

# Analytical Calibration of the Energy Dispersive X-Ray Spectrometer

## I. Preparation of the Reference Samples for the Determination of Main and Minor Elements in Airborne Dust\*

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Received 16 October 2002

The airborne dust particles and the reference powder samples for energy dispersive X-ray spectrometers need to be captured on the membrane filters under identical physical conditions. Therefore, a special spray chamber was developed for the powder capturing process.

The preparation of the thin-layer reference powder samples is a basic problem of the analytical calibration of energy dispersive X-ray spectrometers.

Substantial aim of the present work is the determination and verification of the optimum capturing conditions for particles of the reference powder materials for the analytical calibration process. The chemical analysis of the airborne dust particles captured on the membrane filters is a very complicated experimental problem [1, 2]. The quantitative separations of the dust particles from the surface of membrane filters are unfeasible. Therefore it is necessary to dissolve the membrane filters with the captured dust particles before the analysis, or to use an indirect physicochemical method for the direct analysis of membrane filters. The application of the energy dispersive X-ray spectrometry is a sufficient effective method [3] for this problem. But the analytical calibration of thin-layer samples is especially problematic [4].

### EXPERIMENTAL

The reference samples are prepared either by suction of dispersed reference solutions on membrane filters [5], or by the capturing of aerosols of the reference powder samples on the PRAGOPOR 4 membrane filters [2, 6]. In the concrete case the direct method of the use of powder materials [1, 2, 7, 8] was chosen. The preparation of powder thin layers of reference samples was realized in quartz vessel (Fig. 1). The dispersion of powder materials was reached by vibration [9] and the transport of dispersed sample was conditioned by N<sub>2</sub> flow gas. The applied amplitude of the vibration

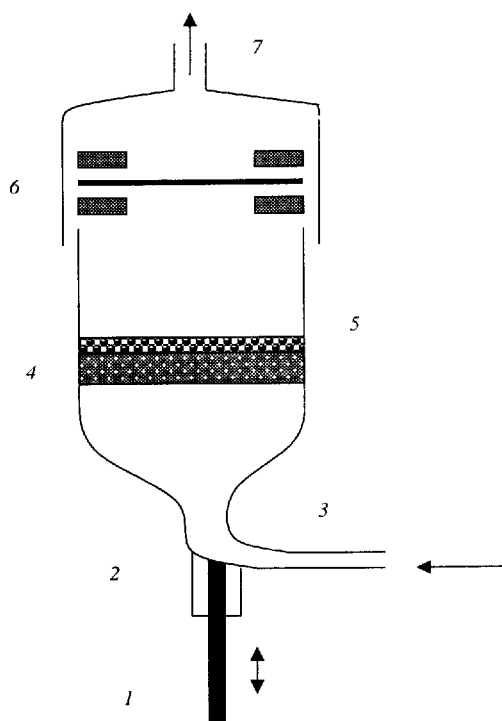


Fig. 1. Scheme of the sputtering vessel of reference samples. 1. The shoulder of the vibrator, 2. holder of the vessel, 3. inlet of the flow gas, 4. the glass frit, 5. the sputtered sample, 6. the membrane filter, 7. exhaust of the flow gas.

was  $\pm 0.5$  mm, the number of vibrations  $100 \text{ s}^{-1}$ , the flow rate of N<sub>2</sub> carrier gas was  $1 \text{ dm}^3 \text{ min}^{-1}$  and the mass of powder material in the vessel was *ca.* 400 mg.

\*Presented at the XVth Slovak Spectroscopic Conference, Košice, 23—27 June 2002.

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**Table 1.** Composition of the Reference Samples of Airborne Dust

Component	Reference samples <i>w</i> /%			
	I	II	III	IV
C (graphite)	32.7	30.0	23.6	30.0
SiO <sub>2</sub>	30.0	33.0	35.0	30.0
CaO	17.0	9.0	2.0	15.0
MgO	2.0	12.0	20.0	15.0
Fe <sub>2</sub> O <sub>3</sub>	17.0	5.0	10.0	5.0
Al <sub>2</sub> O <sub>3</sub>	1.0	9.0	4.0	5.0

This dispersion process guaranteed under the 60 s long exposure a compact thin layer of the mass 5–10 mg. The membrane filters powder thin layer was fixed by varnishing hair spray.

