18. *Choice of the Optimum Quantity and Constitution of the Tracer Used for Isotopic Dilution Analysis.*

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A detailed treatment of the dependence of the error in a mass-spectrometric determination on the constitution of the tracer or the quantity used has been made. Relations are derived between the measured isotopic ratios and the required quantity, so that uncertainty in the latter can be related to experimental errors in the former; they allow the most suitable tracer and the optimum quantity to be chosen. Errors caused by mass discrimination are also considered. The principles involved are outlined, illustrated, and applied to the rubidium–strontium method of age determination.

For isotopic dilution, used in the mass-spectrometric determination of very small quantities of elements, part of a sample is mass-analysed and part mixed with a known quantity of a tracer and also mass-analysed. The tracer is composed of isotopes of the element to be determined, but in different proportions so that the isotopic composition of the mixture differs from that of either component. These three mass analyses and a knowledge of the quantity of tracer used give the results required.

To assess the reliability of the procedure Radin [1] and Christian and Pinajian [2] have considered the effect of experimental errors. Their brief treatment is similar for radioactive and stable tracers and shows that the errors are magnified in the result to an extent which depends on the ratio in which tracer and sample are mixed: the lower this is the nearer is the magnification factor to unity. However, this assumes that the natural abundance employed is accurate, which is rarely true; this aspect has been considered by Jamieson and Schreiner [3,4] whose treatment, though an advance on that of Radin, is open to criticisms. It is developed in isotopic abundances rather than ratios, but available mass spectrometers do not allow direct determination of abundance. Their detector [4] permits a determination of the ratio for a di-isotopic mixture, and the determination of an abundance is approached only as the number of isotopes in the mixture becomes large. Thus, their deductions concerning the choice of the rubidium isotope to be used as the basis

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[1] Radin, *Nucleonics*, 1947, **1**, 48.

[2] Christian and Pinajian, *J. Amer. Pharmaceut. Assoc.* (*Sci. Edn.*), 1953, **42**, 301, 304.

[3] Jamieson and Schreiner, " Electromagnetically Enriched Isotopes and Mass Spectrometry," Butterworths Scientific Publns., London, 1956, p. 169.

[4] Jamieson and Schreiner, *Proc. Roy. Soc.*, 1956—57. *B*, **146**, 257,

for measurement cannot be accepted. Further, their conclusions on the effect of systematic errors would not apply to an instrument measuring isotopic ratios; no account is taken of the differing atomic weights of normal and tracer element, and only one case is considered.

We attempt to overcome these deficiencies and to extend the treatment. First, we develop a general equation that can be modified to suit other circumstances. From this an expression is derived by statistical methods to show how the total error is composed of the various individual errors; in this way means of minimising the total error become apparent. Consideration is then given to the errors involved in the determination of tracer by isotopic dilution, to systematic errors, and to the elimination of errors due to chemical contamination. The principles are illustrated from past work.

GENERAL TREATMENT

It is assumed that the mass analyses are expressed as ratios, $D_{ij} = a^{D}_{i}/a^{D}_{j}$, where a^{D}_{i} is the abundance of the i'th isotope of the matrix element to be determined, etc.

An estimate of the experimental error of D_{ij} will be represented by a variance $V(D_{ij})$ which includes only physical errors. But experimental errors can arise from other causes; usually the "matrix element" is a minor constituent of rocks, irradiated fissile materials, etc., and must be isolated chemically in a suitable state. This treatment may introduce isotopic impurities, a point to be considered later, but in the initial treatment it will be assumed that $V(D_{ij})$ does not include such errors. The procedure depends on whether the tracer is composed of the same isotopes as the matrix element or contains isotopes which the matrix element does not, or *vice-versa.* In the first instance a general equation governing mixtures of matrix element and tracer when each includes at least two given isotopes but in different relative proportions is derived. Equations applicable to other circumstances are obtained from this by applying general rules.

Matrix Element and Tracer having Two Isotopes in Common.—Let a^{D}_{i} and a^{S}_{i} be the fractional abundance of the i'th isotope in the matrix element and the tracer, respectively. Then $\sum\limits_{x} a^{D}_{x} = 1$, $\sum\limits_{y} a^{S}_{y} = 1$. When d atoms of matrix element are mixed with s atoms of tracer, the ratio of the i'th to j'th isotope, M_{ij}, is such that

$$M_{ij} = \frac{da^{D}_{i} + sa^{S}_{i}}{da^{D}_{j} + sa^{S}_{j}}, \text{ or } d = s\,\frac{M_{ij}a^{S}_{j} - a^{S}_{i}}{a^{D}_{i} - M_{ij}a^{D}_{j}}.$$

Now $D = dW^{D}/\boldsymbol{N}$ and $S = sW^{S}/\boldsymbol{N}$, where D and S are the weights of the matrix element and of the tracer, $\boldsymbol{N}$ the Avogadro number, and W^{D} and W^{S} the atomic weights of the matrix element and tracer, respectively. If W_{x} is the atomic mass of the x'th isotope, then $W^{D} = \sum\limits_{x} W_{x}a^{D}_{x} = a^{D}_{i}\sum\limits_{x} W_{x}D_{xi}$. Similarly $W^{S} = a^{S}_{j}\sum\limits_{y} W_{y}S_{yj}$, and thus

$$D = S\,\frac{M_{ij} - S_{ij}}{1 - M_{ij}D_{ji}} \cdot \frac{\sum\limits_{x} W_{x}D_{xi}}{\sum\limits_{y} W_{y}S_{yj}}. \tag{1}$$

If D^{k} is the mass of the k'th isotope in the matrix element, then

$$D^{k} = D\,\frac{W_{k}a^{D}_{k}}{\sum\limits_{x} W_{x}a^{D}_{x}} = D\,\frac{W_{k}D_{ki}}{\sum\limits_{x} W_{x}D_{xi}},$$

and thus, from (1),

$$D^{k} = S\,\frac{M_{ij} - S_{ij}}{1 - M_{ij}D_{ji}} \cdot \frac{W_{k}D_{ki}}{\sum\limits_{y} W_{y}S_{yj}}. \tag{2}$$

When k takes the value i, $W_k D_{ki}$ becomes W_i. If the quantity of matrix element is required in atoms rather than mass, then noting that $a^D{}_i = a^D{}_i/\sum_x a^D{}_x = 1/\sum_x D_{xi}$, we see that d is given by:

$$d = NS\frac{M_{ij} - S_{ij}}{1 - M_{ij}D_{ji}} \cdot \frac{\sum_x D_{xi}}{\sum_y W_y S_{yj}},$$

and the appropriate expressions for d^k and d^i are obtained with the relations $d^k = dD_{ki}/\sum_x D_{xi}$ and $d^i = d/\sum_x D_{xi}$.

