RADIATION AS AN AID TO ANALYSIS

Radiochemical methods of analysis possess some special advantages, such as rapidity and great sensitivity, and can on occasion provide results which would not be attainable by other means. They are finding an increasing number and variety of applications not only in pure research, but in medicine and health, in many industries such as mining, textiles, metallurgy and the oil industry, and in some other fields such as archaeology and criminology.

Professor G. de Hevesy, whose historical article on this subject appears elsewhere in this issue, reminds us that "the first application of radioactivity in analytical chemistry is as old as the discovery of radioactivity". The technique, however, is constantly developing as new requirements stimulate the development of new methods, and as new forms of equipment - the nuclear reactor, the particle accelerator, the electronic computer - open up wider possibilities.

These matters were discussed at an IAEA symposium at Salzburg, 19 - 23 October 1964, in which 278 participants joined, from 28 countries and five international organizations.

Most of the emphasis at the conference was on radioactivation analysis, which occupied six out of the nine sessions. Under this method, the material to be studied is exposed to neutrons or charged particles, or electromagnetic radiation such as X-rays. This causes nuclear transformations in the material, followed by radioactive decay. Each element forms nuclides which emit radiation of characteristic energy and half-life, by which the element can be identified and measured. Sessions were devoted to various applications, using as the source of radiation nuclear reactors, accelerators, and radioisotope sources ; experimental techniques and the application of computers to activation analysis were also considered. Two sessions were devoted to the use of radioactive tracers in analysis, and one to the use of radioactive sources for elementary analysis by observing how radiation is absorbed and scattered, or how, when a sample is exposed to radiation, it emits secondary radiation.

In opening the symposium, the IAEA Deputy Director-General (Research and Isotopes), Dr. H. Seligman, noted that the major part of the proceedings would be devoted to activation analysis - the most widely used of the radioactive techniques in analysis. The advance of this subject in recent years, he said, had been linked with technological advances in other fields, notably multi-channel analysers, small accelerators and computors. "Although activation analysis plays a leading role in isotope methods of analysis, it is by no means the only technique with advantages to offer," he said. "There is a considerable variety of ideas applied to a wide variety of samples. Several of these papers describe techniques which have potential use as continuous methods of analysis - a possibility that is increasingly demanded by industry today."

In an introductory survey, W.W. Meinke (USA) stressed that radiochemical analysis is by no means novel - even activation analysis had its inception almost 30 years ago in the laboratories of Professor Hevesy. In such a mature field, it is no longer sufficient to develop or improve techniques for their own sakes. The present-day analyst is confronted with an ever-increasing number of methods and techniques based on physical, chemical and biological principles ; to be adopted, one particular method must compete favourably with all other methods in the arsenal of the analyst. Activation analysis is now fashionable and it is without doubt an interesting and very important field, but it does in general require rather elaborate and expensive equipment, Mr. Meinke pointed out. In contrast tracer methods are being neglected, although often a new tracer method may be developed for a much smaller investment than is required for activation analysis.

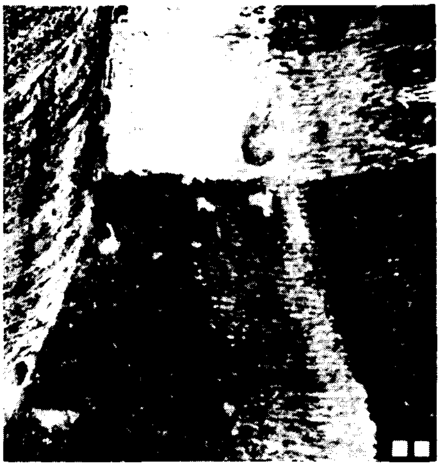
PORTABLE FIELD EQUIPMENT

Even activation analysis was felt by some of the participants to be used less widely than it should be, because it has customarily been done by means of an expensive nuclear reactor or accelerator, with somewhat costly supplementary equipment. There has been a recent tendency to use small accelerators, which do not give quite such good results as the large equipment but still perform satisfactory work. In the United States an accelerator with its equipment can be installed for about $50 000 and some industrial firms have found this to be a worth-while investment. The outstanding advantage is the speed of the method, as, for example, in oxygen determinations. These have become increasingly important in the last few years as the demand has grown for materials of high purity for nuclear, space, and other special uses. Metals frequently are oxidised to some slight extent right through, and rather tedious methods have been employed to determine this. Activation analysis, however, had made possible determinations at the rate of about one per minute, instead of one hour, and the method is accurate and sensitive.

