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BARIUM IN AIRCONDITIONER FILTERS IN THE CITY OF SKOPJE (REPUBLIC OF NORTH MACEDONIA)

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A b s t r a c t: The presence of metals in the ambient air (ambient dust) in the urban environment is a frequent subject for research, and so far it has been worked out in many urban centers in the world. The systematic research for the contents of the ambient dust in the city of Skopje is not made before, so we cannot present such information. However, it should be emphasized that such information which refer on the contents of the urban dust exist in many towns, but that information is very changeable depending on the seasons in which the data is measured. As an example, on the basis of a large number of researches the metals which are present in the urban dust are divided in three groups: – Urban elements (Ba, Cd, Co, Cu, Mg, Pb, Sb, Ti, Zn). – Natural elements (Al, Ga, La, Mn, Na, Sr, Th, Y) – Elements with mixed background (Ca, Cs, Fe, Mo, Ni, Rb, Sr, U). There is accepted opinion that the background of the urban elements is primarily connected with the development of the traffic, the processes of corrosion of the materials build in the objects in the towns (buildings, houses, roads, etc.) as well as the emission of dust which appears in the soils, and fields with no grass. In order to be able to make any correlation of the obtained data which refer to a small number of measured samples (only of two locations) many deeper researchers are needed. From the other side, the influence of the contents of dust (as well as the ambient air) upon the health of the people is a topic which requests more serious and longer measures.

Key words: barium, urban elements, natural elemnets

БАРИУМ ВО ФИЛТРИТЕ НА КЛИМАТИЗЕРИТЕ ВО ГРАДОТ СКОПЈЕ (СЕВЕРНА МАКЕДОНИЈА)

Р е з и м е: Концентрациите на бариум во филтрите од климатизерите на одредени објекти во градот Скопје се зголемени како последица на сообраќајот во градот Скопје (во надворешните филтри) и како последица на вградувањето на пластични материјали во подовите на објектите (линолеум, внатрешни филтри).

Клучни зборови: бариум, природни елементи

INTRODUCTION

Soluble barium components are highly toxic when ingested into the human body, while insoluble components, such as the often present barium sulphate, are generally non-toxic. The soluble barium components that are inhaled cause benign pneumoconiosis or called baritosis). Intake of soluble barium components through food causes muscle stimulation, including the heart, irritation of the digestive system, and irritation of the central nervous system. (Browning, 1961).

The main source of barium components emitted into the atmosphere are industrial processes, including mining, refining, and production of barium and barium chemical compounds that are used as additives in fuels to reduce smoke emission in diesel engines. There is certain information concerning the emission of barium in diesel engines that ranges up to a maximum of 48 $\mu g/m^3$. (Fiorello, 1968).

There is very little information regarding the aspects of air pollution with barium and barium components. Most of the information relates to the concentration of barium in the atmosphere as a result of the impact of diesel engines (Golothan, 1967).

Barium soluble salts are highly toxic when ingested in the digestive system in humans. Barium chloride and barium carbonate are two soluble salts for which there are published results concerning toxicity (Browning, 1961, Patty, 1962), but it should be noted that the consequences of their toxicity are not fatal. One case has been reported (Browning, 1961) in which 7 grams of barium chloride were taken orally, with the occurrence of abdominal pain and a complete collapse but without fatal consequences.

Insoluble barium sulphate is generally not toxic when ingested in the human digestive system. For example, barium sulphate is the most common insoluble component used in X-ray imaging of the human digestive system.

So far, no data have been published on the impact of barium compounds on domestic animals.

Miller (1967) published the results of the impact of the gases from diesel engines on white mice, whereby no visible effects were observed during liver analysis of the experimental mice.

No results have been reported regarding the impact of the concentration of barium on plants. In 1961 Browning mentioned that barium was toxic to plants, but he did not provide information on the chemical form and concentration, as well as on the type of plants.

Data relating to the environmental barium concentration standards can be found in the documents of the 29th Annual Conference of the US State Hygiene Office (1967), which mention the upper limit of exposure to soluble components of barium during 8 hours, which is 500 μg/m^3.

Mode of occurrence and usage

Barium is a soft metal with a silver color that in nature appears in association with other elements. It occurs most often in the form of veins in the lead and zinc deposits. There are two known major minerals of barium: baryte (barium sulphate $BaSO_4$) and witherite (barium carbonate $BaCO_3$). Baryte is mainly the most commercial mineral of barium. Smaller amounts of barium can also be found in the magmatic rocks, and as isomorphically present in feldspars and micas (Kirk-Otmer, 1964). Small amounts of barium are also present in coals (Abernathy et al, 1963) (Liu et all, 1983), (MacDonald et all, 1984) (Zierock, 1983), (Small, 1983).

Baryte (barium sulphate, $BaSO_4$) finds a great application in the chemical industry, as a pigment and as a filler it is used in the production of linoleum and other chemical products. The use of barium sulphate for medical purposes is important. Barium carbonate ($BaCO_3$) also has a significant usage (as a filler in glass industry), then barium chloride ($BaCl_2$) for medical purposes, barium nitrate ($Ba(NO_3)_2$ in the production of pyrotechnics and medical preparations, barium oxide (BaO) is used in the production of barium peroxide, barium hydroxyode and barium methoxide, and they are further used in the production of detergents.

Organometallic components of barium are used as additives in diesel fuels to reduce the presence of smoke in the exhaust fumes of diesel engines (Stern, 1968). In 1967 Miler published the results of research on the effects of barium additives on the reduction of smoke during the operation of diesel engines (Figure 1).

