Analytical Chemistry in Atomic Energy

By L. E. Smythe*

The requirements for analytical chemistry in atomic energy are outlined and the impact of increasing instrumentation is discussed. Some recent developments in analytical chemistry instrumentation are reviewed and their possibilities and uses in the atomic energy field are assessed. These include automatic coulometry, square wave polarography, gamma spectrometry, low background beta counting, infra-red spectrometry, mass spectrometry, emission spectrography, X-ray spectrography and vacuum fusion analysis.

INTRODUCTION

The terms "analyst" and "chemical analysis" still conjure up visions of rather boring repetitive laboratory work in the minds of many scientists. This is indeed to be expected upon reflection of their contact with chemical analysis in various courses of instruction. The contact with "cookery book" conventional qualitative and quantitative chemical analysis is often quite enough to daunt any but perhaps a few apparently misguided individuals with a liking for precise and accurate measurements.

However, a new outlook on analytical chemistry closely associated with the renaissance of inorganic chemistry has developed overseas. Nyholm (1956) clearly links the great progress in inorganic chemistry with the development of atomic energy, and there is little doubt that this in turn has influenced the need for refined methods of chemical analysis. It is hoped that this paper will draw attention to some of the developments.

LITERATURE

Modern analytical chemistry, particularly as applied to atomic energy, covers an exceptionally large part of chemistry and draws on the resources of many important branches of science. While "conventional" methods of "beaker, burette and test-tube chemical analysis" are by no means discarded, many complex instruments and a mastery of basic theory are required to meet the multitude of challenging problems. The rapid growth of analytical chemistry may be gauged from surveys carried out in 1946 and 1955 and reported by Fischer (1956). In 1955, one in every fourteen papers abstracted by Chemical Abstracts dealt with analytical chemistry. This represented nearly 5,500 papers and compares with a ratio of one in 26 for 1946.

As in any scientific field, it is difficult to keep pace with the literature and, in analytical chemistry particularly, it is important that a rapid assessment of past work be made prior to commencing work on a problem. In the A.A.E.C. Research Establishment, the Analytical Chemistry Group uses a comprehensive punched card system as a key to work in this field. Often in the field of atomic energy it is found that no ready-made solution to an analytical chemistry problem is available in the literature. As a result, a proportion of research effort is required for the development of new methods of analysis. This may apply to as many as one-third of the problems, and consequently the boredom of routine and uninteresting work is seldom met in this field.

ANALYTICAL REQUIREMENTS

In atomic energy it is difficult to give examples of research projects in chemistry, chemical engineering, metallurgy, or of reactor control, where exacting chemical analysis is not required. Reactor fuel elements, moderators and structural materials, for example, can tolerate only extremely minute traces of impurities.

Determinations of the order of parts per 20,000,000 are quite common. The chemical analysis of multi-component fission product mixtures in the development and testing of fuel elements, or the determination of traces of fission products in biological materials, may involve analyses by remote control manipulation or concern the estimation of sub-microgram amounts.

The scope for developing new equipment and for automatic instrumentation is almost unlimited. In recent years it has been found possible to determine simultaneously several components of a radioactive mixture using a multichannel gamma ray spectrometer. With the availability of high flux reactors of the Australian Atomic Energy Commission's "Hifar" type the extreme sensitivity of radioactivation analysis reviewed by Jenkins (1956), merits attention. Additional instrumental techniques such as beta ray spectrometry, alpha pulse analysis, and the automatic recording of radioactive decay rates are now extensively used in chemical analysis in this field.

LABORATORIES

Rapid developments are also taking place in the design and construction of analytical chemistry laboratories in this field. In the early stages of the nuclear energy programme, fairly simple shielding or glove boxes provided adequate protection of personnel carrying out the chemical analysis of the alpha and beta active samples which comprised the majority of samples.

