in intensity as concentration of the determinand varies. This is dependent on many things, but lines with an almost linear intensity-concentration relationship for over five orders of magnitude are known. However, such long ranges can only be used with phototube reading; the limitations of film usually limit the use of a line with film to under three orders of magnitude. Usually, for very wide concentration range variations, several analytical lines will be used, ranging from a very intense line, used for low concentrations to a very faint line used only for very high concentrations. A typical such series is: Silicon 288.1 nm (for traces), 251.6 nm and 250.7 nm for intermediate concentrations, 212.4 nm for percent and 212.3 nm for high concentrations. Internal standard lines are usually medium to low intensity lines as such standards are usually used at relatively moderate to high concentrations, but exceptions are known.

The real shape of a working curve is somewhat ess-shaped, curving up from a limiting value due to background light plus electronic noise or film opacity to an almost linear slope (the portion of use for analysis), finally curving away upwards due to absorption and other effects in the source; it may even in some circumstances loop round above itself at concentrations approaching 100% for resonant lines. Rarely, for solid and other samples where a phase change with concentration occurs which markedly affects element volatility, zigzag or dog leg curves are known. Copper 510.5 nm emission from some light alloys is a classic example. Such curves are hazardous to use close to the phase change concentration, and if used at all, it is essential to know the expected sample concentration to ensure that the correct portion of the curve is used (see Ref 37).

For analysis of high alloys and some other complex mixtures, either an addition must be made of a known amount of suitable substance to act as an internal standard, or recourse must be made to a reference material whose concentration varies. In the latter case either a computer must be programmed to use the full equations or families of curves must be drawn up for constant reference element concentrations, the curves varying by successive increments in reference element concentration. For water, sludge and soil analysis the internal standard addition technique is usually used. Scandium and indium are sometimes used as standards as they are rarely sought and occur only infrequently. Even so, an initial qualitative analysis is advisable to ensure that the chosen element is absent.

### 3.8.1 Band Spectra

Molecules and radicles can be excited under similar conditions to free atoms and ions, but because the energy levels of molecular excited states are more numerous and much closer together, the emission from molecules and radicles consists of series of lines getting closer and closer together to a limiting wavelength which is called the band head. A whole such series is called a spectral band. Such bands may approach the band head from either the long or short wavelength side. In a few cases the band head is in the centre of the band. Component lines in bands can be mistaken for element lines, or be so close together as to completely smother an otherwise useful region of the spectrum. Cyanogen bands (from nitrogen in the air and carbon of the electrode) are a great nuisance, as are also carbon monoxide and silicon monoxide bands.

Unfortunately most spectral bands are not listed in the Tables of Line Spectra referred to above, but are published separately (Ref 28). A few of these molecular lines have been used for element detection and determination provided excess of the other unsought element in the molecule is known to be present in the sample (by addition prior to analysis if necessary). Some flame photometers use metal oxide band heads for analytical measurement and fluoride and chloride have been determined by measuring the calcium fluoride and calcium chloride band heads in the presence of excess calcium ion. Although band spectra can cause interference, this can sometimes be overcome, as the line intensity varies regularly with wavelength along a band. Hence any anomalous intensity due to the presence of an element line coincident with a band line will appear as an anomalously intense line in the band (see Figure 1). If necessary such lines can be used quantitatively provided a background correction is made. This can be computed from the intensities of the band lines immediately on either side.

Band spectra can sometimes be eliminated by jacketing the analytical source in an inert gas such as argon or helium. This will only work provided the components of the band are not all present in the sample itself. Thus cyanogen bands can usually be so suppressed, but not the silicon monoxide ones if silicates are present.

## 3.9 Quantitative Analysis: Measurement of Light Intensity

Light intensity is rarely measured merely by visual comparison with a standard light, though instruments of this type have been made. The only reliable methods of measuring the emitted light intensity are by means of phototubes and by the use of calibrated film. If phototubes are used, there are various ways in which the intensity may be read, but ultimately it will be in the form of a digital readout, dial or chart reading. Even with direct reading instruments calibrated in concentration, this may not be the real concentration, but the apparent concentration due to interference effects. This will be discussed later. If films or plates are used, it is best to study the specialist texts (Refs 29-34). Use of film in quantitative analysis is becoming increasingly rare because of the poor availability of photographic instruments, the consequent reduction in the production of film for them and the increase in cost of silver and gelatine. Such special precision film is still made (though expensive), but not in Britain. Some modern instruments are made solely for qualitative analysis and fitted with self developing cameras. Despite this, the use of film for both qualitative and quantitative analysis will be discussed in detail in this and subsequent sections, firstly because second hand equipment exists, secondly because photographic spectrographs are the simplest to make in the workshop, and thirdly, because a knowledge of the use of film for quantitative measurements will enable users to get better results than expected even from ordinary commercial film. At the time of going to press, at least two well known makers are offering quantitative photographic spectrographs. Films which do not use silver are being developed.

Prior to the advent of reliable commercial film, calibration exposures were included on each plate. Such a method, whilst wasteful of time and film would greatly increase the accuracy of results obtained using ordinary shop bought film; however with film made specially for spectroscopy, it is only necessary to standardize for each batch of film, provided good results are obtained from the periodic standard samples analysed along with the routine samples as analytical quality controls. The following effects are important:

i. Form - plate, roll film, or sheet film (governed by the type of film holder in the spectrograph. Prism instruments usually use plate film, instruments based on the Rowland Circle use roll or sheet film because of its flexibility in the curved mount). Several spectra are usually recorded across the width of a plate or along a length of roll film, arranged side by side across the film. (If plates are not available, roll or sheet film can be used instead by mounting it in a tight frame).

ii. Sensitivity - the sensitivity of film to light of different wavelengths varies. Makers of film will readily supply curves showing the relative sensitivities of the different films they make, in fact, many publish information on this in their handbooks on black and white films for expert photographers. It is therefore desirable to choose the correct film for the wavelengths to be used. Several film manufacturers supply special films for spectrographic use. With some films, it is possible to use sensitizers and pretreat the film to change its range, but this is difficult to do reproducibly.

iii. Grain - a photographic film consists of particles, usually of silver halide or other photosensitive material, set on to a gelatine base. The size of these particles determines the degree of resolution that can be photographed. With very coarse grained particles it is possible for the spectrograph to resolve two lines of similar wavelength, but for the film not to record this as the lines fall on the same grains. Light falling onto a grain tends to sensitize the whole grain.

iv. Speed - films vary in their sensitivity to light. This is dependent, partly on grain size, and partly on the photosensitive material used. It is sometimes necessary to compromise between resolution (grain size) and light sensitivity (speed). Unfortunately, due to the use of direct reading spectrographs the range of commercially available film types is decreasing.

### 3.9.1 Effect of Light on Photographic Film

This is a very complex effect, not well written up in most texts. There are two basic "laws" - the Bunsen-Roscoe reciprocity law and the Hurter-Driffield also called the Characteristic, Contrast or Gamma Curve. The Reciprocity Law states that Exposure (E) equals intensity (I) multiplied by time (t), or as an equation: $E = It$, which is the fundamental relationship used when relating aperture to exposure time in ordinary photography. There are three important instances when for practical purposes this law fails. Firstly the Hurter-Driffield curve shows that there is a limit to the effect of exposure on the film (over exposure, when all the silver is completely sensitized and will all be reduced by the developer). Associated with this is a slight failure of reciprocity with rate of exposure. This is usually quite small, but becomes important if very long exposures are used to detect very faint emission due to low concentration, or very short exposures are used for very bright lines. Fortunately most elements have sufficient spectrum lines to allow constant, or almost constant exposure times to be used, though the sequential volatilization of some elements may create minor problems. The other failure, which is also a real one, applies to multiple exposures. If a film is exposed to light, with interruptions in the exposure, the integration of the intensity and time is not quite equal to the exposure that would have been obtained if there had been no interruptions. Whatever the action of light is on the silver halide particles, not only is there an energy of activation (apparent from the Hurter-Driffield relation) but part of this energy can be lost to the surroundings. The practical aspect of this is that the shorter the interruption the less effect it has on the exposure, but to be insignificant the interruption times have to be very short indeed. This becomes important if rotating step sectors are used to interrupt part of the light beam to produce a series of spectra of graded exposures either for analytical or film calibration purposes (see below). Rotating sectors should therefore rotate as fast as possible. In consequence, for film calibration, precision made wire mesh screens obscuring an accurately known amount of light are often preferred or alternatively for spectrographs with reflectance gratings covers or masks which reduce the effective area of the grating thus reducing the light diffracted are also used. (The high speed of rotation, plus the irregular edge of step sectors makes it essential to fit them with edge guards, otherwise they can be as hazardous as mechanical saws). The Hurter-Driffield Curve relates the density of the developed film to the logarithm of the exposure. This form is preferred as it is more linear than direct plots of exposure against density, opacity, or transmission of the developed film.

A typical curve is shown in figure 6. The curve does not pass through zero density even for zero exposure as there is always a residual density due to the film itself. Similarly extrapolation of the main straight line portion of the curve shows that there is a minimum exposure for practical purposes required to activate the film. At very high exposures all the silver halide or other chemical becomes exhausted and the curve bends over to constant density. At exposures far beyond that needed to completely blacken the film, partial bleaching may occur. Measurement of film density is not used for such exposures as self absorption in the plasma (self reversal) also causes problems at such intensities. (Phototubes can measure self reversed lines. The effect of self reversal on line intensity is mentioned in section 3.11 on Interference. Line width measurements are occasionally used with film in such circumstances, see Section 3.10.2).

The equation for the linear portion of the Hurter-Driffield curve is $D = \gamma \text{ Log} \frac{A}{E}$. Where D is the density produced by an exposure E, $\gamma$ (gamma) is the contrast and A is the inertia of the film.

The slope of the gamma curve varies slightly with wavelength used, especially at wavelengths close to the limits of sensitivity of the film. Separate curves can be plotted, but it is rarely necessary to use separate gamma curves for each section of the spectrum, as long as standards, control samples and a rigorous emphasis on reproducibility are maintained. The analytical result is obtained by comparison with standard samples treated in exactly the same way, hence small errors of this type tend to cancel out.

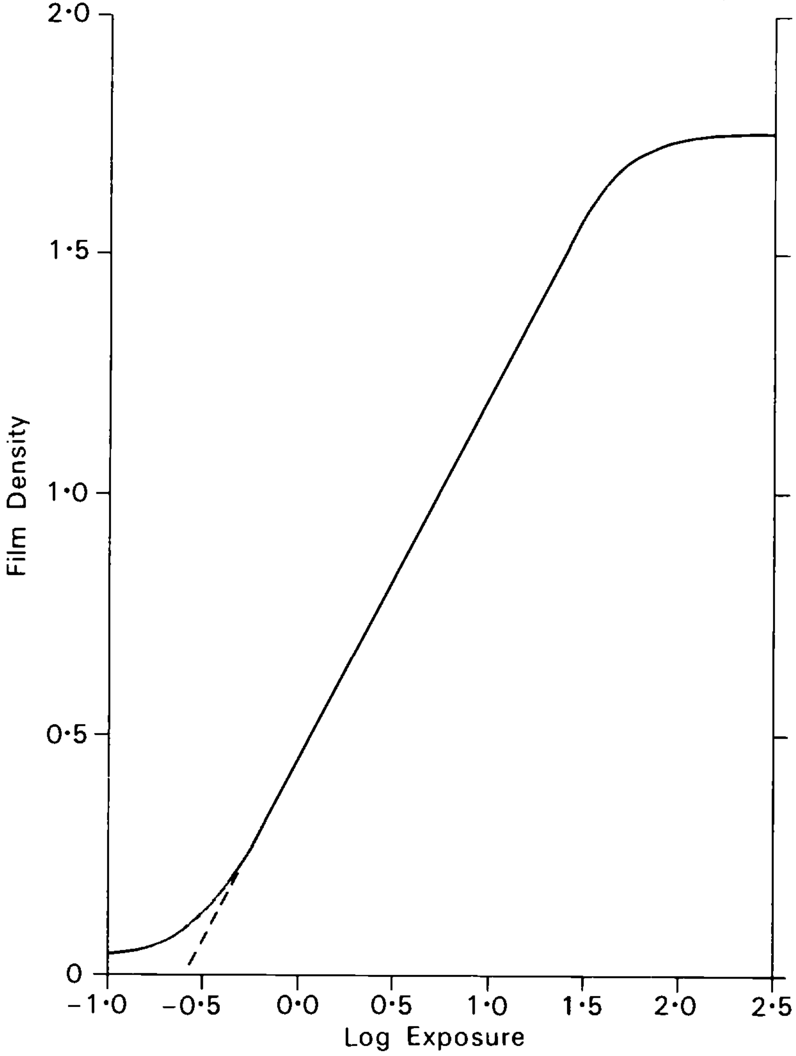
A procedure for determining the Hurter-Driffield Curve is appended (see 3.14). From the above, it should be obvious that film used for measurement of light intensity should not be exposed to any light other than that to be measured. It is strongly recommended that all handling of such film from the time it is unwrapped until after it has been developed, fixed and washed, should be done in complete darkness.

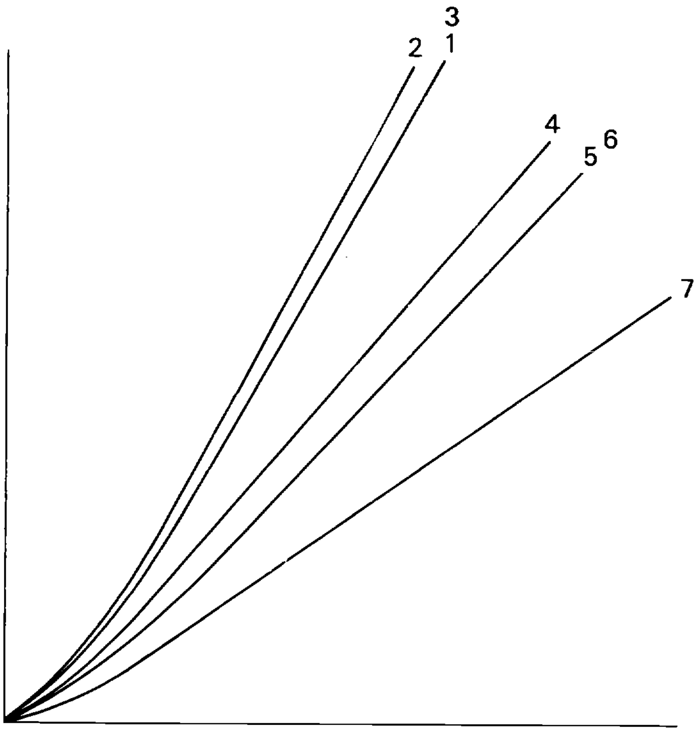
### 3.9.2 Effect of Film Development on Film Density

After exposure, film is developed first by reduction of the activated silver halide to silver, then fixed by dissolution of the residual unactivated silver halide with a complexing agent, and finally washed thoroughly to remove all the soluble silver derivative. The film itself may need hardening again as it tends to become soft during the developing process and so liable to be scratched. Finally it needs careful drying, often in a frame to prevent shrinkage or stretching which would cause uncertainties in line identification; Roll or sheet film is usually handled in a rigid wire frame to keep its dimensions constant during processing.

For really reliable results, the whole development process needs careful quality control, as the density given by a given exposure is dependent on the reagents and reagent strength, time of treatment and temperature. Accurate thermostatically controlled water baths are used to keep the various solutions at the optimum temperature during development. Solutions are changed regularly with respect to usage and age since preparation and are never allowed to reach anywhere near exhaustion. Local temporary depletion of reagents around any local high concentration of activated or unactivated silver halide in the film is

6a A TYPICAL HURTER-DRIFFIELD CHARACTERISTIC CURVE (GAMMA CURVE)





6b The graph (left) shows the way Gamma can vary with wavelength for one make and type of film.

Curve 1 at 496nm
2 at 453nm
3 at 400nm
4 at 341nm
5 at 294nm
6 at 247nm
7 at 233nm

Fig 6. HURTER-DRIFFIELD CURVES

guarded against by efficient agitation (no mechanical parts should be able to come in contact with the exposed film surface).

Information on suitable solutions, formulae for making such solutions and the optimum procedures and conditions can be obtained from the various film manufacturers and from photographic handbooks.

For many purposes development to maximum density is recommended, otherwise very accurate control of the time in each solution is essential for good results. If many films are used, a rigid logging and handling routine is necessary to avoid mix-ups which will cause the wrong allocation of results to the original samples.

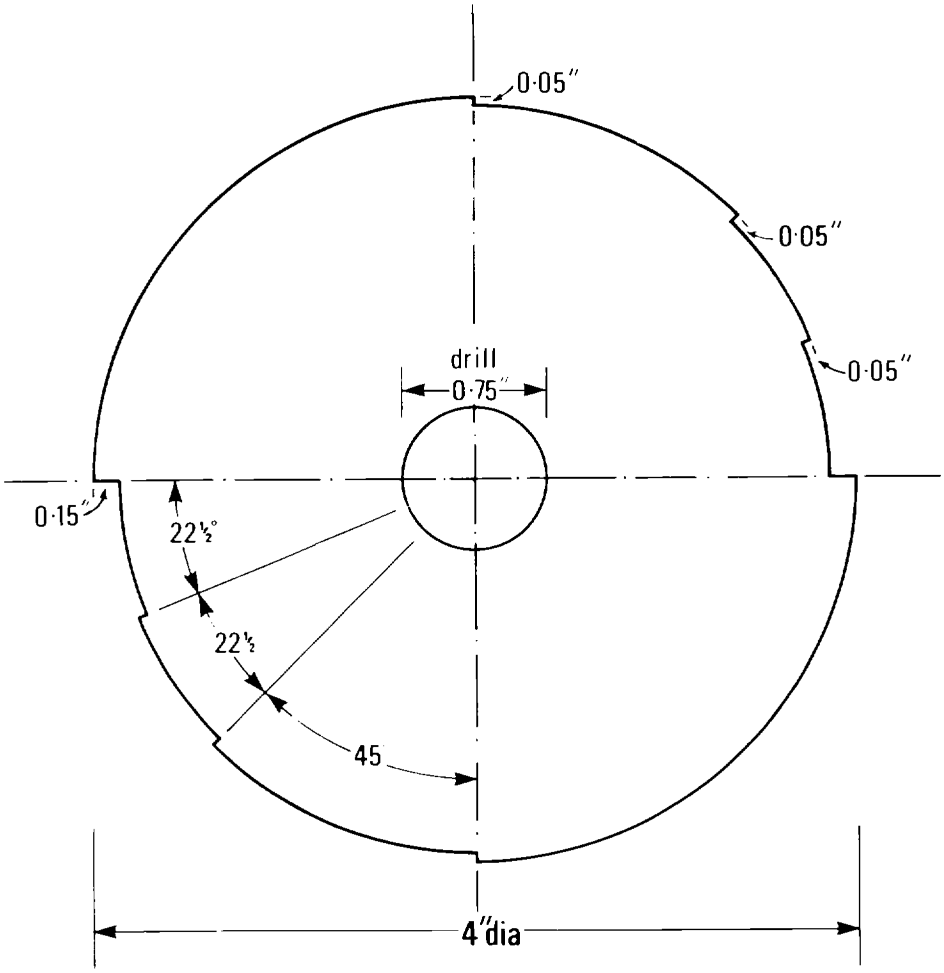
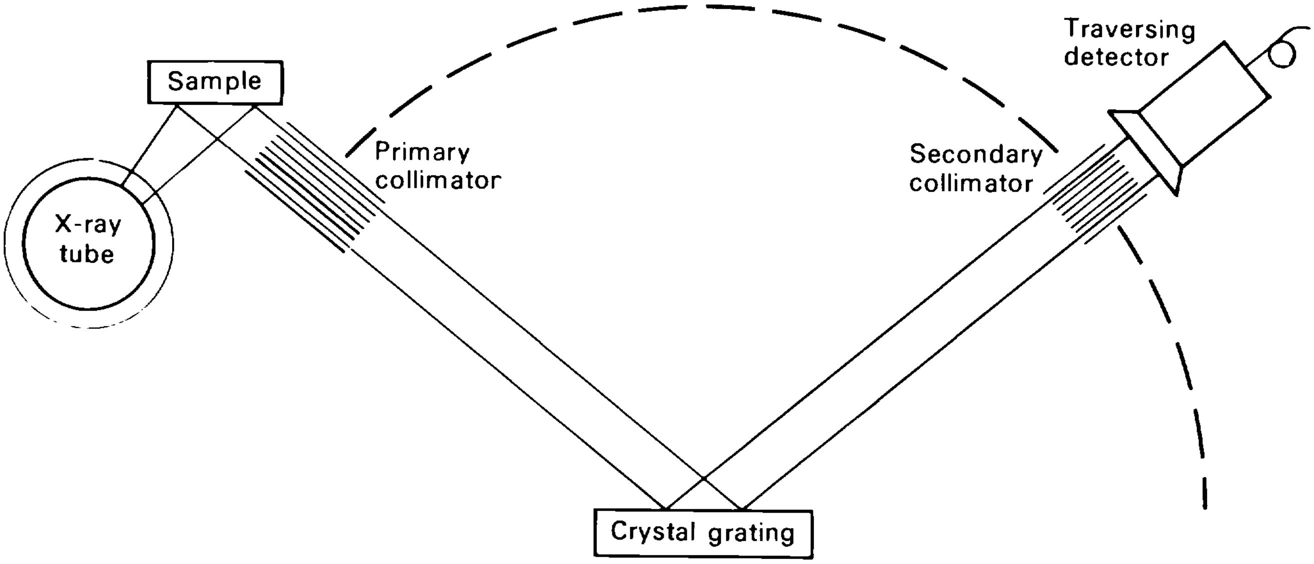


Figure 7. Rotating step sector plan view (Material: 1/16″ Brass sheet.)

