CHAPTER 1

ACTIVATION ANALYSIS

Although neutron activation analysis was proposed by von Hevesy and Levi in 1936 followed in 1938 by charged particle activation analysis applied by Seaborg and coworkers, the method was considered as rather a curiosity until the mid-forties. With the development of nuclear reactors, making available neutron fluxes of the order of 10^{12} neutrons cm^{-2}s^{-1}, the possibilities of neutron activation analysis as a highly sensitive technique were rapidly recognized. This development was particularly welcome as high purity materials were attracting more and more attention as semiconductors. Although little agreement is found in the literature about sensitivities, no doubt can exist that for the moment few if any analytical techniques offer as high a sensitivity as activation analysis. The majority of the elements of the periodic system can be determined in the part per million (ppm) or even part per billion (ppb) range by thermal neutron activation at a flux of approximately 10^{12} neutrons cm^{-2}s^{-1}. Obviously higher neutron fluxes can theoretically be applied if necessary, as nuclear reactors with fluxes up to 10^{15} neutrons cm^{-2}s^{-1} are available, thus increasing the sensitivity by several orders of magnitude. It should however be kept in mind that the use of such high fluxes is quite limited, not only because of the very high cost of such irradiations, but also because of all the problems arising from the applied high neutron and gamma ray doses.

Besides the high sensitivity of thermal neutron activation analysis, this technique offers a number of other advantages such as the simplicity of the nuclear reaction, transparency of most materials to thermal neutrons and the isotropy of the neutron flux. In principle this means that in most cases only neutron capture reactions have to be considered and that consequently there is no change in the chemical nature of the irradiated elements. As neutrons have no electrical charge, their absorption in matter is relatively small and problems in this connection can be ignored or can easily be corrected. When irradiating in the core of a nuclear reactor the flux density can be considered as essentially isotropic so that flux gradient problems are also quite simple.

Unfortunately thermal neutron activation cannot solve a number of important trace analysis problems, as for instance those of the light elements, e.g. carbon, nitrogen and oxygen, which are also highly important in a number of scientific and technological fields. These problems can sometimes be solved by applying another type of activating particle, for instance photons or charged particles such as protons, deuterons, helions 3 or 4, etc. The former activation mode has a number of similarities with thermal neutrons. On principle the induced reaction is again quite simple and is often the inverse, namely a (γ, n) reaction. Moreover the absorption of photons in samples is also quite small so that this type of problem is also not a major one. New parameters are however considerably more difficult to take into account than in the case of thermal reactor irradiation. The photons are usually produced from high energy electrons in a linear electron accelerator (LINAC). Thus the photons obtained by the interaction with a conversion target give a quite complex Bremsstrahlung spectrum which is continuous and has a non-isotropic intensity and energy distribution. High sensitivities can be achieved for the above mentioned elements as well as for many others. Extremely intense photon fluxes can be produced from a modern LINAC, thus compensating for the relatively low cross sections.

If neutrons and photons essentially analyze the whole mass of the sample, this is not true for charged particle analysis, as these have a very short range. One would thus classify this type of activation analysis as being restricted to the sample surface or to a thin layer. New parameters have also to be taken into account as for instance particle energy and type of induced reaction. Target heating can obviously also be a major obstacle. However, excellent sensitivities can be expected and have indeed already been achieved in practice.

All the above required activation sources are obviously very expensive and can only be operated in relatively large specialized institutes or industries. The development of smaller, easily operated neutron sources would clearly be extremely useful in establishing activation analysis as a more widespread analytical tool. Two main approaches can be considered, namely isotopic sources and small accelerators. The first approach can only be applied for the determination of major or minor constituents, as high intensity isotopic neutron sources would be too

expensive. Indeed, as a general rule a one curie source yields a neutron flux at the sample of only 10^5 neutrons $cm^{-2}s^{-1}$. In the future, californium sources will perhaps achieve a wider use, as they yield approximately 10^9 fission neutrons $mg^{-1}s^{-1}$. For the time being, the second approach is by far the most promising and actually applied solution. By accelerating deuterons to approximately 150 kV and bombarding a tritium target, the (d, T)-reaction can yield 10^{11} neutrons $mA^{-1}s^{-1}$ thus allowing many activations with reasonably good sensitivity. The situation with this type of activation is also rather more complex than in the case of thermal neutron activation. The neutrons from the (d, T)-reaction are essentially monoenergetic 14 MeV neutrons. Thus the (n, γ)-reactions become of minor importance and (n, 2n), (n, p) and (n, α) reactions are dominant, giving rise to more complex activities. Thermalization is of course also possible, but not to the extent where a "pure" thermal flux can be realized at a still reasonably high intensity. The (d, T)-reaction being isotropic, means also that a neutron generator can be considered as a disk source (foil of titanium tritide on copper or silver). Thus neutron gradients are extremely important and not easy to control. Besides, high fluxes are only available in the immediate vicinity of the target. The number of neutron generators in research institutes is already important now and can be expected to develop rapidly, also in industry.

