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THE DETERMINATION OF THE MINERAL PERCENTAGES IN GRANITE

27.1 INTRODUCTION

Crystalline minerals in solid materials can be quantitatively determined usually by powder X-ray diffraction (Ward and Taylor, 1996; Wertz and Collins 1998), by scanning electron microscope (SEM) methods (e.g. Finkelman, 1988) and/or by recalculation of chemical analysis of slag on normative minerals (e.g. Nicholls, 1962; Cohen and Ward, 1991). The CQMA method belongs to the last group of methods. All above described methods have some limitations that are generally known (e.g. X-ray diffraction methods give usually low intensities of diffraction patterns, have high signal noise; SEM methods are of a point character of analysis; methods based on the recalculation of the bulk chemical analyses on quantitative mineral analyses calculate selected minerals with simple chemical formulae cascaded in selected priority). This disadvantage is somewhat minimized by CQMA (Klika at al., 2016) method based on the optimization principle.

Goal of this paper is to show CQMA method on example of quantitative determination of minerals in granite sample.

27.2 CHEMICAL QUANTITATIVE PHASE ANALYSIS (CQMA) OF GRANITE

This method is based on the recalculation of chemical analysis of solid crystalline material on quantitative mineral analysis. For the recalculation the following steps are used:

1) Determination of the bulk chemical analysis (CHA).
2) Identification of minerals in analysed material.
3) Selection of chemical formulae for minerals present in sample.
4) Calculation of mineral contents from data obtained in previous points 1, 2 and 3 using optimization CQMA procedure.
5) Reverse control calculation of CHA from calculated mineral contents (point 4) by CQMA.

Step 1 – Chemical analysis (CHA)

X-ray fluorescence, atomic absorption spectroscopy, atomic emission spectroscopy, classical gravimetric and titration analytical methods and/or other ones can be used for the determination of all major elements or their oxides in slag. Determined concentrations of the i-th element (or its oxide) in bulk analysed material is denoted as $(ci)_{exp}$.

Step 2 – Mineral identification

The identification of minerals present in bulk analysed material can be performed by any available method. Especially methods like SEM, X-ray powder diffraction, FTIR spectroscopy, image analysis, optical microscopy are for this purpose are used.

Step 3 – Crystallochemical formula of identified minerals

For more complicated minerals as are e.g. some clay minerals (muscovite, illite, montmorillonite, chlorite, etc.) the crystallochemical coefficients must be estimated or determined. On the other hand oxides, sulphides, sulphates, carbonates phosphates have usually very simple chemical formulae (Table 1).

Step 4 – Calculation of mineral contents

The calculation of mineral contents is performed using the optimization procedure (Chemical Quantitative Phase Analysis). This method is based on the assumption that concentration of chemical elements (or theirs oxides) can be express using the following equation (1):

$$(c_i)_{calc} = \sum_{j=1}^{n} w_{i,j} \cdot c_j \tag{1}$$

where $(c_i)_{calc}$ – is calculated percentage of the i-th element (or its oxide) in inorganic sample; $w_{i,j}$ is weight fraction of the i-th element (or its oxide) in the j-th mineral; c_j is the calculated percentages of the j-th mineral in inorganic sample; n – is number of calculated minerals in inorganic sample.

The weight fraction of the i-th element (or its oxide) in the j-th mineral ($w_{i,j}$) can be calculated from crystallochemical formula of the j-th mineral. The calculation of the j-th mineral content (c_j) in inorganic sample is then performed using optimization formula (2):

$$\sum_{i=1}^{m} \left((c_i)_{\exp} - \sum_{j=1}^{n} w_{i,j} \cdot c_j \right)^2 = \min \tag{2}$$

where $(c_i)_{exp}$ - is percentage of the i-th element (or its oxide) in inorganic sample determined by chemical analysis; m – is number of elements or theirs oxides (in chemical analyses) used for the calculation.

This procedure was originally prepared for calculation of minerals present in sedimentary or igneous rocks (Klika et. al., 1986).

Step 5 – Reverse calculation of chemical analysis from calculated mineral contents.

Validation of calculated mineral percentages (c_j) is performed by theirs reverse calculation on chemical analyses from Eq. (1). From the difference between the calculated $(ci)_{calc}$ and experimental concentrations of elements (or its oxides) $(ci)_{exp}$ we can estimate accuracy of calculated percentages of minerals cj in analysed sample.