## DISCUSSION

The calibration of energy dispersive X-ray spectrometers is realized by the powder reference samples or certified standards (guaranteed reference materials). These do not always express truly the chemical character of the analyzed matrices. Powder reference samples have to be comparable with real airborne dust particles not only from the chemical viewpoint but also from the physical one. And it is a fundamental problem to prepare these samples [1, 2]. The chemical composition of the main and minor components of four types of the Slovak airborne dusts [10] is given in Table 1. The particle size of the single oxide of Al, Ca, Fe, Mg, Si and the graphite (C) and also of the mixture IV was measured on the Micro Photo Sizer, Seishin, Japan instrument. In Table 2 are given the used solutions in which the size of particles was classified and their abundances determined.

**Table 2.** Measuring of the Frequency of Particles Diameter Classes of the Used Chemical Compounds for the Analytical Calibration

Diameter classes $\phi/\mu\text{m}$	<i>w</i> /%						
	Al <sub>2</sub> O <sub>3</sub> (C <sub>2</sub> H <sub>5</sub> OH)	C (H <sub>2</sub> O)	CaO (H <sub>2</sub> O)	Fe <sub>2</sub> O <sub>3</sub> ((CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> OH)	SiO <sub>2</sub> (H <sub>2</sub> O)	MgO (H <sub>2</sub> O)	Mixture of oxides (C <sub>2</sub> H <sub>5</sub> OH)
0.0–2.0	47.41	42.78	66.81	65.91	34.11	45.77	53.98
2.0–4.0	4.23	11.48	23.57	8.02	8.55	20.40	17.25
4.0–10.0	7.64	12.69	9.62	10.56	23.34	19.78	13.69
10.0–20.0	14.44	13.09	0.00	9.44	15.08	10.32	7.75
20.0–30.0	19.96	12.68	0.00	4.05	10.58	3.51	6.20
30.0–40.0	6.32	7.28	0.00	2.03	8.34	0.22	1.13
0.0–10.0	59.28	66.95	100.0	84.49	66.0	85.95	84.92

**Table 3.** Statistical Figures of Merit of the Particles Sizes

X	Al <sub>2</sub> O <sub>3</sub>	C	CaO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	MgO	Mixture of oxides
$\bar{d}(X)/\mu\text{m}$	21.78	21.00	2.66	15.32	20.35	11.07	14.39
$s_d(X)/\mu\text{m}$	± 9.66	± 11.06	± 2.66	± 11.40	± 11.43	± 8.64	± 10.71
$\tilde{d}(X)/\mu\text{m}$	23.91	23.30	3.01	15.29	22.02	10.16	14.70

$\bar{d}(X)$  – arithmetical mean of the X particle diameters,  $s_d(X)$  – standard deviation,  $\tilde{d}(X)$  – median value.

**Table 4.** Change of Particles Size during the Sputtering

Diameter classes $\phi/\mu\text{m}$	Remains of oxide mixtures after sputtering/%	Sputtered oxide mixtures on the filter/%
0.0–2.0	41.58	41.06
2.0–4.0	22.92	15.39
4.0–10.0	20.82	24.74
10.0–20.0	7.60	16.26
20.0–30.0	3.15	2.54
30.0–40.0	3.93	0.00
0.0–10.0	85.32	81.20
Dispersive solution	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>5</sub> OH

The particle size analysis (Table 2) confirmed that pure oxides of Al, Ca, Fe, Mg, Si as well as the graphite (C) are characterized by high proportionality of grain size diameter to  $10\ \mu\text{m}$ . From the atmospheric particles mainly this grain size is captured by the sampling of the airborne dust. The measuring confirmed that in the case of Ca, Mg, and Fe oxides just this grain size range is dominant. By adding of graphite powder the amount of particles of grain size under  $10\ \mu\text{m}$  increases. Identity of figures of the merit (the arithmetical mean  $\bar{d}(X)$  with the median  $\tilde{d}(X)$ ) confirmed the validity of the statistical evaluation (Table 3). The average grain size diameter is *ca.*  $14.4\ \mu\text{m}$ . This value is near to the optimal  $10\ \mu\text{m}$  value. Finally the problem of the eventual change of the grain size classes by the dispersion process was verified. The results also confirmed that the 10 min long dispersion did not change markedly the grain diameter of the sprayed material (Table 4).

Novel equipment was developed for the analytical calibration of membrane filters. In this equipment the model powder mixtures of reference samples were sputtered by the gas flow and actual vibration. The powder particles of the size between  $1\text{--}10\ \mu\text{m}$  were captured on the PRAGOPOR 4 membrane filter. So prepared filter was used for the analytical measurement.

*Acknowledgements.* This work was supported by the Slovak Grant Project No. 1/7418/2000 and the Slovak-German International Cooperation Project No. SVK-005-1998. The authors are obliged to express their gratitude for these supports.

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