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**Adjusting of Isotope Ratios Measurements by the Method of Least Squares  
on a Programmable Pocket Calculator**

Wyrównywanie mierzonych stosunków izotopowych metodą najmniejszych kwadratów  
za pomocą kieszonkowego kalkulatora programowanego

Исправление измеряемых изотопных отношений методом наименьших квадратов  
с помощью программированного калькулятора

INTRODUCTION

Three or more isotopic elements as strontium and lead are widely utilized in the dating of rocks. Thus a need arises for faster data processing with statistical methods. The usual way of meeting this demand in the case of new instruments is an incorporation of a computer, via an interface and a direct statistical adjustment of the data obtained during mass spectrometric measurements. However, many older instruments still working in scientific laboratories are not equipped with such devices and statistical processing of the data obtained must be performed in a computer centre. The purpose of this paper is to eliminate such inconvenient step by using a simple programmable calculator which can be even communicated with the mass spectrometer employing a home-made interface similar to that described by Hałas and Skorzynski [2].

The Authors have accomplished this goal using inexpensive TI Programmable 59 calculator produced by Texas Instruments. This calculator has up to 100 registers available for data storage or up to 960 for program storage. The memory area can be optionally divided between these two needs. The calculator reads and writes magnetic cards.

TERMINOLOGY AND METHODS

Let us consider a mass spectrum of an element for which three peaks are measured. As

an example may serve the mass spectrum of strontium (Fig. 1) in which the isotopic ratio  $^{87}\text{Sr}/^{86}\text{Sr}$  is of geological interest.

However, if the measurements will be limited merely to this ratio, the obtained result can be altered by both systematic and random errors. In order to reduce the systematic error the final value of isotopic ratio is normalized by the following equation [3]:

$$\frac{^{87}\text{Sr}}{^{86}\text{Sr}} = \left[ \frac{(^{87}\text{Sr}/^{86}\text{Sr})_m (^{88}\text{Sr}/^{86}\text{Sr})_n}{(^{88}\text{Sr}/^{87}\text{Sr})_m} \right]^{1/2}, \quad (1)$$

where index  $m$  refers to measured ratios and  $n$  to a normalized one (known with a higher accuracy). In order to reduce the random errors, the measured ratios, being utilized in the above equation, should be adjusted by the Least Squares Method. For this reason all major peaks should be measured and three ratios must be calculated.

To unify the notation for strontium and lead isotopes (Fig. 1, 2), the heights of peaks  $^{86}\text{Sr}$ ,  $^{87}\text{Sr}$  and  $^{88}\text{Sr}$  will be denoted as  $x_2$ ,  $x_3$  and  $x_4$ , and their ratios as:

$$\begin{aligned} y_4 &= x_3/x_2 \\ y_5 &= x_4/x_2 \\ y_6 &= x_4/x_3 \end{aligned} \quad (2)$$

These three values are not independent, but are connected by the following rigorous equation:

$$\eta_4 \eta_6 - \eta_5 = 0, \quad (3)$$

where  $\eta$ 's denote the true values of respective  $y$ 's.

Each of the determined ratios will be considered as a sum of true value and of an attached error. A set of the measured values, generally, does not satisfy the rigorous equation. According to the Method of Least Squares, however, the weighted sum of squares of errors can be minimized, thus providing the most reliable estimates of the determined values which satisfy the rigorous equations (see, for instance [1]).

In the formulation of general equations it is convenient to use the ordinary matrix notation. In this notation the determined values, in our example the strontium isotope ratios, will be denoted as one column matrix, i.e. vector:

$$y = \begin{bmatrix} y_4 \\ y_5 \\ y_6 \end{bmatrix} = \begin{bmatrix} ^{87}\text{Sr}/^{86}\text{Sr} \\ ^{88}\text{Sr}/^{86}\text{Sr} \\ ^{88}\text{Sr}/^{87}\text{Sr} \end{bmatrix}. \quad (4)$$

The variances of  $y$ 's, i.e. squared standard errors, will be represented by diagonal elements of the variance-covariance matrix:

