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INSTD: A Computer Program to Perform Internal Standard Calculations for Isotopic Ratio Mass Spectrometric Data Using General Solutions to the Equations

D. H. Smith

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ABSTRACT

A computer code has been developed to perform internal standard calculations on isotopic ratio mass spectrometric data. Solutions to the relevant algebraic equations are completely general and applicable to any element. The program incorporates two methods of bias calculation: one is through analytical solution of the equations and the other through an iterative process. Derivation of the equations is outlined, and examples of results are given. Also discussed is an attempt to incorporate calculation of unspiked sample bias into the calculations.

INTRODUCTION

One of the most intractable problems confronting the isotope ratio mass spectrometrist is that of isotopic bias during evaporation in the analysis of solid samples. Because evaporation is a function of the mass of the moiety in question, light isotopes evaporate at different rates than heavy. This is an extremely difficult process to control in a reproducible manner. Recent research has led to advances in this area. Rokop et al. have developed a rhenium overplating technique to provide better control of the evaporation process (1). Smith and Carter have used an overlayer of rhenium powder to the same end (2). While these techniques help, they are cumbersome to use and in any case do not eliminate the problem. Internal standards address the situation in an entirely different way. Instead of trying to control evaporation, this technique attempts to calculate the bias applicable to the particular filament in question. This is done by spiking the sample with a tracer composed of a mixture of two highly enriched isotopes. The ratio of these isotopes in the internal standard (also called a double spike) is known to the highest possible degree of accuracy and precision. By comparing the measured value of this ratio to the known, calculation of the bias correction per mass for that particular analysis can be made; bias is assumed to vary linearly with mass, a good approximation over the relatively small mass ranges involved in isotopic ratio measurements. In this way, precision of analyses is improved by about a factor of five over using an average bias correction.

Dietz et al. were the first to suggest use of a synthetic mixture for this purpose (3). Since then it has been widely adopted and used for many elements. Work in this laboratory has concentrated on uranium and plutonium (4,5). Computer codes applicable only to our pulse-counting data

system were developed (6,7); this procedure manipulated the counts collected for each isotope to make the necessary corrections. Recent acquisition of a Vacuum Generators VG-354 isotopic ratio mass spectrometer and receipt of funding to explore its application to gas samples requiring the highest possible accuracy and precision led to the need for a completely general computer program to perform the necessary calculations. An additional incentive was our participation in ISPO project A-126 (8) and the desirability of processing results generated in laboratories other than ORNL.

DERIVATION OF THE EQUATIONS

General application of the internal standard technique requires that the equations involved operate on isotopic ratios rather than counts. I have adopted the general approach of Callis (9), but, unlike him, I have derived the analytical solution for the quadratic equation. The symbols used in the following derivation are summarized in Table 1.

Table 1: Symbol Summary

Symbol	Description
R	ratios
N	numbers of atoms
F	atom fractions
M	masses
B	bias correction
f	bias correction per mass
m	mixture
s	sample
t	tracer (spike)
a	first isotope of tracer (internal standard)
b	second isotope of tracer
c	sample isotope for isotope dilution calculations
d	other sample isotopes

Thus the internal standard ratio to which the measured value is to be corrected is denoted by R_{abt}.

Any measured ratio in the analysis of the mixture of sample and tracer can be defined as the actual ratio times a bias; this ratio is in turn comprised of contributions from the unspiked sample and the tracer. In equation form:

$$B_{ij}R_{ijm} = (N_sF_{is} + N_tF_{it})/(N_sF_{js} + N_tF_{jt}) \tag{1}$$

where i, j represent the relevant isotopes a, b, c, d. We also know that

$$R_{ijx} = F_{ix}/F_{jx} \tag{2}$$

where x represents m, s, t. By solving Equation (1) when expressed in terms of b and c for the mixture ($B_{bc}R_{bcm}$), we get:

$$\frac{N_s}{N_t} = \frac{F_{tc}(R_{bcs} - B_{bc}R_{bcm})}{F_{sc}(B_{bc}R_{bcm} - R_{bcs})} = \frac{F_{tc}A_{bc}}{F_{sc}} \quad . \tag{3}$$

