PHASE QUANTIFICATION OF CERAMIC RAW MATERIALS

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1 INTRODUCTION

The mineralogical composition of a given material is defined by the type and quantities of minerals that constitute such a material. Through the combination of quantitative chemical and qualitative mineralogical analyses, enough information can be obtained to solve the problem of quantitative determination of mineralogical phases. This concept is usually called *Rational Mineralogical Analysis*. There are two well-known procedures for these calculations: the *conventional* and *IRTEC* methods. In this paper an alternative rational mineralogical analysis method, which we call the UFSC method, using the nonnegative least squares routine for solving a system of linear equations is proposed.

2 UFSC METHOD

The UFSC method is based on the same sources as the IRTEC method. The IRTEC method proposes the simultaneous resolution of linear equations. The experimental errors are divided among all the phases present. The unknown quantities of the system correspond to each mineralogical phase present in the sample, while the number of equations is determined by the number of "useful constituents" from chemical analysis. These constituents are considered useful only if they are present in at least one of the mineral species detected by XRD. For each constituent a linear equation is built, in such a way that the sum of the mineralogical phase constituents is proportional to the resulting amount of the chemical analysis. Therefore, for a constituent *m* with *n* mineralogical phases present, a system with *m* equations can be built:

$$a_{11}x_1 + a_{12}x_2 + \dots + a_{1n}x_n + 0.0acess = b_1$$

$$a_{21}x_1 + a_{22}x_2 + \dots + a_{2n}x_n + 0.0acess = b_2$$

$$\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots$$

$$a_{m1}x_1 + a_{m2}x_2 + \dots + a_{mm}x_n + acess = b_m$$

The system is subjected to the restrictions:

$$x_1 + x_2 + \dots + x_n = 100$$

with $x_j > 0,\ j = 1..\ n,\ i = 1..\ m$

where x_j = amount of the mineral *j* to be calculated;

a_{ij} = amount of the element *i* in the mineral *j* from the theoretical composition of this mineral;

b_i = amount of the element *i* from the chemical analysis of the sample;

acess = hypothetical phase termed "accessories", to complete 100%.

The calculation of each mineralogical phase can be then performed as follows:

- each mineralogical phase identified in the qualitative analysis should have a theoretical formula expressed in the form of oxides;
- the fraction in mass is calculated for each oxide in the theoretical formula from the atomic masses;
- a matrix is built where a line corresponds to the amount of each oxide, except for the last one that represents the sum of each phase in the sample;
- a matrix column corresponds to each phase, except for the last one that represents the amount of each oxide in the sample;
- the amount requested by the theoretical formulas can be lower than that determined by chemical analysis; in this case, this amount is added to a hypothetical phase called "accessories" to complete 100%.

The following sets out a simple example of Rational Mineralogical Analysis.

Minerals present: *kaolinite* $(Al_2O_3.\ 2SiO_2.\ 2H_2O)$, *quartz* (SiO_2) *and accessories.*

Chemical analysis:

35.22% Al_2O_3

48.81% SiO_2

1.12% TiO_2

0.25% CaO

0.10% Na_2O

0.52% Fe_2O_3

0.07% MgO

0.17% K_2O

13.74% Ignition Loss (I. L.)

The following system of linear equations can be set up:

$$\begin{array}{lll}
0.395\ kaolinite + 0.000\ quartz + 0.000\ accessories = 35.22 & & (\mathrm{Al_2O_3\ row}) \\
0.465\ kaolinite + 1.000\ quartz + 0.000\ accessories = 48.81 & & (\mathrm{SiO_2\ row}) \\
1.000\ kaolinite + 1.000\ quartz + 1.000\ accessories = 100.00 & & (\mathrm{sum\ row})
\end{array}$$

To solve the system ($AX \approx B$) an algorithm is used, for the constrained least squares problem subject to $X \geq 0$ (*Nonnegative Least Squares* – NNLS).

Using the NNLS algorithm to solve the example, we have:

89.2% kaolinite

7.2% quartz

3.6% accessories

Sometimes the linear equations system can be overdetermined (more oxides than phases in the sample, or more rows than columns) or underdetermined (more phases than oxides, or more columns than rows). In these cases, a kind of approximation method to a solution is necessary. Most frequently *Least Squares* is the approximation criterion chosen. The basic linear least squares problem can be stated as follows: *given a real $m \times n$ matrix A, a real m-vector B, find a real n-vector X minimizing $AX - B$.*

3 RESULTS AND DISCUSSION

For the validation of the method, a series of pure ceramic phases was used as hypothetical raw materials. A total of 6 random mixtures were defined, considered in this case as standard compositions.

From the chemical composition and qualitative analysis of each mixture, the UFSC method was applied. Most of the calculated mixtures are very close to the standard, however some of them presented at least a phase with null result, although this phase had been identified by the qualitative analysis. In these two cases, all the other calculated values were incorrect.

To solve this problem, a new calculation was performed, at first not using the null phases and their chemical compositions. It was observed that the results, again, were very close to the standard, except for the accessories, which had included the previous null phases. Finally, a calculation only with the null phases and the accessories was made, allowing the quantification of these phases.

4 CONCLUSIONS

The UFSC method presented results very close to the hypothetical standard compositions. In addition, the method guarantees:

- the resolution of overdetermined systems;
- the resolution of underdetermined systems;
- the elimination of solutions that satisfy mathematically but not physically (negative amount of a phase);

The rational analysis method presents some sources of errors, common to other methods, such as:

- the improper identification of crystalline phases, with the subsequent alteration of the numeric matrix;
- the occurrence of amorphous or sparsely crystallized phases in the sample, which are not sufficiently evidenced in the XRD;
- the presence of mixed-layered clay minerals;
- the simplification of theoretical formulas of some complex phases;

Eventually, the UFSC method may present specific errors due to:

- the presence of two (or more) phases with the same theoretical formula;
- the presence of a large amount of impurities which has a chemical element present in some other identified phases.

From this calculation approach a computational routine was developed, allowing anyone – and not necessarily a specialized technician – to quantify mineralogical phases of ceramic raw materials. The UFSC method can then be a fast and reliable alternative for the direct quantitative determination of phases.