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Characterization of size, morphology and elemental composition of nano-, submicron, and micron particles of street dust separated using field-flow fractionation in a rotating coiled column

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ABSTRACT

For the first time, nano- and submicron particles of street dust have been separated, weighted, and analyzed. A novel technique, sedimentation field-flow fractionation in a rotating coiled column, was applied to the fractionation of dust samples with water being used as a carrier fluid. The size and morphology of particles in the separated fractions were characterized by electronic microscopy before digestion and the determination of the concentration of elements by ICP-AES and ICP-MS. The elements that may be of anthropogenic origin (Zn, Cr, Ni, Cu, Cd, Sn, Pb) were found to concentrate mainly in <0.3 and 0.3–1 μm fractions. It has been shown that the concentrations of Cr, Ni, Zn in the finest fraction (<0.3 μm) of street dust can be one order of magnitude higher than the concentrations of elements in bulk sample and coarse fractions. For example, the concentrations of Ni in <0.3, 0.3–1, 1–10, and 10–100 μm fractions were 297 ± 46, 130 ± 21, 36 ± 10, and 21 ± 4 mg/kg, correspondingly. Though the finest particles present only about 0.1 mass% of the sample they are of special concern due to their increased mobility and ability to penetrate into the deepest alveolar area of the lungs. For rare earth elements (La, Ce, Pr, Nd, Sm) that are evidently of natural source and may be found in soil minerals, in contrary, higher concentrations were observed in large particles (10–100 μm). Sc was an exception that needs further studies. The proposed approach to the fractionation and analysis of nano-, submicron, and micron particles can be a powerful tool for risk assessment related to toxic elements in dust, ash, and other particulate environmental samples.

1. Introduction

Street dust, which has both natural and anthropogenic sources, is an important pathway in the exposure of people to toxic elements. Nowadays, it is recognized that the impact of metal/metalloids on the environment and human health cannot be evaluated by measuring merely the total concentration of individual elements, because the mobility, bioaccessibility and, consequently, toxicity strongly depend on their associations with particles of different size, density, and surface properties. The composition of dust is very variable and is affected by climate, soils and rocks of the surrounding areas, as well as by human activities. However, fine particles (in particular, particles less than 10 μm) are in all cases considered to be the most dangerous to human health and need a special consideration because: (i) they have a large surface area that favors the retention of increased amounts of metals and metalloids, (ii) they are easily dispersible, (iii) they are more likely to traverse the gastric mucosa and be more efficiently absorbed in human tissues than coarse fractions and (iv) they have the ability to enter the respiratory tract. In addition, the fine dust particles are easily re-suspended into the air by wind or traffic and hence are mobile in the environment [1,2]. It should be noted that nano- and submicron particles are of particular importance for environmental and human health studies due to their increased mobility and ability to penetrate into the deepest alveolar area of the lungs [3].

Recently determining heavy metals concentrations in particle size fractions from street dust has been considered as the basis for risk assessment [1]. For all investigated land-uses of Murcia (Spain), the enrichment of all metals under study (Pb, Cu, Zn, and Cd) in the finest fractions were higher than those reported for undisturbed use, indicating that the accumulation in the finer fractions is higher when the metals have an anthropogenic origin.

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It should be noted that the samples were fractionated into eleven particle size fractions (< 2, 2–10, 10–20, 20–50, 50–75, 75–106, 106–150, 150–180, 180–425, 425–850, and 850–2000 μm). For coarse particles (> 50 μm), a stack of sieves was used. Finer particles (< 50 μm) were dispersed in sodium polyphosphate and then separated by repeated sedimentation and decanting. However, the finest separated fraction (< 2 μm) may also contain particles of different size and origin that, as has been mentioned above, are of particular importance for environmental and human health studies [3]. Hence, particles less than 2 μm require to be further fractionated. A novel method for dry extracting large volumes of fine particulate matter from bulk soil samples, which employs an inclined elutriator connected to a vacuum cleaner, might be attractive for this purpose [4]. However, this method provides the most efficient recovery for particles between 1 and 10 μm, with an optimum around 5 μm.

