STUDIA UBB CHEMIA, LXVI, 2, 2021 (p. 105-116)
(RECOMMENDED CITATION)
DOI:10.24193/subbchem.2021.2.09

A STRAIGHTFORWARD METHOD FOR DETERMINATION OF Ba AND Sr TOTAL CONTENT IN NATURAL ZEOLITES BASED ON MICROWAVE-ASSISTED DIGESTION AND INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY

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ABSTRACT. Ba and Sr may occur in relatively high content in natural zeolites and can contribute to the zeolites ion-exchange properties. In addition, some soluble compounds of Ba and Sr can be toxic, thus their determination is important. The aim of this paper was the development and validation of a method for determination of Ba and Sr in zeolites based on microwave-assisted acid digestion and inductively coupled plasma optical emission spectrometry (ICP-OES). For validation, a certified reference material (BCS-CRM 375/1) was used in the accuracy study, and the obtained recoveries were 92 ± 10 % for Ba and 95 ± 12 % for Sr. A mixture of HNO_3:HCl:HF of 3:9:2 (v/v/v) and a digestion time of 40 min were found to give recoveries in the range of 80-120 %. The obtained LOQs in ICP-OES allowed the quantification of concentrations above 5.0 mg kg^{-1} Ba and 3.8 mg kg^{-1} Sr. The method was applied for the determination of Ba and Sr in five zeolite samples, and concentrations of 422 – 580 mg kg^{-1} for Ba and 115 – 183 mg kg^{-1} for Sr were found. The obtained performance parameters were in agreement with the requirements of international guidelines regarding methods validation.

Keywords: *trace metal, aluminosilicate, barium, strontium, ICP-OES, microwave digestion*

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INTRODUCTION

Zeolites are aluminosilicates materials having porous crystalline structures and well-defined channels or cavities. They have a negative charge in their extended structures, which make them to have strong affinity for cations [1]. Natural zeolites have in their composition significant amounts of Na^+, K^+, Mg^{2+}, and Ca^{2+} that can be substituted by other cations (e.g. cations of heavy metals and radionuclides from contaminated environments), in ion-exchange processes. Due to their occurrence in relatively high amount in nature, zeolites are among the most studied potential inorganic ion-exchange materials [2-4].

The affinity for cations makes natural zeolites useful in many applications, but this property can also conduct to the accumulation in their structure of potentially toxic cations at trace levels [5]. Depending on their origin, the determination of the whole chemical composition of natural zeolites is extremely important mainly when the intended use is human ingestion, animal feed supplements or purification of drinking water. Furthermore, since the zeolites can be used for the removal of different trace elements from contaminated environments, the quantification of elements adsorbed by zeolites is required in order to evaluate their adsorption efficiency [6,7]. Ba and Sr may occur in relatively high content in natural zeolites that can contribute to the zeolites ion-exchange properties. In addition, some soluble compounds of Ba and Sr can be toxic. Therefore, when the zeolite is used as food supplement or as filtrating material it is important to know the content of the two elements.

In several works, zeolites were studied for the removal of radionuclides of barium (Ba) and strontium (Sr) from waters [1,8,9]. The insoluble salts of Ba are nontoxic, being poorly absorbed by organisms, while Sr(II) was reported to be an important mineral for the health of human bones and teeth, thus these elements have no regulated levels in environment [10]. However, the radioisotopes of these elements are of a high concern for human health and their removal from the environment is of high importance [9]. Also, the water-soluble Ba species was reported to affect the mammalian cardiovascular system [11,12]. Sr is an alkaline earth metal naturally occurring in soluble compounds which make it highly mobile and reactive. Sr has four stable isotopes (^{88}Sr, ^{86}Sr, ^{87}Sr, ^{84}Sr), and thirty-one unstable isotopes [13]. Its anthropogenic radionuclides form (^{134}Cs,^{135}Cs and ^{137}Cs) are used in nuclear power plants. Thus, the determination of Ba and Sr both occurring in natural zeolites and those that can be retained by zeolites from contaminated environment is very important.