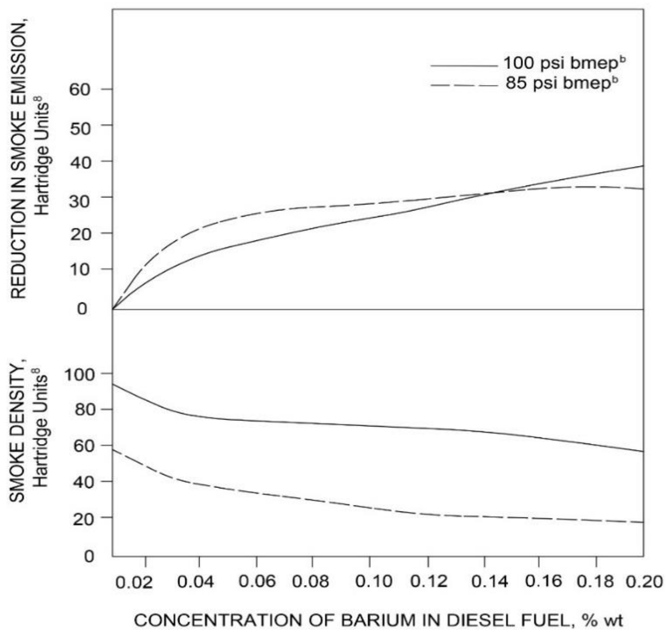


Fig. 1. Effects of barium additive on the reduction of smoke during the operation of diesel engines

METHODOLOGY

The following research methods were applied for the research activities:

- collecting samples of separate materials in the objects and determination of the presence of Ba and other elements with application of appropriate analytical techniques and methods. For that purpose, samples are collected from two locations in Skopje:
  - Skopje-Centar (outer filters, inside filters, walls, used poly-color, used agglomeration for leveling of floors, abrasive cleaning powder (Ajax) and liquid washing splendor (Glos), samples of the air and samples of the floor)
  - Skopje-Biser (outer filters, inside filters, walls, used poly-color, samples of the air)
- Determination of the presence of Ba and other metals with application of the methods ICP-MS
- Determination of the presence of Ba-phases in the samples from the walls and floors with application of Scaning Electronic Micoroscopy-SEM-EDS,

Methods of preparation of the specimens

Dry samples are extracted with a compound of acids, HCl/HNO_3, 16 hours at room temperature and reflux ion of 2 hours according to ISO 11464:1996 (E). The extract is filtered until the final volume and rarefied with nitrate acid. The contents of the metals in traces is determined with ICP-AES, Liberty 110, Varian, according to ISO 11885:1996 (E)

Reactants

All the used reactants are with cleanliness p.a. The cleanliness of the reactants is verified with an experiment.

Water: The quality of the redistilled water is according to ISO 3696, Grade 2.

HCl, 37%, ρ = 1.19 g/mol

HNO_3, 65%, ρ = 1.40 g/mol

H_2O_2, >30%, ρ = 1.11 g/mol

Standard dilutions

Basic standard dilution: ICP- Multi-element standard dilution, Merck IV, 23 elements in a diluted nitrate acid with a concentration for each element separately of 1000 mg/L: Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, Zn

Table 1

Conditions of work of the Inductive Linking Plasma

Conditions for ICP- AES, Liberty 110, Varian					
Introducing a sample					
Sprayer	V-groove				
Spray chamber	Inert Sturman-Masters				
Peristaltic pump	12 rollers, 1 turn/min increment				
Conditions for the program					
Power of plasma	1,0 kW				
Speed of pump/rpm	25				
Flow of Ar for plasma	15 L/min				
Time for stabilization	30 s				
Flow of axial Ar	1,5 L/min				
Time of flushing	30 s				
Pressure of sprayer	200 kPa				
Time of stagnation	30 s				
Correction of fon	dynamic				
High of plasma	Opt. SBR				
Conditions for elements					
Element	Wave length/nm	Slitt	Time for integration/s	Filter	Line of fender
As	193.696	0.02	7	1	1
Ni	352.45	0.02	5	6	1
Sr	407.77	0.02	5	7	1
Ba	455.403	0.02	5	7	1
Mn	257.61	0.01	5	6	2
Fe	259.94	0.01	5	6	2
Cr	267.72	0.01	5	6	2
Zn	213.86	0.007	5	6	1
Cu	324.75	0.01	5	6	2
Pb	220.35	0.007	7	6	1
Co	228.62	0.007	5	6	1
Cd	226.50	0.007	5	1	3

One-element standard dilution for As, Titirisol, Merck, 1000 mg/L.

Tools

The entire tool used for synthesis of the extracts and preparation of the standards is overflow in Nitrate acid for at least +6 ours, and then it is washed with redistilled water.

Analytical conditions for the work of the instruments

Conditions for work of Scanning Electronic Microscope.

The records of the samples and the chemical analyses are made with Scanning Electronic Microscope from the brand of JEOL JSM-6610LV which is equipped with energetic-dispersed spectrometer (EDS) from the brand *X-Max Large Area Analytical Silicon Drift*.

The recording of the samples is made with high vacuum of 20 kV whereas the source of electrons is LaB6 (Lantan-heksa-boridien) filament. The shown photographs are obtained with a help of detector for free electrons (SEI). The samples are blushed with gold and the unmarked piques of the spectrums belong to this element.

RESULTS AND DISCUSION

The obtained results of the research are shown in the Tables 2.

T a b l e 2

Results of the presence of Ba and other metals in the analyzed samples (method, ICP-AES, controlled with ICP-MS)

	1	2	3	4	5	6 (1)	6(2)	7	8	9	10	11	12	13
mg/kg	Outer filter Center	Inside filter Center	Section of wall Center	Agglomeration for allignment	Poly color Center	Cleaning abrasive Ajakx/$mg l^{-1}$	Cleaning abrasive Glos/$mg l^{-1}$	Sample from the floor	Inside filter Biser	Outer filter Biser	Section of wall Biser	Poly color Biser	Filtres (1+2+3+4)	Filtres (5+6+7+8)
Ba	292.6	282.7	0.54	27.7	7.56	<0.73	4.5	129.5	183.9	199.5	0.43	7.68	1.2	0.4
Sr	76.6	112.8	413.8	46.9	38.0	1.0	65.6	38.2	75.0	71.6	406.2	40.5	1.6	0.9
Fe	16562.7	12477.5	46.1	4237.6	298.7	<100	<100	162.7	12430.9	13980.8	63.5	267.2	58.3	31.1
Mn	461.4	355.2	<1	189.1	10.6	<1.33	<1.33	4.1	356.3	424.2	<1	9.9	<1	<1
Zn	1890.9	4277.7	6.4	38.2	9.4	<8	<8	38.6	4722.6	1154.2	4.3	8.4	6.4	3.9
Ni	66.7	60.3	4.9	16.6	6.9	32.0	28.0	<1.3	61.5	69.4	3.5	6.3	4.2	1.2
Cr	65.1	70.2	0.9	15.6	9.8	10.6	14.4	0.6	55.0	47.0	0.7	8.6	1.4	1.3
Cu	184.6	370.3	<3	0.5	<3	49.0	<7	2.6	600.4	116.6	<3	<3	32.1	26.0
Pb	243.2	360.5	<1.5	6.0	7.4	<1.5	<6	<1.5	543.0	164.4	<1.5	8.3	6.2	4.4
Co	7.4	13.1	0.4	1.8	0.6	2.5	<0.7	0.1	16.8	6.6	0.1	0.5	<0.7	<0.7
Cd	7.6	22.1	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	32.6	4.6	<0.5	<0.5	<0.5	<0.5
As	<2.5	<2.5	<2.5	<2.5	1.1	<2.5	<2.5	<2.6	<2.6	<2.6	<2.6	0.1	2.0	1.2

The results obtained are showing significant amounts of Ba, Cu and Pb in analysed filters. Also is very important to concluded that concentration of barium is too high in floor samples of linoleum. Results obtained with SEM-EDS techniques are presented in following Figures and Tables.

