

Certification of Reference Material - Zeolite 1

PAVOL LUČIVJANSKÝ and DANIELA MACKOVÝCH

Geological Survey of Slovak Republic, Markušovská cesta 1, 052 40 Spišská Nová Ves

Abstract. Certified reference material named "Zeolite 1" has been prepared in Geo-analytical Laboratories of Geological Survey of Slovak Republic, accredited testing laboratories in Spišská Nová Ves within the project "Programme of Metrology Development in Slovak Republic" and research projects "Reference Laboratory of Ministry of Environment of Slovak Republic for Geology and Analyses of Geological Material and Rock Environment". The project includes a description of the sampling sites of candidate reference material, sample preparation, testing of homogeneity, inter-laboratory comparative tests and determination of certified values. 21 foreign and 6 Slovak laboratories took part in the certification of chemical composition of zeolite. 27 certified values for the main and trace elements were determined from the recorded values.

Key words: zeolite, reference material, inter-laboratory test

Introduction

The main target of preparation of the certified reference material "Zeolite 1" [1], [2], [3] was to prepare and widen the selection of reference materials by a new type, which is on the base of natural geologic material with aluminosilicate matrix, and which provides quality control of analytic data, precision and accuracy of analytical processes and validity of methods that are used in laboratories.

Characteristics of Deposit and Zeolite Composition

From several occurrences and deposits of zeolite tuffs the deposit of Majerovce [4] was selected for the preparation of certified reference material. The zeolite of deposit Majerovce represents the part of zeolite-rhyodacite tuffs of Earlier Badenian, which occurs on the surface from the northwestern border of Vranov nad Topľou to Pusté Čemerné (Fig.1).

The natural zeolite tuffs are composed of large group of minerals. The information about structure and thermic analyses are very important before beginning the certifying chemical analyses of the composition. The mineralogical composition of zeolite tuff sample from the Majerovce deposit was determined by X-ray diffraction analyses with the use of CuK_α radiation (Hricová 1999) [5]. The mineral clinoptilolite that composed a substantial part of the tuff was identified from a X-ray record (Fig.1). This mineral is accompanied by cristobalite (C), quartz (Q) and carbonate (D). The reflections of feldspar were filtered out from the X-ray record. The values of measured inter-planar distances are presented in 10⁻¹⁰ m and they are compared with table values of card register JCPDS [6].

The curve of differential thermic analyses of clinoptilolite does not show strong thermic effects in temperature

range 40 – 1000°C. A gradual loss of molecular water is characteristic for zeolite minerals, which course is recorded by thermo-gravimetric curve (Diagram 2) [5].

Preparation of Zeolite Sample as Reference Material

A zeolite sample with weight about 100 kg was taken from the open pit mine at the Majerovce deposit and delivered for subsequent processing to Geo-analytical Laboratories of Geological Survey of Slovak Republic in Spišská Nová Ves. The preparation of candidate reference material consisted of the following steps: sample adaptation, check of granularity, homogeneity test, stability test, inter-laboratory comparative tests, statistic evaluation of recorded data and determination of certified values.

Sample Treatment

The whole 100 kg sample was dried at a temperature of 40°C, crushed in a jaw crusher in two steps to granularity of 2 and 0.5 cm. The sample was reduced to two 50 kg samples by quartation. Both parts of the sample were then milled in a cylindrical mill to samples with granularity less than 0.1 cm. The sample was then reduced to 25 kg weight by quartation in rotary quartering equipment and then homogenised in an abrasionless agate mill to an analytical fineness with a grain size under 0.09 mm. The whole agated sample underwent grain size control by dry screening through a screen with holes 0.09 mm.

