SIMPLE AND FAST METHOD FOR CHARACTERIZATION OF CLAY MATERIALS

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INTRODUCTION

- Clay represents a type of material that has been used since long ago. In the present they are used in large variety of industries such as food, construction, ceramics, pharmaceuticals etc.
- The domains in which a certain type of clay is used depends on their chemical and mineralogical composition which determines its properties. In certain domains these characteristics must strictly abide by imposed standards of stability and safety.
- This study aims to realize a fast elemental composition analysis for clay materials for which the XRF spectrometry was used because it is a modern technique which proved its usefulness in studies from different domains, as it does not require any preprocessing of the samples, is time and cost efficient and it does not produce waste.
- In the case of this study the aim of this method was the determination of heavy metals compositions present in clays. The results presented are collected from over a hundred samples of clay.
- The samples were acquired from the commercial market, originating from both Romania and other countries. The place of origin is actually very important for clay, as it determines certain compositions or properties, which may affect or limit their utilization.
- Given the fact that the influence of radioactivity, be it natural or artificial is also an important factor to take into consideration, the samples were also analyzed with the gamma spectroscopy method for a complete overview and characterization, which may be used for determining the use of each type of clay.

GAMMA SPECTROMETRY METHOD

- Gamma-ray spectrometry is a nuclear technique used to analyse gamma-ray emmiting radionuclides present in various types of samples.
- It has two stages: *radionuclide identification* (qualitative analysis) and *determination of specific activity for the identified radionuclides*(quantitative analysis).

Method description

- The samples were dried in a temperature-controlled furnace at 105^{0}C for 24 h to remove moisture.
- To determine radium, the samples are sealed and measured after 3-4 weeks to permit the establishment of the radioactive equilibrium between ^{226}Ra and its gaseous radioactive progeny ^{222}Rn (radon). The samples were measured in 3 intervals of 86400s (24h), while also establishing the background count rate.
- Then, ^{214}Pb and ^{214}Bi radon's radioactive progenies are measured by gamma-ray spectrometry. U, Th and K concentrations can be determined by measuring uranium (^{238}U), thorium (^{232}Th) and potassium (^{40}K) radioactivity in the sample.

RESULTS

- The decontamination of liquids using clays is not a new method, but it has proved efficient in certain cases. The efficiency for each case must be analysed and if the results are satisfying then further proceed to the determination of the decontamination's limit. For this purpose, it is necessary for a characterization study of the clays to be done and to have a study of controlled contamination in order to be able to determine the decontamination factor. This paper refers to the first stage – the characterization of the available clays.
- The results of the determination of the heavy metal content in the clay samples are presented in Table 1 and the radioactivity concentration determined are presented in Table 2. From the elemental XRF it has been found that:
  - ❑ 87% of the clay samples contain 0.0012 ÷ 0.0067 ppm Cr, 0.0014 ÷ 0.0039 ppm Pb, 0.0014 ÷ 0.0067 ppm As,
  - ❑ 75% of the clay samples contain 0.0027 ÷ 0.0099 ppm Cu, 0.001 ÷ 0.0026 ppm Co
  - ❑ Only in 3 samples contained Mo with a concentration of 0.0001 ÷ 0.0013
  - ❑ All samples contained elements such as Zn, Ni, Mn, V, Ti, in quantities with a higher order of magnitude than Cr, Pb, As.
  - ❑ The most abundant element found in the samples was Fe.
  - ❑ There were no traces of Cd and Hg detected in the samples.
- The chemical composition of clays may vary depending on the geographical area and the environmental conditions. Factors that may influence the quantitative determination of heavy metals in the samples analysed are the soil characteristics (which may be more or less rich in Fe), the natural waters from the area, the rainfall (rains), the pollution, the equipment used for extraction, etc.

Name of the sample	Cr [ppm]	Cu [ppm]	Fe [ppm]	Pb [ppm]	Zn [ppm]	Co [ppm]	Cd [ppm]	Hg [ppm]	Mo [ppm]	As [ppm]	Ni [ppm]	Mn [ppm]	V [ppm]	Ti [ppm]
Clay T1	< LOD	< LOD	1.6551	< LOD	0.0029	< LOD	< LOD	< LOD	0.0011	< LOD	0.0037	0.0112	0.0081	0.5992
Clay T2	0.0041	0.0049	4.1703	0.0024	0.0109	0.0015	< LOD	< LOD	0.0013	0.0018	0.0139	0.0752	0.0102	0.2538
Clay T3	0.006	0.0099	4.6053	0.0014	0.011	0.0026	< LOD	< LOD	< LOD	0.0014	0.0096	0.084	0.0076	0.2843
Clay M1	0.0032	0.0027	3.4335	0.0022	0.0062	0.001	< LOD	< LOD	< LOD	0.003	0.005	0.0372	0.0051	0.2498
Clay M2	0.0067	0.0047	3.8228	0.002	0.0096	0.0019	< LOD	< LOD	0.0006	0.0016	0.01	0.0344	0.0111	0.4938
Clay M3	0.0016	0.0044	4.2321	0.0019	0.0111	0.0021	< LOD	< LOD	< LOD	0.003	0.0111	0.0505	0.007	0.3151
Clay M4	0.0049	0.0035	4.231	0.0025	0.0109	0.0014	< LOD	< LOD	< LOD	0.0067	0.0081	0.0655	0.0044	0.2476
Clay M5	0.0012	< LOD	0.6661	0.0039	0.001	< LOD	< LOD	< LOD	< LOD	0.0039	0.0098	0.0031	0.0038	0.2588

