

INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY
ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON RADIOANALYTICAL
CHEMISTRY AND NUCLEAR MATERIALS

RADIOACTIVE TRACERS IN
INORGANIC CHEMICAL ANALYSIS
(A GUIDE)

Prepared for publication by

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RADIOACTIVE TRACERS IN INORGANIC CHEMICAL ANALYSIS (A GUIDE)

INTRODUCTION

The impact that the popularization of radioisotope techniques has had in the chemical analysis field in recent years is usually recognized as due mainly to the spectacular development of activation analysis. This is, however, only one of the important lines of work in the application of radioactivity to chemical analysis and, because of the necessity for the laboratories using it regularly to have access to reactor facilities or costly particle accelerators, certainly not the more apt for widespread usage.

Because of these special characteristics of activation analysis, radioisotope techniques in general are still too frequently considered as a rather exotic subject, reserved for specialists with advanced training in radiochemistry and for laboratories having ample budgets at their disposal.

As a consequence of these misconceptions, many analytical laboratories not directly connected with nuclear energy work do not realize that the second important line of application, namely, the use of radioisotopes as chemical tracers, is within their easy reach, and that its application can lead in many instances to better and quicker solutions for many everyday problems than more classical approaches. Satisfactory radioactive tracers are nowadays available around the world for many elements, and measuring equipment is not prohibitive in cost or too sophisticated to be useful only to specialists. Safety requirements also are not very demanding. Most tracer applications are feasible with levels of activity of a few microcuries per operation, for which fume cupboards with good ventilation and rudimentary radiation precautions are quite appropriate.

When one considers that tracer techniques were employed in analysis much before the discovery of artificial radioactivity, using naturally occurring nuclides, one is bound to speculate on the reasons why they are not more generally used at the present time. A first reason is probably the one mentioned above, namely, their identification in the mind of the everyday analyst with activation analysis. The glamour of this last technique has also had, no doubt, great influence in the direction of the research efforts of workers with good radiochemical background interested in contributing to the development of analytical chemistry. A third, and more serious, reason, is the general feeling that analysis by radiotracers is not as precise or accurate as classical methods due to the inherent statistical nature of the property measured, a fluctuation that is added to those introduced by the chemical operations performed.

This last aspect deserves some comment. Measurements of radioactivity to one per cent standard deviation or better are currently made in the laboratory in a few minutes of counting. This level of precision is rarely achieved in radiochemical analysis, where the errors of more than one radioactivity reading are combined in the result, and most papers on specific methods report

reproducibilities of a few per cent. There does not seem to be any inherent disadvantage in tracer methods not permitting the improvement of this precision, however, and in any case the situation is not worse than in most instrumental methods for amounts of unknown in the p.p.m. level or less. In this range, radiochemical methods of analysis are certainly competitive with other techniques and they require less skill from the analyst than most conventional procedures, since often they do not demand quantitative recoveries. The tracer approach shows the further advantage that, because of the wet chemistry generally involved in the method, it is more independent of matrix effects than most other instrumental methods of similar sensitivity, a factor of special importance in the light of the evergrowing modern array of very pure materials.

The present situation in favour of activation methods of radiochemical analysis outlined above can be easily grasped by just examining recent symposia on analytical chemistry or perusing the analytical journals. For instance, over a total of 62 papers given at the Symposium on Radiochemical Methods of Analysis held at Salzburg in October 1964¹, only 13 (21 per cent) were concerned with tracer applications and 7 (11 per cent,) with other techniques, not discussed here, while 42, that is, 68 per cent, were devoted to different aspects of activation analysis. In the following years, at least four more international symposia were organized for activation methods in analysis and none for non-activation radioanalytical techniques.

The Analytical Chemistry Division of IUPAC feels that this heavy unbalance of interest is unfair to the potentialities of the tracer methods and publishes this guide with the idea to help stimulate the use of these techniques by the conventional analyst not specially familiar with radioisotope techniques but desirous to use the better and shortest approach within his reach to cope with a particular problem. It is hoped that it will contribute to taking the subject out of the realm of specialization and to foster its sound development by promoting a real critical evaluation of its possibilities in competition with other techniques in the field where it belongs.

The guide is not intended to replace current textbooks or reviews on the subject, to which references are given, but rather to point out the highlights of special interest to the analyst to help him in his further reading and to advise him critically on the selection of a radioisotope for the tracing of a particular element.

PART I. GENERAL

(1) Criteria for tracer selection

1.1. Tracers

The basis of tracer methodology is the identical behaviour of the isotopes of an element in chemical and biological phenomena. This identity is not absolute, since slight isotope effects which differentiate the isotopes of the same element do exist and are, in fact, put into operation when isotopes are separated or when second order factors are sought for in delicate reactions, but it can be taken as certain as far as the use of tracers in chemical analysis is concerned. With the exception of special cases involving the very precise determination

of light elements, the influence of isotope effects on the precision of the methods applied is negligible.

The discovery of natural radioactivity led to the identification of 40-odd nuclear species with radioactive properties existing in nature. These were isotopes of some of the heavier elements. The development of particle accelerators and nuclear reactors enlarged this domain very quickly in recent decades by making available synthetic radioisotopes, and a modern table of nuclear species² contains nowadays over 1500 entries, most of them radioactive. With the exception of hydrogen, for which only one radioactive isotope, ³H, has been identified, all the other elements have several, in some cases well over 20. Not all of them are useful for chemical tracing, however, as will be seen below, but those which are hold an ideal position in this respect, since they can be measured in any stage of the process they trace without prior separation and with large sensitivity.

1.2. Nuclear transitions

Two general types of spontaneous nuclear transitions take place in radioactive nuclei: *disintegrations* and *isomeric transitions*. In the first type, a change occurs in the atomic number Z , the mass number A , or both, giving origin to a different nuclear species. On the contrary, no change in Z or A takes place in an isomeric transition.

Both types of phenomena are usually present in radioactive events, since most disintegrations leave the new nuclear species in an excited state which goes down to the ground state immediately afterwards emitting one or several quanta of electromagnetic energy (gamma rays). Because of this, many disintegrations can be detected directly (by means of the particle carrying the excess Z or A actually ejected) or indirectly (detecting the de-excitation that follows the disintegration). Pure disintegrations take place only in a few nuclei which decay directly to the ground state of the daughter nucleus (f.i., ³²P, a pure beta emitter) and pure internal transitions appear when excited nuclei exist as such for a relatively long period of time (f.i., ^{80m}Br, decaying by gamma emission to beta-active ⁸⁰Br with 4.5 h half-life).

The tracers of importance for general chemical use are those which can be measured through their emission of gamma rays, x-rays or electrons. Measurements of other types of radioactivity are employed in some special cases, but they are a forced choice even for the specialized laboratory.

Electrons are emitted by nuclei in *beta decay processes*, which lead to new nuclear species isobaric with the initial ones but with atomic number $Z + 1$ (negatron emission) or $Z - 1$ (positron emission). Negatrons can be detected as such. Positrons, on the contrary, can coexist with matter for a very short time only, since when they collide with negatrons both particles disappear giving origin to two simultaneous gamma rays of 0.511 MeV energy (the energy equivalent to the rest mass of each particle) emitted in opposite directions. This 'annihilation radiation' is present whenever positrons are emitted by nuclei and can be used for their detection.

A mode of disintegration competing with positron emission and equivalent to it in its effects is *electron capture*, in which an orbiting electron from the K -layer is taken up by the nucleus, leading also to a change of -1 in the value of Z . Electron capture is detected by the characteristic x-rays of the daughter

element emitted when the vacant orbital electron positions are refilled. Alternatively, low-energy ('Auger') electrons, originated by the photoelectric effect of the x-rays on the electron cloud of the atom, are emitted.

Another source of electrons in nuclear transitions is the phenomenon called *internal conversion*, occurring when the energy of an isomeric transition is not emitted as a gamma photon but taken up by an orbital electron which is ejected from the atom with the energy of the converted gamma ray less the work function of the electron in its orbit. Internal conversion electrons appear, therefore, as peaks of monoenergetic electrons competing with gamma emission and are counted by beta-counting equipment.

In many cases the new nuclide formed in a nuclear disintegration is not stable but also radioactive, and it may occur, for instance, that after the separation of a traced element from a chemical system the radioactive properties of the separated material change with time. When the daughter's half-life is shorter than the parent's, the total activity of the separated fraction grows to a maximum and then decays with the parent's half-life (*transient equilibrium*). A limiting case, called *secular equilibrium*, appears if the parent's half-life is much longer than the daughter's. In it, the total activity stays constant after the maximum during many daughter half-lives, since the parent does not decay measurably during that period.

These phenomena do not invalidate the use of a radioisotope as a chemical tracer provided they are allowed for in the measurements (see, f.i., ^{28}Mg , ^{99}Mo and ^{103}Ru in Part II) or a measuring procedure that discriminates its radiations from those of its disintegration products is used (filters, spectral analysis). In some instances, the presence of the daughter activity may be of real help, making the measurement easier (see ^{106}Ru and ^{137}Cs in Part II as examples).

In general, the best analytical tracers are those measurable through their gamma rays, since the negligible attenuation of these rays by matter makes possible the direct measurement of the activity in solutions or in thick solid precipitates. They are the obvious choice whenever the efficiency of beta particle measurement is not much higher or other factors of the particular problem studied do not outweigh their advantages.

1.3. Half-life considerations

Radioactivity is measured in Curie units. One Curie (Ci) is defined as the quantity of a radioactive nuclide in which the number of disintegrations per second is 3.700×10^{10} . The corresponding number of disintegrations per minute is 2.220×10^{12} .

The disintegration of a radioisotope follows the fundamental law of radioactive decay

$$A = A_0 e^{-0.693t/T} \quad (1)$$

where A is the activity at time t remaining from an initial activity A_0 at time $t = 0$ and T a constant characteristic of the nuclear species involved, the *half-life*, defined as the time interval in which any activity decays to one half of its value. *Table I* gives values of the factor $e^{-0.693t/T}$ in terms of time expressed in half-lives (t/T).

The half-lives of the radioactive nuclides cover a very wide range, from fractions of a microsecond to more than thousands of millions of years.

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Table 1. Radioactive decay

Assuming an initial activity $A_0 = 1$ at time $t = 0$, the table gives the approximate activity remaining at time $t = t$ as a function of t/T , where T is the half-life of the radioisotope expressed in the same unit as t . Formula 1 in text can be used for better values. Note that zero activity is reached theoretically at infinite time.

t/T	0.00	0.02	0.04	0.06	0.08
0.0	1.000	0.986	0.973	0.959	0.946
0.1	0.933	0.920	0.908	0.895	0.883
0.2	0.871	0.859	0.847	0.835	0.824
0.3	0.812	0.801	0.790	0.779	0.768
0.4	0.758	0.747	0.737	0.727	0.717
0.5	0.707	0.697	0.688	0.678	0.669
0.6	0.660	0.651	0.642	0.633	0.624
0.7	0.616	0.607	0.599	0.591	0.582
0.8	0.574	0.566	0.558	0.551	0.543
0.9	0.536	0.529	0.521	0.514	0.507
	0.0	0.2	0.4	0.6	0.8
1.0	0.500	0.435	0.379	0.330	0.287
2.0	0.250	0.218	0.190	0.165	0.144
3.0	0.125	0.109	0.095	0.083	0.072
4.0	0.063	0.054	0.047	0.041	0.036
5.0	0.031	0.027	0.024	0.021	0.018

Table 2. Mass of some pure nuclides corresponding to

1 μCi .
 (1 $\mu\text{Ci} = 2.22 \times 10^6$ d.p.m.)

Nuclide	Half-life	Mass (microgrammes)
^{36}Cl	3×10^5 y	30
^{14}C	5.8×10^3 y	0.22
^{63}Ni	120 y	2.1×10^{-2}
^{85}Kr	10.6 y	2.5×10^{-3}
^{54}Mn	314 d	1.3×10^{-4}
^7Be	53 d	2.6×10^{-5}
^{122}Sb	2.74 d	2.5×10^{-6}
^{28}Mg	21.4 h	1.9×10^{-7}
^{18}F	110 m	1.0×10^{-8}

Because of this, the actual mass associated with the same amount of radioactivity varies widely from one nuclide to another but, with the exception of the very long lived ones, the mass associated with easily measured activities is very low. Table 2 shows this mass for several nuclides and for an activity of 1 microCi, that is, 2.2×10^6 disintegrations per minute. The minimum detectable activity with simple equipment depends on the particular radioisotope and on the method used, but is often less than one thousandth of the values of Table 2.

It is obvious that radioisotopes of a very short half-life are useless as tracers for analytical purposes, since they disappear during the quickest chemical operations. Radioisotopes with a few hours half-life can be used provided corrections of the decrease of activity during the decay are allowed for, since this factor will be in general of significance for the results. *Table 1*, or graphs obtained from it on semilogarithmic paper, are suitable for this purpose.

Another disadvantage of the short-lived tracers is that they are not stockable or, if not too short, that its stock has to be renewed at very frequent intervals.

From this point of view, the best tracers for chemical purposes are those with half-lives between, say, a few weeks and a few years. The very long-lived ones present the intrinsic disadvantage of having low sensitivity because of the relatively large mass associated with low activities.

Some elements have only radioisotopes of very short half-life to be useful and they cannot be studied by the tracer method. This is specially significant in the case of the very important elements oxygen and nitrogen, for which stable isotopes have to be used. However, some special studies have been made with the positron emitter ^{13}N , of ten minutes half-life.

1.4. *Specific activity*

The specific activity of a sample of a radioactive substance is the ratio of its activity to its mass (or volume of solution, or moles, or any convenient unit proportional to its mass) and gives a relative measurement of the strength of the sample. The specific activity of a pure radioisotope is the maximum value attainable for the nuclide concerned. In the examples of *Table 2*, the maximum specific activities expressed in $\mu\text{Ci}/\mu\text{g}$ would be the inverses of the values of the last column.

These maximum specific activities are rarely obtained in practice, as a radioisotope is normally used and stored together with small amounts of the corresponding inactive element. This 'carrier' may have origin in the method of preparation of the radioisotope or may be added on purpose, in certain cases, to improve the stability of the very dilute solutions against significant losses from adsorption on the walls of the container. When the radioactive nuclide does not contain an isotopic diluent above its chemical detection limit and it is known that none has been deliberately added, it is called 'carrier-free'.

In analytical applications it is convenient in general to have as high a specific activity as possible to improve the sensitivity of the detection and, therefore, carrier-free isotopes should be preferred. When this is not possible, second-best should be used.

For practical purposes, the specific activity is expressed in *counts per minute/unit mass* for a particular measuring procedure. This is a fraction of the absolute activity of the sample in *disintegrations per minute/unit mass*, the value of this fraction depending on the efficiency of the counting arrangement. Comparative values are obtained by adhering strictly to the same measuring procedure when following the fate of a tracer in one experiment. Delicate measurements of absolute activities are seldom, if ever, necessary in analytical tracer applications.

1.5. Cost

Cost is also an important factor in tracer selection. The prices of radioisotopes vary widely for many reasons (production in nuclear reactors or in accelerators, activation of natural elements or of stable isotopes artificially separated, etc.) and frequently the 'second-best' nuclide will cover the necessities at much less expense.

1.6. Availability

Radioisotopes can be ordered from producers or authorized distributors in most countries. Even small research reactors can produce about 30 short-lived useful ones. Local regulations as to its free use vary from country to country, but in general an authorization from the national atomic energy authority is required. In tracer use for chemical purposes, the activities involved are small and there is usually no difficulty to obtain that authorization provided that evidence of the necessary expertise in the laboratory can be proved. Also, no licence is required for small amounts, fixed by local regulations, of many radioisotopes. Often these amounts are sufficient for analytical use.

Appendix I contains information on some radioisotope producers and suppliers and their catalogues.

(2) Total activity necessary

No general rule can be laid as to the amount of activity to be used in analytical applications, since the values vary for each particular technique and radioisotope. For instance, it is obvious that if the result depends on the measurement of a small fraction of the total it will be convenient to start with a bigger amount than if only relatively large percentages are measured during the experiment. At the same time, the efficiency of measurement differs widely from one radioisotope to another, and values as high as 95 per cent for ^{36}Cl in liquid scintillation counting and as low as 0.5 per cent for ^{65}Zn in conventional gamma scintillation equipment can be encountered.

In this respect, it is always advisable to check the real 'count-per-minute' (c.p.m.) specific activity of the stock of radioisotope with the same equipment that will be used in the experiment and to decide on the amount to take on the basis of this measurement and of the envisaged operations.

Whenever possible, enough activity to allow all the readings to fall not below the 5000–10000 c.p.m. range should be taken, since these activities are measurable to a precision of one per cent and better in a few minutes. Usually it will be found that this condition can be met with an initial amount of 1 to 5 μCi , or even less, for each complete experiment.

(3) Factors affecting tracer behaviour

There are some factors other than the non-controllable but negligible isotope effects discussed in 1.1 above which may give origin to differences of behaviour between the tracer and the traced material. These can be easily controlled by the alert analyst, however, and represent a problem only if they are not taken into account.

In the first place, to ascertain identical chemical behaviour it is essential that the chemical form of the problem element or compound originally

present in the sample is the same as that contained in the tracer added. When the total amount of an element in a mixture is traced, this is easily controlled by taking the whole chemical system, after the tracer has been added, to a condition in which the problem element is known to exist in a single chemical form. This is obviously not possible when it is wanted to trace a particular form in a system also containing others as, for example, dichromates in the presence of chromic salts. In cases of this kind, the tracer should be totally and certainly taken to the appropriate chemical form before mixing and no isotopic exchange should take place between the different chemical states of the elements coexisting in the system. Alternatively, this exchange can be slow enough to be allowed for or just not taken into account. When these conditions do not hold, the tracer method is not applicable and should be discarded for the particular problem studied.