Sample from floor 1:

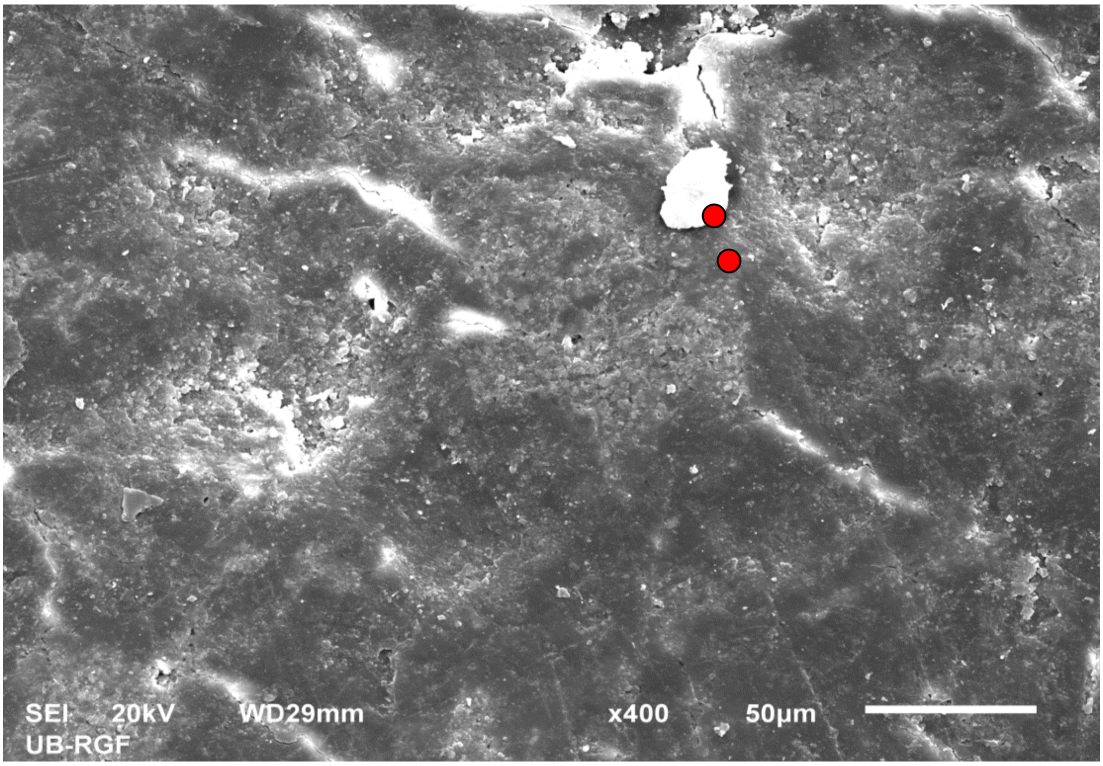


Fig. 2. Morphological view of the sample 1 (zoom 400×)

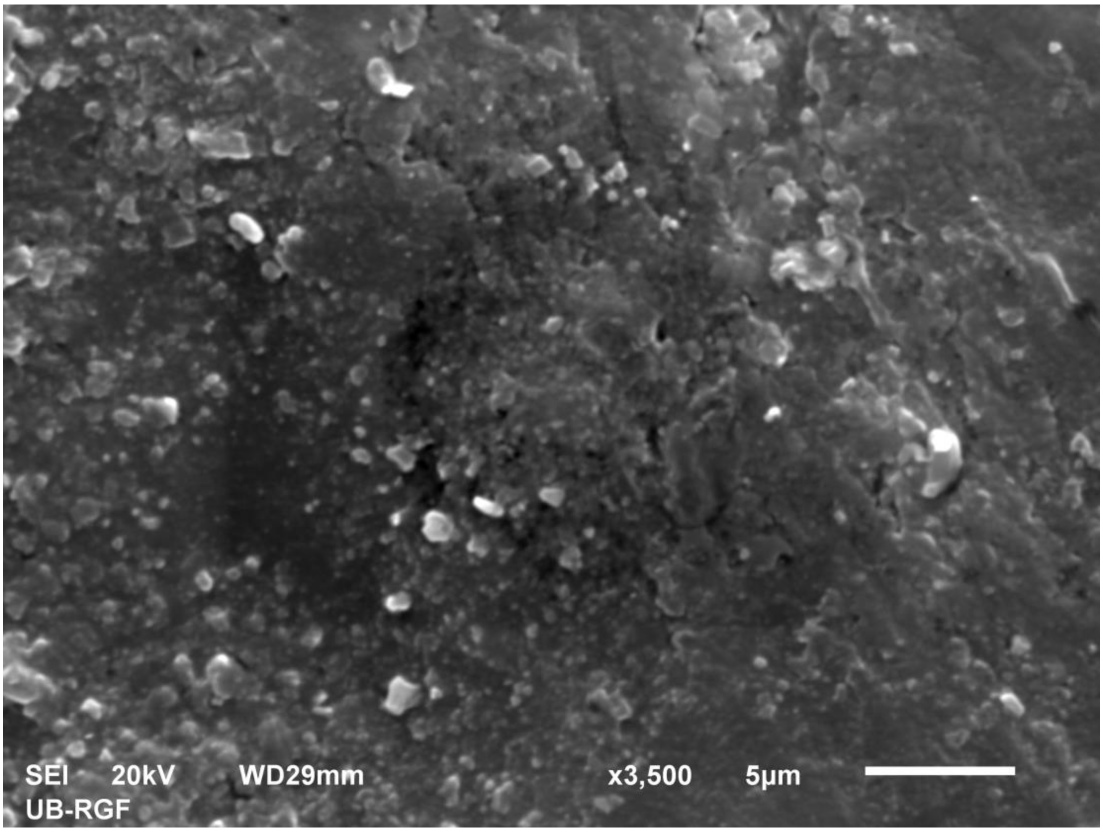
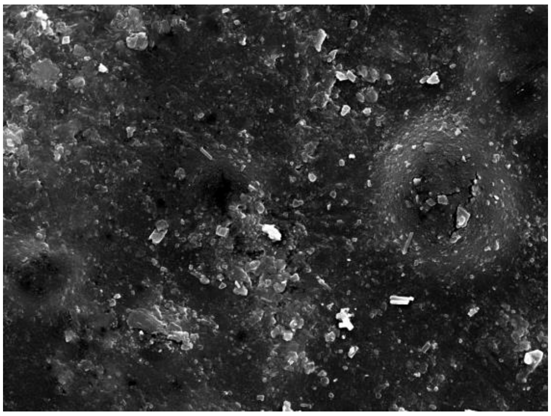
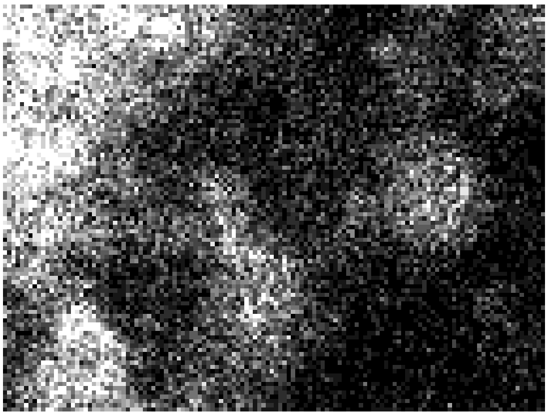