Current increases in the neutron flux of reactors with a consequently greater build-up of fission products and gamma activities has resulted in increasing analyses of samples with high gamma activity. Furthermore, there is

---

* Australian Atomic Energy Commission. Manuscript received March 14, 1958.

the present tendency towards processing spent fuels with short cooling periods in order to reduce inventories of fissionable materials.

The problem of analysis of fuel elements and similar materials thus concerns samples with high concentrations of fission products and correspondingly lower concentrations of uranium. Dilution of samples in order to reduce activity prior to analysis is now less feasible and the present situation tends to be one requiring complete shielding by four to eight inches of lead or two to three feet of concrete with analysis completely by remote control. Analyses of solutions with activities of one or two curies per ml. are becoming more common.

Many of the earlier (1945-1952) radiochemical laboratories, while suitable for alpha, beta and low gamma work, are not entirely suitable for high gamma cell work as pointed out by Spence (1956). High gamma analytical cells are often miniature laboratories in themselves, and what is required is not conventional benches and fume cupboards, but open floor space with adequate services where cells can be constructed. The design of modern radiochemical laboratories is detailed in many papers, of which those of Felds (1956) and Dykes (1956) are typical.

FACILITIES

The more important facilities required for chemical analysis in this field are as follows: spectrometry (emission, infra red, mass and X-ray); electrochemistry (polarography, coulometry, titrimetry); ultra violet and visible spectrophotometry; chromatography (including gas chromatography); radiochemical counting equipment (conventional, plus alpha, beta and gamma spectrometry, special low background beta counting equipment for strontium 90 analysis, etc.); gas analysis equipment (including vacuum fusion analysis of gases in metals) and instrumentation associated with techniques of solvent extraction and ion exchange.

Basic equipment for these facilities costs more than £100,000, assuming no demands by industrial atomic energy processing or fabrication. In the latter cases, requirements would be greater.

Some recent developments in analytical chemistry are outlined and their possibilities and uses in the field of atomic energy are now assessed.

RECENT DEVELOMENTS IN TECHNIQUES

Automatic coulometry

Coulometric analysis, reviewed recently by Smythe (1957), is now widely employed as a

