

# Mobility of Important Toxic Analytes in Urban Dust and Simulated Air Filters Determined by Sequential Extraction and GFAAS/ICP-OES Methods\*

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The modified BCR three-step sequential extraction procedure has been applied to homogenized urban dust samples and to simulated air filters loaded with the prepared urban dust *via* the wet deposition procedure. This work has been focused on comparative study of the distribution of trace elements in both samples and evaluation of the factors influencing the reliability of results with respect to the proposed extraction procedure. Extracted chemical fractions were analyzed by ICP-OES and GFAAS depending on the concentration levels of investigated trace elements As, Cd, Cr, Mn, Ni, and Pb, selected according to their adverse effect on the human health. Statistically evaluated results indicate significant differences between the extracted portions of analytes in urban dust and simulated air filters, where the mobility of some analytes in simulated air filters was higher than that in urban dust samples. The impact of surfactant Triton X-100 (0.05 vol. %) on the extraction procedure was also investigated.

**Keywords:** sequential extraction, trace elements, urban dust, air filter, ICP-OES, GFAAS

## INTRODUCTION

Urban dust is an important carrier of heavy metals and metalloids, which are introduced into the atmosphere with the movement of wind, cars, trains, *etc.* Depending on the particle size, the inhalation and deposition of dust particles in the alveolar regions occurs and then, the biologically available toxic elements can affect human health.

In the frame of a large-scale project “System of Monitoring the Environmental Impact on Population Health in the Czech Republic”, established in 1994, the group of trace elements As, Cd, Cr, Mn, Ni, Pb, (Zn) in outdoor air is monitored. For that purpose, dust samples are collected on acetyl cellulose filters (diameter of 47 mm and pore size 0.45  $\mu\text{m}$ ) and the total element concentrations are evaluated in order to assess the overall pollution level of individual pollutants [1]. However, more precise estimation of the po-

tential toxicity and risk of trace elements is based on the knowledge of the distribution of pollutant chemical forms. Useful information about environmental metal activity, mobility and possible bioavailability can be obtained by the methods based on a sequential chemical extraction, applied to solid samples, including urban dust, fly ash, and atmospheric deposits [2]. Unfortunately, reliability of the element determination and speciation is insufficient due to the lack of proper quality assurance programs and suitable standard reference materials. Until now, validation and harmonization of the BCR sequential analytical scheme was fulfilled only for two sediments, namely CRMs BCR 601 and 701.

In the present study slightly modified 3-step BCR sequential extraction procedure was applied to the urban dust samples and to the simulated air filters prepared by the filtration of a suspension of the same urban dust sample [3–5]. Additionally, a comparative

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study was carried out in the presence of surfactant Triton X-100. Based on the experimental data, a new procedure of sequential chemical extraction was proposed having potential to be included to the methods used by running the program of the System of Monitoring.

## EXPERIMENTAL

### Sampling

Sample of urban dust was collected in a sedimentation chamber of the ventilation system of Prague automobile tunnel, Letná, which was not cleaned at least for one year before the sampling. Collected sample was sterilized by irradiation with photons of  $^{60}\text{Co}$  at 25 kGy and sieved to obtain a fraction of the particulate matter with the particle size  $< 50$  mesh. This fraction was jet-milled twice and homogenized in V-shape blender for 48 h. According to the particle size distribution curve, the most populated was the fraction of particles with diameter of 3–4  $\mu\text{m}$ . Details of the sampling and homogenization procedure were published elsewhere [4, 6, 7].

Simulated air filters were prepared by the filtration of water suspension of homogenized urban dust containing TRITON X-100 surfactant (0.05 vol. %) through acetyl cellulose membrane filters (diameter of 47 mm and pore size 0.45  $\mu\text{m}$ ). The suspension of urban dust was vigorously stirred using ultra sound and mechanical stirrer. During the measurement, the suspension was kept circulating through the measuring cell. From 1  $\text{dm}^3$  of the suspension containing on an average 60 mg of dust, 12–13 filters were prepared, each of them loaded with approximately 4 mg of dust particles. This amount of dust corresponds to that usually collected weekly by the System of Monitoring [4]. Changes of the particle size occurred during equilibration of the particulate material in suspension, broadening and shifting the most populated fraction of particles (3–4  $\mu\text{m}$ ) towards higher values [6, 7].

