

MODERN TRENDS IN RADIOCHEMICAL ANALYTICAL METHODS

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ABSTRACT

Instrumentation for the analysis of mixtures of radionuclides by purely instrumental techniques has improved greatly in recent years both because of increased resolution of the detectors and increased sophistication of data processing equipment. As a result the role of chemical separation techniques is limited to those cases which the instrumental approach alone cannot solve. However, some outstanding applications for solvent extraction, extraction chromatography, and ion exchange chromatography are being made. Large numbers of radiochemical analyses can be performed both more precisely and more cheaply than in the past.

In describing recent trends in radiochemical analysis, it is not my intent to present an extensive review of the voluminous literature on the subject, since a very excellent recent review¹ already exists. I want to acknowledge at this point the very willing and able assistance of the authors of that review in assembling the material for this paper. Instead, I will try to present a picture of trends in radiochemical analysis as we see it practised in the laboratories where considerable numbers of such analyses are regularly performed.

The classical pattern for radiochemical analysis, firmly established in the early days of the development of nuclear energy, involved a series of chemical separations usually based on precipitation reactions, culminating finally in the separation of the nuclide sought (along with added carrier) as a 'pure' precipitate, which could be weighed for yield determination. The measurements were mostly 'gross' alpha, beta, or gamma activity measurements. Hopefully, the series of chemical separations gave sufficient 'decontamination' from other activities present that the gross activity of the separated nuclide, when corrected for yield and counting geometry, could be assumed to represent the amount of the nuclide contained in the original sample. It is a tribute to the capabilities of the radiochemists who developed the original methods for the fission products, that these methods were used with little change for perhaps fifteen years. To be sure this period did see a gradual introduction of solvent extraction and ion exchange separations in radiochemical analysis, but for the most part the methods saw little change.

The developments which have been responsible for the 'revolution' in radiochemical analysis have been those providing detectors capable of measur-

ing the energy of the emitted radiations and providing spectral analysers capable of making maximum use of these energy measurements.

These developments have been closely parallel to the development of electronic computers, obviously using many of the same techniques. Also the increasing complexity of the output from such analysers requires the assistance of electronic computers in its interpretation.

As a consequence of these developments, the character of radiochemical analysis has changed greatly in the last decade. The role of chemical separations has decreased, often to a relatively minor one. Only in the case of nuclides emitting beta radiation unaccompanied by significant gammas is it necessary to resort to the complete decontamination separations which characterized classical methods. In these cases, such as for the analysis of ^{89}Sr – ^{90}Sr , separations are still required since the spectrum of energies of beta particles does not in general permit their resolution into separate and distinct components, although even in this case some selectivity on the basis of energy can be attained.

I will cite as examples of several types of chemical separations which have been developed in recent years, some techniques used in separations of the radionuclides of the transplutonium elements. I have chosen these because they present particularly difficult separation problems, and also because our laboratory is involved in work involving these elements.

Of the transplutonium elements probably the measurement of ^{249}Bk (berkelium) presents one of the most difficult problems, since it decays with the emission of a beta particle accompanied by very little gamma radiation. Its separation is further complicated by the fact that for this element, as for all of the transuranium elements, no inactive isotopic carriers exist. Therefore, the procedures must not only attain a satisfactory decontamination from other radioactivities but must give a quantitative recovery. Since ^{249}Bk is produced by successive neutron captures on plutonium, it is usually encountered in mixtures with large quantities of fission products, since much more of the original plutonium undergoes fission than undergoes capture to yield the berkelium product. Of these the most troublesome are the high-fission-yield lanthanides. The +4 state of berkelium allows separation from the trivalent lanthanides, but cerium likewise has a +4 state and the chemistry of two elements is almost completely similar. Fortunately, it has been possible to find several properties in which the two elements do differ enough to effect a separation.

Illustrating the very effective and rapid separation that can often be effected by anion exchange chromatography is a technique² using a column 5×50 mm of Dowex 1-X4 mixed with lead dioxide. When samples containing mixed berkelium and cerium in 8 M HNO_3 are passed through the column, both elements are oxidized to the +4 state. When 8 M HNO_3 wash solution is passed through the column, berkelium is eluted in the first 5 ml (in 15–20 minutes) essentially free of cerium. The cerium can be recovered by elution with 0.5 M HNO_3 if desired. The procedure is highly advantageous in that the wanted berkelium is eluted first and the use of PbO_2 oxidant introduces very little excess oxidant.