### 3.9.3 Measurement of Exposure (Density) of a Film

This is done using special instruments called Densitometers. As mentioned earlier the film is usually examined for identification purposes by projecting a magnified image of a section of it onto a frosted glass viewing screen.

The projector is fitted with means of moving the film (or photographic plate) in any direction in its own plane. Density measurements are made by passing a narrow beam of light from a slit aligned with the "lines" (images of the spectrograph entrance slit), through the "line" to be measured and on to a photocell, the densitometer slit being smaller than the image line being measured. Correct alignment of the light beam and photocell with the "line" to be measured is usually done by guide marks appearing on the screen. Usually a small mirror is used to divert the appropriate section of the image to the photocell, the mechanism simultaneously inserting a mask with a slit into the light path to prevent unwanted light falling on to the photocell. There are various arrangements which will work satisfactorily. Commercial instruments are recommended. Measurement and electronic circuitry are similar to that in ordinary spectrophotometers. The reading is obtained either as percentage between full light (no absorption) and no light (100% absorption) or as an absorbance. Some analysts set the zero absorption using unexposed but developed film, Fig 5 gives a typical densitometer layout.



8a. OUTLINE DIAGRAM OF A DIFFRACTION TYPE SPECTROPHOTOMETER (COURTESY OF PHILIPS LTD)

DIRECT READING INSTRUMENTS WITH A SERIES OF FIXED SINGLE-ELEMENT CHANNELS ARE ALSO MADE

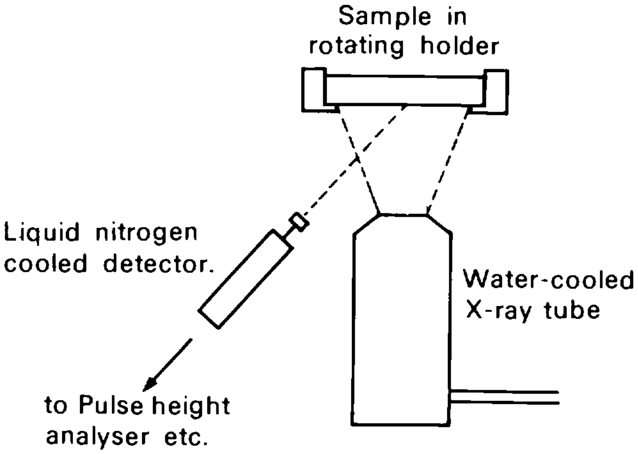
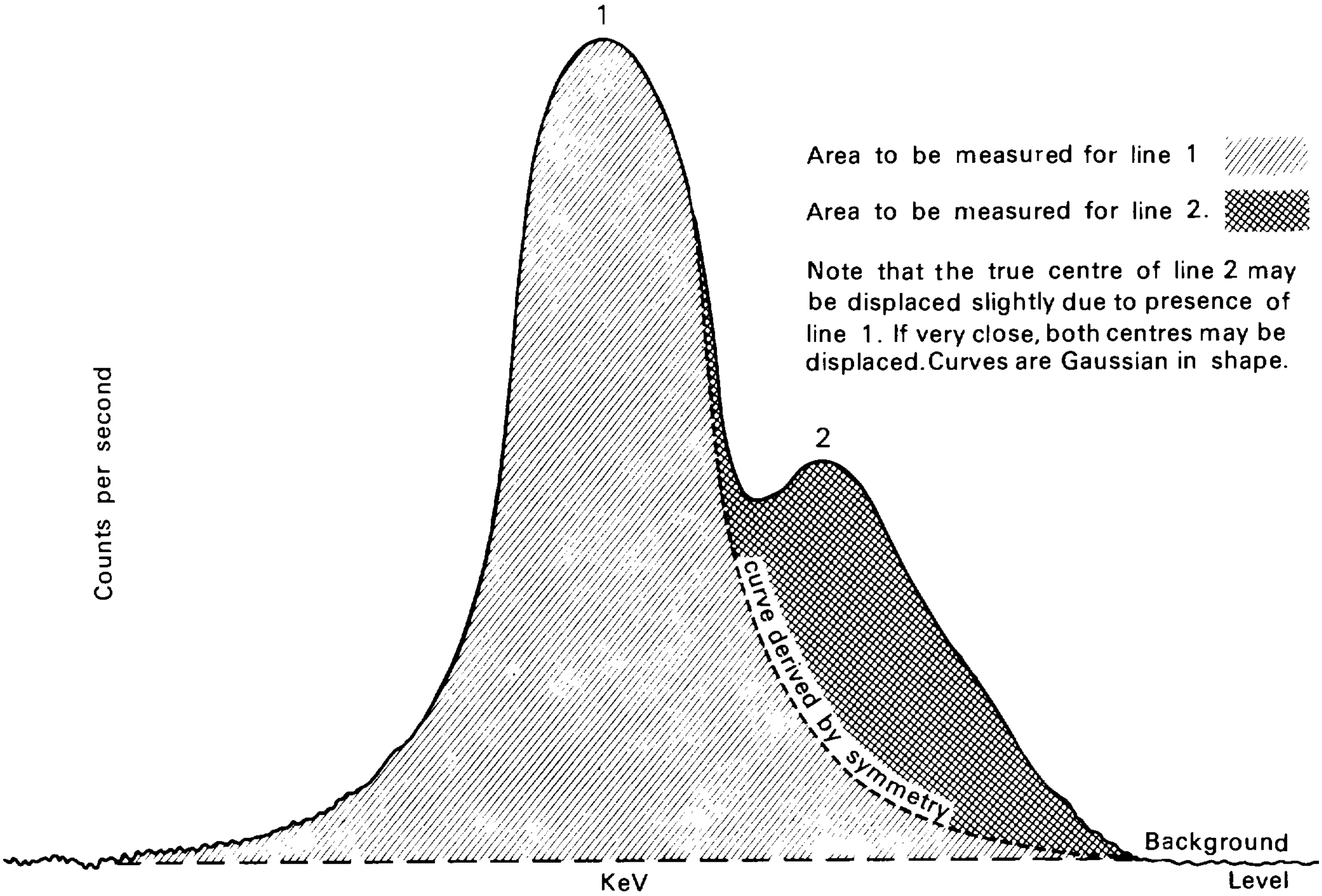


Figure 8. Types of X-ray fluorescence spectrophotometers

Densitometers can be home made, but require good instrument workshops for their production. One of the most versatile – the Sturrock design may not be commercially available. In this instrument, whilst the main image is projected in the conventional way, the region round the selected line is partially diverted through a half silvered mirror and examined by a moving slit – photocell unit oscillated by a servomotor, the photocell output being fed to the vertical control of a cathode ray oscillograph, the horizontal control of which is controlled by the scanning servomotor. The oscillograph therefore gives a density trace across the region concerned. Maximum density is measured either manually with a scale or by electronic devices pretuned to zero and 100%.

One alternative form of densitometer traverses the film slowly at constant speed past the slit and light beam, the phototube output being recorded on a chart recorder against traverse of the film. Such charts are similar to those produced by traversing phototube spectrographs. Interpretation is similar to the more usual technique. Another instrument compares the film absorbance with that of a density wedge. Operators familiar with one technique often need a little practice when adjusting to the other.

With both this latter densitometer and the Sturrock instrument, separation of overlapping lines becomes easy using the concept of general line symmetry and curve analysis outlined for energy dispersive X-ray fluorescent spectrometry in Figure 9.



Note that the true centre of line 2 may be displaced slightly due to presence of line 1. If very close, both centres may be displaced. Curves are Gaussian in shape.

Figure 9. Principle of separation of overlapping spectral lines- example from X-ray fluorescence spectrometry

### 3.10 Determination of Concentration

As with many other methods, measurement of concentration is dependent on accurately prepared standards. Here the water chemist has an advantage, as synthetic solutions similar in composition to sample concentration or pretreated samples are usually easy to prepare. If a solid electrode charge is prepared from liquid samples, similar treatment of liquid synthetic standard solutions is recommended. However, except for reagent blanks, it may not be necessary to put standards through any initial treatment used to remove interfering substances and bring the sample into a standard initial form.

With solid samples, unless these are first dissolved, which may be a needless complication, care is necessary to ensure that the small amount of sample used is not only typical, but homogenous. For quantitative analysis care should be taken to ensure that the sample and standard matrixes are as alike as possible. Phase differences, even variations in the degree of graphitization of carbon, or form of aluminium oxide or silica can alter the emission of light by substances incorporated in them. The same care also applies to any addition of spectroscopic graphite or carbon to a solid sample concentrate prepared from solution. Such additions are often necessary prior to ultimate analysis in order to make such concentrates conductors. Solids should be accurately weighed, finely ground in mortars (usually agate) and then if necessary thoroughly mixed with the required amount of special graphite or carbon. The same graphite or carbon should be used with samples as was used with the standards.

Working curves, as spectrographic calibration curves are usually called, are prepared by making a series of analyses of synthetic standards with varying concentrations of the sought substances in the desired matrix material. The matrix material can be carbon, a carrier or diluent. Sometimes, as mentioned earlier, solutions may be used with special electrodes or sources. Analyses are usually made in triplicate at each concentration, each point being plotted separately on the first draft curve. There are various different ways of making the analytical measurement, but regardless of whether the light intensity is measured directly by a photoelectric system, or indirectly by measuring the blackening of a photographic film with a densitometer, as described earlier, the principle on which the commonest methods are based is the same.

Very rarely, provided the power supply and other parameters are very well controlled, it is possible to plot the light intensity of the analytical wavelength against concentration directly. Light intensity is obtained from the Hurter-Driffield curve, or for direct reading spectrographs some function of the integrated phototube output, usually a condenser charge, may be read and plotted. Precision is usually poor for this method, though some analysts use this technique for inductively coupled plasma source units. Even so, use of an internal standard greatly improves both accuracy and precision and is preferred by most analysts regardless of source type (see below).

For both direct reading and film spectrographs, the most precise methods use an internal standard, and the working curve is a plot of concentration against the ratio of the intensities of the sought element to internal standard analytical lines. Direct, logarithmic or log-log plots may be used depending on circumstances. As mentioned earlier, the internal standard is usually a substance neither sought nor likely to be present in the original sample, which is added in known amount during the preparation of both the standards and samples. With the carrier-concentration technique, the carrier itself is usually used as the internal standard. Just occasionally carbon has been used, but it only has one good wavelength – 247.86nm* which is usually rather too strong to measure except by direct reading photocell instruments, or other special methods. For inductively coupled plasma sources a carrier gas line has been used. If the sample is solid and the main ingredient element concentration is known, this may be used as internal standard and correction made for departure from a constant amount in each sample. This technique is rarely used for water, geological or biological samples, though it is used routinely for the direct analysis of metal samples and for the determination of isotopic ratios where the isotopes have spectra which differ sufficiently for spectroscopy to be a practical method of determination.

### 3.10.1 Use of Phototubes for Quantitative Measurement

Direct reading spectrographs usually give a reading which is some function of the intensity ratio, and the working curves used for their calibration are plots of reading against concentration, or more usually log concentration. Log concentration is used firstly because the plot is almost linear over much of the analytical range, and secondly because such plots extend the usability of the plot for two or more orders of magnitude of concentration. Even a range of five orders of magnitude with only minimal curvature is not unknown. Furthermore, logarithmic plots are the most accurate way of coping with such long ranges of concentration. However with modern instruments such plots are only needed for calibration purposes, concentrations are then read directly.

As phototubes are used in most modern instruments, some information on their use is advisable. Phototubes vary in type. Most consist of a material which under certain conditions emits electrons when exposed to light. Tubes vary in their response to light from different parts of the spectrum. Hence it is essential to use the correct type of tube for

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* Other lines exist in the vacuum region.

the wavelength and intensity to be measured. For many applications, photomultiplier tubes are used in which the electrons emitted from the initial source are accelerated in a field by a charged grid so that they hit a plate which thereupon emits more than one electron. These electrons are accelerated by a second charged grid to hit a second plate where a yet larger number of electrons are produced, and so on. Decade photomultipliers such as IP28 are usually preferred as the signal is greatly amplified before it even leaves the phototube.

In many systems, the phototube output is used to charge a suitable condenser. The size of condenser needed is dependent on several factors such as, the phototube, the concentration in the sample (in other words how much the phototube is excited), and the overall circuitry. For simple measurements the charge on the condenser is measured as a measurement of light intensity, but for analyses with an internal standard the ratio of charge on the sought element and standard element condensers is measured. There are many ways of doing the latter. The simplest method is to measure all the charges individually using a high resistance voltmeter or similar device drawing negligible current. In more complicated devices the condensers are coupled in opposition and the nett charge measured. This may again be performed by direct measurement or by more sophisticated means. In one such system, the standard element charge is bled away to ground through a standard resistor. The circuit used contains an electronic device which times how long the charge takes to match the charge on the sought element condenser. The whole device is so designed that the initial charge on the reference condenser is higher than that on any sought element condenser. Many other similar systems can be devised. Great care has to be taken against switches and relays jamming and causing accidental loss of charge. In some instruments, all circuits are disconnected before being reconnected in a new arrangement.

### 3.10.2 Use of Film for Quantitative Measurement

For film, the working curves can be plots of concentration, or its logarithm, against the intensity ratio or its logarithm. However, if many analyses are made for several elements, much time is saved by the use of a calculating board. A Hurter-Driffield plot of density or transmittance against exposure is put on the board, exposure being a function of intensity under the standardized conditions which are used for analysis. The board is fitted with a Tee-square for accurately finding values on the "exposure" scale corresponding to given densities of film, and the exposure scale is covered by a long slide on which are marked the concentration scales for several elements. As logarithms are subtractive for ratios, the concentration scales are arranged from a line drawn on the slide corresponding to $\frac{IR}{IR}$, in other words one. In use, the reference line density is used to set the scale by this fiducial line. Then concentrations for the various elements can be read directly from the corresponding density measurements. (Ref 35). For background correction see Section 3.10.6.

An alternative proceduring using a multiple step sector is as follows:
For each spectrum line to be used, including the reference line, take density readings for each of three different exposures given by the step sector, such that if possible the density readings straddle a value of about 40%. If a background correction is to be made, take a similar set of two or three readings at a suitable clear piece of film with typical background intensity. Convert these to Seidel function densities ($\log \frac{To}{T} - 1$), where To and T are the transmittances for clear film and exposed film respectively. From the steps used for each line calculate the log relative exposures for each reading. For each line, plot the three values of the Seidel function densities against the log relative exposures. The resultant plots should be a series of virtually straight lines. By means of the 40% density line on the graph, measure the distance between the various sought element and reference element curves and the background curve (or curves if the background differs and different readings are used for the analytical and reference lines) and from these calculate the log intensity ratio. Use this to obtain the sought element concentration from a concentration/log density ratio working curve obtained using synthetic standards. (Ref 36).

Other techniques can be used. Occasionally a single external standard may be used. In this case the standard is a separate sample or set of samples included on each film. This technique is rarely used as it does not correct for any variation in source during the exposure.

In a few instances such as in the monitoring of lubricating oil, mentioned earlier, to give warning of equipment breakdown, it is not necessary to calculate actual concentrations. A simple plot of intensity ratios suffices. Trends and sudden changes provide the warning required.

The use of a phototube scanning device, whether to read a spectrum directly or the record of a spectrum on film produces a slight artificial broadening and flattening of the lines.

Provided the instrument is properly housed such that there is no risk of frame distortion, for direct reading (photocell) instruments, there is no need for the reference line wavelength to be as close as practicable to other wavelengths used. For film this is advisable as it reduces any variations due to change in film response with wavelength.

It is possible to use spectral line width ratio instead of intensity ratio. Due to a number of effects such as Doeppler Broadening (shift of wavelength due to movement of the emitting atoms towards or away from the direction of the entrance slit) and the field effects on emission, spectral wavelength lines have a width distribution which is approximately gaussian. Hence the higher the concentration the broader the spectrum line appears to be. It is possible to measure this on the projected image by use of a travelling microscope and so to use line width as a function of the intensity. (See Ref 48). The precision is not as good as with direct measurement of the line density. However, it does allow lines suffering from self absorption (self reversal) to be used (see below) in which the centre of the line has faded. For merely obtaining the order of magnitude of a spectrum line, a Hodge scale system can be used. Lines are compared with a logarithmic exposure scale. Such a scale can be prepared by exposing film to an arc between two electrodes (preferably metal, usually copper or iron), for a logarithmically increasing series of times (for instance 1,2,4,8,16,32 secs and so on), then a line is selected which is barely detectable at the shortest exposure, and a scale of intensities is prepared using the series of exposures of this line. Other spectral lines are then graded by comparison with this scale.

If it is necessary to use wavelengths which are too intense for conventional methods along with other more useable lines, use may be made of a longer entrance slit to the spectrograph, giving longer spectrum lines in the film, but a rotating step sector (see fig 7) is used to interrupt parts of the light beam for accurately divided ratios of the exposure time, thus apparently reducing the intensity of parts of the line by different amounts. Step sectors are preferable to smoothly logarithmically graded sectors as it is easier to work out the attenuation ratio; the spectrum line has a correspondingly stepped appearance. Step sectors can also be used for order of magnitude determinations by noting at which ratio the line no longer produces an image of the slit (line) on the film. (See Fig 1).

For some accurate work, especially in the presence of faint band spectra or continuous light emission, the density value obtained for a spectrum line may be corrected for the background emission. This is done by measuring clear film on either side of the line being measured and correcting the readings just as would be done in conventional absorptiometry (Spectrophotometry) for cell correction. If the background is due to a band spectrum which can be clearly resolved and there is a band line exactly under the sought element line, measurement should be made of the band lines immediately adjacent on either side of the sought element line. See section 3.10.6 for more information.

It is possible to use small desk computer-calculators for all these computations. For some of these calculations analog computers are particularly suitable due to the logarithmic functions in the calculations. Decade thyratron tubes and other devices can also be used.

### 3.10.3 Quality Control by Standard Samples

It is a well established practice in Emission Spectroscopy to use Standard Samples for Quality Control purposes. However reliance should not be placed on a single analysis. Experience has shown that such standard samples, especially solids and powdered solids are liable to segregation during preparation, and in the latter case, also on storage. Trace level solutions may plate out or exchange with storage bottles. The Geochemical and Spectrographic literature has plenty of examples of debates as to the composition and homogeneity of internationally available standard samples. Care should therefore be exercised when using such samples. Even so, if great care is taken and attention paid to detail, accuracy and precision of better than 1% is not impossible for some emission spectrographic analyses.

