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SERIES IX

ANALYTICAL CHEMISTRY

VOLUME 3

Parts 1-3

Editor

CARL E. CROUTHAMEL

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RADIOCHEMICAL SEPARATIONS OF LOW-LEVEL RADIOACTIVITY*

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THE widespread use and occurrence of radioactivity and the increasing interest in less probable nuclear reactions have forced many nuclear and radiochemists to use low-level methods of isolating and detecting radioactivity. It is the purpose of this review to consider some of the general aspects of low-level radiochemical separations and discuss a few specific procedures. Since it is difficult in many cases to know from a paper's title, its abstract, or sometimes even from its text, whether a low-level method was used, the author makes no claim as to completeness of the literature surveyed in preparing this review. Furthermore, since many separation methods used at ordinary levels may be converted to low-level procedures with only minor alterations, there exist potentially an infinite number of low-level separation schemes. The references cited here should be taken to be only representative ones, and are, of course, those about which the author knows the most. No doubt many other low-level methods, published and unpublished, are extant, and the author would appreciate receiving information about them. Unfortunately, few papers discuss the details of the precautions taken to achieve high radiochemical purity and other characteristics of a low-level method.

The major use of low-level methods has been in (1) environmental studies of naturally occurring or artificial radioactivity[66], (2) research in cosmic-ray-induced radioactivity in meteorites[52] and atmospheric nuclei[74, 104], (3) determination of nuclear-reaction cross-sections in the submicrobarn region[28, 82], (4) studies of nuclear reactions in which the available beam intensities are very low (e.g. pion-induced reactions[118] or resonance fission[92]) although cross-sections are large, and (5) trace-element determination by activation analysis[90].

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Low-level radioactivity can be defined in terms of a signal-to-noise ratio (sample-to-background ratio) — for example, an activity for which this ratio is approximately one. For radiochemical purposes, however, this is not necessarily adequate. One of the important criteria for evaluating a low-level procedure is the blank, as will be discussed below. A blank of one count/min (c.p.m.) may be negligible in a counter system whose background is 25 c.p.m., but it is of very great importance when the background rate is of the order of 0·2 c.p.m., a typical rate in many beta counters in common use[50, 78, 107]. Thus in this discussion we shall be concerned with small absolute amounts of activity ($<$ 10 disintegrations/min (d.p.m.)) as well as signal/noise ratios of the order of unity.

The kinds of counters used and the ingenious methods devised to reduce background are outside the scope of this chapter. A number of specific* and review[7, 33, 59] articles have appeared on the subject in the past few years.

Generally speaking, low-level radiochemistry shows some strong resemblances to trace-element determination by colorimetry[98]. Many of the injunctions applicable to the latter area have counterparts in low-level radiochemistry.

For a low-level procedure to be a good one, the following specific requirements must be met:

(1) zero or small and constant blank,
(2) high chemical yield,
(3) high radiochemical purity, and
(4) ease of preparing sample in chemical form suitable for counting.

All of these criteria apply, of course, to radiochemical separations at ordinary levels, and so do some others, such as speed, which in general is not so important in low-level work. We shall give attention below to the difference in relative importance of some of these factors.

BLANK DETERMINATIONS

A blank in radiochemical separations means approximately what it does in trace element analysis, i.e. the contribution of the added reagents and other constituents of a sample to the quantity measured. A given procedure may, of course, have a different blank for a counting method using γ-ray pulse analysis as compared to one which involves gross β-activity.

* Beta proportional or Geiger counting — references 10, 12, 35, 57, 62, 74, 78, 84, 87, 101, 107; solution scintillation counting — references 1, 8, 15, 18, 31, 55, 56, 88; NaI scintillation counting — references 5, 14, 21, 36, 48, 111.

It is frequently not simple to decide how a blank is to be measured. For example, consider the following case. Low-level measurements are to be made of fallout Ce^{144} in samples of sea water. A procedure is devised which isolates cerium chemically. A blank is determined by adding inert cerium carrier to a volume of distilled water comparable to that of sea water in an actual sample; this is followed by the procedure using the same reagents in the same amounts as in isolation of a real sample, and finally the cerium fraction is counted. This does not necessarily constitute a satisfactory blank determination, since it determines only the contribution of added reagents. Sea water may contain non-cerium activities (referred to as X below) that tend to follow cerium chemistry, particularly when holdback carriers are not present. Ideally, the blank should be determined in a sea water system containing X, but no Ce^{144}; however, in this particular case and at this time there do not exist sea water samples which we can be sure are free of Ce^{144}. Even samples collected at 1500 m appear to contain measurable amounts[108].

