Method for constructing a mineralogical composition from a measured sample of single components

S. KONSULKE[1*], S. HOPFE[2], R. TOLOSANA-DELGADO[1], S. MATOS CAMACHO[1] and K. G. VAN DEN BOOGAART[1,3]

[1] Helmholtz Zentrum Dresden-Rossendorf, Helmholtz Institute Freiberg for Resource Technology, Dept. Modelling and Valuation, Germany - s.konsulke@hzdr.de
[2] Helmholtz Zentrum Dresden-Rossendorf, Helmholtz Institute Freiberg for Resource Technology, Dept. of Processing, Germany
[3] TU Bergakademie Freiberg, Institute of Stochastics
[*] presenting author

Abstract

Our aim is to infer the mineral composition from the chemical composition of a material. Several difficulties occur: Different mineral compositions can lead to the same chemical composition. Not all chemical compositions can be reached by compositions of certain minerals, while e.g. due to measurement errors impossible chemical compositions will typically be observed. In principle the dependency between mineral composition and chemical composition is linear. Inversion of the linear system however often leads to negative portions for some mineral components. Only the first problem is properly solved by state of the art linear end member calculation methods. Here we want to present a way of treating the second problem with a combination of different mathematical methods. As an example we will discuss a sample of waste material consisting of Rare Earth Elements (REE).

1 Introduction

We established a method to calculate mineral components from measured chemical elements. This calculation is not straight forward since the combination of the same chemical element in different amounts result in different mineral components. So there is the problem of an underestimated equation system, since there can be fewer chemical elements than mineral components. The usual way to solve such problems is to construct a linear equation system:

$$Tx = b \tag{1}$$

relating the chemical elements to the mineral components.

Unfortunately there is the possibility for a given measured sample of chemical components, that there is no analytic solution which fit the conditions: The solution vector $\hat{x}$ should have a constant sum and only positive entries. This lack of a solution is due to the measurement errors.

If in other samples there are solutions to the restricted problem (1) a representative solution can be found by using geometric methods. With those we are calculating a solution in a lower dimensional subspace. Following an algorithm is seeking a fitting solution in the original space using the simplex geometry of compositional data. See here for example Tolosana-Delgado (2011).

The possibility of doping the minerals add even more complexity to the problem. Some minerals in the composition can be doped with other chemical elements. So we have an other set of unknowns - the percentage of doping of each mineral component, which we assume to know to have a certain range.

2 The Method

The conversion of chemical components to mineral elements is usually done by creating the linear system (1). T be a weight matrix linking the chemical elements to the mineral components.

The columns contain the mineral components, the rows represent the chemical elements. The matrix entries are derived from the chemical formulas of the mineral components and are positive integers. If you have for example Yttrium(III)oxide (Y_2O_3) you get an entry in the column of Yttrium oxide: a two in the row for Yttrium and a three in the row for Oxygen. A simplified example for such a matrix T can be seen in table (1). The x-vector in equation (1) is the vector of amounts of mineral components and b is the measured vector of chemical elements.

	Y_2O_3	Al_2O_3	$LaPO_4$	...
Al	-	2	-	...
O	3	3	4	...
Y	2	-	-	...
La	-	-	1	...
P	-	-	1	...
⋮	⋮	⋮	⋮	

Table 1: This table shows a simplified example of a matrix T like they are used in equation (1). As can be seen, there will be a lot of zero entries.

In the scope of this work the minerals in the composition can be doped with different chemical elements. To deal with this difficulty we extended the matrix T with columns representing the doped mineral components also and allowed non-integer values. This is shown in table (2).

	Y_2O_3	$(Y,Eu)_2O_3$	Al_2O_3	$LaPO_4$	$(La,Tb)PO_4$	...
Al	-	-	2	-	-	...
Eu	-	0.326	-	-	-	...
O	3	3	3	4	4	...
Y	2	1.674	-	-	-	...
La	-	-	-	1	0.999	...
P	-	-	-	1	1	...
Tb	-	-	-	-	0.001	...
⋮	⋮	⋮	⋮	⋮	⋮	

Table 2: This table shows a modified example of a matrix T like they are used in equation (1). Here the doped parts of the minerals are taken into account.

