

# Determination of C<sub>(total)</sub> and O<sub>(total)</sub> in the Calcite Rich Limestones by WD-XRF Spectrometry

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**Abstract:** Carbon and oxygen XRF spectra were studied using a WDXRF (WD X-ray fluorescence) spectrometer S8 TIGER (Bruker AXS, Germany). XRF spectra were obtained from the samples of the calcareous spar (CaCO<sub>3</sub>) (pure calcium carbonate), the limestones, the graphite, the microcrystalline cellulose, various organic compounds and prepared mixtures on the basis of the calcareous spar with addition of the graphite and the microcrystalline cellulose. The studied samples of the limestones are characterized by high concentrations of calcite (98.5-99%). Main objective of this investigation is to develop WDXRF technique for the determination of  $C_{(total)}$  and  $O_{(total)}$ . Optimal instrumental measuring conditions were selected experimentally for quantitative determination of  $C_{(total)}$  and  $O_{(total)}$ . The calculated values of the ILD (instrumental limit of the detection) vary from 0.0215% for  $C_{(total)}$  to 0.0331% for  $O_{(total)}$ . The obtained values of the LDM (limit of determination of the XRF method) do not exceed 0.08% for  $C_{(total)}$  and  $O_{(total)}$ . The RSDs (relative standard deviations) values do not exceed 1.0% in all cases.

Key words: XRF spectrum, LDM, carbon, oxygen, graphite, calcite, limestone, calcareous spar.

# **1. Introduction**

As you know, most of the carbon and oxygen are found in the calcite and the dolomite in the carbonates which relate to the sedimentary rocks. Also, these elements are part of the organic compounds, the contents of which do not exceed 1% in most cases in the carbonate rocks. A large number of various organic compounds of a complex structure such as amino acids, proteins and peptides have been isolated from the sedimentary deposits and soils [1]. Most of the plant residues are carbohydrates in the sedimentary rocks. The significant proportion of carbohydrates is in the form of polymerized sugars and cellulose in the sedimentary rocks. Cellulose is the most abundant polysaccharide in the sedimentary rocks [1].

It should be noted that dispersed organic matter in sedimentary rocks is transformed into graphite under

the influence of deep regional metamorphism of these rocks [2]. So, graphite was identified in the marbles of the Ol'khonskiy complex [3] and the limestones of the Ol'khovskiy deposit (the Eastern Sayan Mountains) [4].

Despite the fact that the X-ray fluorescence method of analysis is used to study organic compounds [5], significant difficulties arise in the quantitative determination of the light elements, which include C and O. It is associated with the low fluorescence yield as well as the insignificant penetration depth of X-rays  $(1-3 \ \mu m)$  [6, 7].

The stronger influence of oxygen on carbon is observed in the XRF spectra obtained from samples of carbonates under selected measurement conditions in this work. The C/O ratio values obtained from theoretical chemical formulas differ significantly for carbonates and organic compounds. So, the C/O ratio value is 0.25 for carbonates (Li<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, CaCO<sub>3</sub>, MgCO<sub>3</sub>, MnCO<sub>3</sub>, FeCO<sub>3</sub>, CoCO<sub>3</sub>, SrCO<sub>3</sub>, PbCO<sub>3</sub>, BaCO<sub>3</sub>), for sodium bicarbonate (NaHCO<sub>3</sub>) as well as for dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>). The C/O ratio values are 0.75 for glycine and 0.90 for cellulose,

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respectively. The value of this ratio rises to 1.20 for chitinte (polysaccharide).

## 2. Objects

The objects of research are samples of the light-gray chemically pure limestone of the Bilyutinskiy deposit (Zaigraevskiy district, Republic of Buryatia (51°50′06″ N and 108°15′47″ E)) [8].

The mineral composition of the studied samples was investigated by powder diffraction method (diffractometer DRON-3 (Russia)) [9]. Measurements of the samples were performed at the following conditions: 30 kV electric potential difference and 20 mA electric current intensity of the X-ray tube with a copper anode, the range of the 2 $\theta$  angles from 3 to 65 degrees.