Table 1 – Heavy metals content in clay samples

Fig 1 – Clays (From left to right: white, red, green, yellow)

Elemental composition and radioactive ANALYSIS

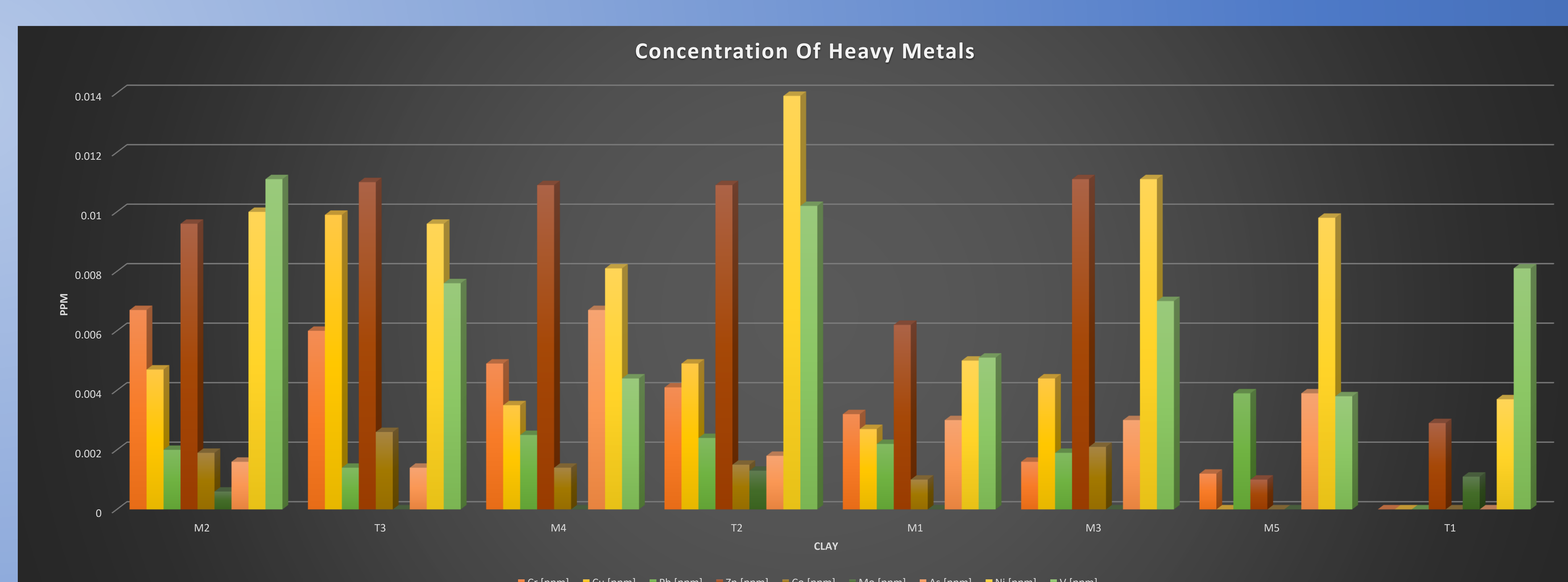
- ❖ Chemical analysis focused on several parameters for the purity of sample, in generally heavy metals or radioactive elements. In the most of case, the concentration of cobalt, copper, chromium, zinc, iron, lead, etc, in the samples was determined by Atomic Absorption Spectroscopy or HPLC.
- ❖ The methods mentioned above are difficult, requires the processing and destruction of the sample, reagents and laborious calculations. They also has a by-product a series of chemical wastes which needs to be treated. In this context, a simple and fast method with a satisfying accuracy is the X-ray Fluorescence (XRF). Also, it is desired because it is non-destructive towards the sample and does not produce any waste.
- ❖ Clay represents the common name for hydrated laminar magnesium-aluminum-ironsilicate and is a material used in a wide range of fields and sectors; from the building industry to pharmaceuticals industry, cosmetics and even gardening.
- ❖ This study aims to study them for usage in the nuclear, chemical field, cosmetic, pharmaceutic or building materials. In many countries, clays are already part of large application, manly for the study of radioactive wastes found in the clay layers of the ground.
- ❖ This paper presents an elemental composition and radiological characterization of some types of clays from Romania, which is available on the market.
- ❖ The samples were both purified and unpurified and have different geographical origins.
- ❖ The importance of their characterization comes from their high capacity of retaining cations, anions and water.

