Isoconcentration principle – an effective tool of (radio) analysis in environmental protection

J Klas†, J Lesny[1,2], M Hornik[1], I Matusikova[1] and V Adamcova[1]

†With memory of our departed colleague, RNDr. Ing. Ján Klas, DrSc. Such an honourable professor and a faithful friend will be incredibly missed, especially his exceptional scientific inventiveness and his warm heart

[1]Department of Ecochemistry and Radioecology, Faculty of Natural Sciences, University of SS. Cyril and Methodius in Trnava, Nám. J. Herdu 2, Trnava, SK-917 01, Slovak Republic

E-mail: lesny@ucm.sk

Abstract. The paper brings two determination methods for non-radioactive analytes based on isoconcentration principle. The first method represents a determination procedure for a non-radioactive substance by use of its radio-labelled form of known concentration by help of a (non-quantitative, but selective) separation method. The main advantage of this method consists in the fact, that the determination is executable only by the detection of radioactivity. The second described procedure enables the determination of the chosen analyte without requirement of radioactive form of the substance to be determinate.

1. Introduction

An effective protection of the environment puts extremely high demands on the implementation of analytical methods for an extremely wide range of analytes in an extremely wide range of matrices. This is due to many reasons. For humans, the environment presents a crucial part of the material world. According to the definition, the environment is everything which creates natural conditions for the existence of organisms, including humans, and is the precondition of their further development [1]. Components of the environment are mainly water, soil, air and organisms. Therefore, the list of analytes in the environment is particularly long. Analogically, the list of components of the respective matrices, which can naturally contain many potential interferences, is also extremely long.

Analytes of the environment are mostly present in concentrations which are several orders of magnitude lower than the concentrations of the components in the relevant matrices. All the stated facts contribute to the occurrence of a wide range of sources of incorrect results mainly in the application of relative methods requiring calibration.

A series of publications appeared in the 1970s and 1980s developing the isotope dilution analysis by the application of an isoconcentration principle [2–7]. These publications focused mainly on the radioactive analytes. The aim of our paper is to contribute to the possible methodological solutions of the stated problems by proposing and modifying the isoconcentration principle for determination of non radioactive analytes.

2. Methods of determination

2.1. Determination process by use of radio-labeled analyte of known chemical concentration

The modified process of the isotope dilution analysis for the determination of non radioactive analytes (provided that selective separation procedures (reagents) are available, and provided that the radio-labelled analyte of known chemical concentration is also available) consists of the following steps.

2.1.1. Step 1

Creation of two series (I, II) of aliquot volumes and an addition of known equal volumes of unknown concentration, i.e. the same unknown amounts (**x**) of the non radioactive substance, which is be determined, to the individual elements of the first series.

2.1.2. Step 2

Addition of known increasing volumes of known concentration, i.e. known increasing amounts (y_1,...y_Φ...y_j) of the radio-labeled analyte to the elements of the first series and an addition of Φ-multiple of these amounts ($\Phi.y_1$,…$\Phi.y_\Phi$...$\Phi.y_j$), to the individual elements of the second series.

2.1.3. Step 3

The same adjustment of reaction conditions (pH, temperature…), the addition of the same amounts of the separation reagent to all the elements in both series and refilling of all elements from both sets to the same volume.

2.1.4. Step 4

Implementation of the separation process for all elements of both sets. Execution of radioactivity detection of separation products. Theoretically, for one of the elements of the first, and second set a condition can occur for which the following applies:

$$\frac{(\mathbf{x}+\mathbf{y}_{\phi})}{\mathbf{V}} = \frac{(\Phi.\mathbf{y}_{\phi})}{\mathbf{V}} \quad (1)$$

Separated masses:	$M_{1;1}$	$M_{1;2}$	$M_{1;3}$	$M_{2;1}$	$M_{2;2}$	$M_{2;3}$
Separated activities:	$A_{1;1}$	$A_{1;2}$	$A_{1;3}$	$A_{2;1}$	$A_{2;2}$	$A_{2;3}$
General symbols:		$(M_{1j}\,;\,A_{1j})$			$(M_{2j}\,;\,A_{2j})$	

