Acta Geodyn. Geomater., Vol. 7, No. 4 (160), 453–460, 2010

DETERMINATION OF MINERALS IN COAL BY METHODS BASED ON THE RECALCULATION OF THE BULK CHEMICAL ANALYSES

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(*Received* May 2010, *accepted* September 2010)

ABSTRACT

Chemical Quantitative Phase Analysis (CQPA) suggested originally for magmatic rocks (Klika et al., 1986) now is tested for the quantitative mineral determination of coal. This method is based on the optimization procedure. For the evaluation of mineral contents, 5 coal samples were selected and the following analytical data were determined: a) chemical analyses (XRF, titrimetric and gravimetric analytical methods), b) qualitative mineral composition (the X-ray powder diffraction, SEM-EDX and image analyses), c) crystallochemical formulae of minerals. The calculated percentages of minerals obtained by CQPA were compared with calculated percentages of minerals obtained by Raask´s method. Simple statistical evaluation showed that calculation of minerals by CQPA program delivers considerable improvement of results.

KEYWORDS: coal, phase analysis, chemical analysis

1. INTRODUCTION

Inorganic matter of coal consists of three basic groups (Ward, 2002). They are:

a) inorganic compounds dissolved in pore solutions of coal;
b) chemical elements bonded on organic parts of coal; and
c) crystalline or amorphous forms of minerals.

From these three groups of inorganic matter of coal, the crystalline minerals prevail and therefore the qualitative and quantitative determination of minerals in coal is very important. The reviews of analytical methods used for these determinations can be found elsewhere (e.g. in Vassilev and Tascón, 2003; Huggins, 2002; Ward, 2002).

The powder X-ray diffraction (XRD) is probably the most utilized method both for qualitative and quantitative determination of minerals in coal (e.g. Querol et al., 1993; Acharya, 1992; Mandile and Hutton, 1995; Ward and Taylor, 1996; Wertz and Collins 1998; Ward et al., 1999, 2001). For quantitative mineral determination the methods of internal standard or spike (e.g. Gaigher, 1983; Ward, 1989) and/or Rietveld´s method (Rietveld, 1969; Weiss et al., 1983; O'Connor and Raven, 1988; Taylor, 1991; Bish and Post, 1993) are widely used.

Scanning electron microscopy with XRF combination (SEM-XRF) is also widespread (Finkelman, 1988; Birk, 1989; Martínez-Tarazona et al., 1990). This method is based on the elemental determination of individual minerals present in sample. More sophisticated methods use automatic analysis that enables to identify thousands of mineral particles. Computer-controlled SEM (CC-SEM) and automatic image analysis SEM (AIA-SEM) belong among electron microscopy methods (e.g. Huggins et al., 1980; Creelman and Ward, 1996; Galbreath et al., 1996). Methods based on the recalculation of chemical analysis of coal to normative minerals are often used (e.g. Nicholls, 1962; Pollack, 1979; Raask, 1985; Felgueroso et al., 1988; Brons et al., 1989; Ward and Taylor, 1996; Cohen and Ward, 1991). They are often favoured for their simplicity.

Other methods such as FTIR (e.g. Estep et al., 1968; Painter et al., 1981) and/or Mössbauer spectroscopy (Huffman and Huggins, 1978; Evans et al., 1990) have much less significance in studying minerals in coal and they are used to identify specific minerals, e.g. FTIR for determination of quartz, kaolinite, and carbonates and Mössbauer spectroscopy for Fe species.

All above described methods have some limitations. The disadvantage of XRD is low detection limit, especially for determination of minerals with low ash content (Wertz, 1990). Therefore the analyses are usually performed on low temperature ashes prepared at about 200 °C (Gluskoter, 1965). But even at low temperature some minerals can be altered, e.g. pyrite oxidizes on iron sulphate minerals and/or oxides (Allen et al., 1986; Pike et al., 1989; Ward, 1991; Ward, 1992). Principal disadvantage of SEM

Table 1 List of the coal samples used in this study.