Similar expressions for A_{ab}, A_{dc} may also be derived from the appropriate version of Equation (1). Going now to the version of Equation (3) for R_{ab}, we have:

$$\frac{N_s}{N_t} = \frac{F_{bt}(R_{abt} - R_{abm}B_{ab})}{F_{bs}(R_{abm}B_{ab} - R_{abs})} \quad . \tag{4}$$

By rearranging and substituting for N_s/N_t from the following relationship:

$$N_s/N_t = A_{bc}F_{ct}/F_{cs} \tag{5}$$

we obtain:

$$B_{ab}(A_{bc}R_{abm} + R_{abm}R_{bct}/R_{bcs}) = R_{bct}R_{abt}/R_{bcs} + A_{bc}R_{abs} \quad . \tag{6}$$

Since the term A_{bc} in Equation (6) contains in turn a term for the bias, B_{bc} (see Equation (3)), it is necessary to derive an expression relating the two bias terms (B_{ab} and B_{bc}); they are not independent and both are integral multiples of the bias correction per mass. We know that:

$$(1-B_{ab})/(M_b-M_a) = (1-B_{bc})/(M_c-M_b) = f \quad . \tag{7}$$

By rearrangement we can get B_{bc} in terms of B_{ab}:

$$B_{bc} = 1-(M_c-M_b)(1-B_{ab})/(M_b-M_a) = 1-p(1-B_{ab}) \tag{8}$$

where p is the ratio of mass differences, $(M_c-M_b)/(M_b-M_a)$. By substituting the full expression for A_{bc} (Equation (3)), incorporating in it the relationship described in Equation (8), we arrive at a quadratic equation in B_{ab} whose solutions are, of course, readily obtained. Using the standard algebraic form for a quadratic equation ($ax^2 + bx + c = 0$) and for the solutions ($x = (-b \pm (b^2 - 4ac)^{1/2})/2a$), we obtain for the coefficients a, b, c:

$$a = - pR_{abm}R_{bcm} + pR_{abm}R_{bct}R_{bcm}/R_{bcs} \tag{9}$$

$$b = R_{abm}R_{bct} - R_{abm}R_{bcm}(1-p) + R_{abm}R_{bct}R_{bcm}(1-p)/R_{bcs}$$
$$- R_{abm}R_{bct} - pR_{bct}R_{abt}\ R_{bcm}/R_{bcs} - pR_{abs}R_{bcm} \tag{10}$$

$$c = - R_{bct}R_{abt}R_{bcm}(1-p)/R_{bcs} + R_{bct}R_{abt} - R_{abs}R_{bcs}$$
$$+ R_{abs}R_{bcm}(1-p) \quad . \tag{11}$$

Equations 9-11, together with the general solution of a quadratic equation, allow an analytical value for the bias to be obtained. Once a value for B_{ab} is known, values for the bias for any ratio may be readily calculated through use of equations similar to Equation (8). The ratios of most interest are the one used in isotope dilution calculations (R_{bcm}

or R_{acm}: either will yield exactly the same result in this context) and those represented by R_{dcs}, which include the ratios, such as 235/238, whose values are to be refined by application of the internal standard protocol. R_{bcm} is calculated by applying the calculated bias correction, B_{bc}, to the measured value of R_{bcm}. Unspiked sample ratios are calculated from the following equation:

$$R_{dcs} = R_{dcm}B_{dc} - (R_{dct} - R_{dcm}B_{dc})/A_{bc} \tag{12}$$

where

$$B_{dc} = 1 - (M_c - M_d)(1 - B_{ab})/(M_b - M_a) \quad . \tag{13}$$

While Equations 9-13 allow direct calculation of all desired parameters, algebra of such complexity must be checked to verify its correctness. With the analytical solutions in hand, it is a simple matter to implement an iterative process that circumvents much of the algebra. Using Equation (6) as a starting point, we can obtain a value for B_{ab} for use in the iterative loop:

$$B_{ab} = (R_{bct}R_{abt}/R_{bcs} + A_{bc}R_{abs})/(A_{bc}R_{abm} + R_{abm}R_{bct}/R_{bcs}). \tag{14}$$