If X is a function of independent variates $x_1, x_2 \ldots$, then

$$V(X) = \left(\frac{\partial X}{\partial x_1}\right)^2 V(x_1) + \left(\frac{\partial X}{\partial x_2}\right)^2 V(x_2) + \cdots\cdot$$

where $V(X)$ is the variance * of X, and $V(x_1)$ the variance of x_1, etc.; [5,6] the related forms, $V(X)/X^2$, $V(x_1)/x_1^2 \ldots$, will be represented by $\bar{V}(X)$, $\bar{V}(x_1)$, etc. Application of this to equation (1) yields the following relation for the variance of D in terms of the variances of the measured ratios and that of the quantity of tracer used:

$$\bar{V}(D) = \bar{V}(S) + \left[\frac{S_{ij}}{M_{ij} - S_{ij}} + \frac{W_i S_{ij}}{\sum_y W_y S_{yj}}\right]^2 \bar{V}(S_{ij}) + \left[\frac{M_{ij}D_{ji}}{1 - M_{ij}D_{ji}} + \frac{W_i D_{ji}}{\sum_x W_x D_{xi}}\right]^2 \bar{V}(D_{ji})$$

$$+ \left[\frac{M_{ij}(1 - S_{ij}D_{ji})}{(M_{ij} - S_{ij})(1 - M_{ij}D_{ji})}\right]^2 \bar{V}(M_{ij}) + \frac{\sum_y^{y \neq i} W_y{}^2 S_{yj}{}^2 \bar{V}(S_{yj})}{(\sum_y W_y S_{yj})^2} + \frac{\sum_x^{x \neq j} W_x{}^2 D_{xi}{}^2 \bar{V}(D_{xi})}{(\sum_x W_x D_{xi})^2}. \tag{1a}$$

Expressions for $\bar{V}(D^j)$ and $\bar{V}(D^i)$ are obtained from expression (1a) by deleting the last term and modifying the coefficient of $\bar{V}(D_{ji})$ to $[1/(1 - M_{ij}D_{ji})]^2$ and $[M_{ij}D_{ji}/(1 - M_{ij}D_{ji})]^2$, respectively. For other isotopes, $\bar{V}(D^k)$ is obtained by adding the term $\bar{V}(D_{ki})$ to the expression for $\bar{V}(D^i)$. When both the tracer and the matrix element consist solely of two isotopes, equations (1) and (1a) reduce to:

$$D = S\frac{M_{ij} - S_{ij}}{1 - M_{ij}D_{ji}} \cdot \frac{W_i + W_j D_{ji}}{W_i S_{ij} + W_j}; \tag{3}$$

$$\bar{V}(D) = \bar{V}(S) + \left[\frac{S_{ij}}{M_{ij} - S_{ij}} + \frac{W_i S_{ij}}{W_i S_{ij} + W_j}\right]^2 \bar{V}(S_{ij}) + \left[\frac{M_{ij}D_{ji}}{1 - M_{ij}D_{ji}} + \frac{W_j D_{ji}}{W_i + W_j D_{ji}}\right]^2 \bar{V}(D_{ji})$$

$$+ \left[\frac{M_{ij}(1 - S_{ij}D_{ji})}{(M_{ij} - S_{ij})(1 - M_{ij}D_{ji})}\right]^2 \bar{V}(M_{ij}). \tag{3a}$$

Expressions for $\bar{V}(d)$, etc., are obtained in an analogous way. They may be derived from those of the D's by making the W's in the coefficients of $\bar{V}(D_{ji})$ and $\bar{V}(D_{xi})$ equal to unity.

Other Cases.—It has been assumed above that matrix element and tracer each have the same isotopes, but in different proportions. This would be so with a naturally

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* The variance of x_i is the mean value of the squares of the deviations of the observations of x_i from their mean. The standard deviation is the square root of the variance. Similarly the coefficient of variation is the square root of the fractional form $V(x_i)/x_i^2$, denoted by $\bar{V}(x_i)$.

[5] Kendall, " The Advanced Theory of Statistics," Griffin, London, 1945, 2nd edn., Vol. I, p. 208.

[6] Davies, " Statistical Methods in Research and Production," Oliver and Boyd, London, 1949, 2nd edn., pp. 35 *et seq.*

occurring element and a tracer prepared by the electromagnetic enrichment of one of the natural isotopes. However, for a radiogenic matrix element, it may happen that one or more of the isotopes it contains is absent from the tracer or *vice-versa*, or that each contains an isotope not present in the other. Then the equations for D, etc., and their variances will be modified. Equations (1) and (1a) are written so that these modifications can be obtained readily. Thus, if the i'th isotope is in the matrix but not in the tracer, and the j'th isotope is present in both, then expressions for D and $\bar{V}(D)$ are given when $S_{ij} = 0$ in (1) and (1a); for a monoisotopic tracer consisting of the j'th isotope alone, S_{ij} and S_{yj} are put equal to zero, so $\sum_y W_y S_{yj} = W_j$. Values for D^k, d, etc., and their variances again follow from the substitution rules above.

Similarly if the j'th isotope is present in the tracer but not in the matrix element, and the i'th isotope occurs in both, $D_{ji} = 0$ in (1) and (1a); and again in the limiting case of a monoisotopic matrix element, D_{ji}, $D_{xi} = 0$, and $\sum_x W_x D_{xi} = W_i$.

Finally, if the i'th isotope is in the matrix element, but not in the tracer, and the j'th isotope in the tracer but not the matrix element, S_{ij}, $D_{ji} = 0$ in (1) and (1a); if the tracer is monoisotopic, then in addition $S_{yj} = 0$. If both are monoisotopic, S_{ij}, S_{yj}, D_{ji}, $D_{xi} = 0$, and the problem is reduced to its simplest form:

$$D = SM_{ij}W_i/W_j; \tag{4}$$

$$\bar{V}(D) = \bar{V}(S) + \bar{V}(M_{ij}). \tag{4a}$$

Choice and Quantity of Tracer.—These expressions relate the error in the required quantity of the matrix element to those in the isotopic ratios. Clearly the former error depends, not only on the precision of mass-spectrometric measurements, but also on the values of the ratios, and so it can be minimised by manipulating the isotopic ratios in the tracer and the mixture; this involves the choice of tracer and adjusting the ratio of tracer to matrix element. It will be assumed that all the isotopic ratios have the same coefficient of variation, $100K$; so:

$$\bar{V}(M_{ij}) = \bar{V}(S_{ij}) = \bar{V}(D_{ji}) = K^2. \tag{5}$$

Without this assumption the relative precisions of the isotopic ratios must be included in assessing the optimum mixture ratio. First, the component parts of (1a) will be considered. The first, $\bar{V}(S)$, represents the precision with which the quantity of tracer in the mixture is known. If determined chemically it may be small; it will be independent of the various isotope ratios and so is ignored. Determination of S by isotopic dilution is treated below. The coefficients of $\bar{V}(S_{ij})$ and $\bar{V}(D_{ji})$ are very similar in form and are minimised by choosing i and j so that S_{ij} and D_{ji} are as small as possible. If we assume expression (5), then $\bar{V}(D)$ in (1a) is minimised with respect to M_{ij} when

$$\frac{\partial}{\partial(M_{ij})}\left[\left(\frac{S_{ij}}{M_{ij}-S_{ij}}+\frac{W_iS_{ij}}{\sum\limits_y W_yS_{yj}}\right)^2+\left(\frac{M_{ij}D_{ji}}{1-M_{ij}D_{ji}}+\frac{W_jD_{ji}}{\sum\limits_x W_xD_{xi}}\right)^2+\left(\frac{M_{ij}(1-S_{ij}D_{ji})}{(M_{ij}-S_{ij})(1-M_{ij}D_{ji})}\right)^2\right]=0. \tag{6}$$

The largest term of equation (6) is the last, and it is minimised with respect to M_{ij} when $M_{ij} = \sqrt{(S_{ij}/D_{ji})}$. This also satisfies the complete expression when $W_iS_{ij}/\sum_y W_yS_{yj} = W_jD_{ji}/\sum_x W_xD_{xi}$, *i.e.*, if the weight fraction of the i'th isotope in the tracer equals that of the j'th isotope in the matrix element. Usually this condition is not satisfied, and $\bar{V}(D)$ is then minimised by adopting a value of M_{ij} close to $\sqrt{(S_{ij}/D_{ji})}$ and found precisely by substituting possible values in expression (6). The last two terms of (1a) can be written $\sum_{y}^{y \neq i,j} (W_y a^S_y)^2 K^2/(W^S)^2$, and $\sum_{x}^{x \neq i,j} (W_x a^D_x)^2 K^2/(W^D)^2$. The latter is unalterably fixed by the constitution of the matrix element, but the former can be minimised by selecting a tracer with the minimum of isotopes other than the j'th.

