INSTYTUT CHEMII I TECHNIKI JĄDROWEJ

POLISH CERTIFIED REFERENCE MATERIAL

FOR MULTIELEMENT TRACE ANALYSIS WITH THE SPECIAL EMPHASIS ON RARE EARTH ELEMENTS

APATITE CONCENTRATE (CTA-AC-1)

GENERAL INFORMATION

INTENDED USE:	CHECKING THE ACCURACY OF ANALYTICAL WORK OF THE LABORATORIES ENGAGED IN THE DETERMINATION OF TRACE ELEMENTS IN MINERAL SAMPLES. CALIBRATION OF APPARATUS AND METHODS.
ELEMENTS FOR WHICH CERTIFIED CONCENTRATIONS COULD BE ESTABLISHED:	Ba, Ca, Ce, Co, Cu, Eu, Gd, Hf, La, Lu, Mn, Na, Nd, Sc, Si, Sm, Ta, Tb, Th, Ti, U, V, Y, Yb, Zn.
ELEMENTS FOR WHICH NON-CERTIFIED "INFORMATION" VALUES ARE AVAILABLE:	Al, Dy, Er, Fe, Ho, K, Mg, Ni, Pr, Sr, Zr.

Produced and certified by:

COMMISSION OF TRACE ANALYSIS OF THE COMMITTEE FOR ANALYTICAL CHEMISTRY OF THE POLISH ACADEMY OF SCIENCES
and
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ORIGIN, PREPARATION AND TESTING

Apatite concentrate (ca. 50 kg) originating from Kola Peninsula (USSR), and used in Polish chemical industry as a raw material for the production of phosphoric acid, was supplied by prof. dr U. Glabisz (Polytechnic Institute, Szczecin). The material was sieved to get the particle size of $\varnothing < 0.125$ mm. The material was further homogenized by mixing for 16 hrs. in a plastic drum rotated in three directions. Preliminary homogeneity testing was performed determining Fe and Y contents by X-ray fluorescence in several subsamples of the material taken from the drum.

Distribution of 50 g portions into wide-mouthed, air-tight polyethylene bottles was achieved with the aid of a specially constructed teflon scoop. Final homogeneity testing was performed by instrumental neutron activation analysis, analyzing several subsamples taken from 6 individual bottles chosen at random and comparing the results with the results for 6 subsamples taken from one bottle.

Statistical comparison of results for Eu, La, Na, Nd, Tb and Th obtained in the two series of measurements confirmed good homogeneity of the material, at least for sample weight of $\geqslant 100$ mg.

CERTIFICATION

Assigning of "recommended" (certified) values was done on the basis of world-wide intercomparison in which 58 laboratories participated. Their cooperation is gratefully acknowledged.

The laboratories contributed 3101 bits of chemical information (802 laboratory means) on 67 elements.

Statistical evaluation of results for individual elements was performed by the method published previously [1].

The outlying results from the population of laboratory averages were rejected by concurrent use of the four criteria i.e. those of Dixon, Grubbs, coefficient of skewness, and coefficient of kurtosis at significance level of 0.05, followed by calculation of overall mean, confidence limits etc.

The criteria used to decide whether the overall mean can be given the status of "recommended" (certified) value were as follows:

1. Relative uncertainty of the overall mean:

$$\frac{S.D. \cdot t_{0.05}}{\sqrt{N} \cdot \bar{X}} \leq 20\% \text{ (trace element)}$$
$$\leq 10\% \text{ (major elements)}$$

or relative standard deviation

$$\frac{S.D.}{\bar{X}} \leq 25\% \text{ (trace elements)}$$
$$\leq 15\% \text{ (major elements)}$$

For the purpose of this work elements with concentration exceeding 0.5 % (5000 ppm) were considered to be major elements.

2. The overall mean was calculated from at least 3 laboratory averages obtained by more than one analytical technique. If results from only one analytical technique are available the number of laboratory averages cannot be smaller than 5.

3. If the conditions (1) and (2) are fulfilled but the number of outliers exceeds 50 %, the additional procedure is activated which checks the changes of the mean and standard deviation respectively accompanying successive rejections.

The process of rejecting of outliers is then stopped when the change in both the mean and standard deviation becomes lower or equal to 15%.

"Information" values were assigned to those elements for which the results while not fulfilling conditions (1)–(3) still fulfilled the following condition:

$$\frac{S.D. \cdot t_{0.05}}{\sqrt{N} \cdot \bar{X}} \leq 50\% \text{ (trace element)}$$
$$\leq 30\% \text{ (major elements)}$$

"RECOMMENDED" VALUES FOR CTA-AC-1

MAJOR ELEMENTS

Element	Concentration [wt%]
Ca	32.7 ± 3.1
Si	0.57 ± 0.13

TRACE ELEMENTS

Element	Concentration [mg/kg (ppm)]	Element	Concentration [mg/kg (ppm)]
Ba	767 ± 79	Sc	0.244 ± 0.035
Ce	3326 ± 175	Sm	162 ± 24
Co	2.72 ± 0.28	Ta	2.65 ± 0.23
Cu	54.0 ± 4.5	Tb	13.9 ± 1.5
Eu	46.7 ± 1.3	Th	21.8 ± 2.1
Gd	124 ± 23	Ti	2927 ± 554
Hf	1.13 ± 0.17	U	4.4 ± 0.9
La	2176 ± 94	V	104 ± 10
Lu	1.08 ± 0.16	Y	272 ± 53
Mn	317 ± 50	Yb	11.4 ± 2.0
Na	3841 ± 564	Zn	38.0 ± 7.6
Nd	1087 ± 124		

"INFORMATION" VALUES FOR CTA-AC-1

MAJOR ELEMENTS

Element	Concentration [wt%]
Al	0.41
Fe	0.50
Sr	2.0

TRACE ELEMENTS

Element	Concentration [mg/kg (ppm)]
Cr	13
Dy	78
Er	26
Ho	9
K	2088
Mg	435
Ni	9
Pr	353
Zr	51

The preparation and certification of the CTA-AC-1 certified reference material was performed by the staff of the Department of Analytical Chemistry, Institute of Nuclear Chemistry and Technology, under the direction of prof. dr hab. R. Dybczyński

[1] R. Dybczyński, Analytica Chimica Acta, 117, 53-70 (1980)

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