Sample	Type of coal	Origin of coal	Geological period
1	lignite	Mine Mír, Dubňany, (Hodonín)	Miocene
2	subbituminous coal	Mine ČSA, Most	Miocene
3	subbituminous coal	Mine ČSA, Most	Miocene
4	subbituminous coal	Mine ČSA, Most	Miocene
5	bituminous coal	Mine Darkov, Karviná	Carboniferous

method is its point character. Coal is a very heterogeneous material and therefore point analyses can be burdened with relatively high errors. Much better results can be obtained using e.g. CC-SEM, AIA-SEM or XAFAS but also here error can be significant because analyses are performed on one plane of sample. Methods based on the recalculation of the bulk chemical analyses of coal to mineral analyses also fumble with many problems (e.g. Vassilev and Tascón, 2003). One of them is a rigid selection of minerals present in coal; often a simple crystallochemical formula is not adequate to characterize clay minerals.

The goal of this paper is to test and verify the CQPA method and study the quantitative mineral composition of typical Czech coals. For this study, the CQPA and Raask´s methods, both based on the recalculation of the bulk chemical analyses, have been used and their application for coal has been compared.

2. EXPERIMENTAL

2.1. SAMPLES

For this study, one sample of lignite, three subbituminous and one bituminous coal samples from the Czech Republic were selected. Their list is given in Table 1.

Coal samples were carefully ground, and fractions of grain size 1 – 2 mm were obtained by sieving. From these coal fractions, the polished sections for image analyses and SEM-EDX determinations were prepared. For XRF, titrimetric and gravimetric analytical methods and powder X-ray diffraction, the fractions below 0.1 mm were prepared by powdering of 1 – 2 mm coal fractions. The ashes of coal samples were obtained by coal combustion (fractions below 0.1 mm) at 850 °C.

2.2. EQUIPMENTS AND METHODS

Bulk chemical analyses of coal were performed using XRF spectrometer XEPOS (Spectro), and proximate analyses and determination of sulphur species (pyritic, sulphate, organic and total sulphur) were performed by classical gravimetric and titrimetric analytical methods. The minerals in coal were identified by X-ray diffractometer D8 Advanced (Bruker) and SEM-EDX measurements (XL-30 with X-ray spectrometer EDAX, Philips). An image analysis was performed using optical microscope BX 300 (Olympus) whereas the evaluation of pyrite content and grain sizes performed by method described by Kožušníková (1992). The Raask´s method (1985) and CQPA methods were applied for the quantitative determination of minerals in our set of 5 coal samples.

a) The Raask´s (1985) method.

The Raask´s method uses the successive calculation of quartz (Q), kaolinite (K), pyrite (Py) and calcite (Cal) percentages from the following equations (1 - 4):

$$Q = SiO_2 - 1.5 \times Al_2O_3 \tag{1}$$

$$K = \left(SiO_2 + Al_2O_3 + K_2O\right) - \left(Q + 9.1 \times K_2O\right) \tag{2}$$

$$Py = \frac{130 \times \left(S_{(C)} - 0.3\right)}{A} \tag{3}$$

$$Cal = \frac{228 \times CO_{2(C)}}{A} \tag{4}$$

where Q, K, Py and Cal are weight percentages of quartz (Q), kaolinite (K), pyrite (Py) and calcite (Cal) in ash; SiO_2, Al_2O_3 a K_2O are weight percentages of related oxides in ash; $S_{(C)}$ and $CO_{2(C)}$ are weight percentages of total sulphur and carbon dioxide in coal; A is ash content. The method of Raask (1985) was selected as a typical normative method.

b) Chemical Quantitative Phase Analysis (CQPA)

This method was originally designed for magmatic rocks (Klika et al., 1986). In this study, this method is tested for its possible use for quantitative determination of minerals in coal.

CQPA method is based on the assumption that concentration of chemical elements (or theirs oxides) can be express using the following equation:

$$(c_i)_{calc} = \sum_{j=1}^{n} w_{i,j} \times c_j \tag{5}$$

Table 2 Proximate and chemical analyses of coal and ash samples.