### 3.10.4 Residual Sought Element Concentration

Sometimes when preparing standards for making working curves, especially for trace element determinations, it is impossible to obtain reagents sufficiently free from sought element. In this case, the residual concentration in the supposed zero standard must be estimated. One method, due both to Pierce and Nachtrieb and to Duffendach and Wolfe (Ref 35) is as follows: First correct all readings for Background. Then plot the intensity ratio against percent sought element. The resultant curve will not pass through the zero/zero point. Extrapolate this curve to cut the concentration axis at a negative intercept. Shift the concentration scale to make this intercept the new zero for the concentration scale. To check this curve, plot the log intensity ratio against log concentration. This should give a straight line relationship. If this plot is still curved and cuts the log concentration axis, an over correction has been made. If it cuts the log intensity ratio axis an under correction has been made. Try again until you do achieve a linear log-log plot. The zero shift necessary corresponds to the residual concentration.

Care is necessary in making the background correction correctly, because a background effect has a similar effect on the working curve. Background appears as extra light intensity added to the reference and sought element lines, and will cause all working curves eventually to curve round towards the concentration axis.

Note that this device can also be used to determine very low concentrations which are detectable, but for which standards are unobtainable, by making a series of samples with varying standard additions of sought element, starting with a pure sample.

### 3.10.5 Self Absorbance

As light produced by an electronic shift to a given lower energy level can also excite an atom already in that lower energy level if absorbed by it, not all the light produced in a source will necessarily be emitted. Some will be reabsorbed. This is the principle of atomic absorption spectrophotometry. This loss of light is especially important for atoms in the centre and back of the source plasma, the light from which must traverse a lot of plasma if it is going towards the entrance slit. The effect is also worse for lines due to electrons terminating in low energy levels especially the ground state, as this is the commonest state in most plasmas. The result of this appears as a fading of the centre of such lines at higher concentration, though their width continues to spread in the normal manner. With photoelectric read out, self absorption causes working curves to curve round to lower than expected readings. Background effect on such instruments causes the working curve to curve round to a constant intensity ratio reading. The combined effect makes the curve into an elongated S shape.

### 3.10.6 Background Correction

Background, its effects, and the possibility of correction for it has been mentioned in several places in this chapter. This is most important for plasma emission and the higher wavelength DC arc measurements, especially for trace range determinations. There are several contributory factors causing background. The easiest to remedy is a light leak into the spectrometer case. Stray light can also enter via the spectrometer entrance slit, but if properly sited and screened this should be negligible. However, if improperly positioned, the glowing tips of electrodes can send unwanted light along the optical path. Unavoidable background can be caused by either band or continuous emission in the source. When film is used to record the spectrum, there is a slight background due to absorption of light by the clear film itself. This is apparent from the Hurter-Driffield curve (figure 6) and can be kept to a minimum by careful film storage and good developing. A similar effect would be produced in spectrophotometers if the instrument noise varied widely in the different phototube circuits.

Correction begins by measuring either the background emission or, if film is being used, this emission as recorded on the film. If the background is due to band emission, the emission due to band lines located symetrically on either side of the analytical line should be measured. With film, care should be taken that these measurements are made close enough to the line to be the true background, yet not so close that any anamolous darkening due to the Eberhard effect* is measured. If, as is often the case within experimental error, the background is almost the same on either side of the analytical line,

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* The Eberhard effect is an effect that can occur in the development of very highly exposed photographic film which falsely broadens the image at the expense of under developing the centre (see Ref 35). It should not be confused with the similar real broadening due to the Drappler effect (see Ref 48) or the reduction in intensity due to self absorption (self reversal) of resonant spectral lines. (See section 3.10.5).

only a single background measurement may be made. For phototube instruments this means provision of an extra phototube circuit to make this measurement.

Care has to be taken when making background correction and some information in the literature is wrong. Ultimately, the effect of background, however caused, appears as an addition to the light measured. The safest way to correct for background is to calculate the analytical line and background signals or readings back to light intensity or some directly proportional number. Then deduct the background intensity (or mean intensity if the background is read on both sides of the line) from the analytical line intensity. Then use this corrected value for calculating the true concentration. Do not use a number proportional to the logarithm of the intensity, nor merely deduct initial readings unless these are directly proportional to the intensity. These latter mistakes are common when film or logarithmically responding phototube readings are used.

## 3.11 Interference Effects

Interference effects can be due to:

i. other substances emitting at the same wavelength (or for grating instruments at a multiple of that wavelength - see earlier) - an apparent enhancement.

ii. substances which either form less volatile compounds or dissolve the sought elements lowering their vapour pressure in the plasma - an apparent reduction.

iii. substances which collide with the atoms or ions of the sought elements changing them into a different excitation state without light of the wavelengths used being emitted - an apparent reduction.

iv. mechanical effects which alter the rate at which the sample reaches the source. These are dependent on instrument used and the form of the sample or standard, but can be compensated for by use of an internal standard; however these effects are similar to an interference effect if only the sought element emission is measured. If the effect acts proportionally on both the sought and internal standard element, use of an internal standard suffices to correct for this effect. For some mechanical effects, such as the sought element not vaporizing uniformly throughout the arc burn, the solution to the problem may be to measure the light emitted by the sought and internal standard elements only during part of the burn. A study of light intensity with time at the various analytical wavelengths will give the optimum measuring interval. Change of electrode design is also sometimes useful. This will not be discussed further, but ref 20 contains examples.

The hotter the source the less problems are caused by effects ii, iii and iv above, but the more complex the spectra become and the more overlapping line interference (i above) is liable to occur. In addition, background light can be affected by the anions present.

The converse of ii. and iii. may also occur and will also cause interference, but in these cases enhancement. Usually every attempt is made to remove or otherwise eliminate interferents. If possible, an alternative spectrum line can be used. This is the preferred solution if the interference is due to an overlapping line, but is rarely any use for other types of interference. Sometimes, change of source excitation, usually to a hotter source will eliminate interference, as for instance increasing source temperature reduces the effect of sulphate on barium. Other alternatives are the addition of fluxes or suppressants to the sample. These act by changing volatilization in the source, fluxes by increasing the volatility of the determinand relative to the interferent, suppressants by reducing the volatility of the interferent. Lithium and other alkali metal halides are typical fluxes, aluminium and lanthanum salts are sometimes used as suppressants. Thus aluminium salts will suppress the interference of calcium with sodium emission, but at the price of slight repression of the sodium emission as well. If these methods fail recourse is sometimes made to chemical or physical separation procedures during the preparation of the sample. The potential disadvantages of such pretreatment procedures are the risk of loss and contamination and the time taken. With solid samples one of the biggest interference problems is the matrix effect. The same effect could also apply for liquid samples in different solvents or with grossly different solutes present in high concentration. The commonest solutions to this problem are either to use different working curves for each matrix (often a matrix element provides the reference line) or to bring all the samples to a common matrix, either by pretreatment or by use of a flux in the source sample. The relative success of these techniques depends on whether it reduces the determinand emission significantly and on how effective it is in producing uniform source conditions. However, the effects are proportional to the concentration of interferent and accurate corrections are possible if the interferent concentration is measured. The light emitted by a spectrographic source can be given by the following equation due to Malpika (Ref 49)

$$I = a\ C^n.$$

Much more complicated equations exist (Ref 50), but at constant source conditions they can be simplified to the above. If the line is resonant (self absorbing), the self absorption in the source becomes important at higher concentrations and the above equation becomes:

$$I = a\ C^n b^{tC}$$

Absorption of light is governed by the Beer Lambert law, the absorbing path length will depend on the flame or arc geometry, but is virtually constant throughout the analysis. If, in addition there is stray light or other background, then an additional term B is added to obtain the observed intensity:

$$I = a\ C^n b^{tC} + B$$

where I is the light intensity,

C is the concentration of the light emitter (in the last two equations it occurs twice once as a product term and once as a power term),

a and n are constants covering emission, (n is usually one and so can be omitted),

b is a constant covering self absorption,

t is a constant based on source flame dimension, and

B is the background light intensity which should be as negligible as possible.

If light emitted by another element also contributes to the intensity, then in addition to the background light an extra emission term dependent on the concentration of this element must be added:

$$I = a_1\ C_1^{\ n_1} + a_2\ C_2^{\ n_2} + B$$

or $$I = a_1\ C_1^{\ n_1}\ b_1^{\ tC_1} + a_2\ C_2^{\ n_2} + B \text{ (for a self absorbing line),}$$

Where subscript 1 refers to the determinand terms and subscript 2 to the interferent terms. It is unlikely that a line with interference from a self-absorbing line would be used, but if it were the extra term would be $a_2\ C_2^{\ n_2}\ b_2^{\ tC_2}$. As with $n_1$, $n_2$ is usually one and omitted. If as can happen, there are several overlapping interferent lines, extra terms of this type with subscripts 2, 3 and so on are needed.

Interference affecting the concentration of the emitting state in the source obeys the Mass Law. Admittedly a source is not in true equilibrium, but for a steady source there is a state of dynamic equilibrium, which as Guldberg and Waage showed (ref 87) obeys the Mass Law but with a different constant from that for true equilibrium.

Hence in such cases

$$I = a_1\ C_1\ f_2\ C_2$$

where $f_2$ is a constant relating to the Mass Law proportional effect and the other terms are as before. If an element produces both added light and concentration change or mass law interference (as calcium can with some aluminium lines and aluminium with some copper lines), both types of interference terms must be added

$$I = a_1\ C_1\ f_2\ C_2 + a_2\ C_2 + B \text{ and so on.}$$

Added light terms cause the intensity ratio concentration working curve to bend round towards the intensity measurement axis. Interference which changes the emitting concentration in the source produces parallel shifts in the working curve. A combined interference gives rise to both changes.

Some interferences only occur above a limiting threshold interferent concentration at which a new phase with a different volatility starts to form in the sample electrode; occasionally interference may affect the internal standard or reference element emission. All such effects can be computed, and if a suitable series of mixed standards are first analysed can be corrected for by simultaneous analysis for the determinand and interfering element concentrations. For more detail see Ref 37.

As mentioned earlier desk computer-calculators can be used, even for interference corrections provided the interferent concentrations are known and their effects have been quantified. As these effects give families of smooth curves, it is also possible to make corrections using nomograms or a series of tables, if necessary correcting for one factor at a time. Once set up the extra calculation may only take a minute or less. Sometimes this is preferable to attempting to eliminate the interference.

With plasma emission, the source is sufficiently hot for the volatility effect to be negligible. The chief interference is due to line overlap, though collision effects may occasionally occur. With simple flame photometry, all the effects may occur, but are chiefly confined to the volatility and collision ones. Type iv interference will effect these two sources unless internal standards are used.

Correction can be made either by solving the equations for these effects, by using families of curves prepared from mixtures of determinand and interferents, or by swamping out the effect by means of a suppressant, though this latter technique often also suppresses the determinand sensitivity as well. Volatility effects are reduced by control of the anions in the solution by either ion exchange or treatment with acid.

## 3.12 Criteria for Accurate, Precise results

There is no substitute for careful clean workmanship. Much of the accuracy of spectroscopic analysis depends on almost monotonous attention to detail. Temperament of the technician is often more important than academic knowledge provided the supervisor has adequate technical knowledge.

The following points need careful attention:

temperature — affects source emission, film sensitivity and development, and instrument alignment. It should be kept constant.

humidity — affects source emission and film sensitivity and should be kept constant.

vibration — affects alignment. Instrument mounts should be as vibration proof as possible. Instruments should never be on the upper floors of building and should be firmly mounted.

optical alignment — affects line focus and line identification, this applies both to the spectrograph and to the densitometer or comparator if used.

slit width — the best compromise must be found and kept constant thereafter. Narrow slits improve resolution, but reduce the incident light, lower sensitivity and raise the limit of detection.

sample preparation — affects everything except alignment and should be rigidly controlled for all quantitative analyses.

film storage and development — affects measurement of light intensity if film is used. Should be as perfect as possible. The makers will advise on the optimum conditions.

power supply — affects source and measurement — this should be regulated as closely as possible.

radio screening — radio frequency emission by spectrographs annoys neighbours, it can also upset ancillary equipment such as densitometers. Incorporation of radio screening in the walls or around the arc itself is necessary. The latter is preferred.

analytical gap — the space between the electrodes tends to increase as they burn away. This enlarges the arc and changes its characteristic by changing its geometry and resistance. Some analysts project an image of the arc on to a small screen on which they mark the image of the starting positions of the electrode tips and, using suitable insulated racks, adjust the electrode positions during the exposure to keep them as constant as possible. The initial gap must always be correctly aligned.

line identification — affects the whole analysis. Great care must be taken to ensure that the right spectral line is used, and if necessary background corrections made. When making an initial qualitative analysis, it is advisable to check using at least two other lines of the same element and/or check the absence of other possible elements with which the sought element line might be confused by looking for their strongest lines in the exposed portion of the spectrum.

## 3.13 Other Uses in the Water Industry

### 3.13.1 Metals and Solid Materials

Emission Spectroscopy can often also be used for the analysis of equipment, treatment chemicals, and the identification of unknown inorganic materials. By suitable sample preparation the methods described above can usually be used. Metal samples are often analysed by means of a special electrode stand in which a clean flat surface of the sample is one electrode with a carbon rod as the counter electrode. If the metal can be readily machined into two pins, these are often used as the electrodes. For further information consult specialist texts, especially those on metallurgical or geochemical analysis.

### 3.13.2 Oils (for maintenance supervision)

A rotating disc electrode procedure (see Refs 3 and 20) has been used with a DC arc for controlling the maintenance of engines and similar machinery. Samples of sump oil are analysed at regular intervals and the intensity ratios of various elements are plotted against an added internal standard element. Trends or sudden changes in ratio indicate the need for maintenance, the elements concerned indicating the type of maintenance required.

## 3.14 Procedures for plotting a Gamma (Hurter-Driffield) Curve

3.14.1 Several detailed procedures are given in the ASTM publication Methods for Emission Spectrochemical Analysis. (Ref 20). Others are included in methods given in Spectrochemical Methods for the Analysis of Soils Plants and Other Agricultural Materials (Ref 36) (see also Refs 29-34), and yet more are described in photographic and analytical chemical journals. The basic procedure is as follows:

3.14.2 Expose the film for a standard time such as 5 seconds to an arc struck between a positive graphite upper electrode and a negative soft iron lower electrode (a large nail is often suitable). The spectrograph slit width should be as for routine analysis. To ensure that the arc is as uniform as possible, a short preburn time such as 3 seconds should be used prior to exposing the film. Make each series of exposures at least in triplicate. Depending on the type of spectrograph and its ancillary equipment, vary the intensity of the light, but keep the intensity constant throughout each exposure. Alternatively vary the total exposure. Typical methods are:

i. variation in the grating area used,

ii. a multistep rotating step sector

iii. wire mesh screens of known dimensions

iv. filters (care must be taken if filters are used as the degree of absorption will vary with wavelength. In consequence, most laboratories do not use them)

v. change the exposure time.

When using a rotating step sector or variation in exposure time, it is advisable to check for any effect of reciprocity failure and so on. Do this by having sets of exposures of approximately identical total light exposure, but obtained by different means.

3.14.3 Develop the film as for routine analysis and measure the density (blackening) of selection iron spectrum lines. The range should cover from almost zero to almost 100% exposure of the film. If need be make extra exposures. If several film portions or slides are used, which is advisable to ensure uniformity, ensure that there is a degree of repetition between them.

3.14.4 Calculate the relative light intensities used and plot the Intensity/Density (Gamma Curve).

3.14.5 If a wide range of wavelengths is to be used, a compromise calibration may be used using a spectrum line or line pair in the middle of the range. But for precise work a series of calibration curves may be advisable. Which technique is used will depend on the type of film available. If film with an almost constant gamma value over the whole range of wavelengths to be used is available the single calibration curve procedure is to be preferred; if not, then the use of several curves each for its own part of the spectrum is advised. If in doubt, initially check the curve when changing to a new production batch of film, and also after prolonged storage. To prevent undue recalibration it is advisable to buy film in quantity all from the same production batch.

## 3.15 Information on Calculations related to Sections 3.9, 3.10 and 3.11

Although the calculations which follow are not essential, and direct calibration or use of a supplied computer programme is the usual procedure, there are times when a knowledge of how the formulae were derived can be useful. This is especially the case when analyses have to be made under conditions that are not ideal and a knowledge of how the departures made will affect the results obtained is desired. Only the simple cases will be given below.

3.15.1 The simple equation for observed light intensity is:

$I = a C^n m + B + i$,

(under ideal conditions this equation would be $I = aC^n$),

where I is the observed intensity

where C is the concentration of the emitting element

where a and n are constants related to the emission

where m is a proportionality factor relating the concentration of atoms or ions of the emitting element actually in the correct energy level for emission to the total sample concentration. For most analyses, m can be combined in a, but where a variable concentration of an interferent causes this change, then a term containing the interferent concentration may be included. (See section 3.11 and ref 37).

where B is the background light, and

where i is interferent light from other elements emitting at wavelengths received at the same detection point as the sought element light.

3.15.2 For self absorption (self reversal or resonant lines), light absorption obeys the Beer-Lambert Law

$$\frac{I}{I_o} = b^{Ct}$$

where b is the absorption coefficient

C is the concentration as above

t is the absorbing path length, a constant dependent on flame geometry when the effect of each individual atom in the flame is integrated

$I_o$ is the light actually emitted by the atoms going to the spectrometer ($aC^n$ above), and

I is the light observed at the spectrometer etc.

Substituting for $I_o$ gives:

$I = aC^n b^{Ct}$ as given in section 3.11.

For simplicity, in the following calculations, self absorption, interference effects of both types (m and i in 3.15.1 above) and background will be assumed to be negligible. Strictly they should be included, but the calculations become much more complicated. For the effects of interference, see also Section 11 and ref 37.

3.15.3 Use of an internal standard with phototubes or film

For each element $I = aC^n$,

so designating the reference line terms by r,

$$\frac{I}{I} = \frac{aC^n}{a_r C_r^{n_r}}$$

but as the reference element is used at constant concentration, $a_r C_r^{nr}$ is constant, so

$\frac{I}{I_r}$ = fcn, where f is another constant

and $\log \frac{I}{I_r} = n \log C + \log f$.

3.15.3.1 As the read out from many photoelectric devices is proportional to the logarithm of the light intensity,

$$R = x \log C + y,$$

where R is the read out signal, and

x and y are constants based on n and f above.

Theoretically there may be problems if the phototube response varies markedly for the two wavelengths, but as long as the reference element concentration is kept constant, this effect is lost in the constants, which then have slightly different values. There are analyses, such as of a range of high alloy steels using iron as internal standard, where the reference element concentration varies. Such analyses are hardly ever encountered in the water industry, but are solved by means of considering families of curves for different constant reference element concentrations, noting the consequent shift in the working curve and programming accordingly (see ref 37). This also applies for film response below.

3.15.3.2 For film, the calculation is more involved; for a continuous exposure (no reciprocity failure, see section 3.9.1)

$$D = \gamma \log \frac{E}{A} = \gamma \log E - \gamma \log A$$

where D is the film density,

E is the film exposure, and

$\gamma$ and A are the film constants.

Then when comparing with a reference line,

$$D - D_r = \gamma \log E - \gamma \log A - (\gamma \log E_r - \gamma \log A)$$

If the film response to light is approximately uniform for both wavelengths, $\gamma$ and A, the film constants are the same. (If the film response to light is markedly different, or if the reference element concentration is not constant, see the similar cases for phototube response immediately preceding this calculation).

Then $D - D_r = \log \frac{E}{E_r}$, and

as E = It, and t is the same for both elements, being, in this instance, exposure time,

$$D - D_r = \log \frac{I}{I_r}$$

Normally, densitometers do not read film density (D) but film transmittance (T) where

$D = \log \frac{1}{T}$, so by susbtitution in the equations already obtained,

$$\log \frac{T_r}{T} = \log \frac{I}{I_r} = (n \log C + f)$$

3.15.4 Note that as similar laws of emission and absorption apply to other forms of electromagnetic radiation and to fluorescence, the principles behind these calculations can be adapted to other techniques.