A method which appears to be better — but is not — is to add inert cerium carrier and recover it from a sea water sample that has already been processed once. The first cerium separation (assumed to be quantitative for simplicity) should remove (1) Ce^{144} originally present in the sample, (2) Ce^{144} in the reagents used, (3) some or all of X, and (4) some or all of Z (as we shall call non-cerium activities contributed by the reagents which follow cerium chemistry; X and Z may or may not be the same). The second cerium separation may contain only (2) and (4). If so, obviously this is no measure of X. If a constant amount of X were to follow each cerium separation, then the second cerium fraction is a reasonable measure of the blank. But this is an unlikely occurrence, and this method does not provide an unambiguous blank determination.

If a small cross-section is being measured in a charged-particle reaction, a satisfactory blank may frequently be determined by placing the target at a position beyond the range of the charged particle and isolating and measuring the activity of interest. The blank here includes contributions from reactions of long-range particles (usually neutrons) as well as from contaminants in target and reagents. Fung and Turkevich[34] have described at some length the precautions they have taken to insure an authentic measurement of the very small cross-section for the $Cu^{65}(p,p\pi^+)Ni^{65}$ reaction. A similar discussion is given by Metzger and Miller[82] of the reactions induced by secondary charged particles produced by the interaction of high-energy protons with gold. The formation cross-sections of bismuth and lead nuclides were very much less than a microbarn. The blank problem in studies of bismuth fission has been described by Fairhall[28] and by Sugihara *et al.*[109].

At ordinary levels of activity, small amounts of radiochemical impurities are frequently tolerable if their half-lives are substantially different from that of the nuclide to be measured. In the low-level case, this is less true. For example, a great many laboratories are determining Sr^{90} at low levels in samples of geochemical or biochemical importance. All of the methods used involve the measurement of the 64-hr Y^{90} in secular equilibrium with its parent. One might think that a small amount of a long-lived activity would be of only minor consequence in such a determination, since the amount of Y^{90} can be deduced from the resolution of the decay curve. In fact, however, counting statistics are not so good, because in the resolution, the sum of the counter background and long-lived activity must be subtracted from each measured point. In effect, the counter background has been increased, thus defeating the purpose of the elaborate shielding methods used to achieve a low counter background. An obvious point to be made is that design of procedures of minimum blank is as important as engineering low backgrounds.

Blanks, like counter backgrounds, are usually not zero; at best they usually have small positive values even though statistically they may be taken to be zero. Such a blank is of course satisfactory. In less fortunate cases, the blank may not be negligibly small, and yet may not be large enough to apply the usual nuclear identification methods such as pulse analysis or absorption curves. Thus one does not know how to change his procedure to remove the contaminating nuclide or nuclides. In such cases, a standard practice is to determine the blank as a function of the chemical yield of the substance counted. If the relationship is simple and reproducible, a blank correction is readily applied to an actual sample (sacrificing some precision, of course). If not, the procedure must be altered (according to the intuition of the radiochemist) until either a negligible or small and constant blank is obtained.

REDUCING THE BLANK CORRECTION

The general problem of obtaining a negligible blank is a most complex one, and only a few statements can be made that are applicable to a wide variety of systems. There are two parts to the problem. One is concerned with the removal of contaminating activities present in the sample or in the reagents not isotopic with the nuclide to be determined. The other involves the contribution from the reagents of nuclides isotopic or identical with that determined. The first is solved by good chemical separations; the second by proper choice of reagents.

1. Contamination of analytical reagents. This subject has recently been thoroughly reviewed[23a] and no general discussion is presented here.