	Samples									
	1		2		3		4		5	
	coal	ash	coal	ash	coal	ash	coal	ash	coal	ash
W	35.45	-	8.27	-	7.28	-	7.22	-	0.77	-
A	8.69	-	15.24	-	10.62	-	9.04	-	2.50	-
VM	58.69	-	48.67	-	45.38	-	52.92	-	26.30	-
SiO_2	2.40	27.62	6.17	40.49	5.22	49.15	3.97	43.92	0.75	30.00
TiO_2	0.04	0.42	0.35	2.30	0.35	3.30	0.24	2.65	0.07	2.80
Al_2O_3	2.48	28.54	2.30	15.09	3.64	34.27	2.21	24.45	0.36	14.40
Fe_2O_3	0.61	7.02	3.50	22.97	0.49	4.61	0.81	8.96	0.78	31.20
CaO	2.46	28.31	0.17	1.12	0.54	5.08	0.43	4.76	0.05	2.00
MgO	0.56	6.44	<0.03	<0.20	<0.03	<0.30	0.09	1.00	0.04	1.60
K_2O	0.04	0.46	0.08	0.52	0.04	0.38	0.06	0.66	0.01	0.40
P_2O_5	0.03	0.35	0.06	0.39	0.04	0.38	0.05	0.55	0.01	0.40
S_{tot}	0.81	-	2.94	-	1.37	-	1.58	-	0.46	-
S_{pyr}	0.03	-	0.36	-	0.02	-	0.29	-	0.01	-
S_{sul}	0.17	-	1.45	-	0.28	-	0.33	-	0.07	-
S_{org}	0.61	-	1.13	-	1.06	-	0.96	-	0,37	-
CO_2	<0.03	-	<0.03	-	<0.03	-	<0.03	-	<0.03	-

Note: W – moisture; A - ash content; VM - volatile matter of coal; S_{total} *- total sulphur;* S_{pyr} *- pyritic sulphur;* S_{sul} *- sulphate sulphur;* S_{org} *- organic sulphur.*

The percentages of Na_2O and CO_2 are below detection limits 0.20 % and 0.03 % (*w/w*), respectively.

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 evaluated from optimization formula:

$$\sum_{i=1}^{m}\left(\left(c_i\right)_{\exp}-\sum_{j=1}^{n} w_{i,j}\times c_j\right)^2=\min \qquad (6)$$

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. The CQPA calculation consists of the following steps:

1. Identification of minerals present in coal.
2. Selection of crystallochemical formula for identified minerals.
3. Calculation of mineral contents (c_j) in coal sample using optimization formulae (Eq. 6).
4. Using calculated mineral contents (c_j) from step 3 and data from point 1 and 2, the $(c_i)_{calc}$ values are calculated from Eq. (5). Validation of the total calculation was then performed by comparison of agreement among $(c_i)_{calc}$ and $(c_i)_{exp}$ data.

The details to this method are given in Klika et al. (1986).

3. RESULTS AND DISCUSSION

3.1. *CHARACTERIZATION OF COAL AND ASH SAMPLES*

Proximate and chemical bulk analyses of coal samples are given in Table 2. Ash content (A), volatile matter (VM) and chemical analyses of coal are related to the coal dry basis. Analyses of ashes were recalculated from coal analyses using ash content (A). This recalculation ensures the same type of input data for mineral evaluation by CQPA and Raask methods. All data are in weight %.

The significant differences in proximate characteristics and in sulphur species among coal samples 1 - 5 are observed. In contrast to lignite and subbituminous coal samples, the lowest contents of sulphur species are in bituminous coal. Except for sample 2, the relations among the concentrations of sulphur species are: $S_{org} > S_{sul} > S_{pyr}$ (Table 2). Predominance of sulphates (mikasaite, basanite and anhydrite) over pyrite was identified by X-ray powder diffraction, and pyrite was identified only in samples 2 and 4 (Table 3, Fig. 1). In contrast to chemical analyses and X-ray powder diffraction, the sulphates were not identified by SEM-EDX. Using SEM-EDX (Fig. 2a) and image analysis (Fig. 3), only the presence of pyrite was proved (Table 3). In coal samples 1 to 4, grains of pyrite varied in size from about 1 to 400 µm and pyrite content ranged from 0 to 17 %. In coal sample 5, the size of pyrite grains were below 15 µm and its maximal content less than 0.16 %.

Table 3 Minerals identified in coal samples.