But we could show, analyzing the measured sample of those chemical elements in the REE example following in the text, that there is no solution at all - not to speak of a solution which fit the conditions. Viewing the equation system (1) with the boundary conditions for this measured sample as a dual problem we could show the lack of a solution using the Farkas' Lemma (Gyula Farkas (1902)).

Believing that the nonexistence of a positive solution is due to the measurement errors of the chemical elements measures we seek for a solution which minimizes the difference between the actual measurement b and assumed real values Tx. This would correspond to the maximum likelihood estimation with normal distributed errors in the sense of a least squares solution. So the equation to solve is:

$$||Tx - b||^2 \rightarrow \min \tag{2}$$

with boundary conditions as follows:

$$\begin{aligned} \sum_i x_i &= c \\ x_i &> 0 \end{aligned} \tag{3}$$

while c is some constant, for example the amount of the measured sample or 1 respectively 100 for percentage values. Equation (2) with the boundary conditions (3) is known as a quadratic program. Solving routines for this kind of problems are already known and widely implemented, see for example the `R` (R Development Core Team (2008)) package `quadprog` or similar ones. The problem here is you need a non-singular matrix T^tT. But since our matrix T has viewer lines than columns, the matrix T^tT is singular. Which makes solving the problem more difficult.

We transformed problem (2) in the following way:

$$||\hat{T}x - \hat{b}||^2 = \left|\left|\begin{pmatrix} T \\ \alpha\tilde{T} \end{pmatrix} x - \begin{pmatrix} b \\ \alpha\tilde{T}x \end{pmatrix}\right|\right|^2 \to \min \tag{4}$$

keeping the boundary conditions (3).

So we have a new quadratic program with a new matrix $\hat{T} = \begin{pmatrix} T & \alpha\tilde{T} \end{pmatrix}^t$. Setting $\tilde{T}$ equals the $m \times m$ identity matrix, with m being the number of columns of T we have a non singular matrix $\hat{T}^t\hat{T}$. Now we view equation system (4) as an iteration problem and iterate as long as the minimal value of (4) is still falling. As a starting value we use solution x_0 from equation (5) with $\hat{b} = \begin{pmatrix} b \\ 0 \end{pmatrix}$. Than we optimize

$$x_0 \quad = \underset{x}{\operatorname{argmin}} \left|\left|\begin{pmatrix} T \\ \alpha Id \end{pmatrix} x - \begin{pmatrix} b \\ 0 \end{pmatrix}\right|\right|^2 \tag{5}$$

with the same boundary conditions (3) as in the original problem. The iteration would than be:

$$x^j = \underset{x}{\operatorname{argmin}} \left|\left|\begin{pmatrix} T \\ \alpha Id \end{pmatrix} x - \begin{pmatrix} b \\ \alpha Id x^{j-1} \end{pmatrix}\right|\right|^2 \qquad \text{with} \qquad \begin{aligned} &\sum_i x_i = c \\ &x_i > 0. \end{aligned} \tag{6}$$

If system (6) converges against a solution it is obvious, that it has to be a solution of (2) also. This is confirmed by the simulations in case of the example data. With such a solution $\hat{x}$ from iteration (6) we can calculate a new vector of chemical elements with equation (1). So we get a new "corrected" vector $\tilde{b}$ for the "measured" chemical element and therefore a new equation system

$$Tx = \tilde{b} \qquad \text{with} \qquad \begin{aligned} &\sum_i x_i = c \\ &x_i > 0. \end{aligned} \tag{7}$$

The equation system (7) has one most important difference to equation system (1): it has a solution $\hat{x}$ which also fits the conditions of having only positive entries and sum up to a known constant c.

