Method for determination of exchangeable cations in natural zeolites using inductively coupled plasma optical emission spectrometry

ICIA
INCDO - INOE 2000
Subsidiary Research Institute for
Analytical Instrumentation Cluj-Napoca

Marin Senila, Oana Cadar, Maria-Alexandra Hoaghia, Zamfira Dinca, Lacrimioara Senila, Ioan Aschilean, Cecilia Roman

Introduction

The laboratory techniques used for the determination of the elements in solid samples require total or partial destruction for extraction of analytes into a liquid solution.

The exchange capacity is one of the most important properties that influence the zeolites applicability. The higher ability of zeolitic materials to exchange movable Na^+, K^+, Ca^{2+} and Mg^{2+} cations is equivalent with their high adsorption capacity in different processes. The amounts of exchangeable cations within zeolites pores/channels strongly depend on Si/Al ratio in its structure, as it influences the negative charge available to attract cations.

Although the cation-exchange capacity laid the foundation for applications in different industries, no international standard method is available for the determination of this exchange capacity of zeolites. Also, the literature is very scarce in presenting methods for CEC determination in zeolites.

A methodology to calculate the CEC of zeolites is based on the measurement of the content of the exchanged cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) from zeolite samples by NH_4^+ ion. The purpose of this study was to perform validation of a method used for the determination of exchangeable cations in zeolites by ICP-OES after their replacement by NH_4^+ ions from an ammonium chloride solution, and to evaluate the measurement uncertainty for this method.

Material and methods

Analyses were carried out using a dual viewing inductively coupled plasma optical emission spectrometer Optima 5300DV Perkin Elmer, USA (Figure 1).

ICP multi-elemental standard solution IV 1000 mg L-1 and mono-element standard solution Si 1000 mg L^{-1} purchased form Merck (Darmstadt, Germany) were used for ICP-OES calibration.

As no standard method for the determination exchangeable cations in zeolites is available, in this study we used a modification of several methods based on the replacement of Na^+, K^+, Ca^{2+} and Mg^{2+} ions from zeolite by NH_4^+ from NH_4Cl solution.
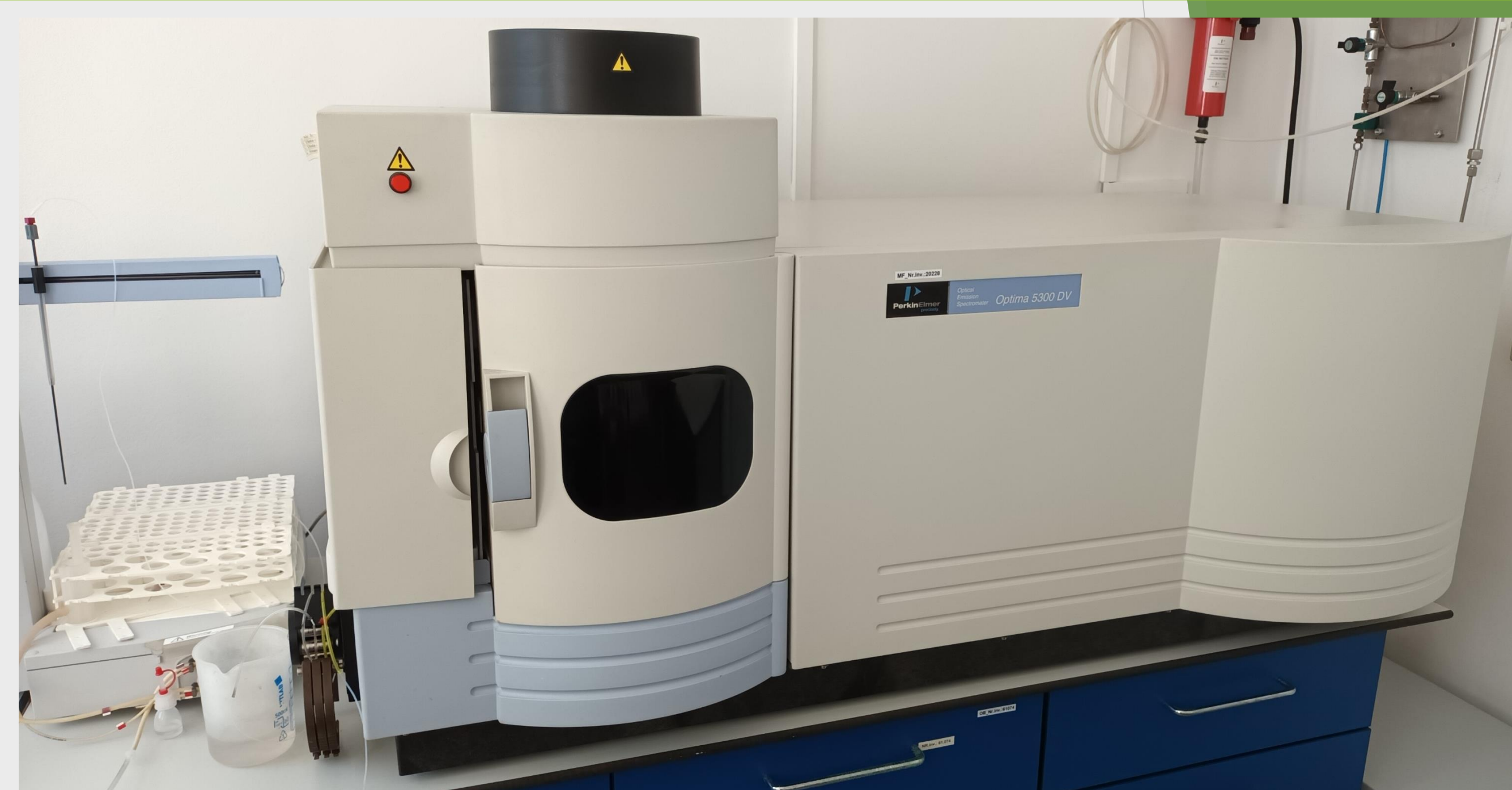

