

list of errors it can be concluded that activation analysis is a complex analytical technique and that experience is required to obtain satisfactory results.

The complexity of the technique and the high costs of the irradiations and of the measuring equipment have apparently not prevented activation analysis from developing rapidly. Since the Symposium on Activation Analysis organized in 1959 by the International Atomic Energy Agency, the progress has been spectacular.

From perhaps 10 specialists in this field and few publications per year, the technique has now hundreds of users and the number of publications reaches several hundreds per year, as appears from the International Conferences on Modern Trends in Activation Analysis. Clearly not only the quantity of research has increased spectacularly over the last decade but also the quality and variety of the new applications has been striking. If in the beginning activation analysis was mainly used in the field of trace determination in high purity materials, applications are now widespread in the biological sciences, geochemistry, criminology, environmental sciences, etc.

Obviously activation analysis is not the answer to all analytical problems of trace analysis. It has to be judged on its own merit by comparison with the rich arsenal of all analytical techniques.

## CHAPTER 2

### GENERAL ASPECTS IN TRACE ANALYSIS

Trace analysis is today no longer a very specialized activity, restricted to particular problems, but constitutes an important part of the daily routine work of many analytical laboratories. Indeed, the qualities of several industrial materials, applied in the development of new branches in technology, are largely dependent on the impurities present in these products. An element with a purity of 99.9999%, means that  $10^{16}$  impurity atoms and  $10^{22}$  atoms of the main element are present in 1 cm<sup>3</sup> of this material yielding an impurity atom versus main element atom ratio of  $10^{-6}$ . In semiconductor applications however sometimes impurity to main element ratios of  $10^{-12}$  or  $10^{-13}$  are required. This implies that determinations down to or even below the ppb level are required in a wide variety of metals, nonmetals, reagents, etc. (1). The choice of the method will depend on the equipment present in the laboratory and on the training and personal preference of the analyst.

#### I Methods Suitable for Trace Analysis

Apart from the sensitivity, the methods should fulfil a number of additional requirements. During the analysis contamination must be avoided or kept as low as possible in order to obtain a low blank value. Analytical grade reagents contain impurities sometimes well above the ppm level, which can be disastrous in trace analysis. Together with the blank of the reagents, interference should be considered. Both constitute a signal to noise ratio problem, which can cause serious restrictions on the sensitivity of the method.

Good reproducibility is an essential condition for all analytical techniques. In the field of trace analysis however, a spread in the results is not always due to the method, but is often caused by the nonhomogeneous distribution of the element of interest in the matrix material.

The accuracy of an analytical method is completely dependent on the availability of standards. Whereas in higher concentration regions standards can be obtained commercially, in trace analysis however,

they are almost completely missing. So, the analyst has to look for techniques such as standard addition or comparison with another independent method.

The amount of sample needed also constitutes a determining factor in the choice of a technique. Although for the sake of homogeneity large samples are preferred, this is not always possible due to the small amount of sample available or to the high cost of the ultra pure sample.

Other conditions, which can determine the choice of an analytical technique, are high speed and reasonable cost.

In view of the considered requirements, the techniques generally applied in trace analysis are:

Activation analysis

Emission spectrometry

Flame emission, absorption or fluorescence photometry

Gas analysis

Mass spectrometry

Polarography and coulometry

Spectrophotometry

X-ray fluorescence spectrometry

None of these techniques presents a general answer to the large variety of problems involved in trace analysis. The method allowing the determination of the largest number of elements in the greatest variety of matrices will of course be the most powerful.

It is a very delicate task to compare the sensitivities of the different methods, because they are extremely dependent on the matrix material. In the literature, one practically always encounters a tendency of the author to overestimate the sensitivity of his favored technique. Furthermore, there exist about as many definitions of sensitivity and detection or determination limit as there exist analytical laboratories, which makes comparison all the more difficult.

Sensitivities can generally be enhanced by concentration of the element prior to analysis. However, one should bear in mind that the probability of contamination and interference becomes quite high, so that there is an optimum limit. The same rule is also true for the application of chemical separations. As previously stated, chemical reagents can contain impurities at the ppm level. Therefore it becomes very difficult to predict the recommended way for increasing sensitivities of trace analytical methods (2,3,4,5).