Another important factor is the certainty that future measurements of activity in the chemical system or in fractions separated from it do represent the behaviour of the element or compound studied and not a different one. It is obvious that the control of the purity of the tracer used, and its purification if necessary, are the only ways to ascertain that this source of error is absent. What is perhaps not so obvious is that this purity control must be repeated periodically, since an impurity may build up with time from negligible amounts to really significant ones. For instance, a sample of 1 mCi of ^{109}Pd ($T = 13.6$ h) containing one per cent ($10\mu\text{Ci}$) of ^{106}Ru ($T = 1.0$ y) will be transformed, through radioactive decay, in a ^{106}Ru activity contaminated with about ten per cent of ^{109}Pd in 5.5 days. Chemical effects due to self-radiolysis, and leading to changes in the oxidation state of the tracer or to the release of free ions or elements from labelled molecules and complex ions, may also be of importance as a source of impurification, especially with radioisotopes used at high specific activities.

(4) Measurements

Radioactivity is measured by counting the whole or a definite fraction of the individual disintegrations produced in the measured sample during a chosen time interval. In some instruments, the number of events in a fixed period of time is integrated and a signal proportional to this number recorded. The basic equipment is formed by the detector itself, where the individual events are transduced into electrical pulses, an amplifier to enlarge these pulses and a scaler or integrator to display the results. The various types of detectors (Geiger-Müller, proportional, solid state, scintillation, etc.) differ in counting efficiency for different particles and, therefore, some are better suited than others for a particular measurement.

Measurements are essentially comparative (see 1.4 above) and, therefore, extreme care must be taken to ensure that comparable conditions are kept as much as possible in related measurements. Sources should be roughly of the same composition to ensure the same self-absorption effect and, when liquids are measured, adsorption on the walls should be controlled by adding carrier. These and similar precautions are less important the more penetrating is the measured radiation; in this respect, gamma rays and energetic betas are the best, and soft betas and x-rays the worst.

4.1. Measurement of gamma rays

Gamma rays are normally detected and measured by means of solid scintillation or semiconductor counters. A large array of equipment with all imaginable degrees of sophistication is presently available for the purpose, but for analytical tracer applications the simplest apparatus, based on the classical thallium-activated sodium iodide scintillator, is quite appropriate. The detector itself is optically coupled to a photomultiplier tube and covered over the rest of its surface by a light-tight metal enclosure through which the gamma rays emitted by the sample reach the activated crystal. The light photons generated in the crystal by the gamma rays are seen by the cathode of the photomultiplier and transformed into electrical pulses which, after further amplification, are registered by the scaler or recorder.

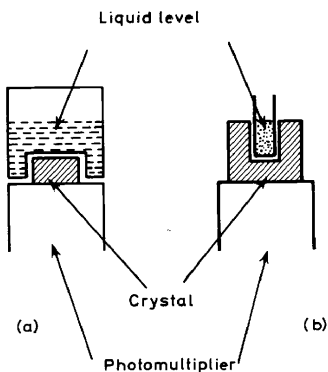


Figure 1. Usual systems for measurement of gamma-active tracers. (a) Common crystal; (b) Well-type crystal.

Because of the penetration of the gamma rays, gamma-active nuclides can be measured directly in solution. The two systems shown in *Figure 1* for the most popular shapes of sodium iodide crystals are very convenient for tracer work with this type of radioisotopes. The second one, called 'well type' crystal, is specially appropriate, since it takes directly small test tubes and has a high counting efficiency.

An elaboration of the simple scintillation counter convenient in some special problems is the one-channel spectrometer, in which the gamma rays corresponding to a predetermined energy interval can be selected and counted separately from the other ones present in the sample, facilitating in this way simultaneous work with two or more tracers. More refined equipment, like solid state detectors and multi-channel analysers, are hardly necessary for analytical tracer work, though they are of everyday growing importance for activation analysis, where they help to avoid chemical separations of activated elements.

4.2. Measurement of beta emitters

The classical detector for beta emitters is the well-known Geiger-Müller (GM) counter. This counter is also the usual choice for general use when only one detector is installed, as it can measure gamma radiation (though much

less efficiently than a scintillator) and, being less demanding on electronics excellence than other counters, it is relatively cheap and easy to handle and maintain.

Its disadvantages when compared with proportional counters are the lack of energy discrimination (GM pulses are independent of the energy of the particle detected) and the relatively long period of insensitivity that follows each event (the 'dead time'). Both are of small importance in analytical applications, since multiple tracer problems are rare and are better solved by gamma-active isotopes and scintillation spectrometry, and corrections for dead time losses are straightforward at the activity levels usual in tracer work. The extent of the insensitivity period depends on the particular counter, being usually of the order of 100 to 300 microseconds. While it can be determined, it is generally better to fix its value by means of an external electronic quenching unit which keeps the counter 'dead' for a prefixed interval after each event. The correction formula is

$$N_0 = -N/(1 - N\tau) \quad (2)$$

where N is the number of counts observed in unit time and τ the dead time in the same units. The denominator is the real time the counter is 'alive' and, therefore, N_0 is the corrected count rate. *Table 3* gives the correction $\Delta N = N_0 - N$ of a reading in counts per minute for a dead time of 400 microseconds. Intermediate values can be corrected by interpolation from the table or from a graph constructed from it.

There are several kinds and many different shapes of GM counters which have been developed for different uses. The two most important for tracer work are the 'bell' or 'end window' type and the 'liquid' counter, both

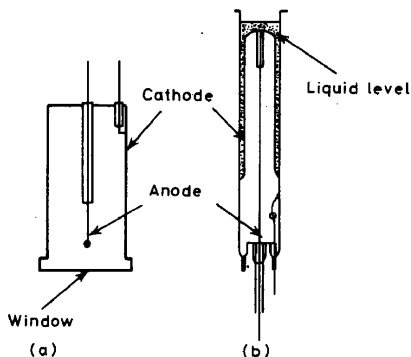


Figure 2. Geiger-Müller tubes. (a) End-window. (b) Liquid.

illustrated in *Figure 2*. The second one, much favoured by British workers, is used for the direct measurement of tracers in solution. The end window type requires previous separation by precipitation or evaporation to prepare a solid source for measuring.

To be counted in a GM counter, a beta particle must be energetic enough to emerge from the sample (solid or liquid) with enough energy to pass

Table 3. Correction of losses due to dead time

The table gives the correction to be added to a reading in counts per minute for a dead time of 400 microseconds. The formula used is $\Delta N = N^2 \tau / (1 - N \tau)$, obtained from equation 2 in text. Intermediate values should be interpolated and the next whole number taken in all cases.

	0	100	200	300	400	500	600	700	800	900
0	—	—	—	0.60	1.07	1.67	2.40	3.27	4.28	5.42
1000	6.70	8.12	9.66	11.4	13.2	15.1	17.2	19.5	21.8	24.4
2000	27.0	29.8	32.7	35.8	39.0	42.3	45.8	49.4	53.2	57.1
3000	61.1	65.3	69.7	74.1	78.7	83.5	88.4	93.5	98.7	104
4000	109	115	121	127	133	139	145	152	159	165
5000	172	179	187	194	201	209	217	225	233	241
6000	250	258	267	276	285	294	303	313	323	332
7000	342	352	363	373	384	394	405	416	427	439
8000	450	462	474	486	498	510	523	535	548	561
9000	574	587	600	614	628	642	656	670	684	699

through the window of the counter. In general, beta energies over 0.3 MeV can be considered 'hard' and easy to measure in solid samples or in solution. Some pure beta-active nuclides, like ^{14}C ($E_{\text{max.}}$ 0.2 MeV) and ^3H ($E_{\text{max.}}$ 0.02 MeV) emit particles of very low energy which are detected with low efficiency or not at all. Their measurement demanded special counters to obtain a reasonable efficiency of detection before the liquid scintillation counter was developed.

In this system, the nuclide in a convenient chemical form is dissolved in a mixture of organic substances, the *phosphor*, which absorbs the energy of the particle and emits light photons. As in solid scintillators, the light is picked up by a photomultiplier and transformed into an electric pulse which can be properly processed electronically. The contact between the disintegrating atoms and the phosphor is direct, without intermediate obstacles, and no part of the energy is wasted before reaching the counting medium.

The technique is also used for the measurement of nuclides which decay by electron capture emitting x-rays and low-energy electrons, like ^{37}Ar and ^{71}Ge .

(5) Techniques

The applications of radioactive tracers to chemical analysis fall under two general types depending upon whether the label is put on the element of interest (*isotopic methods*) or on another one reacting in some way during the analytical procedure (*non-isotopic* or *radio-reagent methods*).

The simplest situation appears when isotopic labelling is applied to follow in a qualitative way the path of an element or a substance in a course of separations or reactions. This does not demand the exact measurement of the radioactivity but only to know whether the element 'is' or 'is not' in a certain phase. Of course, a rough quantitative judgement must usually be applied, since separations are rarely absolute, but the important point is that no careful radioactivity measurement is necessary.

An approach as simple as this may save hours of work with untraced material during the study of an analytical procedure. The washing of a precipitate, the elution of a component from an ion-exchange column, the extraction of an ion by a solvent, the coprecipitation of an impurity and its decontamination in reprecipitation, and many other operations frequently performed in the analytical laboratory, can be easily followed and controlled, saving time and trouble, by just adding a radioactive tracer to the system at some convenient stage of the work. Of course, sometimes qualitative or roughly quantitative detection may not be sufficient and more exact measurements may be necessary, but usually only comparative values of the *total* radioactivity of samples are required.

A more complicated situation appears in quantitative applications aimed at the *determination* of a specific element or substance with the help of radioactive tracers. These methods usually require the knowledge of *specific activities*, that is, not only the measurement of the radioactivity but also of the mass associated with it. Even in this case, however, methods have been developed for special problems in which no mass determination is necessary.

A general approach of great importance, though as yet seldom applied, is the use of radioisotopic tracers to avoid control analysis in pilot and industrial

plants and in many manufacturing operations. By adding convenient tracers at the beginning or at some stages of the process, it is frequently possible to substitute chemical determinations to be performed later by measurements of radioactivity, saving hours and even days of manpower effort. The danger of leaving the final product contaminated with radioactivity is easily controlled by selecting tracers of half-life long enough to be useful during the process but, at the same time, short enough to allow the residual activity to die off quickly after its completion.

The most important quantitative applications of radioactive tracers in analytical chemistry have been summarized in the following discussion. The grouping adopted represents one of the convenient ways of classification and is not intended to cover all the possibilities or to convey the relative importance of the methods. This, it is hoped, will appear from the individual discussions.

5.1. Isotopic methods

5.1.1. *Direct isotope dilution*—This method is specially useful for the determination of an element or compound impossible, difficult or just inconvenient to separate quantitatively from a mixture. It consists in separating and determining a part of the component only and measuring at the same time the yield of the separation by means of an isotopic tracer previously added to the mixture. A classical example is found in the work of Hevesy and Hobbie³ on the determination of a few parts per million (p.p.m.) of lead in some rocks. The gravimetric form used for the determination, PbO_2 , was obtained by anodic oxidation after a long procedure involving many operations in which variable losses of lead very probably occurred. Adding a known activity of the radioisotope lead-210 (RaD) to the initial solution and measuring the radioactivity of the final weight of lead peroxide, Hevesy and Hobbie were able to determine the yield of the lead recovery and, therefore, to calculate the total initial amount of the element, which in some of the determinations was more than two times the quantity recovered.

In the example just mentioned, the tracer was in carrier-free condition and the only data necessary were the total activity added and that recovered, as the mass of the lead tracer added was negligible compared with the amount of the same element present in the sample. This is not valid in the general case, however, in which it may be necessary to take into account the increase in the mass of the element traced introduced into the system by the tracer. The treatment involves the specific activities instead of the total ones, and is as follows.

Let m_x be the unknown mass of the element or substance to be determined present in the sample and s_0 the known specific activity of the tracer. A known mass m_0 of the tracer is added to the sample and complete mixture achieved. The specific activity s_f of the element or substance in the sample will be now

$$s_f = m_0 s_0 / (m_x + m_0) \quad (3)$$

and from this expression, the mass originally present can be calculated as

$$m_x = m_0 [(s_0/s_f) - 1] \quad (4)$$

if s_f is measured.

It is clearly seen here that it is not necessary to recover quantitatively the element or substance sought, since s_f can be measured in any fraction of the total.

An alternative form of equation 3 is

$$a_f/m_f = a_o/(m_x + m_o) \quad (5)$$

in which a_o and a_f are the total activities of the tracer added and of the fraction of mass m_f recovered, respectively. Equation 4 then takes the form

$$m_x = m_f(a_o/a_f) - m_o \quad (6)$$

which may sometimes be more convenient.

When a tracer is used in carrier-free condition or with specific activity high enough for the weight m_o to be negligible when compared with $m_x(m_o \ll m_x)$, equation 6 takes the form

$$m_x = m_f(a_o/a_f) \quad (7)$$

which is the simplest one for the isotope dilution equation and corresponds to the example of lead determination with high-activity tracer given above.

Besides its use in inorganic analysis, isotope dilution has been employed very frequently in organic and biological chemistry using labelled substances as tracers. The determination of γ -hexachlorocyclohexane by means of the ^{36}Cl labelled tracer, of benzylpenicillin with the help of ^{14}C and of vitamin B_{12} with ^{60}Co are a few^{4, 5, 6} of the many examples where isotope dilution methods contributed significantly to improving the analytical situation.

5.1.2. Substoichiometric isotope dilution—In the case of trace analysis, a severe limitation of isotope dilution methods is the necessity to determine the mass associated with the final activity. The sensitivity of mass determination is much less than the one attainable for radioactivity and it is very difficult indeed to measure specific activities with submicrogramme amounts of a product.

This difficulty is elegantly overcome in the technique called substoichiometric isotope dilution analysis, in which a weight of reagent below the amount necessary to react with the mass of element or substance present in the *tracer* used is made to react under the same conditions *both* with the traced sample and with a new volume of the original tracer solution equal to that added to the sample. Since the mass of the reaction products obtained in both cases is the same, the ratio of the specific activities in equation 4 may be replaced by that of the total activities separated, giving

$$m_x = m_o[(a_o/a_f) - 1] \quad (8)$$

which allows m_x to be calculated without measuring m_f .

The method has also been employed in biological and organic chemistry, where it is better known under the name of *saturation analysis*, for the determination of insulin⁷ and other proteins. In the inorganic field, it has given significant results in the submicrogramme region for the determination of some ions with dithizone, cupferron, EDTA and other complexing agents giving highly stable metal complexes easy to extract by solvents or to separate by ion exchange.

Zinc, copper, mercury, indium and other cations have been determined in this way at levels as low as 10^{-9} to 10^{-10} g in model experiments⁸. The limit of satisfactory determination is fixed at present by the blank and the degree of selectivity of the reagent which, of course, is essential for the success of the technique.

5.1.3. *Inverse isotope dilution*—This technique is a variation of the isotope dilution principle frequently used in organic and biological chemistry to determine the amount m_x of a specific component of a mixture of *labelled* compounds of known specific activity s_0 . The determination is made by adding a known amount m_0 of the chemically pure *inactive* compound and, after mixing, measuring the new specific activity s_f on a carefully separated and purified sample. The basic relation corresponding to formula 3 in direct isotope dilution is

$$s_f = m_x s_0 / (m_x + m_0) \quad (9)$$

and instead of equation 4 one has

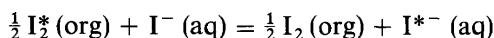
$$m_x = m_0 / [(s_0/s_f) - 1] \quad (10)$$

When s_0 is not known, *double dilution* can be applied by adding different weights of inactive material to two portions of the original mixture or by repeating the procedure with the mixture left after the determination of s_f . The error of this procedure is, of course, larger than when fewer measurements are involved.

One application of inverse isotope dilution in general analytical chemistry is the measurement of the radiochemical purity of the stock of a *carrier-free* tracer. This is done by adding pure inactive carrier in the same chemical form of the tracer and measuring the apparent specific activity s_1 after mixing with the stock. A new measurement s_2 is made on a carefully purified fraction, and the percentage radiochemical purity of the initial stock is readily calculated as $100 (s_2/s_1)$.

If the tracer is not carrier-free, the relation s_2/s_1 will depend on both the radiochemical *and* the chemical purity and further information obtained by paper or thin-layer chromatography and other methods will be necessary to establish each. The double dilution method mentioned above may be applied in some cases, though the error is usually large. In general, as indicated under 1.4, inorganic tracers should be employed in analysis, whenever possible, in carrier-free condition.

5.1.4. *Exchange methods*—Isotopic exchange reactions can be applied to chemical analysis when the exchangeable species are easily separable. Consider, as an example, a solution of labelled iodine in benzene. If such a solution is contacted with an aqueous one containing inactive iodine as iodide ion the mass concentration of both phases will remain unchanged but the exchange reaction



will take place until the specific activity of the *elemental* iodine in both phases

becomes the same. In this condition, the ratio of the total activities of aliquots of both phases is equal to the ratio of the mass atom concentrations

$$a_{\text{org}}/a_{\text{aq}} = 2(I_2)_{\text{org}}/(I^-)_{\text{aq}} \quad (11)$$

and the concentration in one phase can be calculated from that of the other and the measured activity ratio.

The procedure has been applied⁹ to the determination of traces of iodine in water down to concentrations of 1 $\mu\text{g}/\text{l}$. A known carrier-free iodine activity is added to the water and, after conversion of all forms of iodine present to elemental iodine, this is extracted with benzene. The yield of the extraction is measured by the activity recovered and the iodine determined by equilibrating with an aqueous iodide solution of known concentration as just described.