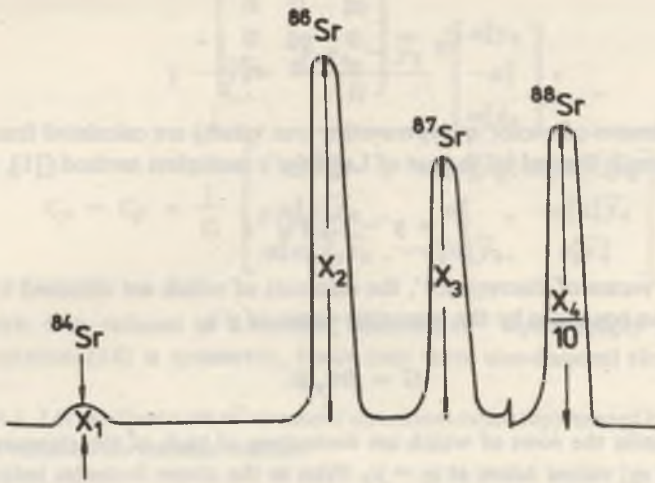


Fig. 1. Mass spectrum of strontium; the height of peaks are proportional to the abundances of the respective isotopes. Three major peaks are measured to reduce static error of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio; note that the height of the  $^{88}\text{Sr}$  peak has been reduced by one-tenth

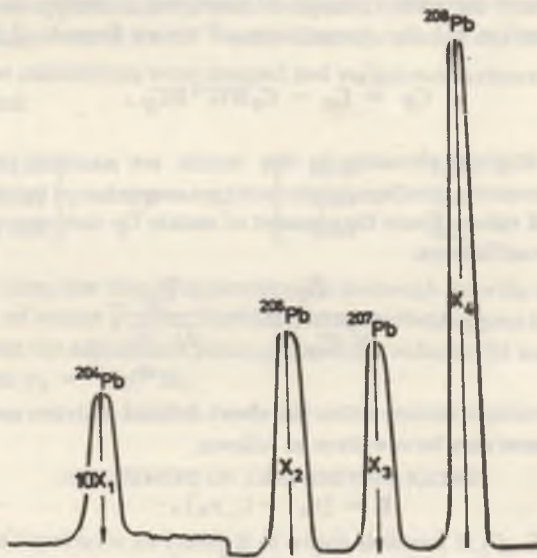


Fig. 2. Mass spectrum of lead, note that the height of the  $^{204}\text{Pb}$  has been enlarged by tenfold

$$C_y = \begin{bmatrix} \sigma_4^2 & 0 & 0 \\ 0 & \sigma_5^2 & 0 \\ 0 & 0 & \sigma_6^2 \end{bmatrix}. \quad (5)$$

The first estimates of vector  $\eta$  (representing true values) are calculated from the following general formula derived by the use of Lagrange's multipliers method ([1], chapter 9):

$$\tilde{y} = y - C_y B' G^{-1} c \quad (6)$$

where  $c$  is the 'vector of discrepancy', the elements of which are obtained by replacing  $\eta$ 's in the rigorous equations by the respective values of  $y$ 's,

$$G = B C_y B', \quad (7)$$

and  $B$  is the matrix the rows of which are derivatives of each of the rigorous equations with respect to  $\eta_j$ ; values taken at  $\eta_j = y_j$ . Prim in the above formulas indicates that a given matrix is transposed.

As usual in nonlinear problems the first estimates may not sufficiently satisfy the rigorous equation, therefore iterative procedure should be used: the second approximation of the vector  $\eta$  can be calculated again from the above equations by putting  $\tilde{y}$  instead of the initial vector  $y$  in matrix  $B$ , vector  $c$  and equation (6). Further approximations, if necessary, can be calculated in the same way.

Finally, the variance-covariance matrix of improved  $\tilde{y}$  vector can be calculated by applying to equation (6) the propagation of errors formula ([1], chapter 4-5):

$$C_{\tilde{y}} = C_y - C_y B' G^{-1} B C_y. \quad (8)$$

Square roots of diagonal elements in this matrix are standard errors of improved values  $\tilde{y}$ , whereas symmetric nondiagonal elements are covariances between the individual pairs of the improved values. From the element of matrix  $C_{\tilde{y}}$  one may calculate the estimates of correlation coefficients:

$$\rho_{ij} = \frac{\tilde{c}_{ij}}{\sqrt{\tilde{c}_{ii} \tilde{c}_{jj}}} = \frac{\tilde{c}_{ij}}{\tilde{\sigma}_i \tilde{\sigma}_j}. \quad (9)$$

In the case of strontium isotope ratios the above defined matrices and formulas of the Method of Least Squares may be rewritten as follows:

$$B = (y_6, -1, y_4), \quad (10)$$

$$B C_y = (\sigma_4^2 y_6, -\sigma_5^2, \sigma_6^2 y_4), \quad (11)$$

$$G = \sigma_4^2 y_6^2 + \sigma_5^2 + \sigma_6^2 y_4^2, \quad (12)$$

$$y - \tilde{y} = \frac{y_4 y_6 - y_5}{G} \begin{bmatrix} \sigma_4^2 y_6 \\ -\sigma_5^2 \\ \sigma_6^2 y_4 \end{bmatrix}, \quad (13)$$