Strictly, in any given example, a unique value of M_{ij} is required to minimise $\bar{V}(D)$, but it is often sufficient to use $\sqrt{(S_{ij}/D_{ji})}$, for $\bar{V}(D)$ usually changes slowly with M_{ij} in this region. Thus, when $D_{ji} = 1$, $S_{ij} = 0{\cdot}01$, $W_j D_{ji}/\sum_x W_x D_{xi} = 0{\cdot}5$, and $W_i S_{ij}/\sum_y W_y S_{yj} = 0{\cdot}01$ (a matrix element with two isotopes of similar abundance), then M_{ij} as given by $\sqrt{(S_{ij}/D_{ji})}$ is 0·1 [cf. 0·089 from (6)]. Equation (3a) gives $1{\cdot}882K^2$ and $1{\cdot}875K^2$, respectively, so in this case the substitution of $\sqrt{(S_{ij}/D_{ji})}$ for the ideal M_{ij} value increases $\bar{V}(D)$ by a factor of only 1·004, or raises a minimum uncertainty of, for example, 1% to 1·002%. Sometimes a value of M_{ij} different from the theoretical value should be used to avoid other errors. In the determination of natural uranium (^{235}U 0·72%, ^{238}U 99·27%) with enriched ^{235}U as the tracer (^{235}U 93·41%, ^{238}U 5·44%), the optimum value of M_{ij} is 2·83. The use of unity, however, avoids the possible errors associated with changing amplifier ranges at the expense of a very small increase in $\bar{V}(D)$, the values being $\bar{V}(S) + (1{\cdot}045K)^2$ and $\bar{V}(S) + (1{\cdot}076K)^2$ respectively.

Only equation (1a) leads to a unique finite value for M_{ij}. For other cases the coefficient of $\bar{V}(M_{ij})$ either tends asymptotically to unity as M_{ij} approaches zero ($S_{ij} = 0$) or infinity ($D_{ji} = 0$), or is independent of M_{ij}. This clearly ignores the fact that equation (5) will not be valid for very large or very small ratios. For example, when isotope j is absent from the matrix, $D_{ji} = 0$ in (1a) and the coefficient of M_{ij} is $M_{ij}/(M_{ij} - S_{ij})$. This decreases as M_{ij} takes a larger value. Thus, for $S_{ij} = 0{\cdot}1$, if $M_{ij} = 1$, 10, 100, $M_{ij}/(M_{ij} - S_{ij}) = 1{\cdot}1$, 1·01, 1·001, showing the diminishing return for each ten-fold increase in M_{ij}. When the quantity of matrix element is small, M_{ij} can be increased only by adding smaller quantities of the tracer, and it is possible that the determination of M_{ij} will then become less precise. With sufficient material the precision of a mass-spectrometric determination of an isotopic ratio is largely controlled by random fluctuations in the intensity of ion beams, and these are independent of the ratio. Decrease in quantity, however, reduces the beam intensity and, when the latter falls below about 10^{-15} amp., precision depends more on statistical fluctuations in the electron multiplier detection system than on variations in the ion source. This statistical fluctuation is approximately proportional to $\sqrt{N'}$, where N' is the number of ions striking the first dynode of the multiplier per second, so that the fractional statistical error is proportional to $1/\sqrt{N'}$. Thus when the matrix isotope i is kept constant and the ratio M_{ij} is increased by decreasing the tracer isotope j, the relative precision will become proportional to $\sqrt{M_{ij}}$, *i.e.*, $\bar{V}(M_{ij}) \propto M_{ij}$. When this begins to control the precision of the isotope ratio, then, although further increase of M_{ij} reduces the coefficient $M_{ij}/(M_{ij} - S_{ij})$, it also increases $\bar{V}(M_{ij})$. These two opposing effects define an optimum value for M_{ij}.

Choice of Reference Isotope.—With reference to rubidium, Jamieson and Schreiner[4] suggest that error magnification depends on the choice of reference isotope. Although possibly true for an instrument giving isotopic abundance directly and possessing a coefficient of variation independent of the abundance, for a di-isotopic element most instruments, including theirs, can determine only the isotope ratio. If this is found with the coefficient of variation, C_v, then the coefficients of variation for the two calculated abundances differ, being $(1 - a)C_v$, where a is the abundance of the isotope in question. Hence it is preferable to examine the problem in terms of the quantity measured, in this case the isotope ratio. Equation (3), relating to di-isotopic elements, may also be expressed as:

$$D = S\,\frac{M_{ij} - S_{ij}}{D_{ij} - M_{ij}} \cdot \frac{W_i D_{ij} + W_j}{W_i S_{ij} + W}.$$

In (3a) $\bar{V}(D_{ij})$ replaces $\bar{V}(D_{ji})$ with the coefficient

$$\left[\frac{D_{ij}}{D_{ij}-M_{ij}}-\frac{W_iD_{ij}}{W_iD_{ij}+W_j}\right]^2 \text{instead of} \left[\frac{M_{ij}D_{ji}}{1-M_{ij}D_{ji}}+\frac{W_jD_{ji}}{W_i+W_jD_{ji}}\right]^2$$

These in fact are identical, which demonstrates algebraically a result which seems obvious, that precision in the result sought is not affected by merely rearranging the calculation to use reciprocals of the measured isotope ratios.

When an element contains more than two isotopes, then in expression (1a) the coefficients of $\bar{V}(D_{ji})$ and $\bar{V}(S_{ij})$ will depend upon whether i or j is used as a reference for the additional isotopes, as in D_{xi} or D_{xj}, S_{xi} or S_{xj}. It will be assumed that any ratio, R_{ab}, is determined by recording the a'th and the b'th isotope alternately, and then drawing a smooth curve through the b'th peaks to provide reference for the recordings of the a'th isotope. This process gives *independent* determinations of all the isotope ratios in the sample. It also minimises the effect of fluctuations in ion currents and so should be used to obtain the highest precision. We assume throughout this paper that such a procedure is used to provide independent estimates of ratios. Equation (1), when expressed in terms of the ratios D_{ij}, D_{xj}, becomes

$$D = S\frac{M_{ij}-S_{ij}}{D_{ij}-M_{ij}} \cdot \frac{\sum\limits_{x} W_xD_{xj}}{\sum\limits_{y} W_yS_{yj}}. \qquad (1b)$$

This equation (1b) refers to a physically different situation from that defined by (1), for different ratios D_{xj} and D_{xi} are measured. The term in $\bar{V}(D_{ji})$ from (1a), rearranged to allow the simplest numerical comparison, becomes

$$\left[\frac{D_{ij}}{D_{ij}-M_{ij}}-\frac{W_iD_{ij}+\sum\limits_{x}^{x\neq i,j} W_xD_{xj}}{\sum\limits_{x} W_xD_{xj}}\right]^2 \bar{V}(D_{ji});\ \text{cf.} \left[\frac{D_{ij}}{D_{ij}-M_{ij}}-\frac{W_iD_{ij}}{\sum\limits_{x} W_xD_{xj}}\right]^2 \bar{V}(D_{ij})$$

from (1b).

This comparison shows that when $D_{ij} > M_{ij}$ it is advantageous to measure the ratios D_{xi}; when $D_{ij} < M_{ij}$, then the ratios D_{xj} should be measured. The origin of this difference is readily seen on comparing those parts of (1) and (1b) which involve D ratios; rearranged these are

$$\frac{W_iD_{ij}+W_j+D_{ij}\sum\limits_{x}^{x\neq i,j} W_xD_{xi}}{D_{ij}-M_{ij}} \text{ and } \frac{W_iD_{ij}+W_j+\sum\limits_{x}^{x\neq i,j} W_xD_{xj}}{D_{ij}-M_{ij}},$$

showing the different dependence on D_{ij} when either D_{xi} or D_{xj} ratios are determined. In this paper equations have been written to correspond to the relation $D_{ij} > M_{ij} > S_{ij}$, and thus in terms of D_{xi} and S_{yj}. When $D_{ij} < S_{ij}$, they should be expressed in terms of D_{xj} and S_{yi}.