A method based on extraction chromatography³ uses a column 5×70 mm packed with Teflon-6 powder coated with 0.5 M HDEHP (di(2-ethyl hexyl) orthophosphoric acid). When mixtures of berkelium and cerium (in the +3 state) are adsorbed on the column, the cerium is readily eluted in 5 ml of 0.15 M

HNO₃. The berkelium can then be recovered in a similar volume of 4 M HNO₃. The cerium contamination in the berkelium product is slightly higher (0.3% vs. 0.005%) than in the anion exchange method, and it has the further disadvantage that the wanted element is eluted last. However, the method illustrates the usefulness of extraction chromatography as a radiochemical separation. In fact, an almost identical procedure can be used to separate ²⁵²Cf from ²⁴⁴Cm.

Another technique⁴ for the separation of berkelium from cerium depends upon the extraction of cerium (+ 4 state) from 2 M HNO₃ with 0.2 M NaBrO₃ as the oxidant. Using a 30% solution of a long-chain amine nitrate, Aliquot-336-S-NO₃, in xylene as the extractant, cerium is strongly extracted while berkelium is extracted hardly at all despite its similarity to cerium in most chemical properties. This illustrates dramatically the high degree of selectivity in extraction procedures often shown by such long-chain aliphatic amines, sometimes referred to as liquid ion exchangers.

A cation exchange technique⁵ has also been used to separate berkelium from very highly radioactive solutions of fission products. By using very finely divided resin, effective separation from cerium and most other fission products except europium is accomplished. However, in order to obtain a reasonable flow rate, it is necessary to raise the temperature to 80°C and apply pressures up to 100 atmospheres. The sample is loaded onto a Dowex 50-X12 column, 2 × 600 mm, packed in a stainless steel tube. The elution takes place with 0.24 M α-hydroxy isobutyric acid, pH 4.2, and is monitored by following the gamma activity of ¹⁵²Eu–¹⁵⁴Eu which accompanies berkelium in the elution. The Bk–Eu fraction is finally subjected to a TTA extraction from 0.5 H₂SO₄ to separate the berkelium from the europium and other activities. While this sounds like a rather involved procedure, it is ideally suited to operation in a shielded glove box and the rapid flow rate obtained under high pressure minimizes radiation damage to the resin.

These methods demonstrate the importance of solvent extraction, extraction chromatography and both anion and cation exchange chromatography in present day radiochemical analysis.

Another case which frequently requires chemical separation is the removal of a major component (or components) from a mixture in order to permit the analysis of activities occurring at much lower levels. The interference of such major components may be due to their having activities of similar or identical energies to those sought, or if present at high enough levels, the Compton scattering process may obscure very low levels of activity in spite of the sophisticated instrumental techniques now available to minimize such effects.

A commonly encountered problem of this type in activation analysis of materials of biological origin is the very high level of sodium (²⁴Na) activity induced by neutron activation. The Compton background from the high energy gamma rays of ²⁴Na can completely obscure the activities of important trace elements, particularly those with lower gamma energies.

Girardi and Sabbioni⁶ have devised a very useful separation for overcoming the interference of sodium in such cases. They have found that when the sample solution (6 M to 12 M in HCl) is passed through a column of hydrated antimony pentoxide sodium ion is quantitatively retained with a capacity of 31 mg of sodium per gram of antimony oxide. Of other elements tested it was found that only tantalum was retained.

Another example of the separation of interfering activities is reported by Peterson, Tera, and Morrison⁷ who describe a rapid separation technique for a number of ions of interest in activation analysis using an ion exchange technique in an acetone-water hydrochloric acid system. They cite the coincidence of the peak of ¹⁰⁸Ag with the Compton peak of ²⁷Mg as an example of the need for such a separation.