	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
	XRD	SEM	XRD	SEM	XRD	SEM	XRD	SEM	XRD	SEM
Quartz	+	+	+	+	+	+	+	+	+	+
Kaolinite	+	+	+	+	+	+	+	+	+	+
Anatase			+	+	+	+	+	+		
Hematite	+								+	+
Pyrite		+	+	+		+	+	+		+
Mikasaite			+		+		+		+	
Anhydrite							(+)			
Basanite	+				+		+			

Note: + mineral present; (+) mineral probably present

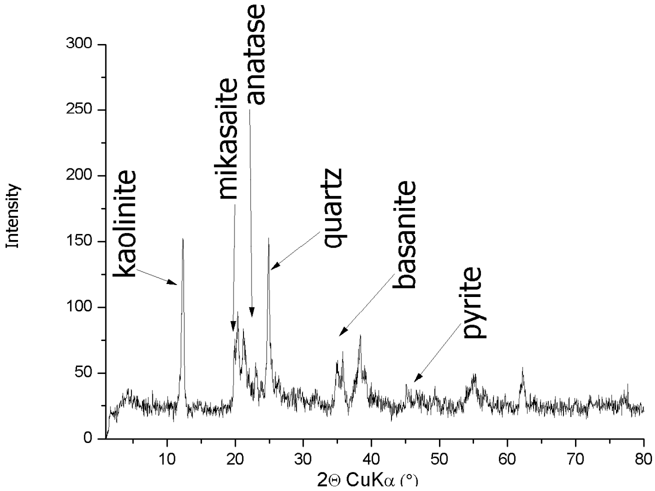

Fig. 1 Powder X-ray diffraction pattern of LTA from coal sample 2.

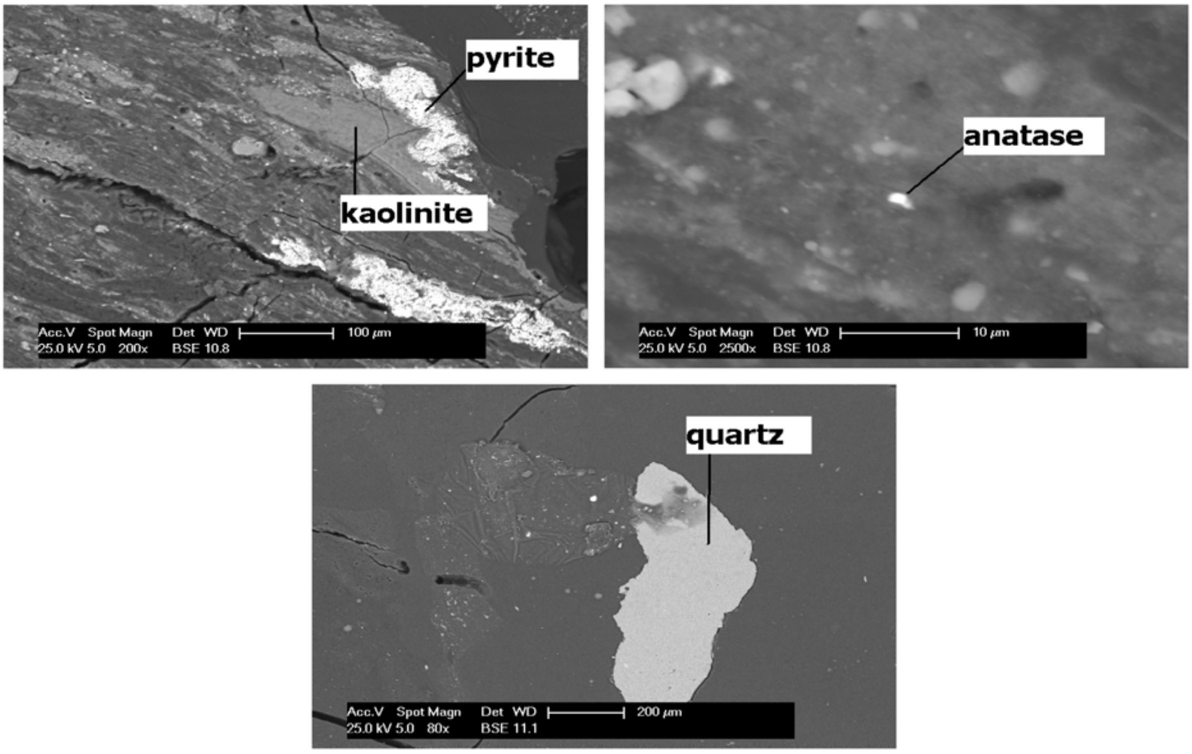

Fig. 2 SEM photos of determined minerals in coal sample 2.