$$C_y - C_{\tilde{y}} = \frac{1}{G} \begin{bmatrix} \sigma_4^2 \tilde{y}_6^2 & , & -\sigma_4^2 \sigma_5^2 \tilde{y}_6 & , & \sigma_4^2 \sigma_6^2 \tilde{y}_4 \tilde{y}_6 \\ -\sigma_4^2 \sigma_5^2 \tilde{y}_6 & , & \sigma_5^4 & , & -\sigma_5^2 \sigma_6^2 \tilde{y}_4 \\ \sigma_4^2 \sigma_6^2 \tilde{y}_4 \tilde{y}_6 & , & -\sigma_5^2 \sigma_6^2 \tilde{y}_4 & , & \sigma_6^4 \tilde{y}_4^2 \end{bmatrix}. \quad (14)$$

Here matrix  $G$  is reduced to a number, therefore  $G^{-1}$  equals simply  $1/G$ . Note that matrix in equation (14) is symmetric, hence only three non-diagonal elements must be calculated.

Example 1. Let us adjust a set of measured strontium ratios represented by the following vector  $y$  and variance-covariance matrix:

$$y = \begin{bmatrix} y_4 \\ y_5 \\ y_6 \end{bmatrix} = \begin{bmatrix} 0.7122 \\ 8.3625 \\ 11.7316 \end{bmatrix}, \quad C_y = \begin{bmatrix} 0.81 \times 10^{-6} & 0 & 0 \\ 0 & 4.84 \times 10^{-6} & 0 \\ 0 & 0 & 7.84 \times 10^{-6} \end{bmatrix}.$$

The initial 'discrepancy vector' is  $-0.00725$ . Using equations (12), (13) and (14) the first and the second approximations were computed. After the first approximation the 'vector of discrepancy' was  $1.9 \times 10^{-7}$  while after the second one it became as small as  $-2.7 \times 10^{-11}$ , so the calculations were stopped and variance-covariance matrix of improved values was calculated:

$$\tilde{y} = \begin{bmatrix} 0.7128 \\ 8.3622 \\ 11.7319 \end{bmatrix}, \quad C_{\tilde{y}} = 10^{-6} \begin{bmatrix} 0.06 & 0.38 & -0.44 \\ 0.38 & 4.65 & 0.22 \\ -0.44 & 0.22 & 7.58 \end{bmatrix}.$$

Actually, in this case, one step of approximation is enough since the differences between the same elements of vector  $\tilde{y}$ , after the first and the second approximations, are smaller than  $10^{-7}$ . Note that the adjustment process essentially reduces the variance of geochemically important ratio  $y_4 = {}^{87}\text{Sr}/{}^{86}\text{Sr}$ .

#### ADJUSTMENT OF LEAD ISOTOPE RATIOS

In the case of lead spectrum an example of which is shown in Fig. 2, the accurate determination of three isotope ratios, namely  ${}^{206}\text{Pb}/{}^{204}\text{Pb}$ ,  ${}^{207}\text{Pb}/{}^{204}\text{Pb}$  and  ${}^{208}\text{Pb}/{}^{204}\text{Pb}$ , is important in many geo- and cosmochemical studies. These ratios are well known as  $X$ ,  $Y$  and  $Z$  values in scientific papers. In our notation they will be represented by  $y_1$ ,  $y_2$  and

$y_3$  values, respectively. Further three ratios which can be determined from four peaks at the mass spectrum, are usually chosen in the following order:

$$y_4 = {}^{207}\text{Pb}/{}^{206}\text{Pb}, \quad y_5 = {}^{208}\text{Pb}/{}^{206}\text{Pb}, \quad y_6 = {}^{208}\text{Pb}/{}^{207}\text{Pb}.$$

We will denote the heights of peaks by  $x_1, x_2, x_3$  and  $x_4$ . Let vector  $y$  represent six ratios to be determined:

$$y = \begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ y_4 \\ y_5 \\ y_6 \end{bmatrix} = \begin{bmatrix} x_2/x_1 \\ x_3/x_1 \\ x_4/x_1 \\ x_3/x_2 \\ x_4/x_2 \\ x_4/x_3 \end{bmatrix} \cdot \quad (15)$$

From the above matrix equation it follows that these measurements are connected by three independent equations. Further calculations will be based on the following set of rigorous equations:

$$\begin{aligned} \eta_1 \eta_4 - \eta_2 &= 0 \\ \eta_1 \eta_5 - \eta_3 &= 0 \\ \eta_2 \eta_6 - \eta_3 &= 0 \end{aligned} \quad (16)$$

This set provides the design matrix

$$B = \begin{bmatrix} y_4 & -1 & 0 & y_1 & 0 & 0 \\ y_5 & 0 & -1 & 0 & y_1 & 0 \\ 0 & y_6 & -1 & 0 & 0 & y_2 \end{bmatrix} \quad (17)$$

and the vector of discrepancy<sup>3</sup>

$$c = \begin{bmatrix} y_1 y_4 - y_2 \\ y_1 y_5 - y_3 \\ y_2 y_6 - y_3 \end{bmatrix}, \quad (18)$$

which can be used in the data adjustment with general formulas (6) and (8). Let us consider a numerical example.

