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The possibilities of analysis of limestone chemical composition

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Abstract. The aim of this work is to show commonly used procedures and methods for limestone analysis. The samples were measured with Inductively Coupled Plasma with Optical Emission Spectrometry (ICP-OES) for chemical compositions determination. For these measurements, the samples were decomposed by dissolving in acid, melting into solution and decomposed by microwave. Due to the time and financial demands of these analyses, there were an effort how to find a satisfactory method providing sufficient results with less time and financial demands. The X-ray diffraction (XRD) method was first tested, followed by X-ray fluorescence (XRF). Samples were measured in powder and melted into pearls. The evaluation was carried out by using of the Fundamental parameters method and by means of instrument calibration. The method of combustion elemental analysis was selected to determine of the sulfur content.

1. Introduction

The limestone has been used by humans for several thousand years, and there still grow the possibilities of processing and using of this raw material. Limestone was formed mainly as sedimentary rocks. Most limestones originated in the seas and their genesis was associated with rock-forming organisms. Limestones were also created in fresh waters, lakes, rivers and caves. The main conditions for the formation of limestone were the climate and the absence of clay or sandy material. Calcium carbonate has several polymorphic modifications. In nature, it is predominantly as minerals of calcite and aragonite. Calcite is usually sediment from organic origin. Aragonite secreted from solutions at higher temperatures or in the presence of sulfates. It may also have a biogenic origin from the shells of some molluscs [1].

Limestones are rocks predominantly made by minerals of calcite (calcium carbonate with trigonal structure, CaCO_3). They are solid and grained sedimentary rocks of organic or chemical origin. The calcium carbonate content is often above 95%. Most of the limestones were formed by the settling of limestone canals of animals and plants, mainly in the sedimentary basins of the sea. These limestones are called organogenic. In a small amount, limestones were excreted from aqueous solutions in karst lands. Conversion of limestones at high temperature and pressure resulted in crystalline limestones (marbles) in which calcite recrystallized so that the calcareous shells of animals did not appear in marble. Limes only rarely occur clean. Mostly they have admixtures of clay, carbonates, dolomite, sand, or phosphates or iron-containing minerals [1].



Limestone analysis is one of the basic chemical analyzes needed in every company focusing on the production and processing of this raw material. The aim of this work is to introduce commonly used methods and procedures for this analysis and to show what errors can occur in these analyses.

2. Sample preparation

All samples were dried at 110°C for 4h. If water content was required, they were weighed before and after drying. To determine the chemical and phase composition, the dried samples were first milled on a vibratory mill.

2.1. Acid decomposition

Determination by decomposition with hydrochloric acid left a large amount of non-degradable fraction after decomposition. The process has been progressively modified. The smallest insoluble fraction was obtained by using aqua regia ($\text{HCl}/\text{HNO}_3 = 3/1$) followed by addition of HF. After 1 hour of decomposition, the mixture was filtered, diluted with water and then analyzed. Despite the multiple workflow adjustment, satisfactory acid decomposition results have not been achieved since a small amount of undiluted portion of silicon was left in the samples.

2.2. Melting into liquid

Although the standard ČSN 721216 [2] allows the decomposition of samples in acids, the preferred method of decomposition for rocks and minerals is alkaline or alkaline oxidation melting, especially the decomposition of the sample by melting with sodium carbonate. This standard also allows degradation in borate fluxes which are more expensive but have many advantages over carbonates. The use of this mixture resulted in the complete decomposition of all components, and therefore it was not necessary to use HF fumigation, which is problematic for many reasons. In this type of decomposition, the sample was totally distributed. Determined samples were transferred to the solution by picking in platinum crucibles on a Fluxana Vulcan melt. A series of experiments found that the optimal melt ratio is 3 parts of lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) and 1 part of lithium metaborate (LiBO_2). LiBr as a wetting agent was added to this mixture. The whole mixture was melted using propan-butane + air heating gas. The melt thus formed was poured into dilute HNO_3 and boiled at 170°C with constant stirring. It was then cooled in air, quantitatively transferred to a volumetric flask, supplemented on 500 ml with distilled water and then determined by ICP-OES.

2.3. Pearl preparation

The specimens were melted into a pearl by drawing in platinum crucibles on a Fluxana Vulcan device. A series of experiments showed that the optimal melt ratio is 3 parts lithium tetraborate ($\text{Li}_2\text{B}_4\text{O}_7$) to 1 part lithium metaborate (LiBO_2) as well as samples for melting into solution. The resulting melt was mixed several times automatically and poured hot into a preheated dish, where it was controlled by software programmed refrigeration program.

2.4. Distribution by microwave decomposition

Samples were distributed on the CEM MARS instrument. The samples were decomposed into HNO_3 . In such an environment, silicon is only decomposed to a minimum. The analysis was performed using ICP-OES.

2.5. Powder form measurement

For samples in the form of powder, samples were placed in special containers supplied by manufacturers of measuring instruments on these instruments. For measurements on the air atmosphere on a handheld XRF spectrometer, they were overlaid with the polyethylene film over which the measurements were made. In the case of vacuum measurements, the samples were equipped with a special foil for vacuum measurement.