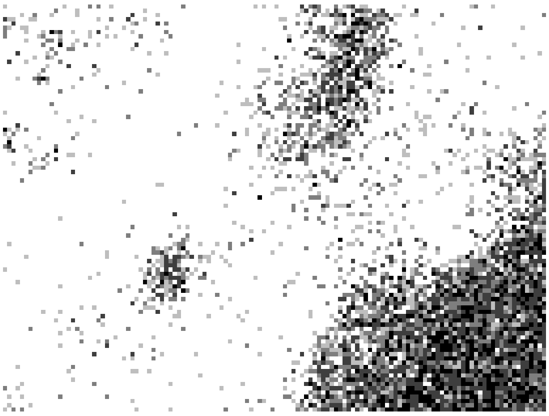
Fig. 3. Morphological view of the sample 1 (zoom 3500×)



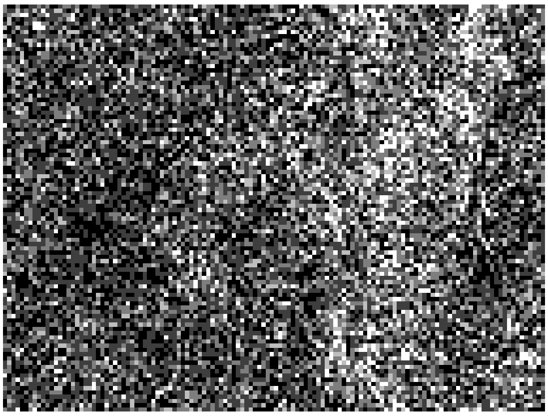
a) view of a scanned field



b) distribution of Ca



c) distribution of Cl



d) distribution of C

Fig. 4. Results of the scanning of sample 1

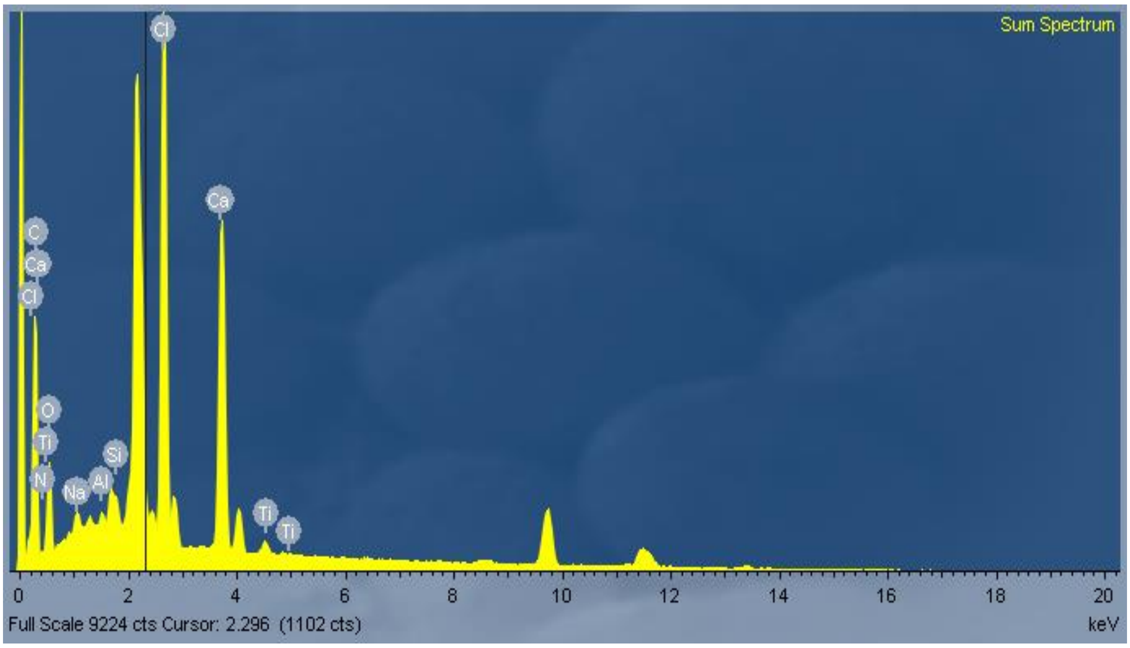


Fig. 5. Compound EDS spectrum of the analyzed field

T a b l e 3

Contents of the elements of the compound spectrum (Figure 5)