For the determination of chemical composition of zeolites, instrumental techniques such as X-ray fluorescence spectrometry (XRF), X-ray diffraction (XRD), magnetic resonance spectrometry (NMR), atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma atomic emission spectrometry (ICP-OES) can be used [14]. Each of these analytical tools has some particular advantages and disadvantages associated with sample preparation procedures, consuming of time, interpretation of analytical results. ICP-OES is widely accepted technique due to the speed of analysis, multi-elemental capability and wide dynamic range [15].

The determination of elements in solid samples by ICP-OES requires, however, sample preparation to extract the analyte into solution [16]. In this way, a homogeneous solution is obtained, which can be more representative than in case of direct analysis of surface of solid sample. The step of sample preparation is essential in obtaining recovery of the analyte, and thus accurate results.

There are several methods of sample preparation, many of them based on dissolving in a mixture of acids (HCl, HNO_3, HF, H_2SO_4) [17,18]. The chosen acid mixtures, digestion devices, amount of necessary sample may influence the quantitative extraction of analyte in solution. Closed microwave-assisted wet digestion/decomposition based methods have several advantages including fast heating, little risk of contamination, use of low amounts of acids and prevention of loss of volatile elements [19,20].

The present work was initiated with the aim to develop a simple and reliable microwave-assisted extraction method in combination with ICP-OES technique for the determination of Ba and Sr in zeolite samples. The digestion step involves closed microwave extraction using a mixture of concentrated HNO_3, HCl, and HF. The optimum composition of acid mixture for the best recovery of Ba and Sr was established by using a Certified Reference Material (CRM) BCS-CRM 357/1 soda feldspar with known amounts of Ba and Sr. The figures of merit, such as limit of detection, limit of quantitation and precision of ICP-OES were also estimated. Finally, the proposed method was applied to measure Ba and Sr content in five natural zeolites samples.

RESULTS AND DISCUSSION

Optimization of microwave-assisted acid digestion procedure

In order to deliver quantitative results, a spectrometric method should provide recoveries in the range of 80-120% [21]. The dissolution of silicate materials is difficult and time-consuming due to refractory nature of their numerous constituents. Two essentially different approaches were suggested as possible ways to digest this type of samples. One is based on fusion with different salts (e.g. Na_2CO_3, $LiBO_2$), and the other is wet digestion based on dissolution in a mixture of acids (HCl, HNO_3, HF, H_2SO_4) [22].

The wet acid digestion is preferable since, comparing with fusion, is simple and rapid. The recovery in this procedure strongly depends on the solubility of analytes and type of matrix. In the case when the spectrometric method is not used for determination of silica content in this type of samples, the digestion with a mixture of inorganic acids which includes HF is preferable [23]. Insufficient amount of acids or incomplete wetting of solid samples can conduct to an incomplete digestion. The ratio of mineral acids used for digestion may influence the recovery rate. In order to evaluate this factor for the digestion of 0.500 g of sample, mixtures of concentrated HNO_3, HCl and HF were used. The ratio between HNO_3 and HCl was kept at 1:3 (v/v), as in *aqua regia* mixture, but the volume of concentrated HF was varied, in order to have the following HNO_3:HCl:HF ratios: 3:9:1 (v/v/v), 3:9:2 (v/v/v), 3:9:3 (v/v/v), 3:9:4 (v/v/v), 3:9:5 (v/v/v). The applied digestion program was similar for all the experiments. The CRM BCS-CRM 375/1 soda feldspar with known amounts of Ba and Sr was used to evaluate the recovery.

At the end of each microwave extraction process, the sample digest was diluted to required volume with ultrapure water for subsequent determination of Ba and Sr by ICP-OES. The extraction efficiency was evaluated by recovery of each analyte. Three replicates were carried-out for this assay, with an average standard deviation of repeatability of 5%. The results are illustrated in Figure 1.

