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PHYSICO-CHEMICAL INVESTIGATIONS OF LIMESTONES FROM DIFFERENT LOCALITIES IN THE REPUBLIC OF MACEDONIA

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A b s t r a c t: Physico-chemical investigations were carried out for limestone samples at different localities in the Republic of Macedonia: mine for nonmetals "Ogražden", Strumica (sample-granulation below: 4, 10, 20, 32, 40, 63 and 90 μm), A.D. "Mikrogranulat", Gostivar, mine "Banjani" – Skopje, mine "Toplica" near Demir Hisar and from the separation of GP Mavrovo, Skopje, located near Pletvar. Investigation of samples from the previously mentioned localities were carried out using different methods: volumetry, gravimetry, UV-VIS and infrared spectroscopy, as well as atomic absorption and X-ray fluorescence spectrometry, X-ray diffraction and flame photometry. The obtained results lead to the conclusion that all granulometric classes of the limestone samples from "Ogražden", Strumica, are of the best quality.

Key words: limestone; infrared spectra; X-ray diffractograms; UV-VIS spectrophotometry; atomic absorption spectrometry; X-ray fluorescence spectrometry

INTRODUCTION

According to its presence, limestone is the second mineral in the earth crust. Republic of Macedonia is rich with calcite form of limestone. The application of limestone in different areas of industry is very high, Remi (1963), Čopin and Džafi (1972), Fedorchenko (1977), which makes the world production of limestone on the level of hundreds millions of tons.

Different types of limestone are found in nature: organogenetic (which are the most widespread type), homogeneous and mixed. Organogenetic limestone is build from the skeletons and shells of different sea organisms. In homogeneous limestones pelitomorphous, oolitic and pseudoolitic limestones are incorporated. Calcite is a hexagonal crystal system of calcium carbonate. Natural limestone is not a chemically pure substance. Namely, most of minerals contain extraneous substances, which can change their characteristics. These extraneous substances can be magnesium carbonate, silica, glauconite, gypsum, siderite, or sulfides and oxides of iron, phosphates, clay etc.

The potential use of limestone for different industrial purposes imposes the need for its characterization. That is why limestone samples from different locations in Republic of Macedonia were investigated. The samples were taken from: mine for nonmetals "Ogražden" near Strumica (with a granulation below: 4, 10, 20, 32, 40, 63 and 90 μm), A.D. "Mikrogranulat" – Gostivar, mine "Banjani" – Skopje, mine "Toplica" near Demir Hisar and mine of GP Mavrovo – Skopje, located near Pletvar.

The chemical composition of the limestone samples was determined by different methods: volumetry, gravimetry, UV-VIS spectrophotometry, atomic absorption spectrometry, X-ray fluorescence spectrometry, flame photometry. Infrared spectroscopy and X-ray diffraction were used for obtaining some structural information for the samples. Different physical parameters were also determined.

EXPERIMENTAL

Volumetric determinations

The content of calcium carbonate in the investigated limestone samples was determined by a classical volumetric method, GOST 7619.2-81 (1981).

Spectrophotometric determinations

The quantitative analysis of silica in the limestone samples was performed by spectrophotometric method, GOST 7619.4-81 (1981), using Hewlett Packard UV-VIS Diode Array spectrophotometer, Model 8452A.

Determination of some elements by X-ray fluorescence spectrometry

Simultaneous X-ray fluorescence spectrometer ARL 7000 S was used for the determination of elements in the investigated limestone samples. For the construction of calibration curves for determination of Ca, Mg, Si, Fe, Mn, Al and P, referent mineral and ore standard samples were used.

Limestone samples were milled and fused with $Li_2B_4O_7$ in ratio of 1:50 (0.2000 g samples and 10 g fusing material) at 1100 °C for 10 min in a platinum crucible. After fusing, the melted mass was casted in platinum moulds and heated before at 1000 °C. The obtained discs were then analyzed for 30 s. Calibration coefficients for Ca, Mg, Si, Fe, Mn, Al and P were calculated from the obtained linear equations for each element:

$$w_i = A \cdot I + B$$

where w_i is the content of the element given in % and I is the X-ray intensity of the analyzed element in kiloimpulses/s.