5.2. Radioreagent techniques

The general principle of these *non-isotopic* methods is to make the non-radioactive problem element or compound react with an active reagent and to calculate its amount by measuring the radioactivity involved in the reaction.

5.2.1. *Isotope derivative*— We take as a general example of this technique a precipitation reaction giving the insoluble compound RX formed from R and X according to the equivalent weight ratio e_X/e_R . This reaction can be used to determine X by forming RX with labelled R of known specific activity, s_R , and separating the precipitate from the excess of reagent. The precipitate is formed with the mass relation

$$g_X/g_R = e_X/e_R \quad (12)$$

and, as the specific activity *does not vary* during the reaction, g_R can be calculated from the original s_R and the total activity a_R present in the precipitate. Therefore

$$g_X = (e_X/e_R) g_R = (e_X/e_R)(a_R/s_R) \quad (13)$$

Three general conditions essential for the application of the technique are apparent from this example. First, the reaction chosen must be quantitatively well defined, as relation 12 must hold; secondly, it must be selective or interferences must be absent, for the same reason; thirdly, the recovery of the compound must be quantitative, or its yield known, as a_R is the *total* activity associated with it. Provided these conditions hold, it is not necessary for the separated material to be free from other non-radioactive substances, since only its total activity and not its mass is used in equation 13.

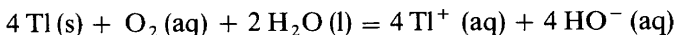
An example of the application of this technique to general analysis is the determination of traces of lead, calcium, strontium and barium using ³⁵S-labelled diluted sulphuric acid as a spraying reagent on their spots on a strip of chromatographic paper¹⁰. After eluting the excess reagent with water, amounts of the order of 0.01 μg of the individual ions were determined.

The method is frequently used in organic chemistry for the analysis of mixtures of related substances. The labelled derivatives are formed and the individual recoveries measured afterwards by reverse isotope dilution (see above). The whole application is usually called *isotope derivative dilution*.

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Sometimes, *double isotope derivative dilution* is applied. This consists in having the inactive compounds used in the reverse dilution stage labelled by a second different tracer to facilitate the recovery measurement. An example is the determination of testosterone in plasma¹¹.

5.2.2. *Radiorelease and isotope displacement reactions*—The same general radioreagent principle applies in this case, but the reactions involved are such that the radioactive tracer, instead of forming a new compound with the problem substance, is displaced or liberated in an amount proportional to it. An example is the measurement of oxygen dissolved in water by passing the water sample through a column filled with copper turnings on which thallium labelled with ²⁰⁴Tl has been electroplated¹². The reaction is



and the amount of the quantitatively liberated radioactivity can be readily determined directly in the water solution.

The necessary condition in this type of application is, of course, that the tracer liberated can be separated from the non-displaced excess without difficulties. Various electrochemical reactions, displacements of tracers from complexes of lower stability than those formed by the problem elements with the same complexing agent and other similar types of reactions, have been applied for the purpose.

5.3. Radiometric titrations

This denomination covers *isotopic* and *non-isotopic* methods, since the label may be placed on the element to be titrated, on the titrating reagent or on both. Furthermore, applications have been described in which neither of them but a third element acting as end point indicator is traced.

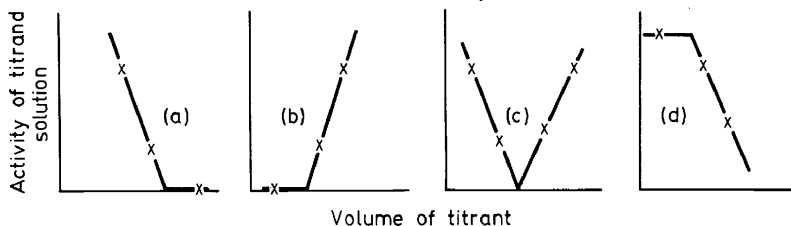


Figure 3. Ideal radiometric titration curves. Activity of solution titrated as a function of the volume of titrant added. (a) Titrand labelled; (b) Titrant labelled; (c) Titrand and titrant labelled; (d) Labelled indicator.

The general principle involved is the detection of the end point by measurements of radioactivity. This is clearly seen in the ideal curves given in Figures 3(a), 3(b) and 3(c) for the three most important cases. The curves represent the radioactivity of the solution titrated as a function of the volume of titrant added obtained after the portion already reacted has been separated. This separation is necessary and constitutes a drawback of the method. In principle, two measurements for each sloping line and one for each horizontal one are enough to determine the end point though, of course, it is convenient to plot as many as possible to have better accuracy.

The main advantage of the technique is the sensitivity of the end-point detection, which can be made very high even at low concentrations by using tracers of high specific activity. Also, radiometric titrations can be employed in coloured, heterogeneous, non-aqueous and other unusual media, since radioactivity measurements are not affected by these properties.

Precipitation reactions have been applied to determine many ions by this technique separating the solids by filtration or centrifugation. However, their sensitivity is seldom very good because of the limitations due to the solubility product and to the fact that precipitates must be large enough to be handled. A better situation is offered when complex-forming reactions and separation by the selective extraction of metal-organic complexes are used, a technique often able to handle quantitatively even carrier-free amounts and, therefore, of sensitivity limited only by the specific activity of the sample and the blanks of the reagents. For instance, cobalt has been determined at the 0.2 μg level by means of a 10^{-4} M solution of dithizone in carbon tetrachloride using ^{60}Co as isotopic tracer. The same radioisotope was used as non-isotopic indicator for the titration of 0.4 μg of zinc also with dithizone. In this case, the more stable zinc complex is extracted first and the titration curve has the shape shown in *Figure 3(d)*, where the end point is marked by the initiation of the extraction of the radioactively traced cobalt¹³.

(6) References

- ¹ *Radiochemical Methods of Analysis*, two volumes. STI/PU B/88, IAEA, Vienna (1965).
- ² *Chart of the Nuclides*, 3rd ed. Ministry of Scientific Research, Bonn, Germany (1968). (Available from Gersbach u. Sohn Verlag, 8 München 34, Barer Str. 32, Germany.)
- ³ G. Hevesy and R. Hobbie, *Z. Anal. Chem.* **88**, 1 (1932).
- ⁴ J. T. Craig *et al.*, *Analyt. Chem.* **25**, 1661 (1953).
- ⁵ G. C. Ashton and M. C. Foster, *Analyst*, **80**, 123 (1955).
- ⁶ F. A. Bacher *et al.*, *Analyt. Chem.* **26**, 1146 (1954).
- ⁷ C. N. Hales and D. J. Randle, *Biochem. J.* **88**, 137 (1963).
- ⁸ J. Ruzicka and J. Stary, *Atomic Energy Review*, **2** (No. 4), 3 (1964).
- ⁹ H. G. Richter, *Analyt. Chem.* **38**, 772 (1966).
- ¹⁰ G. A. Welford *et al.*, *Analyt. Chem.* **36**, 2350 (1964).
- ¹¹ A. Riondel *et al.*, *J. Chim. Endocrin. Metab.* **23**, 620 (1963).
- ¹² H. G. Richter and A. S. Gillespie Jr, *Analyt. Chem.* **34**, 1116 (1962).
- ¹³ J. F. Duncan and F. G. Thomas, *J. Inorg. Nucl. Chem.* **4**, 376 (1957).

PART II. CRITICAL LIST OF TRACERS

The list covers the radioactive isotopes more appropriate for use as tracers in analytical chemistry. Entries have been grouped under the corresponding element and elements listed according to their atomic numbers. The following information is given under each element.

(a) *Symbol of the nuclide*, followed by: (i) Half-life, in parentheses (h denotes hours, d days, y years). (ii) Microgrammes of carrier-free nuclide corresponding to 1 μCi , useful to obtain an orientation on the theoretical mass sensitivity of the tracer (see 1.3 above). (iii) Modes of decay (β^- denotes negatron; β^+ positron; EC electron capture; IT isomeric transition; α alpha). Only the more important are indicated, when more than one. After the corresponding symbol, data on the energy or other characteristic of the radiation are included when considered convenient. (iv) Information (yes or no) on whether the isotope is easily measurable by gamma-counting equip-

ment. (v) Decay product, indicating whether it is stable(St) or radioactive(R).

(b) *Comments.* If necessary, further information or clarification on the above is given here. The tracer (or tracers) considered more appropriate for analytical work are indicated and advice on the more convenient stockable form is given. (NOTE. In general, stocks are kept in N/1 or N/10 acid, usually hydrochloric, to minimize losses from adsorption in the walls of the container.)

(c) *References.* A few selected papers describing analytical work with radioactive tracers for the element covered are quoted.

(1) Hydrogen

^3H (12.3 y) $1 \times 10^{-4} \mu\text{g}$ β^- (very weak) No ^3He (St)

Comments. The only active isotope of hydrogen. Liquid scintillation counting is the best technique for tracer measurement. An alternative in the absence of LSC equipment is to measure in special gas GM counters as hydrogen. (See J. F. Cameron and B. J. Puckett, *UKAEA Rep. AERE-R 3092*(1960), and M. B. Crespi and H. Perschke, *Int. J. App. Rad. Isot.* **15**, 569 (1964)).

Stock. Tritiated water. Traced gaseous hydrogen can be prepared from it when required by complete reduction with magnesium metal.

References

- D. J. Chleck *et al.*, *Int. J. App. Rad. Isot.* **7**, 182 (1960). (Determination of active hydrogen in organic compounds by reaction with tritium-labelled lithium aluminium hydride.)
 C. Evans and J. Herrington, *Radioisotopes in the Physical Sciences and Industry*, Vol. II, p309. I.A.E.A.: Vienna (1962). (Determination of hydrogen in metals by isotope dilution with tritium.)
 J. F. Cameron *et al.*, *Brit. J. Appl. Phys.* **10**, 463 (1959). (Measurement of solubility of water in a halogenated oil by means of tritiated water.)
 G. Joris and H. Taylor, *J. Chem. Phys.* **16**, 45 (1968). (Solubility of water in benzene.)
 G. H. Aylward *et al.*, *J. Inorg. Nucl. Chem.* **16**, 350 (1961). (Radiometric titration of copper with tritium-labelled reagent.)

(2) Helium

No radioactive tracer available.

(3) Lithium

No radioactive tracer available.

(4) Beryllium

^7Be (53.4 d) $3 \times 10^{-6} \mu\text{g}$ EC Yes ^7Li (St)

Stock. Carrier-free beryllium chloride solution.

References

- T. Y. Toribara and R. E. Sherman, *Analyt. Chem.* **25**, 1594 (1963). (Studies on separation of microamounts and determination by fluorimetry.)
 I. Feldman *et al.*, *J. Am. Chem. Soc.* **77**, 878 (1955). (Ion-exchange studies on the beryllium citrate system.)

(5) Boron

No radioactive tracer available.

(6) Carbon

^{14}C (5730 y) $0.2 \mu\text{g}$ β^- (weak) No ^{14}N (St)

Comments. Liquid scintillation counting is the best technique for tracer measurement, with over 90 per cent efficiency, compared with less than one per cent for counting of solid sources with most thin end-window GM counters. It can be purchased as barium carbonate at a ^{14}C isotopic abundance of over 70 per cent, more than adequate for any analytical applications. *Stock.* Solid barium carbonate, from which gaseous carbon dioxide and other carbonates can be easily obtained.

References

NOTE. Most analytical applications of ^{14}C belong to organic chemistry and correspond to the use of labelled compounds (see, f.i., 5.1.1, 5.1.2 and 5.2.1 above).

H. Wuttkowski, *Giesserei Praxis*, **17**, 343 (1961). (Carbon determination in steel.)

A. A. Cochran *et al.*, *J. Metals*, **15**, 914 (1963). (Carbon distribution in steel by autoradiography.)

(7) Nitrogen

No radioactive tracer available. ^{13}N , a 100 per cent positron emitter of ten minutes half-life, is the only choice for laboratories adjacent to a reactor or an accelerator. Most tracer work with nitrogen, very important in biological studies, is made with the stable isotope ^{15}N and requires a mass spectrometer for the measurements.

(8) Oxygen

No radioactive tracer available. As in the case of nitrogen, stable ^{18}O is used for tracer work when necessary.

(9) Fluorine

^{18}F (110 m) $1 \times 10^{-8} \mu\text{g}$ β^+ Yes ^{18}O (St)

Comments. The only radioactive tracer for fluorine. It is an excellent one, very easy to measure by the annihilation radiation of the positron and very sensitive, but unfortunately has a half-life too short to make it appropriate for general use. It can be employed near its source of production in experiments of short duration. It is available carrier-free as sodium fluoride.

References

J. H. Fremlin *et al.*, *Nature, London*, **180**, 1179 (1957). (Determination of small amounts of fluorine by isotope dilution.)

R. Muenze, *Kernenergie*, **3**, 429 (1960). (Fluorine coprecipitation on barium sulphate.)

(10) Neon

No radioactive tracer available.

(11) Sodium

^{22}Na (2.6 y) $1.5 \times 10^{-4} \mu\text{g}$ β^+ Yes ^{22}Ne (St)

^{24}Na (15 h) $1 \times 10^{-7} \mu\text{g}$ β^- Yes ^{24}Mg (St)

Comments. Both are good analytical tracers, but the short half-life of ^{24}Na is inconvenient unless supply from a reactor or accelerator is close at hand. ^{24}Na is available at much higher specific activities than ^{22}Na (about 300 times).

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It is advisable to keep a permanent stock of ^{22}Na for general use and to order ^{24}Na when necessary for special work.

Stock. Sodium chloride solution.

References

C. V. Robinson *et al.*, *J. Clin. Invest.* **34**, 134 (1955). (Determination of exchangeable sodium in body by isotope dilution.)

H. Koch, *Kernenergie*, **3**, 315 (1960). (Separation and determination by isotope dilution.)

A. H. A. Heyn and H. L. Finston, *Analyt. Chem.* **32**, 328 (1960). (Separation of sodium and potassium from magnesium.)

(12) Magnesium

^{28}Mg (21.3 h) $2 \times 10^{-7} \mu\text{g}$ β^- Yes ^{28}Al (R)

Comments. The situation with magnesium is not very satisfactory. The only usable tracer is short-lived and decays to radioactive ^{28}Al which, in turn, leads by negatron emission to stable ^{28}Si . The half-life of ^{28}Al is 2.3 minutes; therefore, a sample of the magnesium tracer becomes contaminated with practically the same activity of an aluminium tracer in about 15 to 20 minutes (6 to 8 half-lives, necessary to reach secular equilibrium). The tracer should be used taking this into account, and the measurement of the magnesium activity should be made after equilibrium is reached in the separated sample. The tracer is available, in small amounts only, as magnesium chloride.

Reference

V. Shvedov, *Zh. Anal. Khim.* **3**, 147 (1948). (Study of the coprecipitation of magnesium with calcium oxalate using 10-minutes ^{27}Mg .)

(13) Aluminium

^{26}Al (7.4×10^5 y) $2 \mu\text{g}$ β^+ Yes ^{26}Mg (St)

Comments. The aluminium situation is also unsatisfactory. The only usable tracer is available at low specific activities (less than 10^3 dpm/mg), is very expensive and has small mass sensitivity. It has found practically no use in analysis up to now.

(14) Silicon

^{31}Si (2.6 h) $2 \times 10^{-8} \mu\text{g}$ β^- No ^{31}P (St)

Comments. Because of its short half-life, is non-stockable and should be obtained for immediate use when necessary. It can be detected by gamma-measuring equipment but with extremely low efficiency, since only less than one per thousand of its disintegrations take place with gamma ray emission. It has found practically no use in analysis up to the present time, though it is a potentially interesting tracer for laboratories near a source of production.

(15) Phosphorus

^{32}P (14.3 d) $3 \times 10^{-6} \mu\text{g}$ β^- (strong) No ^{32}S (St)

^{33}P (25.3 d) $6 \times 10^{-6} \mu\text{g}$ β^- (weak) No ^{33}S (St)

Comments. Both phosphorus tracers are appropriate for analytical purposes, but ^{32}P is to be preferred because it is easier to measure due to its much harder beta radiation (1.7 MeV against 0.2 for ^{33}P). The only advantage of ^{33}P is its capability to trace for a longer time at equal initial activity, but this is seldom important in analytical applications, since the half-life of ^{32}P is enough for this type of work. Also, ^{33}P is available at higher specific activities than ^{32}P and it is cheaper.

Stock. Disodium orthophosphate solution or phosphoric acid.

References

- A. Langer, *J. Phys. Chem.* **45**, 639 (1941). (Radiometric titration of various ions with labelled phosphate.)
 J. Fodor, *Acta Chim. Acad. Sci. Hung.* **19**, 13 (1959). (Phosphorus in steel by isotope dilution.)
 O. T. Quimby *et al.*, *Analyt. Chem.* **26**, 661 (1954). (Triphosphate and pyrophosphate in mixtures by isotope dilution.)
 J. Rijkheer, *J. S. Afr. Chem. Inst.* **13**, 1 (1960). (Phosphate in rocks by isotope dilution.)
 C. Sapetti, *Ann. Sper. Agrar. (Rome)*, **13**, 99 (1959). (Phosphate in soil by isotope dilution.)
 M. Thackray, *Nature, London*, **190**, 434 (1961). (Microanalysis of beryllium and magnesium by precipitation with radioactive phosphate.)
 A. R. Landgrebe *et al.*, *Analyt. Chem.* **38**, 1265 (1966). (Determination of various metals by separation by paper chromatography and precipitation with radioactive phosphate.)
 A. Mizuike *et al.*, *Bunski Kagaku*, **7**, 588 (1958). (Radiometric determination of magnesium by precipitation with radioactive phosphate.)
 I. P. Alimarin *et al.*, *Int. J. App. Rad. Isot.* **2**, 117 (1957). (Radiometric titration of various ions with radioactive phosphate.)
 J. M. Peixoto-Cabral and H. Goette, *Z. Naturforsch.* **10b**, 440 (1955). (Determination of fluorine by liberation of radioactive phosphorus from labelled zirconium phosphate.)
 A. I. Osipov *et al.*, *Zavod. Lab.* **21**, 391 (1955). (Rapid determination of phosphorus in slag.)