In our laboratory, we find many reagents whose activity is $> 0{\cdot}1$ c.p.m. per 10 mg. For example, a rare earth of high chemical purity, such as 99·99% La_2O_3, may contain easily measurable amounts of Ac^{227}; Y_2O_3 and CeO_2 frequently are contaminated with thorium, but we have not been able to detect Ce^{144} in reagent cerium compounds. Barium salts usually contain measurable amounts of radium isotopes. Reagent cesium salts are inevitably contaminated with K^{40} and Rb^{87}. Recently Honda[54] has found that reagents containing chlorine or sulphur also contain measurable amounts of P^{32}, produced by cosmic-ray interactions. At sea level, the saturation P^{32} activity is 0·22 d.p.m./kg as chlorine in HCl or CCl_4, and 0·46 d.p.m./kg as sulphur in H_2SO_4. Reagents stored (for a time which is long compared to the half-life of P^{32}) at a location of the order of a mile above sea level should contain about three times as much P^{32} activity. Thus considerable care needs to be exercised in the choice of reagents for very low-level determinations of P^{32}, P^{33}, or S^{35}. The latter two nuclides are also produced by cosmic rays in chlorine- or sulphur-containing reagents.

2. Obviously, potassium salts and reagents of other elements which have naturally occurring activities should be excluded from a procedure if the counting method is sensitive to the natural activity.

3. Aqueous solutions should be prepared with de-ionized water or water that has been distilled from a glass or quartz still. This is especially important for solutions used near the end of a low-level procedure. The activity found in ordinary distilled water, as prepared in the usual metal still, varies widely, and may be negligible in some laboratories. A very rough rule of thumb is that if the ordinary distilled water has a measurable blank when titrated with EDTA or when used in trace-element colorimetry, it is probably not safe to use in a low-level method.

4. Frequently, the major contribution to the blank is made in the last step. Consider the case of isolating Cs^{137}. A number of methods capable of separating cesium from Rb^{87} and K^{40} are known[20, 107]. Suppose such a method is used, and a very clean cesium-containing solution is obtained. Let us assume that a solid cesium sample is desired for counting. The magnitude of the blank may depend very critically on the choice of precipitant among perchlorate, chloroplatinate, silicotungstate, or tetraphenylborate. There are essentially no reliable rules that can be used at this point. Heavy-metal-containing reagents are usually avoided; yet in our experience[20] chloroplatinate appears to be superior to perchlorate.

5. Airborne contamination. Many radiochemical procedures require suction filtration in the final step to deposit a precipitate on filter paper for subsequent determination. A number of investigators have pointed out that a substantial amount of a 30–40 min β-activity (several c.p.m.) is

readily collected on a filter by drawing a few litres of air through it[16, 79]. This effect is large when the humidity is high. The activity in question is probably a complex mixture of the daughters of Rn^{222}. There appears also to be a long-lived activity (believed to be Pb^{212} and its daughters[54]) whose contribution is of the order of 5–10 per cent of that of the short-lived activity at the time the air stream is stopped. Thus it is of some importance to exclude the air contribution to the reagent blank. Methods that have been used include the following:

(*a*) Complete avoidance of suction filtration. This is certainly possible in procedures in which speed is of little consequence. Evaporation may often be used instead.

(*b*) Prefiltration of the air that eventually passes over the sample with a high-efficiency filter such as Millipore HA. This method is perhaps only 90 per cent efficient even if several such filters are used[79].

(*c*) Purification of the air by a series of traps designed specifically to remove radon and its decay products. Usually a trap containing an aqueous solution and one with charcoal at dry-ice temperature are adequate.

6. Use of non-isotopic carriers. Frequently, the inert carrier for a nuclide to be isolated is difficult to obtain free of active contaminants. In such a case, a non-isotopic carrier of suitable chemical characteristics may be much more desirable from the point of view of reagent blanks. For example, in determining Sr^{90} in geochemical samples, the usual chemical procedure is to add inert strontium carrier, finally recovering the strontium in a form free of other activities (except other strontium nuclides)[78]. The final strontium sample is allowed to stand for a time long enough to allow 64-hr Y^{90} to grow into secular equilibrium. Yttrium carrier is added and an yttrium fraction free of strontium is recovered and counted. The point here is that low-blank yttrium carrier is difficult to obtain; in general, it must be chromatographed under conditions in which separation from thorium is substantially complete. This is tedious and unnecessary.