Determination of Zn, Fe, Cr, Cu, Pb and Mn by atomic absorption spectrometry

Determination of Zn, Fe, Cr, Cu, Pb and Mn was performed by atomic absorption spectrometry using a Perkin-Elmer atomic absorption spectrometer, Model 303. Hollow cathode lamps of the investigated elements were used. Acetylene-air gas mixture of was used for flame.

Determination of Na and K by flame photometry

Determination of Na and K was performed by flame photometer Flammenphotometer M6a, D.R.B. Lange, Berlin.

Infrared spectroscopy

The infrared spectra were recorded using the infrared interferometer Perkin Elmer System 2000 FT-IR (resolution 4 cm^{-1}, OPD rate 1 cm/s, 16 background and 32 sample scans) from KBr pellets. The software package GRAMS 2000 was used for acquisition of spectra, and GRAMS/32 was used for analysis of spectra.

X-ray diffraction

The X-ray powder diffraction patterns were obtained on a Jeol-diffractometer, model JDX-7E with a goniometer model DX-GO-F, using Cu-Kα-radiation with a Ni-filter.

Determination of granulometric content

Granulometric content of some of the investigated samples (Ogražden) was performed by laser granulometer Cilas model Granulometer 715 F036. Granulometric analysis was performed because of the influence of the particle size on the application of the grinned limestone.

RESULTS AND DISCUSSION

Determination of chemical composition

The most important parameter is the purity of the limestone, e.g. the content of $CaCO_3$. The content of $CaCO_3$ was determined by volumetric method GOST 7619.2-81 (1981) and the content of total CaO and MgO by X-ray fluorescence spectrometry. In Table 1 the content of $CaCO_3$, MgO and CaO was presented. As it can be seen, the highest content of $CaCO_3$ was found in the samples from Ogražden mine (over 98 %), whereas the other limestone samples were poorer in $CaCO_3$.

The results from the determination of the content of MgO show that the samples from Ogražden mine have the lowest presence of dolomite (below 1 %) compared to the other samples with higher content of dolomite, which is here considered as an impurity.

The high quality of the samples from Ogražden mine owing to their purity was also confirmed by the analysis of trace elements. The content of various trace elements is very important when making a decision about the potential use of limestone in different processes in the industry. Namely, the results given in Table 2 show that the content of Zn, Cu, Mn, Cr, Pb and Fe are the lowest in the Ogražden samples, whereas the content of Na and K are low in all investigated samples.

Table 1

Content of $CaCO_3$, CaO, MgO and loss of ignition (LI) of limestone samples from different localities in Republic of Macedonia (given in mass fraction / %)

Locality/Sample	$CaCO_3$	CaO	MgO	LI
Ogražden, < 4 μm	98.34	55.75	0.60	43.44
Ogražden, < 10 μm	97.30	56.64	0.96	43.24
Ogražden, < 20 μm	97.41	55.75	1.28	43.34
Ogražden, < 32 μm	98.25	55.75	0.25	42.98
Ogražden, < 40 μm	98.33	56.20	0.96	43.46
Ogražden, < 63 μm	98.43	55.75	0.25	43.15
Ogražden, < 90 μm	96.07	55.30	1.28	42.57
Banjani	95.43	53.52	1.92	42.37
Mavrovo (Pletvar)	96.58	54.41	1.60	42.72
Gostivar, < 20 μm	94.63	53.90	2.57	44.01
Gostivar, < 40 μm	93.83	53.96	3.53	44.09
Gostivar, < 63 μm	93.70	53.96	2.89	44.10
Gostivar, < 90 μm	96.54	53.98	1.28	44.00
Demir Hisar	96.15	54.86	2.24	44.15

Table 2

Content of Zn, Cu, Mn, Cr, Pb, Fe, Na and K in the investigated limestone samples obtained by AAS (given in mass fraction / %)