Example 2. For a lead sample the following data were experimentally obtained, represented by the vector

$$y = \begin{bmatrix} 16.07 \\ 15.49 \\ 36.78 \\ 0.9651 \\ 2.2891 \\ 2.3726 \end{bmatrix}$$

and variance-covariance matrix

$$C_y = 10^{-4} \begin{bmatrix} 624 & 0 & 0 & 0 & 0 & 0 \\ 0 & 556 & 0 & 0 & 0 & 0 \\ 0 & 0 & 3472 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0.0441 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.2025 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0.3136 \end{bmatrix}.$$

The initial 'discrepancy vector' is

$$c = \begin{bmatrix} 0.0192 \\ 0.0058 \\ -0.0284 \end{bmatrix}.$$

while after the first step of iterative process (equation (6)) its elements are as small as about  $10^{-7}$ . After the second step they are comparable with machine error  $\approx 10^{-11}$ . Calculations are, therefore, stopped at the second step of approximation, and the improved values and their variance-covariance matrix are obtained:

$$\tilde{y} = \begin{bmatrix} 16.0624 \\ 15.5002 \\ 36.7715 \\ 0.9650 \\ 2.2893 \\ 2.3723 \end{bmatrix}, \quad C_{\tilde{y}} = 10^{-4} \begin{bmatrix} 211 & 200 & 476 & -0.23 & -0.49 & 0.06 \\ 200 & 197 & 458 & 0.24 & -0.02 & -0.62 \\ 476 & 458 & 1109 & -0.08 & 1.23 & 1.47 \\ -0.23 & 0.24 & -0.08 & 0.029 & 0.028 & -0.042 \\ -0.49 & -0.02 & 1.23 & 0.028 & 0.146 & 0.082 \\ 0.06 & -0.62 & 1.47 & -0.042 & 0.082 & 0.189 \end{bmatrix}.$$

This example illustrates that estimates of covariances between the improved ratios  $\tilde{y}_4$ ,  $\tilde{y}_5$ ,  $\tilde{y}_6$  and the others are very small. In contrast to these values, the ratios  $\tilde{y}_1$ ,  $\tilde{y}_2$ ,  $\tilde{y}_3$  are strongly correlated with correlation coefficients approaching the limit value  $\rho = 1$ . Such a behaviour of the elements of variance-covariance matrix and the strong convergence of iterative process indicate that our problem is nearly linear. Actually, as the height of the minor peak is by one order smaller than the rest, its small variation produces large and strongly correlated variations in  $\tilde{y}_1$ ,  $\tilde{y}_2$  and  $\tilde{y}_3$  ratios. Moreover, these three ratios show percentage errors by one order higher than three others. Hence  $\eta_4$ ,  $\eta_5$  and  $\eta_6$  in the set of rigorous equations (16) may be considered as nearly constant.

One may conclude from this discussion that the problem of the adjustment of lead isotope ratios can be divided into two smaller problems: adjustment of  $y_4$ ,  $y_5$ ,  $y_6$  and, then,  $y_1$ ,  $y_2$ ,  $y_3$  ratios. The first problem is identical with that demonstrated above for strontium isotopes, whereas the second problem may be solved in the same way. However, it includes two independent rigorous equations and three measurements to be adjusted. Hence, the method of elements ([1], chapter 9-3) is more convenient than the method of Lagrange multipliers used above.

Putting the adjusted values  $\tilde{y}_4$ ,  $\tilde{y}_5$ ,  $\tilde{y}_6$  into equations (16), one may obtain three

linear equations, but only two linearly independent. Let us choose the following set for further calculations:

$$\begin{aligned}\eta_1 \tilde{y}_4 - \eta_2 &= 0 \\ \eta_1 \tilde{y}_5 - \eta_3 &= 0\end{aligned}\quad (19)$$

Taking  $\eta_1$  as the element, from equation (19) we obtain

$$\boldsymbol{\eta} = \begin{bmatrix} \eta_1 \\ \eta_2 \\ \eta_3 \end{bmatrix} = \begin{bmatrix} 1 \\ \tilde{y}_4 \\ \tilde{y}_5 \end{bmatrix} \eta_1 = F \eta_1. \quad (20)$$