2.1.5. Step 5, Construction of the isotope dilution function

The ratio of separated activities of the individual elements in the second set and the respective separated activities of the individual elements in the first set (which is the function of the known increasing amounts $\mathbf{y_1,...y_\Phi...y_j}$ of radio-labelled analyte) is identified by the symbol $\mathbf{i_j}$ (equation (2)):

$$\frac{\mathbf{A_{2j}}}{\mathbf{A_{1j}}} = i_j = f(y_j) \quad (2)$$

The total activity of the separated products of individual elements in both sets can be expressed as the product of the total mass and its relevant specific activity. We can write (see equations (3)(4)(5)):

$$\Phi(x+y_j)(A_{1j}/M_{1j}) = \Phi y_j (A_{2j}/M_{2j}) \quad (3)$$

$$(x+y_j)(A_{1j}/M_{1j}) = y_j (A_{2j}/M_{2j}) \quad (4)$$

$$i_j = \frac{x+y_j}{y_j}\frac{M_{2j}}{M_{1j}} = \frac{M_{2j}}{M_{1j}}\left(1+\frac{x}{y_j}\right) \quad (5)$$

Theoretically, two extreme situations may happen:

- separation of the whole quantities of analyte from all elements of both sets;
- separation of the same quantities of analyte from all elements of both sets.

In case of separation of the whole quantities of analyte from all elements of both sets the following equation (6) applies:

$$M_{1j} = x + y_j \quad \text{and} \quad M_{2j} = \Phi . y_j \tag{6}$$

Under these circumstances (equation (7)):

$$i_j = \frac{x + y_j}{y_j}; \; i_j = x \tag{7}$$
$$di/dy = 0$$

In case of separation of equal quantities of analyte of all the elements of both sets the following equations (8) (9) applies:

$$M_{1j} = M_{2j} \tag{8}$$

$$i_j = \frac{x + y_j}{y_j} = \frac{x}{y_j} + 1 \tag{9}$$

If we introduce a substitution:

$$z = \frac{1}{y_j}$$
$$i_j = z \,.\, x + 1$$
$$di/dy = x$$

2.1.6 Step 6

Determination of the unknown amount of non-radioactive analyte (**x**) from the curve $\mathbf{i_j = f(z)}$. In the intersection of all isotope dilution curves $i_j = f(z)$ at the same time applies the separation of the whole quantities as well as equal quantities of analyte from all the elements in both sets. In this situation equation (10) is:

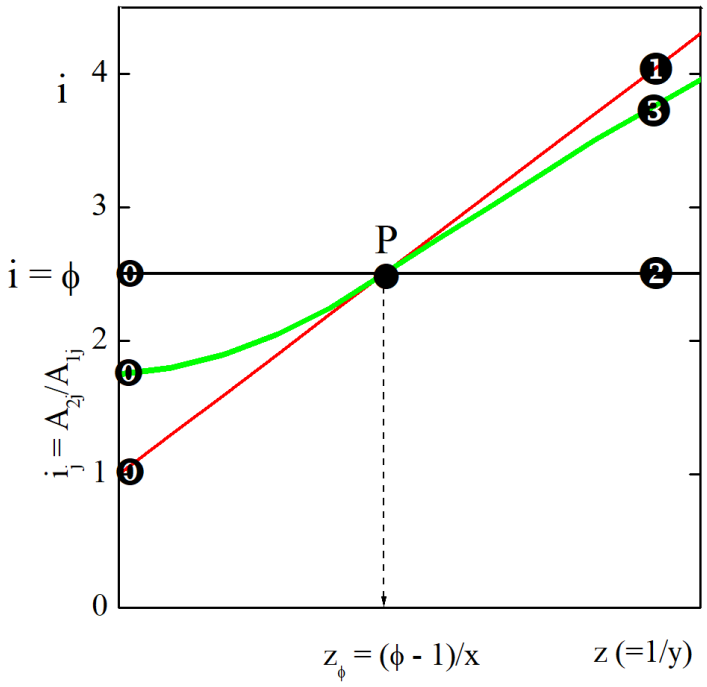
$$i_j = \Phi; \qquad z_\Phi = \frac{(\Phi - 1)}{x} \tag{10}$$

Thus, according to equation (1) we can write (see equations (11)(12)):

$$x + y_\varphi = \Phi . y_\varphi \tag{11}$$

$$x = \frac{(\phi - 1)}{z_\phi} \tag{12}$$

Thus, according to the equation (12), the determination of the unknown quantity x is in this case executable without the determination of separated quantities, i.e. only by the radioactivity detection (figure 1).



❶ $\frac{di}{dy} = x = constant$
The same amounts of separation product are isolated from all elements in both sets

❷ $\frac{di}{dy} = 0$
Full amount of analyte is isolated from all the elements in both sets.

❸ $0 < \frac{di}{dy} \leq constant$
Useful area of the subject method.

Figure 1. Construction of the isotope dilution function.