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	18.90	0.1965	57.58	0.54	71.67
N K	0.00	0.0305	0.00	0.00	0.00
O K	6.48	0.1848	20.98	0.51	19.60
Na K	0.55	0.6880	0.48	0.05	0.31
Al K	0.29	0.7969	0.22	0.03	0.12
Si K	0.47	0.8861	0.32	0.03	0.17
Cl K	13.93	0.7612	10.95	0.14	4.62
Ca K	13.42	0.8919	9.01	0.12	3.36
Ti K	0.58	0.7394	0.47	0.04	0.15
Totals			**100.00**		

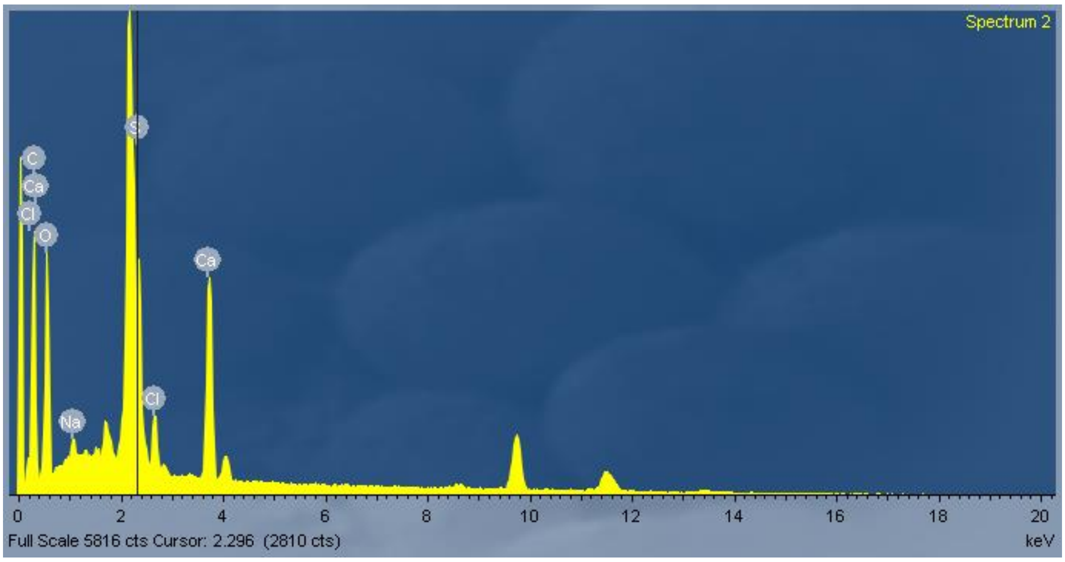


Fig. 6. EDS spectrum of the brightest point from picture

T a b l e 4

Contents of the elements of the compound spectrum (Figure 6)

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	19.24	0.2891	46.29	0.77	56.80
O K	15.34	0.2587	41.28	0.74	38.02
Na K	0.49	0.6155	0.56	0.09	0.36
S K	4.98	0.8189	4.23	0.13	1.95
Cl K	1.50	0.7160	1.46	0.06	0.61
Ca K	8.00	0.9008	6.18	0.13	2.27
Totals			**100.00**		

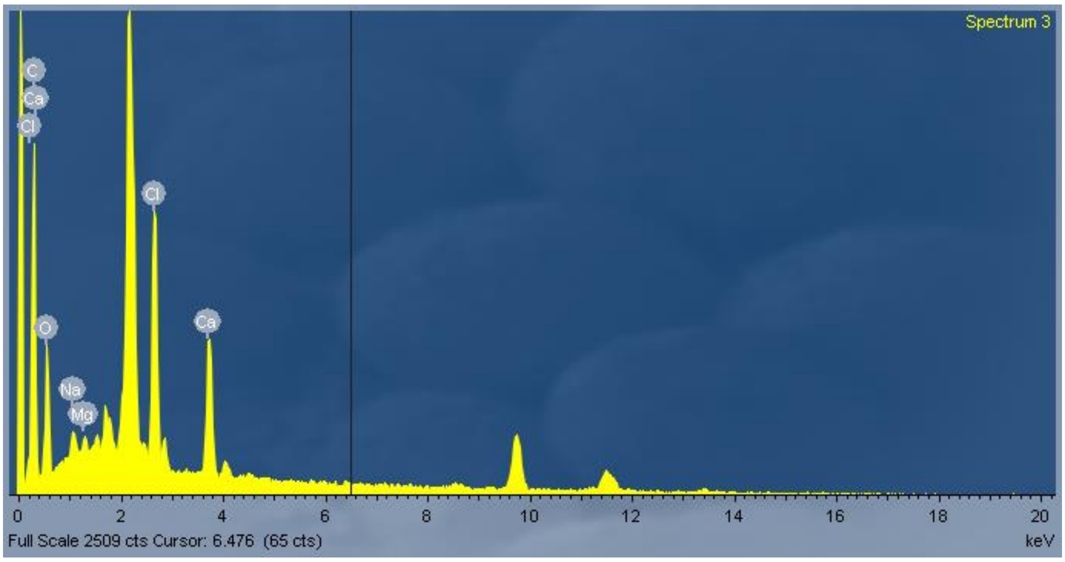


Fig. 7. EDS spectrum of the grey basis of Fig.1

Table 5

Contents of the elements of the compound spectrum (Figure 7)

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	16.05	0.2872	60.59	1.14	70.75
O K	5.62	0.2148	28.36	1.12	24.86
Na K	0.42	0.6714	0.68	0.13	0.42
Mg K	0.20	0.6604	0.34	0.09	0.19
Cl K	4.14	0.7466	6.01	0.19	2.38
Ca K	3.32	0.8950	4.02	0.15	1.41
Totals			**100.00**		

From the presented results we can conclude that the most dominant elements in the sample are carbon, oxygen, chlorine and calcium. This copy is very unstable under the electron beam because of the presence of organic compounds.