### Instrumentation and Analysis

Higher concentrations of Cd, Cr, Mn, Ni, and Pb were determined by ICP-OES (Varian, VistaPro, Australia) equipped with an autosampler (SPS-5), an inert parallel flow nebuliser, an inert spray chamber, and demountable torch with an inert injector tube. For the determination of As and low concentrations of other elements AAS (Perkin—Elmer, model 4000, Germany) equipped with a graphite furnace (HGA 500) and an autosampler (AS-40) was used. The decomposition of samples was performed in a microwave oven (Plazmatronika, Poland), extraction steps in shaker (LT2, Czech Republic), and sedimentation in centrifuge (Hettich Universal 30 RF, Germany). Particle size distribution measurements were

performed by a Mastersizer X device with a He—Ne laser (Malvern Instruments, UK) in laboratory of the International Atomic Energy Agency (IAEA) in Austria and described by *Kučera et al.* [6, 7].

ICP-MS analyses were carried out in an accredited laboratory Ecochem (Prague, Czech Republic), INAA (neutron activation analysis) and PIXE (proton induced X-ray emission) experiments were performed in the Nuclear Physics Institute of the Czech Academy of Sciences [4].

### Reagents

Ultrapure water with the resistivity of 18.2  $\text{M}\Omega \text{ cm}^{-1}$  was produced by a NANOpure system (Barnstead, USA). All other chemicals used in experiments, *i.e.*  $\text{CH}_3\text{COOH}$  (p.a.),  $\text{CH}_3\text{COONH}_4$  (p.a.),  $\text{NH}_2\text{OH} \cdot \text{HCl}$  (p.a.), 65 %  $\text{HNO}_3$ , 30 %  $\text{H}_2\text{O}_2$ , 48 % HF (Suprapur), and Pd modifier (10  $\text{g dm}^{-3}$ ), were supplied by Merck, Germany. As a reference material SRM 1648 Urban Particulate Matter (NIST, USA) was used.

### Sample Preparation

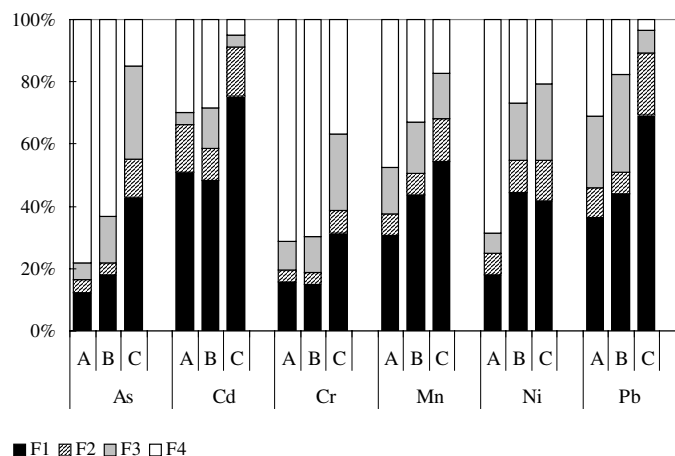
The homogenized urban dust sample (20 mg) was digested in a microwave oven using a mixture of high-purity concentrated acids  $\text{HNO}_3$  and HF and  $\text{H}_2\text{O}_2$  with the volume ratio of constituents of  $\varphi_r = 5 : 1 : 1$ . Samples prepared for ICP-OES and GF AAS measurements were stored in 5 vol. %  $\text{HNO}_3$  at +4°C. Reference material, SRM 1648 Urban Particulate Matter (NIST, USA), was used to verify the method reliability. Details of the verification procedure were described elsewhere [5].

The urban dust sample (100 mg) or 10 loaded filters were placed into centrifuge tubes and sequentially extracted. Exchangeable fraction (F1) was obtained by the sample extraction with 0.11  $\text{mol dm}^{-3}$   $\text{CH}_3\text{COOH}$  using a sample mass to solvent volume ratio of 1 : 50 for 16 h. The fraction bound to Fe/Mn oxides and carbonates (F2) was prepared by extraction with 0.1  $\text{mol dm}^{-3}$   $\text{NH}_2\text{OH} \cdot \text{HCl}$  using the ratio 1 g of solid matter per 50  $\text{cm}^3$  of solvent at pH = 2 for 16 h. The fraction bound to organic matter and sulfides (F3) was extracted in two steps, firstly with 8.8  $\text{mol dm}^{-3}$   $\text{H}_2\text{O}_2$  using a sample mass to solvent volume ratio of 1 : 20. The extract was evaporated at 80°C to get a moist residue, which was extracted again by 1  $\text{mol dm}^{-3}$   $\text{CH}_3\text{COONH}_4$  employing the sample/solvent ratio of 1 : 50 at pH = 2 for 16 h. Residual fraction (F4) was calculated as the difference between the total element concentration in the sample and the sum of the concentrations estimated in the three above-mentioned fractions. The fractions were centrifuged at 2500  $\text{min}^{-1}$  for 15 min, supernatants were acidified by  $10^{-4} \text{ dm}^3$  of 65 vol. %  $\text{HNO}_3$ , filled up to  $10^{-2} \text{ dm}^3$  by water and stored at +4°C until measurements [5].