At the symposium considerable interest was displayed in the development of simple portable equipment – radioisotope sources being used to produce neutrons or X-rays. Although such equipment lacks the precision of the larger installations, it can prove extremely useful for work in the field, as, for instance, in the determination of the metal content of ore *in situ.*

Radiochemical techniques, however, are by no means solely of economic interest. J.P.W. Houtman and J. Turkstra (Netherlands) described how a scientific approach to art objects is becoming popular. Non-destructive investigation is especially interesting, but methods which need only very small samples taken from the object can be useful as well. Since the Middle Ages, white lead has been used in paintings as primer and as a white pigment. Methods of purifying white lead have changed appreciably during the centuries, and therefore the impurities contained in the white lead may provide an indication of the age of the paintings in which it is used.

Neutron activation analysis carried out with a few samples from 1800 and 1875 and present-day paints, shows that the concentrations of all elements are different in the modern and old white lead samples. Twenty-five samples from authentic old paintings made between 1510 and 1909 were analysed, and 18 samples of known date from pigment and paint factories. Up to about



■ Neutron activation analysis makes it possible to differentiate between the materials of different ancient quarries. This Hellenistic tomb monument at Bellevi (Turkey) was built into a marble hill which was quarried out to form a mausoleum (Photos : L. RYBACH and H.U. NISSEN)

■■ Very regular linear carvings (Iscihissar, Turkey) show the careful hand-quarrying of marble blocks in ancient Greece.

1850 the content of copper, silver, mercury and manganese was found to be relatively high and constant, but after that date these dropped to about one tenth of the original value. On the other hand, contained zinc and insoluble antimony were low before 1940 and have since increased sharply.

Neutron activation has also been used to find the origin of marble used in statuary and buildings of ancient Greece. L. Rybach and H.U. Nissen (Switzerland) said that white marble, although a particularly pure rock chemically, can vary in a number of its visible properties. From a large number of thin sections of pure marble from Greece and Anatolia, it was found that the specimens from a majority of localities could not easily be uniquely differentiated. The method chosen was that of measuring the variations of trace element contents in the carbonate crystals composing the marble. Small samples of the marble were exposed to neutron activation in order to determine the sodium present, and it was found that the manganese content could be determined simultaneously. By this means it was possible to to establish characteristics for marbles from a number of ancient quarries. In some instances there is overlapping - e.g., in samples from Samos and from Priene, which have a geological connection - but there was a clear differentiation between many places of origin.

IDENTIFYING A HAIR

Identification of human hair may be important in criminology. F.W. Lima, H. Shibata and L.T. Atalla (Brazil) pointed out that criminal investigation is frequently faced with problems where the fundamental trace is the presence of hair in the hands of the victim, or in the instrument of the crime, or in the surroundings where the crime took place. In some cases that trace is reduced to only a single hair. Identification of hair with an individual by classical means is not always reliable, and hairs from the same person's scalp are similar to each other but not identical in respect of characteristics such as size, shape, degree of pigmentation or length. Mere similarity is not enough, as another person may have hair similar to that examined. However, a definite improvement in identification can be achieved by using activation analysis to determine inorganic elements present in the hair. By establishing the copper, bromide, zinc and sodium content of a single hair it is feasible to detect the person from whom it originated. The possibility of encountering two persons with similar compositions of these elements in hair is about one in 15 000, but by comparing ten of a possible thirty elements present in the hair, it is possible to identify the hair of one person out of 15 000 million.