2.6. Sulfur content determination

To determine the total sulfur content, samples in powder form were placed in special ceramic crucibles for measurement using a combustion elemental analyser.

3. Description of the methods used

3.1. ICP-OES (inductively coupled plasma with optical emission spectrometry)

ICP-OES or inductively coupled plasma with optical emission spectrometry is a trace analytical method for determining trace and significant concentrations of individual elements in the analysed sample. This technique allows analysing almost all elements of a periodic table that can be converted into a solution with sensitivity from ppb to hundreds of ppm. The analyses were carried out on the HORIBA ULTIMA 2 instrument.

3.2. XRD (x-ray diffraction)

X-ray diffraction analysis is a method of determining the structure of crystalline substances. The method is based on the fact that the dimensions of the crystal lattice are comparable to the wavelength of X-rays. Thus, the diffraction (bending) of the radiation can occur on the crystal lattice. Since the pattern of the crystal is periodic, the diffraction pattern of the radiation, after passage through the crystal, has a relatively good relationship with the crystal structure. The method is used to determine the structure understood as a spatial arrangement of crystalline substances. Because of the low detection limit, it is not suitable for the determination of impurities below 1%.

3.3. XRF (x-ray fluorescence)

X-ray fluorescence (XRF) uses the emission of characteristic secondary or X-rays from material that has been excited by high energy X-rays. This phenomenon is widely used for elemental analysis and chemical analysis. Samples were measured primarily on the XENOMETRICS EX-6600 SSD energy dispersion device. The measurements were carried out in vacuum both in pearls and in powder. The evaluation was performed using both the Fundamental Parameter and the instrument calibration using the ICP-OES samples. From the measured values it can be said that this analysis can be used for rapid analysis of the sample for regular quality control. For comparison, measurements were also performed on the Olympus VANTA handheld XRF Spectrometer.

3.4. Combustion sulfur analysis in solids

This analysis is mainly used in the metals, ceramics, minerals, cement industry and other industries. The sample is placed in a ceramic crucible along with a so-called accelerator that promotes the combustion process. Next, the sample is burned in a high-frequency furnace in an oxygen stream. The resulting C, S containing flue gases are converted to CO₂ and SO₂ by reagents and detected by IR detectors. Samples were measured on a Brooker G4 ICARUS CS instrument.

4. Results and discussion

Two samples were observed during analyses. One very pure limestone from the Forest Quarry in Líšeň and the second sample was a polluted limestone used as a quarry stone in the FCH BUT laboratory. The results are shown in Tables 1–5 and Figure 1. Acid decomposition was performed only on a pure limestone sample, as a large amount of non-decomposed portion containing mostly Mg and Si was found in contaminated limestone.

4.1. The comparison of XRF and ICP-OES analysis

The values from comparison between XRF and ICP-OES techniques are present in wt. % in Tables 1 and 2.

Table 1. The results of analysis of limestone from Forest Quarry in Líšeň.

Pure limestone	Fe₂O₃	Al₂O₃	SiO₂	MgCO₃	CaCO₃
Powder without calibration	0.73	3.08	2.94	1.68	91.57
Powder with calibration	0.15	0.18	0.56	0.56	98.55
Pearl without calibration	0.72	0.14	0.17	0.21	98.77
Pearl with calibration	0.08	0.30	0.57	0.56	98.50
XRF handed analyzis	0.10	0.19	0.67	2.12	96.92
ICP-OES acid	0.09	0.22	0.59	0.87	98.23
ICP-OES fusion	0.09	0.25	0.68	0.81	98.17
ICP-OES microwave decomposition	0.12	LOD	0.02	1.37	98.49

Table 2. The results af analysis of Quarry stone.

Quarry stone	Fe₂O₃	Al₂O₃	SiO₂	MgCO₃	CaCO₃
Powder without calibration	0.95	5.38	23.9	0.45	69.33
Powder with calibration	0.54	0.70	5.69	0.45	92.62
Pearl without calibration	2.00	0.25	2.10	0.21	95.43
Pearl with calibration	0.38	1.08	7.95	0.98	89.61
XRF handed analyzis	0.42	1.21	7.61	1.25	89.51
ICP-OES acid	0.27	0.58	1.78	1.20	96.17
ICP-OES fusion	0.38	1.09	8.31	1.18	89.04
ICP-OES microwave decomposition	0.28	LOD	0.02	1.53	98.10

4.2. XRD analysis results

Another option is XRD (X-ray diffraction) analysis. The evaluation was performed by semi-quantitative analysis. This analysis was made for a pure limestone sample. Since this sample is quite clean, it is possible to determine the sensitivity of this method for limestone analysis. From this analysis the data in Figure 1 and Table 3 were obtained.