To execute the loop, one initializes all biasses to 1.0, calculates a value for A_{bc}, and then evaluates B_{ab}. This value is compared to the one obtained in the previous iteration (B_{ab} = 1.0 for the first iteration); when successive iterations yield values for the bias that are analytically indistinguishable, the process has converged and iteration is terminated. The test value for convergence is arbitrary but should be well below expected analytical uncertainties; I have used 1×10^{-8} in this program. It usually takes four to six iterations before convergence occurs.

A case that occurs with some frequency is to have the internal standard incorporated in the sample rather than in the spike. This will be

the case, for example, when one is calibrating a proposed internal standard for concentration. It is highly desirable to exploit the enhanced accuracy accessible through the internal standard and relatively easy to do so with a few algebraic manipulations. To address this situation, one interchanges sample and spike ratios prior to data processing; R_{abs}, R_{abt}, R_{bcs}, and R_{bct} are the ratios involved. The equation for calculation of relevant ratios (R_{dct}) takes on a different form:

$$R_{dct} = A_{bc}(R_{dcm}B_{dc} - R_{dct}) + R_{dcm}B_{dc} \quad . \qquad (15)$$

R_{dct} appears in this equation rather than R_{dcs} because sample and spike have been interchanged.

The isotopic ratios derived from the unspiked sample in the above derivations (R_{abs}, R_{bcs}, etc.) are nearly always calculated from analyses in which an average bias correction has been used. It is tempting to include another variable in the derivations that represents the correction necessary to apply to the average bias correction used for processing unspiked sample data to make it consistent with the internal standard analysis. This can be accomplished by including the appropriate term in Equation (3):

$$N_s/N_t = F_{jt}/F_{js}(R_{ijt} - B_{ijm}R_{ijm})/(B_{ijm}R_{ijm} - B_{ijs}R_{ijs}) \qquad (16)$$

where B_{ijs} represents the sample bias and B_{ijm} the mixture bias; it is calculation of B_{ijm} that was the goal of the earlier derivation. In Equation (16), i, j represent a, b, c as they did before. The parameters which we wish to extract algebraically are the bias to be applied to analysis of the mixture whose data we are currently processing, B_{abm}, and the bias adjustment to apply to the ratios of the unspiked sample, B_{dcs}. By following logic analogous to that used to arrive at equations 9-13, we obtain:

$$B_{abm} = (R_{bct}R_{abt}/(R_{bcs}B_{bcs}) + A_{bc}B_{abs}R_{abs})/(A_{bc}R_{abm} + R_{abm}R_{bct}/(R_{bcs}B_{bcs}) \quad (17)$$

and

$$B_{dcs} = (A_{bc}R_{dcm}B_{dcm} - R_{dct} + R_{dcm}B_{dcm})/(A_{bc}R_{dcs}) \quad (18)$$

where A_{bc} is defined in a manner similar to Equation (5). The algebra involved in obtaining an analytical solution to these equations is quite formidable and wasn't attempted. An iterative approach similar to that already described was relatively straightforward and was implemented to evaluate the validity of this approach. All biasses were initialized to 1.0 and values of B_{abm} and B_{dcs} repetitively calculated until both biasses converged.

One more case remains to be described: that of a "built-in" internal standard. This arises in the case of an element among whose isotopes are at least two that are not radiogenic and whose ratio is thus invariant in nature. This ratio can then be used as the internal standard ratio to calculate the bias necessary to apply to ratios involving radiogenic isotopes whose values will vary from sample to sample. The calculations involved in addressing this situation are much simpler than for those already described. This is because no corrections for "unspiked sample" contribution are necessary; the bias is calculated directly by comparing the measured ratio to the known. Examples where this situation arises are for strontium, where internal standard procedures have been applied for many years in geological age-dating studies, and for krypton and xenon.