An analytical method of determining the boron content of steel was described by H. Spenke, T. Cless-Bernert and B. Karlik (Austria). Steel containing boron is coming into increasing use for the construction of nuclear reactors, and where good temperability is required. Chemical analysis of boron at low concentrations is tedious and slow, so that an activation method was developed; this is much quicker, more economical and also more accurate than normal chemical analysis. Under this method, steel samples are irradiated in a reactor; the boron contained in the steel absorbs neutrons with the result

Many Roman slaves, originally condemned to death, worked in these quarries at Iscihissar (the ancient Synada) near Afyoukarahissar, Turkey. Fine white marble was exported as far as Rome, and is still worked today.

that the steel becomes less radioactive, and the difference in radioactivity can be measured. Steel samples containing 0.1 per cent boron reach about 90 per cent of the activity attained by the standard boron-free steel sample. With samples containing as little as 0.008 per cent of boron, the difference of activity as compared with the boron-free sample can just be detected.

The prospect that some material from the surface of the moon will become available for analysis within the foreseeable future was cited as a prime motive for enhanced interest in analytical methods for use on meteorites, by D.E. Fisher and R.L. Currie (USA). They hope that by the activation method they described it will be possible to analyse something like a few hundreds milligrams of lunar material for seven or eight elements. Not only does this gather more information per milligram than may be available by wet chemical analysis, but the sample remains in existence for inter-laboratory comparisons and for future investigations. The authors described how the method had been applied to meteorites. A vast amount of information has been published concerning the abundance of the elements in meteorites, from major constituents down to those appearing only in trace amounts. Such information is important to theories of the origin and history of the solar system, but much of it has been unreliable, because some elements are recalcitrant to chemical analysis, and (in respect of trace elements) because of contamination from impurities in the chemical reagents in the laboratory. Activation analysis avoids both difficulties, and has the further advantages of being non-destructive and rapid.

ANALYSING SNAKE VENOM

Experiments aimed at tracing the migration and action mechanisms of snake venom were described by B. Moav, S. Gitter, Y. Welwart and S. Amiel (Israel). These venoms are complex mixtures of toxic agents containing considerable amounts of trace metals. Venoms of various snakes were examined and found to contain large concentrations of copper (in the range 0.1 per cent) and zinc (0.05 per cent). A systematic activation analysis study was carried out with the aim of using these trace metals as internal tracers, and studying the relation between the chemical nature, biological activity and trace metal content.

Methods of tracing oxygen by means of the stable isotope oxygen-18 were discussed. As the radioisotopes of oxygen have half-lives too short to enable them to be used as tracers, oxygen-18 is used to "label" substances of interest. Determination of oxygen-18 then becomes important in studying processes involving oxygen and in tracing oxygen in chemical and biological systems. D.C. Auman and H.J. Born (Federal Republic of Germany) pointed out that although oxygen-18 can be measured with high accuracy by mass spectrometry, this is a long and costly procedure. However, by irradiating the material with fast neutrons, fluorine-18 is produced and this provides a measure of the content of oxygen-18. The method was described as simple and non-destructive, though less accurate and sensitive than mass spectrometry. In the ensuing discussion, S. Amiel (Israel) questioned the use of fluorine-18; by using nitrogen-17, he said, a precise, simple and very rapid analysis could be made. Dr. Aumann replied that this method was not for trace impurities of oxygen but for determining the isotopic composition of oxygen, and extreme sensitivity was therefore not needed. S. Amiel and A. Nir (Israel) also presented a paper describing a method of using alpha particles, neutrons are emitted in proportion to the concentration of oxygen-18 in the sample.

The possibilities of using a neutron generator in place of the nuclear reactor in activation analysis of lubricating oils were discussed by D. Gibbons, W.J. McGabe and G. Olive (UK). The 14 MeV neutron generator is a useful source of activating particles ; although the neutron flux is relatively low, it is adequate for a range of analyses where extreme sensitivity is not of prime importance, and offers the advantages of relatively low cost and ease of operation. The two elements, barium and phosphorus, which are commonly added to oils, undergo convenient reactions with 14 MeV neutrons, and can be determined rapidly without involving chemical operations. Iron and chlorine can also be measured with the same method, for which, however, it is less sensitive. The authors concluded that neutron activation analysis of oil additives should be a relatively simple procedure with the possibility of rapid non-destructive analysis for several elements simultaneously.