## 3.16 Construction of a Calculating Board

To construct a calculating board, first plot the Hurter-Driffield Curve as detailed in Section 3.14, and put a transmittance scale on in addition to a density scale; the latter can even be omitted. Then, using standard samples obtain the relationship between sought element concentration and intensity, trying to keep the reference element intensity as constant as possible. Then using the same scale as on the Hurter-Driffield curve plot a concentration scale on a slide to fit over the intensity scale, and mark the reference line intensity on the slide scale. Use this as a fiducial line to set the sliding concentration scale. As both scales are logarithmic, if convenient, provided the same convention is used each time the board is used, a factor of ten or one hundred times may be introduced when locating the fiducial line.

## 3.17 Calculations with Interference or Reference Line Variation Problems

Using synthetic or preanalysed standards attempt to draw up a family of curves for a series of constant values of the additional variant. If there are several variants then there will have to be sets of families and so on.

If preanalysed real samples must be used rather than synthetic standards, allowance may need to be made statistically for variations in the desired ideal values. From these construct correction curves, equations, nomograms or tables to correct the readings obtained when the problem is absent (no interferent present, or a constant or most commonly occurring reference element concentration). During an analysis, note the interferent concentration (or reference element signal) and correct the sought element result accordingly. This correction can also be done by incorporation in the computer programmes.

## 4. X-Ray Fluoresence 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 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 are described in Ref 5, which contains a review of applications of XRF to water analysis. 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 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 74). 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 on to 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. Most X-ray detectors now in use are solid state devices which emit electrons when X-rays are absorbed, the energy being proportional to that of the incident X-rays and the quantity proportional to the intensity. Some such devices are cooled for greater sensitivity. For some purposes however decade photomultipliers can be used, fitted with a screen which luminesces when X or gamma radiation is absorbed, the photomultiplier measuring the degree of luminescence. Such tubes are not suitable for energy dispersive applications. Fig 8 illustrates typical instruments.

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 the use of La Chance correcting equations (Ref 73). Secondary fluorescent effects are due to radiation from one sample component being absorbed by another component and re-emitted at its own wavelength; one element is reported at a lower concentration than the truth, the other at a higher concentration. The effect is concentration dependent and correction can be made using interference equations similar to those mentioned in section 3.11. Matrix effects can cause a slight shift in the position of maximum emission. For instance a peak due to sulphur in calcium sulphide is displaced slightly from that due to sulphur in calcium sulphate (Ref 81A). Some instruments rotate the sample during exposure to compensate for any inhomogeneity or lack of symmetry in the sample. Typical, instruments will determine from percent down to part per million 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 with or without lithium fluoride flux is the commonest of these, but has the disadvantage diluting the sample, hence it is mainly used for major element analyses of rocks and sediments. Typically 0.5g of dry sample is fused with 14.5g of lithium tetraborate in a metal crucible in an induction furnace. Crucibles of platinum 10% Rhodium or Platinum 3% gold are often used, the same diameter as the spectrograph sample holder as they do not stick to samples. Some work has been done on the analysis of dried sewage by this method. Samples may also be concentrated by precipitation (Ref 77), absorption (Refs 78 and 79) or freeze drying (Ref 80).

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 in ordinary emission spectroscopy, which is both an advantage and a disadvantage. There are a few instances of elements for which overlapping lines make 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 enable lines to be resolved (see Figure 9 for details). 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. See also Refs 75 and 76. Recent information on interference effects can be found in Ref 81.

### 5. Electron Microprobe X-ray Emission Spectrometry

This is very much a specialized instrument, but it is very useful for the identification of small inclusions in solids. The basic instrument is an electron microscope, but all or part of the electron beam can be focused 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. See also Refs 82-85.

These instruments are expensive and are not for routine analysis; 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. It is possible to buy component parts to make equipment, but careful design is necessary, X-rays are hazardous and leaks must be avoided. Energy dispersive measuring devices are most commonly used. Interference effects do occur. These are chiefly caused by fluorescent emission and matrix effects described in Chapter 4. Corrections can be made.

Auger Electron Spectrometry, Electron Energy Loss Spectroscopy and X-ray Photo-electron Spectrometry are related methods suitable for the determination of elements with atomic numbers down as far as lithium, especially in small particles and surface films. When atoms are excited by electron beams or by X-rays, electrons are emitted with energies characteristic of the emitting element. Analysis of these electrons by energy and rate of emission allows identification and determination of the emitting element to be carried out on the target sample. These techniques require special equipment and expertise. It is suggested that interested laboratories contact Harwell and similar laboratories for information and advice. (See Refs 85A, B and C).

## 6. Gamma Ray Spectrometry

Analyses for radioactive isotopes can often be made using a gamma ray spectrometer. Energy dispensive 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. These two techniques are not strictly photometric as particles are measured not electromagnetic radiation, but the methodology is similar.

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) analysis based on single radiation measurements, especially if the natural decay series has been interrupted by chemical or metallurgical processes in the past.

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Table 1

## 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.

Table 2

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

| | 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) | 249.7; (548, 521 and 495(3)) | |
| Calcium (3) | 854.2, 422.7, 396.8 and 393.4 | 0.2 (for 422.7) |
| Caesium | 894.3 and 852.1 | 0.1 (for 852.1) |
| Chromium (2) | 425.4 | |
| Copper | 578.2, 327.4, 324.8 | |
| Europium | 576.5, 459.4, 462.7, 466.2<br>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, 398.8, 369.4 and 328.9 | – |

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 3

## Elements determined by Ultra Violet-Visible Emission Spectroscopy

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

| | |
|---|---|
| ( ) | free element in gases by discharge tube technique |
| / / | usually analysed by some other method but obtainable routinely by special techniques. |

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/

Table 4

## Approximate appearances and extinctions of selected lines of Elements, suitable for prism spectrographs.

(An explanation of the intensity scale and notes used in this table, together with a summary of the excitation conditions immediately follow the end of this table.)

(A similar line extinction system for use with grating spectrographs is given in reference 5.)

| Line | Percent in Carbon | | | | | | | Elements liable to overlap |
|---|---|---|---|---|---|---|---|---|
| nm | 10 | 1 | 0.1 | 0.01 | 0.001 | 0.0001 | 0.00001 | |
| **Ag Silver** | | | | | | | | |
| 241.3 | ft | vft | | | | | | Mo,V ,Pt,Co,Fe |
| 243.8 | ft | vft | | | | | | Mo,Ni,Fe |
| 293.8 | vft | vvft | | | | | | Fe,Mn,Bi |
| 328.0 | vh | h | m | t | ft | vft | vvft | Fe,Mn,Zn |
| 338.3 | h | t | vt | vft | | | | Fe,Ti,Cr |
| **Al Aluminium** | | | | | | | | |
| 216.8 | vft | | | | | | | |
| 217.4 | vft | | | | | | | |
| 220.4 | vft | | | | | | | |
| 221.0 | ft | vft | vvft | | | | | Si |
| 225.8 | vft | | | | | | | |
| 226.3 | t | vft | | | | | | |
| 226.9 | t | vft | | | | | | Sn |
| 232.1 | vft | | | | | | | Ni |
| 236.7 | t | ft | vft | | | | | Fe |
| 237.2 | ft | vft | | | | | | Mn,Ti |
| 237.3 | t | ft | vft | 4 | | | | Sb,Cr |
| 256.8 | m | ft | vft | | | | | Zr |
| 257.5 | m | t | ft | 5 | | | | Mn |
| 265.2 | t | ft | vvft | | | | | Re,Hg,Rh,Ta |
| 266.0 | m | ft | vvft | | | | | Pt,Cd,Fe,Ag,Mo,Mg |
| 308.2 | h | m | t | ft | vft | | | Mn,V,Co |
| 309.3 | h | m | t | ft | vft | vvft | | V ,Na,Fe,Mg |

*Table 4 continued*

| Line | | Percent in Carbon | | | | | | | Elements liable to overlap |
|---|---|---|---|---|---|---|---|---|---|
| nm | 25 | 10 | 1 | 0.1 | 0.01 | 0.001 | 0.0001 | 0.00001 | |
| As Arsenic (E) | | | | | | | | | |
| 216.5 | | vvft | | | | | | | Cu,As,Ni,Fe,Sr |
| 228.8 | | m | t | ft | vvft | | | | Cd,Ni |
| 234.9 | | m | t | ft | vft | | | | Be |
| 236.9 | | ft | vft | | | | | | Cu |
| 237.0 | | vft | vvft | | | | | | Cr |
| 238.1 | | vft | vvft | | | | | | Fe,Ru |
| 245.6 | | ft | vft | vvft | | | | | Ru,Zr |
| 249.3 | | vft | vvft | | | | | | Cu |
| 278.0 | | t | ft | vft | | | | | Mn,Ce,Mo,Nb,Bi,Cr |
| 286.0 | | ft | vft | vvft | | | | | Co, V,Pt,Cr,Os |
| 289.9 | | vft | vvft | | | | | | Fe,Mo,Mn,Hf,Ta |
| 303.3 | | m | t | ft | vvft | | | | Fe,Ni,As,Sn,Cr |
| Au Gold (L) | | | | | | | | | |
| 235.2 | | vft | | | | | | | Hg,Mo,Nb,Co,Mn |
| 242.8 | | h | m | t | ft | vft | | | Ta,Pt |
| 259.0 | | vvft | | | | | | | Ti,Co,Mn |
| 267.6 | | h | m | t | ft | vft | | | Ta |
| 270.1 | | vft | | | | | | | Zr,Mo,Cr,V ,Cu,Mn |
| 274.8 | | t | ft | vft | | | | | Pt,Cr,Mo,Ta |
| 3 12.3 | | t | ft | vft | | | | | Fe,V ,Ti,Rh |
| B Boron (E) | | | | | | | | | |
| 208.89 | | ft | vvft | | | | | | |
| 208.96 | | ft | vft | | | | | | |
| 249.7 | | vh | h | m | ft | vft | | | |
| 249.8 | | vh | h | m | ft | vft | | | |
| Ba Barium | | | | | | | | | |
| 224.5 | | ft | vft | | | | | | Pt,Co,Fe,Ir,V ,Sn |
| 225.4 | | vft | | | | | | | Nb,Ni |
| 230.4 | | h | m | t | ft | vft | | | Co,Ir,Mo |
| 233.5 | | h | m | t | ft | vft | | | Sn,Co |
| 234.7 | | ft | vft | | | | | | Hf |
| 259.6 | | m | t | ft | vft | | | | Ta,Ti,Mo |
| 263.5 | | t | ft | vft | | | | | Mo,Hg,Ce |
| 264.7 | | vvft | | | | | | | Pt,Re,Mo,Hf,Ta,Nb, Fe,V |
| 277.1 | | ft | vft | | | | | | Zn,Mo, V,Mn,Cr |
| 307.1 | | vft | vvft | | | | | | Ti,Cr,Mo,Nb,Ce,Pt |
| Be Beryllium | | | | | | | | | |
| 217.5 | | ft | vft | vvft | | | | | Co,Fe,Pt,Ni |
| 234.8 | | vh | h | m | t | ft | vvft | | As |
| 235.0 | | ft | vvft | | | | | | Hf |
| 249.5 | | vh | h | m | ft | vft | 5 | | Mn,Fe |
| 265.1 | | vh | m | t | ft | vvft | | | Pt |
| 313.0-1(d) | | vh | m | t | ft | vft | 5 | | Fe,Ta,Nb,Os,Hg |
| 332.1 | | m | t | ft | vft | | | | Co,Sr,Ni,Fe,Rh |
| Bi Bismuth | | | | | | | | | |
| 222.8 | | ft | vft | vvft | | | | | |
| 223.0 | | ft | vft | | | | | | |
| 227.6 | | ft | vft | | | | | | Co,Hf |
| 240.1 | | vft | | | | | | | Co,Pt,Ni |
| 289.8 | | m | t | ft | vft | | | | Mo,Mn,Nb,Pt,Fe |
| 298.9 | | m | ft | vft | | | | | Fe,Cr,Ru,Ta,Co |

*Table 4 (continued)*

| Line<br>nm | 25 | Percent in Carbon<br>10 | 1 | 0.1 | 0.01 | 0.001 | 0.0001 | 0.00001 | Elements liable<br>to overlap |
|---|---|---|---|---|---|---|---|---|---|
| Bi Bismuth (contd.) | | | | | | | | | |
| 299.3 | | t | vft | vvft | | | | | Re,Ni,Mo,Fe,Nb,Cr |
| 302.4 | | m | ft | vft | | | | | Cr,Fe |
| 306.8 | | h | m | t | ft | vft | | | Fe,Re,Ta |
| Ca Calcium | | | | | | | | | |
| 227.5 | | vft | | | | | | | |
| 239.8 | | ft | ft | vft | | | | | B |
| 299.5 | | vft | | | | | | | Fe,Ni,Nb,Cr,Co |
| 299.7 | | vft | | | | | | | Cr,Cu |
| 299.9 | | vft | | | | | | | Fe,Re |
| 300.1 | | vft | | | | | | | Fe,Co,Ti,Mo,Cr |
| 300.6 | | ft | vft | | | | | | Co,Fe |
| 315.9 | | t | ft | vft | vvft | | | | Mo,Co |
| 317.9 | | m | t | ft | vft | vvft | | | Cr,Fe |
| Cd Cadmium (E) | | | | | | | | | |
| 214.4 | | ft | vft | vvft | | | | | As,Pt,Fe,Sb |
| 226.5 | | t | ft | ft | vft | vvft | | | Ni,Fe,Co |
| 228.8 | | vh | h | m | t | ft | vft | | Ni,As |
| 267.7 | | ft | vft | vvft | | | | | Pt,Cr,V ,Fe |
| 276.4 | | t | ft | vft | | | | | Co,Cr,Pd,Fe,Mo |
| 288.1 | | ft | vft | vvft | | | | | Si,Ta |
| 298.0 | | ft | vft | 5 | | | | | Fe,Cr,Hf,Ni |
| Ce Cerium | | | | | | | | | |
| 254.8 | | ft | vft | | | | | | Fe,Mo,Ni |
| 257.3 | vft | | | | | | | | Mn,Mo,Co |
| 261.4 | | t | ft | vft | | | | | Pb,Fe,Mo,Ta |
| 263.5 | | ft | vft | | | | | | Hg,Ba,Mo,Zr |
| 265.1 | | ft | vft | 4 | | | | | Pt,Be,Ge |
| 269.1 | vft | | | | | | | | W,Cr,Ta,Ge |
| 269.5 | | ft | vft | | | | | | Mg,Mn,Fe |
| 276.1 | | vvft | | | | | | | Co,Mo,W,Ta,Cr,Fe |
| 278.4 | | vft | | | | | | | Mo,Fe,V |
| 283.7 | t | ft | vft | 3 | | | | | Cr,Mn,Fe |
| 297.6 | | ft | vvft | | | | | | Cr,Ta,Hf,Fe,Re |
| 297.7 | ft | vft | | | | | | | Ru,W , V |
| 298.0 | | vft | | | | | | | Fe,Cd |
| 298.2 | | vft | | | | | | | Fe,Cd,Ni,Nb,Mo |
| 299.5 | | ft | vft | | | | | | Cr,Ti |
| 300.9 | | ft | vft | | | | | | Fe,Sn |
| 305.1 | | vft | | | | | | | Ni,Os,Co,Hf,V |
| 305.5 | | ft | vvft | | | | | | Fe,Mo |
| 305.6 | | ft | vvft | | | | | | Ti,Mo,Hf |
| 320.1 | | ft | vft | 6 | | | | | Fe,Ti,Pt |
| 321.8 | | ft | vft | 4 | | | | | Cr,Sn,Pd,Co,Ti |
| Co Cobalt | | | | | | | | | |
| 217.4 | | t | ft | vft | | | | | Ni,Pt |
| 224.5 | | t | ft | vft | | | | | Pt,W |
| 226.8 | | vft | | | | | | | Nb,Cr,Sn |
| 228.6 | | h | m | ft | vvft | | | | |
| 237.8 | | h | m | ft | vvft | | | | Al |
| 238.8 | | h | m | ft | vvft | | | | Pb,Fe,Ni,V |
| 240.7 | | h | t | ft | vft | | | | Fe |
| 240.9 | | t | ft | vft | | | | | |
| 241.0 | | ft | vft | | | | | | Fe |
| 241.1 | | h | m | ft | vft | | | | Fe,Pb |
| 241.4 | | t | ft | vft | | | | | Zr |

| Line | | Percent in Carbon | | | | | | | | Elements liable |
|---|---|---|---|---|---|---|---|---|---|---|
| nm | 25 | 10 | 1 | 0.1 | 0.01 | 0.001 | 0.0001 | 0.00001 | 0.000001 | to overlap |
| Co Cobalt (contd.) | | | | | | | | | | |
| 241.5 | | m | t | ft | vft | | | | | Mo,V |
| 242.5 | | h | m | t | vft | | | | | Pt |
| 251.1 | | m | t | vft | | | | | | Fe |
| 252.1 | | h | m | ft | vft | | | | | Fe,W , In |
| 304.4 | | t | ft | vvft | | | | | | Mn,Os,Ni,Fe |
| 304.9 | | t | ft | vvft | | | | | | Fe, Ta |
| 307.2 | | t | ft | vvft | | | | | | Ba,Zn,V |
| 308.7 | | m | t | ft | vft | vvft | | | | |
| 325.4 | | m | t | ft | vft | 7 | | | | Fe,Zr,Mn |
| 340.5 | | m | t | ft | vft | 3 | | | | Pd |
| 341.2 | | m | t | ft | vft | | | | | Ni |
| 341.7 | | m | t | ft | vft | | | | | Ni |
| 346.6 | | m | t | ft | vft | 2 | | | | Re,Cd |
| 347.4 | | m | t | ft | vft | 2 | | | | |
| Cr Chromium | | | | | | | | | | |
| 236.4 | t | ft | | | | | | | | Au,Fe |
| 236.8 | | ft | | | | | | | | Ir,Pt,Fe |
| 238.3 | | t | ft | vft | | | | | | Te |
| 240.8 | | m | t | vft | | | | | | Sn,Co |
| 249.6 | | t | vft | | | | | | | Sn,Fe,Zr,B |
| 250.2 | | vft | | | | | | | | Zn,Ir,Re,V |
| 250.4 | | m | t | vft | | | | | | Pt,Ta |
| 251.9 | vft | | | | | | | | | Fe,Ce,Cd,Ti,Si |
| 267.7 | | vh | m | t | ft | vft | | | | Pt,Cd,V |
| 272.6 | | m | ft | vft | | | | | | Mn,Fe |
| 273.2 | | m | ft | vft | | | | | | V,Ti |
| 273.6 | | t | vft | | | | | | | Fe,Ta,Rh |
| 274.8 | | h | t | ft | vft | | | | | Pt,Au,Mo,Ta |
| 275.3 | | t | ft | vft | | | | | | Ta,Hg |
| 275.7 | | m | t | ft | vft | | | | | Zn,Fe |
| 276.1 | | h | m | t | vft | | | | | Ta,Fe |
| 276.4 | | t | ft | vft | vvft | | | | | Cd,Co |
| 277.0 | | m | ft | vft | | | | | | Sb,Re,Zn |
| 278.1 | | h | t | ft | 8 | | | | | Au,Bi,As,Fe |
| 283.5 | | vh | h | m | t | vft | | | | Fe |
| 284.0 | | t | ft | vft | vvft | | | | | Sn,Al,Fe |
| 284.3 | | vh | h | m | t | ft | vft | | | Ta,Fe |
| 284.9 | | h | m | t | vft | | | | | Ta,Mo,Ru,Hf,Fe |
| 298.6* | | h | m | t | ft | vft | | | | Be,Rh,Co,Fe,Si |
| 299.9* | | m | ft | vft | 9 | | | | | Pt,Fe,Re |
| 301.5(t) | | m | t | ft | 5 | | | | | Fe |
| 301.7 | | h | m | t | ft | vft | | | | Co,Fe,Os,Zn |
| 304.1 | | m | ft | vft | | | | | | In,Fe,Mn,Os |

*There is a series of lines at 298.64, 298.86, 299.19, 299.51, 299.66, 299.88 and 300.09, which are visible depends on concentration

