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Analysis of Pure Materials – Some General Comments

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Some general observations are made on the part to be played by the analytical scientist in the field of pure materials research, his outlook, and his relationship with other research scientists. Some desirable characteristics of analytical techniques are listed; and, in the light of that list, an assessment is made of each of a selection of techniques available at present.

1. General Observations

This paper is concerned entirely with the determination of *impurities*; broadly, at levels below an upper limit of 100 parts per million by weight, down to levels of parts per thousand million or even less. It does not deal with major elements, but it should be understood that the accurate and precise determination of them is a highly important and difficult field in its own right.

The range of *materials* is wide. Individual materials will not be considered, except as examples in one or two cases, though it should be stressed that from the analytical point of view each material needs individual consideration.

The impurity elements to be determined can occasionally be specified by the "customer". More often however, it is a question of: "what impurities are present and how much of each?"; sometimes, "whereabouts in the material?"; and occasionally, "in what chemical form?". Clearly, the analytical scientist must collaborate closely with the colleague requiring the analysis, so that each can appreciate the other's problems with a view to saving time and expense.

Sampling is extremely important in this work. It is of little value to spend considerable time and effort in analysing a sample which later turns out to be unrepresentative. Equally, contamination of a sample must be avoided, and the containers must be carefully selected. (For example, an envelope sealed with gum moistened by saliva would be useless if sodium or chloride were to be determined on a sample so contained.) Again, it is desirable that full collaboration exists.

The methods available for determining minute quantities of elements are many, and they are discussed in the remaining part of this paper. The choice of method must be based on experience and judgement, and often, at very low impurity levels, it may be felt important to use more than one method for a particular impurity, to be quite sure of accuracy. Frequently, new methods of separation or determination must be developed, and, as it is rarely possible to analyse new materials without some investigation, in some cases long programmes may be necessary. So early discussion of new requirements is advisable.

2. Desirable Characteristics

What are the "desirable characteristics" of an analytical technique in this field of trace impurity determination? Perhaps the following may be suggested.

2.1. Sensitivity

This is clearly very important both in *absolute* terms (i.e. what is the smallest mass of a given element which can be determined by a given method under ideal conditions), and, even more important in practice, in *comparative* terms (i.e. in parts per million by weight or volume in a matrix). It is the latter which is more meaningful in a general consideration, and sensitivity will be discussed in this context.

2.2. Ability to Deal with Several Elements Simultaneously

Clearly, not only is this economical in time (and money), but may often be economical in sample weight, and this is sometimes very important. If a sample is heterogeneous, then it may well be important to have comparative measurements of several elements in the same piece.

2.3. Specificity

This simply means how sure one can be that the measurement being made really refers to the element one hopes is being determined.

2.4. Accuracy

A very important consideration meaning nearness to the true value – but to be considered for each specific case. For example, a major element might be required to an accuracy within 0.1% or even 0.01% of the true value, whereas for an impurity at the level of a part in a thousand million, a figure accurate to within a factor of two or three might be quite adequate.

2.5. Freedom from Contamination and Reagent Blanks during the Analysis

This is fairly obvious, although difficult enough to minimise and almost impossible to avoid completely.

2.6. Possibility of Overcoming Surface Contamination

It is extremely difficult to avoid surface contamination in sampling, and if some methods are available which minimise or overcome such surface contamination then clearly this is a desirable characteristic of such a method. Of course, the determination of such surface contamination may well be the purpose of the analysis. But such cases are not considered here – this review deals with samples where the composition of the bulk is important and the surface is not representative of the bulk.

3. A Selection of Techniques and a Consideration of their Characteristics

3.1. Absorption Spectroscopy

The technique of absorption of light in the ultraviolet, visible, and infrared regions is of long standing. Generally speaking, the methods are for individual elements, usually after separation from the matrix and formation of a complex with some organic reagent. Although the level of determination is usually at the level of a microgram or above, the possibility of concentration of a trace impurity from a large sample may make sensitivity quite high – in the range 0.1 to 1 ppm, but the limitation is often the reagent "blank". Infrared absorption is more widely used in organic group identification and measurement, with which this paper is not really concerned, but it is also extremely valuable in some gas analysis problems, although not usually with very high sensitivity.

3.2. Fluorescence Spectroscopy

This again is an individual element method of fairly recent general interest. The particular advantage seems to be a potential improvement in sensitivity over "straight" absorption spectroscopy, perhaps 10^{-7} g is a likely level, although there may be individual cases where even better sensitivity can be achieved. The use of the yellow fluorescence of hexavalent uranium in a *solid* phosphor of sodium fluoride is a classical example of a highly sensitive, highly specific method of determining as little as 10^{-9} g.

3.3. Emission Spectroscopy

This method has been of major importance in all nuclear energy work. Its advantages are that several elements may be determined simultaneously, in some cases directly on the sample material; then contamination is low – in this case only that from the electrode material is involved, and the method is rapid. Direct determination usually restricts sensitivity, but it is sometimes possible to differentiate between surface impurities and those in the body of the material. For reasonable accuracy by this direct method, analysed standards of materials similar to those being examined are desirable but not always readily obtained.