(16) Sulphur

^{35}S (88 d) $2 \times 10^{-6} \mu\text{g}$ β^- (weak) No ^{35}Cl (St)

Comments. As with ^{14}C , the best measuring technique is liquid scintillation, with over 90 per cent efficiency. Solid sources can be counted with thin window GM counters, but efficiency is usually less than one per cent.

Stock. Sulphuric acid in N/10 or N/100 solution.

References

- Z. N. Tarasova *et al.*, *Zavod. Lab.* **21**, 396 (1955). (Radiometric determination of combined sulphur in rubber.)
 G. A. Welford *et al.*, *Analyt. Chem.* **36**, 2350 (1964). (Determination of various cations by separation by paper chromatography and precipitation with radioactive sulphate.)
 P. C. van Erkelens, *Nature, London*, **172**, 357 (1953). (Radioactive hydrogen sulphide for quantitative paper chromatography of traces of metals.)
 S. L. Eisler, *Plating*, **39**, 1019 (1952). (Sulphate on chromium plating baths by isotope dilution.)
 A. I. Busev and V. M. Byr'ko, *Talanta*, **8**, 492 (1961). (Radiometric titrations with ^{35}S -labelled reagent.)

(17) Chlorine

^{36}Cl (3×10^5 y) $29 \mu\text{g}$ β^- No ^{36}Ar (St)

Comments. The only general purpose radioactive tracer for chlorine (^{38}Cl , of half-life 37 minutes) is also available, but due to its short duration can be

applied only in special cases and locations). Unfortunately, it is not very mass sensitive and is not available at specific activities of over 1 mCi/g. Measured with high efficiency (over 90 per cent) by liquid scintillation and reasonably well by conventional GM counting.

Stock. Sodium chloride solution.

References

- V. P. Maksimchuck and I. L. Rosenfel'd, *Dokl. Akad. Nauk SSSR*, **131**, 354 (1960). (Mechanism of the activating action of chloride ions on chromium electrodes.)
 J. K. Johannesson, *Analyst*, **86**, 72 (1961). (Microgram amounts of chloride by isotope dilution.)
 J. Yoffe *et al.*, *Bull. Res. Council. Israel*, **9A**, 253 (1960). (Radiometric titration of chloride with silver using ^{36}Cl .)

(18) Argon

^{37}Ar (34.5 d) $1 \times 10^{-5} \mu\text{g}$ EC No $^{37}\text{Cl}(\text{St})$

Comments. Measured by liquid scintillation counting only (0.0026 MeV chlorine x-rays). ^{41}Ar , measurable by gamma equipment, is also available, but its half-life is only 110 minutes.

Stock. Argon gas in ampoules.

(19) Potassium

^{42}K (12.4 h) $1.6 \times 10^{-7} \mu\text{g}$ β^- Yes $^{42}\text{Ca}(\text{St})$

^{43}K (22 h) $3 \times 10^{-7} \mu\text{g}$ β^- Yes $^{43}\text{Ca}(\text{St})$

Comments. No potassium tracer of half-life longer than one day is available. The only long-lived isotope is ^{40}K , present at about 0.01 per cent in natural potassium and responsible for the radioactivity of the normal element. It can be purchased at over 80 per cent enrichment, but is very costly (\$1400/mg) and unpractical for tracer use due to its very low maximum specific activity.

The usual tracer is ^{42}K , available from most radioisotope suppliers and satisfactory for many analytical applications. In special cases, costlier ^{43}K , which is available carrier-free, can be used.

Stock. Both are stocked (for a few days only) as potassium chloride solution.

References

- L. Corsa Jr *et al.*, *J. Clin. Invest.* **29**, 1280 (1950). (Exchangeable potassium in man by isotope dilution.)
 W. Geilmann and W. Gebaur, *Z. Anal. Chem.* **139**, 161 (1953). (Determination by precipitation of the tetraphenylboron compound.)
 J. Toperczer, *Z. Anal. Chem.* **180**, 265 (1961). (Potassium in phosphors by isotope dilution.)

(20) Calcium

^{45}Ca (165 d) $6 \times 10^{-5} \mu\text{g}$ β^- No $^{45}\text{Sc}(\text{St})$

Comments. Rather soft (0.3 MeV) betas, measured by liquid scintillation with over 90 per cent efficiency and with only 0.2 per cent by end-window GM counters on solid sources.

Stock. Calcium chloride solution.

References

- N. B. Mikheev, *Zh. Anal. Khim.* **14**, 735 (1951). (Determination of exchange capacity of ionites by isotope dilution.)
 J. T. Corless, *J. Chem. Educ.* **42**, 421 (1965). (Calcium in sea water.)
 J. Takanaka and Y. Minogami, *Yosui To Haisui*, **6**, 389 (1964). (Hardness of water by isotope dilution.)
 G. Barbier and E. Tiszkiwicz, *C.R. Acad. Sci., Paris*, **236**, 2105 (1953). (Diffusible calcium in soils.)
 J. Toperczer, *Z. Anal. Chem.* **180**, 265 (1961). (Calcium in phosphors by isotope dilution.)
 B. F. Scott and W. J. Driscoll, *Nucleonics*, **19** (No. 6), 49 (1961). (Determination of phosphate by precipitation with radioactive calcium.)
 J. Majer *et al.*, *Schweiz. Apoth. Ztg.* **98**, 631 (1960). (Radiometric titration of drug preparations containing calcium.)
 D. S. Berry and B. F. Scott, *Proc. 6th Conf. Anal. Chem. in Nucl. React. Technol.* (Gatlinburg, Tenn., 1962), *USAEC Rep. TID-7655*, 291 (1963). (Radiometric titration of fluoride used to determine silica in silicates.)

(21) Scandium

^{46}Sc (84 d) 3×10^{-5} μg β^- Yes ^{46}Ti (St)

^{47}Sc (3.4 d) 1×10^{-6} μg β^- Yes ^{47}Ti (St)

Comments. The usual tracer is ^{46}Sc . In special cases requiring high specific activities, costlier ^{47}Sc , which is available carrier-free, can be used.

Stock. Scandium chloride solution.

References

- G. K. Schweitzer and M. R. Bomar, *J. Am. Chem. Soc.* **77**, 4528 (1955). (Adsorption of scandium ions on various materials.)
 C. G. Warren *et al.*, *J. Inorg. Nucl. Chem.* **12**, 336 (1960). (Solvent extraction by monoalkylorthophosphoric acids.)
 K. Kimura *et al.*, *Bunseki Kagaku*, **6**, 719 (1957). (Cocprecipitation of scandium on ceric iodate.)

(22) Titanium

^{44}Ti (47.3 y) 5×10^{-3} μg EC Yes ^{44}Sc (R)

Comments. Very difficult to use. Gamma rays are of low energy (about 70 keV) and daughter ^{44}Sc decays with 3.9 days half-life by electron capture and positron emission, interfering with titanium detection. Scandium hold-back carrier, highly selective separations and quick measurements are necessary for perhaps only mediocre success. These circumstances and its high cost (about \$300/ μCi) are serious drawbacks discouraging its use. Unfortunately, it is the only tracer now available for titanium.

(23) Vanadium

^{48}V (16.2 d) 6×10^{-6} μg β^+ , EC Yes ^{48}Ti (St)

^{49}V (330 d) 1×10^{-4} μg EC No ^{49}Ti (St)

Comments. Both are available carrier-free and are apt for analytical use, but ^{48}V is cheaper and measurable by gamma equipment and should be preferred.

Stock. Vanadium oxychloride solution.

Reference

G. Leliaert *et al.*, *Talanta*, **1**, 369 (1958). (Vanadium in steels by isotope dilution.)

(24) Chromium

^{51}Cr (27.8 d) 1×10^{-5} μg EC Yes ^{51}V (St)

Stock. Chromic chloride solution.

References

R. Fukai. *Radiochemical Methods of Analysis*, STI/PUB/88, IAEA, Vienna, Vol. II, 335 (1965). (Chromium in marine organisms by isotope dilution.)

H. G. Richter, *Analyt. Chem.* **37**, 1146 (1965). (Radiorelease determination of dichromate in natural waters.)

(25) Manganese

^{52}Mn (5.7 d) 2×10^{-6} μg EC, β^+ Yes ^{52}Cr (St)

^{54}Mn (303 d) 1×10^{-4} μg EC Yes ^{54}Cr (St)

^{56}Mn (2.6 h) 5×10^{-8} μg β^- Yes ^{56}Fe (St)

Comments. The three tracers indicated can be purchased and are appropriate for analytical work. The best choice for general use is ^{54}Mn , which is available carrier-free and can be stocked for long periods. It is dearer than the other two, but its longer half-life makes it cheaper in the long run.

Stock. Manganous chloride solution.

References

L. Gordon *et al.*, *Analyt. Chem.* **26**, 992 (1954). (Coprecipitation of manganese on tin compounds.)

J. Mikulski and I. Stronski, *Nukleonika*, **6**, 295 (1961). (Separation of manganese, iron, cobalt and zinc by partition chromatography.)

J. T. Byrne and L. B. Rogers, *J. Electrochem. Soc.* **103**, 442 (1956). (Determination of manganese deposited with anodic lead dioxide.)

(26) Iron

^{55}Fe (2 60 y) 4×10^{-4} μg EC No ^{55}Mn (St)

^{59}Fe (45 d) 2×10^{-5} μg β^- Yes ^{59}Co (St)

Comments. ^{59}Fe is available at high specific activities (several mCi/mg) and, being measurable by gamma equipment, is recommended for general use. Measurement of ^{55}Fe is through low-energy 6 keV manganese x-rays by liquid scintillation; it is also available as a carrier-free, accelerator-produced isotope, and, while more expensive, it should be used when this condition is imperative. The mixture of both isotopes (elemental iron activated in a reactor) is also available at a lower price than any of them alone.

Stock. Ferric chloride solution in hydrochloric acid.

References

S. V. Bleshinskii and V. F. Abramova, *Izvest. Akad. Nauk SSSR*, **37**, 45 (1955). (Determination of beryllium with radioactive iron.)

I. M. Gibalo and V. M. Byr'ko, *Zavod. Lab.* **24**, 281 (1960). [Radiometric titration of zinc and cadmium by iron-labelled potassium hexacyanoferrate(II)].

- M. Mori and R. Tsuchiza, *Nippon Kagaku Zasshi*, **77**, 1525 (1956). (Partition of ferric chloride between organic solvents and hydrochloric acid.)
 J. Stary and J. Ruzicka, *Talanta*, **8**, 775 (1961). (Iron determination by substoichiometric isotope dilution.)
 C. N. La Rosa *et al.*, *Analyt. Chem.* **28**, 1447 (1956). (Interference of iron in the determination of tin in brass and bronze.)
 I. P. Alimarin and V. S. Sotnikov, *Trudy Kom. Analit. Khim., Akad. Nauk. SSSR*, **9** (12), 213 (1958). (Iron determination by phenyl-selenious acid.)
 J. Konecny *et al.*, *Acta Chim. Acad. Sci. Hung.* **51**, 245 (1967). (Radiometric titration of iron with EDTA.)

(27) Cobalt

^{56}Co (77d)	3×10^{-5} μg	EC, β^+	Yes	^{56}Fe (St)
^{57}Co (270d)	1×10^{-4} μg	EC	Yes	^{57}Fe (St)
^{58}Co (71d)	3×10^{-5} μg	β^+ , EC	Yes	^{58}Fe (St)
^{60}Co (5.3 y)	9×10^{-4} μg	β^-	Yes	^{60}Ni (St)

Comments. The situation with cobalt is particularly favourable, since four different satisfactory tracers are available. Of these, ^{60}Co is the cheapest, because of its bulk production at high specific activities for gamma radiation sources, and is the obvious choice for general analytical use. The other three are dearer. ^{58}Co is recommended if a carrier-free cobalt tracer is mandatory. *Stock.* Cobaltous chloride solution.

References

- P. C. Van Erkelens, *Analyt. Chim. Acta*, **26**, 46 (1962). (Trace analysis of cobalt using ^{60}Co and ^{35}S -labelled diethyl dithio carbamate.)
 N. Ishibashi *et al.*, *Bunseki Kagaku*, **15**, 637 (1966). (Radiometric titration of trace amounts of cobalt by EDTA.)
 A. R. Landgrebe *et al.*, *Radiochemical Methods of Analysis*, STI/PUB/88, IAEA, Vienna, Vol. II, 321 (1965). (Substoichiometric determination of trace amounts of cobalt.)
 T. Braun *et al.*, *Acta Chim. Acad. Sci. Hung.* **49**, 131 (1966). (Radiometric titration of cobalt.)
 H. Kohara and N. Ishibashi, *Bunseki Kagaku*, **15**, 642 (1966). (Determination of cobalt by paper chromatography and isotope dilution.)
 H. Koch, *Kernenergie*, **3**, 609 (1960). (Thallium radiometric titration with hexamminecobalt trichloride.)
 I. M. Korenman *et al.*, *Trudy Khim. i Khim. Tekhnol.* **94** (1959). (Determination of potassium by labelled hexanitrocobaltate.)
 D. I. Eristavi *et al.*, *Zh. Anal. Khim.* **14**, 631 (1959). [Radiometric titration of cobalt with potassium hexacyano ferrate(II).]
 H. H. Bradhurst *et al.*, *J. Inorg. Nucl. Chem.* **4**, 379 (1957). (Radiometric titration of tungstate ions with cobalt.)
 J. F. Duncan and F. G. Thomas, *J. Inorg. Nucl. Chem.* **4**, 376 (1957). (Radiometric titration of submicrogram amounts of cobalt and zinc with dithizone using ^{60}Co as indicator.)
 T. Ishimori and K. Ueno, *Bull. Chem. Soc. Japan*, **28**, 200 (1955). (Determination of small amounts of antimony with ^{60}Co -labelled organic reagent.)
 K. F. Sporek, *Analyt. Chem.* **33**, 754 (1961). (Cobalt determination by isotope dilution.)
 D. Salyer and T. R. Sweet, *Analyt. Chem.* **28**, 61 (1956). (Cobalt determination by electrodeposition with isotope dilution.)
 D. A. Lambie, *Analyst*, **84**, 173 (1959). (Cobalt determination with help of ^{60}Co . A new approach to radiochemical tracer analysis resulting in increased accuracy.)

(28) Nickel
 ^{63}Ni (92 y) $1.5 \times 10^{-2} \mu\text{g}$ β^- (soft) No ^{63}Cu (St)

 ^{65}Ni (2.6 h) $5 \times 10^{-8} \mu\text{g}$ β^- Yes ^{65}Cu (St)

Comments. ^{65}Ni is included here because it is the only nickel radioisotope available carrier-free and measurable by gamma equipment. Its short half-life is a serious drawback; for regular use, supply from a nearby reactor is necessary. ^{63}Ni is the normally stocked nickel tracer; it is measured by liquid scintillation with about 60 per cent efficiency.

Stock. Nickelous chloride solution.

References

- A. Kohn, *Chim. Analyt. (Paris)*, **44**, 425 (1962). (Nickel determination in Armco iron.)
 R. H. Herber and J. W. Irvine Jr, *J. Am. Chem. Soc.* **76**, 987 (1954). (Ion exchange separation.)

(29) Copper
 ^{64}Cu (12.8 h) $3 \times 10^{-7} \mu\text{g}$ β^- , EC, β^+ Yes ^{64}Zn (St); ^{64}Ni (St)

 ^{67}Cu (62 h) $1 \times 10^{-6} \mu\text{g}$ β^- Yes ^{67}Zn (St)

Comments. No isotope longer lived than ^{67}Cu is available. This can be obtained carrier-free and is preferable for analytical applications, but it is expensive, not regularly produced and offered only as a special product. The tracer currently available, with which most work has been done, is ^{64}Cu , which can be bought at specific activities high enough for analytical use.

Stock. Cupric chloride solution.

References

- K. Kudo, *Radioisotopes (Tokyo)*, **15**, 209 (1966). (Determination in aluminium by isotope dilution.)
 R. H. Herber and J. W. Irvine Jr, *J. Am. Chem. Soc.* **76**, 987 (1954). (Ion exchange separation.)
 J. Ruzicka and J. Stary, *Talanta*, **9**, 617 (1962). (Traces of copper with dithizone.)

(30) Zinc
 ^{65}Zn (245 d) $1 \times 10^{-4} \mu\text{g}$ EC Yes ^{65}Cu (St)

Comments. The isomeric mixture $^{69m}\text{Zn} + ^{69}\text{Zn}$, decaying with about 14 h half-life to stable ^{69}Ga , is also available, but it has no advantages over ^{65}Zn , which can be obtained at higher specific activities and is stockable for long periods.

Stock. Zinc chloride solution.

References

- P. Lerch and L. Kreienbuehl, *Chimia*, **15**, 519 (1961). (Determination in gallium by isotope dilution.)
 J. Stary and J. Ruzicka, *Talanta*, **8**, 296 (1961). (Determination of zinc with dithizone.)
 D. W. Margerum and F. Santacana, *Analyt. Chem.* **32**, 1157 (1960). (Tracer evaluation of some methods for zinc analysis.)
 K. Theurer and T. R. Sweet, *Analyt. Chem.* **25**, 119 (1953). (Determination in aluminium by electrodeposition with isotope dilution.)
 I. M. Korenman *et al.*, *Zh. Anal. Khim.* **12**, 48 (1957). (Radiometric titration of mercury and zinc with dithizone using ^{65}Zn as indicator.)