A much simpler technique is to isolate Y^{90} carrier-free by co-precipitation on ferric hydroxide[107]. The Fe(III) carrier used is very simply obtained in a form that gives a zero blank. An HCl solution of reagent iron wire or powder is prepared. Because of air oxidation, there is always an appreciable concentration of Fe(III) in the $FeCl_2$ solution; thus, if the pH is adjusted to $\sim$4, some $Fe(OH)_3$ will precipitate. The $Fe(OH)_3$ purifies the $FeCl_2$ solution by the usual scavenging action. A trace of H_2O_2 may be added if the scavenging is to be repeated. Finally, excess H_2O_2 is added and the Fe(II) is oxidized to Fe(III).

One might object to using Fe(III) as a carrier for yttrium because of the

lack of specificity of $Fe(OH)_3$; on the other hand, if the strontium sample has been properly purified, no activity other than Y^{90} is present which would be carried on $Fe(OH)_3$. The co-precipitation of carrier-free yttrium and rare earths on $Fe(OH)_3$ is quantitative[107]. Furthermore, since small amounts of $Fe(OH)_3$ are recovered quantitatively on a Millipore filter, no chemical yield determination is necessary. Repeated application of this method to a standard Sr^{90}-containing solution has shown that the Y^{90} recovery is reproducible and indeed quantitative[107].

7. Re-use of iron exchangers. Ion-exchange resins are commonly used in low-level radiochemical procedures. Some authors[80] have stated that a given batch of resin should not be used more than once in a low-level separation. Several metal ions which are strongly adsorbed by ion exchangers are erratically eluted and their re-use may lead to contamination of subsequent samples. On the other hand, repeated use of the same colloidal Dowex-50 in rare-earth separations[107] has caused no difficulty. In the latter case, a basic citrate wash has been used between runs. According to Harley[47], some batches of Dowex-50 have been found to contain Sr^{90}. The activity is in a form that is not removed by the usual acid-base washing cycles. It is apparent only when the resin is ashed and counted; that is, samples are not contaminated when the resin is used in the usual column or batch manner. The activity level is about 10 d.p.m. Sr^{90} per 100 ml of wet resin.

8. Equipment and facilities. There are obvious complications in attempting to do low-level work in a laboratory devoted otherwise to ordinary levels of activity, particularly if others work with the same nuclide as that being measured at a low level. A very strict segregation of the usual laboratory glassware, hardware, and counting and other equipment (such as counters, absorbers, balances, ovens, centrifuges, etc.) is highly important. While not demonstrable that it is absolutely necessary, in the author's laboratory polyethylene ware is used where possible. It is conceivable that potassium and perhaps other naturally occurring activities can be leached from glass.

IDENTIFYING NUCLIDES IN LOW-LEVEL DETERMINATIONS

In many low-level determinations involving long-lived fallout nuclides, naturally occurring or cosmic-ray-induced activities, the counting measurement shows only that a certain amount of activity has been observed. If a properly determined blank correction is known, the difference should be attributable to the nuclide being investigated. How can one be sure that the activity measured is what one expects it to be?

Only in a few fortunate cases such as Si^{32}, Sr^{90}, or Ac^{227}, which have

daughter activities of convenient half-life, is it possible to base the identification on a decay curve. In most cases there is no appreciable decay over the time of the experiment. In general, pulse analysis of γ-rays does not appear to be feasible for a few d.p.m. of activity, at least at the present level of sophistication of instrumentation. A unique identification of low-level positron emitters is made possible by the angular correlation of annihilation radiation[5, 21]. Nuclides decaying by electron capture or isomeric transition can frequently be identified at low levels by X-ray counting.

A standard chemical method used is to re-cycle to constant specific activity. From the constancy, the chemical nature of the measured nuclide is deduced. Usually there is no difficulty in assigning the correct mass number. It is worthwhile to point out, however, that constant specific activity is not necessarily adequate if the *same* chemical procedure is used in each cycle. This can be illustrated by an example. Suppose nuclide *A*, which is the nuclide being studied, is separated, poorly or not at all, from radionuclide *B* (a different chemical element) in the procedure used, and thus the first sample of *A* contains some *B*. On re-cycling through the same procedure, *A* and *B* are not appreciably fractionated. Thus virtually the same specific activity as before will be obtained, even though the contamination level of *B* is appreciable; on the other hand, a different procedure which provides better fractionation between *A* and *B* should show a change in specific activity. Pairs of elements like rubidium and cesium, which are very similar chemically, may cause this kind of difficulty. Generally speaking, then, rather different chemical procedures should be used in successive cycles in the process of re-cycling to constant specific activity.