XRF - OVERVIEW

- The application of the analysis method using X Ray Fluorescence can be used for qualitative and quantitative determination of primary composition for a material sample. Nowadays, X Ray Fluorescence (XRF) can be easily utilized with the help of modern equipment.
- Portable Tracer 5i Spectrometer made by Bruker Instruments has a working principle based on X Ray Fluorescence and energy dispersion (EDXRF) and presents a high level of analysis speed and sensibility. The spectrometric analysis of elemental chemical composition for samples is calculated for elements in the range between magnesium (Mg) and uranium (U).
- The device presents a detection system for Fluorescence X Ray, with a sensor for detection and control of scattered radiation. This system has a preamplifier and analog electronic circuits. The data acquisition is made real-time and is interpreted using a software for digital multichannel spectrometric acquisition and analysis, type Bruker. Also, for being able to visualize the analysed sample it is also equipped with a CCD camera.

XRF – SPECIFICATIONS

- The spectrometer has, as a source of excitation, a tube of X rays with Rh anode installed behind the beryllium window. During the sample analysis the voltage used is in the range of 6-50 kV and the amperage is the range of 5-500 uA.



Name of the sample	Specific activity (Bq/kg)						
	^{226}Ra	^{214}Pb	^{214}Bi	^{228}Ac	^{40}K	^{212}Pb	^{212}Bi
Argila T1	54 ± 15,9	17 ± 1,4	16 ± 1,4	40 ± 3,7	160 ± 16,6	40 ± 3,6	41 ± 8,6
Argila T2	70 ± 20,4	10 ± 0,8	12 ± 1,0	50 ± 4,4	560 ± 58,2	30 ± 2,7	50 ± 10,3
Argila T3	75 ± 21,7	40 ± 3,2	40 ± 3,4	30 ± 2,8	420 ± 43,7	30 ± 2,7	30 ± 6,5
Argila M1	74 ± 22,0	18 ± 1,8	17 ± 1,5	67 ± 6,1	493 ± 51,3	56 ± 5,1	95 ± 19,4
Argila M2	88 ± 26,0	25 ± 1,0	20 ± 1,7	54 ± 5,0	615 ± 64,0	53 ± 4,8	719 ± 153,1
Argila M3	64 ± 19,4	16 ± 1,3	15 ± 1,3	65 ± 5,3	633 ± 65,9	51 ± 4,6	84 ± 17,3
Argila M4	140 ± 39,8	48 ± 3,8	53 ± 4,5	81 ± 7,3	851 ± 88,5	59 ± 5,3	100 ± 20,7
Argila M5	170 ± 49,8	50 ± 4,0	40 ± 3,4	220 ± 19,6	<AMD	200 ± 18,0	230 ± 45,8

Table 2 - **Specific activity of gamma emitting radionuclides identified in clay samples**

CONCLUSIONS

- ❖ Clays, zeolite volcanic tuffs (from Romania) and sands (from Romania) were radiologically characterized and their content of heavy metals was analysed, as they are capable of isotopic exchange and migration from their structure. These materials were studied with the purpose of using them as filtering and absorbent materials in the nuclear field, namely for retaining and concentrating the radioisotopes in liquid wastes resulted from decontamination processes or radioactive pollution. The ultimate goals are:
  - to obtain a non-aggressive decontaminate method that results in as little radioactive waste as possible
  - to separate afterwards the radioisotopes from the absorbent and filter materials for research studies at low costs
- ❖ It is important to determine the heavy metals content for each of those materials because chemically contaminated liquids may appear as a result of the isotopes' recovery.
- ❖ Considering the multitude of uses of clays, especially in the fields that requires the direct contact between the user and the clay or the products that contains it, kowing the amount of impurities is compulsory, especially heavy metals and natural radioisotops that it may possibly contain.
- ❖ All the values obtained for the concentration of transition metals are lower than the admitted limits for their use.
- ❖ Most of the materials examined in this work showed fairly low levels of radioactivity. The values obtained are lower than the internationally recommended limits for building materials. The results indicate an acceptably low radiological risk arising from the use of these row materials in buildings construction and probably in other industrial field (sugar industry, metallurgic industry, etc).
- ❖ The results obtained are very well in agreement with those reported in many European country.
- ❖ The surveillance of the natural mineral rocks is not a new subject. This must be done continuously to get consistent data with international rules. The analyses performed on the samples of natural mineral clays are consistent with the European Directive 59/ transposed into Romanian standards of Ministry of Environment, National Commission for Nuclear Activity Control (CNCAN) and Ministry Health and others.
- ❖ The assessment presented in this paper on the natural radioactivity in mineral clays samples comes to update at least some data on activity concentrations and effective doses due to intake of natural radionuclides.
- ❖ The obtained data provide basic information for consumers and competent authorities to be aware of radiation effects on human health.

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ACKNOWLEDGEMENTS

- ❖ This work has been funded by the project PN 19 06 02 04, phase 9/2022 and phase 10/2022
- ❖ This work was sponsored by the Gritsablare Company from Constanta (http://www.gritsablare.ro) and the authors would like to express their sincere appreciation for providing some of the materials used in this study.