INSTYTUT CHEMII I TECHNIKI JĄDROWEJ

POLISH CERTIFIED REFERENCE MATERIAL

FOR MULTIELEMENT TRACE ANALYSIS

FINE FLY ASH (CTA – FFA – 1)

GENERAL INFORMATION

INTENDED USE:

CHECKING THE ACCURACY OF ANALYTICAL WORK OF THE LABORATORIES ENGAGED IN THE DETERMINATION OF TRACE ELEMENTS IN MINERAL AND ENVIRONMENTAL SAMPLES. CALIBRATION OF APPARATUS AND METHODS.

ELEMENTS FOR WHICH CERTIFIED CONCENTRATIONS COULD BE ESTABLISHED:

Al, As, Ba, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, F, Fe, Gd, Hf, La, Li, Lu, Mn, Na, Nd, Ni, P, Pb, Rb, Sb, Sc, Si, Sm, Sr, Ta, Tb, Th, Tm, U, V, W, Y, Yb, Zn.

ELEMENTS FOR WHICH NON-CERTIFIED „INFORMATION" VALUES ARE AVAILABLE:

Be, Ca, Cd, Ga, In, K, Mg, Mo, Se, Ti.

Produced and certified by:

COMMISSION OF TRACE ANALYSIS OF THE COMMITTEE FOR ANALYTICAL CHEMISTRY OF THE POLISH ACADEMY OF SCIENCES

and

INSTITUTE OF NUCLEAR CHEMISTRY AND TECHNOLOGY, UL. DORODNA 16, 03-195 WARSZAWA, POLAND

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ORIGIN, PREPARATION AND TESTING

Fine fly ash (ca. 60 kg) originating from the 3rd zone of electrofilters at Kozienice power station (Poland), was supplied by Mrs. M. Małusecka (Department of Power Stations' Waste Utilization, Katowice). Over 93% of the material passed trough the 0.06 mm sive. The material was 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 50g 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 for 6 subsamples taken from one bottle. Statistical comparison of results for Co, Cr, Fe, La, Sc, and Th obtained in the two series of measurements confirmed good homogeneity of the material, at least for sample weight of $m \geq 100$ mg.

CERTIFICATION

Assigning of "recommended" (certified) values was done on the basis of world–wide intercomparison in which 63 laboratories participated. The laboratories contributed 4282 bits of chemical information (1041 laboratory means) on 65 elements. Their cooperation is gratefully acknowledged.

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:

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

$$\leqq 10\% \text{ (major elements)}$$

or relative standard deviation

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

$$\leqq 15\% \text{ (major elements)}$$

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%, and the condition (1) is rechecked.

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

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

$$\leqq 30\% \text{ (major elements)}$$

"RECOMMENDED" VALUES FOR CTA–FFA–1

MAJOR ELEMENTS

Element	Concentration [wt%]
Al	14.87 ± 0.39
Fe	4.89 ± 0.14
Na	2.19 ± 0.08
Si	22.48 ± 0.92

TRACE ELEMENTS

Element	Concentration [mg/kg (ppm)]	Element	Concentration [mg/kg (ppm)]
As	53.6 ± 2.7	Ni	99.0 ± 5.8
Ba	835 ± 56	P	725 ± 74
Ce	120 ± 7	Pb	369 ± 46
Co	39.8 ± 1.7	Rb	185 ± 5
Cr	156 ± 8	Sb	17.6 ± 2.5
Cs	48.2 ± 2.6	Sc	24.2 ± 1.1
Cu	158 ± 9	Sm	10.9 ± 0.6
Dy	9.09 ± 1.45	Sr	250 ± 13
Er	4.52 ± 1.12	Ta	2.11 ± 0.16
Eu	2.39 ± 0.06	Tb	1.38 ± 0.14
F	198 ± 39	Th	29.4 ± 0.7
Gd	10.0 ± 2.6	Tm	0.705 ± 0.200
Hf	6.09 ± 0.45	U	15.1 ± 0.8
La	60.7 ± 4.0	V	260 ± 10
Li	128 ± 22	W	10.5 ± 1.1
Lu	0.658 ± 0.043	Y	45.0 ± 13.5
Mn	1066 ± 41	Yb	4.24 ± 0.19
Nd	56.8 ± 3.7	Zn	569 ± 58

"INFORMATION" VALUES FOR CTA–FFA–1

MAJOR ELEMENTS		TRACE ELEMENTS	
Element	Concentration [wt%]	Element	Concentration [mg/kg (ppm)]
Ca	2.29	Be	27
K	2.20	Cd	2.8
Mg	1.55	Ga	49
Ti	0.58	In	0.34
		Mo	17
		Se	4.6

The preparation and certification of the CTA–FFA–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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It has been complied
with the requirements of ISO Guide 34

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FINE FLY ASH (CTA-FFA-1)

1. **The stability of Fine Fly Ash (CTA-FFA-1) has been monitored during storage. On the basis of the obtained results, the shelf life is extended until 31 December 2027.**
2. The material is stored in an air conditioned room, in which the temperature does not exceed 22°C. Its stability is monitored at appropriate time intervals.
3. The users should store the material at room temperature [(20±5)°C] in tightly closed original containers.
4. For chemical analysis and simultaneous determination of water content, samples of the material of adequate size should be taken. Immediately after sampling, it is necessary to cover firmly the container. The unused part of samples must not be placed back in the container.

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