Fig. 1. ICP-OES Optima 5300DV Perkin Elmer, USA

RESULTS and DISCUSSION

Characteristics of the zeolite samples

Fourteen natural zeolites samples (Z1–Z14) from a quarry located in Racos, Brasov County, Romania were collected and analyzed. The samples were preliminary characterized regarding chemical composition for major elements using ICP-OES after microwave assisted digestion. The measured concentrations of major elements (Si, Al, Fe, Na, K, Ca, and Mg) were converted to oxides using atomic and molecular masses and the results are presented in Table 1.

In Figure 1 is presented the XRD pattern of sample Z1. According to X-ray diffraction analysis, the investigated zeolites from the Racos quarry contain clinoptilolite (C, $KNa_2Ca_2(Si_{29}Al_7)O_{72} \cdot 24H_2O$, PDF 00-039-1383) as the main crystalline phase, accompanied by quartz (Q; SiO_2, PDF 00-005-0490), muscovite (M; $KAl_2(AlSi_3O_{10})(OH)_2$, PDF 00-007-0025) and albite (A, $NaAlSi_3O_8$, PDF 00-019-1184) in lower concentrations.

Table 1. Major oxides concentrations (%) in zeolite samples

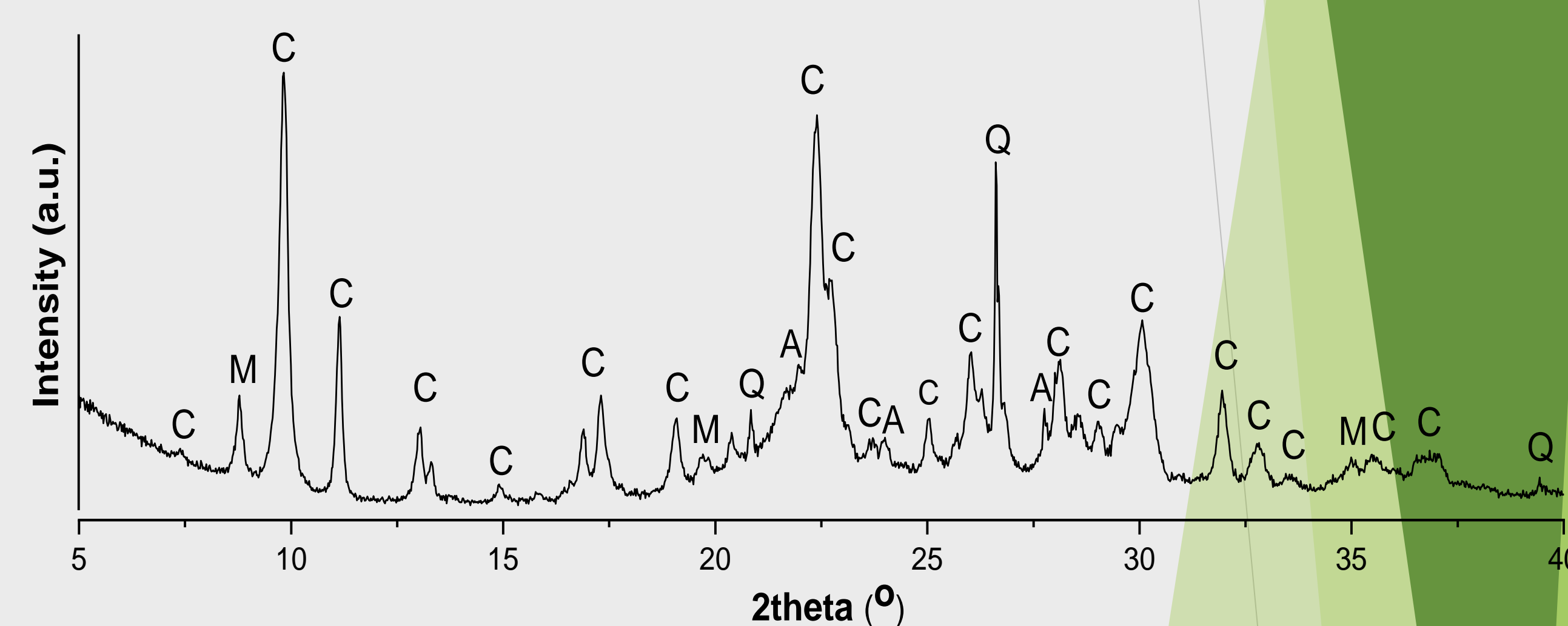| Sample	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	Fe_2O_3	MnO
Min.	57.09	9.87	2.05	0.54	1.97	0.16	1.04	0.01
Max.	71.79	11.19	2.85	0.82	2.50	0.88	1.70	0.14
Mean	62.38	10.48	2.42	0.68	2.25	0.55	1.36	0.04
Median	62.81	10.45	2.40	0.70	2.25	0.55	1.40	0.03
Stdev.	4.11	0.42	0.28	0.09	0.15	0.21	0.21	0.03
Skewness	0.791	0.231	0.186	-0.185	0.145	-0.346	-0.114	2.356
Kurtosis	0.637	-0.783	-1.431	-0.777	-0.379	-0.214	-1.138	6.025