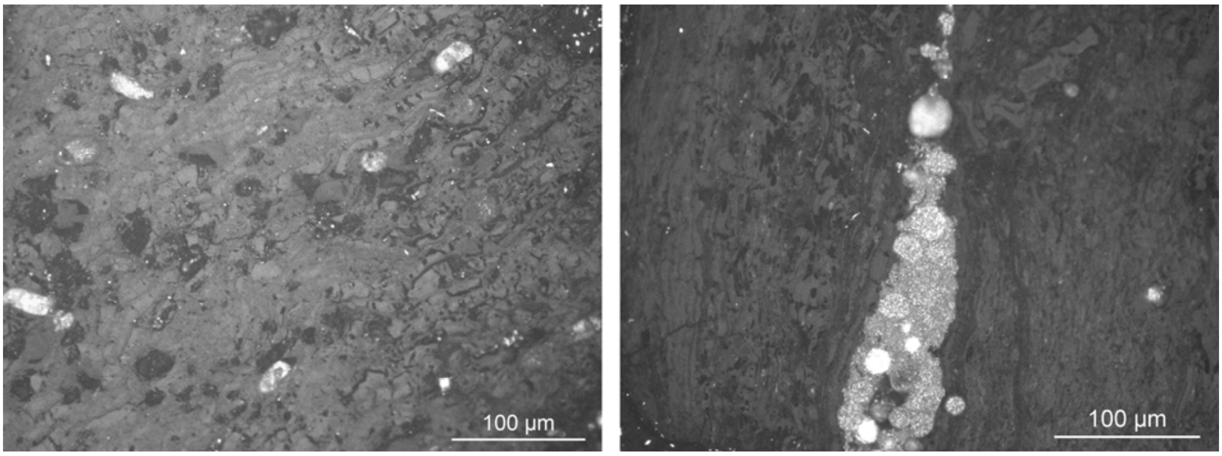

Fig. 3 Pyrite in coal sample 2 (image analysis).
Pyrite filling of cells (left); framboidal pyrite (right).

Mikasaite and basanite are not usually reported as primary minerals present in coal (e.g. Vassilev and Vassileva, 1996; Ward, 2002). Their occurrence is usually attributed to reaction between pyritic and/or organically bonded Fe and Ca with newly formed sulphates (Allen et al., 1986; Pike et al., 1989; Ward, 1991; Ward, 1992). Therefore the presence of sulphate minerals identified by powder X-ray diffraction and chemical analyses in our samples can be explained by transformation of pyrite into mikasaite and basanite during coal samples powdering to grain size below 0.1 mm. Moreover, the X-ray diffraction data were obtained from powdered samples of ashes obtained at about 350 °C. This opinion is also in agreement with e.g. Pearson and Kwong (1979) who, as many others, observed oxidation of pyritic sulphur to sulphate species during grinding. Therefore, for quantitative determination of the minerals in our coal samples the sulphate minerals identified by X-ray diffraction were treated as an artefact of the sample preparation and were not taken into account.

3.2. EVALUATION OF MINERAL PERCENTAGES IN COAL SAMPLES

The percentages of minerals in coal samples 1 - 5 were evaluated using the methods of Raask (method I) and CQPA (method II) described above. The following input data were used:

a) **Method I - chemical analyses of ashes (SiO_2, Al_2O_3, K_2O) and coal (S_{tot} and CO_2) in Table 2.** (Note: chemical analyses of SiO_2, K_2O and Al_2O_3 of coals were recalculated on ash basis (i.e. ash was not analysed) using ash contents, while total sulphur (S_{tot}) and carbon dioxide contents (CO_2) were taken from analyses of coal. Recalculation of SiO_2, K_2O and Al_2O_3 percentages of coal on ash basis provides the equivalent input data with that for methods II.)

b) **Method II – chemical analyses of coal (Table 2), mineral identification by SEM-EDX (Table 3) and the following crystallochemical formulae:**

Quartz: SiO_2

Kaolinite: $Al_4(OH)_8Si_4O_{10}$

Hematite: Fe_2O_3

Anatase: TiO_2

Pyrite: FeS_2

(Note: The determination of pyritic sulphur for coal samples 1 – 4 is burdened by big error with regard to its oxidation during subbituminous coal grinding. For these coal samples the pyritic sulphur was calculated using the formula: $S_{pyr} = S_{tot} - 0.3$ (see also Eq. 3), where $S_{org} = 0.3$ % wt is assumed).