CHECKING ATOMSPHERIC POLLUTION

Routine neutron activation analyses of many varied elements in rocks and minerals can be carried out easily and fairly cheaply with the help of computers, R. Coulomb and J.C. Schitz (France) said. The methods and computer programmes they described are helping to meet the need of geochemistry and geology, which require an ever-increasing number of quantitative determinations of elements in rocks, soil, water and plants. An advanced integrated automatic system and computer programme for neutron activation analysis was described by R.E. Wainerdi, F.E. Fite, D. Gibbons, W.W. Wilkins, P. Jimenez and D. Drew (USA). This is a high-speed system used to analyse samples whose minor variations in composition are of research interest - e.g., determination of cobalt and iron levels in blood serum. The system permits individual sample activation or the simultaneous activation of many samples. The cost of the system is about $170 000 working with IBM units costing about $100 000. With a counting time of 60 seconds per sample, data on 4040 samples can be collected per day.

In the sessions devoted to radioactive tracers, a variety of ingenious methods was described, applicable to many different purposes. S.C. Ellis and J.H. Barrett (UK) discussed a radiometric method for determining the quantity of gelatin size on a single yarn in textile manufacture. In many processes a small coating is applied to the yarn in order to make it less liable to shrink and more water-resistant. It is highly desirable to be able to measure the coating along the length of the yarn, which has not yet been easy to do because the coating is extremely thin. Moreover it was not desired to use radioactive materials until after yarn samples had been removed from the industrial plant. The method employed was therefore to measure the coating by means of a radioactive reagent – in this case, radioactive sulphur. Small quantities of copper were added to the gelatin, and afterwards the yarn was exposed to gas containing the radioactive sulphur. The sulphur combined with the copper in the gelatin, and the amount of radiation emitted was proportional to the amount of gelatin on the yarn. The method allows convenient measurement of average gelatin content as well as an examination of the lengthwise content with a degree of accuracy which would be extremely difficult to attain by any other method.

A method of measuring sulphur dioxide in the atmosphere was described by H.H. Ross and W.S. Lyon (USA). Pollution of the atmosphere is causing growing concern in many countries, and it has become important to make such measurements. The radio release technique employed in this case is sensitive, selective, and rapid, and would lend itself to self-contained automatic systems. The method consists of forcing air through a solution containing radioactive iodine. Sulphur in the air reacts with the solution, and elementary iodine is released. By measuring the radioactivity of the released iodine, it is possible to calculate the amount of sulphur which has been absorbed in the solution. Minute traces of sulphur, as in normal air, or relatively large amounts, as found near industrial outlets, can be readily measured by the same routine method. The judgment of a skilled operator is not required.

A different principle – that of measuring "backscatter" radiation – of particular interest in the manufacture of pharmaceutical products, was described by P. Schiller (Czechoslovakia). Under this method, beta radiation directed at the substance to be examined produces a "backscattering" of radiation bounced back towards the source, which can be accurately measured. Elements having a high atomic number* such as iodine or mercury produce more backscattered radiation than the light ones, so that variations in the composition of a product are revealed by variations in the backscatter measurement. This provides a rapid and effective means of checking ingredients on line. The time required to check a number of preparations for iodine content was reduced from 19 hours to about ten minutes. The possibilities of rapid analytical control are improved mainly in intermediate process control – because there is no long wait for determination results. The method is simple, and the analysed sample remains intact and useable, which may be commercially significant where relatively expensive materials are being processed.