Homogenisation of Analytic Sample

For the purpose of ensuring of perfect homogeneity, the sample was homogenised for 24 hours in 50 litres PE container with sealed glass ampoule of technetium solution with activity 3.7 Gbq. The technetium solution caused ionisation of the container's content to prevent the

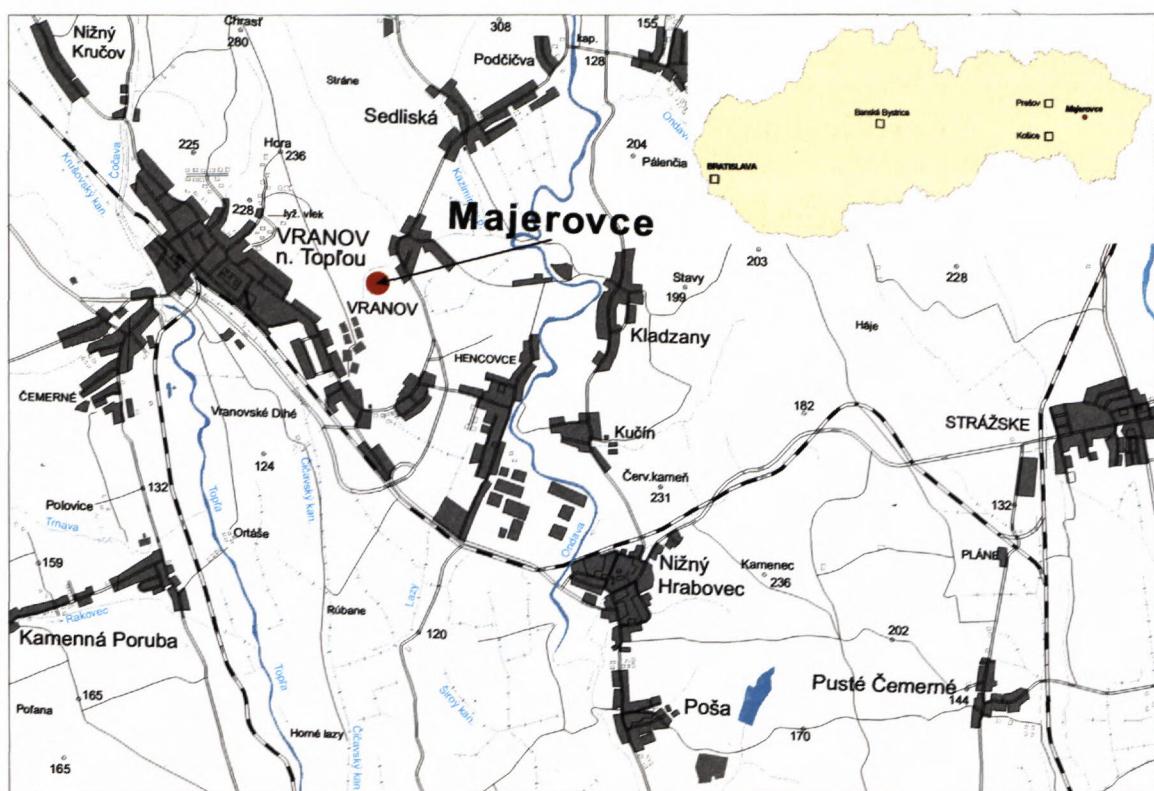


Figure 1 Map of the sample site at the Majerovce deposit

forming of an electrostatic charge and sample clustering during mixing. Immediately after homogenisation the sample was weighted by 50 g and 100 g into 100 and 200 ml PE vessels with a screwing seal, labelled and stored in a dark and dry chamber.

Homogeneity Control

Twenty vessels from the whole set of 500 vessels were selected by random sampling. The samples were then tested on variance of concentrations of selected elements, so-called tracers of inhomogeneity (macro elements Fe, K, Ti, and trace elements Ba, Pb, Sr, Zn), the variances were tested within a sample and among the samples. The concentrations represent also various concentration levels. The homogeneity control was made by quantitative analyses of the above-mentioned elements in energo-dispersion X-ray fluorescence spectrometer SPECTRO X-LAB 2000, (Mackových 1999) [7].

The evaluation of homogeneity was done in accordance with Slovak Technical Standard (STN) No. 01 2841 [8] and ISO Guide 35 [9]. Because the tests confirmed the suitable homogeneity of all monitored components, the inter-laboratory comparative testes could be performed.