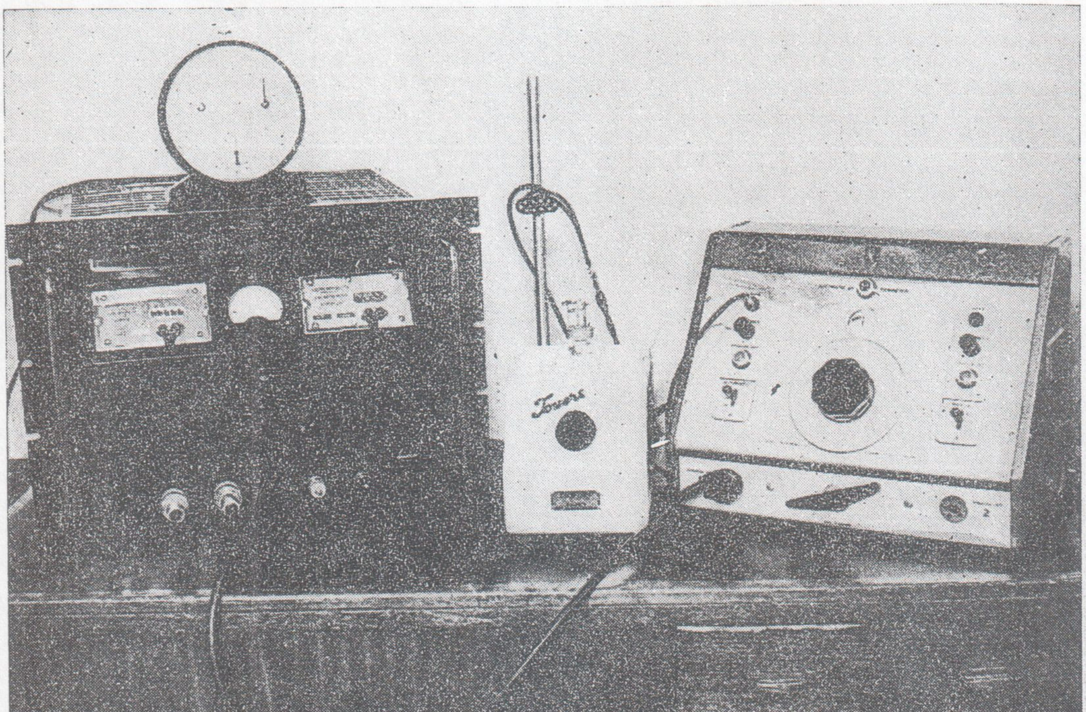

FIGURE 1:—Integrated current source for automatic coulometric titrations.

highly sensitive and accurate electroanalytical method. The large conversion factor from chemical equivalents to coulombs and the ease of measurement and interpretation of electrical and time-based phenomena, with which coulometry is concerned, have led to the development of highly accurate automatic coulometric analysis apparatus similar to that described by Smythe (1957).

In coulometric titrations with electrogenerated ferrous ions using an integrated current source and a 1mA current range, Smythe (1957) showed that the registration of 1.0 count on the counter was equivalent to the addition of 1.0 ml. of an N/17,000 ferrous solution. The counter could be read to ±0.01 count. In the analysis of radioactive solutions the control equipment may be set up some distance from the coulometric cell itself which is appropriately shielded. The whole titration is then carried out automatically by equipment similar to that shown in Figure 1.

Examples of such determinations are the coulometric titration of chloride and of chromium in homogeneous reactor solutions reported by Schults and Thomason (1955), the coulometric determination of plutonium in the 3γ to 10mg range by Carson et al. (1957), and the determination of cerium in the presence of uranium by Smythe (1957).

A versatile instrument for automatic controlled potential analysis and precision coulometric integration described by Booman (1957), controls electrolysis potential within 3mV with response to changes occurring in as short a time as 10 micro sec., for the range 10 μA to 100mA.

Controlled potential methods of analysis have not yet been used to the extent merited by their versatility and selectivity, but such equipment opens up a wide range of applications.

Basic equipment for automatic coulometric titrations costs approximately £200, while that for controlled potential coulometry, approximately £400.

Square wave polarography

Square wave polarography, conceived and developed by Barker (1952) and recently reviewed by Milner (1957), is a development of the alternating current polarography of Breyer and Gutmann (1950), and has played an important part in chemical analysis in U.K.A.E.A. laboratories.

In this method, a small alternating square wave voltage is superimposed on the usual slowly changing D.C. voltage and the amplitude of the resulting A.C. component of the cell current is measured shortly before each change in sign of the alternating voltage. A greatly increased sensitivity, particularly for reversible reductions, results and the square wave polarograph has found wide applications in the determination of trace amounts of substances in inorganic analysis. This is reviewed by Milner (1957).

The square wave polarograph designed and built at A.E.R.E. Harwell is now available commercially. Its sensitivity and accuracy are illustrated by the fact that reversibly reduced metallic ions in the range 10^{-4} to 10^{-7} M can be estimated with an accuracy of from 0.5 to 2.0 per cent. This polarograph is at least 200 times as sensitive as a conventional polarograph for reversible reductions, and the resolving power compares favourably with that of other alternating current methods. Milner (1957) gives some details of its applications. A square wave polarograph costs approximately £2,000.

Gamma spectrometry

The gamma ray scintillation spectrometer has found wide acceptance in the field of radiochemical analysis in the past four years. Connally (1953, 1956) reviews this method, which is both speedy and specific and suitable for the analysis of gamma-emitting radioisotopes. It is often possible to analyse up to 5-component mixtures without recourse to preliminary chemical separations and in the majority of cases the samples are recoverable in their original condition.