Locality/Sample	Zn	Cu	Mn	Cr	Pb	Fe	Na	K
Ogražden, < 4 μm	0.0016	0.0026	0.0044	0.0044	0.0110	< 0.001	0.21	0.0033
Ogražden, < 10 μm	0.0064	0.0014	0.0022	0.0044	0.0094	< 0.001	0.23	0.0038
Ogražden, < 20 μm	0.0118	0.0025	0.0043	0.0042	0.0076	< 0.001	0.23	0.0035
Ogražden, < 32 μm	0.0108	0.0022	0.0043	0.0038	0.0110	< 0.001	0.21	0.0082
Ogražden, < 40 μm	0.0102	0.0019	0.0022	0.0028	0.0110	< 0.001	0.23	0.0031
Ogražden, < 63 μm	0.0025	0.0011	0.0040	0.0027	0.0058	< 0.001	0.14	0.0022
Ogražden, < 90 μm	0.0096	0.0026	0.0030	0.0035	0.0101	< 0.001	0.22	0.0032
Banjani	0.0197	0.0030	0.0250	0.0052	0.0104	0.245	0.18	0.0085
Mavrovo (Pletvar)	0.0150	0.0024	0.0021	0.0023	0.0090	–	0.15	0.0038
Gostivar, < 20 μm	0.0107	0.0028	0.0043	0.0063	0.0030	–	0.26	0.0040
Gostivar, < 40 μm	0.0096	0.0018	0.0021	0.0038	0.0088	–	0.22	0.0019
Gostivar, < 63 μm	0.0060	0.0016	0.0044	0.0050	0.0094	–	0.26	0.0070
Gostivar, < 90 μm	0.0030	0.0017	0.0084	0.0042	0.0090	-	0.25	0.0036
Demir Hisar	0.0016	0.0027	0.0086	0.0044	0.0116	-	0.17	0.0050

Table 3

Content of SiO_2 and insoluble part in the investigated limestone samples (given in mass fraction / %)

Locality/Sample	Insoluble part in HCl	SiO_2
Ogražden, < 4 µm	0.14	0.037
Ogražden, < 10 µm	0.16	0.044
Ogražden, < 20 µm	0.16	0.038
Ogražden, < 32 µm	0.11	0.120
Ogražden, < 40 µm	0.02	0.000
Ogražden, < 63 µm	0.02	0.027
Ogražden, < 90 µm	0.18	0.190
Banjani	1.75	0.600
Mavrovo (Pletvar)	0.29	0.290
Gostivar, < 20 µm	0.09	0.070
Gostivar, < 40 µm	0.05	0.130
Gostivar, (< 63 µm)	0.12	0.130
Gostivar, < 90 µm	0.10	0.110
Demir Hisar	0.05	0.160

Another parameter important for the use of limestone is the content of SiO_2 and materials insoluble in HCl (25 %). The results of this analysis presented in Table 3 show that all investigated samples have very low content of SiO_2 and insoluble materials (except the sample from the Banjani mine).

Investigation of some physical properties of limestone samples

The values of some physical properties of the investigated limestones (density, volumetric mass and moisture content) are given in Table 4. The content of moisture in all samples is low. The values for density (between 2.68 g/ml and 3.0478 g/ml) and for volumetric mass (from 1.5 to 3.0 $g \cdot cm^{-3}$) are in the range which is characteristic for limestone Федорченко (1977).

The granulation is also considered as an important parameter for the conclusion of the use of limestone in the industry. This is especially important for samples obtained by special treatment of grinding and separation by granulation. This kind of treatment is utilized in the mines of Ogražden and "Mikrogranulat". The granulometric content of the samples taken from those two mines was assayed using a laser microanayzer. The results of granulometric content for samples from Ogražden mine are presented in Table 5.

Table 4

Physical characteristics (density, volumetric mass and moisture content) of the investigated limestone samples

Sample	ρ $g \cdot cm^{-3}$	Volumetric mass $g \cdot cm^{-3}$ (with shaking)	Volumetric mass $g \cdot cm^{-3}$ (without shaking)	w (H_2O) %
Ogražden, < 4 µm	2.9372	1.8503	0.9527	0.05
Ogražden, < 10 µm	2.7146	1.7870	1.0006	0.09
Ogražden, < 20 µm	2.7132	1.8292	0.9167	0.02
Ogražden, < 32 µm	2.6889	2.0902	1.1535	0.05
Ogražden, < 40 µm	2.642	2.1907	1.1823	0.03
Ogražden, < 63 µm	2.7618	2.1607	1.1693	0.06
Ogražden, < 90 µm	2.6858	2.1534	1.2222	0.07
Banjani	2.6999	2.4918	1.5135	0.12
Mavrovo (Pletvar)	2.7545	2.2348	1.2255	0.01
Gostivar, < 20 µm	2.8176	1.5950	0.6918	0.07
Gostivar, < 40 µm	2.7787	1.6696	0.8900	0.06
Gostivar, < 63 µm	2.7418	1.7331	0.8110	0.07
Gostivar, < 90 µm	2.6709	2.0300	0.9836	0.04
Demir Hisar	2.6924	2.0750	1.1347	0.20