Analytic Data Evaluation and Statistical Analyses

21 foreign and 6 Slovak laboratories took part in certification of reference material (Tab.1).

The analysed sample was from 4 separate charges. Delivered analytical data were statistically evaluated by programme for inter-laboratory test - ISO 5725 [10] and according to following standards: STN 01 2841 [8] and ISO Guide 35 [9]. Statistical analyses and expertise were used to identify the statistically outlying values, which were excluded from the data set used in the following evaluation process. The prepared analytical data were evaluated according to ISO Guide 35 criteria for preparation of RM and they were divided into certified and un-certified values (Tab. 2) (Lučivjanský, Mackových 1999) [11].

The following criteria were chosen for determination of certified values:

- data, entering certification process of one element, must be obtained minimally from two independent analytical methods,
 - the set of processed data must be from 6 laboratories at least,
 - the uncertainty of measurement must be smaller than: 6 % from base value of element for concentration range 0.1 – 100 %
12 % from base value of element for concentration range 1 – 999 µg/g
18 % from base value of element for concentration range 1 – 999 ng/g

The components of which the recorded data set has not fulfilled these criteria have been included among informative, uncertified values.

Tab.1. Names of participating laboratories

No.	Organisation	City	Country
1.	<i>British Geological Survey</i>	Nottingham	Great Britain
2.	<i>CEVA, s.r.o.</i>	Trenčín	Slovakia
3.	<i>Czech Geological Survey, Analytical Laboratory</i>	Prague	Czech Republic
4.	<i>ECOCHEM-stredisko ICP,</i>	Prague	Czech Republic
5.	<i>Ekologické laboratória, s. r. o.</i>	Spišská Nová Ves	Slovakia
6.	<i>Federal Institute for Geosciences and Natural Resources</i>	Hannover	Germany
7.	<i>Geoekologické laboratóriá š.p.</i>	Turčianske Teplice	Slovakia
8.	<i>Geological Institute of Hungary, Laboratory</i>	Budapest	Hungary
9.	<i>Geological Institute of Romania, Environmental Geochemistry Department</i>	Bucharest	Romania
10.	<i>Geological Survey of Austria</i>	Wien	Austria
11.	<i>Geological Survey of Estonia</i>	Tallinn	Estonia
12.	<i>Geological Survey of Finland, Chemical Laboratory</i>	Espoo	Finland
13.	<i>Geological Survey of Norway, Laboratory Section</i>	Trondheim	Norway
14.	<i>Geologická služba SR, Geoanalytické laboratóriá</i>	Spišská Nová Ves	Slovakia
15.	<i>Geologický ústav SAV</i>	Bratislava	Slovakia
16.	<i>Institute of Geology of Lithuania, Spectroscopy Laboratory</i>	Vilnius	Lithuania
17.	<i>Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Wrocław University of Technology</i>	Wrocław	Poland
18.	<i>Katedra chemie, Zemědělská fakulta</i>	Ceske Budejovice	Czech Republic
19.	<i>Netherlands Inst. of Applied Geoscience TNO – National Geological Survey, Section of Geochem. Lab.</i>	Haarlem	The Netherland
20.	<i>Okręgowa Stacja Chemiczno-Rolnicza w Warszawie</i>	Warszawa	Poland
21.	<i>Polish Geological Institute, Central Chemical Laboratory</i>	Warszawa	Poland
22.	<i>U.S. Geological Survey, Colorado</i>	Denver	U.S.A.
23.	<i>University of Pavia, Laboratorio Energia Nucleare Applicata</i>	Pavia	Italy
24.	<i>University of Ljubljana, Dep. of Chemistry, National Institute of Chemistry</i>	Ljubljana	Slovenija
25.	<i>Vernadsky Institute of Geochemistry and Anal. Chemistry RSA</i>	Moscow	Russia
26.	<i>VSEGEI HIMLAB</i>	St.- Petersburg	Russia
27.	<i>VSŽ LABORTEST s.r.o</i>	Košice	Slovakia