The light-gray limestone studied samples are characterized by high concentrations of calcite (98.5-99%). So, the main identified phase is calcite with unit cell parameters a = 4.978 (2); c = 17.03 (1) Å in the studied limestone samples. These parameters are lower than unit cell parameters of pure calcite [10]. It can be associated with the presence of magnesium, manganese and iron, which take part in isomorphic substitutions in calcite [11].

Mineral composition data obtained by the method powder diffraction are in good agreement with the data of silicate analysis [12]. CaO and CO<sub>2</sub> are the dominant components in the chemical composition of all studied samples of the limestone. So, concentrations of CaO and CO<sub>2</sub> in one of the representative samples of limestone are 55.32% and 42.84%, respectively. Contents (%) of  $Fe_2O_{3(total)}$  (0.35) and MgO (0.35) are low. Also, trace concentrations (%) of Na<sub>2</sub>O (0.02) and MnO (0.04) are present in the chemical composition of this limestone. Concentration of hygroscopic water  $(H_2O^-)$  is 0.10%, and value of lost on ignition is 0.89% after subtracting of CO2 concentration. Lost on ignition was determined by calcining a weighed portion of the sample in a porcelain crucible at a temperature of 1,000 °C to constant weight. Weight

loss on ignition occurs due to the release of water (bound and free), carbon dioxide, volatile components and organic substances. Value of lost on ignition after additional subtracting of hygroscopic water (H<sub>2</sub>O<sup>-</sup>) concentration (0.10%) and total content of the volatile components such as F, S<sub>(total)</sub>, and Cl (0.0252%) is 0.764% for the studied limestone. The obtained value indicates the presence of relatively low content of TOC (total organic carbon) in the studied limestone.

# 3. Methodology

## 3.1 Samples Preparation for Analysis

The studied samples preparation was carried out in accordance with the requirements given in Ref. [13]. The selected samples were powdered manually with the addition of a few drops of an ethyl hydroxide of high purity for the elimination of a particle aggregation in the agate mortars for 7 h. The average particle size was 35 µm after this grinding stage. It was obtained using a laser particle-size analyzer "Analysette 22" COMPACT (FRITSCH, Germany). C and O are elements of the long-wave region of the spectrum. Smaller particles ( $< 2.5 \mu m$ ) are required for quantitative determination of these elements [6]; therefore the resulting powdery material was subjected to further grinding in solution of an ethyl hydroxide of high purity in the agate mortars of larger volume for 5 h. The particle sizes did not exceed 1.5 µm after second grinding stage. The prepared powdered samples weighing  $1 \pm 0.0001$  g were used for the determination of the concentrations of C<sub>(total)</sub> and O<sub>(total)</sub>. The prepared samples were pressed into tablets on a base from boric acid with a diameter of 40 mm using the HERZOG HTP 40 semiautomatic press (Germany) with a pressure of 100 kN as in Ref. [14].

#### 3.2 WDXRF Set-Up and X-Ray Spectra

Investigations were performed in a vacuum condition using a WDXRF spectrometer S8 TIGER (Bruker AXS, Germany), which is equipped with a 4 kW power X-ray tube with a rhodium anode and a beryllium window of 75 µm thickness [15]. Optimal instrumental measuring conditions were selected as a result of research. So, the contents of C<sub>(total)</sub> and O<sub>(total)</sub> were determined using the XS-C and XS-55 crystals, respectively. Flow proportional counter and a  $0.46^{\circ}$ collimator were used in all cases. Also, for the determination of C<sub>(total)</sub> electric current intensity and electric potential difference of the X-ray tube were 50 mA and 50 kV, for the determination of O<sub>(total)</sub> these parameters were 20 mA and 80 kV, respectively. Values of the ILD (instrumental limit of the detection) for  $C_{(total)}$  and  $O_{(total)}$  were calculated for the calcareous spar (pure calcium carbonate) for various measurement conditions. The ILD can be detected by an instrument in a given analytical context with a 99.95% confidence level. It was calculated using the equation from [16]:

$$ILD = \frac{4.65}{S_i} \sigma_b, \qquad (1)$$

where  $S_i$  is sensitivity (Cps/concentration),  $\sigma_b$  is the standard deviation calculated from several background intensity measurements (n = 10) performed in both sides of peak position of the analytical lines.