In the case of β-emitters, absorption curves may be taken to help identify the nuclide. But with, for example, only 0·5 c.p.m. of activity against a background of 0·2 c.p.m. the absorption characteristics cannot be measured very precisely. Usually all one needs to know is that the absorption curve is consistent with what one expects. The parameter compared is normally the half-thickness or sometimes the general (unresolved) shape of the absorption curve. When working with thick samples of low specific activity, Libby and co-workers[77, 106, 110] have used with considerable success a close cylindrical geometry among sample, absorber, and counter. Under these conditions a simple β-emitter exhibits a truly exponential absorption curve, and a measured half-thickness can be correlated with β-energy in a straightforward way.

Radiochemists who are accustomed to working at much higher levels may suggest that a measured absorption curve on a low-level sample of,

say, Cs^{137} should be compared with that measured under the same conditions with an authentic (and much higher activity) sample of Cs^{137}. The reaction of most low-level radiochemists is that under no circumstances would they want 1000, or even 100 d.p.m., of Cs^{137} measured on a counter intended for 1 d.p.m.

Absorption curves are usually taken with plastic absorbers since they are generally uncontaminated. Aluminium and other metals frequently have an appreciable blank correction. Polyethylene and Mylar have been used successfully in several laboratories[10, 80, 107]. A disadvantage in working with plastic absorbers is that it is easy to build up an appreciable electrostatic charge on them by rubbing with tissue, as one might do in cleaning them. The charge leaks off only gradually, and the effect is readily observable as an increase in the background rate on a thin-wall β-counter. It has been the practice in our laboratory to place the absorber over the sample several hours before a count is taken and thereafter avoid handling the absorber until the count is complete.

RELATIONSHIP BETWEEN ORDINARY AND LOW-LEVEL PROCEDURES

Generally speaking, a procedure designated as suitable for low-level use may be very similar to those used at much higher levels, as will be seen in the procedures described at the end of this review. Usually, decontamination steps are repeated more times and extra care is exercised to maximize yield, since reducing the chemical yield is tantamount to increasing background. In a statistical sense the effect is still greater, because the figure of merit for a method depends on (sample activity)^2/(background rate).

Particular attention is paid to specificity, for a low-level separation frequently starts with a very large amount of sample, containing nearly all possible contaminants. It is not easy to decide what holdback carriers to use in each step of the procedure. Thus a low-level procedure for nuclide A will often contain a step that is known to be specific for A in the presence of B, C, D, . . . when the latter are present carrier-free. Methods most successful for such steps are ion exchange, solvent extraction, and volatilization which are applicable at very low concentrations.

Seldom, if ever, is a low-level procedure done carrier-free if the element exists in stable form. Because of extra decontamination or other steps that tend to reduce yields, somewhat larger amounts of carrier are used than in work at ordinary levels. In the low-level determination of nuclides such as Pm^{147}, for which no stable isotope is available, non-isotopic carriers have been used (in this case, neodymium and samarium)[107].

SOME GENERAL RULES

The following general rules are suggested to aid in the design of a low-level procedure.

1. Devise a fast and efficient first step to remove the nuclide to be determined from the bulk of the sample (frequently very large). Poor decontamination from other nuclides in this first step is perfectly acceptable. Since samples may be rocks, meteorites, sea water, earth, cyclotron targets, etc, little specific advice can be offered.

2. List all possible activities that might be present in the sample at levels that would interfere with the determination. Introduce appropriate holdback carriers and scavenging agents to take care of each extraneous activity. All radiochemical procedures do this to a greater or lesser extent.

3. Devise a step that is highly specific for the nuclide in question. Generally speaking, this is always possible if appropriate preliminary removal of interferences can be carried out.