To solve our adjusting problem one column matrix  $F$ , thus obtained, must be put in the following expressions:

$$C_{\tilde{y}} = \frac{FF'}{H} = \frac{1}{H} \begin{bmatrix} 1 & \tilde{y}_4 & \tilde{y}_5 \\ \tilde{y}_4 & \tilde{y}_4^2 & \tilde{y}_4 \tilde{y}_5 \\ \tilde{y}_5 & \tilde{y}_4 \tilde{y}_5 & \tilde{y}_5^2 \end{bmatrix}, \quad (21)$$

where

$$H = F' C_y^{-1} F = \frac{1}{\sigma_1^2} + \frac{\tilde{y}_4^2}{\sigma_2^2} + \frac{\tilde{y}_5^2}{\sigma_3^2}, \quad (22)$$

and

$$\tilde{\mathbf{y}} = C_{\tilde{y}} C_y^{-1} \mathbf{y} = C_{\tilde{y}} \begin{bmatrix} y_1/\sigma_1^2 \\ y_2/\sigma_2^2 \\ y_3/\sigma_3^2 \end{bmatrix}. \quad (23)$$

Note that all correlation coefficients followed from the expression's (21) equal unity, as expected.

Example 3. In order to compare the results obtained in this very simplified way with those obtained by the method demonstrated above, let us consider again the same set of initial values  $\mathbf{y}$  and  $C_y$  as in Example 2. Our simplified approach provides the following first estimates:

$$\tilde{\mathbf{y}} = \begin{bmatrix} 16.0624 \\ 15.5002 \\ 36.7715 \\ 0.9650 \\ 2.2893 \\ 2.3723 \end{bmatrix}, \quad C_{\tilde{y}} = 10^{-4} \begin{bmatrix} 209 & 202 & 478 & 0 & 0 & 0 \\ 202 & 195 & 461 & 0 & 0 & 0 \\ 478 & 461 & 1095 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0.029 & 0.029 & -0.043 \\ 0 & 0 & 0 & 0.029 & 0.147 & 0.083 \\ 0 & 0 & 0 & -0.043 & 0.083 & 0.190 \end{bmatrix}.$$



This example clearly shows that in the case of lead isotopes, and also in other cases when one peak is small in comparison with the other to be measured, both methods provide nearly identical adjusted ratios. Also the standard errors and correlation coefficients, derived from simplified  $C_{\bar{y}}$ , are close to those derived from a strict variance-covariance matrix. Even those correlation coefficients which correspond to covariances are estimated here as zero. Therefore, a calculator program will be presented for the simplified procedure only. The program for the strict method on TI Programmable 59 calculator is available from the authors.

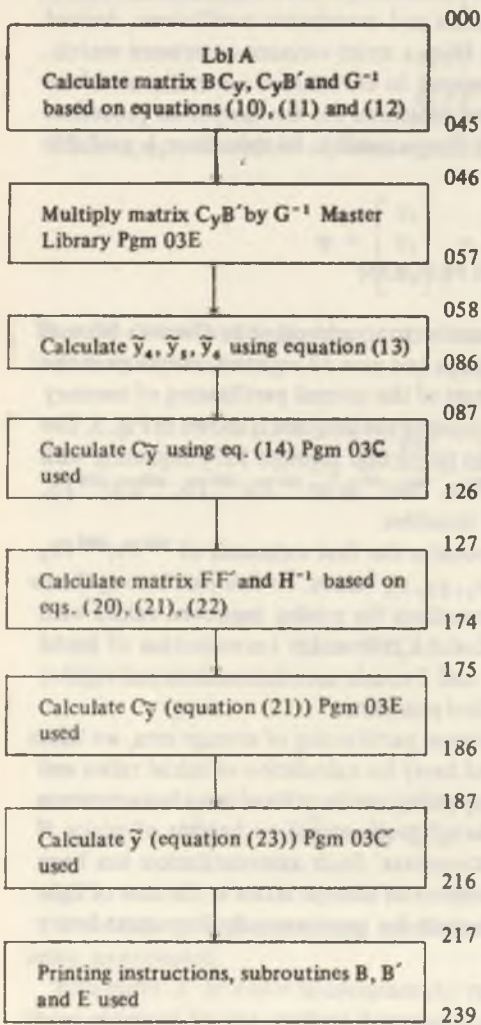
### THE CALCULATOR PROGRAM

The program listed in the Appendix has been written according to Owner's Manual for TI Programmable 58/59. It consists of 316 steps and uses 33 registers, therefore it can be written on one magnetic card without the reset of the normal partitioning of memory storage area in TI Programmable 59. The flow diagram of the program is shown in Fig. 3. The program consists of two basic parts. The first part (steps 000 through 127) beginning with label A enables the adjusting of  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $^{88}\text{Sr}/^{86}\text{Sr}$ ,  $^{88}\text{Sr}/^{87}\text{Sr}$  or  $^{207}\text{Pb}/^{206}\text{Pb}$ ,  $^{208}\text{Pb}/^{206}\text{Pb}$ ,  $^{208}\text{Pb}/^{207}\text{Pb}$  ratios, i.e.  $y_4$ ,  $y_5$ ,  $y_6$  in our unified notation.