It should be noted that the selected aforecited parameters correspond to the minimum values of the ILD for  $C_{(total)}$  and  $O_{(total)}$  (Fig. 1).

As seen from Fig. 1, further increase of electric potential difference of the X-ray tube from 50 to 60 kV does not lead to reduction of the ILD values for  $C_{(total)}$ . Increase of electric potential difference from 20 to 60 kV causes rise of the ILD values for  $O_{(total)}$ . The minimum calculated values of the ILD for the calcareous spar (pure calcium carbonate) for the selected measurement conditions are 215 mg kg<sup>-1</sup> (0.0215%) for  $C_{(total)}$  and 331 mg kg<sup>-1</sup> (0.0331%) for  $O_{(total)}$ , respectively.



Fig. 1 Values of the ILD for  $C_{(total)}$  and  $O_{(total)}$  for the calcareous spar (pure calcium carbonate) for various measurement conditions.

The lines peaks position and background were selected experimentally. It was found that selected peak position of  $CK_{\alpha 1}$ -line for carbonate rocks differs from peak positions for graphite and organic

compounds. It can be associated with the stronger influence of O on C in the XRF spectra obtained from samples of carbonates unlike the organic compounds (Figs. 2a and 2b).



Fig. 2 (a-c) XRF spectra of analytical line of C from samples of the calcareous spar, the microcrystalline cellulose and the graphite (measurement time is 300 s).



Fig. 3 (a and b) XRF spectra of analytical line of C from samples of mixture of the calcareous spar and the microcrystalline cellulose in ratio of 9:1 and mixture of the calcareous spar and the graphite in ratio of 9:1 (measurement time is 300 s).

So, peak position of  $CK_{\alpha 1}$ -line for the calcareous spar (pure calcium carbonate) and the microcrystalline cellulose are 43.407 ° and 43.582 °, respectively. Peak position of  $CK_{\alpha 1}$ -line is 43.821 ° for graphite (Fig. 2). Also, angular deflection of peak position of  $CK_{\alpha 1}$ -line (43.407 °) is observed in the XRF spectra obtained from samples of mixture of ascorbic acid and glucose in ratio of 1:9 (43.582 °), glycine (43.698 °), acetylsalicylic acid (43.767 °). Similar changes of peak position of  $CK_{\alpha 1}$ -line are identified in the XRF spectra obtained from samples of mixture of the calcareous spar and the microcrystalline cellulose in ratio of 9:1 (43.525 °) and mixture of the calcareous spar and the graphite in ratio of 9:1 (43.629 °) (Fig. 3).

Also, intensity of  $CK_{\alpha 1}$ -line increases by 1.19 and 1.79 times after adding to the calcareous spar 10% of microcrystalline cellulose and 10% of graphite, respectively (Figs. 2a, 3a and 3b).

Background intensity changes slightly. Background position of  $CK_{\alpha 1}$ -line is 39.497 °. It remains constant in all cases as well as positions of peak and background of  $OK_{\alpha 1}$ -line, which are 49.947 ° and 47.820 ° for XS-55 analyzing crystal, respectively. Measurement time of intensities of the analytical lines and the

background from C and O was 300 s and 60 s, respectively. Processing the X-ray spectra, numerical peak separation, and the correction of the matrix effects were carried out using the software SPECTRA<sup>plus</sup> [17].

#### 3.3 RMs (Reference Materials)

The RMs with the high content of calcium oxide (more than 20%) such as GPOS302 (dolomitic limestones) and GPOS303 (dolomite containing of feldspars 35.3%) were used for performing of metrological studies [18, 19].

GPOS301 (dolomitic limestones), the calcareous spar (CaCO<sub>3</sub>) (pure calcium carbonate),  $Li_2CO_3$ (chemically pure), CaCO<sub>3</sub> (chemically pure), BaCO<sub>3</sub> (chemically pure), and prepared mixtures on the basis of the calcareous spar with addition of the graphite and the microcrystalline cellulose were used for constructing of calibration curves. The calcareous spar and aforecited mixtures were prepared similarly to the studied samples. So, the graphite contents vary from 0.124 to 10% in mixtures of the first type, while the total concentrations of entered equal amounts of the graphite and the microcrystalline cellulose vary from 0.156 to 10% in mixtures of the second type.