A technique which has continued to receive considerable development in the past few years is that of substoichiometric isotopic dilution. This method is reported by Růžicka and coworkers⁸ to offer advantages of high sensitivity with relatively simple equipment. Recently reported work⁹ using automated equipment is reported to greatly facilitate the application of this technique to practical monitoring problems.

It is in the field of measurements of radioactivity that the developments having the greatest impact on radiochemical analysis have taken place. While probably the greatest attention has been given to the gamma measurements, there have likewise been improvements in beta activity measurements.

Liquid scintillation counting of beta emitters, especially low energy ones, such as ¹⁴C and ³H, has been a tremendous boon to the organic and biochemists using these activities for tracer applications. There has continued to be intensive study of new scintillation mixtures and of the problems of quenching and ways to correct for this effect. Commercial vendors have devised very sophisticated machines for counting huge numbers of samples automatically, a fact which certainly attests to the great usefulness of this technique, and the advanced state of its development.

However, a relatively new development, although certainly not a new phenomenon, in the measurement of beta emitters is the counting of Cerenkov radiation.^{10, 11} This method does not require an organic scintillator and is not subject to chemical quenching effects. However, since it has a threshold of 263 keV, it is consequently not useful at all for beta emitters of lower energy, although some lowering of the threshold can be accomplished by increasing the refractive index of the medium. The Cerenkov emission has directional properties and consequently shows considerable sensitivity to the volume and shape of the sample, as well as to the configuration of the detectors, especially at energies near the threshold. Although free from chemical quenching, it does show colour quenching, and since its emission peaks in the ultraviolet it may show quenching from materials absorbing in this region even though they may show no visible colour. However, for beta emitters with energies appreciably above the threshold the measurement by means of Cerenkov radiation using water as the medium is a sensitive, simple, and highly reproducible technique.

However, the greatest changes in radiochemical analysis in recent years have come in the field of analysis by purely instrumental techniques without chemical separation. These techniques not only offer the advantage of lower cost, but also offer the feature of essentially non-destructive analysis. The improvement of semi-conductor detectors in recent years as well as a concomitant improvement in electronic data processing equipment has led to a tremendous increase in the sophistication of instrumental techniques.

By far the greatest emphasis in purely instrumental radiochemical analysis is on the resolution of the components of gamma spectra. Efforts at resolution of gamma spectra in the early part of the past decade used primarily NaI(Tl)

detectors. The multichannel analysers of that period had a relatively few channels and resolution was accomplished mostly by integrating peaks or using standards and the subtractive mode of the analyser itself. The relatively poor resolution of the NaI(Tl) detectors led to a demand for multidimensional analysers to permit the three-dimensional display of coincidence peaks for nuclides having multiple gamma emissions. The large number of channels demanded by this technique has likewise proved to be desirable with Ge(Li) detectors, since the greatly improved resolution of the semiconductor detector has made the use of an analyser with a large number of channels imperative to resolve complex mixtures.

In order to illustrate the capabilities of the gamma spectrometers available today, I will describe briefly the salient features of some of the systems that have been assembled and some aspects of the treatment of the data acquired by such systems.

The resolution offered by the lithium-drifted germanium detector is obviously very much better than that of the thallium activated sodium iodide scintillator, typically ~ 2 keV at 1 MeV vs. $\sim 8\%$, and it is consequently obviously vastly superior for studying complex mixtures of gammas. However, as will be seen in the following descriptions, the NaI scintillator still has its uses. Up to the present time it has not been possible to make Ge(Li) detectors which approach in size and counting efficiency the NaI crystals which are available. Typical large Ge(Li) detectors may have volumes approaching 500 cc while volumes of large NaI detectors may be 5 litres or more. Thus for measurement of low levels of activity in fairly simple mixtures the NaI(Li) detector is still to be preferred. This is further aggravated by the fact that the small volumes of the Ge(Li) detectors also give much higher Compton scattering contributions from the higher energy components of the activity of the sample. While the ratio of the peak to the Compton background can be greatly increased by instrumental techniques, as we will point out, the NaI(Tl) spectrometer is still the method of choice for the study of low levels of activity.

That this is the case is amply illustrated by the fact that the system which was assembled at the Lunar Receiving Laboratory¹² at the Manned Spacecraft Centre at Houston, Texas, for the study of the radio-activities in the returned lunar samples used large NaI(Tl) detectors.