The program CQMA includes for calculation about 55 various minerals from which 5 have general formulas that can be adapted to any crystallochemical formula. In Table 1 are shown some of them.

Table 27.1 Examples of crystallochemical formulas of some minerals.

Mineral	Crystallochemical formula
Quartz	SiO_2
Rutile/Anatase	TiO_2
Hematite	Fe_2O_3
…………………	…………………………
Pyrite/Markazite	FeS_2
Pyrhotine	FeS
Calcite	$CaCO_3$
Siderite	$FeCO_3$
Dolomite/Ankerite	$CaMg_{1-x}Fe_x(CO_3)_2$
Anhydrite	$CaSO_4$
Basanite	$CaSO_4$ 0.5 H_2O
Gypsum	$CaSO_4$ 2 H_2O
Apatite	$Ca_3(PO_4)_2$
K/Na feldspar	$Na_xK_{1-x}AlSiO_8$
Plagioclase	$Na_{1-x}Ca_xAl_{1+x}Si_{3-x}O_8$
Kaolinite	$Al_4Si_4O_{10}(OH)_8$
……………………	………………………..
General formula (1)	$x_1SiO_2.x_2TiO_2.x_3Al_2O_3.x_4Fe_2O_3.x_5FeO.......x_{10}.H_2O$
General formula (1)	$x_1SiO_2.x_2TiO_2.x_3Al_2O_3.x_4Fe_2O_3.x_5FeO.......x_{10}.H_2O$
…………………….	…………………………

Note: crystallochemical coefficients x_i can be selected according to any mineral.

27.3 RESULTS

27.3.1 Reference granite sample

Table 27.2 The reference bulk chemical analysis (in wt. %) of granite rock sample.

	GM	
	$\bar{x}$	s
SiO_2	73.50	0.18
TiO_2	0.213	0.023
Al_2O_3	13.55	0.22
Fe_2O_3	0.75	0.21
FeO	1.14	0.17
MnO	0.043	0.007
MgO	0.377	0.08
CaO	1.04	0.13
Na_2O	3.76	0.14
K_2O	4.74	0.18
P_2O_5	0.063	0.010
CO_2	0.278	0.047
H_2O^+	0.349	0.052

Note: GM – Granite;

$\bar{x}$ – reference value, s – standard deviation

In addition to elemental analysis (Table 2) the reference mineral percentages of granite and identified our identified minerals (by X-ray diffraction) are given in Table 3.

Table 27.3 The percentages of minerals (wt. %) of granite sample.

No.	Minerals	Reference data	XRD identification
1	Quartz	32	+
2	Biotite	6	+
3	K-feldspar	25	+
4	Plagioclase (albite)	35	+
5	Calcite	0.7	n.i
6	Apatite	0.2	n.i
Total		99	

Note: + identified by XRD; n.i. not identified by XRD

The presence of other accessoric minerals in reference mineral analysis was identified by optical methods. They are:

- zircon, magnetite, hematite, pyrite, sericite, chlorite, kaolinite, anatase, xenotime and monazite in the GM sample.

27.3.2 Determination of mineral contents and comparison with reference data

The percentages of minerals in granite sample were identified by XRD and the crystallochemical formulas calculated by the Rietveld technique. They are listed in the following Table 4.

Table 27.4 Calculated crystallochemical formulas in granite sample calculated using XRD and Rietveld technique.

Mineral	Crystallochemical formula
Quartz	SiO_2
Biotite	$K_{1.00}(Mg_{1.35}Fe(II)_{1.65})[Al_{1.00}Si_{3.00}]O_{10}(OH)_2$
K-feldspar	$KAlSi_3O_8$
Plagioclase	$Na_{0.75}Ca_{0.25}(Al_{1.25}Si_{2.75})O_8$

As was described above the CQMA method was used for the calculation of mineral percentages in studied granite sample. The calculation was performed using the chemical analysis of granite (Table 2), identified minerals by XRD (Table 3) and crystallochemical formulas (Table 4). The calculated percentages of minerals are given in Table 5 (column b).

Table 27.5 Percentages of minerals determined in granite.

Minerals	Percentages of minerals	
	a	b
Quartz	32	33.5
Biotite	6	4.4
K-feldspar	25	25.1
Plagioclase	35	35.6
Calcite	0.7	-
Apatite	0.2	-
Total	98.90	98.6

Columns: a) reference mineral analyses (see Table 3),
b) mineral analyses calculated by CQMA.