**Table 1.** Averaged Element Total Content in Urban Dust and Simulated Air Filters

Element	Content/(mg kg <sup>-1</sup> )		Difference/%
	Urban dust	Simulated air filters	
As	25.6 ± 0.529	19.4 ± 1.00	-24
Cd	1.98 ± 0.113	1.9 ± 0.22	-4
Cr	182 ± 9.77	176 ± 18.4	-3
Mn	984 ± 55.8	492 ± 83.4	-50
Ni	63.6 ± 6.05	63.2 ± 7.9	<1
Pb	1746 ± 89.7	1514 ± 118	-13

$n = 10$  (the number of independent experiments).



**Fig. 1.** Distribution of elements present in the urban dust (A), Triton X-100-treated urban dust (B), and simulated air filters (C) samples in extracted fractions F1, F2, and F3 and residual fraction F4.

Unless stated otherwise, the described sequential extraction was performed in five replicates, mean and standard deviations were calculated.

### Determination of Pollutant Concentrations

For the determination of As, the GF AAS technique was used. Detailed experimental conditions are described in [5]. Calibration curve for As was prepared in the range of 0–50  $\mu\text{g dm}^{-3}$  in 1.5 vol. %  $\text{HNO}_3$  and 1000  $\text{mg dm}^{-3}$  of Pd modifier. Employing platform technique the temperature program was ashing at 900°C and atomization at about 2500°C. Low contents of Cd were also measured by GF AAS. Calibration curve of aqueous solutions of Cd was linear in the range of 0–2  $\mu\text{g dm}^{-3}$  using 1.5 vol. %  $\text{HNO}_3$  and the temperature program was ashing at 250°C and atomization at 2100°C. Differences in slopes between aqueous and agents-matched calibration curves did not exceeded 3 % in any case.

The determination of Cd, Cr, Mn, Ni, and Pb was carried out by ICP-OES. Calibration solutions were prepared using the corresponding extraction agents as follows: 5–50  $\mu\text{g dm}^{-3}$  for Cd, 50–500  $\mu\text{g dm}^{-3}$  for Cr and Ni, and 1–10  $\text{mg dm}^{-3}$  for Mn and Pb. Concentrations of each element were measured using two

spectral lines. No significant differences were observed comparing the element concentration calculated from the two intensities. For more details see Ref. [5]. Collected data were statistically evaluated using the analysis of variance employing the Statgraphics Plus 5.0 for Windows software.

### RESULTS AND DISCUSSION

Results of the analytes total content in urban dust and in simulated air filters obtained by different methods are summarized in Table 1. They are expressed as mean value  $\pm$  standard deviation from 10 independent measurements obtained by analytical methods mentioned above (each value used for the statistical calculations represents the mean of 3 to 5 replicate values). Last column in Table 1 demonstrates the major drawback of the preparation of simulated air filters, *i.e.* the sample mass loss during the wet deposition. For the elements present in the dust matrix together with compounds that are highly soluble in water, the resulting analyte concentration estimated for the filter samples is lower than that found in the starting material. All calculated data are related to the respective element total content given in Table 1 either in the samples urban dust or loaded filters.

**Table 2.** Statistical Evaluation of the Content of Pollutants in Individual Fractions

Fraction	Samples	As	Cd	Cr	Mn	Ni	Pb
F1	A (urban dust)	a	b	a	a	a	a
	B (urban dust treated with Triton X-100)	a	a	a	b	b	a
	C (loaded filters)	a	c	a	c	a	b
F2	A (urban dust)	a	b	a	a	a	b
	B (urban dust treated with Triton X-100)	a	a	a	a	a	a
	C (loaded filters)	b	b	b	b	b	c
F3	A (urban dust)	a	a	a	a	a	b
	B (urban dust treated with Triton X-100)	b	b	a	a	b	c
	C (loaded filters)	c	a	b	a	c	a
F4	A (urban dust)	b	b	b	c	c	c
	B (urban dust treated with Triton X-100)	b	b	b	b	a	b
	C (loaded filters)	a	a	a	a	b	a

The same letter represents statistically identical values within one element and/or fraction ( $P < 0.05$ ).