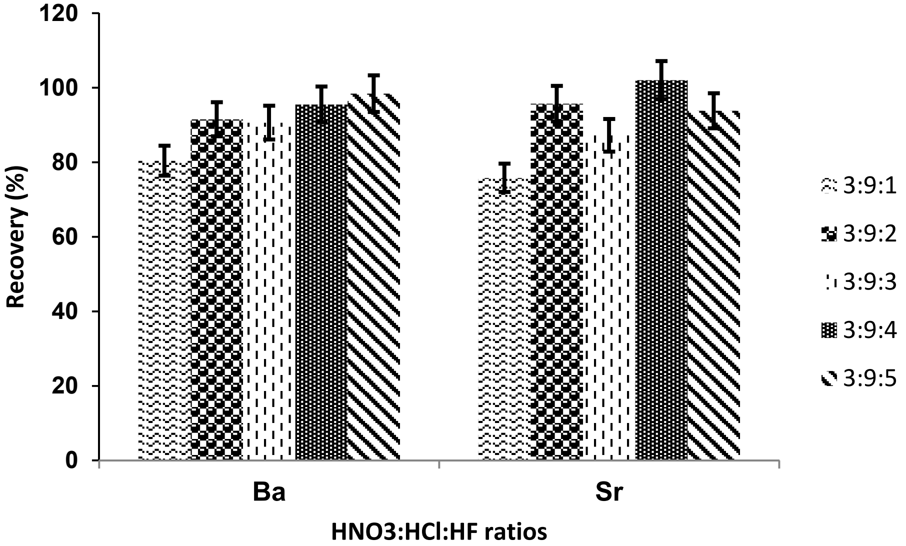

Figure 1. Influence of HNO3:HCl:HF ratios on Ba and Sr recovery (%) from CRM BCS-CRM 357/1 soda feldspar following microwave-assisted digestion. Error bars with CI values are indicated

The recovery of Ba ranged between 80.4 – 98.4 %, with an increase from the ratio HNO_3:HCl:HF of 3:9:1 (v/v/v) to the ratio of 3:9:5 (v/v/v). In all cases, the recovery was in the range of 80-120 %. In case of Sr, for the ratio HNO_3:HCl:HF of 3:9:1 (v/v/v), the recovery rate was of 75.8 %, below 80%, which is an unsatisfactory result, while for the increased HF content, the recovery was in all cases in the range of 80-120 %. Consequently, it was considered that for the quantitative extraction of Ba and Sr from 0.500 g of sample, the use 3 mL of HNO_3 65% (w/w), 9 mL HCl 37 % (w/w) and 2 mL HF 40 % (w/w) is a suitable digestion method.

The validation was performed considering the recommendations of the Cooperation for Analytical Chemistry in Europe (EURACHEM) guide [24].

Selectivity for Ba and Sr measurement by ICP-OES

The emission wavelengths for each metal (Ba – 233.527 nm and Sr – 407.771 nm) which are not affected by spectral interferences according to the recommendation of the instrument manufacturer have been selected. Selectivity was evaluated by recovery of a spike of 1 mg L^{-1} element in the extracted solutions. The recoveries were in the range of 90 –110%, considered as satisfactory [25].

Limits of Detection (LODs), Limits of Quantification (LoQs) and linear ranges

The LODs for both elements were calculated using the $3s_{y/x}/m$ criterion [26] where $s_{y/x}$ is the residual standard deviation of the calibration curve and m the slope of the calibration curve, using the Equation 1:

$$LoD = (3\ s_{y/x} - y) / m \qquad (1)$$

where y is the intercept of the calibration curve.