PROGRAM DESCRIPTION

A FORTRAN computer program, INSTD, was developed to implement the above system of equations. Data sets from various mass spectrometers were

input and stored in files on the disc. Two files were used, ISBOOK.DAT and ISDAT.DAT. The structure and contents of these files are listed in Table 2.

Table 2: Structure and Contents of Data Files

File	Size	Variable	Description
ISBOOK	301,30	ITIT	Descriptive title.
		LREC	Record number in ISDAT where data start.
		NREP	Number of replicates.
		SMWGT	Sample weight.
		SPWGT	Spike weight.
ISDAT	2001,16	ABMIX	Isotopic abundances.

ISBOOK is a bookkeeping file that contains the information necessary for proper access to ISDAT for up to 300 samples. It also contains a descriptive title and the weights necessary to perform isotope dilution calculations. ISDAT contains mass spectrometric data in the form of isotopic abundances in atom percent. From these all necessary initial values for mixture ratios are calculated.

Information concerning the unspiked sample and the spike are read from the appropriate disc files. These files are those used for similar functions in the main data processing programs for isotopic mass spectral data from our four pulse-counting instruments (6,7). The input required for INSTD are the file record numbers in SPIKE.DAT for the spike composition and OUT.DAT for the unspiked sample composition.

The input sequence for INSTD first offers an option to exit, to process old data or enter new, or to edit an existing record. The last option provides the opportunity to correct an old data set that has one or more erroneous entries. Keyboard prompting instructions should be

self-explanatory. One of the provisions in this branch is to allow printing a short table of contents for the data files.

The data processing branch requires first the relevant record numbers for the spike and for the unspiked sample. There is then an option for input of mixture data: they may come from an already existing disc file or they may be input manually from the keyboard either as isotopic ratios or as isotopic abundances in atom percent form. If isotopic ratios are the form of input, the program asks for the mass of the denominator; it is necessary to enter all ratios with the same denominator. Isotopic ratios are converted to atom percents, and all data are stored on the disc in files ISBOOK and ISDAT. Maintenance of these files is automatically carried out by the program: the last record of each file contains the record number in that file last written into, and these indices are kept updated by the program. The title is entered, and weight information for the sample and spike follow. Ratios or atom percents are then entered; the number and identity of the isotopes or ratios are assumed by the program; the operator has no choice in the matter. These, however, are the natural ones for the element in question, with isotopic abundances entered in order of increasing mass and isotopic ratios in order of increasing numerator mass; the number of isotopes is determined by the number appearing in the mass and abundance file (MASSAB.DAT) (6,7). Data entry from the disc requires only the relevant record number; the disc files contain all other necessary information.

Data processing proceeds automatically, and output is given for all three methods of calculation: analytical solution, iteration, and iteration including sample bias. The program continues to ask for a record number

for mixture data until a 0 (zero) is entered, at which it branches back to the original option of exit, data processing, or editing.

The computer program was implemented on a DEC 11/23, an LSI-11 system with 20 megabytes of hard disc data storage. The program consists of several modules; it was not possible to use a single module due to dynamic memory overflow during compilation. These modules are INSTD, the main line calling program that consists primarily of subroutine calls; INSTD1, which contains input routines and initializes various parameters; INSTD2, which performs the calculations and outputs results; and ISED, the file editing routine for ISBOOK and ISDAT. These modules are linked in overlay mode, with each in turn being called into core for execution. Variables are transferred between modules via COMMON statements.