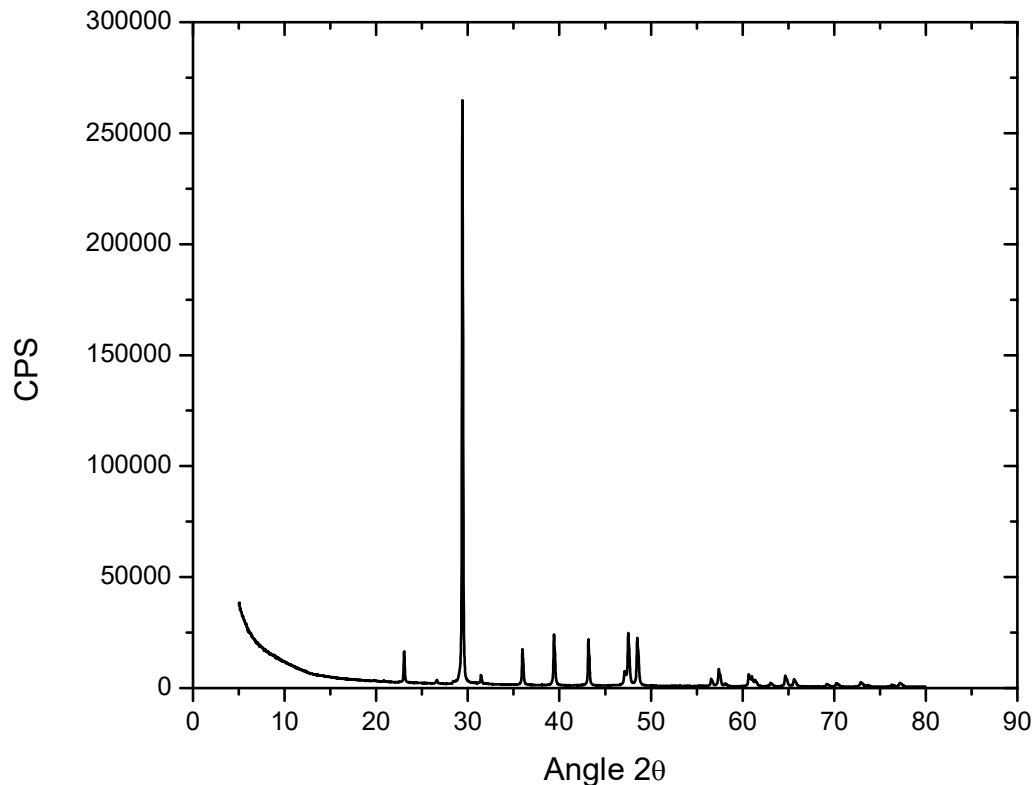


Figure 1. XRD spectrum of pure limestone.

Table 3. The results of limestone analysis by XRD.

Compound	wt. %
Calcite	99.2
Quartz	0.7
Muscovite	0.1

4.3. Sulfur content measurement

The purpose of these tests was to find out the differences when using individual calibrations. Calibration was performed on various standards. First, a one-point calibration on the dolomite stone certified material SX09-11 ($\text{SO}_3 = 0.064\%$) was used because the limestone certified materials mostly do not contain sulfur data. Subsequently, the multi-element calibration was performed on steel standards CRM CZ 2004 A, CRM CZ 2005 A, CRM CZ 2007, CRM CZ 2015 A, CRM CZ 2021 A, CRM CZ 2024 A (with amount of S = 0.0091 – 0.0464) and blast furnace slag NCS HC 15803, NCS HC 13825, NCS HC 13824 with amount of S = 0.535 – 0.98%. Samples were measured five times. The results are given in wt. % of sulfur in Tables 4 and 5. In measurements based on different calibration curves, slight changes in the resulting values occur. The results of all calibrations used are almost the same, but in the calibration of the steel, repeated measurements lead to a smaller amount of scattering, which is also due to a larger number of calibration points with concentrations closer to the actual sulfur concentration in the limestone samples.

Table 4. Sulfur amount in Forest Quarry in Líšeň sample.

Calibration type	Average value	Value difference
Dolomite stone	0.041	± 0.007
Steel	0.042	± 0.004
Slag	0.044	± 0.012

Table 5. Sulfur amount in Quarry stone sample.

Calibration type	Average value	Value difference
Dolomite stone	0.062	± 0.008
Steel	0.061	± 0.004
Slag	0.065	± 0.014

5. Conclusion

The aim of this work was to analyse limestone using the available methods and to evaluate the influence of the applied method on the results of the analyses. The best results were achieved by melt-decomposition into the solution and subsequent ICP-OES analysis. With acid decomposition and microwave pressure decomposition, a higher amount of undiluted fraction containing Mg and Si mainly resulted in a distortion of the result. Samples were also measured using XRF. The best results were obtained by measuring in the form of pearls in the vacuum by means of calibration, however the measurement in the powder form by means of calibration can be also used for standard quality control. The sulfur content was measured by combustion sulfur analysis in solids. The smallest value scatter was achieved by calibration on steel. This calibration contained the largest number of calibration points at near sulfur levels as in limestone. Other calibrations are also useful for determining the sulfur content of limestone. XRD was used to determine the phase composition. This method is suitable for measuring crystalline phases in contents above 1%.

Acknowledgments

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