By the use of chemical concentration, it is possible to obtain much higher sensitivity and probably improved accuracy, but of course the reagent blank problem is introduced.

Location of impurities using laser probes is an important recent development in direct emission spectroscopy.

3.4. Fluorescent X-ray Spectroscopy

The use of secondary X-ray emission after excitation with either X-rays or electrons has developed enormously over the past 10 years. While sensitivity is not high with the more conventional commercial X-ray fluorescence equipment, there are advantages still in the ability to carry out non-destructive analysis on small samples for several elements; for some materials, such as beryllium, at the level of

10 to 100 ppm. Recently, our work on automation of the Philips instrument has allowed the emission from line and background for up to 5 to 7 elements to be counted successively over many hours, thus permitting the optimum use of time to obtain good statistics. The developments in scanning instruments have been most striking – our work on a cheap instrument using X-rays for excitation has provided equipment, at a cost of a few hundred pounds, which is capable of scanning over a few square centimetres with resolution of a square millimetre, and which is thus able to locate and identify at any rate some of the major elements in small inclusions. The much more costly electron probe microanalyser is a major development capable of resolving and identifying components in areas of a few square microns, and the instrument has become a metallurgical tool of prime importance. X-ray diffraction should perhaps be mentioned in its analytical aspect of identification of compounds.

3.5. Mass Spectrometry

3.5.1. Isotope Dilution

In combination with mass spectrometry, isotope dilution has proved, during the last few years, to be one of the most sensitive methods available (another being radioactivation); sensitivity down to 10^{-12} g or less is possible, and sensitivity down to 10^{-9} g has been obtained at Harwell for a number of elements, taking careful precautions and with specially clean laboratories. Single elements are generally determined, although recent work at Harwell indicates the possibility of groups of elements (e.g. rare earths) being tackled. Contamination and reagent blanks are difficulties, although in the latter case, as quantitative separations are not essential, it often proves possible to carry out adequate separations using readily purified reagents, e.g. distillable acids, ammonia, and solvents, recrystallisable organic reagents, and well-washed ion exchangers.

3.5.2. Vacuum Spark Mass Spectrometry

Although used by Dempster in the USA during the early atomic energy programmes, vacuum spark mass spectrometry has only come into prominence again with the commercial availability of instruments during the last few years. The potential advantages are great – speed of analysis, wide range of elements determined simultaneously, high sensitivity (0.01 to 0.001 ppm seems possible), direct examination of sample, and possibility of differentiation between surface and bulk sample are examples. There are some doubts about absolute accuracy, and although, at the highest sensitivity, factors of five or ten may still be tolerable, it seems that improvement of accuracy is the area where most work is still needed. It may well prove that one answer to this problem of accuracy is the use of separated stable isotopes in an isotope dilution manner. Certainly, this is an instrument whose potential cannot be ignored in an analytical department faced with problems of high purity materials.

3.6. Resonance Methods

Nuclear magnetic resonance hardly qualifies for consideration in the context of analysis for trace impurities, but it deserves a brief mention for its ability to identify the different forms in which, for example, protons might exist in a material. In this connexion, it has been useful for examining magnesium oxide specimens and detecting protons existing as OH, H_2O (chemisorbed), and H_2O (freely movable).

Electron spin resonance has been of value to radiation chemists but may also prove to be useful in a more general analytical fashion, by its ability to detect some elements quite sensitively and in some cases to differentiate between the chemical forms in which a particular element exists in a sample.

3.7. Vacuum Extraction and Fusion

Vacuum extraction has been used mainly for determination of hydrogen, while vacuum (or inert gas) fusion (i.e. where the sample is allowed to react with carbon at high temperature (2000° C) and low pressure) has been mainly used for determining oxygen content, although in certain cases hydrogen and possibly nitrogen can also be determined.

3.8. Gas Chromatography

This has been a major advance in sensitive gas analysis during recent years, and it has been used by staff at the Warren Springs laboratory, in analysis of gases evolved from samples of rocks, for example.

3.9. Electrochemical Methods

The development of high sensitivity polarographs (for example, square wave, pulse, and radiofrequency instruments) by Barker at Har-

A selection of methods available for analysis of high purity materials.