The second part (steps 128 through 240) provides the first estimates of  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ ,  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios noted here as  $y_1$ ,  $y_2$ ,  $y_3$  values. To this part belong three subroutines (labels B, B' and E) including instructions for printing improved values with their standard errors. Subroutine C is designed for a convenient introduction of initial data: ratios and their standard errors. Tables 1 and 2 contain user instructions and register contents. Figure 4 shows two examples of standard printouts.

As numerous free steps are available at the normal partitioning of storage area, we have extended our program to a subroutine (not listed here) for calculation of initial ratios and errors directly from the heights of peaks. This capability can be utilized in an instantaneous adjustment of readouts of digital voltmeter, being proportional to heights of peaks, if the calculator is interfaced with a mass spectrometer. Such automatization has been accomplished in our laboratory for the measurements of isotope ratios in the case of light elements and we are going to extend this technique for geochemically important heavy elements.

## MAIN PROGRAM



## SUBROUTINES

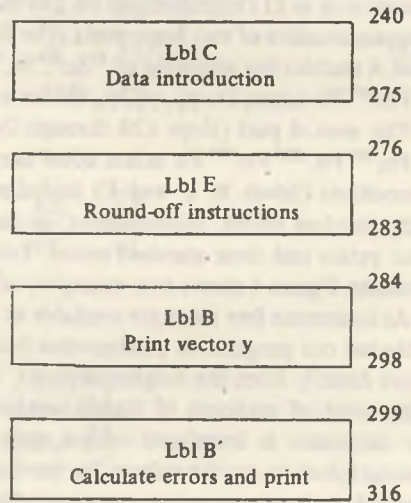


Fig. 3. The flow diagram of the program for adjusting strontium and lead isotope ratios

Tab. 1. User Instructions

Step	Procedure	Enter	Press	Display
1	Initialize		C	28
2	Enter elements of vector $y$	$y_1$	R/S	$y_1$
		$y_2$	R/S	$y_2$
		$y_3$	R/S	$y_3$
		$y_4$	R/S	$y_4$
		$y_5$	R/S	$y_5$
		$y_6$	R/S	6
3	Enter standard errors	$\sigma_1$	R/S	$\sigma_1^2$
		$\sigma_2$	R/S	$\sigma_2^2$
		$\sigma_3$	R/S	$\sigma_3^2$
		$\sigma_4$	R/S	$\sigma_4^2$
		$\sigma_5$	R/S	$\sigma_5^2$
		$\sigma_6$	R/S	$\sigma_6^2$
4	Perform the adjustment of the entered values		A	see note 1

NOTES: 1. Subroutine A provides standard printout, shown in Fig. 4, with 4 decimal places. One may reset this number occupying step 279 of the program.

2. For strontium isotopes perform all above steps with any number as  $y_1, y_2, y_3$  and  $\sigma_1, \sigma_2, \sigma_3$  values.

3. Elements of variance-covariance matrix may be recalled after computations from appropriate registers, see Tab. 2.

Tab. 2. Register Contents

$R_{00}$		$R_{20}$	
$R_{01}$		$R_{21}$	} Used
$R_{02}$		$R_{22}$	
$R_{03}$		$R_{23}$	
$R_{04}$	} Used	$R_{24}$	} Used
$R_{05}$		$R_{25}$	
$R_{06}$			$R_{26}$
$R_{07}$	Pointer	$R_{27}$	
$R_{08}$	Used, $\tilde{c}_{11}$	$R_{28}$	$y_1$
$R_{09}$	Used, $\tilde{c}_{21}$	$R_{29}$	$y_2$
$R_{10}$	Used, $\tilde{c}_{31}$	$R_{30}$	$y_3$
$R_{11}$	$-\tilde{c}_{46}, \tilde{c}_{12}$	$R_{31}$	$y_4, \tilde{y}_4$
$R_{12}$	$-\tilde{c}_{56}, \tilde{c}_{22}$	$R_{32}$	$y_5, \tilde{y}_5$
$R_{13}$	$c_{44} - c_{66}, \tilde{c}_{32}$	$R_{33}$	$y_6, \tilde{y}_6$
$R_{14}$	, $\tilde{c}_{13}$	$R_{34}$	$c_{11}$
$R_{15}$	Used, $\tilde{c}_{23}$	$R_{35}$	$c_{22}$
$R_{16}$	Used, $\tilde{c}_{33}$	$R_{36}$	$c_{33}$
$R_{17}$	Used, $\tilde{y}_1$	$R_{37}$	$c_{44}, \tilde{c}_{44}$
$R_{18}$	Used, $\tilde{y}_2$	$R_{38}$	$c_{55}, \tilde{c}_{55}$
$R_{19}$	$-\tilde{c}_{45}, \tilde{y}_3$	$R_{39}$	$c_{66}, \tilde{c}_{66}$