If the major advantage of all types of activation analysis is high sensitivity, the absence of reagent blank problems is also highly important. A number of other analytical techniques are indeed sometimes competitive with activation analysis for some elements as far as sensitivity is concerned. Usually however they require some chemical treatment before the analysis, whereas in activation analysis the chemical treatment, if required, is only after irradiation and often after removal of surface contamination.

One further advantage of neutron activation analysis is in many cases the selectivity or even specificity of its nature. Firstly it should be remembered that the activation is a reaction of the nucleus, and thus independent of the chemical state of the considered element. Further, the relatively simple nature of the nuclear reaction allows to establish with great certainty the isotope or isotopes which gave rise to the measured species. Besides chemical criteria, nuclear ones can further increase the certainty of identification, as for instance half-life measurements, type of disintegration and energy measurement of the emitted radiation. Gamma-ray spectrometry appears to be a powerful tool in this respect. By applying gamma scintillation spectrometry to activation analysis, it becomes possible to analyze simultaneously a number of different elements. In cases for instance where the matrix is not activated or only weakly activated or has a short half-life, nondestructive analysis can be applied. With the use of germanium lithium drifted detectors, gamma spectrometry has developed in a spectacular way. These detectors have a resolving power which is more than an order of magnitude better than the NaI(Tl) scintillators. Thus chemical separations can be limited to the removal of high intensity high energy gamma emitters and a simultaneous determination of a large number of isotopes is possible.

If the high resolving power of Ge(Li) detectors can considerably reduce the number of chemical separations, the interpretation of the spectra causes new problems. In the case of NaI(Tl) detectors, sufficient information can indeed be obtained in 200 to 400 channels, whereas for their Ge(Li) counterpart 2000 to 4000 channels are obviously required. Interpretation of this large amount of numerical data thus becomes hopelessly long and can only be avoided with an adequate computer facility. If this is available the most logical step is to automate the analysis as far as possible, i.e. by providing a program for optimum sample size and for optimum irradiation, decay and measuring time. A program for qualitative and quantitative analysis of the spectra and computation of the final results from a standard library is of course also possible. The task of calculating the precision, the detection limit of undetected elements, etc. is obviously also greatly shortened by adequate computer programs.

Precision and accuracy are evidently factors of high importance in activation analysis as in any other analytical method. This problem has apparently been somewhat neglected in activation analysis. This is understandable to a certain extent as activation analysis is concerned in the majority of cases with trace determinations where the knowledge of the order of magnitude of the impurity is often sufficient. Lack of standards in trace analysis has also led to uncertainties as far as accuracy is concerned, i.e. the absolute error in a determination. Standard materials at the ppm and even at the ppb level are therefore highly desirable and will make intercomparison of the results more easy. The precision, i.e. the reproducibility of an analysis, is often not clear from a statistical treatment of the results. At the trace level, the distribution of many elements can be highly irregular, so that the standard deviation on a number of analyses gives a picture of the homogeneity of the material rather than of the precision of the analysis itself. The above factors have unfortunately led some analysts to believe that activation analysis is inherently incapable of yielding precise results. A careful statistical treatment can however demonstrate that activation analysis can be as precise and even better than other analytical methods, if proper attention is paid to all the parameters determining the final result. In a number of cases activation analysis was used as eventual arbiter for other instrumental methods or for standardization purposes of more routinely applied techniques.

A superficial analysis of the results is perhaps also caused by the fact that activation analysis is an apparently simple technique. The procedure is often rightly summarized as follows: irradiate a sample and a standard under the same conditions; count both under the same conditions; the ratio of these rates will be equal to the ratio of the masses of the element of interest. One should however keep in mind that activation analysis is an instrumental method. Consequently the user should have received an adequate training in analytical chemistry, and should moreover have a sound knowledge of nuclear chemistry, of the measuring devices and instruments and of the irradiation sources. Apparently simple determinations can therefore be, in fact, quite complex. If one takes activation in a thermal reactor as an example, one should remember among many other parameters that the neutron energy varies from a thermal energy of 0.025 eV up to about 20 MeV. Consequently activation not only occurs with thermal neutrons, but also with epithermal and fast neutrons. Thus other reactions can and do occur apart from the simple radiative neutron capture. Besides the activation can vary from place to place in the reactor. The flux gradient may not be the same in standard or sample or even over the entire sample itself. Unsuspected reactions may influence the results such as "burn up" of the reaction product, production of the isotope of interest by second order reactions or radioactive growth of a daughter isotope, etc. The measurements can also be complex and difficult: unreproducible geometry, absorption of radiation, instability of the instrumentation, nonlinearity in detector response, etc. If chemistry is used one should not forget that the Szillard–Chalmers effect can have occurred, that isotopic exchange between carrier and isotope is not always simple, etc. From this short 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^3 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,