Sample from wall Biser 1:

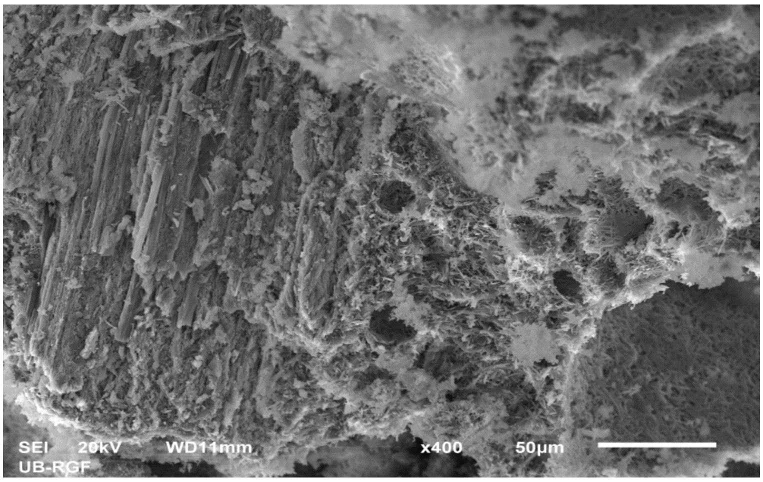


Fig. 8. Morphological view of the sample of wall 1 Biser (zoom 400×)

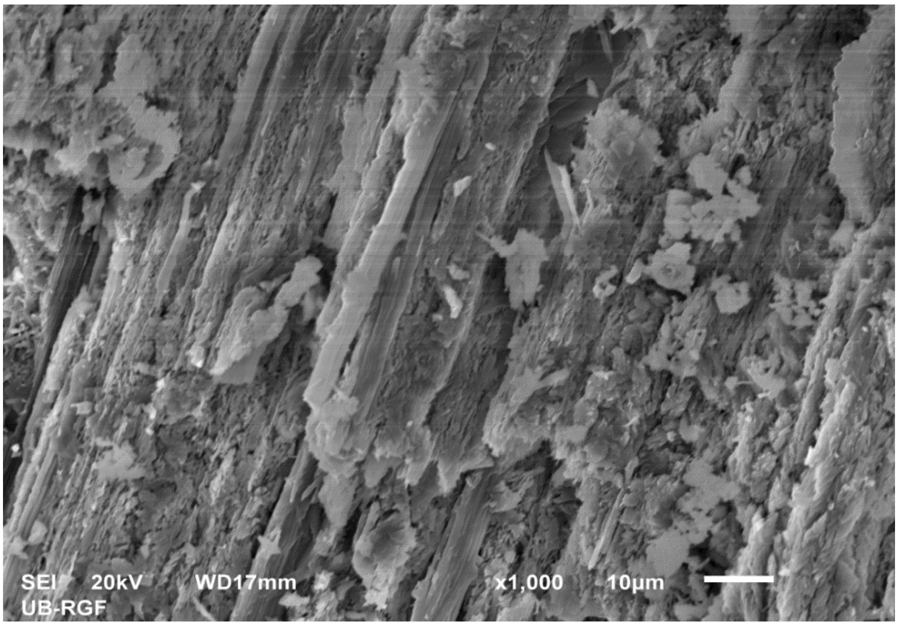


Fig. 9. Morphological view of the sample of wall 1 Biser (zoom 1000x)

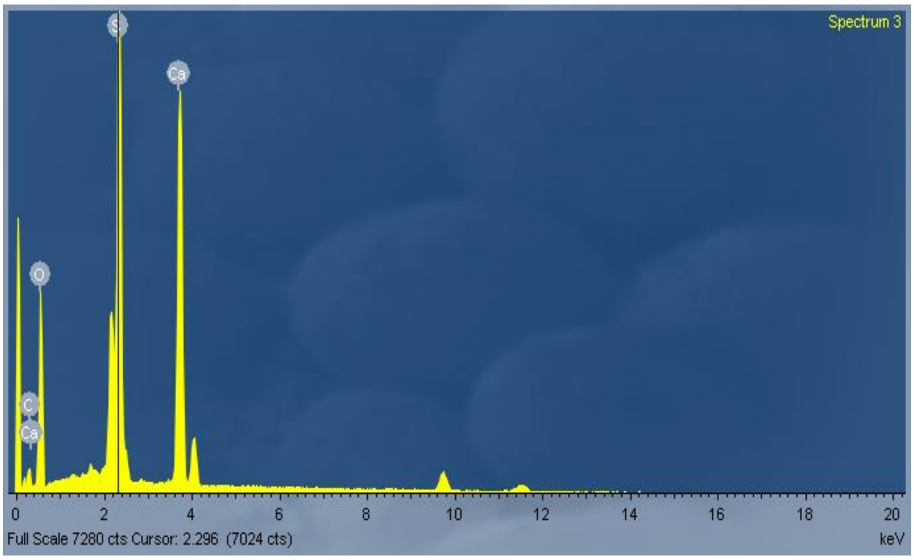


Fig. 10. EDS spectrum of the surface on Fig.8

Table 6

Contents of the elements (spectrum of Figure 10)

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	1.63	0.1461	10.02	1.14	15.95
O K	17.01	0.2807	54.57	0.85	65.21
S K	15.03	0.8294	16.33	0.31	9.74
Ca K	19.05	0.8990	19.08	0.34	9.10
Totals			100.00		

From the performed analyses it can be concluded that this sample represents the plaster that has a certain amount of calcium carbonate. Within the sample there are no visible phases containing Ba. Certain amount of Ba method ICP-AES and ICP-MS values are in ppm and as such they are isomorphic mixed in the carbonate and sulphate phases.

Sample from wall Centar 1.