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	Total number	*Calibration	Line overlap	Influence coefficients	S <sup>a</sup> (%)	
Element	of the RMs and prepared mixtures	range (%)	correction	( <i>a</i> -correction)	$\mathbf{I}^{\mathrm{b}}$	IIc
C(total)	23	6.081-20.800	OK <sub>α1</sub> [2], RhL <sub>α1</sub> /Rayleigh	$FK_{\alpha 1}$ , $MgK_{\alpha 1}$ , $AlK_{\alpha 1}$ , $SiK_{\alpha 1}$ , $CaK_{\alpha 1}$ , $TiK_{\alpha 1}$ , $MnK_{\alpha 1}$	1.86	0.14
O(total)	22	24.324-52.163	RhL <sub>a1</sub> /Rayleigh	$\begin{array}{l} FK_{\alpha 1},ClK_{\alpha 1},PK_{\alpha 1},MgK_{\alpha 1},SiK_{\alpha 1},\\ MnK_{\alpha 1},FeL_{\alpha 1} \end{array}$	5.43	0.29

Table 1 Calibration data obtained for C<sub>(total)</sub> and O<sub>(total)</sub>.

\* Calibration ranges are present by calculated concentrations of  $C_{(total)}$  and  $O_{(total)}$ . Calculated values of  $C_{(total)}/O_{(total)}$  vary from 0.238 (RM GPOS301 (dolomitic limestone)) to 0.481 (mixture of the calcareous spar and the graphite in ratio of 9:1).

<sup>a</sup> Standard deviation.

<sup>b</sup> Without correction of the matrix effects.

<sup>c</sup> With accounting of the matrix effects ( $\alpha$ -correction).

## 4. Result and Discussions

#### 4.1 Quantitative Analysis

The method based on the use of  $\alpha$ -coefficients was realized to take into account the interelement influences. The corrected concentrations were calculated using the equation:

$$C_{i} = m_{i}I_{i}\left(1 + \sum_{j} \alpha_{ij}^{'}I_{j}\right), \qquad (2)$$

where  $C_i$  and  $I_i$  are concentration and intensity of the determined element analytical line corrected for background,  $m_i$  is slope of the calibration curve,  $I_j$  is matrix elements intensity corrected for background,  $\alpha_{ij}$  is  $\alpha$ -coefficients used to account for matrix effects.

The coefficients for accounting of the contribution of the lines overlap were calculated using the equation:

$$I_{i} = I_{i} + \sum_{overlap} k_{j} \cdot I_{j}, \qquad (3)$$

where  $I_i$  is the corrected intensity for an *i*-th line,  $I_i$  is the intensity of the determined element analytical line corrected for background (net intensity),  $I_j$  is the intensity of the element that gives the interfering line,  $k_j$  is the regression coefficient.

Table 1 shows the calibration data.

As seen from Table 1, the standard deviation (S) values obtained using the fixed  $\alpha$ -coefficients were less than the S values achieved without the matrix correction by 13.29-18.72 times. Values of the standard deviation were derived from linear regression equation

using least-squares fit [20]. The scatter of points was reduced significantly after accounting the matrix effects and the introduction of improvements for the lines overlap both on the calibration curves and on the plot expressing the dependence of I Net of  $CK_{\alpha 1}/I$  Net of  $OK_{\alpha 1}$  on measured values of  $C_{(total)}/O_{(total)}$  (Fig. 4).



Fig. 4 Dependence of the ratio of the analytical line intensities of  $CK_{\alpha 1}$  and  $OK_{\alpha 1}$  corrected for background on measured values of  $C_{(total)}/O_{(total)}$ .