- H. Spitzy, *Microchim. Acta*, 789 (1960). (Radiometric titrations using ^{65}Zn as indicator.)
 A. D. Babko and P. V. Marchenko, *Zavod. Lab.* **25**, 1047 (1959). (Microimpurities in zirconium.)
 I. M. Korenman *et al.*, *Zavod. Lab.* **22**, 1143 (1956). (Radiometric titration of zinc.)
 J. Konecny and J. Tolgyessy, *Isotopenpraxis*, **3**, 479 (1967). (Radiometric titration of lead with EDTA and ^{65}Zn indicator.)

(31) Gallium

^{67}Ga (78 h)	2×10^{-6} μg	EC	Yes	$^{67}\text{Zn}(\text{St})$
^{68}Ga (1.1 h)	2×10^{-8} μg	β^+ , EC	Yes	$^{68}\text{Zn}(\text{St})$
^{72}Ga (14 h)	3×10^{-7} μg	β^-	Yes	$^{72}\text{Ge}(\text{St})$

Comments. The usual gallium tracer is ^{72}Ga , available at high specific activities but not carrier-free and non-stockable more than a few days due to its short half-life. When a carrier-free tracer is wanted, costlier ^{67}Ga should be used, which also cannot be stocked for long periods. ^{68}Ga , on the contrary, and in spite of its very short proper half-life, can be kept on hand by stocking its mother nuclide, 275-days ^{68}Ge , with which it coexists in secular equilibrium and from which a carrier-free activity of ^{68}Ga practically equal to the one of ^{68}Ge can be separated at any time. The gallium activity is regenerated in a few hours in the mother nuclide. At the time of writing (1968), ^{68}Ge 'cows', from which the ^{68}Ga could be easily 'milked', are being developed at various radioisotope producing centres.

Stock. Gallium trichloride or germanium-68 tetrachloride solutions in 4-6N hydrochloric acid.

References

- H. M. Irving and F. J. C. Rossotti, *Analyst*, **77**, 801 (1952). (Solvent extraction and separation of gallium, indium and thallium.)
 R. H. Herber and J. W. Irvine Jr, *J. Am. Chem. Soc.* **76**, 987 (1954). (Ion exchange separation.)

(32) Germanium

^{71}Ge (11 d)	6×10^{-6}	EC	No	$^{71}\text{Ga}(\text{St})$
^{77}Ge (11 h)	3×10^{-7}	β^-	Yes	$^{77}\text{As}(\text{R})$

Comments. The usual tracer, ^{71}Ge , is measured through the 9 keV gallium x-rays resulting from electron capture. Liquid scintillation efficiency is about 30 per cent. Gamma-active shorter-lived ^{77}Ge can be used but is not advisable, since its daughter nuclide is also gamma-active and of longer half-life (39 h) and, consequently, more elaborate radiochemical and measurement techniques than with other tracers are necessary for its successful application. The same considerations, though less serious because of the relative half-lives, are pertinent for ^{68}Ga (see gallium, above).

Stock. Sodium germanate in alkaline solution.

References

- L. K. Bradacs *et al.*, *Mikrochim. Acta*, 229 (1953). (Germanium determination in various materials using ^{71}Ge .)
 G. O. Brink *et al.*, *J. Am. Chem. Soc.* **79**, 1303 (1957). (Solvent extraction separations.)

(33) Arsenic

^{73}As (76 d)	$4 \times 10^{-5} \mu\text{g}$	EC	Yes	$^{73}\text{Ge}(\text{St})$
^{74}As (18 d)	$1 \times 10^{-5} \mu\text{g}$	β^- , β^+ , EC	Yes	$^{74}\text{Se}(\text{St})$: $^{74}\text{Ge}(\text{St})$
^{76}As (26.5 h)	$6 \times 10^{-7} \mu\text{g}$	β^-	Yes	$^{76}\text{Se}(\text{St})$
^{77}As (38.7 h)	$9 \times 10^{-7} \mu\text{g}$	β^-	Yes	$^{77}\text{Se}(\text{St})$

Comments. The longest lived isotope available, ^{73}As , can be obtained only in small amounts and is expensive. For general use, ^{74}As is the best, as it can be stocked for longer periods than ^{76}As , the usual arsenic tracer, which is also the cheapest. Both ^{74}As and ^{76}As can be purchased at high specific activities (10 to 100 mCi/mg), appropriate for most analytical applications. When very high values are needed, ^{77}As , available from one supplier at least at 1 Ci/mg, can be used.

Stock. Sodium arsenate solution.

References

- A. Kohn, *Chim. Analyt. (Paris)*, **44**, 425 (1962). (Determination of arsenic in iron and steel.)
 R. L. Bersin, *Nucl. Sci. Eng.* **23** (Sept), 21 (1965). (Determination of atomic hydrogen at very low pressures by reaction with radioactive arsenic.)
 P. Daudel, *C.R. Acad. Sci., Paris*, **220**, 658 (1945). (Microdetermination of silver with labelled arsenite ion.)
 S. Gomiscek, *Nova Proizvodnja*, **11**, 273 (1960). (Determination of arsenic in tin, pig iron and steel.)
 P. De Bruyne and J. Hoste, *Bull. Soc. Chim. Belg.* **70**, 221 (1961). (Separation of traces of arsenic from iron by fractional distillation.)

(34) Selenium

^{75}Se (120 d)	$7 \times 10^{-6} \mu\text{g}$	EC	Yes	$^{75}\text{As}(\text{St})$
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Stock. Sodium selenate or selenite solution.

References

- W. J. Kelleher and M. J. Johnson, *Analyt. Chem.* **33**, 1429 (1961). (Traces of selenium in organic matter by isotope dilution.)
 I. May and F. Cuttitta, *U.S. Geol. Surv. Prof. Paper 424-D*, 394 (1961). (Completeness of precipitation of selenium as the element.)

(35) Bromine

^{77}Br (56 h)	$1 \times 10^{-6} \mu\text{g}$	EC	Yes	$^{77}\text{Se}(\text{St})$
^{82}Br (35.4 h)	$9 \times 10^{-7} \mu\text{g}$	β^-	Yes	$^{82}\text{Kr}(\text{St})$

Comments. No longer-lived isotope is available. The tracer for general use is ^{82}Br , which can be stocked for short periods and is available at specific activities appropriate for analytical applications. When a carrier-free isotope is necessary, cyclotron-produced ^{77}Br , much dearer than ^{82}Br , is the only choice.

Stock. Sodium or ammonium bromide solution.

References

- A. Langer, *Analyt. Chem.* **22**, 1299 (1950). (Radiometric titration of labelled bromide with labelled silver nitrate.)

A. F. Reid, *J. Lab. Clin. Med.* **48**, 63 (1956). (Total body chloride in man by 'isotope dilution' with radiobromide.)

M. Martin *et al.*, *Analyt. Chim. Acta*, **3**, 222 (1949). (Chromatographic analysis of halides on alumina.)

E. Berne, *Acta Chem. Scand.* **5**, 1260 (1951). (Separation of halide ions on silver oxide exchange column.)

(36) Krypton

^{85}Kr (10.8 y) $3 \times 10^{-3} \mu\text{g}$ β^- No $^{85}\text{Rb}(\text{St})$

Comments. Measured by its beta radiation. The percentage of gamma rays emitted is too small (less than one per cent) to be used for measuring except in the case of large activities. Important analytical uses are based on the radio-release reactions which occur when the substance determined reacts with krypton-containing clathrates or with the surface of a solid in which ^{85}Kr has been introduced ('kryptonates') by gaseous diffusion or bombardment.

Stock. Krypton gas in ampoules.

References

D. J. Chleck and C. A. Ziegler, *Nucleonics*, **17** (No. 9), 130 (1959). (Preparation of ^{85}Kr -quinol clathrates.)

C. O. Hommel *et al.*, *Nucleonics*, **19** (No. 5), 94 (1961). (Ozone determination by radioactive clathrates.)

D. J. Chleck, *Radiochemical Methods of Analysis*, STI/PUB/88. IAEA, Vienna, Vol. II, 273 (1965). (Radioactive kryptonates: applications to analysis.)

I. Tolgyessy and S. Varga, *Talanta*, **16**, 625 (1969). (Radioactive kryptonates used to determine oxygen in water.)

(37) Rubidium

^{83}Rb (83 d) $5 \times 10^{-5} \mu\text{g}$ EC Yes $^{83}\text{Kr}(\text{St})$

^{84}Rb (33 d) $2 \times 10^{-5} \mu\text{g}$ EC, β^+ Yes $^{84}\text{Kr}(\text{St})$

^{86}Rb (18.7 d) $1 \times 10^{-5} \mu\text{g}$ β^- Yes $^{86}\text{Sr}(\text{St})$

Comments. The usual tracer is ^{86}Rb , which can be obtained at high specific activities and is apt for analytical use. The other two are produced in cyclotrons in carrier-free condition and are much more expensive. A mixture of 83 + 84 is available at reduced price.

Stock. Rubidium chloride solution.

References

E. S. Burkser and T. G. Kornienko, *Ukrain. Khim. Zh.* **24**, 375 (1958). (Rubidium in silicates.)

W. Geilmann and A. Gaenssle, *Glastech. Ber.* **27**, 80 (1954). (Determination in glass.)

W. Geilmann and W. Gebauhr, *Z. Anal. Chem.* **139**, 161 (1953). (Determination by precipitation of the tetraphenylboron compound.)

H. J. Arnkar, *Nature, London*, **182**, 1230 (1958). (Separation by chromatography.)

M. Ishibashi *et al.*, *Bunseki Kagaku*, **10**, 116 (1961). (Separation by ion exchange.)

(38) Strontium

^{85}Sr (65 d) $4 \times 10^{-5} \mu\text{g}$ EC Yes $^{85}\text{Rb}(\text{St})$

^{89}Sr (50.5 d) $3 \times 10^{-5} \mu\text{g}$ β^- No $^{89}\text{Y}(\text{St})$

Comments. Both are excellent tracers and can be purchased carrier-free or, at a much lower price, at specific activities appropriate for analytical use. ^{89}Sr is easily measured by GM counters in solution or in solid sources and, being cheaper, is to be preferred. The widely known isotope ^{90}Sr decays to radioactive ^{90}Y and is not as good a tracer as those given here.

Stock. Strontium chloride solution.

References

- J. Gilat, *J. Inorg. Nucl. Chem.*, **16**, 147 (1960). (Determination of ^{90}Sr by isotope dilution with ^{85}Sr .)
 J. Toperczer, *Z. Anal. Chem.* **180**, 265 (1961). (Determination in phosphors by isotope dilution.)
 G. Leliaert and J. Eeckhaut, *Analyt. Chim. Acta*, **16**, 311 (1957). (Determination by isotope dilution.)
 L. Berak and J. Muenich, *Coll. Czech. Chem. Commun.* **26**, 276 (1961). (Separation from calcium by sulphate precipitation.)
 S. Yu. Elovich and V. N. Prusakov, *Dokl. Akad. Nauk SSSR*, **112**, 684 (1957). (Separation of bi- and tri-valent ions by ion exchange chromatography.)

(39) Yttrium

^{88}Y (108 d) 7×10^{-5} μg EC Yes $^{88}\text{Sr}(\text{St})$

^{91}Y (59 d) 4×10^{-5} μg β^- No $^{91}\text{Zr}(\text{St})$

Comments. The situation with yttrium is similar to strontium. ^{91}Y is cheaper and should be preferred for general use. It can be easily measured by beta counters in solution or in precipitates.

Stock. Yttrium chloride solution.

References

- P. Sue *et al.*, *C.R. Acad. Sci. Paris*, **244**, 1212 (1957). (Determination in zone melting experiments.)
 B. M. Maryanov and V. V. Serebrennikov, *Sb. Voprosy Khimii, Izd. Tomsk. Gos. Univ.*, 195 (1963). (Radiometric titration of yttrium with cupferron.)
 E. Schumacher and H. J. Streiff, *Helv. Chim. Acta*, **41**, 1771 (1958). (Radiometric titration of yttrium with EDTA.)
 R. Lieberman *et al.*, *BMI-Report-1508* (1961). (Iron determination in cement by radiometric titration with EDTA using yttrium oxalate as solid indicator.)

(40) Zirconium

^{89}Zr (78.4 h) 2×10^{-6} μg EC, β^+ Yes $^{89}\text{Y}(\text{St})$

^{95}Zr (65 d) 5×10^{-5} μg β^- Yes $^{95}\text{Nb}(\text{R})$

Comments. The activity of the usual zirconium tracer, ^{95}Zr , gets contaminated by that of its daughter, ^{95}Nb (35 days, $\beta^- + \gamma$), at about two per cent per day in the first few days after its isolation. This must be taken into account and controlled (f.i., by adding hold-back niobium carrier before separations and measuring as soon as possible), especially when zirconium–niobium studies are made. Preferably, ^{89}Zr , decaying to a stable yttrium isotope, should be employed for this type of investigation. For general use, ^{95}Zr , which is much cheaper and longer lived, can be employed, provided the precautions mentioned above are taken for its measurement.

Stock. Zirconium oxalate complex in oxalic acid solution.

References

- H. Amano, *Sci. Rep. Res. Inst., Tohoku Univ.* **11(A)**, 296 (1959). (Determination in steel.)
 E. Huffman and L. Beaufait, *J. Am. Chem. Soc.* **71**, 3179 (1949). (Separation of zirconium and hafnium by extraction with thenoyltrifluoroacetone.)
 E. Huffman and R. Lilly, *J. Am. Chem. Soc.* **71**, 4147 (1949). (Anion exchange separation of zirconium and hafnium.)
 L. Kosta and L. Ravnik, *Proc. 2nd U.N. Conf. on the Peaceful Uses of Atomic Energy, Geneva*, **28**, 143 (1958). (Separation by precipitation with sodium hypophosphate.)
 I. M. Korenman *et al.*, *Trudy Kom. Anal. Khim., Akad. Nauk SSSR*, **11**, 198 (1960). (Precipitation of zirconium 'oxinate'.)

(41) Niobium

^{95}Nb (35 d) 2.5×10^{-5} μg β^- Yes ^{95}Mo (St)

Comments. As delivered, the tracer usually contains one to two per cent ^{95}Zr .
Stock. Niobium oxalate complex in oxalic acid solution.

References

- G. W. C. Milner and A. A. Smales, *Analyst*, **79**, 425 (1954). (Determination in stainless steel.)
 I. P. Alimarin and G. N. Bilimovitch, *Coll. Czech. Chem. Commun.* **26**, 255 (1961). (Determination by isotope dilution.)
 J. Beydon and C. Fisher, *Analyt. Chim. Acta*, **8**, 538 (1953). (Determination in mixtures with tantalum and titanium.)
 M. N. Bukhsh and D. N. Hume, *Analyt. Chem.* **27**, 116 (1955). (Determination in presence of tantalum.)
 T. E. Boyd and M. Galan, *Analyt. Chem.* **25**, 1568 (1953). (Determination of small amounts.)
 H. Amano, *Sci. Rep. Res. Inst., Tohoku Univ.* **11(A)**, 304 (1959). (Determination in steel.)
 P. Grandjean *et al.*, *Helv. Chim. Acta*, **43**, 848 (1960). (Determination in tantalum by isotope dilution.)
 K. V. Troitsky, *Zh. Analyt. Khim.* **12**, 349 (1957). (Separation by solvent extraction.)
 E. Bruninx *et al.*, *Analyt. Chim. Acta*, **14**, 74 (1956). (Separation of niobium and tantalum by paper electrophoresis.)

(42) Molybdenum

^{99}Mo (67 h) 5×10^{-5} μg β^- Yes $^{99\text{m}}\text{Tc}$ (R)

Comments. Measurements of ^{99}Mo (the only practical molybdenum tracer) are complicated by the presence of the radioactive technetium daughter nuclide, of 6.0 h half-life. The technetium activity grows to nearly ten per cent of the molybdenum one in the first hour after isolation and reaches transient equilibrium in about two days. Because of this, separated molybdenum should be measured not more than 10 to 15 min after the separation (when the contamination is less than two per cent), or at a fixed time after at least 48 hours (8 daughter half-lives), to ensure that the measurements are made under comparable conditions. Alternatively, gamma spectrometry may be used.
Stock. Ammonium molybdate in alkaline solution.

References

- E. H. Huffman *et al.*, *J. Inorg. Nucl. Chem.* **3**, 49 (1956). (Separation from technetium by ion exchange.)
 M. L. Geldhof *et al.*, *Bull. Soc. Chim. Belg.* **65**, 706 (1956). (Determination in steel by isotope dilution.)
 J. Pauly *et al.*, *Radiochemical Methods of Analysis*, STI/PUB/88, IAEA, Vienna, Vol. II, 297 (1965). (Determination in uranium by isotope dilution.)
 H. V. Weiss and M. G. Lai, *Talanta*, **8**, 72 (1961). (Determination in sea water.)

(43) Technetium

Synthetic element, formed only by artificially prepared radioactive isotopes. Some of them are used as non-isotopic tracers in medical applications but have found, so far, no applications in chemical analysis.

(44) Ruthenium

^{103}Ru (40 d) $3 \times 10^{-5} \mu\text{g}$ β^- Yes $^{103\text{m}}\text{Rh}(\text{R})$

^{106}Ru (1.0 y) $3 \times 10^{-4} \mu\text{g}$ β^- Yes $^{106}\text{Rh}(\text{R})$

Comments. Both isotopes decay to radioactive rhodium daughters; however, ^{106}Ru is to be preferred for tracer use as will be seen from the following discussion. $^{103\text{m}}\text{Rh}$ decays by isomeric transition to stable ^{103}Rh with 57 min half-life. As both ^{103}Ru and $^{103\text{m}}\text{Rh}$ emit gamma rays, the measurement of the ruthenium tracer is affected in a way similar to that discussed for magnesium above and requires special precautions, since 8 to 10 h are necessary to reach equilibrium. For ^{106}Ru , on the contrary, the situation is different. This isotope is a pure beta emitter and its daughter, ^{106}Rh , of only 30 sec half-life, decays by negatron and gamma emission to stable ^{106}Pd . Because of this, any isolated ruthenium fraction reaches radioactive secular equilibrium with its rhodium daughter in a few minutes and is measurable through the gamma radiation present. This is a typical case in which the decay of a radioisotope to a nuclide which is also radioactive is not a drawback but an advantage for the use of the first one as chemical tracer.