TABLE 2.1  
Survey of the quality of different trace analysis techniques

Technique	Several elements simultaneously	Sensitivity (ppm)	Specificity	Accuracy	Freedom from contamination and interferences	Possibility of overcoming surface contamination
Activation analysis	in several cases	0.001	good	good	good	good
Atomic absorption and flame spectro-photometry	no	0.01	good	good	bad	reasonable
Emission spectro-metry	yes	0.1	good	reasonable	reasonable	reasonable
Gas analysis (reducing fusion)	O, N, H <sub>2</sub>	1	reasonable	reasonable	reasonable	bad
Mass spectrometry	yes	0.01	good	needs stand.	good	good
spark source isotope dilution	no	0.001	good	reasonable	bad	bad
Polarography (cathode ray, pulse)	yes	0.01	reasonable	good	bad	reasonable
Spectrophotometry and fluorimetry	no	0.1-0.01	reasonable	good	bad	bad

An attempt has been made to summarize the advantages of different trace analysis techniques in Table 2.1 (6,7).

As for the reproducibility and the accuracy of some methods, a very interesting study has been made by Cook *et al.* (8). The authors submitted to analyses in nine laboratories all over the world a solution containing  $4.92 \pm 0.01 \mu\text{g/ml}$  Cu;  $16.5 \pm 0.1 \mu\text{g/ml}$  Cr;  $4.25 \pm 0.033 \mu\text{g/ml}$  Mn and  $15.2 \pm 0.01 \mu\text{g/ml}$  Hg. The applied techniques were emission spectrography, spectrophotometry, polarography and neutron activation analysis. The statistical analysis of the 511 results shows that the expected reproducibility of the techniques on a routine base are:  $\pm 40\%$  for spectrography,  $\pm 25\%$  for polarography,  $\pm 20\%$  for activation and  $\pm 10\%$  for spectrophotometry on the 0.05 probability level. The accuracy follows about the same pattern, but a wider spread of the results within a technique occurs. A summary of the results obtained by this study is given in Fig. 2.1.

## II. Properties of Neutron Activation Analysis

In order to allow neutron activation analysis, the first condition is that the element of interest gives by some nuclear reaction a radioactive isotope of adequate properties. Therefore the probability of the reaction (cross section), the isotopic abundance of the target nucleus, and the half life of the formed isotope should be large enough to allow measurement of the emitted radiation. The type and the energy of this radiation is also of interest, mainly in overcoming nuclear interferences induced by the matrix and other impurities. Although wide use is made of nuclear reactors, which are the neutron sources with the highest thermal flux (up to  $10^{15}$  neutrons  $\text{cm}^{-2}\text{s}^{-1}$ ), it has to be remarked that neutron generators, yielding 14 MeV neutrons at a flux of about  $10^9$  neutrons  $\text{cm}^{-2}\text{s}^{-1}$ , can be very satisfactory as a neutron source, mainly in industry. Moreover in high flux reactors an appreciable fast fission neutron flux is generally present, which can cause annoying interferences due to threshold reactions.

The sensitivity of the neutron activation analysis method has been described in several places (9,10,11,12) and can be considered to be about the ppb level for reactor irradiations and about the ppm level for irradiations with neutron generators.