Because of the very low levels of some of the activities which were expected, the utmost precautions were taken in this system to reduce the background counting rate to the lowest possible level. Thus the counting equipment is located in an underground chamber, 15 metres below the surface, shielded by walls 0.9 metre thick composed of crushed dunite and supplied with radon-free air. All the interior materials were selected for low radioactive contamination level. The detector system consists of two NaI(Tl) detectors at 180° orientation with respect to the sample. The dimensions of the cylindrical detectors are 23 cm in diameter by 13 cm in length coupled optically to a light pipe of pure NaI of the same diameter but 10 cm in length. The light pipe helps to attenuate gamma radiation originating in materials in the four photo-multiplier tubes used to detect the light pulses from each detector.

The principal detectors are surrounded by a cylindrical annulus of plastic scintillator 30 cm thick viewed by a bank of 22 photomultipliers. The output from these photomultipliers is connected in anticoincidence with the NaI(Tl)

detectors both to help suppress background events and to improve the peak-to-total ratio by rejecting those counts in which a gamma transfers only part of its energy to the NaI(Tl) and emits a degraded photon which can be captured in the plastic scintillator. The background is further reduced by enclosing the whole assembly inside a lead shield 20 cm thick and weighing 24 metric tons.

The data acquisition system includes coincidence-anticoincidence logic circuits and dual analog-to-digital converters interfaced to a Digital Equipment Company PDP-9 computer with 16 384 words of 18-bit memory. The programmes for the PDP-9 provide for the simultaneous acquisition of singles data from each detector in 255 channels each, a sum-coincidence spectrum in 255 channels, and finally a gamma-gamma coincidence spectrum in a folded matrix of 127×127 channels, but requiring only 8192 storage locations. Some measure of the performance of such a system is seen in the background which for the interval of 0.1–2.0 MeV in the singles mode was 476 counts per minute without anticoincidence and 79 counts per minute with anticoincidence. This demonstrates the effectiveness of the anticoincidence shield in reducing the background of such a system.

In analysing the data from this system, four selected areas containing peaks for the nuclides to be measured are summed so that each sum can be treated as a single spectrum, and these as well as the singles spectra are analysed with a least squares technique on a Univac 1108 computer using a programme called Alpha M.¹³ This programme contains provisions for correcting for gain and threshold shifts of the detector-amplifier system.

For precise analysis of data from NaI(Tl) systems it is necessary to have a library of standard spectra for all of the nuclides measured with exactly the same geometrical relationships as the sample. With samples which are nearly weightless point sources such standard spectra are easily prepared by counting a suitable portion of the standard at a specified position. However, with samples of considerable volume and mass, such as the moon rocks, which it was desired to analyse entirely non-destructively, it was finally necessary to prepare replicas to approximate the size, shape, and density of the rocks themselves. Initial measurements were made using prepared standards of various weights, but for the utmost refinement in the analysis of the data, standards were prepared by filling aluminium foil shells shaped around the individual rock samples with a mixture of iron powder and polyurethane spheres of the same average density as the rock itself and containing a uniform dispersion of the radionuclide. Thus a library of standards was prepared for each of the lunar samples analysed. Fortunately, it is not necessary to go to such lengths in most radiochemical analyses.

When the library of standard spectra has been prepared, the Alpha-M programme evaluates the content of each of the radionuclides by a matrix inversion technique. It is beyond the scope of the present paper to report the results of the analysis of the moon rocks, but some results from a test mixture approximating one of the samples will provide a measure of the precision and accuracy which can be attained by such purely instrumental techniques even at these very low levels of activity.

While this is certainly a very specialized application, NaI(Tl) detectors still find considerable use in the analysis of fairly simple mixtures of radionuclides, and especially where the activity level is low. Reliable analysis is usually limited

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to about 10 to 12 components. As already pointed out, the computer programmes for the analysis of NaI(Tl) spectra require a library of standard spectra collected on the system in use under the conditions used for measuring the sample. Also, in order to obtain precise results, it is usually necessary to include standards for all the radionuclides present at measurable levels whether analysis for that particular nuclide is desired or not.