Table 2 Certified Values:

Component	Al ₂ O ₃	CaO	Fe ₂ O ₃ Total	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅	SiO ₂	TiO ₂	As	Ba	Be	Ce	Cs
Unit	%	%	%	%	%	%	%	%	%	%	µg/g	µg/g	µg/g	µg/g	µg/g
Certified value	12.21	4.51	1.75	2.19	1.41	0.045	0.612	0.055	67.11	0.190	1.96	779	1.96	52.3	3.88
Uncertainty U _c	0.16	0.08	0.03	0.04	0.02	0.001	0.011	0.003	0.31	0.003	0.09	13	0.08	2.6	0.13
np	70	79	79	68	75	18	63	54	58	63	38	60	26	21	18

Component	Cu	Ga	Hg	La	Pb	Rb	Sb	Sr	V	Y	Zn	Zr
Unit	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Certified value	5.12	13.9	0.329	32.6	20.8	95.7	0.379	617	12.6	21.8	38.2	158
Uncertainty U _c	0.25	0.2	0.008	1.2	0.4	1.9	0.025	6	0.4	0.7	1.2	3
np	58	31	30	16	67	44	22	48	51	48	87	24

np – number of accepted laboratory measurements

Uncertified Values:

Component	LOI	Ag	Bi	Cd	Co	Cr	Dy	Er	Eu	Gd	Ge	Hf	Ho	In
Unit	%	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Uncertified value	9.49	0.040	0.198	0.065	2.26	4.33	3.72	2.51	0.565	3.31	1.62	4.05	0.693	0.026
Uncertainty U _c	0.36	*	*	0.011	0.21	0.52	*	*	0.059	*	*	0.63	*	*

Component	Li	Lu	Mo	Nb	Nd	Ni	Pr	Sc	Se	Sm	Sn	Ta	Tb
Unit	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Uncertified value	14.1	0.337	1.57	11.9	22.0	2.86	6.54	5.13	0.260	3.66	3.05	0.94	0.570
Uncertainty U _c	2.5	*	*	1.8	0.9	0.29	*	0.36	*	0.12	0.23	*	*

Component	Th	Tl	Tm	U	W	Yb
Unit	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Uncertified value	10.40	0.467	0.420	4.51	2.60	2.69
Uncertainty U _c	0.72	0.109	*	0.43	*	0.33

* number of accepted laboratory means < 2

Evaluation of Used Analytical Methods

The most frequently used analytical method for determination of certified values of the main elements (10 elements) was atomic emission spectrometry with inductively coupled plasma (AES-ICP) – 69 times, X-ray fluorescence spectrometry (RFS) – 66 times and atomic absorption spectrometry (AAS) - 24 times. Except of these methods, the methods as gravimetry and photometry were used – 25 times. Some of the used analytical methods do not have the same level of precision or reproducibility of repeated measurements. The assessment of the standard deviation values for repeatability and reproducibility of the measurements found as the most suitable methods: atomic emission spectrometry with inductively coupled plasma and X-ray fluorescence spectroscopy methods (Figure 2).

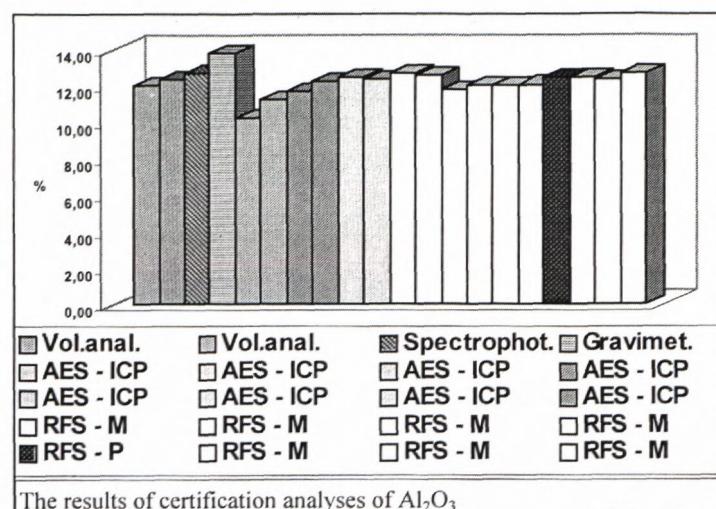


Figure 2. Comparison of analytic methods for determination of aluminium gained from 20 laboratories