Fig. 2. X-ray diffraction pattern of the zeolite sample Z1 from Racos quarry

Figures of merit

Data in Table 2 shows the LoD, LoQ and the measured RSD and recovery for LoQ confirmation. Internal repeatability for the measurement of exchangeable cations was evaluated by analysis of 6 parallel zeolite samples, and the obtained data are presented in Table 3.

Table 2. LOD and LOQ for exchangeable cations in extracting solution

Element	λ (nm)	LoD (mg L^{-1})	LoQ (mg L^{-1})	RSD at LoQ (%)	Recovery at LoQ (%)
Na	589.592	0.021	0.070	8.84	109
Mg	285.213	0.025	0.083	7.63	94.2
K	766.490	0.014	0.047	10.8	95.6
Ca	317.933	0.011	0.037	8.46	92.5

Table 3. Results from the repeatability study

Element	Average (mg/L)	s_r (mg/L)	RSD_r (%)	r (%)
Na^+	154	6.93	4.50	12.6
Mg^{2+}	35.3	1.92	5.43	15.2
K^+	705	46.2	6.55	18.3
Ca^{2+}	742	41.0	5.53	15.5

We evaluated the recovery using a CRM (BCS-CRM 375/1 soda feldspar) with certified values for total content of Na_2O, K_2O, CaO, and MgO. The results obtained in the analysis of CRM presented in Table 4 indicate good recoveries in the range of 92 – 103%.

Table 4. Certified values of CRM BCS-CRM 375/1 soda feldspar, measured values by ICP-OES

Components	Certified Values ± U (%)	Measured Values ± U* (%)	Recovery ± U* (%)
Na_2O	8.89 ± 0.11	9.06 ± 0.62	102 ± 7
K_2O	1.47 ± 0.03	1.37 ± 0.12	93 ± 8
MgO	0.180 ± 0.016	0.185 ± 0.018	103 ± 10
CaO	0.78 ± 0.03	0.72 ± 0.07	92 ± 9

The main sources of uncertainty of this method are: uncertainty of reference materials used for instrument calibration, uncertainty of dilutions for preparation of reference solutions and samples, uncertainty of the calibration curves, uncertainty of samples weighting, and repeatability of the replicate analysis.

CONCLUSION

Fully validated method for exchangeable cations analysis in zeolites after extraction in NH4Cl solution is presented. The fast and precise ICP-OES technique allows the quantification of selected cations in this type of samples. The performance parameters (LOD and LOQ, selectivity, working and linear range, accuracy, precision and measurement uncertainty) satisfied the imposed targets.

"Agriculture and Food - current and future challenges, AGRIFA"
8rd of October 2021, Cluj-Napoca