Qualitative analysis may be undertaken by carrying out a gamma scan with suitable equipment and locating the full energy peaks on the energy axis. If necessary, the location of a particular energy peak can be confirmed by following with the scan of a standard sample. When two or more energy peaks do not differ by sufficient magnitude to be resolved, or when a full energy peak is obscured by the Compton continuum of the more energetic gamma photons, preliminary chemical separations are necessary.

Quantitative radiochemical analysis by gamma spectrometry presents some difficulties when applied on a routine basis. The measurement and interpretation of peaks can be carried out by different methods, as described by Connally (1956) and McIsaac (1956). These are based on the fact that the net area under each photopeak is directly proportional to the abolute gamma emission rate of the corresponding isotope.

Gamma spectrometry can be undertaken with a variety of equipment, ranging from single crystal single channel analysers, double crystal anti-coincidence gamma spectrometers, as described by Pierson (1957), multi-peak analysers, or 20-, 100-, and 256-multi-channel analysers with provision for automatic analog readout. The choice of equipment requires some experience, but a great deal of work can be undertaken with a single crystal single channel spectrometer costing approximately £1,500.

The accuracy (standard deviation) of gamma spectrometry is approximately 5 per cent. with a precision ranging from 1 to 5 per cent., depending on the equipment used. The method is extremely sensitive and γ to microgram quantities of gamma emitters can be determined in a variety of samples as detailed by Iredale (1957).

Low background beta counting

Nuclear explosions produce strontium 90, together with other fission products, and there is considerable interest in accurate estimations of strontium 90 in soils, vegetation, animal and human bones and milk. The development of, and requirements for, low background beta counting illustrate well the type of analytical chemistry work which is now a feature of atomic energy.

In 1953, the first systematic sampling and analysis for strontium 90 was commenced in the U.S.A. under the direction of Libby, details being given by Martell (1956). Bryant (1956) gives details of British sampling which was begun in 1954, and in this case the analytical procedure is based on the separation of active strontium 90, with added carrier, as nitrate in strong nitric acid solution.

Three types of counting sets are in use in the U.K., but the most familiar is a three position anti-coincidence counter in which the background and two samples can be measured. The counts are usually recorded on a printing register. The counting tubes are either E.H.M.2 or special thin window G.M.4 tubes, with thirteen G.M.5 glass envelope guard tubes arranged to 180°. The assembly is shielded with 2 inches of lead. The normal background using the special G.M.4 tube is approximately 1 count per minute, with an efficiency for Y90 counting of about 25 per cent.

Current Canadian practice reported by Bovy (1954) and Atomic Energy of Canada Ltd. (1957) uses an ion-exchange separation which is said to be more rapid and efficient. The samples are also counted in an anti-coincidence low background counter with a background of 1-2 counts per minute, as described by Grummitt (1956).

A special low background beta counting laboratory is now available for a wide range of work at the Australian Atomic Energy Commission's Research Establishment. A counting set for low background beta work costs approximately £1,200. Two sets are desirable for routine measurements.

Infra red spectrometry

Infra red spectrometry has long found extensive applications in organic chemistry, but its inorganic analytical applications have, until recently, been fairly limited. The availability of relatively inexpensive infra red spectrometers using gratings, coupled with the use of the potassium bromide pressed disc technique, described by Kirkland (1955), has led to an increasing number of inorganic analytical applications.

Current uses of infra red spectrometry in chemical analysis in the atomic energy field include gas analysis; the analysis of ceramics and other inorganic materials, and the determination of the isotopic purity of heavy water, as described by Gaunt (1953, 1956). A fixed wavelength (2.95μ) infra red spectrometer using a Merton-N.P.L. grating, provides a rapid and accurate method for the estimation of the isotopic purity of heavy water at concentrations greater than 99.5 per cent. w/w of D_2O. The fundamental absorption band of HOD (O-H stretching vibration), which has a high extinction coefficient, is used.

A commercial continuous infra red heavy water monitor (Perkin Elmer "Trinon" Analyser) is also used in the chemical control of heavy water moderated reactors of the "Hifar" type. An infra red spectrometer of the Gaunt type costs approximately £1,000.