Cs Caesium

No good lines visible in the ultra violet, see table 2

| Line | | Percent in Carbon | | | | | | | | Elements liable |
|---|---|---|---|---|---|---|---|---|---|---|
| nm | 25 | 10 | 1 | 0.1 | 0.01 | 0.001 | 0.0001 | 0.00001 | 0.000001 | to overlap |
| Cu Copper | | | | | | | | | | |
| 223.0 | | t | ft | vft | | | | | | Bi |
| 224.4 | | ft | vft | | | | | | | Ni |
| 226.0 | | vvft | | | | | | | | Fe |
| 240.6 | | t | ft | vft | | | | | | Co,Fe,V |
| 244.1 | | vft | | | | | | | | Ti,Co,Mo |
| 249.2 | | ft | vvft | | | | | | | Zn,Rh,Os |

*Table 4 (continued)*

| Line | Percent in Carbon | | | | | | | | | Elements liable to overlap |
|---|---|---|---|---|---|---|---|---|---|---|
| nm | 25 | 10 | 1 | 0.1 | 0.01 | 0.001 | 0.0001 | 0.00001 | | |
| Cu Copper (contd.) | | | | | | | | | | |
| 261.8 | | t | vft | vvft | | | | | | Fe,Mn |
| 276.6 | | vft | | | | | | | | Fe,Cr,V , Co |
| 282.4 | | vft | | | | | | | | Fe,At |
| 296.1 | | vft | | | | | | | | Fe |
| 299.7 | | vvft | | | | | | | | Cr,Pt |
| 324.7 | | vh | vh | h | m | m | t | ft | vft | |
| 327.4 | | vh | vh | h | m | m | t | ft | vvft | |
| Dy Dysprosium | | | | | | | | | | |
| 214.4(n) | | ft | | | | | | | | As,Cd,Fe |
| 231.9 | | ft | vft | | | | | | | |
| 232.5 | | ft | vft | | | | | | | Ag,Zr,Hf,Co,Ni |
| 238.2 | | t | ft | c5 | | | | | | Ru,Fe |
| 242.2 | | ft | vft | | | | | | | Sn,V , Co |
| 263.4 | | ft | vft | | | | | | | Ba,Hg |
| 281.6 | | ft | vft | | | | | | | Fe,Mo,Co |
| 313.5 | | t | ft | 3 | | | | | | Mo,Ni,Cd |
| 325.1 | | t | ft | vft | | | | | | Fe,Pd,Cd |
| Er Erbium | | | | | | | | | | |
| 210.7 | ft | | | | | | | | | |
| 211.4 | ft | | | | | | | | | |
| 212.5 | ft | | | | | | | | | Si |
| 213.3 | ft | | | | | | | | | Bi |
| 214.1 | ft | | | | | | | | | Te |
| 244.6 | | m | ft | vft | | | | | | Pb |
| 258.6 | | m | t | vft | | | | | | Fe,Re |
| 267.0 | | m | t | vft | | | | | | Zn |
| 275.0 | | t | ft | | | | | | | Ta,Fe |
| 275.5 | | m | t | ft | | | | | | Fe |
| Eu Europium | | | | | | | | | | |
| 255.4 | | vft | | | | | | | | Zr,Ta,Sb,V , Fe |
| 255.9 | | vft | | | | | | | | Ta,In |
| 256.4 | | ft | vft | | | | | | | Mn,Re,V |
| 256.8 | | ft | | | | | | | | Al,Zn,V , Fe,Zr |
| 257.7 | | ft | vft | | | | | | | Pb,Ta,Fe |
| 263.5 | | ft | | | | | | | | Hg,Ba,Ce,Zr,Mo,Fe, Ru,Pd |
| 263.8 | | h | t | vft | vvft | | | | | Mn,Mo,Hf,Zr,Pt |
| 264.1 | | t | ft | | | | | | | Ti,Hf,Fe,Cr |
| 266.8 | | m | t | vft | | | | | | Fe |
| 267.8 | | t | ft | | | | | | | Cd,Zr,Ru,Fe |
| 268.5 | | t | ft | | | | | | | Co |
| 269.2 | | m | t | vft | | | | | | Ru,Fe,Sb,Ta,Mn |
| 270.1 | | t | ft | vft | | | | | | Au,V , Cu,Mo,Mn, Pt,Cr |
| 270.2 | | t | ft | vft | | | | | | Cr,V ,Pt,Ba |
| 272.8 | | h | m | t | ft | vft | | | | Ta,Fe,V ,Rh |
| 272.9 | | m | t | vft | vvft | | | | | Fe,Rh,Pt |
| 274.0 | | ft | vvft | | | | | | | Fe,Cu,Ti,v ,Ta,Co |
| 281.3 | | h | m | t | ft | vvft | | | | Mn,Ti,Fe,Sn,Ta |
| 282.1 | | m | t | ft | vft | | | | | Ni |
| 285.9 | | t | ft | | | | | | | Fe,Cr,V ,As |
| 286.2 | | t | ft | | | | | | | Hf,Fe,Cr,Co |
| 290.6 | | h | m | ft | vft | | | | | Ti,Pt,Fe,V ,Rh |
| 305.5 | | t | ft | vft | | | | | | Co,Fe |

*Table 4 (continued)*

| Line | Percent in Carbon | | | | | | | Elements liable |
|---|---|---|---|---|---|---|---|---|
| nm | 10 | 1 | 0.1 | 0.01 | 0.001 | 0.0001 | 0.00001 | to overlap |
| Fe Iron | | | | | | | | |
| 212.5 | vft | | | | | | | |
| 219.2 | ft | vft | 2 | | | | | |
| 226.7 | vft | | | | | | | Sn,Cd,Ni |
| 227.8 | ft | vft | | | | | | |
| 229.2 | m | t | ft | vft | | | | Pt |
| 229.6 | vft | | | | | | | Co,Ni,Cr |
| 229.8 | vft | | | | | | | Zr,Ni |
| 233.2 | ft | vft | | | | | | Pb,Hf |
| 233.8 | ft | vft | | | | | | Mo |
| 2 34.8 | ft | vft | | | | | | Ba,W ,Bi,Be |
| 239.9 | m | ft | vft | vvft | | | | Ca,B |
| 240.4 | h | m | t | ft | vft | | | Co |
| 246.2 | t | ft | vft | | | | | |
| 247.3 | m | t | ft | vft | | | | Mn |
| 248.3 | h | m | t | ft | ft | vft | | Rh,Sn |
| 248.4 | m | t | ft | vft | vvft | | | Re |
| 248.8 | h | m | m | t | ft | vft | | Mn |
| 248.9 | t | t | ft | vft | vvft | | | Pt |
| 249.0 | t | t | ft | vft | vvft | | | Ni,Mn,Rh |
| 249.1 | t | t | ft | vft | vvft | | | Mn,Ni,Au,Cr |
| 250.1 | t | t | ft | vft | | | | Ni,Rh |
| 251.0 | t | ft | vft | vvft | | | | Ni |
| 251.8 | t | ft | vft | vvft | | | | |
| 252.3 | m | t | ft | vft | vvft | | | |
| 252.4 | t | ft | vft | 3 | | | | Si,Ni,Bi |
| 252.7 | t | ft | vft | vvft | | | | Mn |
| 259.9(d) | m | t | t | ft | vft | vvft | | Ta |
| 261.2 | m | t | t | ft | vft | | | Ru |
| 271.9 | t | ft | vft | 4 | | | | |
| 296.5 | h | m | t | ft | vft | vvft | | Re,Ti,Ta |
| 296.7 | h | m | t | t | ft | vft | | Hg |
| 297.0 | m | m | t | t | ft | vft | | Ta |
| 297.3(d) | vh | h | m | t | ft | vft | | Co,Zr |
| 302.0-1(t) | vh | h | h | m | t | ft | see note below | |
| 304.8 | t | ft | vvft | | | | | |

at about this level this triplet starts resolving as follows:
one thick line at concentration 0.00004%
two lines at concentration 0.00002%
three lines at concentration 0.00001%
However, finally perhaps about 0.000008% only one thin line is left.

| Line | Percent in Carbon | | | | | | | Elements liable |
|---|---|---|---|---|---|---|---|---|
| nm | 10 | 1 | 0.1 | 0.01 | 0.001 | 0.0001 | 0.00001 | to overlap |
| Ga Gallium (E) | | | | | | | | |
| 223.4(n) | vft | | | | | | | Co,Pt |
| 225.5(n) | vft | | | | | | | Hf |
| 225.9(n) | vft | | | | | | | V ,Fe,Ni,In |
| 229.4 | ft | vft | | | | | | Co,Zr,Fe,W |
| 229.8(n) | vft | vvft | | | | | | Hf,Mn,Tl |
| 233.8 | ft | vft | | | | | | Co |
| 237.1 | vft | vvft | | | | | | As,Mo |
| 241.8 | ft | vft | | | | | | Pt |
| 245.0 | ft | vft | | | | | | Fe,Pt,Ti,Ni |
| 250.0 | ft | vft | vvft | | | | | |
| 250.1 | ft | vft | vvft | | | | | Fe,Ni,Rh,V ,Re |
| 262.5 | vft | | | | | | | Mn,Hg,W,Cr,Pt,Fe,Ce |

*Table 4 (continued)*

| Line | Percent in Carbon | | | | | | | Elements liable |
|---|---|---|---|---|---|---|---|---|
| nm | 10 | 1 | 0.1 | 0.01 | 0.001 | 0.0001 | 0.00001 | to overlap |
| Ga Gallium (E) (contd.) | | | | | | | | |
| 266.0 | ft | vft | vvft | | | | | Pt,Cd,Al,Fe,Ag,Mg |
| 271.9 | ft | vft | vvft | | | | | Sb,Fe,Pt,Ru |
| 287.4 | h | m | t | ft | vft | | | Pb,Ta,Fe |
| 294.3 | m | t | ft | vft | vvft | | | V ,Re,Co,Ni |
| Gd Gadolinium | | | | | | | | |
| 216.8 | vft | | | | | | | |
| 217.0 | ft | vft | | | | | | Pt,V |
| 217.7 | vft | vvft | | | | | | V ,Fe |
| 217.8 | vft | vvft | | | | | | Cu,Sb |
| 219.1 | vft | vvft | | | | | | Mn,Fe |
| 219.2 | vft | vvft | | | | | | |
| 226.1 | ft | vft | | | | | | |
| 246.8 | ft | vft | | | | | | Pt,Co,In,Fe |
| 248.7 | ft | vft | | | | | | Pt,Zr,Re |
| 248.8 | ft | vft | | | | | | Fe,Ta |
| 276.4 | t | ft | vft | | | | | Cd,Co,Cr |
| 276.8 | t | ft | vft | | | | | Fe,Tl |
| 278.1 | t | ft | vft | | | | | Cr |
| 281.0 | t | ft | vft | vvft | | | | Ru,Ta |
| 283.4 | t | ft | vft | | | | | Ta,Co,Re,Mo,Pt |
| 299.9 | m | t | ft | vft | vvft | | | Cr,Fe,Re |
| 300.9 | t | t | ft | vft | | | | Sn,Fe |
| 307.2 | m | t | ft | vft | | | | Ba,Zn,Co,V ,Ti |
| Ge Germanium | | | | | | | | |
| 209.4 | vft | | | | | | | |
| 212.3 | ft | vft | | | | | | Si |
| 218.5 | vvft | | | | | | | |
| 219.9 | m | t | ft | vft | | | | Sn,Cu,Fe |
| 225.5 | vft | | | | | | | Os |
| 231.4 | ft | vft | | | | | | Ni |
| 232.8 | ft | vft | | | | | | |
| 237.9 | ft | vft | | | | | | Tl |
| 239.8(n) | vft | | | | | | | B,Ca |
| 241.7 | m | t | ft | vft | | | | Ta,V ,Fe,Pt |
| 243.6(n) | t | vft | | | | | | Fe,Co,Pt |
| 253.3 | t | ft | | | | | | Zr,Fe,Bi,Mn,Ir |
| 258.9 | ft | vft | | | | | | Ar,Au |
| 259.2 | h | m | t | ft | vvft | | | Cr,Ir,Cu,Fe,Mn,Ta |
| 264.4 | vft | | | | | | | Fe,Ti,Mo |
| 265.1 | h | m | t | ft | vft | | | Pt,Ce,Fe,Ru,V ,Re,Hg |
| 269.1 | h | m | ft | vft | | | | Ta,Ce,Ru |
| 303.9 | t | ft | 3 | | | | | |
| 312.4 | vft | | | | | | | Ce,In |
| Hf Hafnium | | | | | | | | |
| 227.7 | ft | vft | vvft | | | | | |
| 232.2 | ft | vft | | | | | | |
| 232.3,232.4 | ft | vft | | | | | | both lines same |
| 234.7 | vft | | | | | | | Co,Ni,Ba |
| 235.1 | t | ft | vvft | | | | | Mo |
| 239.3 | ft | vft | | | | | | Pb |
| 239.4 | ft | vft | | | | | | Pb |
| 240.5 | ft | vft | | | | | | Re |
| 260.7 | t | ft | vft | vvft | | | | Fe |

*Table 4 (continued)*

| Line | Percent in Carbon | | | | | | | | Elements liable to overlap |
|---|---|---|---|---|---|---|---|---|---|
| nm | 25 | 10 | 1 | 0.1 | 0.01 | 0.001 | 0.0001 | 0.00001 | |
| Hf Hafnium (contd.) | | | | | | | | | |
| 262.2 | | t | ft | vvft | | | | | Fe,Co,Cr,Mn |
| 263.8 | | t | ft | vft | vvft | vvft | | | Mn,Mo |
| 264.1 | | vft | | | | | | | Ti,Fe |
| 282.0 | | t | ft | vvft | | | | | Zr,Co,Fe,Cr,Ni |
| Hg Mercury | | | | | | | | | |
| 253.6 | | m | t | ft | vft | vvft | | | Fe,Ru |
| 265.2 | | ft | 2 | | | | | | Re,Al,Rh |
| 296.7 | | vft | | | | | | | Fe,Cr |
| 312.6 | | vft | | | | | | | Fe,Cu,V ,Cr |
| 313.1(d) | | ft | vft | vvft | | | | | Be,Ta,Nb,V ,Mo |
| Ho Holmium | | | | | | | | | |
| 259.1 | | vvft | | | | | | | Fe,Co,Cr,Mo |
| 260.5 | | vft | | | | | | | Fe,Mo,Co,Mn |
| 271.3 | | ft | vvft | | | | | | V,Pt,Mn,Cu,Mo,In,Fe |
| 273.4 | | ft | vft | | | | | | Cd,Pt,Fe,Ru,Zr,Ti |
| 275.0 | | ft | vft | | | | | | Ta,Ti,Fe,Ru,Cr |
| 288.0 | | ft | vft | vvft | | | | | Sn,Mg,Mn,Mo,As,Bi, Cr,Au |
| 288.1 | | ft | vft | vvft | | | | | Cr,Zn,Mg,Fe |
| 289.5 | | vft | vvft | | | | | | Fe,Ta,Mn |
| 290.9 | | ft | vft | | | | | | V,Fe,Ta,Cr,Os,Mo |
| 291.9 | | ft | vft | | | | | | Co,Pt,Hf,Os,Fe |
| 297.3 | | vft | | | | | | | Mo,Fe |
| In Indium (E) | | | | | | | | | |
| 230.7 | | ft | vft | | | | | | Co,Pt |
| 246.0 | | vft | | | | | | | Co,Hf,Mn |
| 246.8 | | vft | | | | | | | Co,Mo,Fe |
| 256.0 | | t | vft | | | | | | |
| 260.2 | | ft | vft | | | | | | Mo,Mn,Cd |
| 275.4 | | t | ft | vft | | | | | V,Fe,Pt,Mo,Ge |
| 285.8 | | ft | vft | | | | | | Ta,Mn,V,Fe,Cr |
| 293.2 | | t | ft | vvft | | | | | Ta,Mn |
| 303.9 | | m | t | ft | vvft | | | | Ge,Fe,Co |
| 325.6 | | m | t | ft | vvft | | | | V,Fe,Mn,Mo |
| 325.8 | | t | ft | vft | | | | | Co,Mn,Pd,Re |
| Ir Iridium | | | | | | | | | |
| 224.2 | | ft | vft | | | | | | Pb,Cu |
| 226.5 | | vvft | | | | | | | Ni,Cd,Fe |
| 230.4 | | vft | | | | | | | Co,Ir,Ba,Fe,Mn |
| 234.3 | | vft | | | | | | | Hf,Pt,Fe,As |
| 236.3 | | ft | vvft | | | | | | Cu,Zr |
| 237.3 | | t | ft | vft | | | | | Mo,Cr,Al |
| 238.7 | | vft | | | | | | | Co,Cr,Pt,V ,Zr,Mo |
| 239.0 | | ft | vft | | | | | | V |
| 239.1 | | ft | vft | | | | | | Re,Co,Ta |
| 243.2 | | vft | | | | | | | |
| 245.3 | | vvft | | | | | | | |
| 246.7 | | ft | vft | | | | | | Pt |
| 247.5 | | t | ft | vft | vvft | | | | Ta,Mo,Fe,Li,Ru |
| 248.1 | | t | ft | vvft | | | | | Sb,V ,W,Mo |
| 250.3 | | m | t | ft | vft | | | | Zn,Re,Cr,V |
| 254.3 | | m | t | ft | vft | vvft | | | Co,Fe |
| 266.5 | | m | t | ft | vvft | | | | Fe,Pt,Mo |

*Table 4 (continued)*

| Line | | Percent in Carbon | | | | | | | Elements liable |
|---|---|---|---|---|---|---|---|---|---|
| nm | 25 | 10 | 1 | 0.1 | 0.01 | 0.001 | 0.0001 | 0.00001 | to overlap |
| Ir Iridium (contd.) | | | | | | | | | |
| 269.4 | | t | ft | vft | vvft | | | | Co,Fe |
| K Potassium | | | | | | | | | |
| 321.7 | ft | vft | 2 | | | | | | Ta,Ti,V ,Fe |
| 344.6 | ft | vft | vvft | | | | | | Cr,Nb,Ni |
| 344.8 | ft | vft | vvft | | | | | | Fe,Zr,Co,Os |
| La Lanthanum | | | | | | | | | |
| 218.7 | | ft | vft | | | | | | Fe |
| 221.6 | | ft | vft | | | | | | Ni,Si,Pt |
| 225.7 | | vft | vvft | | | | | | V |
| 229.8 | | ft | vft | | | | | | Fe,Hf,Mn,Tl |
| 231.8 | | vft | | | | | | | Pt |
| 231.9 | | vft | | | | | | | Cr,Cu,Ni |
| 237.9 | | ft | vft | | | | | | Tl |
| 289.3 | | ft | vft | | | | | | Mo,Pt,V ,Cr,Hg,Fe |
| 310.4 | | ft | vft | 2 | | | | | Ti,Co,Os |
| 324.5 | | t | ft | vft | | | | | Fe |
| 330.3 | | m | t | ft | vft | | | | Zn,Na,Mn,Fe,Co,Mo |
| 333.7 | | t | ft | vft | 5 | | | | Mg,Co,Fe,Ta,Cu,Re |
| Li Lithium | | | | | | | | | |
| 239.4 | | ft | vft | | | | | | |
| 242.6 | | vvft | | | | | | | |
| 247.5 | | vft | | | | | | | Ru |
| 256.2 | | ft | vft | | | | | | Ta,V ,Fe |
| 274.1 | | t | ft | vft | | | | | |
| 323.2 | | t | ft | vft | vvft | | | | Os,Pb,Sb,Co,Ni |
| Lu Lutetium | | | | | | | | | |
| 219.1 | | vvft | | | | | | | Fe |
| 219.5 | | vft | | | | | | | |
| 223.6 | | vvft | | | | | | | Cu |
| 227.7 | | vft | | | | | | | Co,Bi,Hf,Fe |
| 261.5 | | t | ft | vft | | | | | Ru,Fe,Mo |
| 270.2 | | ft | vft | | | | | | Fe,Cr,V ,Pt,Ba |
| 275.4 | | ft | vft | | | | | | In,Mo,Ge,Pt |
| 289.4 | | ft | vft | | | | | | Pt,Mo,Fe,Ta |
| 291.1 | | t | ft | vft | | | | | Cr,V ,Mo,Fe |
| Mg Magnesium | | | | | | | | | |
| 273.6 | | vft | | | | | | | Ta,Cr,Mo,Fe |
| 277.7 | | t | vft | vvft | | | | | ) these lines are |
| 277.8 | | t | vft | vvft | | | | | ) easy to identify |
| 277.9 | | t | ft | vft | vvft | | | | ) from others by |
| 278.1 | | t | vft | vvft | | | | | ) the symmetrical |
| 278.3 | | t | vft | vvft | | | | | ) pattern they make |
| 279.1 | | ft | vft | vvft | | | | | Ta |
| 279.5 | | t | ft | vft | vvft | vvft | | | Mn |
| 280.3 | | t | t | ft | vft | vvft | | | Co |
| 285.2 | | vh | vh | h | m | ft | ft | vft | Fe,Na |
| Mn Manganese | | | | | | | | | |
| 210.9 | | vft | | | | | | | Re,Bi |
| 219.1 | | vft | | | | | | | Fe |
| 221.4 | | ft | vft | | | | | | Re |
| 230.5 | | ft | vft | | | | | | |