Nano- and submicron particles can be separated using field-flow fractionation (FFF). The general concept of FFF was developed in the 1960 s by Giddings [5]. FFF is a set of liquid chromatography-like elution methods. However, unlike chromatography, FFF requires no stationary phase and only physical interactions are involved in the separation process. The retention and elution of colloidal and particulate matter are achieved by a combined action of a non-uniform flow velocity profile of a carrier fluid and a physical force field (gravitational, centrifugal, electric, etc.) applied at right angles to the thin (0.05–0.5 mm) channel. In general, FFF is a powerful and versatile fractionation and sizing method that covers a size range from about 1 nm to 100 μm. FFF may serve as the basis for hyphenated methods. For example, FFF coupled to multi-angle laser light scattering and inductively coupled plasma – mass spectroscopy (ICP-MS) detectors can be successfully applied to studies on metal compositions of different environmental microparticles, nanocolloids and macromolecules [6,7]. The main limitation of FFF is the maximum sample loading which is less than 1 mg. Therefore samples must be highly homogenized in order to provide representative data.

Split-flow thin-cell fractionation (SPLITT) is similar to FFF but it enables sample loading of particles up to gram levels [8]. Stream splitters are inserted into the flat channel, so that the SPLITT system has two inlets at one side of the channel and two outlets at the opposite side. The separation is achieved by the combined action of controlled flow rates and a gravitational cross-field. SPLITT systems and related techniques can be used for the fractionation and investigation of micron and submicron particles like aquatic colloids [9] and sea sediments [10]. However, when using SPLITT techniques only two fractions can be recovered in one experimental run (for example, particles greater than 1 μm and those less than 1 μm). Thus, for the separation of a number of different fractions multi-step procedures are required.

The fractionation in a rotating coiled column (RCC), which can be attributed to FFF, also enables the loading sample weight to be increased up to 1 g [11]. This technique, named *coiled tube FFF* (*CTFFF*), employs the complex asymmetrical force field generated in planetary centrifuges. Among the other FFF techniques, CTFFF is more similar to sedimentation FFF utilizing a circular channel inserted inside a centrifugal basket. Though both SdFFF and CTFFF are based on the centrifugal force field, there are two important differences between these techniques. Firstly, in the case of CTFFF the mixture to be separated is not introduced into a thin channel but pumped with the carrier fluid (mobile phase) through a long rotating coiled column (inner capacity about 20 mL). Secondly, in the planetary centrifuge used for performing CTFFF, particles and fluid in the coiled tube are under the action of the complex asymmetrical centrifugal force field. This field is dependent on the ratio of the rotation and revolution radii (β-value). CTFFF has been applied to the speciation analysis of environmental solids. Silt (< 2 μm), clay (2–50 μm), and sand (> 50 μm) fractions were successfully separated from soils. It should be noted that rotating columns can be also used for the sequential flow-through extraction of trace elements from solid samples. Determining elemental concentrations in each size-fraction enables a detailed pattern of the distribution of toxic elements in soils to be obtained [12]. So far, submicron environmental particles have not been fractionated in RCC.

Hence, at present there are no readily available methods for the recovery of large amounts of nano- and submicron particles from environmental samples (except aerosol airborne particles, which can be collected and separated according to their aerodynamic diameter by passing a multistage (cascade) impactors [13,14]). The field-flow fractionation in RCC may enable this problem to be resolved.

The aim of the present work is to develop a methodology for studies on both natural and anthropogenic elements associated with nano-, submicron, and micron particles of dust. The methodology is a combination of fractionation of particles in RCC, characterization of size and morphology by scanning electron microscopy with inductively coupled plasma – atomic emission spectroscopy (ICP-AES) and ICP-MS determination of element concentrations in the separated and weighed fractions.

2. Material and methods

2.1. Samples and reagents

For developing the methodology city dust samples were studied. Street dust samples nos 2 and 5 were taken in the eastern area of Moscow not far from the industrial zone where many plants, including an oil refinery, are located. The samples were collected at times of dry and sunny weather conditions from edge parts of roads using a brush and a plastic scoop. Prior to analysis, the samples were dried at 25 °C, homogenized, sieved through a 100 μm screen, and characterized using a scanning electron microscope (JEOL JSM-6700F, Japan).

De-ionized water was used as a carrier fluid for the fractionation of dust particles in the rotating coiled column. All chemicals used for the digestion of both samples and fractions were analytical grade reagents.