The difference arising from the use of i or j as the reference for the isotopes x or y would disappear if some quantity proportional to the number of atoms could be simultaneously found for each of the isotopes. Such a measurement can be approached in a conventional instrument, with relatively slow magnetic or electrostatic scanning, by repeatedly recording the complete mass spectrum instead of that of a selected isotope pair. Usually there will be loss of precision, because thermal-emission ion sources are not very stable and the beam intensity may rise or fall and sometimes oscillates erratically. Comparisons should therefore be made in the shortest possible times, and for this reason individual isotope pairs are preferred. When very rapid scanning of the mass spectrum is possible, virtually simultaneous estimates of the peak heights are obtained by ion counting. Then equation (1) may be expressed in terms of peak heights or their equivalents:

$$D = S\,\frac{P^{\rm M}{}_{\rm i}P^{\rm S}{}_{\rm j} - P^{\rm M}{}_{\rm j}P^{\rm S}{}_{\rm i}}{P^{\rm D}{}_{\rm i}P^{\rm M}{}_{\rm j} - P^{\rm D}{}_{\rm j}P^{\rm M}{}_{\rm i}} \cdot \frac{\sum\limits_{\rm x} W_{\rm x}P^{\rm D}{}_{\rm x}}{\sum\limits_{\rm y} W_{\rm y}P^{\rm S}{}_{\rm y}},$$

where $P^{\rm M}{}_{\rm i}$ is the height of the peak recorded for the i'th isotope in the mixture of tracer and matrix element, etc. An equation corresponding to (1a) relating $\bar{V}(D)$ to $\bar{V}(P^{\rm M}{}_{\rm i})$, etc., can then be derived. To compare this with (1a) it is assumed that all peak heights are determined with the same precision [cf. (5)], and that $\bar{V}(D_{\rm ab}) = \bar{V}(P^{\rm D}{}_{\rm a}) + \bar{V}(P^{\rm D}{}_{\rm b}) = 2\bar{V}(P^{\rm D}{}_{\rm a})$. This comparison shows that the error arising from the determination of the isotopes i and j in the mixture is the same in both cases; that from the determination from peak heights of the isotopes i and j in the matrix element is the mean of the two possible values in the ratio method and, similarly, for the isotopes i and j in the tracer; and the components for all the isotopes other than i and j, both for the matrix element and for the tracer, are halved by peak-height analysis.

Determination of Tracer Element by Isotopic Dilution.—So far, $\bar{V}(S)$ has been assumed to be small. This is true provided there is sufficient tracer for quantitative analysis, for example, if the natural element can be used. Frequently, however, the tracer must be an isotopic mixture made by electromagnetic separation and sometimes radiogenic materials are used. Thus the amount of tracer may not easily be found by chemical means or direct weighing. Usually it is then obtained by mixing the tracer with a known quantity of the naturally occurring element; five mass analyses (for the matrix element, the tracer, their mixture, the naturally occurring form of the element, and its mixture with the tracer) and the quantity, E, of natural element used can then provide the necessary data to find D. If required a joint equation is obtained by writing D in terms of S, and S in terms of E, and then eliminating S. An overall equation for $\bar{V}(D)$ is given by adding two expressions, $\bar{V}(D)$ as (1a) and an analogous one for $\bar{V}(S)$, with the addition of $\bar{V}(S_{\rm fj})$ if different reference isotopes are used in the two parts (*e.g.*, $S_{\rm ij}$ and $S_{\rm if}$ or $S_{\rm ef}$) and the omission of $\bar{V}(S_{\rm yj})$, $\bar{V}(S_{\rm yf})$. Choice of tracer composition to minimise one part will necessarily minimise the other only when the matrix element is similar in isotopic composition to the natural element. This occurs in the determination of a naturally occurring element, when the same two reference isotopes i and j will be used throughout. Then the coefficient of $S_{\rm ij}$ becomes $[S_{\rm ij}(M_{\rm ij} - M'_{\rm ij})/(M_{\rm ij} - S_{\rm ij})(M'_{\rm ij} - S_{\rm ij})]^2$ where $M'_{\rm ij}$ is the mixture ratio for the calibration. This coefficient tends to zero as $M_{\rm ij}$ tends to $M'_{\rm ij}$, and $\bar{V}(D)$ is minimised by choosing $M_{\rm ij}$ to satisfy equation (6) modified by replacing the first term by the coefficient above; again the optimum value is close to $\surd(S_{\rm ij}/D_{\rm ji})$. Strictly, when natural and matrix elements are dissimilar, the best combination of $M_{\rm ij}$, $M'_{\rm ij}$ or $M'_{\rm if}$ or $M'_{\rm ef}$, and tracer must be selected to minimise the complete expression for $\bar{V}(D)$; however, as the precision of calibration is commonly improved by replicate analyses, this part can often be ignored and the problem reverts essentially to minimising (1a).

Experimental Examples.—The operation of these procedures will be illustrated from experience with the determination of the products of fission or neutron capture formed in nuclear reactors. All isotopic ratios are assumed to have the same precision, as defined by (5). The coefficient of variation is the standard deviation expressed as a percentage of the mean value, and for $A_{\rm ij}$, say, is given by $100\surd[V(A_{\rm ij})/A_{\rm ij}{}^2]$, $100\surd[\bar{V}(A_{\rm ij})]$, or $100K$. In practice, $\bar{V}(A_{\rm ij})$ will vary with the time and care devoted to the mass spectrometry. The ratio of two isotopes can usually be determined with a coefficient of variation of 1% without undue effort, and this can often be maintained over a range of ratios of perhaps 0·01—100 if sufficient sample is available. With considerable effort and adequate sample higher precisions of 0·1—0·2% can be achieved,[7] and, for example, the $^{107}Ag/^{109}Ag$ ratio was determined with a coefficient of variation of 0·07% in our determination of the atomic weight of silver.[8]

In the following examples isotopic compositions are given in percentages of atoms.

Tracer element monoisotopic: *cæsium.* Cæsium formed as a fission product in highly irradiated ^{239}Pu had the composition: ^{133}Cs, 24·9; ^{134}Cs, 5·29; ^{135}Cs, 24·9; ^{137}Cs, 44·9%. Natural cæsium is monoisotopic (^{133}Cs) and was the only tracer available at the time of analysis. Expression (1a) with S_{ij}, $S_{xj} = 0$, becomes

$$\bar{V}(D) = \bar{V}(S) + \left[\frac{M_{ij}D_{ji}}{1 - M_{ij}D_{ji}} + \frac{W_jD_{ji}}{\sum\limits_{x} W_xD_{xi}}\right]^2 \bar{V}(D_{ji}) + \left[\frac{1}{1 - M_{ij}D_{ji}}\right]^2 \bar{V}(M_{ij}) + \frac{\sum\limits_{x}^{x \neq j} W_x{}^2D_{xi}{}^2\, \bar{V}(D_{xi})}{(\sum\limits_{x} W_xD_{xi})^2}. \quad (7)$$

Applying (5) and selecting i = 137, j = 133, gives

$$\bar{V}(D) = \bar{V}(S) + \left[\frac{0{\cdot}555\, M_{ij}}{1 - 0{\cdot}555\, M_{ij}} + \frac{73{\cdot}8}{301{\cdot}4}\right]^2 K^2 + \left[\frac{1}{1 - 0{\cdot}555\, M_{ij}}\right]^2 K^2 + \frac{15{\cdot}8^2 + 74{\cdot}9^2}{301{\cdot}4^2} K^2 \quad (8)$$

As M_{ij} is reduced, $\bar{V}(D)$ becomes smaller, and with sufficient ^{133}Cs tracer to make $M_{ij} = 0{\cdot}1$, (8) becomes

$$\bar{V}(D) = \bar{V}(S) + 0{\cdot}092K^2 + 1{\cdot}121K^2 + 0{\cdot}064K^2 = \bar{V}(S) + 1{\cdot}277\, K^2.$$

$\bar{V}(S)$ can be small, since it arises from a weighing, so $\bar{V}(D)$ will be close to $1{\cdot}277K^2$. Thus the coefficient of variation of D would be $113K$; so if isotope ratios are determined with a precision of 1%, D has a precision of 1·13%.