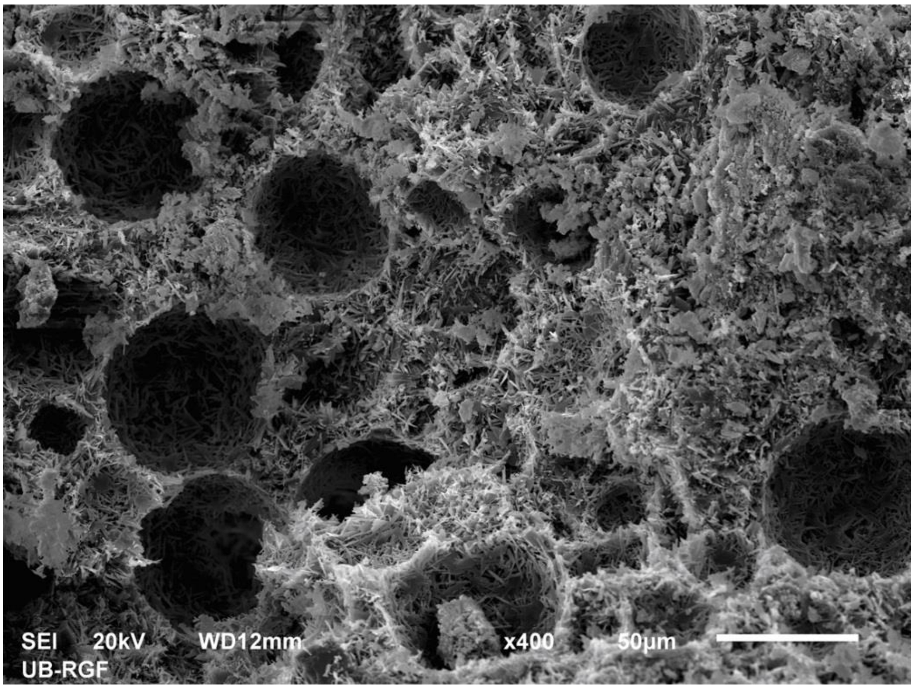


Fig. 11. Morphology of the sample 1 Centar (zoom 400×)

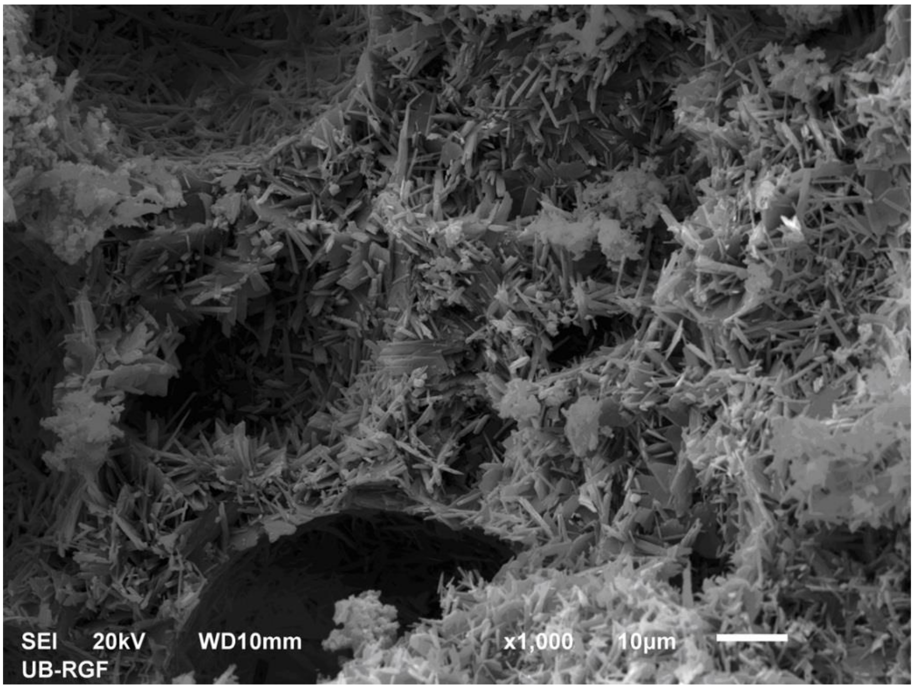


Fig.12. Morphology of the sample 1 Centar (zoom 1000×)

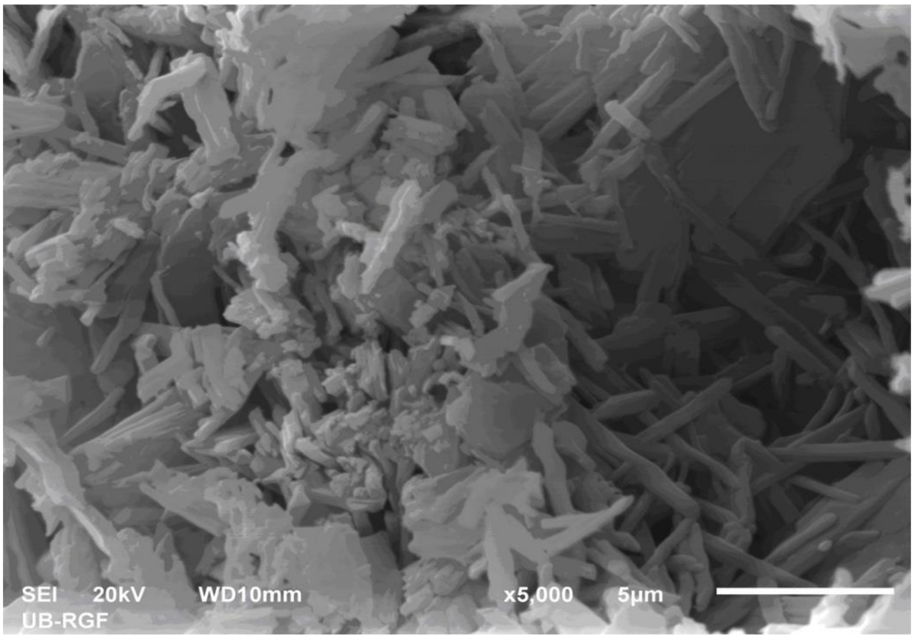


Fig. 13. Morphology of the sample 1 Centar (zoom 5000×)