LoQs were calculated as three times the LoDs. To confirm LoQs, six independent solutions containing Ba and Sr at a level of concentration close to the LoQ (0.10 mg L^{-1}) were analysed, with the targeted relative standard deviation of repeatability (RSD) below 20 % and recovery between 90-115 %. The selected wavelengths, LoDs, LoQs, RSD (%) and recovery (%) at LoQs are presented in Table 1.

Table 1. Selected spectral lines, LoDs, LoQs and LoQ confrmation

Element	λ (nm)	LoD (mg L^{-1})	LoQ (mg L^{-1})	RSD at LoQ (%)	Recovery at LoQ (%)
Ba	233.527	0.008	0.025	5.36	97
Sr	407.771	0.006	0.019	7.73	105

The obtained LoDs were of 0.008 mg L^{-1} for Ba and 0.006 mg L^{-1} for Sr. Lower LoDs of 0.0002 mg L^{-1} for Ba and 0.00007 mg L^{-1} for Sr were reported by Pohl and co-workers [27], but the estimation was based three times standard deviation of blank signal. The performance parameters for LoQs confirmation were well fitted on the targeted values, showing that these values can be measured with good accuracy. Considering the digestion procedure, the calculated LoQs in the solid sample are of 5.0 mg kg^{-1} for Ba and 3.8 mg kg^{-1} for Sr, values that can be lowered by digestion of higher amount of solid sample or by a lower dilution.

Seven-point external calibration curves within the concentration range of 0.02 - 2 mg L^{-1} were used for quantification of studied elements. For concentrations of Sr higher than this value, saturation of the emission signal in axial view of plasma was observed, thus for higher Sr concentrations, sample dilution is necessary. The homogeneity of variances was evaluated by measuring six times the lowest and the highest concentrations of calibration standards. The PG ratios of the standard deviations (s_1) and (s_7), calculated as s_1^2/s_7^2 or s_7^2/s_1^2 were compared with the critical value Fischer $F_{5;5;0.99} = 11$ [28].

The characteristics of the calibration curves for the two elements obtained by ICP-OES are presented in Table 2.

Table 2. Characteristics of the calibration curves
over the range 0.02 – 2 mg L^{-1}

Element	Intercept (a)	Slope (*b*)	PG	Correlation coefficient (R)
Ba	235	18830	3.72	0.9999
Sr	230077	12069102	7.32	0.9999

The variances evaluated from the lowest and the highest concentrations of calibration curves are homogenous, and the correlation coefficients are better than the imposed target value 0.995 [29], therefore linear regressions were accepted.

Precision and Trueness

Precision was assessed in term of repeatability for the 6 parallel measurements on a zeolite sample, which included the whole procedure. Relative standard deviation of repeatability (*RSD_r*) below 10% and limit of repeatability (*r*) below 28% were the imposed targets for this assay. The standard deviations of repeatability/limit of repeatability, within the imposed limits are presented in Table 3.

Table 3. Repeatability study for a zeolite sample (n=6 parallel determinations)

Element	Average (mg kg^{-1})	s_r (mg kg^{-1})	RSD_r (%)	r (%)
Ba	580	43	7.41	20.8
Sr	170	11	6.47	18.1

s_r – standard deviation of repeatability; RSD_r – relative standard deviation of repeatability; r – limit of repeatability (2.8x RSD_r)

The trueness was evaluated from the recovery study using a CRM (BCS-CRM 375/1 soda feldspar) with indicative values for Ba and Sr content. The calculated recoveries are showed in Table 4.

Table 4. Indicative values of BCS-CRM 357/1 soda feldspar, average measured concentrations (n = 6 parallel determinations) and the recoveries (%)

Components	**Indicative Values** µg g^{-1}	**Average values ± CI** µg g^{-1}	**Recovery (%)**
Ba	95	90.1 ± 11.1	95
Sr	101	92.5 ± 9.6	92

The obtained recoveries were of 95 % for Ba and 92% for Sr, which are in the target range of 80-120 % [30].