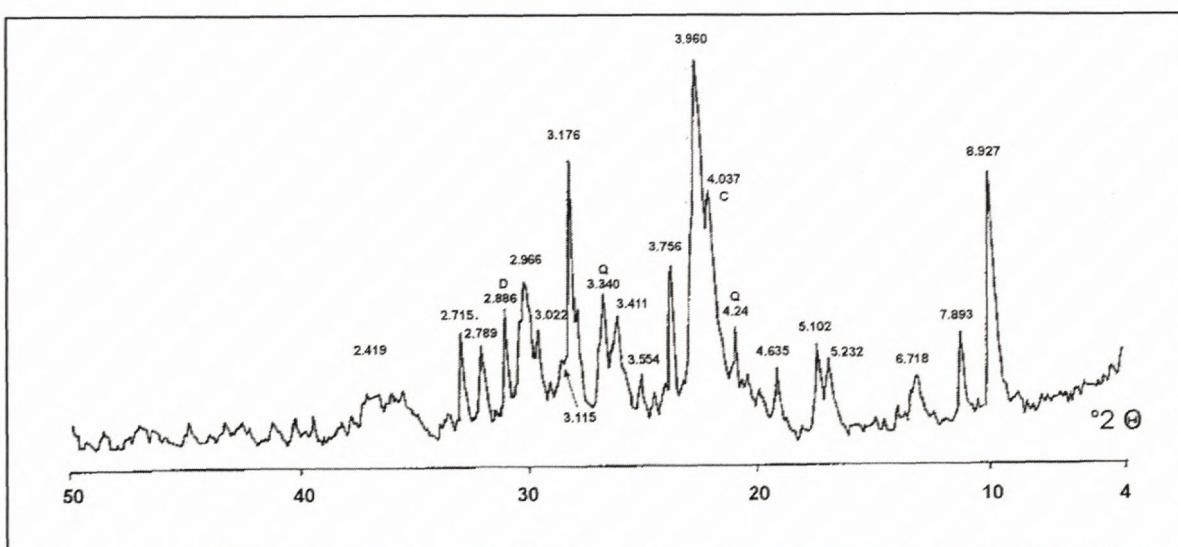


Diagram 1 – X-ray record of zeolite tuff from the Majerovce deposit

Certified values of trace elements (17 elements) were most frequently determined by X-ray fluorescence spectrometry method – 62 times and atomic emission spectrometry with mass detection (AES-ICP/MS) – 62 times. The other used methods were: atomic absorption spectrometry with added techniques – 41 times, atomic emission spectrometry with inductively coupled plasma – 22 times, optic emission spectrometry and neutron activation analyses – 13 times.

The determination of the main and trace elements by AES-ICP and AAS methods were done after absolute decay of sample in mineral acid mixture or after alkaline melting of the sample. In AES-ICP/MS method only decay in mineral acids including HF was used. In RFS method two kinds of sample preparation were used. The main elements were determined from melted borate pearls (RFS-M), and trace elements were analysed from pressed tablets (RFS-P).

Conclusion

The selection of geologic reference materials with aluminosilicate matrix was widened by preparation of the certified reference material "Zeolite 1".

The process of preparation and certification was performed under the patronage of the Slovak Metrology Institute, Bratislava, in accordance with international standards ISO Guide 34 [12] and ISO Guide 35 [9]. 6 Slovak and 21 foreign laboratories took part in the certification.

