Mathematical matrix notation of stoichiometric relations as applied to quantitative x-ray spectral analysis.

Eduard M. Schechter

https://chekhter.de/

Zenodo. https://doi.org/10.5281/zenodo.3986835

The task of spectral analysis is to calculate the concentrations of elements included in the chemical formula. When solving the equations of X-ray spectral analysis, it is often necessary to take into account the constraints in the form of stoichiometric ratios for the elements that make up the analysed sample.

Analysed samples in geology or semiconductor compositions, as well as metal alloys, are compounds with partially known stoichiometric formulas. If the sample consists only of a compound with a known chemical formula, for example Al_2O_3, then from a chemistry course it is known how to find the concentration of elements from linear stoichiometric ratios. If the compound is more complex, for example, $(Al_2O_3)_x(MnO)_{1-x}$ where x is unknown, then the desired concentrations are related by linear relations.

The paper proposes a mathematical matrix notation of stoichiometric relations for an arbitrary chemical formula, which allows us to formulate the problem of solving the equations of spectral analysis as a vector problem of parameter estimation in the presence of such restrictions.

We assume that a sample consist of complexes such as oxides, silicates, sulphides, and so on with known stoichiometric formulas, for example, a metal alloy $(Al_2O_3)_x(MnO)_{1-x}$, where x it is not known. Our goal is to obtain concentration ratios that do not contain an unknown index.

We rewrite this chemical formula for the purpose of further calculations in the form $(Al_2O_3)_{x_1}(MnO)_{x_2} + rest$, $rest$ these are elements that are not included in stoichiometric relationships. The weight concentrations of elements in this sample can be expressed using the indices of the chemical formula as the ratio of the molar weight of the constituent elements to the molar weight of the entire sample, i.e. $c_1 = c_{Al} = \frac{2xM_{Al}}{M_{alloy}}$, $c_2 = c_{Mn} = \frac{(1-x)M_{Mn}}{M_{alloy}}$,

$$c_3 = c_O = \frac{3M_O x + M_O(1-x)}{M_{alloy}}$$

where M_{Al}, M_{Mn}, M_O the atomic weights of aluminium, magnesium, and oxygen, $M_{alloy} = (2M_{Al} + 3M_O)x_1 + (M_{Mn} + M_O)x_2 + M_{rest}$ are the molar mass of the alloy. If there are no impurities in the alloy, then $rest = 0$ and $x_1 + x_2 = 1$. $c = Qx = \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} = \begin{bmatrix} 2\frac{M_1}{M_{alloy}} & 0 \\ 0 & \frac{M_2}{M_{alloy}} \\ \frac{3M_3}{M_{alloy}} & \frac{M_3}{M_{alloy}} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix}$

These relationships can be rewritten in matrix form. Let $M_1 = M_{Al}$, $M_2 = M_{Mn}$, $M_3 = M_O$ be the atomic weights of the corresponding elements. If c is the vector of weighted concentrations of elements, the index x is the vector of indices of the complexes included in the compound, Q is the matrix of transformation of indices in concentration, then in our case

$$c = Qx = \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} = \begin{bmatrix} 2\frac{M_1}{M_{alloy}} & 0 \\ 0 & \frac{M_2}{M_{alloy}} \\ \frac{3M_3}{M_{alloy}} & \frac{M_3}{M_{alloy}} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} \quad (1)$$

Or

$$c = Qx = \begin{bmatrix} c_1 \\ c_2 \\ c_3 \end{bmatrix} = \begin{bmatrix} A \\ B \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} \quad (2)$$

where $A = \begin{bmatrix} 2\frac{M_1}{M_{alloy}} & 0 \\ 0 & \frac{M_2}{M_{alloy}} \end{bmatrix}$, $B = \begin{bmatrix} \frac{3M_3}{M_{alloy}} & \frac{M_3}{M_{alloy}} \end{bmatrix}$.

There are more concentrations than indices, but not all concentrations are independent.