Now we can run the algorithm described in Tolosana-Delgado (2011) on the equation system (7) with the starting solution $\hat{x}$ and we get a subset of possible solutions of system (7). We do that by a singular value decomposition of the matrix $S = TT^t = UD^2V$. S is a square and symmetric $n \times n$ matrix with r ($r < n$) non-zero singular values. The first r columns of matrix U are the right singular vectors of T, the remaining $n - r$ columns of U are the singular vectors belonging to the zero singular values and are therefore orthogonal to the first r columns. Since S is symmetric the right and left singular vectors coincide and for

$$U = \begin{pmatrix} U_r & U_{n-r} \end{pmatrix} \tag{8}$$

we get:

$$x = \hat{x} + \lambda U_{n-r}^t \tag{9}$$

Every solution x in equation (9) for any vector $\lambda \in R^{n-r}$ is an unconstrained solution of equation system (7). We just have to ignore every solution which contains negative values and so we get a subset of restrained solutions.

3 Example

Since recycling of waste materials is getting more and more important. Rare Earth Elements (REE) are used in mostly all new technologies and until now, there is no environmentally friendly recycling-process for fluorescent phosphor. For the development of a suitable recycling method, it is important to know the composition of the materials. Due to company secrecy, in some cases only rough informations about the composition of the material can be found. In the case of fluorescent phosphor, which is collected during the recycling-process of energy saving bulbs, only the type of the dye but not the precise composition is known. Because of different restrictions in the analytical methods and the complex composition, only the elemental concentrations with relatively high measurement errors can be measured.

We got a sample of 1000mg light bulb dust waste. After test measurements and literature research (see for example F. Kummer (1999), A.M. Srivastava and T.J. Sommerer (1998) or E. Gock, et al. (2008)) we assume to have a set of minerals as can be seen in table (3).

yttrium oxide (YOX)	pure or doped with europium
lanthanum(III) phosphate (LAP)	pure or doped with terbium or cerium
sanbornite	pure or doped with europium
aluminum oxide	
glass	soda-lime glass and lead silicate glass
cerium magnesium aluminate (CAT)	pure or doped with terbium or gadolinium
gadolinium magnesium pentaborate (CBT)	pure or doped with cerium or terbium
barium magnesium aluminate (BAM)	pure or doped with europium
halophosphate	pure or doped with antimony or manganese

Table 3: Here you can see the minerals assumed to be present in the sample.

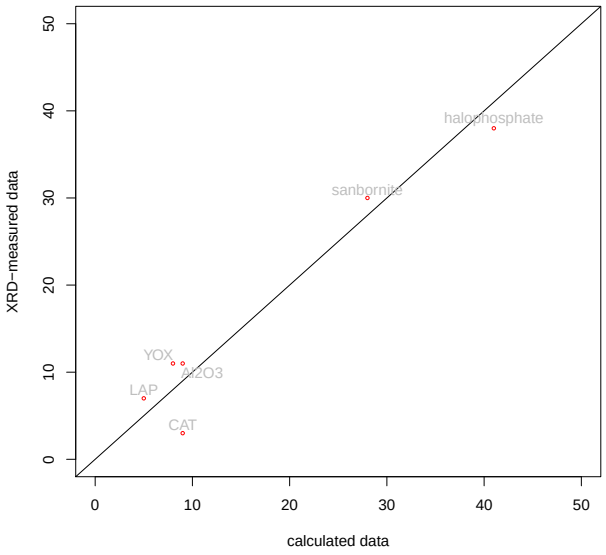

Figure 1: In this figure you can see the estimated weight percentages of the mineral compositions on the x axis and the measured values of the mineral components as weight percentages (using an X-ray diffraction measurement for comparison).

We got 108 valid solutions for equation system (7) which fit the boundary conditions and are all relatively close together. Details can be seen in figure 2. As input data we got a measurement of masses of nineteen different chemical elements, which can be seen in table (4). The estimated mass for the minerals are close to the XRD measured values (see figure 1). But as can be seen the values for the single chemical elements (figure 3 and 4) are not in every case satisfying. We could improve our estimation if we got the error to the single measurements for each chemical element and weigh our estimation with 1/"measurement error".