Mass spectrometry

Current work concerns the use of mass spectrometers for the analysis of gas mixtures in reactor control or in connection with irradiation studies; precise mass number measurement; the determination of isotopic abundance; and isotopic dilution analysis. Dibeler (1956) reviews the subject.

The A.A.E.C. Research Establishment facilities for mass spectrometry comprise the Metropolitan Vickers MS3 and MS5 mass spectrographs. The MS3 is used primarily for gas analysis associated with purity control of the "Hifar" reactor gas blanket. The MS5, which incorporates a vacuum lock, will be used in the high mass number range for precise mass number measurement, isotope abundance determinations and isotope dilution analysis.

Mass spectrometry can also be applied to the determination of absolute fission yields and neutron absorption cross sections. Details are given by Dibeler (1956). A mass spectrometer for gas analysis and low mass number work costs approximately £9,000, and one suitable for high mass work (with vacuum lock) approximately £20,000.

Emission spectrography

Facilities for the spectrographic analysis of both inactive and active samples are an essential in the field under review. While the steel and other large industries require the increasing use of almost fully automatic and instantaneous spectrographs, similar to that described by Hasler (1953), research and control in the atomic energy field tends to favour the more conventional and versatile "research" instruments.

One important requirement is for a sensitive and speedy qualitative examination of samples which can often provide useful information for subsequent "conventional" analytical methods. Quantitative spectrographic analysis, often providing accuracies of ± 5%, is extensively used in the examination of reactor fuel elements, structural materials and moderators.

While it is not a substitute for other instrumental methods, it finds wide application in this field because of its adaptability to the wide range of sample forms and of elements covered. The obvious advantages of sensitivity, speed, the detection of unexpected elements, and permanent records, enhance its usefulness.

With active samples, handling techniques are necessarily slow and difficult compared with those used for inactive samples. The vaporisation of part or all of an active sample in an arc may necessitate glove box techniques, efficient arc vapour extraction and filtration, or appropriate shielding facilities, depending on the type of activity. Basic equipment for emission spectrography costs approximately £9,000, but equipment may well require duplication for both inactive and active requirements.

X-ray spectrography

X-ray spectrography provides a valuable non-destructive method for obtaining analytical data. The method utilises the characteristic X-ray fluorescence which is related to the atomic nature of the constituent elements. It is particularly valuable for metallurgical analyses associated with the development of new fuel elements and reactor materials.

Multi-wavelength X-rays are focused on to the solid, powder or liquid sample, and the characteristic X-ray spectrum is emitted by the atoms of the elements present in the sample. These characteristic X-ray spectra are dispersed by analysing crystals of known spacings, scanned with a radiation detector (generally a Geiger tube of high quantum efficiency, but proportional or scintillation counter detectors are finding increasing use) and recorded automatically.

X-ray spectrography is an essentially rapid method of analysis, which becomes even more rapid as a library of typical spectra is built up. The accuracy ranges from approximately 0.5 to 1 per cent. in the range 1-100% of many elements; to 5 to 10 per cent. in the p.p.m. range. The sensitivity is such that in favourable cases one part of the element in ten million parts of the sample can be detected. Excellent reviews on the subject by Liebhafsky (1956) and others are available, and the applications, which may even extend to adaption to spot test techniques, as described by Pfeiffer (1954), are numerous. Basic equipment for X-ray spectrography costs approximately £5,000.

Vacuum fusion analysis of gases in metals and ceramics

A knowledge of the gas content of metals and ceramics is important in the atomic energy programme. The vacuum fusion technique has been the subject of considerable attention during the past six years, and it owes much to the work of Sloman and co-workers (1935, 1937, 1945) at the National Physical Laboratory some 20 years ago.