Irradiation of natural cæsium produced ^{133}Cs, 94·3; ^{134}Cs, 5·5; ^{135}Cs, 0·2%, which was again determined with natural ^{133}Cs as the tracer. Expression (7) with i = 134, j = 133, contains $(1 - M_{ij}D_{ji})$ which becomes $(1 - 17{\cdot}1M_{ij})$. Here the value of D_{ji} is very unfavourable; the addition of natural cæsium must cause M_{ij} to be less than 0·058, and it would not be convenient to measure an M_{ij} ratio less than 0·01. With this value (7) becomes

$$\bar{V}(D) = \bar{V}(S) + 1{\cdot}321K^2 + 1{\cdot}457K^2 + <10^{-5}K^2 = \bar{V}(S) + 2{\cdot}778K^2.$$

Again, if $\bar{V}(S)$ is small the coefficient of variation of D would be about $167K$; thus a precision of 1% for the ratios results in a precision of 1·67% for D. If a pure radiogenic isotope, ^{131}Cs or ^{137}Cs, had been available D_{ji} would be zero in (7) which, for any reasonable value of M_{ij}, would then become

$$\bar{V}(D) = \bar{V}(S) + K^2 + 0{\cdot}003K^2 = \bar{V}(S) + 1{\cdot}003K^2.$$

Thus, if the ^{137}Cs (or ^{131}Cs) used could be determined accurately, $\bar{V}(S)$ would be small and the coefficient of variation for D would be near the minimum of $100K$, actually the coefficient of variation for one ratio. If $\bar{V}(S)$ were determined by calibration with natural ^{133}Cs, then combining (4a) for the calibration with the above modification of (7) gives $\bar{V}(D) = \bar{V}(E) + 2{\cdot}003K^2$. If we ignore $\bar{V}(E)$, the coefficient of variation is near the minimum of $141{\cdot}4K$ for the calibrated case and is better than that obtained by using natural cæsium directly.

Tracer element polyisotopic: *gadolinium.* Gadolinium from long-irradiated ^{239}Pu had a composition ^{156}Gd, 88·3; ^{158}Gd, 11·4; ^{160}Gd, 0·3%. Two tracers were then available: natural gadolinium containing ^{152}Gd, 0·20; ^{154}Gd, 2·14; ^{155}Gd, 14·7; ^{156}Gd, 20·5; ^{157}Gd, 15·7; ^{158}Gd,

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[7] Webster, Dance, Morgan, Preece, Slee, and Smales, *Analyt. Chim. Acta*, 1960, **23**, 101; Webster, Smales, Dance, and Slee, *ibid.*, 1961, **24**, 371, 509.

[8] Crouch and Turnbull, *J.*, 1962, 161; Crouch, Preece, Swainbank, and Turnbull, *Nature*, 1959, **184**, 358.

24·9; ^{160}Gd, 21·9%; and enriched ^{160}Gd containing ^{154}Gd, 0·13; ^{155}Gd, 0·34; ^{156}Gd, 0·56; ^{157}Gd, 0·66; ^{158}Gd, 3·05; ^{160}Gd, 95·26%.

With the natural gadolinium, the analysis might proceed on the basis of two common isotopes in tracer and matrix element by selecting $i = 156$, $j = 160$ in (1a). With $M_{ij} = \sqrt{(S_{ij}/D_{ji})} = 16{\cdot}6$, (1a) reduces to $\bar{V}(D) = \bar{V}(S) + 1{\cdot}448K^2$, and with $M_{ij} = 20$ to $\bar{V}(S) + 1{\cdot}449K^2$. Thus $\bar{V}(D)$ is not very sensitive to M_{ij}, and the coefficient of variation of D would be about $120K$.

Natural gadolinium has 15·7% of ^{157}Gd, which is absent from the matrix element; so (1) and (1a) modified by $D_{ji} = 0$ might be applied. Thus with $i = 156$, $j = 157$, (1a) reduces to $\bar{V}(S) + 1{\cdot}594K^2$ for $M_{ij} = 10$, and to $\bar{V}(S) + 1{\cdot}301K^2$ for $M_{ij} = 30$. These are comparable with the result from the two-common-isotope analysis; a better precision can be achieved but only by using a less convenient mixture ratio.

For the enriched ^{160}Gd tracer, expression (1a), with $i = 156$, $j = 160$, and $M_{ij} = \sqrt{S_{ij}/D_{ji}}) = 1{\cdot}32$, reduces to $\bar{V}(S) + 1{\cdot}032K^2$; if $\bar{V}(S)$ can be ignored the coefficient of variation of D is $102K$, nearly the minimum value. The alternative approach might be considered with tracers enriched in ^{154}Gd, ^{155}Gd, or ^{157}Gd, now available, but clearly could give little improvement. When the ^{160}Gd tracer is calibrated against natural gadolinium, M_{ij} and M'_{ij} must both satisfy expression (6, modified) to minimise the overall equation. In this example $\bar{V}(D)$ is not very sensitive to M_{ij} and M'_{ij}, and with $M_{ij} = \sqrt{(S_{ij}/D_{ji})} = 1{\cdot}318$, and $M'_{ij} = \sqrt{(S_{ij}/E_{ji})} = 0{\cdot}074$, $\bar{V}(D) = \bar{V}(E) + 2{\cdot}62K^2$. The coefficient of variation of D [$\bar{V}(E)$ being ignored] is then $162K$.

The various methods for gadolinium are compared in Table 1; clearly the best is by isotopic dilution with natural gadolinium unless the enriched ^{160}Gd tracer could be calibrated with greater precision, either by at least five replicate analyses, or by an alternative technique.

TABLE 1.

Determination of radiogenic Gd from highly irradiated ^{239}Pu.

Tracer	M_{ij}	$\bar{V}(D)$ direct	$\bar{V}(D)$ including calibration
Natural Gd (two common isotopes) ……	16·6	$\bar{V}(E) + 1{\cdot}45K^2$	—
Natural Gd (one common isotope) ………	10	$\bar{V}(E) + 1{\cdot}59K^2$	—
	30	$\bar{V}(E) + 1{\cdot}30K^2$	—
Enriched ^{160}Gd ……………………………	1·32	$\bar{V}(S) + 1{\cdot}03K^2$	$\bar{V}(E) + 2{\cdot}62K^2$

THE EFFECTS OF MASS DISCRIMINATION ON RESULTS

Hitherto only random errors have been considered, but systematic errors may also occur through mass discrimination. This causes the relative ion beam intensities to be different from the relative isotopic abundances. Such effects may be due to different diffusion rates in the ion source, to differing responses of the detector to ions of slightly different velocities, or to stray magnetic and electrostatic fields. Some of these may be corrected for, but others are difficult to detect and their assessment involves the preparation of accurately known mixtures of pure isotopes. We therefore consider how mass discrimination affects results determined by isotopic dilution. Suppose that the discriminatory process is defined by the equation

$$R_{j,j+1(\text{true})} = R_{j,j+1(\text{obs})}(1 + \delta),$$

where $R_{j,j+1}$ is the ratio of the j'th to the $(j + 1)$th isotope in the element. δ is small and, if it does not depend absolutely on the mass, similar relations for $R_{j+1,j+2}$, etc., will lead to a general equation

$$R_{j,n(\text{true})} = R_{j,n(\text{obs})}(1 + \delta)^{W_n - W_j} \approx R_{j,n(\text{obs})}[1 + \delta(W_n - W_j)].$$

Substituting in (1) gives an expression which approximates to

$$(D_{\text{obs}} - D_{\text{true}})/D_{\text{true}} = (W^D - W^S)\delta.$$

This involves the assumption that the error introduced by discrimination into an atomic weight is negligible compared with the error introduced into a ratio, which is usually true.