Table 1. Analysis of sample 17 test mixture by use of exact library (1035-minute counting interval).

<i>Nuclide</i>	<i>Added</i>	<i>Found*</i>	<i>Difference (%)</i>
K	2270 ppm	2220 ± 50	-2.2
Th	2.85 ppm	2.82 ± 0.07	-1.1
U	0.70 ppm	0.71 ± 0.03	+1.4
²² Na	101 dpm/kg	103 ± 6	+2.0
²⁶ Al	125 dpm/kg	126 ± 6	+0.8
⁴⁶ Sc	115 dpm/kg	118 ± 5	+2.6
⁵⁴ Mn	106 dpm/kg	111 ± 6	+4.7
⁵⁶ Co	101 dpm/kg	106 ± 8	+5.0

* Errors stated are those due to counting statistics only.

Systems for Ge(Li) spectroscopy can use either a single detector or elaborate anticoincidence systems to aid in improving the peak-to-background ratio. A simple small volume detector drifted from a single face will usually have a superior resolution, but because a relatively small proportion of gamma rays will be completely absorbed within the active region, the peak-to-Compton ratio for such a detector will be low. The resolution of such detectors makes them valuable tools for determining energies of gamma rays, but they are relatively less effective for quantitative analysis, particularly if it is desired to determine the weaker components of mixtures.

Ge(Li) spectra are also complicated by another phenomenon if high energy gammas are present; namely, that of escape peaks. At high energies, over 2.5 MeV, the cross section for pair production becomes quite high and the probability of the escape of one or both of the components of the annihilation radiation is also high; hence, the spectrum will contain single and double escape peaks as well as the full energy peaks.

Systems for Ge(Li) spectrometry can be quite complex if maximum flexibility and sensitivity are desired. Probably the optimum results¹⁴ for the improvement of the peak-to-Compton ratio uses a plastic scintillator shield constructed in the form of a cylindrical annulus similar to that already described for the NaI(Tl) system. The plastic scintillator has the advantage of being relatively inexpensive and it is possible to mould the plastic into a shape which will intercept the maximum number of secondary photons. For this purpose a strict proportionality of peak height to energy is not essential since the pulses from the plastic scintillator are used only for timing purposes in the anticoincidence circuits of the spectrometer. Also the plastic scintillator need not be encapsulated, and is quite resistant to damage by mechanical or thermal shock. Compton background suppressions of a factor of 10 have been reported for 662 keV gamma rays. A system using a large volume five-sided or coaxial detector will probably offer the best sensitivity for Ge(Li) spectra.

However, if it is desired to have a more flexible system, an anticoincidence shield has been described,¹⁵ which was constructed from a cylindrical annulus of NaI(Tl) 20 cm in diameter and 25 cm in length split longitudinally into two halves and canned with an optical separation. The Ge(Li) detector was inserted into the 7.5 cm diameter tunnel in the centre of the annulus. In taking data from the system, the analyser is divided into four quarters. The first receives the pulses from the detector not in coincidence with any from the annulus. The next two receive pulses in coincidence with 511 keV pulses (annihilation radiation) from one or the other of the two halves of the annulus. The fourth quarter receives pulses in coincidence with other events in the annulus. Thus, no pulses are discarded and the spectrum can be reconstituted in the manner which will give the optimum peak-to-background ratio for the particular gamma of interest. In the Compton suppression mode, a suppression of approximately 5 is reported for 662 keV. For high energy gammas it is more advantageous usually to operate the system as a pair spectrometer. If desired, the contents of all of the quarters can be added together to give a spectrum without any type of suppression.