Table 5

Granulometric content of limestone from "Ogražden", Strumica (sample-granulation below 4, 10, 20, 32, 40, 63 and 90 μm)

Granulation μm	W %	Granulation μm	W %
Below 4 μm			
–1	14.1	> 1	85.8
– 1.5 + 1	3.2	> 1.5	82.5
– 2 + 1.5	8.0	> 2	74.5
– 3 + 2	8.7	> 3	65.7
– 4 + 3	8.2	> 4	57.5
– 6 + 4	10.5	> 6	47.0
– 8 + 6	13.9	> 8	33.0
– 12 + 8	18.6	> 12	14.3
– 16 + 12	12.1	> 16	2.2
–24 + 16	2.2	> 24	0.0
Below 10 μm			
–1	13.9	> 1	86.0
– 1.5 + 1	3.3	> 1.5	82.7
– 2 + 1.5	8.1	> 2	74.5
– 3 + 2	8.9	> 3	65.6
– 4 + 3	8.2	> 4	57.3
– 6 + 4	10.9	> 6	46.3
– 8 + 6	14.7	> 8	31.5
– 12 + 8	20.0	> 12	11.5
– 16 + 12	11.5	> 16	0.0
Below 20 μm			
–1	11.9	> 1	88.0
– 1.5 + 1	2.5	> 1.5	85.4
– 2 + 1.5	6.3	> 2	79.1
– 3 + 2	7.7	> 3	71.4
– 4 + 3	7.8	> 4	63.5
– 6 + 4	11.0	> 6	52.4
– 8 + 6	14.0	> 8	38.4
– 12 + 8	20.9	> 12	17.4
– 16 + 12	13.9	> 16	3.4
–24 + 16	3.4	> 24	0.0
Below 32 μm			
–1	6.2	> 1	93.7
– 1.5 + 1	0.9	> 1.5	92.7
– 2 + 1.5	1.1	> 2	91.5
– 3 + 2	1.7	> 3	89.7
– 4 + 3	1.3	> 4	88.4
– 6 + 4	0.0	> 6	88.4
– 8 + 6	2.4	> 8	86.0
– 12 + 8	20.7	> 12	65.2
– 16 + 12	25.8	> 16	39.3
– 24 + 16	33.1	> 24	6.1
– 32 + 24	6.1	> 32	0.0
Below 40 μm			
–1	5.8	> 1	94.1
– 1.5 + 1	0.6	> 1.5	93.4
– 2 + 1.5	1.0	> 2	92.3
– 3 + 2	1.4	> 3	90.9
– 4 + 3	2.2	> 4	88.7
– 6 + 4	0.0	> 6	88.7
– 8 + 6	0.3	> 8	88.3
– 12 + 8	12.5	> 12	75.8
– 16 + 12	24.8	> 16	50.9
– 24 + 16	36.5	> 24	14.4
– 32 + 24	14.4	> 32	0.0
Below 63 μm			
–1	6.4	> 1	93.5
– 1.5 + 1	0.8	> 1.5	92.6
– 2 + 1.5	1.1	> 2	91.5
– 3 + 2	1.3	> 3	90.1
– 4 + 3	1.3	> 4	88.7
– 6 + 4	0.2	> 6	88.5
– 8 + 6	4.7	> 8	83.7
– 12 + 8	18.5	> 12	65.2
– 16 + 12	22.3	> 16	42.8
– 24 + 16	29.6	> 24	13.1
– 32 + 24	10.9	> 32	2.2
– 48 + 32	2.2	> 48	0.0
Below 90 μm			
–1	9.8	> 1	90.1
– 1.5 + 1	2.2	> 1.5	87.8
– 2 + 1.5	4.2	> 2	83.5
– 3 + 2	5.9	> 3	77.6
– 4 + 3	5.2	> 4	72.3
– 6 + 4	8.4	> 6	63.9
– 8 + 6	7.8	> 8	56.0
– 12 + 8	13.4	> 12	42.5
– 16 + 12	10.5	> 16	31.9
– 24 + 16	15.3	> 24	16.6
– 32 + 24	7.0	> 32	9.5
– 48 + 32	8.4	> 48	1.1
– 64 + 48	1.1	> 64	0.0

As it can be seen from the data given in Table 5, the granulometric content is not always the same as declared by the manufacturer. Namely, the average granulation of the class declared as < 4 μm was found to be 5.4 μm, containing 57.7 % particles bigger than 4 μm. Similar situation was found with a class < 10 μm. On the other hand (below 12, 20, 32, 40, 63 and 90 μm) the granulometric content was in the range of the declared values.