*Table 4 (continued)*

| Line | Percent in Carbon | | | | | | | | Elements liable to overlap |
|---|---|---|---|---|---|---|---|---|---|
| nm | 25 | 10 | 1 | 0.1 | 0.01 | 0.001 | 0.0001 | 0.00001 | |
| Mn Manganese (contd.) | | | | | | | | | |
| 254.3 | | ft | vft | | | | | | Na,Fe,Re,Ir |
| 257.2 | | t | ft | vft | | | | | Cr,Co,Mo |
| 257.6 | | vh | h | m | t | ft | vft | | Al,Fe |
| 258.4 | | h | m | t | ft | vft | | | Ta,Fe |
| 259.3 | | vh | h | m | t | ft | vft | | Cu,Ta |
| 259.6 | | h | m | t | ft | vft | | | Pt |
| 260.5 | | vh | m | t | ft | vft | | | Fe,Co |
| 279.5 | | vh | vh | m | t | t | ft | vft | Mg |
| 279.8 | | vh | vh | m | t | ft | ft | vvft | Fe,Ta,Zr,Ni,Bi |
| 280.1 | | vh | vh | m | t | ft | vft | | Ta,Zn,Pb |
| Mo Molybdenum | | | | | | | | | |
| 261.6 | | vft | | | | | | | Co,Fe |
| ·263.9 | | ft | ft | vft | | | | | Pt,Ir |
| 264.9 | | vft | | | | | | | Re,Ti,Co |
| 267.3 | | ft | vft | vvft | | | | | Mg,Fe,Co |
| 277.5 | | t | ft | vft | vvft | | | | Ta,Co,Ru,Cr |
| 278.0 | | t | ft | vft | | | | | Sn,Mg,Mn,As,Bi |
| 278.5 | | ft | vft | | | | | | Ru,Ta,Sn,Ba |
| 281.6 | | m | t | ft | vft | | | | Fe,Co |
| 284.2 | | vft | | | | | | | Ru,Na,Ti,Mn,Co,Ta, Ce,Cr |
| 284.8 | | m | t | ft | vft | | | | Ta,Zr |
| 287.1 | | t | ft | vft | | | | | Rh,Ta,Re,Fe |
| 289.1 | | t | ft | vft | | | | | Ta,Cr,V |
| 291.2 | | t | ft | vft | | | | | Fe,Ti,Pt |
| 293.0 | | t | ft | vft | | | | | Pt,Mn,Re,V |
| 313.2 | | m | t | ft | vft | vvft | | | Hg,Co,Fe,V ,Ta |
| 315.8 | | m | t | ft | vft | | | | Fe,Re,Co |
| 317.0 | | m | t | ft | vft | vvft | | | Co,Fe |
| 319.4 | | m | t | ft | vft | vvft | | | Fe,V ,Os |
| 320.9 | | ft | ft | vft | | | | | Fe |
| Na Sodium | | | | | | | | | |
| 259.4 | vft | | | | | | | | Fe,Mo,Mn,Bi,Co |
| 268.0 | ft | vft | | | | | | | Ti,Co,Fe |
| 285.3 | m | t | ft | vft | vvft | | | | Fe,Mg,V ,Mo |
| 330.3(d) | h | m | t | ft | vft | | | | Sr,Pd,Bi,Zn |
| Nb Niobium (L) | | | | | | | | | |
| 254.5 | | vvft | | | | | | | Fe,Ta,Sb |
| 265.6 | | vft | | | | | | | Mo,Fe,V ,Ru,Ti,Ta |
| 267.1 | | ft | vft | | | | | | Ir,Re,V ,Mg |
| 272.2 | | vft | | | | | | | Ca,Ce,Ag,Fe,Co,V |
| 277.3 | | ft | vft | | | | | | Fe,Pt,Mn,Hf,V,Mo |
| 287.5 | | ft | vft | vvft | | | | | Fe,Re,V ,Zr,Cr,Ta |
| 288.3 | | t | ft | vft | vvft | | | | V ,Mn,Re,Cu,Fe |
| 289.7 | | ft | vft | vvft | | | | | Mo,Mn,Pt,Bi |
| 289.9 | | ft | vft | vvft | | | | | Ta,V ,Cr,Fe,Ce |
| 290.8 | | ft | vft | | | | | | Fe,Pt,Mn,Ce,V |
| 291.0 | | ft | vft | | | | | | V ,Cr,Fe |
| 292.8 | | t | ft | vft | vvft | | | | Ru,Fe,Co |
| 294.1 | | t | ft | vft | vvft | | | | Fe,V ,Cr,Ti,Mg,Ta |
| 295.1 | | t | ft | vft | vvft | | | | Fe,V , Na,Zr, |
| 309.4 | | t | ft | vft | vvft | | | | Fe,Cu,V ,Mo |
| 313.1 | | t | ft | vft | | | | | Ta,Ti,Ce,Be,Os |
| 316.3 | | t | ft | vft | vvft | | | | Ta,Ce,W ,Cr,Fe |

*Table 4 (continued)*

| Line<br>nm | Percent in Carbon<br>10 | <br>1 | <br>0.1 | <br>0.01 | <br>0.001 | <br>0.0001 | <br>0.00001 | Elements liable to overlap |
|---|---|---|---|---|---|---|---|---|
| Nb Niobium (L) (contd.) | | | | | | | | |
| 319.4 | t | ft | vft | vvft | | | | Fe,Au,Ce,Os,Ni |
| Nd Neodymium | | | | | | | | |
| 224.3(n) vft | | | | | | | | Co |
| 242.2(n) vft | | | | | | | | V ,Sb,Y ,Co |
| 270.2 | vft | | | | | | | Fe,Cr,V,Nb,Pt,W,Cu, Mo,Ba |
| 276.5 | vft | | | | | | | Ti,Rh,Mo,Ru |
| 286.4 | vft | | | | | | | Bi,Mo,Fe,Mo,V ,Ta |
| 300.8 | vft | | | | | | | Mn,Mo,Cd,Fe,Zr |
| 301.4 | ft | vft | | | | | | Co,Cr,Mo,Fe,V,Zr,Mn |
| 307.0 | ft | vft | | | | | | Ce,V,Mo,Os,Re |
| 307.1 | vvft | | | | | | | Mo,Ce,Re,Ti,Cr,Ba |
| Ni Nickel | | | | | | | | |
| 216.9 | vft | | | | | | | Pb, |
| 226.4 | ft | vft | vvft | | | | | Fe,Co |
| 227.0 | ft | vft | | | | | | Sb |
| 228.7 | vft | | | | | | | Fe |
| 231.7 | ft | vft | | | | | | Ag,Sn |
| 240.2 | vft | | | | | | | Pt,Pb,Mo,Co |
| 294.4 | ft | vft | vvft | | | | | Co,Ga,Mo,Fe |
| 299.4 | ft | vft | vvft | | | | | Fe,Nb,Cr |
| 301.2 | ft | vft | vvft | | | | | Fe,Zr,Ta,Cu |
| 305.1 | t | ft | vft | vvft | | | | Os,Co,Hf,V |
| 305.4 | ft | vft | vvft | | | | | Mn,Al,Co |
| 310.1 | t | ft | vft | vvft | | | | Mo,Hf,K,V |
| 313.4 | t | ft | vft | vvft | | | | Cd,V ,Fe,Hf |
| 324.3 | t | ft | vft | vvft | | | | Mn,Co,Fe,Pd,Ta,Ir |
| 341.4(t) | t | ft | vft | vvft | | | | Co |
| Os Osmium | | | | | | | | |
| 219.4 | vvft | | | | | | | Sn,W |
| 225.6 | ft | vvft | | | | | | Fe,Ni |
| 228.2 | ft | vft | | | | | | Sn |
| 236.3 | vft | | | | | | | Zr,Co |
| 237.7 | t | ft | vvft | | | | | Co,Pt |
| 242.5 | ft | vft | | | | | | Pt,Co |
| 248.8 | t | ft | vft | | | | | Mn,Fe,Ta |
| 251.3 | vft | | | | | | | Hf,Mo,Cr,Pt |
| 263.7 | t | ft | vft | vvft | | | | Ta,Sn,V |
| 283.8 | t | ft | vft | | | | | Al,Fe |
| 290.9 | m | t | ft | vft | vvft | | | V ,Fe,Ta,Cr |
| P Phosphorus | | | | | | | | |
| 213.5 | vft | | | | | | | Pt,Ni,Fe,Cu |
| 213.6 | ft | vft | | | | | | |
| 214.9 | ft | vft | | | | | | Sn,Cu,Fe |
| 2 15.3 | vft | | | | | | | Bi,Fe |
| 215.4 | vft | | | | | | | Co |
| 253.4 | ft | vvft | | | | | | Ir,Ti,Hg |
| 253.5 | t | vft | | | | | | Ru,Fe,Ti,Cu,Hg |
| 255.3 | ft | vvft | | | | | | Co,Cr |
| 255.5 | vft | | | | | | | V,W,Fe |
| Pb Lead (E) | | | | | | | | |
| 217.0 | ft | vft | | | | | | |

*Table 4 (continued)*

| Line<br>nm | Percent in Carbon<br>10 | 1 | 0.1 | 0.01 | 0.001 | 0.0001 | 0.00001 | Elements liable<br>to overlap |
|---|---|---|---|---|---|---|---|---|
| **Pb Lead (E)** (contd.) | | | | | | | | |
| 220.3 | ft | vft | | | | | | |
| 224.7 | ft | vft | | | | | | Ag,Cu |
| 233.2 | vft | | | | | | | Co,Fe,Hf |
| 238.9 | vft | | | | | | | Fe,Co,V ,Ni,Mo |
| 239.4 | t | vft | vvft | | | | | Hf |
| 239.9 | vft | | | | | | | Ca,Cr,Fe,Hg,V,Co,Bi |
| 240.2 | ft | vft | | | | | | Ni,Pt,Mo,Co |
| 241.1 | vft | | | | | | | Co,Fe,Ag,Ni,V |
| 247.6 | t | vft | | | | | | Pd |
| 257.7 | t | ft | vvft | | | | | Mn,Fe,Ta,Cr |
| 261.4 | m | t | vft | vvft | | | | Fe,Co,Ta,Re |
| 280.2 | m | t | vft | vvft | | | | Zn,Mn,Ta,Ni,Ti |
| 282.3 | m | t | vft | | | | | Ru,Hf,Fe |
| 283.3 | h | t | ft | vft | | | | Fe,Ce,Ta |
| **Pd Palladium** | | | | | | | | |
| 244.8 | ft | vft | | | | | | Fe,Ag,Bi |
| 247.6 | ft | vft | | | | | | Fe,Pb,Co,Ni |
| 276.3 | ft | vft | | | | | | Fe |
| 292.2 | ft | vvft | | | | | | Fe |
| 302.8 | ft | vft | | | | | | Ta |
| 324.3 | m | t | vft | vvft | | | | Ta,Ni |
| 330.2 | t | ft | vvft | | | | | Os,Pt,Na,Bi,Zn |
| 340.4 | t | ft | vvft | | | | | Cd,Co |
| 342.1 | t | ft | vvft | | | | | |
| **Pr Praseodymium** | | | | | | | | |
| 237.3(n) | ft | | | | | | | Al |
| 269.8 | ft | | | | | | | V ,Ta,Pt,Fe |
| 270.2 | ft | | | | | | | Cr,V ,Ba,Pt |
| 270.7 | ft | | | | | | | Sn,Fe,V ,Rh,Mn |
| 297.1 | ft | | | | | | | Cr,Mg,Fe |
| 298.5 | vft | | | | | | | Fe,Cr,Rh |
| 301.3 | ft | vvft | | | | | | Hf,Cr,Co,Os,Mo,Fe |
| 302.9 | vft | vvft | | | | | | Cr,Au,Fe,Ir,Zr,Mn,Y |
| 306.3 | ft | | | | | | | Ce,V,Cu,Fe |
| 308.2 | t | vft | | | | | | Mo,V,Mn,Al,Co,Mn,<br>Ti,Sb |
| **Pt Platinum** | | | | | | | | |
| 246.7 | vft | vvft | | | | | | Ni,Mo |
| 248.7 | vft | vvft | | | | | | Fe,Zr,Re |
| 261.9 | vft | | | | | | | Mn,Ti,Re |
| 262.8 | ft | ft | vft | | | | | Bi,Pb,Fe |
| 264.7 | ft | ft | vft | | | | | Ta,Mo,Ti,Re |
| 265.9 | t | t | ft | vft | | | | |
| 269.8 | ft | vft | vvft | | | | | V,Mo,Fe,Ta |
| 270.2 | t | ft | vft | | | | | V,Cr,Ba |
| 270.6 | t | ft | vft | | | | | Rh,Mn,Fe,Mo,Zr,<br>V,Sn |
| 271.9 | ft | vft | vvft | | | | | Fe,Ru,Cu,Sb |
| 273.4 | ft | vft | vvft | | | | | Fe,Cd,Ru |
| 283.0 | ft | vft | vft | | | | | Mo,Mn |
| 293.0 | t | ft | vft | vvft | | | | Co,Fe,Hf,Mn,Mo |
| 299.8 | t | ft | vft | vvft | | | | Cu,Cr |
| 304.2 | ft | vft | vft | | | | | Fe,Co,Mn,V |
| 306.5 | m | t | ft | vft | vvft | vvft | | Mo,Co,Ni |

*Table 4 (continued)*

| Line<br>nm | Percent in Carbon<br>10 | <br>1 | <br>0.1 | <br>0.01 | <br>0.001 | <br>0.0001 | <br>0.00001 | Elements liable to overlap |
|---|---|---|---|---|---|---|---|---|
| **Rb Rubidium** | | | | | | | | |
| No suitable lines in the ultra violet, see table 2 | | | | | | | | |
| **Re Rhenium** | | | | | | | | |
| 209.7 | vft | | | | | | | Pt,V,Co,Mn |
| 215.6 | vft | | | | | | | Bi,Fe |
| 227.5 | t | ft | vft | vvft | | | | Ca |
| 230.6 | ft | | | | | | | Fe,Sb,In |
| 232.2 | ft | | | | | | | Hf |
| 234.5 | ft | | | | | | | Fe,Ni |
| 236.5 | ft | | | | | | | Au,Fe,Cr |
| 240.5 | t | vft | | | | | | Fe,Hf,Mo |
| 240.6 | ft | | | | | | | Hf,Mo,Co,Fe,Cu |
| 242.0 | t | vft | | | | | | V,Sn |
| 242.8 | m | t | vft | | | | | Ta,Au,Pt,V, Sn |
| 248.3 | t | vft | | | | | | Fe,Rh,Sn |
| 248.7 | t | vft | | | | | | Pt,Rh,Fe |
| 250.9 | m | ft | vft | | | | | Pt |
| 252.1 | t | vft | | | | | | |
| 271.5 | m | ft | | | | | | Fe,Os,Ta,Rh,V |
| 296.6 | t | vft | | | | | | Fe,Ta |
| 299.2 | m | ft | vft | | | | | Fe,Cr,Ni,Bi |
| 299.9 | m | ft | vft | | | | | Cr,Fe |
| **Rh Rhodium** | | | | | | | | |
| 226.3 | ft | | | | | | | Sb,Cu,Al |
| 226.4 | ft | vft | | | | | | Fe,Ni,Cd |
| 227.7 | vft | | | | | | | Pt,Hf,Fe |
| 229.0 | ft | | | | | | | Bi |
| 232.2 | ft | | | | | | | Hf |
| 233.5 | t | ft | | | | | | V,Sn,Ba |
| 246.1 | ft | vvft | | | | | | Co,Mn,Re |
| 247.0 | vft | | | | | | | Fe,Pt,Mo |
| 247.1 | vft | | | | | | | Mo,Fe |
| 248.3 | t | vft | vvft | | | | | Fe,Sn |
| 248.7 | t | vvft | | | | | | Pt,Re,Zr,Fe |
| 249.2 | m | ft | | | | | | Zn,Co,Os |
| 250.1 | ft | | | | | | | Fe,V,Re |
| 265.2 | t | vft | | | | | | Ru,V,Hg,Al,Re |
| 270.3 | t | vft | | | | | | Mn |
| 271.4 | t | vft | | | | | | In,V,Fe,Os,Ta |
| 271.7 | ft | | | | | | | Ru,Fe |
| 272.0 | ft | | | | | | | Mo,Cu,Fe,Ta |
| 272.9 | t | vft | vvft | | | | | V,Mo,Fe |
| 297.7 | t | vft | | | | | | V,Co |
| 298.6 | t | ft | | | | | | Cr,Be,Fe |
| 319.1 | t | ft | vft | | | | | Nb,Fe |
| 326.3 | t | vft | | | | | | Os,Sn,Fe |
| 327.1 | t | vft | | | | | | Fe,Ni,Cu |
| 328.0 | t | ft | vvft | | | | | Fe,Ag |
| 328.3 | t | ft | vvft | | | | | Ti,Zn,Ni,Fe |
| 332.3 | m | t | ft | vft | | | | Co,Sr,Ni,Pt,Fe |
| 343.5 | m | t | ft | vft | | | | Co,Pd,Ni,Ru |
| **Ru Ruthenium** | | | | | | | | |
| 225.5 | ft | | | | | | | Os |

*Table 4 (continued)*

| Line | Percent in Carbon | | | | | | | | Elements liable |
|---|---|---|---|---|---|---|---|---|---|
| nm | 25 | 10 | 1 | 0.1 | 0.01 | 0.001 | 0.0001 | 0.00001 | to overlap |
| Ru Ruthenium (contd.) | | | | | | | | | |
| 225.9 | | vft | | | | | | | Ni,In |
| 227.2 | | ft | | | | | | | Fe |
| 227.8 | | vft | | | | | | | Os,Ni,Fe,Co |
| 227.9 | | ft | vvft | | | | | | Os,Ni,Fe,Co |
| 240.2 | | m | ft | vft | | | | | Pt,Cu |
| 245.5 | | t | vft | | | | | | As |
| 245.6 | | m | ft | vvft | | | | | As |
| 254.9 | | ft | | | | | | | Ta,Pt,Fe,V,Cr |
| 267.8 | | t | ft | | | | | | Fe,Zr |
| 281.0(d) | | t | vft | | | | | | Bi,Fe,V,Ta |
| 287.5 | | m | t | ft | vvft | | | | Fe |
| 343.7 | | m | t | ft | vvft | | | | Pd,Rh,Ni,Co,Zr |
| Sb Antimony | | | | | | | | | |
| 212.7 | | vft | vvft | | | | | | |
| 213.9 | | vft | vvft | | | | | | Zn |
| 214.1 | | vft | vvft | | | | | | Fe,V |
| 214.5 | | vft | vvft | | | | | | As,Cd,Fe |
| 217.6 | | t | t | ft | vft | | | | |
| 217.9 | | ft | vft | vvft | | | | | Hf,Co,Cu |
| 231.1 | | m | t | ft | vft | | | | Ni |
| 252.8 | | t | ft | vft | vvft | | | | Si |
| 259.8 | | m | t | ft | vft | | | | Fe |
| 287.8 | | t | ft | vft | vvft | | | | |
| 323.2 | | ft | vft | | | | | | Fe,Ta,Os,Li |
| Sc Scandium | | | | | | | | | |
| 227.3 | | ft | vft | vvft | | | | | Fe,Hf,Nb |
| 255.2 | | t | ft | vft | | | | | Ta,Re,Pt,Tl,Fe,V |
| 256.0 | | t | ft | vft | | | | | In,Cr,Co,Ni |
| 282.2 | | m | ft | vft | vvft | | | | Ru,Mo,Cr,Co |
| 301.9 | | t | vft | vvft | | | | | Cr,Ni,Os,Fe |
| 326.9 | | t | vft | vvft | | | | | Sb,Fe,Ge,Ta,Os,Mn |
| 327.3 | | m | t | vft | 2 | | | | Nb,Cu |
| Se Selenium | | | | | | | | | |
| no suitable lines in the ultra violet | | | | | | | | | |
| Si Silicon | | | | | | | | | |
| 212.3 | ft | vft | 2 | | | | | | |
| 212.4 | t | ft | vft | vvft | | | | | |
| 220.8 | ft | vft | vvft | | | | | | |
| 221.1 | ft | vft | vvft | | | | | | |
| 221.6 | t | ft | vft | vvft | | | | | Ni,Pt |
| 243.5 | m | t | ft | vft | vvft | | | | Zr,V |
| 250.7 | h | m | t | ft | vft | vvft | | | Re,Pt,Ta,V,Co,Pt* |
| 251.4 | h | m | t | ft | vft | | | | Pt,Ta,Fe * |
| 251.6 | vh | h | m | t | ft | vft | vvft | | Re,Zn,Bi,Pt * |
| 251.9 | h | m | t | ft | vft | | | | V,Cr,Fe * |
| 252.4 | h | m | t | ft | vft | | | | Ni,Sn,Fe,Co * |
| 252.8 | h | m | t | ft | vft | vvft | | | Sb,Fe,Ta,V * |
| 263.1 | t | ft | vft | vft | | | | | Fe |
| 288.1 | vh | h | m | t | ft | vft | vvft | | Cd |

*These lines are relatively stronger than the interfering lines and form a recognizable though irregular pattern. With experience confusion is unlikely.