### 4.2 Analytical Figures of Merit

The LDM (limit of determination of the XRF method) was calculated for  $C_{(total)}$  and  $O_{(total)}$  under selected measurement conditions. The LDM was defined as the smallest concentration of an analyte that can be reliably quantified with a 95.4% confidence level [16]. It should be noted that the limits of the determination took into account errors of sample preparation, instrumental errors and errors in calculating statistics [16]. Values of LDM were calculated from a series of ten replicate specimens (n = 10) prepared from the representative sample of the light-gray limestone according to the equation from works [16, 21]:

Tuble 2	Emilies of the determination (70) of the WBI	in method evaluated in the right gruy innestone, " = 10.
Element	Concentration (%)	LDM <sup>a</sup>
C(total)	12.427	0.0560
O(total)	47.279	0.0737

Table 2 Limits of the determination (%) of the WDXRF method evaluated in the light-gray limestone, n = 10.

<sup>a</sup> The limit of determination of the WDXRF method.

Table 3 Comparison of the results (%) obtained by different methods for representative sample of the light-gray limestone.

Element	Method of the WDXRF	Method of the silicate analysis
C(total)	$12.427 \pm 0.052$	12.448*
O(total)	47.279 ±0.064	47.231*

12.448%\* is the calculated total content of carbon, which consists of concentration of carbonate carbon (11.684%) computed from CO<sub>2</sub> content (42.84%) and value of lost on ignition (0.764%) after additional subtracting of H<sub>2</sub>O<sup>-</sup> concentration (0.10%) and total content of F, S<sub>(total)</sub>, and Cl (0.0252%).

47.231%\* is the calculated total content of oxygen.

Table 4 Concentrations (%) (mean  $\pm$  standard deviation, n = 6) obtained for RMs GPOS302 (dolomitic limestone) and GPOS303 (dolomite containing of feldspars 35.3%) by the proposed WDXRF method and concentrations calculated from the certified values for the RMs (C\*).

Floment	GPOS302				
Element	Cwdxrf	C*			
C(total)	$10.255 \pm 0.059$	10.200			
O(total)	$49.289 \pm 0.068$	49.345			
Flomont	GPOS303				
Element	Cwdxrf	<i>C</i> *			
C(total)	$8.557 \pm 0.058$	8.509			
O(total)	$49.520 \pm 0.072$	49.455			

LDM = 
$$2\sqrt{\frac{\sum_{m=1}^{n} (C_m - \overline{C})^2}{n-1}}; \quad \overline{C} = \frac{\sum_{m=1}^{n} C_m}{n}.$$
 (4)

The concentrations of  $C_{(total)}$  and  $O_{(total)}$  as well as the obtained LDM values are presented in Table 2.

The LDM values do not exceed 0.08% for  $C_{(total)}$ and  $O_{(total)}$ . The RSDs (relative standard deviations) values of the measurement results were calculated for checking purposes of the WDXRF method repeatability as in Ref. [14]. The values of the RSD do not exceed 1.0% in all cases.

The accuracy of this WDXRF method was checked. The comparison of the results obtained by methods of the WDXRD and the silicate analysis was carried out (Table 3).

As can be seen, the results obtained by two different methods are in good agreement which is also observed at the comparison of the data obtained by the proposed WDXRF method after measurement the RMs GPOS302 (dolomitic limestones) and GPOS303 (dolomite containing of feldspars 35.3%) with calculated concentrations of  $C_{(total)}$  and  $O_{(total)}$  in these RMs. Obtained contents of the determined elements were calculated using the certified values (Table 4).

Presented RMs and studied light-gray limestone enriched by calcite are characterized by significant differences in chemical composition. This is reflected in the obtained values of  $C_{(total)}/O_{(total)}$  which vary from 0.173 for RM of dolomite containing of feldspars 35.3% to 0.208 for RM of dolomitic limestone. Measured value of  $C_{(total)}/O_{(total)}$  for studied light-gray limestone is 0.264. This value is very close to calculated value  $C_{(total)}/O_{(total)}$  (0.263) and measured value of this ratio (0.259) which were obtained for prepared mixture consisting of the calcareous spar (CaCO<sub>3</sub>) 99.375% and the graphite 0.625% in accordance with the calculations.

# 5. Conclusions

The proposed WDXRF technique can be applied for quantitative determination of  $C_{(total)}$  and  $O_{(total)}$  in limestones because values of the ILD, the LDM, the RSD and the accuracy of this method are found to be satisfactory. Also, obtained contents of  $C_{(total)}$  can be used to calculate TOC concentrations in limestones.

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