The fractional error due to mass discrimination is the product of δ and the difference between the atomic weights of tracer and matrix element; it is very small when these are nearly the same, but this is rarely compatible with the minimisation of random errors. However, both requirements can be satisfied, for example, in equation (2) if $S_{ij},S_{xj} = 0$; the tracer is then monoisotopic, so $S = S^j$ and (2) becomes

$$D^j = S^j M_{ij} D_{ji}/(1 - M_{ij} D_{ji}).$$

This equation could be used to find the quantity of radiogenic ^{133}Cs in fission products with natural ^{133}Cs as tracer. When the concentration of tracer is determined by isotopic dilution with a standard, the fractional error caused by discrimination is the product of δ and the difference between the atomic weights of the matrix element and the standard, *i.e.*, $(W^D - W^E)\delta$. Discrimination errors can then be minimised simply by choosing a standard having an isotopic composition very similar to that of the element to be determined.

The following examples illustrate the importance of mass discrimination.

(*a*) *Calibration of tracers under different conditions.* (i) In a calibration of ^{6}Li tracer against natural lithium, the ion gun was operated with two different sets of accelerating potentials, giving results of 1·760 and 1·743 μg./ml.[9]

(ii) The concentration of ^{84}Sr tracer solution was determined by means of different mass spectrometers both fitted with triple-filament sources. One employed an electron multiplier detector and gave 9·56 μg./ml. for the sample on the side filament (9·45 μg./ml. with velocity correction). The second used a plate detector; the result was 9·46 μg./ml. when samples were mounted on the side filament, and 9·27 μg./ml. when on the centre filament.[10]

(*b*) *Calibration of instruments with synthetic isotopic mixtures.* (i) Shields *et al.*[11] have measured the mass discrimination for natural silver and find $(1 + \delta)^2 = 0{\cdot}99444 \pm 0{\cdot}00062$. (ii) At Harwell[8] the mass discrimination for silver isotopes was found to vary with the ^{107}Ag : ^{109}Ag ratio, R; two mass spectrometers gave discriminations represented by $(1 + \delta)^2 = 0{\cdot}9894 - 0{\cdot}0092 \log_{10}R$, and $(1 + \delta)^2 = 0{\cdot}9913 - 0{\cdot}0224 \log_{10}R$.

These examples show that systematic errors of about 1% per mass unit are quite common, and clearly results obtained by isotopic dilution should be quoted with an assurance that the effects of mass discrimination are small, or have been avoided.

EXTENSION OF THE METHOD

In equation (1), only one mixture ratio, M_{ij}, is used, but sometimes, by using two or more mixture ratios, the information obtained by separate measurements for the matrix element and its mixture with tracer can be obtained from a single analysis of the mixture. It is of interest to compare the errors in the two procedures.

Tracer with an Isotope not in the Matrix Element.—The conventional equation follows from (1) with $D_{ji} = 0$:

$$D = \frac{S^j}{W_j}(M_{ij} - S_{ij}) \sum_x W_x D_{xi}; \tag{9}$$

but any matrix ratio can be expressed as

$$D_{xi} = (M_{xj} - S_{xj})/(M_{ij} - S_{ij}),$$

and with relations of this form (9) becomes

$$D = \frac{S^j}{W_j} \sum_x W_x (M_{xj} - S_{xj}). \tag{10}$$

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[9] Smales and Webster, *Analyt. Chim. Acta*, 1958, **18**, 587.

[10] Webster, Morgan, and Smales, *Trans. Amer. Geophys. Union*, 1957, **38**, 543.

[11] Shields, Craig, and Dibeler, *J. Amer. Chem. Soc.*, 1960, **82**, 5033.

The appropriate equations for $\bar{V}(D)$ are:

$$\bar{V}(D) = \bar{V}(S^{\mathrm{j}}) + \left[\frac{M_{\mathrm{ij}}}{M_{\mathrm{ij}} - S_{\mathrm{ij}}}\right]^2 \bar{V}(M_{\mathrm{ij}}) + \left[\frac{S_{\mathrm{ij}}}{M_{\mathrm{ij}} - S_{\mathrm{ij}}}\right]^2 \bar{V}(S_{\mathrm{ij}}) + \frac{\sum\limits_{\mathrm{x}} W_{\mathrm{x}}{}^2 D_{\mathrm{xi}}{}^2 \bar{V}(D_{\mathrm{xi}})}{(\sum\limits_{\mathrm{x}} W_{\mathrm{x}} D_{\mathrm{xi}})^2} \tag{9a}$$

$$\bar{V}(D) = \bar{V}(S^{\mathrm{j}}) + \frac{\sum\limits_{\mathrm{x}} W_{\mathrm{x}}{}^2 M_{\mathrm{xj}}{}^2 \bar{V}(M_{\mathrm{xj}})}{[\sum\limits_{\mathrm{x}} W_{\mathrm{x}}(M_{\mathrm{xj}} - S_{\mathrm{xj}})]^2} + \frac{\sum\limits_{\mathrm{x}} W_{\mathrm{x}}{}^2 S_{\mathrm{xj}}{}^2 \bar{V}(S_{\mathrm{xj}})}{[\sum\limits_{\mathrm{x}} W_{\mathrm{x}}(M_{\mathrm{xj}} - S_{\mathrm{xj}})]^2}. \tag{10a}$$

The variance terms $\bar{V}(D_{\mathrm{xi}})$ in (9a) have been replaced by $\bar{V}(M_{\mathrm{xj}})_{\mathrm{x}\neq\mathrm{i}}$ and $\bar{V}(S_{\mathrm{xj}})_{\mathrm{x}\neq\mathrm{i}}$, but this increase in $\bar{V}(D)$ will be offset and sometimes outweighed by the smaller coefficients of $\bar{V}(M_{\mathrm{ij}})$ and $\bar{V}(S_{\mathrm{ij}})$.

Routine uses of (10) for the determination of fissile material in a chemical processing plant are possible for natural uranium, ^{235}U in irradiated enriched uranium, and plutonium from irradiated natural uranium.[7] Typical isotopic compositions are: (*a*) ^{234}U 0·005, ^{235}U 0·72, ^{238}U 99·27%; (*b*) ^{234}U 1·7, ^{235}U 87, ^{236}U 4·3, ^{238}U 7·0%; (*c*) ^{239}Pu 96, ^{240}Pu 3·8, ^{241}Pu 0·2%. The ^{233}U tracer used for (*a*) and (*b*) had ^{233}U 99·8, ^{234}U 0·17, ^{235}U 0·004, ^{238}U 0·02%; and the ^{242}Pu tracer for (*c*) had ^{238}Pu 0·3, ^{239}Pu 0·4, ^{240}Pu 0·5, ^{241}Pu 0·2, ^{242}Pu 98·4, ^{244}Pu 0·2%. The errors in the two procedures may be compared in Table 2, the values of $M_{238/233}$, $M_{235/233}$, and $M_{239/242}$ being made unity. Clearly, if the isotopic composition of the samples is not of prime importance, the second method will reduce the number of mass-spectrometric analyses, and can diminish the overall errors. Both features are attractive in a routine application.