Investigation with infrared spectroscopy and X-ray diffraction

The methods of infrared spectroscopy and X-ray diffraction were used for identification of carbonates and for establishing their purity. The spectra and diffractograms obtained for the samples were compared with those recorded for $CaCO_3$, *p.a.* quality from Merck (min. 99% $CaCO_3$). The samples spectra and diffractograms are very similar to the ones of the standard, which implies that these limestones have a very high calcium carbonate content, as previously shown by chemical analyses (Table 1). The infrared spectra and diffractograms of the standard and samples from Ogražden mine are shown in Fig. 1 and Fig. 2 respectively.

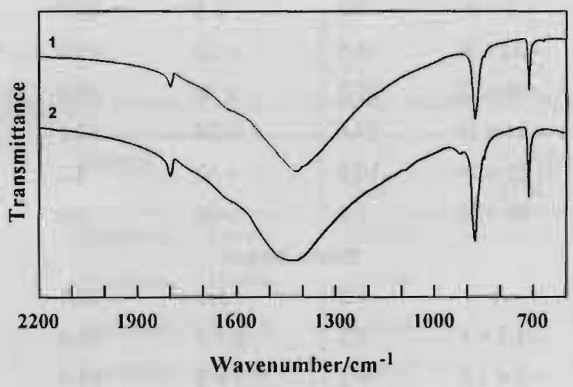

Fig. 1. The FTIR spectra of $CaCO_3$ from Merck (1) and limestone from "Ogražden" – Strumica (2)