The results of the three-step sequential extraction together with the calculated element abundance F4 are shown in Fig. 1. Comparing the mobility of analytes in urban dust and simulated air filters, important differences could be noted and their statistical significance is shown in Table 2. The increase of Cd, Mn, and Pb mobility in filters is represented by their respective content in the fraction F1. In the fraction F2, the concentrations of As, Cr, Mn, Ni, and Pb increased and in the fraction F3 a significant increase of As (43 %), Cr (24 %), and Ni (32 %) can be observed. Details are shown in Table 3.

Since during the filter preparation procedure 0.05 vol. % of surfactant Triton X-100 was added to suspend dust particles in water, a simple experiment was carried out to identify its influence on the extraction of urban dust. The amount of Triton X-100 added to all extraction agents used to obtain the fractions F1—F3 corresponded to the surfactant concentration of 0.05 vol. %. As can be seen in Fig. 1, the addition of surfactant provoked some changes in mobility of investigated elements. Thus, in the fraction F1 solubility of Mn, Ni, and Pb was enhanced. In F2 the presence of surfactant negatively influenced the solubility of Cd and Pb, while no change in solubility of the remaining analytes was observed. In the fraction F3 an important concentration increase for As, Cd, Cr, Ni, and Pb is obvious. The comparison of the amount of analytes extracted with and without the addition of Triton X-100 in separate dust fractions is summarized in Table 4.

Summing up the contents of analytes in mobile and possibly mobile fractions (F1—F3) the overall available amount of As, Mn, Ni, and Pb was increased by the addition of Triton X-100 by 8 %, 12 %, 14 %, and 18 %, respectively. Taking into account that surfactants are used as interesting agents for the remediation of contaminated soils and fly ashes [8, 9], the influence of Triton X-100 on the pollutant extraction is not surprising. This non-ionic surfactant was capable

**Table 3.** Comparison of the Analyte Content of the Urban Dust and Simulated Air Filters Samples in Individual Extracted Fractions

Fraction	Difference/%					
	As	Cd	Cr	Mn	Ni	Pb
F1	0	33	0	25	0	53
F2	20	0	10	10	14	14
F3	43	0	24	2	32	-24

$n = 5$  (the number of independent experiments).

**Table 4.** The Analyte Content Ratio of the Triton X-100-Treated and Original Urban Dust Samples in Individual Extracted Fractions

Fraction	As	Cd	Cr	Mn	Ni	Pb
F1	0.673	0.784	3.10	2.07	2.08	1.62
F2	0.941	0.702	1.37	0.951	1.03	0.788
F3	3.03	n.d.*	1.30	1.0	1.82	1.50

\*Not determined

(in concentration of 0.5 vol. %) to enhance the remediation of Cd and Ni from contaminated soils [10—12]. Moreover, it was found that Triton X-100 with iodide ligand, I<sup>-</sup>, selectively desorbed Cd at conditions used for the acquisition of exchangeable fraction [11].

The optimum concentration of Triton X-100 from the viewpoint of metal extraction from urban dust was not investigated. This experiment was conducted with the aim to adjust the experimental conditions during the pollutant extraction from urban dust to those applied during the preparation of simulated air filters. Assuming loaded filters extraction, availability of the majority of analytes was enhanced (Fig. 1), which cannot be explained by a simple action of surfactant Tri-

ton X-100. The ratio of the sample mass to the volume of extraction agents should be also considered. In all experiments the volume of extraction agents was the same, however, the sample masses were different. For the extraction of urban dust 100 mg of the sample were weighted, while for the extraction of loaded filters ( $n = 10$ ) 40 mg of dust and approximately 700 mg of acetyl cellulose were used. It should be noted that the presence of acetyl cellulose medium during the sample treatment could contribute to the observed differences as well. The adsorption of non-ionic surfactant Triton X-100 on the cellulose surface was investigated recently [13]. It was stated that the adsorption of Triton X-100 is caused by the interactions between the hydrophobic cellulose sites and the hydrophobic groups of the Triton X-100 molecule. Thus, the interaction of Triton X-100 with the surface of acetyl cellulose used for the simulated air filters preparation could be the major reason for significant concentration increase of some analytes in mobile and possibly mobile fractions observed in this study.

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