TABLE 2.

Fissile material accounting analyses.

Sample	$\bar{V}(D)$ from (9a)	$\bar{V}(D)$ from (10a)
a	$\bar{V}(^{233}\mathrm{U}) + 1{\cdot}0004K^2$	$\bar{V}(^{233}\mathrm{U}) + 0{\cdot}986K^2$
b	$\bar{V}(^{233}\mathrm{U}) + 1{\cdot}007K^2$	$\bar{V}(^{233}\mathrm{U}) + 0{\cdot}762K^2$
c	$\bar{V}(^{242}\mathrm{Pu}) + 1{\cdot}011K^2$	$\bar{V}(^{242}\mathrm{Pu}) + 0{\cdot}932K^2$

Matrix Element a Radiogenic Nuclide Contaminated with the Natural Element.—The matrix element consists of a mixture of the desired radiogenic nuclide r with the naturally occurring element also containing r. The latter could be introduced by contamination from reagents or the atmosphere during chemical processing, or might already be present in the matrix material (as often occurs with geological samples).

Let the various isotope ratios for the matrix element be D_{xi}, $\mathrm{x} = 1,2, \ldots$; these will be identical with the ratios C_{xi} for the naturally occurring contaminating element except that $D_{\mathrm{ri}} > C_{\mathrm{ri}}$. The quantity G^{r} of the *radiogenic* part of the nuclide r is $D^{\mathrm{r}} - C^{\mathrm{r}}$, so from (2)

$$G^{\mathrm{r}} = \frac{SW_{\mathrm{r}}}{\sum\limits_{\mathrm{y}} W_{\mathrm{y}} S_{\mathrm{yj}}} \cdot \frac{M_{\mathrm{rj}} - S_{\mathrm{rj}}}{1 - M_{\mathrm{ij}} D_{\mathrm{jr}}} \cdot \frac{D_{\mathrm{ri}} - C_{\mathrm{ri}}}{D_{\mathrm{ri}}}. \tag{11}$$

C_{ri} and the other C_{xi} ratios are known usually by a determination for the normal naturally occurring element. Expression (11) requires separate determinations to find M_{rj}, and the ratios D_{jr}, D_{ri}, but if the latter can be calculated from an additional mixture ratio, the matrix mass analysis may be avoided. Thus D_{ri} is given by

$$D_{\mathrm{ri}} = [M_{\mathrm{rj}} - S_{\mathrm{rj}} + (M_{\mathrm{ij}} S_{\mathrm{rj}} - M_{\mathrm{rj}} S_{\mathrm{ij}}) D_{\mathrm{ji}}]/(M_{\mathrm{ij}} - S_{\mathrm{ij}}),$$

where $D_{\mathrm{ji}} = C_{\mathrm{ji}}$. Using this and $D_{\mathrm{jr}} = D_{\mathrm{ji}}/D_{\mathrm{ri}}$ in (11) gives

$$G^{\mathrm{r}} = \frac{SW_{\mathrm{r}}}{\sum\limits_{\mathrm{y}} W_{\mathrm{y}} S_{\mathrm{jy}}} \cdot \frac{1}{1 - M_{\mathrm{ij}} C_{\mathrm{ji}}} \cdot [M_{\mathrm{rj}}(1 - S_{\mathrm{ij}} C_{\mathrm{ji}}) - S_{\mathrm{rj}}(1 - M_{\mathrm{ij}} C_{\mathrm{ji}}) - C_{\mathrm{ri}}(M_{\mathrm{ij}} - S_{\mathrm{ij}})]. \tag{12}$$

Within the square brackets of (12) the first term defines the total quantity of nuclide r in the mixture, the second the correction for the quantity present in the tracer, and the third the correction for the quantity of r from the contaminating natural element. If i or j is absent from tracer or matrix the equation is modified accordingly. The use of (12) eliminates errors which occur when contamination varies between experiments or when samples are inhomogeneous but, if D_{ri} is not very different from C_{ri}, (11) may be preferable. The problem is considered below for radiogenic ^{87}Sr.

RUBIDIUM–STRONTIUM GEOLOGICAL AGE DETERMINATION

This determination is based on the decay of ^{87}Rb, and the relative quantities of ^{87}Rb and ^{87}Sr in the sample must be found.

Determination of Rubidium and ^{87}Rb.—Natural rubidium consists of ^{85}Rb 72·2, ^{87}Rb 27·8%, and tracers available are: (*a*) ^{85}Rb 0·72, ^{87}Rb 99·28%; (*b*) ^{85}Rb 99·0, ^{87}Rb 1·0%. Table 3, based on (2), (3), and (3a), lists the components of $\bar{V}(D)$ and $\bar{V}(D^{87})$, it being assumed that $M_{\mathrm{ij}} = \sqrt{(S_{\mathrm{ij}}/D_{\mathrm{ji}})}$; optimum M_{ij} values made $\bar{V}(D)$ negligibly smaller and are omitted.

TABLE 3.

Determination of natural Rb and its ^{87}Rb content.

Determn.	Tracer	Coefficients of $\bar{V}(S_{\mathrm{ij}})$	 $\bar{V}(D_{\mathrm{ji}})$	 $\bar{V}(M_{\mathrm{ij}})$	Total * $\bar{V}(D)$ or $\bar{V}(D^{87})$
Total Rb	^{87}Rb	0·004	0·115	1·236	$1{\cdot}35K^2$
	^{85}Rb	0·041	0·829	1·922	$2{\cdot}79K^2$
^{87}Rb	^{87}Rb	0·004	1·115	1·236	$2{\cdot}35K^2$
	^{85}Rb	0·041	0·037	1·922	$2{\cdot}00K^2$

* $\bar{V}(S)$ is ignored.

Clearly for total rubidium, enriched ^{87}Rb tracer is better. This is also used for ^{87}Rb–^{87}Sr age determinations in many laboratories, but, despite the larger error involved in its calibration, ^{85}Rb tracer seems to be preferable. Usually the natural ratio for rubidium is assumed or measured once on a mass spectrometer, rather than for every sample. Because of the lower coefficient of $\bar{V}(D_{\mathrm{ji}})$ the use of ^{85}Rb would reduce the significance of any natural variation of D_{ji}. Furthermore, to reduce errors caused by inhomogeneity, it is preferable to use the same matrix sample in determining rubidium and strontium; in the strontium mass spectrum the residual ^{87}Rb correction is more accurate when the ^{85}Rb : ^{87}Rb ratio is high.

When either tracer is calibrated against a natural rubidium standard the discrimination error in the determination of ^{87}Rb will be about $1{\cdot}5\delta$.

Determination of Strontium and ^{87}Sr.—Tracers employed are natural strontium, fission-product strontium, enriched ^{86}Sr, and enriched ^{84}Sr. Natural strontium is suitable only for fairly pure radiogenic ^{87}Sr. ^{90}Sr would be an ideal tracer, but fission-product strontium also contains ^{87}Sr and ^{88}Sr and constitutes a serious health hazard. Accordingly only the relative merits of tracers enriched in ^{84}Sr or ^{86}Sr are considered. Typical compositions are ^{84}Sr 50·5, ^{86}Sr 12·0, ^{87}Sr 3·6, ^{88}Sr 33·9, and ^{86}Sr 82, ^{87}Sr 4, ^{88}Sr 14%.