Estimation of measurement uncertainty

Two types of sources of uncertainty were identified for Ba and Sr determinations by ICP-OES: those obtained from laboratory experiments (method repeatability and uncertainty of the calibration curves), and those obtained from certificates of used materials: uncertainty of reference materials, uncertainty of devices used for standards and sample preparations (weighting, dilutions). Composed uncertainties (u_c) were assessed by combining individual uncertainties in the traceability chain. Expanded uncertainties (U_e) were calculated for 95% confidence level (cover factor k=2). The relative expanded uncertainties were of 15.2 % for Ba and 13.3 % for Sr. Replicate analysis was the main contributor to the total uncertainty.

Ba and Sr in zeolite samples

Five natural zeolites samples (Z1–Z5) from a quarry located in Chilioara, Salaj County, Romania were collected and analyzed. The measured concentrations of Ba and Sr are presented in Table 5.

Table 5. Ba and Sr concentrations (mg kg^{-1}) in zeolite samples, n=3 parallel determinations

Sample	**Ba** Average values ± U_e mg kg^{-1}	**Sr** Average values ± U_e mg kg^{-1}
Z1	580 ± 88	170 ± 23
Z2	504 ± 77	115 ± 15
Z3	431 ± 66	134 ± 18
Z4	522 ± 79	167 ± 22
Z5	422 ± 64	183 ± 24

U_e – expanded uncertainty, k=2

As showed in Table 5, the content of Ba in the analysed zeolite samples were in the range of 422 – 580 mg kg^{-1}, with an average value of 492 mg kg^{-1}, while the concentrations of Sr ranged between 115 – 183 mg kg^{-1}, with an average value of 154 mg kg^{-1}. In the clinoptilolite zeolite from a qaury from Turkey were reported concentrations of Ba of 454 ± 16 mg kg^{-1} and of Sr of 825 ± 4 mg kg^{-1} [31]. Karapinar [32] reported a concentration of Sr of about 470 mg kg^{-1} in natural zeolite from Germany.

CONCLUSIONS

A microwave-assisted acid extraction method was developed and optimized for the determination of Ba and Sr in zeolite samples. A ratio of HNO_3:HCl:HF of 3:9:2 (v/v) with a total time of digestion of 40 min was found to give recoveries in the target values of 80-120%) for Ba and Sr from a CRM with silicate matrix. The digestion method based on microwave-assisted wet digestion is simple, faster, and it requires less chemicals than other digestion methods like that based on fusion with salts. The obtained LOQs in ICP-OES allowed the quantification of concentrations higher than 5.0 mg kg^{-1} for Ba and 3.8 mg kg^{-1} for Sr. All the performance parameters (LoD and LoQ, selectivity, linearity, trueness, precision and measurement uncertainty) satisfied the imposed targets. The method was applied for the determination of Ba and Sr in five zeolite samples.

EXPERIMENTAL SECTION

Materials

Standard solutions for external calibration of ICP-OES were prepared by stepwise dilution of a Merck Millipore CertiPur ICP multi-elemental standard solution IV 1000 mg L^{-1}, which contains Ba and Sr, purchased form Merck (Darmstadt, Germany). Emsure® ACS premium grade acids HNO_3 65%, HCl 37%, and HF 40%, purchased from Merck (Darmstadt, Germany) were used for digestion of samples. Ultrapure water (18 MΩ cm^{-1}) obtained from a Millipore Direct Q3 (Millipore, France) was used for dilutions.

For the optimization of digestion procedure and for recovery study a Certified Reference Material CRM BCS-CRM 375/1 soda feldspar from Bureau of Analysed Samples Ltd (United Kingdom) was used.

Five natural zeolites samples (Z1–Z5) were collected from a quarry located in Chilioara, Salaj County, Romania. In this region, the predominant zeolite in tuff is represented by clinoptilolite-type minerals [33]. The samples were crushed and further grounded to a fine powder in a tungsten-carbide swing mill and sieved through a 100 µm mesh sieve.