The electronic equipment for use with Ge(Li) detectors must, as we have already pointed out, be capable of storing data in a large number of channels in order to be capable of making optimum use of their excellent energy resolution characteristics. Since the energy resolution of a good detector will be of the order of 2.8 keV full width at half maximum height and it is desirable to have 4 to 10 channels in the peak for adequate data processing capability, it is obvious that analysers of 1000 to 4000 channels are required to cover a reasonable part of the energy spectrum. The system described for NaI(Tl) spectroscopy used a small computer (PDP-9) for both data storage and initial processing. With suitable programming such a system would also be capable of taking and processing data from a Ge(Li) system as well. The use of a small computer as opposed to a hard-wired analyser has the advantage of offering maximum flexibility in the manipulation of data and offers the possibility of introducing new programmes to manipulate the data in new ways to fit changing situations. The computer can also be used for mathematical calculations, although a computer of this size is not sufficient to do a complete resolution of a Ge(Li) spectrum using one of the more sophisticated data reduction programmes. The computer system has the disadvantage that programmes must be provided for all data acquisition and handling operations. More recently, systems have been introduced which combine the best of the two systems. In a system recently delivered to our laboratory, a 4096-channel 24-bit hard-wired analyser is provided and this is coupled to a PDP-15 with 8192 words of 18-bit memory and magnetic tape auxiliary memory. The spectra are taken and stored in the analyser memory and then can be displayed and manipulated by means of the computer. This system offers a very full range of capabilities in scale expansion, integration of peaks, subtraction of background, etc., and it is anticipated that many analyses can be performed without recourse to a larger computer.

Because the spectra from the Ge(Li) detector have been developed more recently and are more complex than NaI(Tl) spectra, the resolution of these spectra on large computers has not reached the degree of standardization and refinement found in programmes for NaI(Tl) spectra. It is beyond the scope of this paper to describe any of the programmes for Ge(Li) spectra in any detail,

but I would like to point out some of the salient features in such programmes and how they differ from NaI(Tl) programmes.

Most such programmes start with a search of the data to identify peaks usually by finding the points at which the slope changes from positive to negative. Then these apparent peaks are subjected to a number of tests, for statistical significance, for resolution (width), asymmetry, and tailing to the right or left. Failure of these tests usually does not eliminate a peak from further analysis, but will be noted in the final printout as a warning that data from that peak should be regarded with scepticism.

The programme then goes to an identification and fitting routine. The situation here is very different from that for NaI(Tl) spectra where standard spectra actually measured on the system in use are required in the library. For the Ge(Li) situation a spectrum is run for some reference source such as ^{226}Ra to provide a precise energy calibration and also a series of counting efficiency curves at different geometries is supplied. The library does not contain standard spectra, but consists of a catalogue of radionuclides with their energies, intensities, and decay rates. Such a library is compiled by critical examination of literature values. To conserve space usually only the four principal gamma lines are considered, and even then the library may be very voluminous. For example, the library of a programme under development at this laboratory contains over 900 nuclides.

Before identification is made, the portions of the spectrum outside the peaks are fitted to a polynomial which is then considered to constitute the background and is subtracted from the spectrum.

Each peak is examined to see if it corresponds within a specified limit of error to a peak listed in the catalogue. If a correspondence is found, then the programme searches for other peaks for the radionuclide tentatively identified. From the presence or absence of these and their ratios to each other, a confidence factor for the identification of that nuclide is calculated.

If a peak is shown to be broader than would be expected for a single peak, or if peaks are incompletely resolved, the programme attempts to fit the data with a combination of modified gaussian curves. Inouye *et al.*¹⁶ have described a technique for using the Fourier transform to resolve overlapping peaks in Ge(Li) spectra, but this method does not appear to be widely used.

When all of the peaks (or those requested) have been examined, the computer then prints out the radionuclides tentatively identified, the quantity calculated based on the principal peaks, the confidence factor and any alternative identification if such exists. Also printed is the information with regard to the failure of the peaks to meet the established criteria. Using programmes of this type, very complex radionuclide mixtures can be analysed without recourse to any chemical separation whatsoever.

In summary, the trends that we see in the development of radiochemical analysis strongly emphasize the use of purely instrumental techniques. The increased resolution of solid-state detector systems, and the increasing capabilities and decreasing costs of small computers are leading to an ever increasing degree of sophistication in data acquisition and processing. The role of chemical separations has less emphasis, and is limited to verification of instrumental results and reducing interferences which are beyond the capabilities of purely instrumental methods. However, some of the newer chemical separation

techniques of solvent extraction, extraction chromatography, and ion exchange are finding effective use where needed in radiochemical analysis.

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