Stock. Ruthenium chloride solution.

References

- M. A. El Guebely, *Analyt. Chim. Acta*, **15**, 580 (1956). (Determination by isotope dilution.)
 J. Brandstet *et al.*, *Coll. Czech. Chem. Commun.* **26**, 2596 (1961). (Determination of the solubility product of ruthenium hydroxide.)
 J. Pauly *et al.*, *Radiochemical Methods of Analysis*, STI/PUB/88, IAEA, Vienna, Vol. II, 297 (1965). (Determination in uranium by isotope dilution.)

(45) Rhodium

^{105}Rh (36 h) $1 \times 10^{-6} \mu\text{g}$ β^- Yes $^{105}\text{Pd}(\text{St})$

Comments. The isotope, as purchased, is contaminated with longer lived ruthenium isotopes arising from its production from a ruthenium target, and it is normally necessary to separate it in the laboratory. It has seldom been applied for analytical purposes up to the present time.

(46) Palladium

^{103}Pd (17 d) $1 \times 10^{-5} \mu\text{g}$ EC Yes (low) $^{103\text{m}}\text{Rh}(\text{R})$

^{109}Pd (13.5 h) $4 \times 10^{-7} \mu\text{g}$ β^- Yes (low) $^{109\text{m}}\text{Ag}(\text{R})$

Comments. As in the case of ruthenium, both tracers lead to radioactive isotopes. Using ^{103}Pd , measurements should be made after 6 to 8 h, a period in which secular equilibrium with $^{103\text{m}}\text{Rh}$, of 57 minutes, which decays to stable ^{103}Rh , is established. With ^{109}Pd , the situation is much better, since $^{109\text{m}}\text{Ag}$ decays to stable ^{109}Ag with a half-life of only 40 sec and reaches equilibrium in a few minutes. For this reason, added to its much lower price,

^{109}Pd is preferred for tracer applications except when supply sources are too far away. Both isotopes are better measured by GM counters, since a large proportion of the gamma rays of its metastable daughters appear as internally converted electrons.

Stock. Palladous chloride solution.

References

- V. Voicu and I. Dema, *Acad. Rep. Pop. Rom., Stud. Cercet. Chim.* **7**, 431 (1959). (Determination by solvent extraction.)
 P. Spacu and V. Voicu, *Acad. Rep. Pop. Rom., Stud. Cercet. Chim.* **10**, 305 (1962). (Radiometric titration with thiocyanate, iodide and chromate.)

(47) Silver

^{105}Ag (41.2 d)	$3 \times 10^{-5} \mu\text{g}$	EC	Yes	$^{105}\text{Pd}(\text{St})$
$^{110\text{m}}\text{Ag}$ (253 d)	$2 \times 10^{-4} \mu\text{g}$	β^-	Yes	$^{110}\text{Cd}(\text{St})$
^{111}Ag (7.5 d)	$6 \times 10^{-6} \mu\text{g}$	β^-	Yes	$^{111\text{m}}\text{Cd}(\text{R})$

Comments. All three tracers have been used in analytical applications. The second one listed, $^{110\text{m}}\text{Ag}$, is by far the best, being cheaper, stockable for long periods, and easy to measure. The only advantage of the other two is that they are available carrier-free, a factor not very important in the case of silver due to the specific activity at which $^{110\text{m}}\text{Ag}$ can be purchased. Furthermore, ^{111}Ag shows the inconvenience of leading to 49-min $^{111\text{m}}\text{Cd}$ on its way to stable ^{111}Cd , demanding several hours to reach secular equilibrium before measurement.

Stock. Silver nitrate solution.

References

- W. J. Driscoll *et al.*, *USAEC Rept. TID-11306* (1961). (Exploration of the precipitation of chloride ion with radioactive silver and of other reactions as industrial process control methods.)
 J. Rygaert *et al.*, *Euratom Rept. EUR-2990f* (1966). (Determination of chloride in water by radioreagent precipitation with silver.)
 A. A. Shatolova and G. I. Meerov, *Biokhimiya*, **25**, 769 (1960). (Id. in blood plasma.)
 J. Ruzicka and P. Benes, *Coll. Czech. Chem. Commun.* **26**, 1784 (1961). (Microdetermination of silver by isotope dilution.)
 J. Govaerts and C. Barcia-Goyanes, *Analyt. Chim. Acta*, **6**, 121 (1952). (Determination of chromium, vanadium and molybdenum by precipitation of their anions with radioactive silver.)
 P. Bebesel and I. Sirbu, *Rev. Chim. (Bucarest)*, **11**, 288 (1960). (Radiometric titrations with radioactive silver.)
 J. Tolgyessy and V. Sajter, *Acta Chim. Acad. Sci. Hung.* **26**, 179 (1961). (Automatic radiometric titration.)
 J. Tolgyessy and M. Sarsunova, *Z. Anal. Chem.* **195**, 429 (1963). (Radiometric titration of phosphate with silver.)
 K. Mueller, *Analyt. Chim. Acta*, **35**, 162 (1966). (Determination of several metals by back-titration with EDTA using radioactive solid silver iodate as indicator.)
 Y. Nakamura and K. Fukami, *Bunseki Kagaku*, **6**, 687 (1957). (Studies on silver losses in cupeling.)
 A. Illaszewicz *et al.*, *J. Radioanal. Chem.* **1**, 39 (1968). (Use of radioactive silver metal as radio-reagent in redox titrations.)
 C. Beaudet and J. Rygaert, *J. Radioanal. Chem.* **1**, 153 (1968). (Portable equipment for chloride determination with labelled silver nitrate.)

(48) Cadmium¹⁰⁹Cd (1.3 y) 4 × 10⁻⁴ μg EC Yes ^{109m}Ag(R)^{115m}Cd (43 d) 4 × 10⁻⁶ μg β⁻ Yes ¹¹⁵In(St)

NOTE. ¹¹⁵In is a very long-lived (β⁻, 6 × 10¹⁴ y) radioisotope which can be taken as stable for our purposes.

Comments. The decay of ^{109m}Ag leads, with 40 sec half-life, to stable ¹⁰⁹Ag, facilitating ¹⁰⁹Cd measurements by reaching secular equilibrium in a few minutes, as in the case of ¹⁰⁶Ru above. The gamma radiation of the silver isomeric transition is largely converted, making beta activity measurements very satisfactory. ¹⁰⁹Cd is available carrier-free and is longer lived than ^{115m}Cd, being cheaper in the long run in spite of its higher price. However, the last one, decaying to ¹¹⁵In directly, without passing through ¹¹⁵Cd, is also satisfactory, and as it is a commonly produced radioisotope and easy to measure by gamma equipment, it has found wider use.

Stock. Cadmium chloride solution.

References

- A. K. Babko and P. V. Marchenko, *Zavod. Lab.* **25**, 1047 (1959). (Determination of cadmium in zirconium.)
 K. Saito *et al.*, *Bunseki Kagaku*, **9**, 299 (1960). (Studies on the determination of cadmium in uranium.)
 J. Konrad-Jakovac and Z. Pucer, *Croat. Chim. Acta*, **33**, 33 (1961). (Electrophoretic separation of cadmium-indium mixtures.)
 I. M. Korenman *et al.*, *Trudy Khim. i. Khim. Tekhnol.* **1**, 109 (1958). (Determination of copper with dithizone, cadmium indicator.)
 I. M. Gibalo and V. M. Byrko, *Zavod. Lab.* **24**, 281 (1958). [Cadmium determination by titration with hexacyanoferrate(II).]

(49) Indium¹¹¹In (2.8 d) 2 × 10⁻⁶ μg EC Yes ^{111m}Cd(R)^{114m}+¹¹⁴In (50 d) 4 × 10⁻⁵ μg IT + β⁻ Yes ¹¹⁴Sn(St)

NOTE. ^{113m}In, decaying with 1.7 h half-life to stable ¹¹³In, can be separated in the laboratory from the stock of ¹¹³Sn and used as a short-lived indium tracer in many applications.

Comments. Both tracers are usable for analytical purposes. ¹¹¹In is available carrier-free, but it shows the disadvantage that its daughter decays (to stable ¹¹¹Cd) with 49 min half-life, requiring 6 to 7 h to reach transient equilibrium and complicating its measurement. The pair ^{114m}+¹¹⁴In exists in secular equilibrium (¹¹⁴In is a pure negatron emitter of 72 sec half-life), behaving as a single nuclide of 50 d half-life. Since it is cheaper than ¹¹¹Cd, stockable for long periods and available at specific activities high enough for most applications, it is the preferred indium tracer for general use.

Stock. Indium chloride solution.

References

- G. M. Budov and V. V. Losev, *Dokl. Akad. Nauk SSSR*, **129**, 1321 (1959). (Electrode processes on indium amalgam.)
 E. B. Owens, *Analyt. Chem.* **32**, 1366 (1960). (Solvent extraction of indium bromide.)
 J. Sary *et al.*, *Talanta*, **11**, 481 (1964). (Radiometric titrations with EDTA and radioactive indium.)

(50) Tin

^{113}Sn (115 d) 1×10^{-4} μg EC Yes $^{113\text{m}}\text{In}(\text{R})$

$^{119\text{m}}\text{Sn}$ (245 d) 2×10^{-4} μg IT Yes $^{119}\text{Sn}(\text{St})$

Comments. Both are satisfactory tracers. The commoner, and cheaper, is ^{113}Sn , which shows the disadvantage that its daughter decays to stable ^{113}In with 1.7 h half-life, requiring about 10 h to reach equilibrium after tin separation to ensure comparable measuring conditions. $^{119\text{m}}\text{Sn}$ is a better tracer in this respect and is also obtainable radiochemically purer, but its price is higher. *Stock.* Stannic chloride in 6N hydrochloric acid.

References

- J. A. Dean *et al.*, *Analyt. Chim. Acta*, **11**, 390 (1954). (Electrodeposition studies.)
 S. Gomiscek, *Nova Proizvodnja*, **11**, 273 (1960). (Determination in pig iron and steel.)
 C. N. La Rosa *et al.*, *Analyst. Chem.* **28**, 1447 (1956). (Determination in brass.)

(51) Antimony

^{124}Sb (60 d) 6×10^{-5} μg β^- Yes $^{124}\text{Te}(\text{St})$

^{125}Sb (2.7 y) 9×10^{-4} μg β^- Yes $^{125\text{m}} + ^{125}\text{Te}(\text{R})$

NOTE. Approximately four fifths of the ^{125}Sb disintegrations lead directly to stable ^{125}Te and the remaining fifth to the isomeric $^{125\text{m}}\text{Te}$, which decays to ^{125}Te with 58 d half-life.

Comments. ^{124}Sb is recommended for tracer use. The apparent advantage of ^{125}Sb of being obtainable carrier-free is not important in this case, since ^{124}Sb can be purchased at high specific activities and it is cheaper and easier to use, decaying straightforwardly to a stable nuclide.

Stock. Antimony trichloride solution.

References

- I. E. Zimakov and G. S. Rozhavskii, *Trudy Kom. Anal. Khim.* **9**, 231 (1958). (Determination in lead by isotope dilution.)
 J. Stary and J. Ruzicka, *Talanta*, **11**, 697 (1964). (Determination by substoichiometric isotope dilution.)
 S. Gomiscek, *Nova Proizvodnja*, **11**, 273 (1960). (Determination in pig iron and steel.)
 K. Kimura *et al.*, *Nippon Kagaku Zasshi*, **74**, 305 (1953). (Separation from tin by ion exchange.)
 P. De Bruyne and J. Hoste, *Bull. Soc. Chim. Belg.* **70**, 221 (1961). (Separation from iron by fractional distillation.)
 D. I. Ryabchikov and M. M. Privalova, *Zh. Neorgan. Khim.* **3**, 1694 (1958); UCRL-tr-607. (Solvent extraction of antimony.)

(52) Tellurium

$^{127\text{m}} + ^{127}\text{Te}$ (109 d) 1×10^{-4} μg IT, β^- Yes $^{127}\text{I}(\text{St})$

$^{129\text{m}} + ^{129}\text{Te}$ (34 d) 3×10^{-5} μg IT, β^- Yes $^{129}\text{I}(\text{St})$

NOTE. ^{129}I is a very long-lived (β^- , 1.7×10^7 y) radioisotope which can be taken as stable for our purposes.

Comments. Both isomeric pairs are in secular equilibrium, as they are genetically related and the half-lives of the fundamental states are 9.3 h for ^{126}Te and 1.24 h for ^{129}Te . Also, both isomeric transitions are nearly 100 per cent

internally converted. Because of this and of the fact that ^{127}Te is a pure negatron emitter, measurement of pure $^{127\text{m}}+^{127}\text{Te}$ is better done by beta counting. However, the isotope as purchased normally contains other tellurium radioisotopes which are gamma active and make possible the use of gamma counting equipment. When measurements of high accuracy are wanted, it is advisable to add iodine hold-back carrier before the separations to control the contamination by iodine activities formed in the decay of these radiochemical impurities.

In the case of $^{129\text{m}}+^{129}\text{Te}$, about 70 per cent of the beta disintegrations of ^{129}Te are accompanied by unconverted gamma rays and measurement by gamma equipment is straightforward. This tracer is available radiochemically pure and is preferable to $^{127\text{m}}+^{127}\text{Te}$, though it is considerably more expensive.

Stock. Sodium tellurite solution.

Reference

G. T. Seaborg, *Chem. Rev.* **27**, 199 (1940). (Study of the coprecipitation with antimony.)

(53) Iodine

^{125}I (60 d) $6 \times 10^{-5} \mu\text{g}$ EC Yes $^{125}\text{Te}(\text{St})$

^{131}I (8.05 d) $8 \times 10^{-6} \mu\text{g}$ β^- Yes $^{131}\text{Xe}(\text{St})$

Comments. Both isotopes are available in carrier-free condition. The common tracer is ^{131}I , which is preferable because of the much higher efficiency with which it is measured by gamma equipment. It can be easily obtained all over the world due to its widespread use in medicine.

Stock. Sodium iodide in sodium thiosulphate solution.

References

M. S. Raben, *Analyt. Chem.* **22**, 480 (1950). (Microdetermination of iodine.)

M. Kahn and A. C. Wahl, *J. Chem. Phys.* **21**, 1185 (1953). (Behaviour of iodine at low concentrations.)

N. A. Kiseleva *et al.*, *Zavod. Lab.* **22**, 1291 (1956). (Determination of small amounts of copper using radioactive iodine.)

J. F. Duncan, *J. Inorg. Nucl. Chem.* **11**, 161 (1959). (Solubility product of lead iodide.)

Z. Herman, *Coll. Czech. Chem. Commun.* **26**, 1925 (1961). (Determination of microamounts of silver and bismuth with radioactive iodine.)

V. P. Pomazkov and V. P. Vasilev, *Izvest. Akad. Nauk SSSR, Ser. Fiz.* **28**, 1354 (1964). (Metallic barium by reaction with radioactive iodine.)

H. G. Richter, *Analyt. Chem.* **38**, 772 (1966). (Iodine in natural waters.)

T. Braun and E. Koros, *Radiochemical Methods of Analysis*, STI/PUB/88, IAEA, Vienna, Vol. II, 213 (1965). (Radiometric titration of thiosulphate with radioactive iodine.)

P. Beronius and A. B. Gabrielsson, *Analyt. Chim. Acta*, **40**, 352 (1968). (Microgram determination of iodide ion by isotopic exchange.)

J. Tolgyessy *et al.*, *Radiochemical Methods of Analysis*, STI/PUB/88, IAEA, Vienna, Vol. II, 199 (1965). (Radiocoulometric titration of iodide.)

H. H. Ross and W. S. Lyon, *Radiochemical Methods of Analysis*, STI/PUB/88, IAEA, Vienna, Vol. II, 285 (1965). (Radiorelease method for evaluation of sulphur dioxide pollution.)

C. B. Oxby and J. B. Dawson, *Radiochemical Methods of Analysis*, STI/PUB/88, IAEA, Vienna, Vol. II, 229 (1965). (Estimation of submicrogram amounts of iodine.)

P. Spacu and V. Voicu, *Acad. Rep. Pop. Rom., Stud. Cercet. Chim.* **10**, 305 (1962). (Determination of palladium with radioiodine.)

(54) Xenon
 ^{133}Xe (5.3 d) $5 \times 10^{-6} \mu\text{g}$ β^- Yes $^{133}\text{Cs}(\text{St})$

Comments. Available at high specific activities.

Stock. Xenon gas in ampoules.

(55) Caesium
 ^{134}Cs (2.1 y) $1 \times 10^{-4} \text{g}$ β^- Yes $^{134}\text{Ba}(\text{St})$
 ^{137}Cs (30 y) $1.5 \times 10^{-3} \mu\text{g}$ β^- Yes $^{137}\text{Ba}(\text{St})$

Comments. ^{137}Cs is a pure negatron emitter decaying to stable ^{137}Ba through gamma-active $^{137\text{m}}\text{Ba}$, of 2.5 min half-life, with which it reaches secular equilibrium 15 to 20 min after separation. Because of this, it is easily measured by gamma equipment (cf. ^{106}Ru). Both isotopes can be recommended for tracer work, since they are obtainable at high specific activities (carrier-free in the case of ^{137}Cs), are of similar price and do not present particular measuring problems.