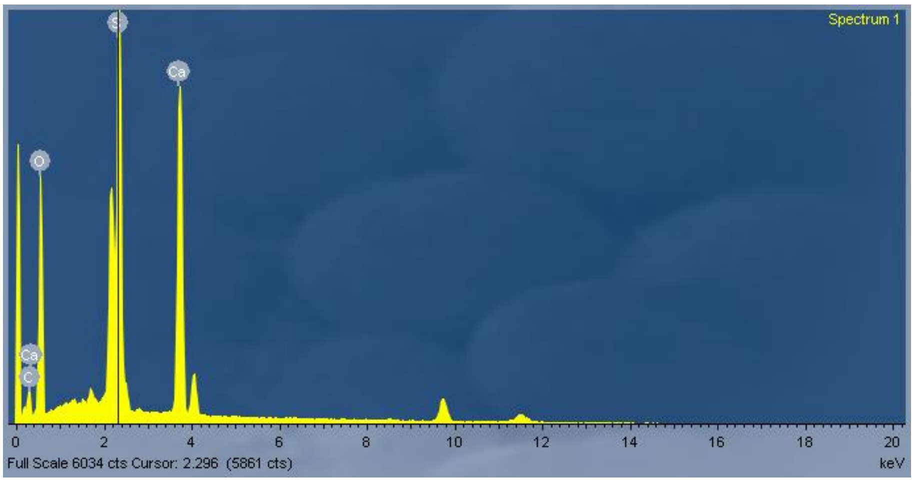


Fig. 14. Spectrum of the surface from Fig.12, sample 1 Centar

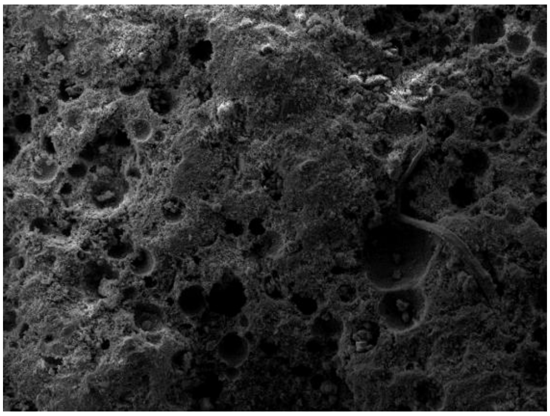
Table 7

Contents of the determined elements (spectrum of Figure 14)

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	2.24	0.1631	12.36	1.12	18.73
O K	20.21	0.3121	58.37	0.87	66.42
S K	12.47	0.8218	13.68	0.27	7.77
Ca K	15.57	0.9000	15.59	0.29	7.08
Totals			100.00		

Figure 15 shows the scanned field of sample from wall 1 Centar, whereas on the pictures 15a, 15b, 15c, 15d, the distribution of separate elements is shown.

From the conducted research it can be concluded that in the samples taken from the walls of the site center there is no presence of phases containing Ba. The deterimend concentration of Ba with the methods ICP-AES and ICP-MS techniques are in ppm values and are isomorphic mixed in calcium carbonate and calcium sulphate stages.



a) view of a scanned field

b) distribution of Ca

c) distribution of S

d) distribution of C

Fig, 15. Results of the scanning by SEM-EDS

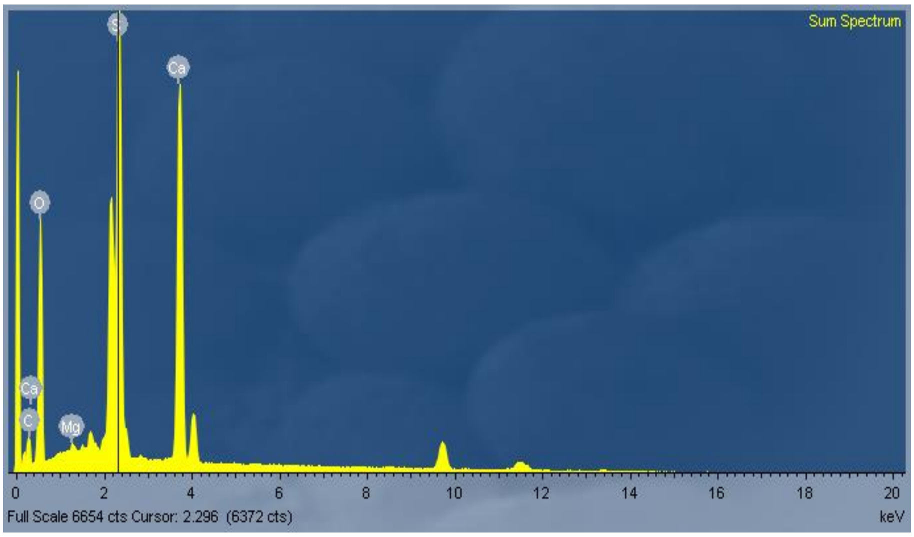


Fig. 16. Compound spectrum of the scanned field

Table 8

Contents of the determined elements (compound spectrum of Figure 16)

Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
C K	3.20	0.1605	12.53	0.81	19.19
O K	26.71	0.2980	56.41	0.63	64.86
Mg K	0.25	0.5770	0.27	0.05	0.21
S K	18.35	0.8233	14.03	0.20	8.05
Ca K	23.98	0.9005	16.75	0.22	7.69
Totals			**100.00**		

CONCLUSION

The main conclusions of the conducted research and the results shown are the following:

- Determined concentrations of Ba (and other metals Fe, Mn, Zn, Cu, Pb) in the inside and outer filters.
- At the object in centar these concentrations range from 282-292 mg/kg Ba.
- At the object Biser these concentrations range from 183-199 mg/kg.
- At the object in Bitola these concentrations range from 200 до 188 mg/kg.
- Higher concentration of Ba is found at the sample from the floor which is a plastic material, linoleum.
- Lower concentrations of Ba are found in the other samples, but these concentrations are not high.
- Concentrations of Ba are determined in the samples of air.
- At the samples of the isolated materials there are determined concentrations of sulphur (S) which are linked in the calcium-sulphate phases.

Determined concentrations of Ba in the inside and outer filters coming from the barium additive on the reduction of smoke during the operation of diesel engines and from the floor plastic materials (linoleum) inside of the buildings.

INSTEAD OF COMMENT

The presence of metals in the ambient air (ambient dust) in the urban environment is a frequent subject for research, and so far it has been worked out in many urban centers in the world. The systematic research for the contents of the ambient dust in the city of Skopje is not made before, so we cannot present such information. However, it should be emphasized that such information which refer on the contents of the urban dust exist in many towns, but that information is very changeable depending on the seasons in which the data is measured.

As an example, on the basis of a large number of researches the metals which are present in the urban dust are divided in three groups:

- Urban elements (Ba, Cd, Co, Cu, Mg, Pb, Sb, Ti, Zn),
- Natural elements (Al, Ga, La, Mn, Na, Sr, Th, Y),
- Elements with mixed background (Ca, Cs, Fe, Mo, Ni, Rb, Sr, U).

There is accepted opinion that the background of the urban elements is primarily connected with the development of the traffic, the processes of corrosion of the materials build in the objects in the towns (buildings, houses, roads, etc.) as well as the emission of dust which appears in the soils, and fields with no grass.

In order to be able to make any correlation of the obtained data which refer to a small number of measured samples (only of two locations) many deeper researchers are needed. From the other side, the influence of the contents of dust (as well as the ambient air) upon the health of the people is a topic which requests more serious and longer measures.

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