Evaluated percentages of minerals by methods I and II are given in Table 4. The Raask´s empirical formulas (Eqs. 1 - 4) were suggested for selected British and U.S. bituminous coal. For our samples (subbituminous rank) with somewhat different proportion of quartz/kaolinite and higher content of pyrite, the results calculated by Raask´s method are less satisfactory than that obtained by CQPA method (see e.g. higher negative content of quartz for sample 1 and 3).

3.3. COMPARISON OF RESULTS

Using Eq. 5, the validation of above methods I and II was performed by reverse calculation of mineral percentages (Table 4) into chemical analyses (methods I and II, Table 5). For comparison the chemical analyses of coals CHA (given before in Table 2) are also included. The percentages of CaO, MgO, K_2O and P_2O_5 in method I and method II equal zero because they are not included in the identified minerals.

In order to compare both analyses (method I and method II), the maximal relative errors (*E*) for each sample and each method were calculated according to

Table 4 Percentages of minerals (% w/w) in coal samples determined by method I and method II.

Sample	Mineral	method I	method II
1	Quartz	-1.32	-0.20
	Kaolinite	5.88	5.58
	Pyrite	0.66	0.93
2	Quartz	2.72	3.76
	Kaolinite	5.11	5.18
	Pyrite	3.43	5.12
	Anatase	-	0.35
3	Quartz	-0.24	1.41
	Kaolinite	8.77	8.19
	Pyrite	1.39	1.27
	Anatase	-	0.35
4	Quartz	0.65	1.65
	Kaolinite	5.04	4.97
	Pyrite	1.66	1.74
	Anatase	-	0.24
5	Quartz	0.21	0.37
	Kaolinite	0.82	0.81
	Pyrite	0.21	0.38
	Hematite	-	0.45

Table 5 Chemical analyses (CHA) and chemical analyses (method I and II) recalculated from mineral contents obtained by methods I and II.

Sample		SiO_2	TiO_2	Al_2O_3	Fe_2O_3	*CaO*	*MgO*	K_2O	P_2O_5	S_{tot}
1	CHA	2.40	0.04	2.48	0.61	*2.46*	*0.56*	*0.04*	*0.03*	0.81
	method I	1.42	*0.00*	2.32	0.44	*0.00*	*0.00*	*0.00*	*0.00*	0.82
	method II	2.40	0.00	2.20	0.62	*0.00*	*0.00*	*0.00*	*0.00*	0.80
2	CHA	*6.17*	*0.35*	*2.30*	3.50	*0.17*	*<0.03*	*0.08*	*0.06*	*2.94*
	method I	5.10	*0.00*	2.02	2.27	*0.00*	*0.00*	*0.00*	*0.00*	1.83
	method II	6.17	0.35	2.04	3.40	*0.00*	*0.00*	*0.00*	*0.00*	3.04
3	CHA	5.22	0.35	3.64	0.49	*0.54*	*<0.03*	*0.04*	*0.04*	1.37
	method I	3.84	*0.00*	3.46	0.92	*0.00*	*0.00*	*0.00*	*0.00*	0.74
	method II	5.22	0.35	3.24	0.84	*0.00*	*0.00*	*0.00*	*0.00*	0.98
4	CHA	3.97	0.24	2.21	0.81	*0.43*	*0.09*	*0.06*	*0.05*	1.58
	method I	3.00	*0.00*	1.99	1.10	*0.00*	*0.00*	*0.00*	*0.00*	0.89
	method II	3.97	0.24	1.96	1.16	*0.00*	*0.00*	*0.00*	*0.00*	1.23
5	CHA	0.75	0.07	0.36	0.78	*0.05*	*0.04*	*0.01*	*0.01*	0.46
	method I	0.59	*0.00*	0.32	0.14	*0.00*	*0.00*	*0.00*	*0.00*	0.11
	method II	0.75	0.00	0.32	0.77	*0.00*	*0.00*	*0.00*	*0.00*	0.51

Note: Oxides CaO, MgO, K_2O and P_2O_5 not included in crystallochemical formulaes of calculated minerals are printed in small italics. The % Fe_2O_3 was determined by recalculation of Fe from % Py (Table 4) for both methods I and II.