Stock. Caesium chloride solution.

W. Cohn and H. Kohn, *J. Am. Chem. Soc.* **70**, 1986 (1948). (Separation of alkali metals by ion exchange.)

M. L. Granstrom and B. Kahn, *J. Phys. Chem.* **59**, 408 (1955). (Absorption of tracers on paper.)

M. Kyrs and L. Kadlecova, *Analyt. Chim. Acta*, **33**, 481 (1965); **36**, 215 (1966). (Determination of specific activity of ^{137}Cs solutions and caesium determination by extraction with dipicrylamine.)

W. Geilmann and A. Gaenssle, *Glastech. Ber.* **27**, 80 (1954). (Determination of caesium in glass.)

M. Ishibashi *et al.*, *Bunseki Kagaku*, **10**, 116 (1961). (Separation of caesium and rubidium by ion exchange.)

A. T. Casey and W. Robb, *Nature, London*, **198**, 581 (1963). [Radiometric titration of hexachloroplatinate(IV) ion with labelled caesium chloride.]

(56) Barium
 ^{133}Ba (10.7 y) $4 \times 10^{-4} \mu\text{g}$ EC Yes $^{133}\text{Cs}(\text{St})$
 ^{140}Ba (12.8 d) $1 \times 10^{-5} \mu\text{g}$ β^- Yes $^{140}\text{La}(\text{R})$

Comments. ^{133}Ba is available at high specific activities and is by far the better tracer of the two. If ^{140}Ba is employed, lanthanum hold-back carrier must be added before isolation and measurements must be done as quickly as possible, since the lanthanum activity grows to nearly two per cent in the first hour. It is impracticable to wait until transient equilibrium is established, as the half-life of ^{140}La is 40 h and about 13 d would be required.

Stock. Barium chloride solution.

References

S. L. Eisler, *Metal Finishing*, **50**, 71 (1952). (Determination of sulphate in chromium baths with radiobarium.)

H. Teicher, *Analyt. Chem.* **27**, 1416 (1955). (Precipitation of barium carbonate.)

E. Tompkins, *J. Am. Chem. Soc.* **70**, 3520 (1948). (Separation of alkaline-earth metals by ion exchange.)

J. Toperczer, *Z. Analyt. Chem.* **180**, 265 (1961). (Determination of barium in phosphors.)

(57) Lanthanum ^{140}La (40.2 h) 4×10^{-5} μg β^- Yes $^{140}\text{Ce}(\text{St})$

Stock. Lanthanum chloride solution.

ReferencesJ. Beydon, *C.R. Acad. Sci., Paris*, **224**, 1715 (1957). (Lanthanum-yttrium separation by sulphate precipitation.)J. Stary, *Coll. Czech. Chem. Commun.* **25**, 86 (1960). (Extraction with benzoylacetone.)A. Kohn, *Chim. Analyt. (Paris)*, **44**, 425 (1962). (Determination in steel.)J. Pauly *et al.*, *Radiochemical Methods of Analysis*, STI/PUB/88, IAEA, Vienna, Vol. II, 297 (1965). (Determination in uranium.)**(58) Cerium** ^{139}Ce (140 d) 1×10^{-4} μg EC Yes $^{139}\text{La}(\text{St})$ ^{141}Ce (32.5 d) 4×10^{-5} μg β^- Yes $^{141}\text{Pr}(\text{St})$ ^{144}Ce (284 d) 3×10^{-4} μg β^- Yes $^{144}\text{Pr}(\text{R})$

Comments. The best tracer by far is ^{139}Ce , which is available carrier-free and radiochemically pure. It is, however, very costly. The other two are less pure. ^{141}Ce may contain other cerium activities and some radioactive praseodymium, and it is important for many applications that this last contamination is kept under control. In the case of ^{144}Ce , measurements should be made after a couple of hours, necessary to reach secular equilibrium with 17 min ^{144}Pr . This nuclide decays to very long lived ^{144}Nd (α , 2×10^{15} y), which can be taken as stable for the present purposes.

Stock. Cerous chloride solution.

ReferencesD. Harris and E. Tompkins, *J. Am. Chem. Soc.* **69**, 2792 (1947). (Separation by ion exchange and determination by isotope dilution.)K. Kimura *et al.*, *Bunseki Kagaku*, **6**, 719 (1957). (Precipitation with potassium iodate from homogeneous solution.)A. J. Freedman and D. N. Hume, *Analyt. Chem.* **22**, 932 (1950). (Determination by isotope dilution.)V. P. Shvedov and F. I. Bei, *Radiokhimiya*, **2**, 234 (1960). (Separation on mercury cathode.)A. A. Cochran *et al.*, *J. Metals*, **15**, 914 (1963). (Radiometric analysis of steel.)J. Pauly *et al.*, *Radiochemical Methods of Analysis*, STI/PUB/88, IAEA, Vienna, Vol. II, 297 (1965). (Determination in uranium.)D. S. Berry and B. F. Scott, *USAEC Rep. TID-7655*, 291 (1963). (Radiometric determination of silica using cerium tracer.)**(59) Praseodymium** ^{142}Pr (19.2 h) 9×10^{-7} μg β^- Yes $^{142}\text{Nd}(\text{St})$ ^{143}Pr (13.6 d) 2×10^{-6} μg β^- No $^{143}\text{Nd}(\text{St})$

Comments. Both isotopes are appropriate for analytical use, but ^{143}Pr , which is longer lived, available carrier-free and measurable by beta counting in solution or solid sources, is preferable for quantitative analytical work. As it is prepared from neutron irradiation of ^{142}Ce , it may need purification from small amounts of extraneous cerium activities for special applications.

Stock. Praseodymium chloride solution.

References

J. Alexa, *Coll. Czech. Chem. Commun.* **25**, 706 (1960). (Separation from europium by ion exchange.)
 A. S. Kostygov and O. F. Saunkin, *Zavod. Lab.* **33**, 678 (1967). (Control of purification of ammonium hexanitrocerate by use of praseodymium tracer.)

(60) Neodymium

^{147}Nd (11.1 d) $1 \times 10^{-5} \mu\text{g}$ β^- Yes $^{147}\text{Pm(R)}$

Comments. The promethium daughter decays with 2.62 y half-life to practically stable ^{147}Sm (α , 1×10^{11} y). Since the half-life of ^{147}Pm is longer than that of ^{147}Nd , no equilibrium (transient or secular) is established and the neodymium tracer changes to promethium with the course of time. The ratio of the promethium activity to that of neodymium varies exponentially and, starting with pure ^{147}Nd , is about 0.01 after 10 days, 0.03 after 20 days and over 0.25 at 50 days.

A general comment on rare-earths tracing is pertinent here. Due to its chemical similarity, an isotope of one of the lanthanides is frequently used as non-isotopic tracer for a neighbour element; f.i., ^{147}Pm has been employed successfully to trace neodymium and even cerium in quantitative applications in the presence of non-lanthanide elements. It is obvious that contaminations such as the one just discussed are insignificant in these cases. On the contrary, when separation or determination of individual rare-earth elements in a mixture are wanted, delicate separations by ion-exchange [cf. O. Samuelson, *Ion Exchange Separations in Analytical Chemistry*, pp 338 ff. Wiley: New York (1963)] and/or a multiple tracer approach with the purest isotopes available and differential detection by gamma spectrometry may be necessary.

In the particular case of the pair ^{147}Nd – ^{147}Pm , the first can be distinguished from the second, if necessary, by using gamma equipment for measuring, since ^{147}Pm is a pure beta emitter.

Stock. Neodymium chloride solution.

Reference

B. M. Maryanov and V. V. Serebrennikov, *Izd. Tomsk. Gos. Univ.* 256 (1962). (Radiometric titration of neodymium with oxalic acid.)

(61) Promethium

^{147}Pm (2.6 y) $1 \times 10^{-3} \mu\text{g}$ β^- (soft) No $^{147}\text{Sm(St)}$

Comments. Only artificially prepared radioisotopes exist for this element. The one mentioned above is best measured by liquid scintillation and has found analytical use as non-isotopic tracer for some lanthanides (see neodymium). It is, of course, inherently carrier-free.

Stock. Promethium chloride solution.

References

A. Bradley and H. Peterson, *J. Chem. Educ.* **37**, 398 (1960). (Solubility of a neodymium salt.)
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 B. M. Maryanov and V. V. Serebrennikov, *Radiokhimiya*, **5**, 347 (1963). (Radiometric titration of ^{147}Pm -labelled neodymium with cupferron.)

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B. M. Maryanov and V. V. Serebrennikov, *Zh. Analyt. Khim.* **18**, 58 (1963). (Identification of neodymium with other reagents.)

(62) Samarium

^{151}Sm (87 y)	$4 \times 10^{-2} \mu\text{g}$	β^- (soft)	No	$^{151}\text{Eu}(\text{St})$
^{153}Sm (47 h)	$2 \times 10^{-7} \mu\text{g}$	β^-	Yes	$^{153}\text{Eu}(\text{St})$

Comments. Both are available at specific activities high enough for analytical applications. ^{151}Sm , much longer lived and stockable, is to be preferred if liquid scintillation counting is available.

Stock. Samarium chloride solution.

Reference

D. Dyrssen and V. Dahlberg, *Acta Chem. Scand.* **7**, 1186 (1953). (Separation by solvent extraction.)

(63) Europium

^{152}Eu (12.4 y)	$5 \times 10^{-3} \mu\text{g}$	EC, β^-	Yes	$^{152}\text{Sm}(\text{St}); ^{152}\text{Gd}(\text{R})$
^{154}Eu (16 y)	$7 \times 10^{-3} \mu\text{g}$	β^-	Yes	$^{154}\text{Gd}(\text{St})$
^{155}Eu (1.8 y)	$8 \times 10^{-4} \mu\text{g}$	β^-	Yes	$^{155}\text{Gd}(\text{St})$

NOTE. ^{155}Gd is a very long lived (α , 1×10^{14} y) radioisotope which can be taken as stable for our purposes.

Comments. The three isotopes are appropriate for analytical use. ^{155}Eu is the only one available carrier-free, but this is not important in the present case due to the high specific activities at which the other two can be purchased. The best buy is a mixture of ^{152}Eu and ^{154}Eu offered by some manufacturers at a lower price than the individual isotopes.

Stock. Europium chloride solution.

References

M. W. Lerner and G. J. Petretic, *Analyt. Chem.* **28**, 227 (1956). (Separation of rare earths from thorium nitrate by solvent extraction.)

E. I. Onstott and W. P. Ellis, *Analyt. Chem.* **28**, 393 (1956). (Radiometric titration of fluoride with samarium nitrate labelled with radioactive europium.)

D. Dolar and Z. Draganic, *Rec. Trav. Inst. Rech. Structure Mat.* **2**, 77 (1953). (Separation from uranyl nitrate by ion exchange and determination.)

(64) Gadolinium

^{151}Gd (120 d)	$1 \times 10^{-4} \mu\text{g}$	EC	Yes	$^{151}\text{Eu}(\text{St})$
^{153}Gd (242 d)	$3 \times 10^{-4} \mu\text{g}$	EC	Yes	$^{153}\text{Eu}(\text{St})$

Comments. The two isotopes are appropriate for tracer use in analysis. For reasons of cost and easier availability, ^{153}Gd is preferred.

Stock. Gadolinium chloride solution.

(65) Terbium

^{160}Tb (72 d)	$9 \times 10^{-5} \mu\text{g}$	β^-	Yes	$^{160}\text{Dy}(\text{St})$
^{161}Tb (6.9 d)	$8 \times 10^{-6} \mu\text{g}$	β^-	Yes	$^{161}\text{Dy}(\text{St})$

Comments. The two isotopes are appropriate for tracer use in analysis. ^{161}Tb is available carrier-free and is costlier, but ^{160}Tb can be purchased at over 1 mCi/mg, more than enough for most applications.

Stock. Terbium chloride solution.

Reference

E. Schumacher and W. Friedli, *Helv. Chim. Acta*, **43**, 1013 (1960). (Determination of terbium by EDTA titration.)

(66) Dysprosium

^{159}Dy (144 d) 2×10^{-4} μg EC Yes ^{159}Tb (St)

Stock. Dysprosium chloride solution.

(67) Holmium

^{166}Ho (27 h) 1×10^{-6} μg β^- Yes ^{166}Er (St)

NOTE. The independent isomer ^{166m}Ho , which does not decay to ^{166}Ho but directly to ^{166}Er by $\beta^- + \gamma$, is also available. It is not appropriate for analytical applications because its half-life is 1.2×10^3 y and it can be purchased only at low specific activities.

Comments. Measurement of ^{166}Ho is best made by beta counting in solution or solid sources, since the gamma rays are weak and largely converted.

Stock. Holmium chloride solution.

(68) Erbium

^{169}Er (9.5 d) 1×10^{-5} μg β^- No ^{169}Tm (St)

Comments. Measurement is best by liquid scintillation counting, since beta particles are not very energetic.

Stock. Erbium chloride solution.

(69) Thulium

^{170}Tm (130 d) 2×10^{-4} μg β^- Yes ^{170}Yb (St)

Comments. Gamma activity is not very large; beta counting in solution or solid sources is preferable.

Stock. Thulium chloride solution.

(70) Ytterbium

^{169}Yb (32 d) 4×10^{-5} μg EC Yes ^{169}Tm (St)

Stock. Ytterbium chloride solution.

Reference

C. E. Crouthamel and D. S. Martin, *J. Am. Chem. Soc.* **72**, 1382 (1950). (Complex-ion formation and solubility in oxalate solutions.)

(71) Lutetium

^{177}Lu (6.7 d) 9×10^{-6} μg β^- No ^{177}Hf (St)

Comments. Measurement is best done by beta counting in solution or solid

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sources. The nuclide can be detected by gamma equipment but with very low efficiency.

Stock. Lutetium chloride solution.

References

B. M. Maryanov and V. V. Serenbrennikov, *Izd. Tomsk. Gos. Univ.* 256 (1962). (Radiometric titration with oxalic acid.)

B. M. Maryanov and V. V. Serenbrennikov, *Radiokhimiya*, **5**, 347 (1963). (Identification with cupferron.)

(72) Hafnium

^{175}Hf (70 d) 9×10^{-5} μg EC Yes ^{175}Lu (St)

^{181}Hf (42.5 d) 6×10^{-5} μg β^- Yes ^{181}Ta (St)

Comments. Both are appropriate analytical tracers. ^{181}Hf is a better choice, since it can be measured by both gamma and beta equipment and is available at very high specific activities. A mixture of the two can be purchased at a lower price from some manufacturers and it is also satisfactory.

Stock. Hafnium chloride solution.

References

H. Amano, *Sci. Rep. Res. Inst., Tohoku Univ.* **11**(A), 367 (1959). (Trace amounts in zirconium by isotope dilution.)

N. Getoff, *Atompraxis*, **5**, 472 (1959). (Determination in zirconium by isotope dilution.)

W. J. Maeck *et al.*, *Analyt. Chem.* **32**, 922 (1960). (Radioreagent method for fluoride.)

K. A. Kraus and G. Moore, *J. Am. Chem. Soc.* **71**, 3263 (1949). (Separation from zirconium by ion exchange.)

(73) Tantalum

^{182}Ta (115 d) 2×10^{-4} μg β^- Yes ^{182}W (St)

Comments. Available at very high specific activities.

Stock. Tantalum oxalate complex in oxalic acid solution.

References

I. P. Alimarin and G. N. Bilimovitch, *Coll. Czech. Chem. Commun.* **26**, 255 (1961). (Determination by isotope dilution.)

L. S. Aleksandrova and K. V. Chmutov, *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk*, No. 5, 801 (1960). (Separation of tantalum and niobium by adsorption chromatography on a charcoal column.)

S. Spauszus and M. Heimer, *Chem. Tech. (Berlin)*, **13**, 96 (1961). (Ion exchange separation and determination in steel.)

H. Amano, *Sci. Rep. Res. Inst., Tohoku Univ.* **11**(A), 360 (1959). (Determination by isotope dilution in presence of niobium.)

K. A. Kraus and G. Moore, *J. Am. Chem. Soc.* **71**, 3855 (1949). (Ion exchange separation of niobium and tantalum.)

J. Hoste *et al.*, *Chem. Weekblad*, **60**, 35 (1964). (Determination of tantalum and other metals by homogeneous precipitation.)

I. P. Alimarin and I. M. Gibalo, *Dokl. Akad. Nauk SSSR*, **109**, 1137 (1956). (Separation with cupferron.)

(74) Tungsten

^{181}W (130 d) 2×10^{-4} μg EC No ^{181}Ta (St)

^{185}W (74 d) 1×10^{-4} μg β^- No $^{185}\text{Re}(\text{St})$

^{187}W (24 h) 1×10^{-6} μg β^- Yes $^{187}\text{Re}(\text{St})$

NOTE. ^{187}Re is a very long-lived (β^- , 5×10^{10} y) radioisotope which can be taken as stable for our purposes.

Comments. ^{187}W is included here because it is the only tungsten radiotracer available which can be measured by gamma equipment. It has a short half-life, however, and can be stored only for a few days. The best general use tracer is ^{185}W , measurable by beta equipment on solution or solid sources and with best efficiency by liquid scintillation. ^{181}W requires liquid scintillation; its apparent advantages of being the only one available carrier-free and stockable for longer periods than ^{185}W are not very significant, since the last one can be purchased at very high specific activity and costs twenty times less.

Stock. Sodium tungstate in alkaline solution.