NOTES: 1. A fraction of memory registers are used twice: the first symbols represent number stored when the first part of the program is running while the second symbols represent numbers which can be recalled after run of the second part.

2. Symbols  $\tilde{c}_{ij}$  were used for the elements of variance-covariance matrix of improved values.

28.0000		16.0700	$y_1$
28.0000		15.4900	$y_2$
28.0000		36.7800	$y_3$
0.7122	$y_4$	0.9651	$y_4$
8.3625	$y_5$	2.2891	$y_5$
11.7316	$y_6$	2.3726	$y_6$
6.0000		0.2498	$g_1$
36.0000		0.2358	$g_2$
1296.0000		0.5892	$g_3$
0.0009	$g_4$	0.0021	$g_4$
0.0022	$g_5$	0.0045	$g_5$
0.0028	$g_6$	0.0056	$g_6$
28.1204		16.0624	$y_1$
20.0435		15.5002	$y_2$
235.1487		36.7715	$y_3$
0.7128	$y_4$	0.9650	$y_4$
8.3622	$y_5$	2.2893	$y_5$
11.7319	$y_6$	2.3723	$y_6$
5.9537		0.1445	$g_1$
4.2436		0.1395	$g_2$
49.7861		0.3309	$g_3$
0.0002	$g_4$	0.0017	$g_4$
0.0022	$g_5$	0.0038	$g_5$
0.0028	$g_6$	0.0044	$g_6$

Fig. 4. Standard format of the printed results; the time of calculation is about 1 min