2.2. Determination process by use of non radio-labeled analyte of known chemical concentration

The procedure for the determination of the substance ***M*** with the use of isoconcentration principle without the use of (radio) isotopic indicator is as follows:

From the solution I with the substance ***M*** to be determined, two sets of aliquot volumes will be taken. The first set (FS) will contain equal aliquot volumes $\Phi.V_I$, where Φ represents an arbitrary selected number **($\Phi > 1$)**. Individual elements in this set contain the amount $\Phi.x$ of the substance to be determined. At the same time, from the solution I we take a second set (SS) of equal aliquot volumes $1.V_I$, which contain the amount x of the substance to be determined. From an other solution (II) of the same studied substance ***M***, we take variable quantities of volumes $\alpha.V_{II}$, where α represents the variable sequence of numbers (α = 0; 0,1; 0,2; ... 1; 1,1; 1,2;...); V_{II} is the volume of the solution II containing a quantity of the substance y to be determined (at α = 1). To aliquots $\alpha.V_I$ we add the volumes of the second (SS) set of aliquots $1.V_I$, which creates a mixed set of aliquots (MS). This results in two sets of aliquots with various volumes of the studied substance: FS with equal $\Phi.x$ content of the substance ***M***, and MS with variable $x + \alpha.y$ content of the substance ***M***. All aliquots shall be completed to the same volume ***V***. The stated two sets of aliquots are in mathematical equations indicated by subscript $_\Phi$ or $_\alpha$.

If we mark the function of a measurable quantity related to the amount of the substance ***M*** (or its concentration), for FS with I_Φ and for MS with I_α, then we can state (see equations (13)(14)):

$$I_\Phi = k_\Phi.\Phi.x \quad (13)$$

$$I_\alpha = k_\alpha.(x + \alpha.y) \quad (14)$$

Where ***k*** is a function between the measurable amount (or concentration) of the substance ***M*** in the first and mixed set of aliquots. This quantity can be optical, electrochemical, physical or nuclear properties associated with the quantity (concentration) of the studied substance ***M***.

Quantities, which can be determined by measurements for the stated sets I_Φ and I_α can be formulated as a function:

$$i = \Phi.I_\alpha/I_\Phi = (k_\alpha/k_\Phi)\,(1 + \alpha.(y/x) = f(k_\alpha, k_\Phi, \alpha) \quad (15)$$

If in isoconcentration point $\boldsymbol{P}$ applies $\boldsymbol{k_{\alpha P} = k_{\Phi P}}$, then the isoconcentration point $\boldsymbol{P}$ with coordinates ($\boldsymbol{\alpha_P}$, $\boldsymbol{\Phi}$) is the intersection of the equation (15) with the a priori selected constant value $\boldsymbol{i = I_P = \Phi}$ (see equation (16)):

$$\boldsymbol{I_P = \Phi.I_{\alpha P}/I_{\Phi P} = (1 + \alpha_P\,(y/x)) = \Phi} \tag{16}$$

of which

$$\boldsymbol{x = y.\alpha_P/(\Phi - 1) \quad or \quad y = x.(\Phi - 1)/\alpha_P} \tag{17}$$

With the use of equations (17), if the value $\boldsymbol{y}$ is known, it is possible to calculate the value $\boldsymbol{x}$, or if the value $\boldsymbol{x}$ is known, the value $\boldsymbol{y}$ can be calculated. If both these values are known, it is possible to calculate their ratio (see equation (18)):

$$\boldsymbol{x/y = \alpha_P/(\Phi - 1)} \tag{18}$$

In case of determination of the quantity $\boldsymbol{x}$ there is a partial compensation of the effect of present substances in the matrix on the substance $\boldsymbol{M}$, because their quantities in the set of aliquots FS and MS are in the ratio $\boldsymbol{\Phi : \alpha}$, while by determination of $\boldsymbol{y}$ there is no such compensation (0 : $\boldsymbol{\alpha}$).

The uncertainty of this method is, in general, consist in the fact, that between the measurable quantity ($\boldsymbol{I_\Phi}$, $\boldsymbol{I_\alpha}$) and a variable amount of the substance $\boldsymbol{M}$ (or its variable concentration) the functions $\boldsymbol{k_\alpha}$ and $\boldsymbol{k_\Phi}$ are not generally equal ($\boldsymbol{k_\alpha \neq k_\Phi}$).

The advantage is an unquestionable fact, that in the isoconcentration point $\boldsymbol{P}$ ($\boldsymbol{\alpha_P}$, $\boldsymbol{\Phi}$) the concentrations of aliquots of the substance $\boldsymbol{M}$ in the set FS and in the set MS are equal and the measured quantities (unless there is an interference of the substance $\boldsymbol{M}$ with other present substances in the matrix, or if the measured quantity is not affected by other factors) are also the same. In this case $\boldsymbol{k_\alpha = k_\Phi}$ and the result of determination can be perceived as reliable.

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