References

V. Pfeifer and F. Hecht, *Z. Anal. Chem.* **177**, 175 (1960). (Determination in steel by isotope dilution.)

V. Pfeifer, *Mikrochim. Acta*, 518 (1960). (Extraction of the tungsten-thiocyanate complex.)

H. Amano, *Sci. Rep. Res. Inst., Tohoku Univ.* **12**, 24 (1960). (Tracer study of spectrophotometric determination.)

I. E. Zimakov, *Zavod. Lab.* **25**, 133 (1959). (Determination of the solubility of barium tungstate.)

(75) Rhenium

^{183}Re (71 d) 1×10^{-4} μg EC Yes $^{183}\text{W}(\text{St})$

^{186}Re (3.8 d) 5×10^{-6} μg β^- . EC No $^{186}\text{Os}(\text{St}); ^{186}\text{W}(\text{St})$

Comments. Gamma rays are present in ^{186}Re disintegrations in too small amounts to permit efficient measurement; the isotope is best measured by beta equipment in solution or solid sources. It is available at very high specific activities and it is quite satisfactory for analytical use. ^{183}Re is a better tracer as it can be purchased carrier-free, is easily measured by gamma equipment and can be stocked for long periods, but is usually reserved for special problems due to its much higher cost.

Stock. Perrhenic acid in nitric acid solution.

References

M. Lederer, *Analyt. Chim. Acta*, **12**, 146 (1955). (Separation by paper chromatography.)

M. Koyama, *Bull. Chem. Soc. Japan*, **34**, 1766 (1961). (Separation from technetium by distillation.)

(76) Osmium

^{185}Os (94 d) 1×10^{-4} μg EC Yes $^{185}\text{Re}(\text{St})$

^{191}Os (15 d) 2×10^{-5} μg β^- Yes $^{191\text{m}}\text{Ir}(\text{R})$

Comments. ^{191}Os is measurable by gamma equipment in spite of being a pure beta emitter because it is in secular equilibrium with its daughter,

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which decays by isomeric transition, and with five seconds half-life, to stable ^{191}Ir . As to ^{185}Os , it is measured through its proper gamma rays.

None of the tracers is available carrier-free, but ^{191}Os can be obtained at a specific activity appropriate for most analytical applications.

Stock. Sodium chloro-osmate solution.

(77) Iridium

^{192}Ir (74 d) $1 \times 10^{-4} \mu\text{g}$ β^- , EC Yes $^{192}\text{Pt}(\text{St})$; $^{192}\text{Os}(\text{St})$

Stock. Ammonium or sodium hexachloroiridate(IV) solution.

Reference

K. W. Lloyd and D. F. C. Morris, *Talanta*, 7, 117 (1960). (Separation from platinum and rhodium by precipitation.)

(78) Platinum

^{197}Pt (18 h) $1 \times 10^{-6} \mu\text{g}$ β^- Yes $^{197}\text{Au}(\text{St})$

Comments. No stockable tracer for platinum is available. ^{193}Pt , a pure EC nuclide of more than 500 years half-life, can be obtained only at specific and total activities not appropriate for analytical use. ^{197}Pt is thus the only usable tracer. It is best measured by GM equipment (on solution or solid sources) and has some limitations, since it is available at moderate specific activities only.

Stock. Platinic chloride solution.

(79) Gold

^{195}Au (183 d) $3 \times 10^{-4} \mu\text{g}$ EC No $^{195\text{m}}\text{Pt}(\text{R})$

^{198}Au (2.7 d) $4 \times 10^{-6} \mu\text{g}$ β^- Yes $^{198}\text{Hg}(\text{St})$

Comments. ^{195}Au is the only tracer stockable for long periods. It can be measured by GM equipment (on solution or solid sources) through its largely converted gamma radiation or, with better efficiency, by scintillation counting. Measurements should be made as soon as possible after separation to avoid contamination by its active daughter, which decays to stable ^{195}Pt with four days half-life and also emits conversion electrons in large proportion.

The tracer commonly used, ^{198}Au , is much cheaper and should be preferred whenever its short half-life does not preclude its use. It is not available carrier-free, as ^{195}Au , but it can be purchased at specific activities of several mCi/mg, more than enough for analytical applications.

Stock. Tetrachlorauric acid solution.

References

S. Hirano *et al.*, *Bunseki Kagaku*, 9, 423 (1960). (Ion exchange separation from copper.)

A. N. Nesmeyanov *et al.* *Zh. Fiz. Khim.* 33, 342 (1959). (Radiometric measurement of vapour pressure in solid solutions.)

(80) Mercury

^{203}Hg (47 d) $7 \times 10^{-5} \mu\text{g}$ β^- Yes $^{203}\text{Tl}(\text{St})$

Comments. $^{197m+197}\text{Hg}$ is also available and can be obtained carrier-free, but it is short-lived and measured less efficiently by gamma scintillation equipment. ^{203}Hg is recommended, as it is available at specific activities high enough for analytical applications.

Stock. Mercuric chloride or acetate solution.

References

- J. W. Irvine and C. Goodman, *J. Appl. Phys.* **14**, 496 (1943). (Determination of gaseous mercury in air.)
 J. Ruzicka and J. Stary, *Talanta*, **8**, 535 (1961). (Determination of trace amounts.)
 H. C. Moser and A. F. Voigt, *J. Inorg. Nucl. Chem.* **4**, 354 (1957). (Extraction of mercuric iodide.)
 P. C. van Erkelens, *Analyt. Chim. Acta*, **26**, 46 (1962). (Radiometric trace analysis of cobalt with radioactive tracers.)
 J. F. Duncan and F. G. Thomas, *J. Inorg. Nucl. Chem.* **4**, 376 (1957). (Radiometric titration of mercury with dithizone.)

(81) Thallium

^{204}Tl (3.8 y) $2 \times 10^{-3} \mu\text{g}$ β^- No ^{204}Pb (St)

Comments. Measurement by GM equipment on solution or solid sources.

Stock. Thallous sulphate or nitrate solution.

References

- T. Ishimori and Y. Takashima, *Bunseki Kagaku*, **6**, 175 (1957). (Radiometric analysis of lead using thallium-204.)
 T. Ishimori and Y. Takashima, *Nippon Kagaku Zasshi*, **76**, 858 (1955). (Determination of traces of thallium.)
 S. A. Sirotina and I. P. Alimarin, *Zh. Analyt. Khim.* **12**, 367 (1957). (Radiometric titration with tetraphenylboron.)
 P. C. van Erkelens, *Analyt. Chim. Acta*, **26**, 32 (1962). (Trace analysis of lead with diethyl-dithiocarbamate and thallium-204.)
 J. Majer *et al.*, *Schweiz. Apoth. Ztg.* **98**, 631 (1960). (Determination of iodine and iodide in presence of each other.)
 C. Beaudet and J. Rygaert, *J. Radioanal. Chem.* **1**, 153 (1968). (Portable equipment for oxygen determination by radiorelease of thallium-204.)

(82) Lead

^{210}Pb (22 y) $1 \times 10^{-2} \mu\text{g}$ β^- (soft) No ^{210}Bi (R)

Comments. The daughter activity decays to α -active ^{210}Po with 5.0 d half-life and this to stable ^{206}Pb . The best measurement technique would be to wait until secular equilibrium is established and count the hard (1.2 MeV) beta radiation of ^{210}Bi (on solution or a solid source) by means of a GM counter. The growing polonium activity is not detected and does not interfere. As a quicker alternative, ^{210}Pb can be separated from the ^{210}Bi grown during the experiment by means of a small cation-exchange column [cf. O. Samuelson, *Ion Exchange Separations in Analytical Chemistry*, pp 406-7, Wiley: New York (1963)] and measured as soon as possible by liquid scintillation counting.

Stock. Lead nitrate solution.

References

- G. Hevesy and R. Hobbie, *Z. Anal. Chem.* **88**, 1 (1932). (Determination of lead in rocks.)
 C. Rosenblum, *Chem. Revs.* **16**, 99 (1935). (Several examples.)
 H. von Buttlar, *Naturwissenschaften*, **42**, 90 (1955). (Determination in minerals by isotope dilution.)
 E. Ledehit *et al.*, *Bull. Soc. Belge Geol. Pal. Hydr.* **65**, 233 (1956). (Age of a mineral.)
 P. C. van Erkelens, *Analyt. Chim. Acta*, **26**, 32 (1962). (Trace analysis.)
 A. Lagrou and F. Verbeek, *J. Electroanal. Chem.* **9**, 184 (1965). (Trace analysis by isotope dilution.)

(83) Bismuth

^{206}Bi (6.2 d)	$1 \times 10^{-5} \mu\text{g}$	EC	Yes	^{206}Pb (St)
^{207}Bi (28 y)	$2 \times 10^{-3} \mu\text{g}$	EC	Yes	^{207}Pb (St)
^{210}Bi (5.0 d)	$8 \times 10^{-6} \mu\text{g}$	β^-	No	^{210}Po (R)

Comments. Both bismuth-206 and -207 are available carrier-free and are excellent bismuth tracers; the second one shows the further advantage that it can be stored for very long periods. They are accelerator-produced, however, and very expensive compared with ^{210}Bi . This is also a very good tracer, measurable by GM equipment; as mentioned under Lead above, its decay products can be taken as stable for this measuring technique. It can be stored as the mother nuclide, ^{210}Pb , fixed in a cation exchanger from which ^{210}Bi can be 'milked' at will when necessary and where secular equilibrium is continuously reestablished (cf. Lead, above).

Stock. Bismuth chloride solution or ^{210}Pb cation exchange column.

References

- B. Sagortschew, *Z. Anal. Chem.* **116**, 24 (1939). (Coprecipitation with lead.)
 M. Ishibashi *et al.*, *Nippon Kagaku Zasshi*, **75**, 13 (1954). (Controlled potential electrolytic separation from copper and lead.)
 J. Stary and J. Ruzicka, *Talanta*, **11**, 697 (1964). (Substoichiometric determination.)

(84–104) Polonium, astatine, radon, francium, radium, actinium, actinides (90 to 103) and 104

All elements after bismuth exist only as radioactive isotopes, natural or artificial. Tracer techniques, using a more active radioisotope to follow the behaviour of a long-lived one, not so easily detectable, have been applied in some cases, especially for thorium and uranium.

In the case of thorium, a good tracer is ^{234}Th (UX_1), of 24 d half-life, which can be obtained in the laboratory from an old (six months or so) uranium salt, which exists in secular equilibrium. A solution of uranyl nitrate, f.i., is passed through a small cation exchange column and the column washed with 2N hydrochloric acid. ^{234}Th is retained in the resin bed and can be eluted afterwards with 0.5 M oxalic acid solution (cf. O. Samuelson, *op. cit.* under Lead above, p 353).

In the case of uranium, ^{237}U (β^- , 6.7 d) and ^{233}U (α , 1.6×10^5 y), both artificial isotopes, have been used.

For the other elements at the end of the periodic table, tracer techniques should be reserved for the specialized radiochemical laboratory, as they

can hardly be included in common analytical practice due to the particular requirements necessary.

References

- J. Govaerts and A. Lambrechts, *Bull. Soc. (Roy.) Sci. Liège*, **11**, 35 (1942). (Application of natural uranium as a possible radioreagent for zinc determination.)
- H. V. Weiss *et al.*, *Analyt. Chim. Acta*, **25**, 550 (1961). (Determination of uranium in sea-water by isotopic dilution with ^{237}U .)
- V. I. Kusnetsov and T. G. Akimova, *Zh. Analyt. Khim.* **13**, 79 (1958). (Use of ^{233}U to study the determination of uranium in sea-water.)
- J. D. Wilson *et al.*, *Analyt. Chim. Acta*, **23**, 505 (1960). (Use of ^{237}U in the determination of uranium in sea-water.)
- D. Ledehet *et al.*, *Bull. Soc. Belge Geol. Pal. Hydr.* **65**, 233 (1956). (Thorium determination in rocks using ^{234}Th .)
- E. D. Goldberg, in *Submicrogram Experimentation*, N. D. Cheronis (ed.), Interscience: New York (1961). (Determination of thorium in sea-water and marine organisms using ^{234}Th .)
- F. Molnar and G. Toth, *Acta Chim. Acad. Sci. Hung.* **19**, 75 (1959). (Study of ion exchange separations using ^{234}Th .)

APPENDIX I—RADIOISOTOPE PRODUCERS AND SUPPLIERS

Most countries nowadays operate nuclear reactors and accelerators of different sizes and are usually able to supply some locally produced radioisotopes of short half-life. Longer-lived isotopes can be obtained from national or international firms, frequently government-owned, which have specialized for many years and now stock a wide assortment of radioactive isotopes and labelled chemicals. Comprehensive lists are periodically published (see refs. 1 and 2 below) and should be consulted for wider information than the one given here.

- ¹ *International Directory of Isotopes (3rd ed.)*. International Atomic Energy Agency: Vienna (1964).
- ² J. L. Sommerville, *The Isotope Index*. Scientific Equipment Co., P.O.B. 19086, Indianapolis 19, Indiana, USA.
- ³ *Radioactive Products*, Catalogue 1969/70. The Radiochemical Centre, Amersham, Bucks., England.
- ⁴ *Radioisotopes, Stable Isotopes and Research Materials*. Catalogue 7-67. Isotopes Development Center, Oak Ridge National Laboratory, P.O.B.X., Oak Ridge, Tenn., USA.
- ⁵ *Radioisotopes Catalogue*. V/O SOJUZCHIMEXPORT, Smolenskaya Square 32/34, Moscow G-200, USSR.
- ⁶ *Radioéléments et Molécules Marquées*. C.E.A. (France), C.E.N. (Belgium), SORIN (Italy). Available from the three institutions. French address: C.E.A., Département des Radioéléments, B.P. No. 2, 91-Gif-sur-Yvette, France.
- ⁷ *Radionuclides 1969*. New England Nuclear, 575 Albany Street, Boston, Mass. 02118, USA.
- ⁸ *Nuclides and Radioactive Compounds Catalogue*. Tracerlab, 1601 Trapelo Rd, Waltham, Mass. 02154, USA.
- ⁹ *Radiochemicals Catalogue*. Mallinckrodt/Nuclear, Box 6172, Lambert Field, Miss. 63145, USA.
- ¹⁰ *Radioactive Products*. MEDIMPEX, Budapest 5, P.O. Box 126, Hungary.
- ¹¹ *Nuclear Chemicals*. Duphar, N. V. Philips-Duphar, Petten, Holland.

APPENDIX II—BIBLIOGRAPHY

(A) Analytical applications

- ¹ D. A. Lambie, *Techniques for the Use of Radioisotopes in Analysis*. Spon: London (1963).

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- ² T. Braun and J. Tolguessy, *Radiometric Titrations*. Pergamon: Oxford (1967).
- ³ A. J. Moses, *Nuclear Techniques in Analytical Chemistry*. Pergamon: Oxford (1964).
- ⁴ L. M. Michejewa and N. B. Michejew, *Radioaktive Isotope in der Analytischen Chemie*. Akademie-Verlag: Berlin (1962).
- ⁵ S. A. Reynolds and G. W. Leddicote, *Radioactive Tracers in Analytical Chemistry*, *Nucleonics*, **21**, No. 8, 128–40 (1963).
- ⁶ J. W. McMillan, *Radioactive Tracer Methods in Inorganic Trace Analysis: Recent Advances*, *Analyst*, **92**, 539–48 (1967).
- ⁷ H. Weiler, 'The accuracy of isotope dilution methods', *Int. J. Appl. Rad. Isot.* **12**, 49–51 (1961).
- ⁸ D. A. Lambie, 'Radiochemical tracer analysis: a new approach resulting in increased accuracy'. *Analyst*, **84**, 173–76 (1959).

(B) General

- ¹ G. Friedlander, J. W. Kennedy and J. M. Miller, *Nuclear and Radiochemistry*, Wiley: New York (1964).
- ² M. Haissinsky, *La Chimie Nucléaire et Ses Applications*. Masson: Paris (1957). [English translation: *Nuclear Chemistry and Its Applications*, Addison-Wesley: Reading, Mass. (1964)].
- ³ S. Glasstone, *Sourcebook on Atomic Energy* (3rd ed.) Van Nostrand: Princeton, N.J. (1967).
- ⁴ J. F. Duncan and G. B. Cook, *Isotopes in Chemistry*, Clarendon Press: Oxford (1968).
- ⁵ R. T. Overmann and H. M. Clark, *Radioisotope Techniques*, McGraw-Hill: New York (1960).
- ⁶ R. A. Faires and B. H. Parks, *Radioisotope Laboratory Techniques*, (2nd ed.), Pitman: New York (1960).
- ⁷ C. E. Crouthamel, *Applied Gamma-Ray Spectrometry*, Pergamon: Oxford (1960).
- ⁸ J. Sharpe, *Nuclear Radiation Detectors* (2nd ed.). Wiley (Methuen): New York (1964).
- ⁹ B. J. Wilson (Ed.) *The Radiochemical Manual* (2nd ed.). The Radiochemical Centre, Amersham, England (1966).
- ¹⁰ W. S. Lyon *et al.* 'Methods for assay of radioisotopes'. *Nucleonics*, **24**, No. 8, 116 (1966).
- ¹¹ *Source Material for Radiochemistry* (1965 revision). *Publication 1351*, National Academy of Sciences–National Research Council: Washington, D.C., USA. (Available from Printing and Publishing Office, N.A.Sc., 2101 Constitution Ave., Washington, D.C. 20418, USA.) Contains a comprehensive list of books and publications of interest for radiochemistry and its applications.
- ¹² B. J. Wilson, *Selected References to Tracer Techniques*. The Radiochemical Centre, Amersham, England.
- ¹³ *Monographs on the Radiochemistry of the Elements*. Individual monographs on one element or a small group of elements sponsored by the Subcommittee in Radiochemistry of the National Academy of Sciences–National Research Council. Available from Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U.S. Department of Commerce, Springfield, Va 22151, USA.