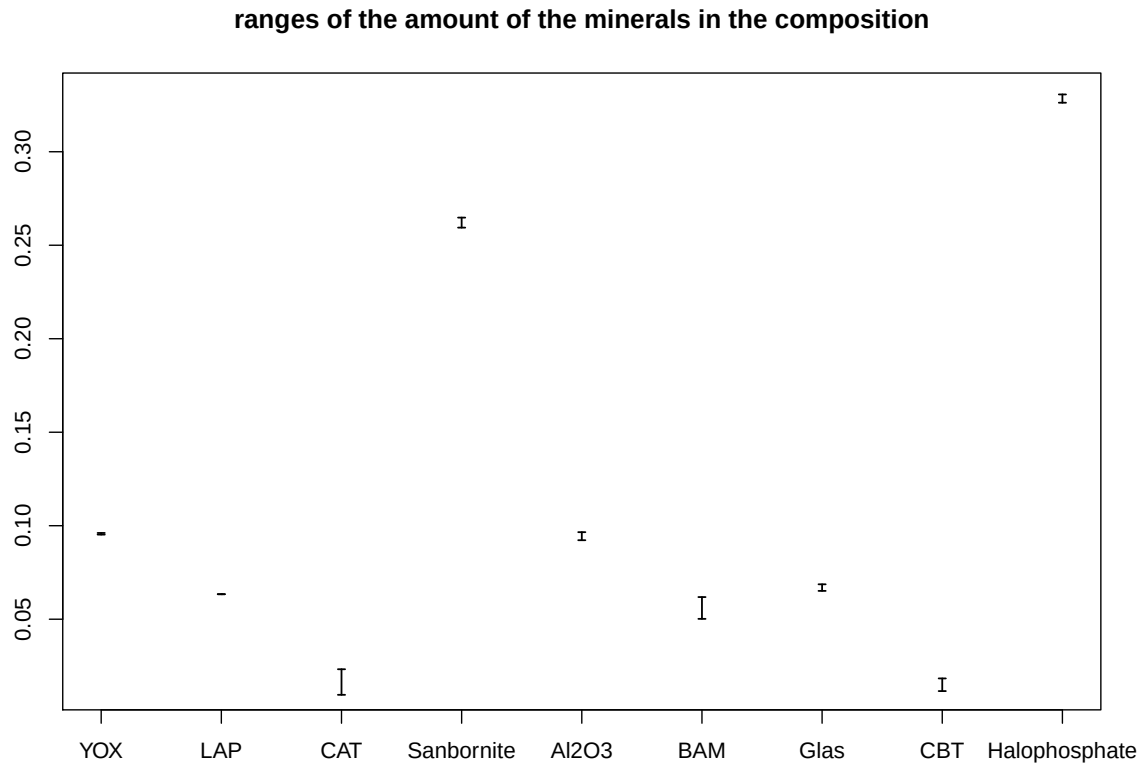

Figure 2: Here you see the ranges of amount of minerals in the composition for all equally probable solutions which fit the conditions of adding approximately to one and have only positive components.

Al	Ba	Ca	Ce	Cl	Eu	F	Gd	La	Mg
Mn	Na	P	Pb	Sb	Si	Sr	Tb	Y	

Table 4: Those are the chemical elements measured in the 1g sample of light bulb dust waste.