The present micro vacuum fusion method has been applied to the determination of the gas contents of boron, copper, chromium, silicon, steel, titanium, zirconium, thorium, tantalum, beryllium, and uranium, as well as to alloys, ceramics or cermets developed from these elements. Booth (1957) gives details of some of this work and states that it is also likely that determinations on molybdenum, vanadium, niobium and tungsten will be successful. The method is applicable to gas contents in the 0.0005 to 1 per cent. range with a precision of approximately 5-10%.

Complete equipment for vacuum fusion analysis is not available commercially, and the principal requirement is a 15kW induction heater, around which the apparatus is built. The approximate cost of a suitable apparatus for micro vacuum fusion is £3,500.

REFERENCES

Atomic Energy of Canada Ltd. (1957).—Report CRC-688. Unclassified.

BARKER, G. C., and JENKINS, I. (1952).—Analyst. 77: 685.

BOOMAN, G. L. (1957).—Anal. Chem. 29: 213.

BOOTH, E., et al. (1957).—Analyst. 82: 50.

BOVY, R., and DUYCHAERTS, G. (1954).—Anal. Chem. Act. 11: 134.

BREYER, B., and GUTMAN, F. (1950).—Aust. J. Sci. Research. 3: 558.

BRYANT, R. J., et al. (1956).—U.K.A.E.A. Report, AERE HP/R 2056.

CARSON, W. N., et al. (1957).—Anal. Chem. 29: 213.

CONNALLY, R. E., and LEBOEUF, M. B. (1953).—Anal. Chem. 25: 1095.

CONNALLY, R. E. (1956).—Anal. Chem. 28: 1847.

DIBELER, V. H. (1956).—Anal. Chem. 28: 610.

DYKES, F. W., et al. (1956).—Anal. Chem. 28: 1084.

FIELDS, P. R., and YOUNGQUIST, C. H. (1956).—Proc. Internat. Conf. on the Peaceful Uses of Atomic Energy, Geneva. 7: 44.

FISCHER, R. B. (1956).—Anal. Chem. 28: 9A (December).

GAUNT, J. (1953, 1956). — U.K.A.E.A. Report. A.E.R.E. C/R 1264 Unclassified; Spectrochim. Acta. 8: 57.

GRUMMITT, W. E., et al. (1956).—Canad. J. Chem. 34: 206.

HASLER, M. F. (1953).—Spectrochim. Acta. 6: 69.

IREDALE, P., and HUMPHREYS, D. L. (1957).—U.K.A.E.A. Report, A.E.R.E. EL/R 2326. Unclassified.

JENKINS, E. N., and SMALES, A. A. (1956).—Quart. Revs. 10. No. 1.

KIRKLAND, J. J. (1955).—Anal. Chem. 27: 1537.

LIEBHAFSKY, H. A., and WINSLOW, E. H. (1956).—Anal. Chem. 28: 587.

MARTELL, E. A. (1956).—U.S.A.E.C. Report. AECU-3262. Unclassified.

McISAAC, L. D. (1956).—U.S. Naval Radiological Defence Laboratory TR-72. Unclassified.

MILNER, G. W. C., and SLEE, L. J. (1957).—The Industrial Chemist. 33: 494.

NYHOLM, R. S. (1956).—The Times Science Review (Summer, 1956), p.3.

PFEIFFER, H. G., and ZEMANY, P. D. (1954).—Nature. 174: 397.

PIERSON, D. H., and IREDALE, P. (1957).—Br. J. Appl. Phys. 8: 422.

SCHULTS, W. D., and THOMASON, P. F. (1955).—U.S.A.E.C. Report ORNL-1846. Unclassified.

SLOMAN, H. A. (1935, 1937, 1945).—The Iron and Steel Inst., Lond., Special Report, No. 9, p. 71; Special Report No. 16, p.82; J. Inst. Metals. 71: 391.

SMYTHE, L. E. (1957a, 1957b).—The Industrial Chemist 33: 501; Analyst. 82: 228.

SPENCE, R. (1956).—Proc. Internat. Conf. on the Peaceful Uses of Atomic Energy, Geneva. 7: 39.