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## APPENDIX

## PROGRAM LISTING

000 76 LBL	049 01 1	098 37 37	147 85 +	196 43 RCL	245 02 2
001 11 A	050 42 STO	099 43 RCL	148 43 RCL	197 35 35	246 08 8
002 43 RCL	051 04 04	100 17 17	149 36 36	198 35 1/X	247 42 STO
003 37 37	052 00 0	101 42 STO	150 35 1/X	199 65 x	248 06 06
004 65 x	053 42 STO	102 15 15	151 65 x	200 43 RCL	249 91 R/S
005 43 RCL	054 06 06	103 36 PGM	152 43 RCL	201 29 29	250 72 ST*
006 33 33	055 36 PGM	104 03 03	153 32 32	202 95 =	251 06 06
007 95 =	056 03 03	105 18 C <sup>^</sup>	154 42 STO	203 42 STO	252 15 E
008 42 STO	057 15 E	106 43 RCL	155 10 10	204 22 22	253 69 OP
009 08 08	058 43 RCL	107 12 12	156 42 STO	205 43 RCL	254 26 26
010 42 STO	059 31 31	108 22 INV	157 14 14	206 36 36	255 97 DSZ
011 16 16	060 65 x	109 44 SUM	158 33 X <sup>2</sup>	207 53 1/X	256 07 07
012 65 x	061 43 RCL	110 38 38	159 42 STO	208 65 x	257 02 02
013 43 RCL	062 33 33	111 43 RCL	160 16 16	209 43 RCL	258 49 49
014 33 33	063 75 -	112 11 11	161 95 =	210 30 30	259 06 6
015 75 -	064 43 RCL	113 42 STO	162 35 1/X	211 95 =	260 42 STO
016 43 RCL	065 32 32	114 19 19	163 42 STO	212 42 STO	261 07 07
017 38 38	066 95 =	115 43 RCL	164 05 05	213 23 23	262 98 ADV
018 94 +/-	067 42 STO	116 18 18	165 43 RCL	214 36 PGM	263 91 R/S
019 42 STO	068 15 15	117 42 STO	166 31 31	215 03 03	264 15 E
020 09 09	069 36 PGM	118 15 15	167 65 x	216 18 C <sup>^</sup>	265 33 X <sup>2</sup>
021 42 STO	070 03 03	119 36 PGM	168 43 RCL	217 01 1	266 72 ST*
022 17 17	071 18 C <sup>^</sup>	120 03 03	169 32 32	218 07 7	267 06 06
023 95 =	072 43 RCL	121 18 C <sup>^</sup>	170 95 =	219 42 STO	268 69 OP
024 42 STO	073 11 11	122 43 RCL	171 42 STO	220 06 06	269 26 26
025 05 05	074 22 INV	123 13 13	172 15 15	221 12 B	270 97 DSZ
026 43 RCL	075 44 SUM	124 22 INV	173 42 STO	222 03 3	271 07 07
027 39 39	076 31 31	125 44 SUM	174 13 13	223 01 1	272 02 02
028 65 x	077 43 RCL	126 39 39	175 03 3	224 42 STO	273 63 63
029 43 RCL	078 12 12	127 01 1	176 42 STO	225 06 06	274 98 ADV
030 31 31	079 22 INV	128 42 STO	177 04 04	226 12 B	275 92 RTN
031 95 =	080 44 SUM	129 08 08	178 04 4	227 98 ADV	276 76 LBL
032 42 STO	081 32 32	130 43 RCL	179 42 STO	228 08 8	277 15 E
033 10 10	082 43 RCL	131 34 34	180 25 25	229 42 STO	278 58 FIX
034 42 STO	083 13 13	132 35 1/X	181 00 0	230 06 06	279 04 04
035 18 18	084 22 INV	133 85 +	182 42 STO	231 17 B <sup>^</sup>	280 99 PRT
036 65 x	085 44 SUM	134 43 RCL	183 06 06	232 03 3	281 22 INV
037 43 RCL	086 33 33	135 35 35	184 36 PGM	233 07 7	282 58 FIX
038 31 31	087 43 RCL	136 35 1/X	185 03 03	234 42 STO	283 92 RTN
039 85 +	088 16 16	137 65 x	186 15 E	235 06 06	284 76 LBL
040 43 RCL	089 42 STO	138 43 RCL	187 43 RCL	236 01 1	285 12 B
041 05 05	090 15 15	139 31 31	188 34 34	237 42 STO	286 03 3
042 95 =	091 36 PGM	140 42 STO	189 35 1/X	238 25 25	287 42 STO
043 35 1/X	092 03 03	141 09 09	190 65 x	239 17 B <sup>^</sup>	288 07 07
044 42 STO	093 18 C <sup>^</sup>	142 42 STO	191 43 RCL	240 76 LBL	289 73 RC*
045 05 05	094 43 RCL	143 11 11	192 28 28	241 13 C	290 06 06
046 03 3	095 11 11	144 33 X <sup>2</sup>	193 95 =	242 06 6	291 15 E
047 42 STO	096 22 INV	145 42 STO	194 42 STO	243 42 STO	292 69 OP
048 03 03	097 44 SUM	146 12 12	195 21 21	244 07 07	293 26 26

294 97 DSZ	299 76 LBL	304 73 RC*	309 25 25	314 03 03
295 07 07	300 17 B	305 06 06	310 44 SUM	315 04 04
296 02 02	301 03 3	306 34 GX	311 06 06	316 92 RTN
297 89 89	302 42 STO	307 15 E	312 97 DSZ	
298 92 RTN	303 07 07	308 43 RCL	313 07 07	

### STRESZCZENIE

Praca zawiera prosty i praktyczny algorytm pozwalający poprawiać stosunki izotopowe dla pierwiastków złożonych z kilku (3–5) izotopów oraz umożliwiający znaczną redukcję błędów losowych obliczanych w ten sposób stosunków.

Algorytm wykorzystuje metodę najmniejszych kwadratów i ma charakter iteracyjny. W przedstawionych przykładach wystarczyły dwa kroki iteracyjne do tego, by różnice między kolejnymi przybliżeniami poprawionych elementów stały się porównywalne z błędem maszynowym (ok.  $10^{-11}$ ). Algorytm został zrealizowany na programowanym kalkulatorze kieszonkowym TI Programmable 59. Opracowany program jest szczególnie użyteczny przy poprawianiu stosunków izotopowych strontu i ołowiu.

Dodatki zawierają sieć działań programu, przykładowe tabulogramy wyników oraz wydruk programu.

### РЕЗЮМЕ

В работе излагается простой алгоритм, который позволяет значительно поправлять экспериментальные данные по изотопным отношениям элементов составленных на 3–5 изотопов. В алгоритме, который имеет итерационный характер, используется метод наименьших квадратов. В представленных вычислениях достигается разницу между последовательными приближениями поправленных отношений порядка  $10^{-11}$  (машинной ошибки) в двух итерационных шагах.

Алгоритм реализован на программированном калькуляторе TI-59. Разработанная программа особенно полезна для поправления изотопных отношений стронта и свинца. В приложениях представлены: диаграмма действий программа и полная форма программа.

Złożono w Redakcji 2 XI 1981 roku.