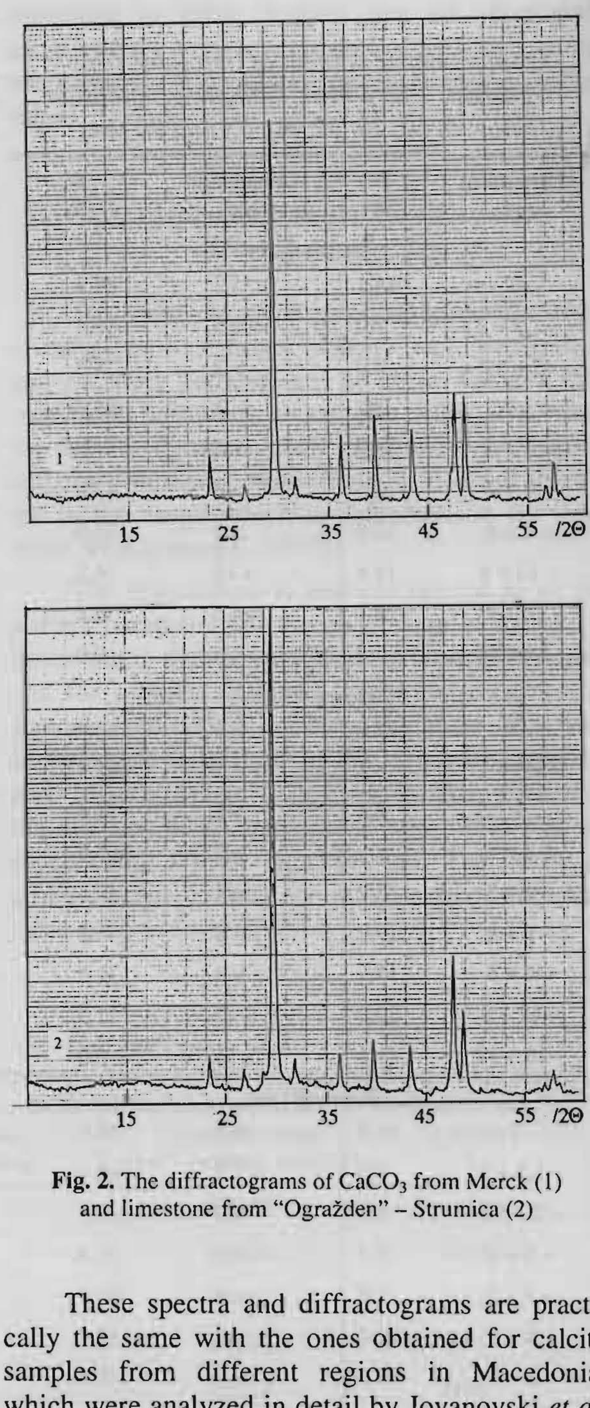

Fig. 2. The diffractograms of $CaCO_3$ from Merck (1) and limestone from "Ogražden" – Strumica (2)

These spectra and diffractograms are practically the same with the ones obtained for calcite samples from different regions in Macedonia, which were analyzed in detail by Jovanovski *et al.* (1999a; 1999b).

CONCLUSION

Some physico-chemical parameters of the limestone samples taken from different localities of the Republic of Macedonia were investigated: mine for nonmetals "Ogražden", Strumica (sample-granulation below: 4, 10, 20, 32, 40, 63 and 90 μm), A.D. "Mikrogranulat" – Gostivar, mine "Banjani" – Skopje, "mine "Toplica" near Demir Hisar, and from the separation of GP Mavrovo, Skopje, located near Pletvar. Different methods and techniques were applied for the investigation of chemical composition, physical properties, granulometric and structural characteristic.

The obtained results show that the limestone samples from the mine of Ogražden near Strumica, containing about 99 % of $CaCO_3$, are of highest quality, especially for the industrial use.

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REFERENCES

Федорченко, И. М., 1977: *Энциклопедия неорганических материалов.* Том 1. Главная редакция Украинской Советской энциклопедии, Киев, с. 469–470.

GOST, 1981: 7619.2-81.

GOST, 1981: 7619.4-81.

GRAMS ANALYST for PE 2000 FTIR, Vers. 3.01 B, Galactic Industries Corporation, 1991–1993.

GRAMS32 for Microsoft Windows, Vers. 4.10, Galactic Industries Corporation, 1991-1996.

Jovanovski, G., Stefov, V., Jovanovski, B., Šoptrajanov, B., 1999: *Minerals from Macedonia: I. Analytical application of powder x-ray diffraction patterns of calcite and aragonite,* Book of Papers of 16th Congress of Chemists and Technologists of Macedonia (with international participation), Vol. **1**, 43–46.

Jovanovski, G., Stefov, V., Jovanovski, B., Šoptrajanov, B., Boev, B., 1999: *Minerals from Macedonia: III. Determination of calcite and aragonite in mineral mixtures using FT IR spectroscopy,* Geologica Macedonica, **13**, 69–74.

Реми, Г., 1963: *Курс неорганической химии,* Издательство иностранной литературы, Москва, с. 310–312.

Чопин, Г. Р., Джафи, Б., 1972: *Хемија. Наука о материји, енергији и променама,* Вук Караџић, Београд, с. 477.

Резиме

ФИЗИЧКО-ХЕМИСКИ ИСПИТУВАЊА НА ВАРОВНИЦИ ОД РАЗЛИЧНИ ЛОКАЛИТЕТИ ВО РЕПУБЛИКА МАКЕДОНИЈА

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Клучни зборови: варовник; инфрацрвени спектри; рендгенски дифрактограми; UV-VIS спектрофотометрија; атомска апсорпциона спектрометрија; рендгенска флуоресцентна спектрометрија

Извршени се физичко-хемиски испитувања на примероци варовник од различни локалитети во Република Македонија: рудникот за неметали „Ограждено" – Струмица (примероци со гранулација под 4, 10, 20, 32, 40, 63 и 90 μm), А.Д. „Микрогранулат" – Гостивар, рудникот „Бањани" – Скопје, рудникот „Топлица" близу Демир Хисар, и од сепарацијата на ГП Маврово, Скопје, лоцирана близу Плетвар. Испитувањата се извршени со примена на различни методи: волуметрија, гравиметрија, UV-VIS и инфрацрвена спектрометрија, како и со атомска апсорпциона спектрометрија, рендгенска флуоресцентна спектрометрија, рендгенска дифракција и пламена фотометрија. Добиените резултати укажуваат дека со најдобар квалитет се сите класи на варовник од „Огражден" – Струмица.