Natural strontium has ^{84}Sr 0·55, ^{86}Sr 9·8, ^{87}Sr 7·0, ^{88}Sr 82·7%. Using (1) with $\mathrm{i} = 88$, $\mathrm{j} = 84$ or 86, and $M_{\mathrm{ij}} = \sqrt{(S_{\mathrm{ij}}/D_{\mathrm{ji}})}$ gives: ^{84}Sr, $M_{88,84} = 10{\cdot}0$, $\bar{V}(D) = \bar{V}(S) + 1{\cdot}52K^2$; ^{86}Sr, $M_{88,86} = 1{\cdot}2$, $\bar{V}(D) = \bar{V}(S) + 1{\cdot}94K^2$. Clearly the precision for *total* strontium is better with ^{84}Sr tracer, but this advantage is somewhat offset by the less convenient M_{ij} ratio.

Radiogenic ^{87}Sr may be determined with (11), or alternatively with a derivative of (2) with $k = \mathrm{r}$:

$$G^{\mathrm{r}} = \frac{SW_{\mathrm{r}}}{\sum\limits_{\mathrm{y}} W_{\mathrm{y}}S_{\mathrm{yj}}} \cdot \frac{M_{\mathrm{ij}} - S_{\mathrm{ij}}}{1 - M_{\mathrm{ij}}D_{\mathrm{ji}}} (D_{\mathrm{ri}} - C_{\mathrm{ri}}), \tag{13}$$

where r is 87, i 88, and j 84 or 86 for the two tracers. Separate mass analyses are made to find M_{rj} (or M_{ij}) and D_{ri}, D_{jr} (or D_{ji}); C_{ri} is determined with reagent strontium, or strontium separated from a strontium-rich mineral associated with that being dated, whichever is the prime source of contamination. Three typical examples are considered

Example	D_{ri}	^{84}Sr	^{86}Sr	^{87}Sr	^{88}Sr
1	0·2	0·5%	8·9%	15·1%	75·5%
2	0·5	0·4%	7·3%	30·8%	61·5%
3	1·0	0·3%	5·6%	47·05%	47·05%

The errors are listed in Table (4): for equation (11) $M_{rj} = \sqrt{(S_{rj}/D_{jr})}$; for equation (13), M_{ji} values are identical with those for total strontium.

TABLE 4.

$[\bar{V}(G^r) - \bar{V}(S)]$ from equations (11) and (13).

Example	Enriched ^{84}Sr			Enriched ^{86}Sr		
	M_{rj}	Eq. (11)	Eq. (13)	M_{rj}	Eq. (11)	Eq. (13)
1	1·46	$2·45K^2$	$5·07K^2$	0·29	$3·20K^2$	$5·47K^2$
2	2·31	$1·36K^2$	$3·00K^2$	0·45	$1·68K^2$	$3·39K^2$
3	3·27	$1·25K^2$	$2·71K^2$	0·64	$1·42K^2$	$3·10K^2$

Evidently it is better here to use enriched ^{84}Sr tracer; also (11) is preferable to (13), which might be expected since, as D_{jr}, D_{ji}, S_{rj}, S_{ij}, and C_{ri} tend to zero, $\bar{V}(G^r) - \bar{V}(S)$ tends to K^2 and $2K^2$, respectively.

TABLE 5.

Coefficients in (14a) and $\bar{V}(G^r)$ for (14) and (11, calibrated).

Example	M_{rj}	Coefficients of						$\bar{V}(G^r)(14)$ *	$\bar{V}(G^r)(11)$ *
		$\bar{V}(M_{rj})$	$\bar{V}(M_{ij})$	$\bar{V}(S_{rj})$	$\bar{V}(S_{ij})$	$\bar{V}(C_{ri})$	$\bar{V}(C_{ji})$		
Tracer ^{84}Sr									
1	9·0	3·06	0·10	—	0·01	0·55	0·18	$5·23K^2$	$3·64K^2$
2	9·8	1·47	—	—	0·01	0·04	0·02	$2·87K^2$	$2·55K^2$
3	12·4	1·21	—	—	0·01	0·01	0·01	$2·57K^2$	$2·44K^2$
Tracer ^{86}Sr									
1	0·61	3·37	0·03	0·01	0·03	0·55	0·32	$6·15K^2$	$5·04K^2$
2	0·87	1·59	—	—	0·03	0·04	0·07	$3·57K^2$	$3·53K^2$
3	1·19	1·28	—	—	0·02	0·01	0·03	$3·19K^2$	$3·26K^2$

* $\bar{V}(E)$ is omitted.

Alternatively, equation (12) may be used to eliminate the effects of sample inhomogeneity and variable chemical contamination. When the tracer is calibrated against the natural element (12) becomes

$$G^r = \frac{EW_r}{\sum\limits_z W_z E_{zi}} \cdot \frac{1 - M'_{ij}E_{ji}}{M'_{ij} - S_{ij}} \left[\frac{M_{rj}(1 - S_{ij}C_{ji}) - S_{rj}(1 - M_{ij}C_{ji}) - C_{ri}(M_{ij} - S_{ij})}{(1 - M_{ij}C_{ji})}\right] \quad (14)$$

The variance expression for terms within the square brackets is:

$$\left[\frac{M_{rj}(1 - S_{ij}C_{ji})}{X}\right]^2 \bar{V}(M_{rj}) + \left[\frac{M_{ij}\,(1 - S_{ij}C_{ji})(C_{ji}M_{rj} - C_{ri})}{(1 - M_{ij}C_{ji})X}\right]^2 \bar{V}(M_{ij}) +$$

$$\left[\frac{S_{rj}(M_{ij}C_{ji} - 1)}{X}\right]^2 \bar{V}(S_{rj}) + \left[\frac{S_{ij}(C_{ri} - M_{rj}C_{ji})}{X} + \frac{S_{ij}}{M'_{ij} - S_{ij}}\right]^2 \bar{V}(S_{ij}) +$$

$$\left[\frac{C_{ri}\,(M_{ij} - S_{ij})}{X}\right]^2 \bar{V}(C_{ri}) + \left[\frac{C_{ji}(M_{rj} - C_{ri}M_{ij})(M_{ij} - S_{ij})}{(1 - M_{ij}C_{ji})X}\right]^2 \bar{V}(C_{ji}), \quad (14a)$$

where $X = [M_{rj}(1 - S_{ij}C_{ji}) - S_{rj}(1 - M_{ij}C_{ji}) - C_{ri}(M_{ij} - S_{ij})]$. Coefficients of $\bar{V}(E_{zi})$, $\bar{V}(E_{ji})$, and $\bar{V}(M'_{ij})$ follow from (1a). Expression (14a) will be minimised by some value of M_{rj}. Table 5 records these minimising values for the three examples, the coefficients in (14a), and the minimum total $\bar{V}(G^{\mathrm{r}})$ for both (14) and (11) modified for calibration of the tracer. Clearly little precision is lost by using (14) unless the percentage of radiogenic ^{87}Sr is small. Then the loss of precision must be balanced against the advantages of eliminating the effects of sample inhomogeneity. Table 5 shows that a slightly improved precision is achieved with ^{84}Sr tracer, but only at the expense of less convenient M_{rj} values. However, $\bar{V}(G^{\mathrm{r}})$ is less sensitive to changes in M_{rj} when ^{84}Sr is used; if M_{rj} is made unity, $\bar{V}(G^{\mathrm{r}})$ rises only to about the optimum values found for the ^{86}Sr tracer. Although there is little to choose between the tracers on these grounds, the ^{84}Sr tracer gives a lower coefficient of $\bar{V}(C_{\mathrm{ji}})$; for these examples it is 0·001 or less, when $M_{\mathrm{rj}} = 1$. In the method based on (14), D_{ji} is assumed to equal C_{ji} determined with C_{ri} for a different source of the element, or obtained from the literature; the error thus introduced will be smaller for the ^{84}Sr tracer.

When either tracer is calibrated against a natural strontium standard, the mass discrimination bias in ^{87}Sr will be about $0{\cdot}7\delta$.

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[*Received, September* 12*th*, 1961.]