ANALYSING ORES IN THE FIELD

The rapidity with which the composition of an ore can be determined on the spot is of great importance in mining, and T. Florkowski, B. Dziunikowski, A. Kosiara and M. Wasilewska (Poland) described how radioisotope sources emitting X-rays could be used to analyse iron, zinc and copper ores in the field, using simple portable apparatus. The X-rays excite characteristic

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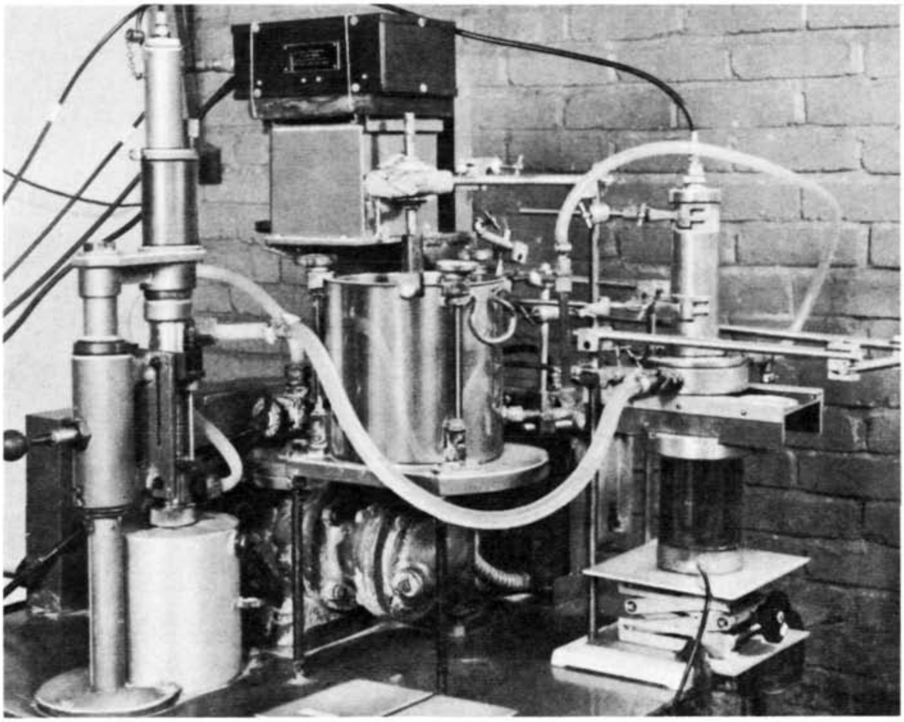
* *Atomic number is the number of protons in the nucleus of an atom. Each chemical element has its own atomic number and together the numbers form a complete series in order of increasing atomic weight.*



A prototype "On Stream" X-ray fluorescence analyser (Photo: Mineral and Technical Developments, Ltd.)

radiation in the sample, which is then analysed with counting equipment. Only two or three minutes are needed for each determination. The accuracy of the results is affected by the conditions to be found in mining, such as variations in moisture and irregular distribution of the element in the sample. Nevertheless the simple inexpensive prototype field instruments have proved very useful in exploiting ore deposits. Two other applications of X-ray fluorescence in tin mining, using radioisotope sources, were described by J.R. Rhodes, T.G. Ahier and I.S. Boyce (UK). One was continuous analysis of process streams, with emphasis on sensitivity, and the second was rapid assay of ore strata *in situ* with a portable analyser. Results for the first show that a considerable increase in sensitivity can be obtained over normal methods.

Conventional methods of X-ray fluorescence are particularly difficult to apply to the analysis of elements of high atomic number and P. Martinelli and P. Blanquet (France) discussed the possibility of measuring these elements by using gamma radiation emitted by radioisotope sources in place of X-rays. The major obstacle to such processes has been the inadequacy of electronic detecting and measuring equipment, but of late this has been improved and simplified. For certain problems of industrial control the method has marked advantages over traditional ones; radiation of very high intensity can be

Prospecting for Tin Ore with the Isotope Portable Analyser (Photo: Hilger and Watts, Ltd.)

obtained. It would allow of automatic sorting of low-grade ores of heavy metals, such as tungsten, gold, mercury, lead and bismuth.

Two methods for rapid determination of tungsten content in steel were submitted by L. Gorski and A. Lubecki (Poland). One uses X-ray fluorescence excited by a radioisotope source, which is particularly suited to concentrations of tungsten up to 11 per cent, and the second, based on backscattering of beta rays, is better for higher concentrations. Rapid tungsten determination in tool steel is most important economically, and by these methods it is possible to control the steel smelt in electric furnaces. Large savings can be achieved by avoiding the use of more tungsten than is called for in the specifications.