Table 27.6 Recalculated (a, b) and reference (ref) bulk chemical analyses.

	Percentages of oxides		
	ref	*a*	*b*
SiO_2	73.50	72.21	73.50
TiO_2	0.213	-	-
Al_2O_3	13.55	13.61	13. 60
Fe_2O_3	0.75	-	-
FeO	1.14	1.52	1.11
MnO	0.04	-	-
MgO	0.38	0.70	0.51
CaO	1.04	2.34	1.88
Na_2O	3.76	3. 06	3.11

K_2O	4.74	4.83	4. 68
P_2O_5	0.06	0.1	-
CO_2	0.28	0.31	-
H_2O^+	0.35	0.23	1.17
Total	99.80	98.90	99.60

Notes:
Columns: ref) reference chemical analysis (see Table 2),

a) chemical analysis calculated from reference mineral analysis (Table 3)
b) chemical analysis recalculated from mineral analysis obtained by CQMA (Table 5, column b) and crystallochemical formula (Table 4).

CONCLUSION

From the comparison of mineral analyses (Table 5) and chemical analyses (percentages of oxides (Table 6) is seen that CQMA gives very good results. Next information can be seen in Klika at al. (2016) and in http://homen.vsb.cz/~kol70/cqma/cqma_en.html where all possibilities of the CQMA are shown in detail.

Described program may be used to improve identification of the mineral content in the geological samples.

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Abstract: *Recently a new method (CQMA) for the quantitative determination of minerals in solid samples has been suggested and verified on 6 standards of rocks samples (Klika at al., 2016). This method is based on the recalculation of the elemental bulk chemical analysis on the quantitative contents of the mineral phases identified in sample. This method is based on the optimization procedure and except elemental bulk chemical analysis requires the identification of minerals and finding their crystallochemical formulas. The mineral phases as well as chemical analysis are determined by usual analytical methods. In this contribution the results of quantitative calculated minerals by Chemical Quantitative Mineral Analysis (CQMA) are compared with the reference analysis of granite. Mineral analysis of granite was performed by optical and XRD methods, chemical analyses by classical and XRF methods and crystallochemical formulas of minerals were identified by Rietveld technique (Rietveld, 1967).*

Keywords: *Quantitative mineral analysis, chemical analysis recalculation, a sample on analysis of granite.*

STANOVENÍ PROCENTUÁLNÍHO OBSAHU MINERÁLŮ V ŽULE

Abstract: *V poslední době byla navržena nová metoda (CQMA) pro kvantitativní stanovení minerálů v pevných vzorcích a ověřena na 6 standardech vzorků hornin (Klika et al., 2016). Tato metoda je založena na přepočtu elementární úplné chemické analýzy na kvantitativní obsah minerálních fází identifikovaných ve vzorku. K výpočtu se využívá optimalizační procedůra a kromě úplné elementární chemické analýzy se vyžaduje identifikace minerálů a jejich krystalochemických vzorců. Minerální fáze stejně jako chemická analýza jsou určeny obvyklými analytickými metodami V tomto příspěvku jsou výsledky vypočtených obsahů minerálů pomocí programu "Chemical Quantitative Mineral Analysis" (CQMA) porovnány s referenční analýzou žuly. Referenční analýzy žuly byla provedenya pomocí optických a XRD metod, chemických analýz pomocí klasických a XRF metod v řadě evropských laboratoří (Klika a kol. 2016). Pro výpočet CQMA byla využita referenční chemická analýza, identifikace a krystalochemické stanovení minerálů byly provedeny v naši laboratoři za použití RTG metody a Rietveldovy techniky (Rietveld, 1967).*

Keywords: *Kvantitativní minerální analýza, přepočet chemické analýzy, ukázka na analyse žuly.*

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Doc., Dr., Ivan KOLOMAZNÍK
VŠB-Technical University Ostrava
Department of mathematics and descriptive geometry
Třída 17. listopadu 15, 708 33 Ostrava-Poruba, Czech Republic
tel.: +470 597 324 128, e-mail: ivan.kolomaznik@vsb.cz

Prof., Ing., CSc., Zdeněk KLIKA
VŠB-Technical University Ostrava
Department of chemistry
Třída 17. listopadu 15, 708 33 Ostrava-Poruba, Czech Republic
tel.: +470 597 321 548, e-mail: zdenek.klika@vsb.cz