10 certified values for the major matrix elements, 17 certified and 33 uncertified values for trace elements have widened the spectrum of possibilities of analysts in providing of reliability verification of analytic data, precision and accuracy of analytic processes and evaluation of methods used in testing laboratories.

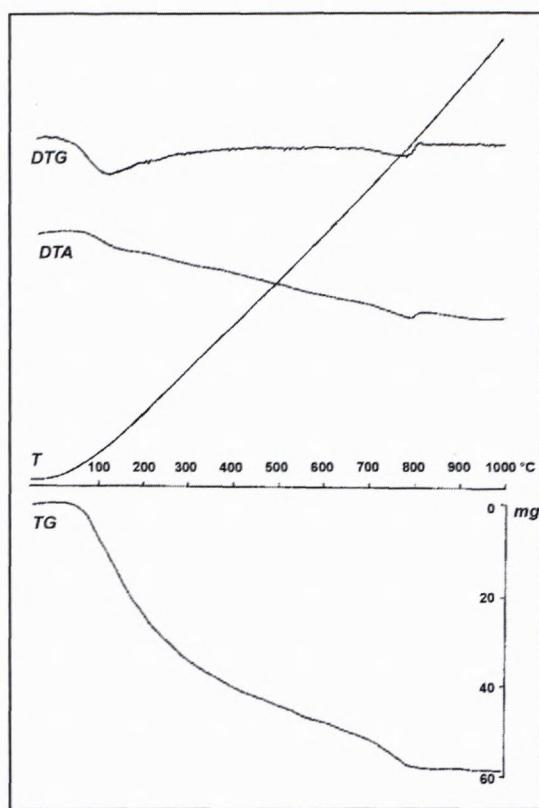


Diagram 2 – Thermic analysis record of zeolite tuff from the Majerovce deposit

References

- [1] TPM 8701-99, 1999: Technický predpis metrologický. Princípy tvorby a certifikácie referenčných materiálov v Slovenskej republike (in Slovak).
- [2] STN 01 2801, 1997: Certifikované referenčné materiály (in Slovak).
- [3] STN 99 8073, 1997: Klasifikácia a metrologické charakteristiky referenčných materiálov (in Slovak).
- [4] Hudáček, J., 1994: Majerovce – Zeolity: Vyhľadávací prieskum č.u. 11 92 1515, Slovenská Geológia š.p. Spišská Nová Ves, Manuscript (in Slovak), 141.
- [5] Hricová, M. & Ondíková, H. 1999: Archív analytickej databázy Geoanalytických laboratórií Spišská Nová Ves, Manuscript (in Slovak).
- [6] JCPDS, 1974: Joint Committee on powder diffraction standards, Pennsylvania 19081, U.S.A.
- [7] Mackových, D., 1999: Štandardizácia- Vývoj analyt. metodiky kvantitatívneho stanovenia hlavných matricových a stopových prvkov v geologických materiáloch a environmentálnych vzorkách metódou energodisperznej röntgenfluorescenčnej spektrometrie a vypracovanie odvetvovej technickej normy MŽP SR, Záverečná správa, Spišská Nová Ves, Manuscript (in Slovak), 22.
- [8] STN 01 2841, 1988: Referenčné materiály- Metodika prípravy atestácie referenčných materiálov zloženia hornín a nerastných surovín (in Slovak).
- [9] ISO Guide 35, Certification of reference materials – General and statistical principles, Second edition 1989 (Certifikácia referenčných materiálov. Všeobecné a štatistické princípy).
- [10] ISO 5725, 1997: Program for Interlaboratory Studies, dánsky softvér z Water Quality Institute, Horsholm.
- [11] Lučivjanský, P. & Mackových, D., 1999: Certifikácia kandidujúceho referenčného materiálu Zeolit I, Záverečná správa, Spišská Nová Ves, Manuscript (in Slovak), 29.
- [12] ISO Guide 34, Quality system requirements for reference materials producers, First edition ISO 1994 (Požiadavky na systém kvality pre výrobcov referenčných materiálov).