		Several elements simultaneously	Sensitivity	Specificity	Accuracy	Freedom from contamination reagent blanks, etc.	Possibility of overcoming surface contamination	Comments
Absorption spectroscopy		No	0.1 to 1 ppm	Reasonable	Good	Bad	Bad	
Fluorescence spectroscopy		No	0.1 ppm	Reasonable	Fairly good	Bad	Bad	
Emission spectroscopy	Direct	Yes	1 ppm	Good	Needs stds.	Good	Good	
	After chem. concn.	Yes	0.1 ppm	Good	Reasonable	Bad	Bad	
Fluorescent X-ray spectroscopy		Yes	10 to 100 ppm	Good	Needs stds.	Good	Possible by precleaning	
Mass spectrometry	Isotope diln.	Limited	Very high	Good	Reasonable	Bad	Bad	
	Vac. spark	Yes	0.01 ppm	Good	Needs stds.	Good	Good	
Resonance spectroscopy	Nuclear magnetic	No	Poor					For chemical form
	Electron spin	Possibly	Fair					For chemical form
Vacuum-fusion (extraction)		Oxygen, hydrogen, and nitrogen	1 ppm	Reasonable	Reasonable	Good	Bad	
Gas chromatography		Yes	1 ppm	Good	Good	—	—	
Electrochemical methods		Fair	0.1 ppm	Reasonable	Good	Bad	Bad	
Radiotracers		No	High	Good	?	Good	Bad	Not direct determination but useful for transfer, etc.
Radioactivation		In some cases	Very high	Good	Good	Good	Good	

well and the cathode-ray and differential cathode-ray instruments by Davis and Seaborn at Woolwich has made methods available for certain elements at the 0.1 to 1 μg level. Coulometric equipment has also been of value in trace element work, particularly in the actinide field. Mention might be made of the potential application of high precision differential polarography to major element analysis, a rather neglected field.

3.10. Radioactive Tracers

This topic is not strictly relevant to the *determination* of impurities, rather is it that tracers provide a method for following the behaviour of some elements in a particular process. Since this is normally done by analysis, it is legitimate to consider the analytical implications.

An example can be quoted from the semiconductor field – in a study of the intake of impurities by pure germanium from a graphite boat during melting. The graphite boat was first irradiated making some of the impurities radioactive. After melting the germanium in the irradiated boat, each was taken into solution and the elements of interest separated by radiochemical methods. The fractionation of the elements could thus be followed.

This does not of course give the absolute amount of a particular element in either phase unless the graphite had been previously analysed – say, spectrographically – in which case very minute transfers become measurable absolutely. There is no doubt that the sensitivity of the technique is high, and much more consideration might be given to its use.

3.11. Radioactivation

This is one of the most sensitive methods available and has the additional great advantage of being free from the reagent blank problem. Sensitivity varies for each element, but with a neutron flux of 10^{12} n/cm^2 sec (available in BEPO) a wide range of elements can be determined at levels between a microgram and a picogram. As sensitivity for a given element is directly proportional to neutron flux available, increases in flux available in newer reactors are very important to analytical chemistry. While the majority of applications use reactor neutrons (usually thermal but sometimes fast), other sources of activating particles or radiations are growing in importance. Non-destructive analysis is sometimes possible for certain elements in favourable matrices, particularly utilising the multichannel analysers and semiconductor detectors now becoming available. Where it is possible, the use of radiochemical separations after irradiation of the sample usually gives somewhat improved sensitivity at the expense of time and effort. Irradiation of a sample followed by autoradiography may be of help in location of impurities in suitable materials.

3.12. Other Methods

It should be stressed that only a *selection* of methods has been considered, certainly there are others – an example is available in *biological* methods, where there is one technique possibly unrivalled for determining traces of molybdenum.

4. Conclusions

Of course, it is attempting the impossible to try to deal in generalities when it is only really possible to deal with specific cases. The summary table reads rather like a league table where the competitors play entirely different games. But, if some readers have caught a glimpse of the tremendous amount of interest there is to be found in analytical science, and if they have seen that it is a developing subject always ready to invent or adopt new principles and techniques for new problems, the purpose will have been served. In concluding, it should be stressed that *collaboration* is the key to many of the problems, both inside the analytical laboratory in choice of method, and outside it between the would-be customer and his analytical colleagues.

5. For Further Reading

5.1. Books Covering Several of the Techniques Discussed

1. "Methods in Geochemistry", edited by A. A. Smales and L. R. Wager (Interscience, 1960).
2. "Trace Analysis of Semiconductor Materials", edited by J. P. Cali (Pergamon Press, 1964).
3. "Handbook of Analytical Chemistry", edited by L. Meites (McGraw Hill, 1963).

5.2. Books or Review Articles on Individual Techniques

1. E. B. SANDELL, "Colorimetric Determination of Traces of Metals", 3rd Edition (Interscience, 1959). (Absorption and Fluorescence Spectroscopy)
2. N. H. NACHTRIEB, "Principles and Practice of Spectrochemical Analysis" (McGraw Hill, 1950).

3. L. S. BIRKS, "X-ray Spectrochemical Analysis" (Interscience, 1959).
4. "Advances in Mass Spectrometry", edited by R. M. Elliott (Pergamon, 1963).
5. C. P. SLICHTER, "Principles of Magnetic Resonance" (Harper & Row, 1964).
6. "The Determination of Gases in Metals", Iron & Steel Institute Special Report 68 (1960).
7. A. B. LITTLEWOOD, "Gas Chromatography" (Academic Press, 1962).
8. G. W. C. MILNER, "Principles and Applications of Polarography and Other Electroanalytical Processes" (Longmans, 1957).
9. H. J. M. BOWEN and D. GIBBONS, "Radioactivation Analysis" (Clarendon Press, 1963).