RESULTS AND DISCUSSION

Results of analyses performed on a variety of mass spectrometers were input. One of the first data sets was of samples analyzed on one of our multi-stage instruments whose data had already been processed by program MSC (6,7) and had been subjected to the internal standard protocol embodied therein. It was gratifying (and a big relief) to find that each program gave identical values for the bias correction per mass for the various samples tested. Data obtained using our Vacuum-Generators VG-354 were entered and processed using INSTD. The power of this instrument was vividly demonstrated by the fact that a precision of $\pm 0.005\%$ was obtained for seven replicate samples of a mixture of a prospective 233-U/236-U internal standard and NBS U-500; the 235/238 ratio of the latter was used as the internal standard ratio.

Calculation of the bias required by the unspiked sample in the iterative process described above was evaluated. Typical results are

presented in Table 3 for both current-integrating and pulse-counting instruments. The mass spectrometers in question are in the IAEA laboratory near Vienna. Tabulated are the 236/238 uranium ratios both with and without calculation of unspiked sample bias. Also included are the values for bias correction per mass calculated in the normal internal standard way (column labeled "Mixture without") and with calculation of unspiked sample bias included; the latter include the bias calculated for the sample-spike mixture (column labeled "Mixture with") and the adjustment to the unspiked sample bias necessary to bring it into conformance with the constraints imposed by the internal standard (column labeled "Sample with").

Table 3: Sample Bias Calculation

Sample	236/238 without	236/238 with	Mixture without	Mixture with	Sample with
Part 1: Current Integration Results					
M115-1	0.39288	0.39281	-0.159	-0.156	-0.562
-2	0.39046	0.39045	-0.023	-0.021	-0.355
M215-1	0.40855	0.40854	-0.016	-0.014	-0.390
-2	0.40838	0.40836	-0.031	-0.029	-0.327
-3	0.40855	0.40854	+0.009	+0.011	-0.231
M315-1	0.39324	0.39323	+0.015	+0.016	-0.253
-2	0.39301	0.39300	-0.011	-0.009	-0.263
Part 2: Pulse-counting Results					
M115-1	0.38939	0.38937	+0.129	+0.132	-0.536
-2	0.39076	0.39077	+0.403	+0.402	+0.133
M215-1	0.40389	0.40839	+0.213	+0.213	-0.060
-2	0.40818	0.40816	+0.068	+0.070	-0.477
M315-1	0.39352	0.39352	+0.132	+0.133	-0.230
-2	0.39260	0.39259	+0.182	+0.183	-0.159

The conclusion I reach by analysis of the results in Table 3 (and others not tabulated) is that calculation of unspiked sample bias is of doubtful value. Changes wrought in the 236/238 ratio, which, due to its use in isotope dilution calculations, is the most important one, are insignificant, generally one part in 40,000 or so. The effect on the calculated bias correction per mass for the mixture is also very small, well below statistical uncertainty. In addition, the adjustment to the bias corrections to be applied to the unspiked sample are suspiciously large. In the section of Table 3 devoted to results from a current-integrating instrument, the biasses calculated for the unspiked sample should be approximately equal to those calculated for the mixture; there is nothing inherent in the mixture that should cause lower bias corrections. Yet the adjustments to the bias correction for the unspiked sample listed in Table 3 are roughly an order of magnitude larger than the corresponding mixture bias corrections (several tenths of a percent per mass versus several thousandths). This does not seem to be a probable reflection of reality. A possible explanation that may mitigate this conclusion to some extent is that the 235/238 ratio, which was used to determine the unspiked sample bias correction, is less than 0.01. It is possible that a higher ratio would yield more realistic adjustments to the unspiked sample bias correction. A firm decision in this matter awaits further experiments.

CONCLUSIONS

There can be no doubt that use of internal standards is justified whenever application is possible. Improvements in precision and accuracy

of factors of five, which can be realized by their application, are not easy to come by. The program described in this paper, embodying general solutions to the system of simultaneous equations, should receive widespread application at ORNL. It will be a relatively simple matter to incorporate it into the principal mass spectral data processing programs (MSC) once the VG-354 is linked in the network to our host computer. It will have direct application to our project to measure accurate inert gas isotopic ratios. The fact that the solutions are general will enhance their flexibility and make them adaptable to any analytical situation in which internal standards are used.

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