4. Isolate the sample in a form suitable for counting, being very careful that any reagents (including water and other solvents) used in the last step are free of activity. Filtered air may be necessary. Contamination from reagents introduced in earlier steps may be removed in the high-specificity operation. The choice of final form is often a compromise between low blank and suitable gravimetric factor. For a soft β-emitter, the total weight of counting sample should be minimized, of course.

5. If the chemical yield of the procedure is reasonable, determine a blank as described earlier, taking care to ensure that an authentic blank is measured. If it is not negligible, introduce additional steps in the procedure, and repeat until the blank is satisfactorily small.

6. Isolate the active nuclide according to your procedure from a real sample. If counted as an external sample on a β-counter, determine the absorption curve (if long-lived) and compare it with what one expects for the nuclide. If the nuclide is sufficiently short-lived, follow the decay until the activity no longer changes appreciably with time. The residual activity is a lower limit to the blank. On a γ-counter a decay curve may be followed in the same way; and possibly with a low-background, highly stable scintillation spectrometer, pulse analysis can be used to check purity and authenticity.

7. Put the sample (if long-lived) back into solution and go through a second processing cycle, using in step 3 a different operation specific for the nuclide. Remeasure the specific activity. If there is no change, the chances are that the procedure is adequate.

8. In general, the blank must be re-determined whenever a different

batch of reagents is used; hence, if a procedure is to be applied to a large number of samples, stock a considerable inventory of reagents from the same batch. Blank determinations should be made periodically as a matter of course, even with the same batch of reagents.

9. If a procedure is devised that appears to be satisfactory and it is to be used routinely for a large number of samples, investigate the possibility of eliminating some steps, or reducing the number of times certain operations such as scavenging are to be repeated. In the long run, a great deal of time may be saved. Low-level procedures generally tend to be over-conservative; that is, in one's attempt to make sure that a procedure will be satisfactory the first time he tries it, particularly from the point of view of a small blank, he usually includes more steps than are really necessary. Eliminating them may result not only in time saved but also in higher chemical yield.

10. Libby[75], who has pioneered in the use of low-level radiochemistry, points out in his Nobel lecture, with regard to the method used in radiocarbon dating, "It is something like the discipline of surgery—cleanliness, care, seriousness, and practice". No further comment seems necessary.

EXAMPLES OF LOW-LEVEL PROCEDURES

Several examples of low-level procedures, chosen for their variety of elements isolated as well as of starting material, will be described below. Experimental details such as volumes and concentrations of reagents have been omitted.

1. Potassium from Iron Meteorites[50]

In this study Honda[50] measured the amount of cosmogenic K^{40} in certain iron meteorites, as produced by the spallation of iron with cosmic rays. The measurement consists essentially in determining the specific activity of a potassium fraction isolated from the meteorites (samples weighing between 170 and 1100 g), and comparing it with the specific activity of natural potassium, which fortunately has a low concentration in iron meteorites (about 0·1 ppm).

Obviously no potassium carrier could be added. In one of the samples, purified cesium carrier was used. After solution of the meteorite in aqua regia, iron, cobalt, copper, and other elements were removed by ether extraction and anion exchange. The resultant solution was made ammoniacal, and was filtered. The filtrate, which contained about 3 moles of NH_4Cl and 0·7 moles of $Ni(NH_3)_4^{++}$, was passed through a cation-exchange column in ammonium form. Potassium and cesium were eluted with ammoniacal ammonium acetate, and the alkali metals were

precipitated with tetraphenylborate in the presence of EDTA. Potassium and cesium were separated on Dowex-50, and $K(C_6H_5)_4B$ precipitated. The chemical yield of potassium (85 per cent) was estimated from the cesium recovery. The actual weight of potassium recovered was evidently much more than that originally in the meteorite, the excess being attributed to the contribution of potassium by reagents and equipment.

The specific activity of the sample was determined, and it was then dissolved in an acetone–water mixture and passed through a cation exchanger. Potassium was eluted with HCl. This fraction was then subjected to scavenging with CuS and $Fe(OH)_3$. The tetraphenylborate was again precipitated. The specific activity was essentially the same for the first and second counting samples and considerably higher than that of a natural potassium sample.