To write this in a formal way, we write

then $\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = A \begin{bmatrix} x_1 \\ x_2 \end{bmatrix}$, $c_3 = B \begin{bmatrix} x_1 \\ x_2 \end{bmatrix}$

Further $\begin{bmatrix} x_1 \\ x_2 \end{bmatrix} = A^{-1} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$, then $c_3 = B \begin{bmatrix} x_1 \\ x_2 \end{bmatrix} = BA^{-1} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$ or $\frac{3}{2}\frac{c_1}{M_1} + \frac{c_2}{M_2} - \frac{c_3}{M_3} = 0$, these are concentration ratios, where chemical indices and molar mass of the alloy are no longer present. If in

matrix form, then $Gc = 0$, where $G = \begin{bmatrix} \frac{3}{2M_1} & \frac{1}{M_2} & \frac{-1}{M_3} \end{bmatrix}$ is the matrix - row. The number of rows in the matrix is equal to the difference in the number of elements included in the stoichiometry equation, minus the number of complexes included in the formula (number of indices). This result could be written right away, but the proposed recording method can easily be generalized to a more complex multicomponent sample using non-square multicomponent matrices Q and G, namely:

- A part of the concentration vector c with n components included in the stoichiometric compound is expressed through the chemical indices of the complexes included in this compound, a vector x with p components, $c = Qx$.

- The coupling matrix Q is divided into two arbitrary matrices, Q_1 (n-p) x (p), Q_2 (p) x (p), $Q = \begin{bmatrix} Q_1 \\ Q_2 \end{bmatrix}$

,

then

$$\begin{bmatrix} c_{1,n-p} \\ c_{2,p} \end{bmatrix} = \begin{bmatrix} Q_1 \\ Q_2 \end{bmatrix} x \tag{3}$$

- Using one of them, the vector x is expressed through part of the vector c. Since the second part of the vector c is also expressed in terms of the vector x, by substituting the vector x, we obtain the relationship of the components of the vector c due to the stoichiometry of the sample.
$c_1 = Q_1 x = Q_1 Q_2^{-1} c_2$, or $c_1 - Q_1 Q_2^{-1} c_2 = 0$, wherein the matrix Q_2 should be square full rank. Then

$$\begin{bmatrix} I_{(n-p)\times(n-p)}, & -\left(Q_1 Q_2^{-1}\right)_{(n-p)\times p} \end{bmatrix} \begin{bmatrix} c_{1,n-p} \\ c_{2,p} \end{bmatrix} = \mathbf{Gc} = \mathbf{0} \tag{4}$$

are equations of restrictions that should be taken into account when solving the inverse problem.

Since in this example $x_1 + x_2 = 1$, then automatically $c_1 + c_2 + c_3 = 1$. But it's not always the case. If the multicomponent sample contains elements that are not included in the stoichiometric formula, then we are forced to make any assumptions about the sum of all analyzed elements.

Let now c_x be the fraction of that part of the concentration vector, which is included in the stoichiometric formula, and c_{1-x} be the fraction of elements that are not included in it. We have received $\mathbf{Gc}_x = \mathbf{0}$ and, in addition, the sum of all the analyzed concentrations is equal to unity, $\sum c_i = 1$ otherwise you will not get the correct solution of the spectral analysis equations. Then the complete equation of a priori restrictions,

$$\begin{bmatrix} \mathbf{G}_x & 0_{1-x} \\ 1'_x & 1'_{1-x} \end{bmatrix} \begin{bmatrix} c_x \\ c_{1-x} \end{bmatrix} = \begin{bmatrix} 0_x \\ 1 \end{bmatrix} \tag{5}$$

Here $\mathbf{G}$ (pxn) is a matrix of stoichiometric bonds, $\mathbf{1}'$ is a unit vector, $\mathbf{0}$ is a zero vector. If there are no impurities and $c_{1-x} = 0$, then (5) is converted to the formula

$$\begin{bmatrix} \mathbf{G_x} \\ \mathbf{1'_x} \end{bmatrix} c_x = \begin{bmatrix} 0_x \\ 1 \end{bmatrix} \tag{6}$$

If concentrations are found, then the vector of indices based on (2) is then

$$x = Q^{+}c = Q'\left(QQ'\right)^{-1} c \tag{7}$$

Literature

1. Representing Reconstructed Networks Mathematically: The Stoichiometric Matrix, Bernhard Palsson, Lecture #4, September 15, 2003, University of California, San Diego, Department of Bioengineering.
2. The Stoichiometry of Reactions—Introduction, Copyright 2015 by Nob Hill Publishing, LLC
3. E. Shekhter, Industrial Laboratory, 1986, v. 52, Nr. 5, p.p. 445-449
4. E. Shekhter, G. Edelstein, Industrial Laboratory, 1991, v. 57, Nr. 5, p.p. 536-545
5. Albert, A. (1972) Regression and the Moore-Penrose Pseudoinverse; A.P., N.Y.