*Table 4 (continued)*

| Line | Percent in Carbon | | | | | | | Elements liable |
|---|---|---|---|---|---|---|---|---|
| nm | 10 | 1 | 0.1 | 0.01 | 0.001 | 0.0001 | 0.00001 | to overlap |
| Sm Samarium | | | | | | | | |
| 228.8 | vft | | | | | | | Cd,As |
| 261.0 | vft | | | | | | | Tl,Co,Fe |
| 264.0 | ft | vvft | | | | | | Pt,Cd,Ir,Mo,Ti |
| 264.9 | vft | | | | | | | Ru,Re,Mo,Co,Pb,Be |
| 265.7 | vft | | | | | | | Ta,Pt |
| 266.2 | ft | vvft | | | | | | V,Ru,Ir,Pb |
| 267.5 | ft | vvft | | | | | | Au,Ta |
| 268.8 | vft | | | | | | | V,Re,Fe |
| 269.3(d) | ft | vft | | | | | | Mn,Ir |
| 278,9 | ft | vft | | | | | | Fe |
| 279.6 | ft | vvft | | | | | | Mg,Fe,Ta,Rh,Os |
| 280.9 | ft | vft | | | | | | Fe,Bi |
| 283.0 | ft | vft | | | | | | Pt |
| 330.6 | t | ft | vft | | | | | Mo,Fe,Zr |
| 330.7 | t | ft | vvft | | | | | Fe,Zr,Mo,Co,Sr,Cu,Au |
| Sn Tin | | | | | | | | |
| 211.4 | vvft | | | | | | | |
| 219.4 | ft | vft | | | | | | Os |
| 224.6 | t | ft | vvft | | | | | Pt,Ag,Cu,Pb |
| 226.9 | m | ft | vvft | | | | | Al |
| 235.5 | m | ft | vft | | | | | |
| 242.9 | m | ft | vft | | | | | Pt |
| 254.6 | t | ft | vvft | | | | | Ni,Fe,V,Ir |
| 257.1 | t | vft | vvft | | | | | Zr,Cr |
| 270.6 | h | t | vft | vvft | | | | Pt,V,Fe |
| 284.0 | vh | m | ft | vft | 5 | | | Fe |
| 285.0 | t | ft | vvft | | | | | Cr,Ta,Mo,Sb |
| 286.3 | m | t | ft | vvft | | | | Rh,Fe |
| 291.3 | t | vft | vvft | | | | | Pt,Cr,Ta |
| 300.9 | m | t | ft | vvft | | | | Fe,Cu |
| 303.4 | h | t | ft | vvft | 5 | | | As,Cr,Fe |
| 317.5 | h | t | ft | vft | vvft | | | Co,Fe |
| 326.2 | m | t | vft | vvft | | | | Ti,Tl,Fe,Os,Rh |
| Sr Strontium (E) | | | | | | | | |
| 215.3 | ft | vft | | | | | | Bi,Ir,Sn |
| 216.5 | ft | vft | vvft | | | | | Cu,Pt,As,Fe |
| 228.2 | vft | vvft | | | | | | Os |
| 330.7 | ft | vft | 7 | | | | | Fe,Ti,Mo,Co,Cu |
| 335.1 | ft | vft | 5 | | | | | Fe,Rb |
| Ta Tantallum (L) | | | | | | | | |
| 243.2 | ft | vft | 6 | | | | | Co,Fe,Ti |
| 250.7 | ft | vft | | | | | | Si,V,Fe |
| 251.3 | vft | | | | | | | Hf |
| 251.9 | vft | | | | | | | Si,Cr,V |
| 252.6(t) | t | ft | vft | | | | | V |
| 253.2 | ft | vft | | | | | | Ni,Co,Si,Zr |
| 255.9 | ft | vft | | | | | | In |
| 257.3(d) | ft | vft | | | | | | Cr,Re,Hf |
| 260.8 | ft | vft | | | | | | Zn,Fe,Tl |
| 269.8 | ft | vft | | | | | | Fe,V,Pt |
| 271.0 | ft | vft | | | | | | Fe,Cr,In |
| 271.4 | t | ft | vft | | | | | In,V,Rh,Fe,Os |
| 279.6(d) | ft | vft | 4 | | | | | Mg,Co,Os |
| 285.1(d) | ft | vft | vft | | | | | Fe,Mg |

*Table 4 (continued)*

| Line | Percent in Carbon | | | | | | | Elements liable |
|---|---|---|---|---|---|---|---|---|
| nm | 10 | 1 | 0.1 | 0.01 | 0.001 | 0.0001 | 0.00001 | to overlap |
| Ta Tantalum (L) (contd) | | | | | | | | |
| 287.9 | vft | | | | | | | V,Cr |
| 288.0 | vft | | | | | | | Cd |
| 290.2 | ft | vft | 4 | | | | | Fe,Re |
| 293.3(d) | ft | ft | vft | | | | | In |
| 295.2 | ft | vft | 6 | | | | | Fe |
| 296.3 | t | ft | vft | | | | | V |
| 301.2 | t | ft | vft | | | | | Fe,Zr,Ni |
| Tb Terbium | | | | | | | | |
| 238.4(n) | ft | | | | | | | Mn,Fe |
| 239.7(n) | ft | | | | | | | Co,Os,V |
| 258.4 | ft | vft | | | | | | Mn,Fe |
| 260.8 | ft | vft | | | | | | Zn,Fe,Tl,Ta |
| 261.7 | vft | | | | | | | Fe,Co,Mn |
| 262.8 | ft | vft | | | | | | Bi,Pt,Pb,Fe,Mn |
| 266.8 | ft | vvft | | | | | | Fe,Ir |
| 266.9 | ft | vft | | | | | | Ti,Ir,Zn |
| 273.6 | ft | vft | | | | | | Fe,Cr |
| 275.9 | ft | vft | | | | | | Hg,Fe |
| 276.9 | t | ft | vft | | | | | Ru,Fe,Cr |
| 280.9 | ft | vft | vvft | | | | | Ti,Bi |
| 281.2 | ft | vft | | | | | | Mn,Ti,Fe |
| 289.4 | ft | vft | | | | | | Mo,Fe,Ta |
| 289.7 | t | ft | vft | | | | | Cr |
| 291.5 | ft | vft | | | | | | Ta |
| 307.0 | ft | vft | | | | | | Os,Re,Mn |
| Te Tellurium (E) | | | | | | | | |
| 214.3 | vft | vvft | | | | | | |
| 214.7 | vvft | | | | | | | |
| 216.0 | vvft | | | | | | | Fe |
| 225.6 | vft | | | | | | | Os,Fe |
| 225.9 | ft | vft | | | | | | V,Fe,Ni |
| 226.6 | vft | | | | | | | Ni,Hf |
| 238.3 | t | ft | vvft | | | | | Sb,Pt,Mn |
| 238.6 | t | ft | vft | vvft | | | | Cr,Vi,Ni |
| 253.1 | ft | | | | | | | Sn,Hf,Ti,Ta |
| Th Thorium | | | | | | | | |
| 249.4 | vft | | | | | | | Co,Fe,Mn,Be |
| 254.8 | vft | | | | | | | Fe,Co,Mo |
| 260.1 | ft | vvft | | | | | | Fe |
| 264.1 | ft | vvft | | | | | | Cr,Fe,Hf,Ti,Mo |
| 268.4 | t | vft | | | | | | Ta,Zn |
| 269.4 | ft | vvft | | | | | | Ir,Co,Fe |
| 274.7 | t | ft | vvft | | | | | Pt,Fe,Ni,Ta |
| 283.2 | t | ft | vft | vvft | | | | Fe,Pb |
| 283.7 | t | ft | vft | vvft | | | | Ta,Cd,Co,Zr,Al,Fe |
| 287.0 | ft | vft | | | | | | V,Cr |
| 298.1 | ft | vft | | | | | | Fe,Ni,Cd,Hf,Cr |
| 307.9 | vft | | | | | | | Fe,Ce,Mo |
| 310.8 | t | ft | vvft | | | | | Ni,Mn,Fe,Cu,Ca,Re, Os,Hf |
| Ti Titanium (L) | | | | | | | | |
| 227.2 | ft | vvft | | | | | | Ru |
| 227.3 | ft | vvft | | | | | | Hf |

| Line | Percent in Carbon | | | | | | | Elements liable to overlap |
|---|---|---|---|---|---|---|---|---|
| nm | 10 | 1 | 0,1 | 0.01 | 0.001 | 0.0001 | 0.00001 | |
| Ti Titanium (L) (contd.) | | | | | | | | |
| 242.4 | vft | | | | | | | Co,Pt,W,Fe,Ni |
| 251.7 | ft | vft | | | | | | Fe,Mo,V,Cr,Hf |
| 251.9 | vft | | | | | | | Cr,Cd,W,Si,V,Fe,Co |
| 252.0 | ft | vvft | | | | | | Rh,Fe |
| 252.5 | t | ft | vft | | | | | Co,Fe,Cd,Mn,Ta |
| 253.1 | ft | vft | | | | | | Sn,Ta,Hf |
| 260.0 | t | ft | vvft | | | | | Fe,Mo,Re |
| 260.5 | t | ft | vvft | | | | | Mn |
| 261.1 | t | ft | vft | | | | | Ir,Ta,Fe |
| 264.1 | m | ft | vft | | | | | Cr,Fe,Hf,Th,Mo |
| 264.4 | t | ft | vft | | | | | Fe,Mo |
| 264.6 | t | ft | vvft | | | | | Pt,Mo,Ta,Ru |
| 294.2 | m | t | ft | | | | | Fe,V,Nb,Ta,Ru,V |
| 294.8 | m | t | ft | | | | | Fe,Mn |
| 295.6 | m | t | ft | | | | | Fe,Mn |
| 307.2 | m | t | ft | vft | | | | Co,Zn,Ba |
| 307.5 | m | t | ft | vft | | | | V,Mo,Os,As,Fe,Zn |
| 307.8 | m | t | ft | vft | | | | Os,Cr,Fe,Co,Mn |
| 308.8 | m | t | ft | | | | | Mo,Co,Ir,V,Cu |
| 316.8 | t | vft | | | | | | Fe,Ce,Ru,Re,Os,Co |
| 318.6 | m | t | vft | | | | | Re,Rh,Ce,Co,Os |
| 319.2 | t | ft | vft | | | | | Fe,Cr,Co |
| 319.9 | m | t | ft | | | | | Fe |
| 323.4 | m | t | ft | vft | vvft | | | Fe,Os,Ni |
| 323.6 | t | ft | vft | vvft | | | | Fe,Zr,Ce,Mn |
| 323.9 | t | ft | vft | vvft | | | | Os,Fe,Ta |
| 324.2 | t | ft | vft | vvft | | | | Ir,Ta,Pd |
| 334.9 | t | ft | vft | vvft | | | | Rb,Nb,Cr,Cu,Ce,Ca |
| Ti Thallium (E) | | | | | | | | |
| 223.8 | vft | | | | | | | Ti |
| 231.6 | vvft | | | | | | | Sb,V,Pt |
| 237.9 | ft | vft | | | | | | Hf |
| 258.0 | ft | vft | | | | | | Mn,Ta,Cd,Ti |
| 266.5 | vft | | | | | | | Fe,V,Mo,Ir |
| 270.9 | ft | vvft | | | | | | Fe |
| 276.8 | h | t | vft | | | | | Ru,Rh,Fe |
| 282.6 | ft | vvft | | | | | | Fe,Zr,Mo,Rh,Co |
| 291.8 | h | ft | vvft | | | | | Fe |
| 292.1 | t | vft | | | | | | Fe,Pt |
| 323.0 | t | ft | vvft | | | | | Os,Ta,Fe |
| Tm Thulium (Tu in Russian journals) | | | | | | | | |
| 222.4 | vft | | | | | | | |
| 223.2 | vft | | | | | | | Sn,Ir |
| 228.5 | ft | | | | | | | Co,Zr |
| 240.9 | ft | vvft | | | | | | Cr |
| 242.6 | ft | vvft | | | | | | Sb |
| 260.7 | ft | vft | | | | | | Fe,Hf,Mo,Ta,Ir |
| 262.4 | ft | vft | vvft | | | | | Fe,Co,Mn |
| 264.0 | t | ft | | | | | | Mo,Ti,Hf |
| 265.8 | t | ft | | | | | | Mn,Mo,Pt,Pd,Fe |
| 266.0 | t | ft | | | | | | Pt,Al,Sn,Ta |
| 282.8 | t | ft | vft | | | | | Fe,Ta,Mn |
| 286.9 | m | t | ft | vvft | | | | Ta,Fe,Zr |
| 301.5 | m | t | ft | vft | | | | Cr,Os,Co,Fe,Re,V |
| 313.1 | m | t | ft | vft | vvft | | | Be,Ta,Nb,Os,Hg,Mo |

*Table 4 (continued)*

| Line | Percent in Carbon | | | | | | | Elements liable to overlap |
|---|---|---|---|---|---|---|---|---|
| nm | 10 | 1 | 0.1 | 0.01 | 0.001 | 0.0001 | 0.00001 | |
| Tm Thulium (Tu in Rumian journals) (contd.) | | | | | | | | |
| 313.3 | t | ft | vft | vvft | | | | Mo,Ta,Cd,Ni |
| 315.1 | t | ft | vvft | | | | | Fe,Os,Co |
| 317.2 | m | t | ft | vvft | | | | Mo,Fe,Os |
| 324.1 | t | ft | vft | vvft | | | | Mn,Mo,Cr,Zr,Ir,Ti, Ta,Y,Pd |
| U Uranium | | | | | | | | |
| 240.6 | vft | | | | | | | Re,Fe,Cu,V |
| 256.3 | vvft | | | | | | | Fe,Mn |
| 256.5 | t | ft | vvft | | | | | |
| 259.7 | vft | | | | | | | Sb |
| 263.5 | ft | vft | | | | | | Fe,Ru,Pd |
| 279.3 | vft | | | | | | | Ru,Fe,Mo,Pt |
| 281.1 | vft | t | | | | | | Ru,Ta,Co,Mo |
| 286.5 | ft | vft | | | | | | Ta,Cr |
| 288.9 | t | ft | vft | | | | | Cr,V |
| V Vanadium (L) | | | | | | | | |
| 252.6 | vft | vvft | | | | | | Ti,Ta |
| 267.7 | t | ft | vft | | | | | Pt,Cr,Cd,Fe,Zr |
| 268.2 | t | ft | vvft | | | | | Fe,Mo,Sb |
| 268.7 | t | ft | vft | | | | | Fe,Mo,Cr,Re |
| 268.8 | ft | vft | | | | | | Fe,Mo,Cr,Re,Ti |
| 268.9 | ft | vft | | | | | | Fe |
| 289.3 | t | ft | vft | vvft | | | | Cr,Hg,Pt |
| 292.0 | t | ft | vft | vvft | | | | Os,Fe,Pt |
| 292.4 | m | t | ft | vft | | | | Mo,Fe |
| 305.6 | ft | vft | vvft | | | | | Mo,Ce |
| 306.0 | ft | vft | vvft | | | | | Ta,Os,Mn,Fe |
| 306.6 | t | ft | vft | | | | | Mn,Pd,Fe |
| 309.3 | m | t | ft | vft | | | | Al,Fe,Mg |
| 310.2 | t | ft | vft | | | | | Ni,Co |
| 318.3 | m | t | ft | 5 | | | | ) these three |
| 318.4 | m | t | ft | vft | | | | ) lines make |
| 318.5 | m | t | ft | vft | | | | ) a pattern |
| W Tungsten (L) | | | | | | | | |
| 227.0 | vft | | | | | | | Sb,Fe,Ni,As |
| 227.7 | vft | | | | | | | Co,Bi,Ti,Pt,Hf,Fe |
| 236.0 | vft | | | | | | | Fe,Sb |
| 236.3 | ft | vvft | | | | | | Ir,Cu,Zr,Co,Fe |
| 239.7 | ft | vft | vvft | | | | | Co,Os,Zr,V |
| 240.5 | t | vft | | | | | | Fe,Re,Hf,Zr,Mo |
| 241.5 | ft | vvft | | | | | | Co,Mo,Y,Rh |
| 242.4 | ft | vvft | | | | | | Ti,Mn,Pt,Co |
| 243.6 | t | ft | vft | | | | | V,Co,Mo,Fe |
| 245.9 | ft | vvft | | | | | | Mo,Rh |
| 246.7 | ft | vvft | | | | | | Ni,Pt |
| 247.2 | vft | | | | | | | Fe,Mn |
| 247.4 | ft | vvft | | | | | | Ag,Cr,Sb,Ta,Mo |
| 248.1 | t | vft | | | | | | Sb,V,Ir,Mo |
| 248.5 | ft | vvft | | | | | | Re,Fe,Mo,Co |
| 254.7 | ft | vft | | | | | | Sn,Fe,Ni |
| 255.1 | t | ft | vft | | | | | Zr,Mo,Ta,Fe,B |
| 256.2 | ft | vvft | | | | | | Ni,Mo,Fe,Ta,Co,Li |
| 258.7 | ft | vft | 5 | | | | | Pt,Fe,B |
| 260.2 | vft | | | | | | | Mo,In,Mn,Cd |