Eq. (7). In these calculations, only the oxides SiO_2, Al_2O_3, K_2O, Fe_2O_3, S_{tot} were taken into account. The calculated E data are given in Table 6 and plotted in Figure 4.

$$E = \left(\frac{\sum_{i=1}^{m} \left| c_{i,cal} - c_{i,\exp} \right|}{\sum_{i=1}^{m} c_{i,\exp}} \right) \times 100 \qquad (7)$$

where $c_{i,cal}$ is the concentration of the i-th oxide obtained from the calculated mineral contents by method I (Raask) or method II (CQPA); $c_{i,exp}$ is the concentration of the i-th oxide from the comparative chemical analysis (CHA).

4. CONCLUSION

The methods based on the recalculation of chemical analysis of inorganic element oxides into quantitative phase (mineral) analysis usually result in

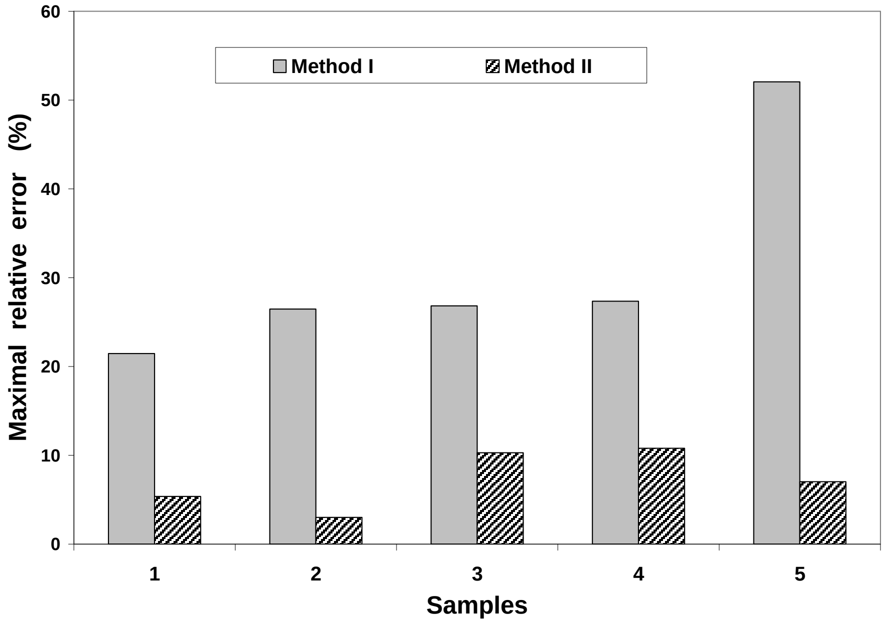

Fig. 4 Maximal relative error (E) of tested methods for samples 1-5.

Table 6 Maximal relative error E (%) obtained for methods I and II.

Sample		Maximal relative error E (%)
1	Method I	21.45
	Method II	5.36
2	Method I	26.47
	Method II	3.01
3	Method I	26.83
	Method II	10.30
4	Method I	27.36
	Method II	10.78
5	Method I	52.07
	Method II	7.02

relative high error of minerals determination. In this paper, the CQPA (Klika et al., 1986) and Raask´s methods are tested and compared for quantitative determination of minerals in the Czech coals. The validation of this method was performed using 5 coal samples. In comparison to the Raask´s method the CQPA has the following advantages:

a) Calculation is based on the minerals identified in coal and not only on the normative minerals; and

b) Optimization principle of CQPA calculation gives very reliable results.

One disadvantage of the CQPA, as well as all similar methods based on the recalculation of chemical analysis, is that the major elements with affinity to organic matter are not excluded from bulk chemical analyses of coal. This gives some uncertainty of the calculation because the analyst does not know whether these elements belong to minerals that were not quantitatively determined or if they are bonded on organic matter.

ACKNOWLEDGEMENTS

We acknowledge the financial support of the Grant Agency of the Czech Republic (grant No.105/08/0913) and project CZ.1.05/2.1.00/01.0040.

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