Preparation of zeolites digest

An amount of 0.500 g of sample, with particulate size <100 µm, was digested with a mixture of 3 mL HNO_3 65%, 9 mL HCl 37%, and 1 - 5 mL HF 40%, for method optimization, in a closed-vessel MWS-3+ microwave system (Berghof, Germany). The three-steps heating program of the microwave system was applied for samples digestion, heating at 160 °C, 200 °C, cooling at 100 °C, in a total time of digestion of 40 min, according to the manufacturer recommendations for similar samples. After cooling at room temperature, 20 mL of saturated H_3BO_3 were added, and then heated again at 160 °C in the microwave system for 15 min. The samples were finally filtered through cellulose filters in volumetric flasks of 100 mL and diluted to final volume using ultrapure water.

Instrumentation

Analyses were carried out using a dual viewing inductively coupled plasma optical emission spectrometer Optima 5300DV (Perkin Elmer, USA). The operating conditions used for ICP-OES determination were 1300W RF power, 15 L min^{-1} Ar plasma support, 2.0 L min^{-1} auxiliary Ar flow, 0.8 L min^{-1} nebulization Ar, and 1.5 mL min^{-1} sample uptake rate, in axial viewing option of the plasma. Axial viewing approach provides an increased sensitivity and lower LoDs in detecting trace elements. 7-point linear calibration curves over the range 0 – 2 mg L^{-1} element were plotted.

Strategy for method validation

The validation of the analytical procedure for quantitative determination of Ba and Sr in zeolites was performed by evaluating limits of detection, limits of quantification, selectivity, linear ranges, trueness and precision. Measurement uncertainty was evaluated based on the bottom-up approach. All the contributions to combined uncertainty were obtained from statistical analysis of repeated measurements and calibration certificates.

ACKNOWLEDGMENTS

The work has been funded by the Competitiveness Operational Programme of the Ministry of European Funds through the Contract No. 7/01.09.2016, code MySMIS 105654.

REFERENCES

1. Y. Li; A. O. Simon; C. Jiao; M. Zhang; W. Yan; H. Rao; J. Liu; J. Zhang; *Microporous Mesoporous Mater.*, **2020**, *302*, 110244.
2. S.A. Maicaneanu; H. Bedelean; *Studia UBB Chemia*, **2020**, *LXV*, *3*, 89-100.
3. E. Neag; A.I. Torok; C. Tanaselia; I. Aschilean; M. Senila; *Water*, **2020**, *12*, 1614.
4. M. Senila; O. Cadar; L. Senila; A. Hoaghia; I. Miu; *Molecules*, **2019**, *24*, 4023.
5. M. Tomasevic-Canovic; *J. Serb. Chem. Soc.*, **2005**, *70*, 1335-1345.
6. S. Chalupnik; W. Franus; M. Wysocka; G. Gzyl; *Environ. Sci. Pollut. Res.*, **2013**, *20*, 7900-7906.
7. A.K. Mosai; H. Tutu; *Miner. Eng.*, **2021**, *161*, 106740.
8. S. Kwon; C. Kim; E. Han; H. Lee; H.S. Cho; M. Choi; *J. Hazard. Mater.*, **2021**, *408*, 124419.