When looking at the selectivity of the method, it shows striking

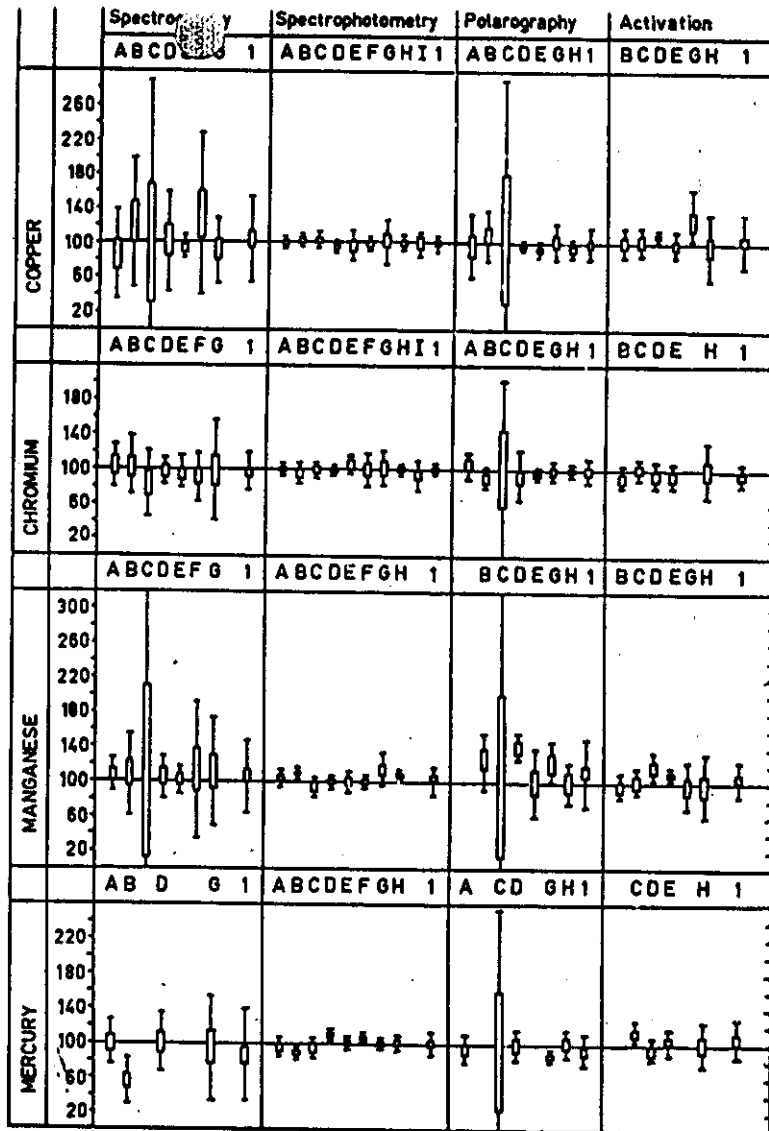


Fig. 2.1. Averages per laboratory and confidence limits at the 0.05 probability level for the given element and the specified technique. The continuous horizontal line is the true value, normalized to 100. The average of each plot is given by the horizontal line, the confidence limits of this average by the white vertical region, whereas the black vertical line represents the confidence limits of a single determination (they are not below zero). A, B, ... represent the different laboratories, 1 represents all laboratories combined) (8).

properties of certainty and versatility in the identification of the activated trace elements. Indeed, not only the half life and the type and energy of the produced isotopes can be measured in an unambiguous way, but also by changing irradiation and decay time before measurement, the ratio of the activity of the isotope of interest to the interfering activities can be enhanced. In fact even a change in the neutron spectrum can be used for minimizing interferences due to fast neutron induced reactions, which is practically performed by choosing an irradiation site in the reactor with a clean thermal flux. When the reaction of interest is a threshold reaction however, irradiations under cadmium in a hollow fuel element yield a practically pure fission neutron spectrum, which favors this type of reaction.

In most cases, surface contamination can be overcome, since the sample can be cleaned after irradiation (13). Although a number of analyses can be performed instrumentally, in trace analysis, chemical separations sometimes become unavoidable. However by application of the inverse isotope dilution method, separations do not constitute a problem. The addition of a carrier allows the separations to be performed on a large scale without the fear of contamination, and quantitative recovery is unimportant, since a yield determination can be achieved.

In the concentration region, where classical chemistry no longer allows quantitative separations of the element to be determined, activation analysis is completely satisfactory.

Several separation techniques however, (solvent extraction, ion exchange, distillation, . . .) can be performed at trace level concentrations and the activity of the element under consideration offers an excellent check on the progress of the separation.

Through its nuclear character, the neutron activation technique allows the analysis of a wide variety of elements in widely differing matrices, making it a powerful analytical tool, not only in trace analysis but also in determining alloy elements and minor constituents. Therefore the field of application of the method is very wide. It has been used to determine traces in ultra pure elements, in biological materials and minerals, in analysis where only small samples are available, in forensic analysis, in identification of industrial products by trace characterization, in industrial analysis of steel, in geochemistry for the determination of isotopic abundancies, etc.

Activation analysis can also be applied as an independent check on a

new classical trace analysis method, making sure no systematic error is affecting the technique.

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