The net β-counting rates due to K^{40} were in the range 0·3 to 2·4 c.p.m. (background 0·17 c.p.m.). While no specific reference is made to contaminants (other than non-cosmogenic potassium), it is clear from the procedure that rubidium is about the only conceivable interference, and should be removed in the cation-exchange steps. The ratio of K^{40} to K^{39} and K^{41}, as deduced from the specific activity measurements, was subsequently verified mass spectrometrically.

2. Barium and Strontium Nuclides in Spontaneous Fission[49] of U^{238}

Kuroda and co-workers[11, 49, 69, 86] have measured the yields of a number of nuclides in the spontaneous fission of U^{238}. The paper by Heydegger and Kuroda[49] is devoted chiefly to measuring the yield of Ba^{140}, although Sr^{91} and Sr^{92} are also mentioned. Since the spontaneous fission half-life of U^{238} is very long (8×10^{15} y), very large samples of uranium compounds (500–2000 g) must be taken as the starting material in order to obtain measurable counting rates of fission products.

The uranium was dissolved in ether, and the solution was extracted twice with small volumes of aqueous barium nitrate solution. Barium sulphate was precipitated, filtered, and converted to the carbonate by fusion with sodium carbonate. The barium was then purified by ferric hydroxide scavenging, by precipitation as barium nitrate, and finally precipitated as the carbonate or chromate. A barium sample isolated from 10 g of uranium showed no activity above the counter background of $1{\cdot}10 \pm 0{\cdot}03$ c.p.m.

When barium was isolated from 758 g of U^{238}, $1{\cdot}11 \pm 0{\cdot}15$ c.p.m. of Ba^{140} was found when counted 410 min after the $BaSO_4$ precipitation step. The observed decay curve was found to fit the calculated growth–decay curve of Ba^{140}–La^{140}.

When three nitrate precipitation and five ferric hydroxide scavenging steps are used, the authors state that there remains 0·06 ± 0·03 c.p.m. of residual contamination, determined presumably by following the decay over a period that was long, compared to the half-life of 12·8-day Ba^{140}. Another method of determining the blank would be to separate barium again from the uranium solution, very soon after the first extraction. Only a little Ba^{140} would have formed by spontaneous fission in a time very short compared to 12·8 days.

Similar experiments were conducted with uranium that had been depleted in U^{235}, reducing the possibility that induced fission would contribute to the observed results. In this case, the residual contamination was 0·15 ± 0·05 c.p.m. The authors speculate that this may be ascribed to radium contamination.

3. Cobalt and Iron from Copper Cyclotron Target[95]

Roy and Kohman[95] were interested in establishing the nuclear characteristics of Fe^{60} which was believed to be long-lived. Beta-decay systematics predict that it should decay, at least in part, to 10 min Co^{60m}. The first step of the experiment consisted of recovering an iron fraction from a copper target that had been irradiated with about 200 μa-hr of 400-MeV protons. The copper target, weighing about 10 g, was dissolved in HNO_3 and the solution was evaporated to dryness and taken up in HCl. Carriers for Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Zn were added, and $FeCl_3$ was extracted into isopropyl ether under conditions that are essentially specific for iron. The iron fraction after purification contained of the order of a millicurie of Fe^{59} and a considerable quantity of Fe^{55}.

The second part of the chemical procedure consisted of milking Co^{60m} from the iron fraction by contacting an aqueous cobalt solution briefly with the solution of $FeCl_3$ in isopropyl ether. The cobalt fraction was then washed with isopropyl ether several times. Cobalt was finally precipitated as the sulphide. Prefiltered air was found to be necessary to eliminate short-lived radioelements in air. The separation took about 9–15 min.

Counting was done on a thin-window β-counter sensitive to the 51-keV conversion electrons of Co^{60m}. The background was 2·8 c.p.m. Residual long-lived activity (presumably Fe^{55} + Fe^{59}) ranged in various separations from 9 to 55 c.p.m. The net rate attributable to Co^{60m} at the time of separation ranged from 9 to 62 c.p.m. This illustrates the difficulties associated with removing a few d.p.m. of an activity from a system containing millicuries of other activities, particularly when only a few minutes may be devoted to the separation because of a short half-life.