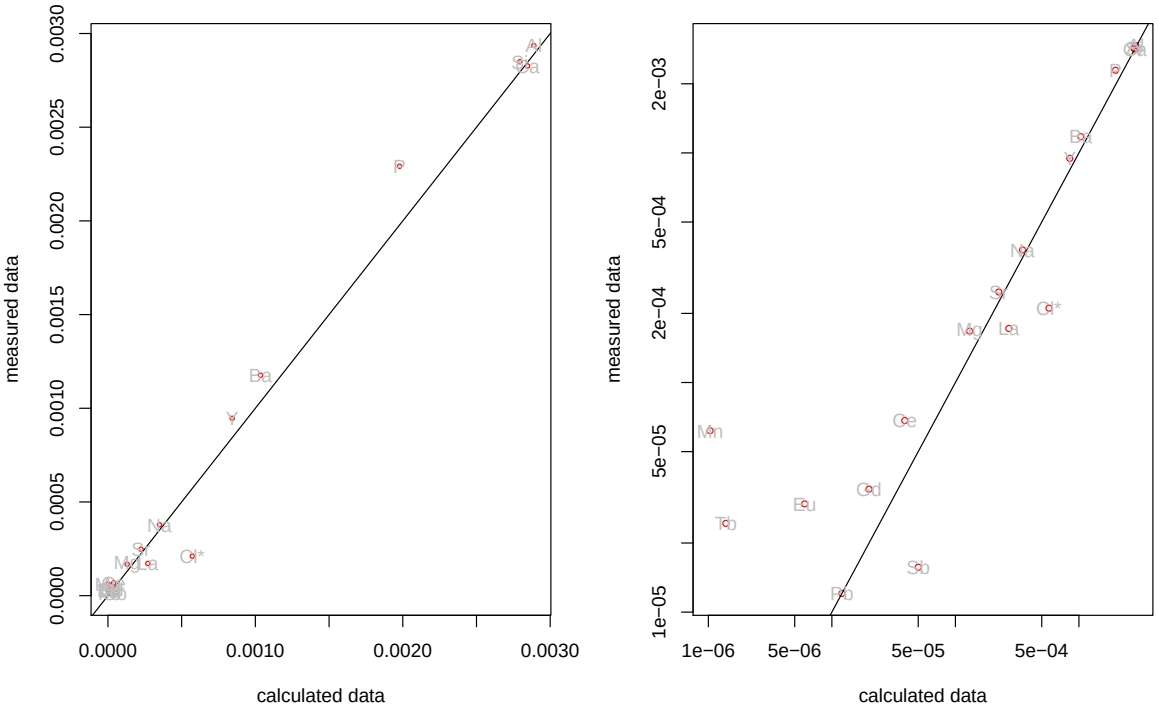

Figure 3: On the left hand side you can see the calculated data for $\hat{x}$ (amount of substance) from equation system (2) on the x-axis versus the measured sample data on the y-axis (also the amount of substance). The other figure shows the same data but with log scaled axis. The Cl^* element presents a linear combination of fluorine and chloride, since those elements only occur in the halophosphate mineral we combined them for our calculations. On the right hand side can be seen, that the estimation of terbium and manganese is worse than the other chemical elements.

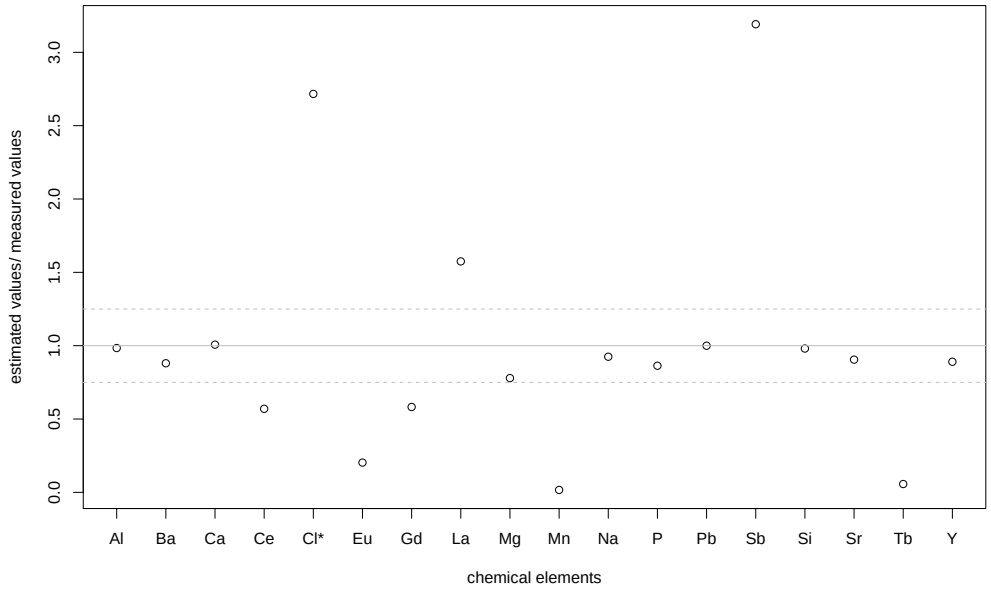

Figure 4: Here you can see the ratio between the estimated chemical amounts and the measured chemical amounts (both in *mg* as well). A ratio of approximately one means the estimation is good enough, a ration below one means we underestimate and a ratio greater than one means we overestimate the value of the chemicals.

References

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