9. D. Alby; C. Charnay; M. Heran; B. Prelot; J. Zajac; *J. Hazard. Mater.*, **2018**, *344*, 511-530.
10. D. Gonzalez-Weller; C. Rubio; A.J. Gutierrez; G.L. Gonzalez; J.M. Caballero Mesa; C. Revert Girones; A. Burgos Ojeda; A. Hardisson; *Food Chem. Toxicol.,* **2013**, *62*, 856-868.
11. I.R. McNeill; K.Z. Isoardi; *Toxicol. Commun*., **2019**, *3*, 88-90.
12. H. Zhang; X. Zhou; L; Wang; W. Wang; J. Xu; *Ecotox. Environ. Safe*., **2018**, *164*, 181-188.
13. Z. Liu; B. Chen; X. Li; L. Wang; H. Xiao; D. Liu; *Sci. Total Environ*., **2019**, *670*, 433-438.
14. Y. Ma; S. Rigolet; L. Michelin; J.L. Paillaud; S. Mintova; F. Khoerunnisa; T.J. Daou; E.P. Ng; *Microporous Mesoporous Mater*., **2021**, *311*, 110683.
15. T. Frentiu; S. Butaciu; E. Darvasi; M. Ponta; M. Senila; D. Petreus; M. Frentiu; *Anal. Methods*, **2015**, *7*, 747-752.
16. M. Miclean; E.A. Levei; M. Senila; C. Roman; E. Cordos; *Rev. Chim. (Bucuresti)*, **2009**, *60*, 1-4.
17. I. Smical; A. Muntean; D. Ciurte; V. Micle; *Studia UBB Chemia*, **2020***, LXV, 4,* 95-107.
18. G.E. Damian; V. Micle; I.M. Sur; *J. Soil. Sediment*., **2019**, *19*, 2869-2881.
19. H. Altundag; M. Tuzen; *Food Chem. Toxicol*., **2011**, *49*, 2800-2807.
20. V.B.K. Mullapudi; K. Chandrasekaran; G. Venkateswarlu; D. Karunasagar; *Microchem. J.*, **2019**, *146*, 807-817.
21. AOAC Guidelines for Single Laboratory Validation of Chemical Methods for Dietary Supplements and Botanicals. (2002). https://members.aoac.org/AOAC_Docs/StandardsDevelopment/SLV_Guidelines_Dietary_Supplements.pdf (accessed Mar 2021).
22. P.K. Srivastava; A.K. Singh; B. Sunilkumar; *At. Spectrosc*., **2003**, *24*, 98-104.
23. M. Balcerzack; *Anal. Sci*., **2002**, *18*, 737-750.
24. B. Magnusson; U. Ornemark (eds.) Eurachem Guide: The Fitness for Purpose of Analytical Methods – A Laboratory Guide to Method Validation and Related Topics, (2nd ed. 2014), available from https://www.eurachem.org/images/stories/Guides/pdf/MV_guide_2nd_ed_EN.pdf, accessed on 22.06.2021
25. A. Drolc; A. Pintar; *Accreditation and Qual. Assur.*, **2012**, *17*, 323–330.
26. E. Covaci; M. Senila; M; Ponta; E; Darvasi; D. Petreus; M. Frentiu; T. Frentiu; *Talanta*, **2017**, *170*, 464-472.
27. P. Pohl; A. Szymczycha-Madeja; M. Welna; *Food Chem*., **2018**, *263*, 171-179.
28. International organization for standardization (1990) ISO 8466-1 Water quality. Calibration and evaluation of analytical methods and estimation of performance characteristics - Part I: Statistical evaluation of the linear calibration function, Geneva, Switzerland.
29. E. Covaci; M. Senila; M. Ponta; T. Frentiu; *Rev. Roum. Chim*., **2020**, *65*, 735-745.
30. M. Senila; E. Covaci; O. Cadar; M. Ponta; M. Frentiu; T. Frentiu; *Chem. Pap*., **2018**, *72*, 441-448.

31. M. Kurudirek; Y. Ozdemir; I. Turkmen; A. Levet; *Radiat. Phys. Chem.*, **2010**, *79*, 1120-1126.
32. N. Karapinar; *J. Hazard. Mater.*, **2009**, *170*, 1186-1191.
33. A. Maicaneanu; H. Bedelean; M. Stanca; Natural Zeolites. Characterization and Applications in Environmental Protection, Editura Presa Universitara Clujeana, Romania, 2008, pp. 59–78 (in Romanian).