*Table 4 (continued)*

| Line<br>nm | Percent in Carbon<br>10 | <br>1 | <br>0.1 | <br>0.01 | <br>0.001 | <br>0.0001 | <br>0.00001 | Elements liable<br>to overlap |
|---|---|---|---|---|---|---|---|---|
| **W Tungsten (L)** (contd.) | | | | | | | | |
| 261.3 | ft | vft | vvft | | | | | Fe,Cr,Co,Mn,Hf,Pb,Ta |
| 263.3 | ft | vft | vvft | | | | | Fe |
| 265.6 | t | ft | vft | | | | | Fe,V,Ru,Mo,Ti,Ta |
| 268.1 | t | ft | vft | | | | | Mo,Fe,Mn |
| 271.9 | t | ft | vvft | | | | | Fe,Pt,Ru,Co,Ce,Rh |
| 272.4 | t | ft | vft | | | | | Fe,Cu,Ti,Mo |
| 294.4 | t | ft | vft | | | | | Ni,Mo,Ce,Fe,Vi,Ti |
| 294.7 | m | t | vft | | | | | Ta,Fe,Ti |
| **Y Yttrium** | | | | | | | | |
| 224.1(n) | ft | vft | | | | | | V,W |
| 224.3 | t | vft | | | | | | Ir,Co |
| 235.4 | vft | | | | | | | Cu,Mo,Sn |
| 237.4 | vft | | | | | | | Al,Sb,Cr,Zr |
| 238.5 | vft | | | | | | | Cr,Te |
| 241.5 | vft | | | | | | | Co,Mo,W |
| 242.2 | t | ft | vft | | | | | Sn,V,Sb,Co |
| 246.0 | ft | vft | | | | | | Co,Hf,Fe,Mn |
| 285.4 | ft | vft | | | | | | Fe,V,Ce |
| 291.9 | ft | vvft | | | | | | Tl,Fe,Ce,Mo,Pt,Co, Hf,Os |
| 319.5 | m | t | ft | vft | | | | Ce,Nb,Os,Ni,Mo,Fe |
| 320.0 | m | t | ft | vvft | | | | Fe,V,Ti,Re,Ni,Ce,Pt |
| 320.3 | m | t | ft | vvft | | | | Ti,Fe,Co,Pt,Ce |
| 321.6 | m | t | ft | vft | vvft | | | Fe,Ta,Mn,Ti,V,K |
| 324.2 | m | t | ft | vft | | | | Ti,Ta,Ce,Pd,Ni,Fe |
| 332.8 | m | t | ft | vvft | | | | Mo,Ce,Co,Cr,Fe,Ti |
| **Yb Ytterbium** | | | | | | | | |
| 211.6 | vft | | | | | | | |
| 212.7 | ft | vvft | | | | | | Nb,Ir |
| 216.1 | vft | | | | | | | |
| 239.0 | t | vft | | | | | | V |
| 239.8 | vft | | | | | | | V,Nb |
| 246.4 | m | ft | vft | | | | | Hf,Co,Fe |
| 251.2 | t | vft | | | | | | Cr |
| 253.8 | t | vft | | | | | | Mo,Fe |
| 255.2 | vft | | | | | | | Pt,Sc,Tl,V,Fe,Mo,Co |
| 265.3 | m | ft | vft | | | | | Ta,Mo,Hg,V,Re |
| 267.2 | t | vft | vvft | | | | | Cr,Ir,Re,Nb,V,Mg |
| 275.0 | m | t | vft | | | | | Ta,Fe,Ru,Cr |
| 285.1 | t | vft | vvft | | | | | Ta,Sn,Hf,Fe,Ce,Mg |
| 289.1 | h | t | ft | vft | | | | Mo,Ta,Ti,Cr,V,Fe |
| 297.0 | m | t | vft | vvft | | | | Fe,Ce,Si,Ti,Cr |
| 303.1 | m | ft | vft | vvft | | | | Os,Hf,Fe,Ni |
| 328.9(d) | vh | m | t | ft | vft | vvft | | Rh,Pt |
| **Zn Zinc** | | | | | | | | |
| 213.8 | m | t | ft | vft | vvft | | | |
| 258.2 | vft | | | | | | | Os,Bi,Mo,Co,Fe |
| 275.6 | ft | vft | | | | | | Fe,Cr |
| 277.1(d) | t | ft | vft | | | | | Cr,Sb,Re,Rh,Pt |
| 280.1(d) | t | ft | vvft | | | | | Ta,Mn |
| 307.2 | t | ft | | | | | | Ba,Pt,Co,Ti |
| 307.6 | t | ft | vft | | | | | Os,Ti,As,Fe,V |
| 328.2 | t | ft | vft | | | | | Ti,Ni,Fe |

*Table 4 (continued)*

| Line<br>nm | Percent in Carbon<br>10 | <br>1 | <br>0.1 | <br>0.01 | <br>0.001 | <br>0.0001 | <br>0.00001 | Elements liable to overlap |
|---|---|---|---|---|---|---|---|---|
| Zn Zinc (contd.) | | | | | | | | |
| 330.3(d) | m | t | vft | 3 | | | | Sr,Pt,Pd,Na,Bi,Mn,Fe |
| Zr Zirconium | | | | | | | | |
| 228.5 | vft | vvft | | | | | | |
| 229.1 | vft | | | | | | | Fe |
| 237.4 | vft | | | | | | | Al,Ag |
| 245.0 | ft | vft | | | | | | Mg,Zn,Co |
| 253.2 | ft | vvft | | | | | | Ta,Co,Si,Fe,Bi,Ir |
| 257.1 | t | ft | vft | vvft | | | | Sn,Cr |
| 267.8 | t | ft | vft | vvft | | | | Fe,V,Mo,Ru |
| 270.0 | t | ft | vft | | | | | W,Mo,V,Cu |
| 272.2 | t | ft | vft | vvft | | | | Fe,Co,W,V,Re,Cr |
| 272.6 | t | ft | vft | vvft | | | | Fe,Mn,Cr,Mo,Sb |
| 273.2 | t | ft | vft | | | | | Cr,Ce,Mo,Ta |
| 273.4 | t | ft | vft | vvft | | | | Pt,Ru,Ti,Fe |
| 275.2 | t | ft | vft | vvft | | | | Hf,Cr,Co,Ce,Ta,Mn, Ru,Hg |
| 275.8 | vft | | | | | | | Fe,Co,Nb,Mo,Mn, Cr,Hg |
| 283.7 | ft | vft | vvft | | | | | Fe,Ta,Cd,In,Co,Ce,Al |
| 284.8(d) | ft | vft | vvft | | | | | Ta,Mo,Mg,Fe,V,Hf, Ru,Cr |
| 298.5 | vft | | | | | | | Fe,Cr,Rh |
| 301.1 | t | ft | ft | vft | | | | Cu,Ta,Fe,Ce,Ni |
| 302.9 | vft | | | | | | | Cr,Au,Fe,Ir,Sb,Ce |
| 316.5 | vft | | | | | | | Fe,Mo,Ca,V |
| 327.9 | t | ft | vft | vvft | | | | Fe,Co,Ti,Ce,Ta,Cu,V |
| 338.8(d) | t | ft | vft | vvft | | | | Fe,Os,Ti,Co,Cr |
| 339.2 | m | t | ft | ft | vft | | | Ni,Fe,Ru |

## Source conditions

**Samples** – carbon chars prepared either by ignition of mixed dithizonates and 8 quinolinolates at 450°C in a closed muffle furnace, or similar chars prepared by ignition of pure cellulose uniformly impregnated with metal nitrates, the ammonium salt of the metallate, or in a few instances the free acid or chloride where the nitrate or metallate was not stable.

**Lower electrode** – high purity graphite, ASTM specification E 130. S13. charged with 8.0 + 0.05 mg of sample.

**Counter electrode** – high purity graphite, ASTM specification E130. C1.

**Initial gap** – 3mm but not kept constant.

**Source** – sample negative 7.5 amp 220v DC arc, controlled as long as possible, but then allowed to fall to breakdown of the arc as the electrodes were consumed.

## Notes on the Table

Lines are compared with a base two scale of line densities. Such a scale may be made by striking arcs between copper electrodes for 2 seconds, 4 seconds, 8 seconds and so on, doubling exposure to 128 seconds at constant current, and developing the plate as above, then selecting a line that is just visible on the 2 second exposure. In the table lines similar to this are called vvft (very very faint trace). The others in order are called as follows: 4 secs vft (very faint trace), 8 secs ft (faint trace), 16 secs t (trace), 32 secs m (moderate), 64 secs h (high), and 128 secs and darker vh (very high), all using the same copper line for comparison. In an actual analysis, the plate is examined carefully to determine which lines of each element are visible and how big or intense they are. Comparison with the Copper line intensity scale may be made in several ways. A densitomer trace may be used, or the copper lines can be on a separate plate mounted in the reference holder of a slide comparator, or projected photographed and mounted on the comparator head. If possible, several lines of the element should be confirmed to avoid mistakes, and if necessary the absence or relative concentrations of elements with overlapping lines should also be checked by looking at lines of these elements as well. Thus a weak line of one element is unlikely to be mistaken for a strong line of a second element at low concentration if strong lines of the first element are absent. On the other hand, for the line of the second element not to obscure the weak line of the first element, the second element must be almost completely absent as indicated by the absence of even stronger lines elsewhere in its spectrum. Always include an iron or copper arc or similar comparison spectrum on each plate for ease of identification, scales fitted to spectrographs are not always precise.

The above table lists typical line appearances at various concentrations for a selection of lines chosen to be as far into the ultra violet region as is practicable. In some cases hitherto unreported lines are used. These are marked. Their wavelengths were measured by calculation from known lines on either side, knowing the dispersive power of the spectrograph for that region. It is highly unlikely that they are due to impurities as all suitable strong lines of every possible impurity were sought and found absent.

If a numerical value is given in a column instead of an intensity indication, as for instance 4, and 5 under 0.01% in carbon for Al 237.3nm and 257.5nm respectively, the line fades rapidly and becomes only just visible (vvft) at this number of times the column value – 0.04 and 0.05% respectively in the example given.

(d) signifies that the spectrum is a doublet,

(t) signifies a triplet,

(n) indicates that this is a newly discovered line not listed in most tables.

(E) these elements are sometimes concentrated in the early part of the burn.

(L) these elements are often only volatilized towards the end of the burn.

Table 5

## Typical Plasma Emission Spectrum Lines (1)

| Element | Wavelength nm | Typical limit of Detection micro g/l |
|---|---|---|
| Aluminium | 308.22 | 20 |
| | 309.3 | 3 |
| | 396.15 | 1 |
| Antimony | 206.8 (vn) | 100 |
| | 217.58(vn) | |
| | 259.80 | |
| Arsenic | 193.59(v) | 10 |
| | 228.81 | 30 |
| | 278.0 | 50 |
| Barium | 233.5 | 3 |
| | 455.40 | 0.04 |
| | 493.4 | 0.04 |
| Beryllium | 234.9 | |
| | 313.04 | 0.1 |
| Bismuth | 223.0 | 20 |
| Boron(2) | 249.68 | 7 |
| | 249.77 | 0.6 |
| Cadmium | 214.4 (vn) | |
| | 226.50 | 2 |
| | 228.80 | |
| Calcium | 317.9 | 6 |
| | 393.37 | |
| | 396.8 | |
| Carbon(3) | 193.9 (v) | |
| | 247.86 | 800 |
| Chromium | 205.55 | 4 |
| | 267.7 | |
| | 283.56 | |
| | 425.4 | |
| Cobalt | 228.6 | 3 |
| | 238.89 | |
| | 343.35 | |
| Copper(4) | 324.75 | 3, 0.3 |
| Indium | 303.9 | |
| Iron | 238.20 | 6 |
| | 259.94 | |
| Lanthanum | 398.8 | 6 |
| Lead | 220.35 | 30 |
| | 280.2 | 30 |
| | 405.78 | 7 |
| Lithium | 670.7 | 3 |
| Magnesium | 279.0 | 30 |
| | 279.55 | |
| Manganese | 257.61 | 0.4 |
| Mercury | 184.9 (v) | |
| | 194.23(v) | |
| | 253.65 | |

*Table 5 (continued)*

| Element | Wavelength nm | Typical limit of Detection micro g/l |
|---|---|---|
| Molybdenum | 202.03 | 9 |
| | 281.6 | |
| | 317.03 | |
| | 379.82 | 1 |
| | 386.4 | 0.6 |
| Nickel | 231.60 | 9 |
| | 341.5 | |
| Nitrogen$^{(5)}$ | 174.3 (v) | |
| | 174.5 | |
| Phosphorus | 178.2 (v) | 60 |
| | 213.62(vn) | 20 |
| | 214.9 (vn) | |
| | 253.56 | 20 |
| Potassium | 404.72 | |
| | 766.4 | 100 |
| | 769.9 | |
| Rubidium | 780.0 | 200 |
| Scandium | 361.4 | 0.05 |
| Selenium | 196.09(v) | 100 |
| | 204.0 (vn) | 120 |
| Silicon | 251.61 | |
| | 288.16 | 20 |
| Silver | 328.07 | 5 |
| Sodium | 330.23 | |
| | 588.99 | 20 |
| | 589.6 | 20 |
| Strontium | 407.77 | 0.2 |
| Sulphur | 180.73(v) | 80 |
| | 182.03 | |
| | 469.4 | 5000 |
| Tellurium | 214.2 (vn) | 20 |
| Tin | 189.99(v) | 7 |
| | 284.00 (283.999) | |
| Titanium | 334.94 | 3 |
| | 337.2 | |
| Tungsten | 207.91(vn) | 20 |
| | 239.71 | |
| Vanadium | 292.4 | 0.5 |
| | 309.31 | 0.3 |
| | 311.07 | 3 |
| Zinc | 202.55(v) | 2 |
| | 213.86(vn) | |
| | 239.71 | |
| Zirconium | 349.6 | 5 |

Notes

(1) It must be remembered that the useful range of an emission spectrograph is dependent on the emission line used and on the source and even plasma sources do vary with design. Choice of line is determined not only by the range required but also by the other elements present in the sample (because of interference effects) and other elements the instrument may be required to analyse (space available in the instrument in which to mount the exit slits).

(2) Boron limits of detection can be degraded due to high blank values due to contact with borosilicate prior to analysis.

(3) Carbon limits of detection can be degraded by the presence of methane in the argon.

(4) The two values quoted for the limit of detection are for the same analytical line but different makes of source unit.

(5) If nitrogen is to be analysed great care must be taken to keep air out of the sample and the source unit.

(v) These lines require an evacuated spectrometer.

(vn) These lines require either an evacuated spectrometer or one purged with nitrogen.

Table 6

## Extraction of Elements by Some Organic Reagents

| Metals tested | Chloride soluble in acid diethyl ether | Extracted by 8-Quinolinol into Chloroform | 8-Quinolinolate insoluble in chloroform or water, or otherwise precipitated | Extracted by Dithizone into Chloroform | Extracted by Diethyldithio-carbonate into Chloroform | Unextracted from Water at all pH |
|---|---|---|---|---|---|---|
| Li | 1 | | | | | 2 |
| Na | | | | | | 1 |
| K | | | | | | 1 |
| Rb | | | | | | 1 |
| Cs | | | | | | 1 |
| Be | 2 | 1 | | | | |
| Mg | 2 | | 1 | | | |
| Ca | 2 | | 1 | | | |
| Sr | 2 | | 1 | | | |
| Ba | 2 | | 1 | | | |
| B | 2 | 1 | 1 | | | |
| Al | 1 | 1 | | | | |
| Sc | 1 | 1 | | | | |
| Y | | 1 | | | | |
| La-Lu | | 1 | | | | |
| Th | | 1 | | | | |
| U | | 1 | | | | |
| Ti | | 1 | | | | |
| Zr | 2 | 1 | | | | |
| Hf | 2 | 1 | | | | |
| V | 2 | 1 | | 1 | 1 | |
| Nb | | 1 | | | | |
| Ta | | 1 | | | | |
| Cr | 2 | 1 | | 1 | | |
| Mo | 2 | 1 | | | | |
| W | | 1 | | | | |
| Ma | 2 | 1 | | 1 | 1 | |
| Fe | 1 | 1 | | 1 | 1 | |
| Ru | | 1 | | 1 | | |
| Os | | 2 | | 1 | | |
| Co | 2 | 1 | | 1 | 1 | |
| Rh | 1 | | | 1 | | |
| Ir | | | | 1 | | |
| Ni | 2 | 1 | | 1 | 1 | |
| Pd | 1 | | | 1 | 1 | |
| Pt | 1 | | | 1 | 1 | |
| Cu | 2 | 1 | | 1 | 1 | |
| Ag | 2 | 1 | | 1 | 1 | |
| Au | 1 | | | 1 | | |
| Zn | 2 | 1 | | 1 | 1 | |
| Cd | | 2 | | 1 | | |
| Hg | 2 | 2 | | 1 | 1 | |
| Ga | 1 | 1 | | | | |
| In | 2 | 1 | | 2 | | |
| Tl | 1 | 1 | | 1 | | |
| Si | | | 1 | | | |
| Ge | 1 | | 1 | 2 | | |
| Sn | 1 | 1 | | 1 | 1 | |
| Pb | 2 | 1 | | 1 | 1 | |
| As | 1 | 1 | | 2 | | |
| Sb | 1 | 1 | | 2 | | |
| Bi | 1 | 1 | | 1 | 1 | |
| Se | 2 | | | | | 1 |
| Te | 1 | 1 | | | 1 | |

*Table 6 (continued)*

Key: 1. Almost completely extracted at some pH between 1 and 9 after several extractions

2. Traces are extracted at some pH between 1 and 9

Note:— Cupferron is also a good extracting reagent into chloroform but is not used in the method outlined in Table 4; some of its salts tend to explode in warm chloroform solution. If cupferron is necessary for a separation, ice must always be present in the extraction funnel, extracts must always be refrigerated or stored in an ice bath and should be back-extracted to decompose the cupferronate and recover the metals without delay. On no account should the chloroform extract be evaporated to recover the metals.

Table 7

## Typical Carrier Internal Standards suitable for the analysis of some waters and effluents(a)

| Determinand | Determinand Wavelength nm | Carrier-Internal Standard | Carrier Internal Standard Wavelength nm | Precipitant |
|---|---|---|---|---|
| Aluminium | 256.80 | Lanthanum(d) | 285.59 | Ammonium Hydroxide |
| Beryllium | 313.04 | Aluminium(b) | 305.01 | ” |
| Cerium | 401.24 | ” | ” | ” |
| Chromium | 283.56 | Lanthanum(d) | 285.59 | ” |
| Dysprosium | 400.05 | Aluminium(b) | 305.01 | ” |
| Erbium | 390.62 | ” | ” | ” |
| Europium | 397.20 | ” | ” | ” |
| Gadolinium | 336.22 | ” | ” | ” |
| Hafnium | 227.72 | ” (e) | ” | ” |
| Holmium | 345.60 | ” | ” | ” |
| Lanthanum | 398.85 | ” | ” | ” |
| Lutetium | 347.24 | ” | ” | ” |
|  | or 291.16 | ” | ” | ” |
| Molybdenum(c) | 317.03 | ” | ” | 8 Quinolinol |
| Neodymium | 430.35 | ” | ” | Ammonium Hydroxide |
|  | or 338.28 | ” | ” | ” |
| Nickel | 341.48 | ” | ” | 8 Quinolinol |
| Praseodymium | 422.52 | ” | ” | Ammonium Hydroxide |
| Samarium | 428.08 | ” | ” | ” |
| Scandium | 402.33 | ” | ” | ” |
| Silver | 328.07 | Bismuth | 279.87 | Hydrogen Sulphide at pH 1 |
| Terbium | 332.44 | Aluminium(b) | 305.01 | Ammonium Hydroxide |
| Tin | 242.95 | ” | ” | ” |
|  | or 317.51 | ” | ” | ” |
| Thulium | 313.12 | ” | ” | ” |
| Titanium | 337.28 | ” | ” | ” |
| Vanadium | 318.40 | ” | ” | 8 Quinolinol |
| Ytterbium | 328.95 | ” | ” | Ammonium Hydroxide |
| Yttrium | 324.23 | ” | ” | ” |
| Zirconium | 343.82 | ” | ” | ” |

Notes

(a) Normally 50mg of carrier element would be added as nitrate per one to five litres of sample. A check should be made that other elements present do not interfere with the analytical wavelength of either the standard or determinand, and whether it can be prevented from coprecipitating either by complexation or prior removal. For simple solid samples the precipitates are washed and dried. For plasma sources, the washed precipitate can be redissolved.

(b) Unless stated otherwise, if used as solid samples, washed precipitates must be ignited at over 1000°C, preferably at 1400°C.

(c) For molybdenum, ignition should be at 400°C, preferably in a closed but vented furnance to prevent volatilization of molybdenum as the trioxide.

(d) A small quantity (about 2ml) of hydrogen peroxide must be added prior to precipitation.

(e) Zirconium can be used as internal standard but usually contains hafnium. Hafnium -Zirconium ratios are occasionally determined this way using mandelic acid as precipitant.

## Address for Correspondence

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

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