2.2. Field-flow fractionation of dust particles in the rotating coiled column

The fractionation of dust samples was performed on a planetary centrifuge with a vertical single-layer coiled column with two symmetrical protrusions (Fig. 1) developed in our research group. The shape of the column drum was designed on the basis of theoretical modeling [15] for the retention and separation of nano- and submicron particles. The device was fabricated in the Institute of Analytical Instrumentation, St. Petersburg, Russia. The column drum rotates around its own axis and at the same time revolves around the central axis of the device. The two axes are parallel. The planetary centrifuge has a revolution radius $R=90$ mm and a rotation radius $r=40$ mm. The β value ($\beta=r/R$) is therefore 0.44. The height of the protrusions is 10 mm. The separation column is made of PTFE tube with an inner diameter of 1.5 mm and a total inner capacity of 18.5 mL. The tube length is approximately 10 m.

Before commencing the fractionation procedure, the column was filled with de-ionized water using a peristaltic pump (MasterFlex L/S series, USA), after which the solid sample (about 100 mg) was introduced into the column (which was not rotating) as a suspension in 2 mL of water at a flow rate of 15 mL min^{-1}. Then the column was rotated at 800 rpm and water was continuously fed into the column at a flow rate of 0.2 mL min^{-1}. The separation

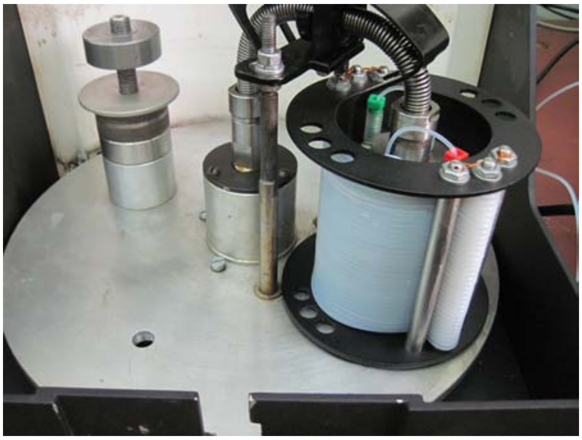


Fig. 1. A prototype of a planetary centrifuge equipped with a vertical single-layer coiled column drum with two symmetrical protrusions.

of different size fractions was achieved by a flow rate step gradient up to 21 mL min^{-1}. The particulate matter in the column effluent was monitored using a flow spectrophotometer (Institute of Analytical Instrumentation, St. Petersburg, Russia) at $\lambda=254$ nm. After the procedure has been finished, the residue (the final coarse fraction) of the dust sample was removed from the stopped column by pumping water at a flow rate of 21 mL min^{-1}.

2.3. Investigation and elemental analysis of dust samples and their fractions

The separated fractions (as well as the initial dust samples) were characterized by scanning electron microscopy. After the operational conditions of field-flow fractionation (flow rates and volumes of the eluent needed for the separation) have been optimized for each sample, the different separated size fractions were filtered, dried, weighted, digested, and analyzed by ICP-AES and ICP-MS techniques.

The particulate matter was precipitated on *Millipore* cellulose filters (pore diameter of 50 nm) under pressure of 2 bars using a filtration cell with a magnetic stirring rod. Then, the filters were dried in a desiccator with silica gel to constant weight (about 2 days). The digestion of the filters were performed in a mixture of 0.5 mL HNO_3 (Nitric acid 65%, max. 0.0000005% Hg, GR, ISO, Merck) and 1.0 mL HCl (Hydrochloric acid fuming 37% GR, ISO, Merck) using an autoclave system (ANKON-AT-2, Russia) at 160 °C (1 h), 180 °C (2 h) and finally 200 °C (1 h).

Samples of the initial dust were digested in an open beaker using a combination of three acids. The particulate samples (0.1 g) and the standard gabbro GSO 521-84P sample (Russian Standard Sample) were put into 50 mL Teflon beakers together with 0.5 mL $HClO_4$ (Perchloric acid fuming 70% Supratur, Merck), 3 mL HF (Hydrofluoric acid 40% GR, ISO, Merck), 0.5 mL HNO_3 (Nitric acid 65%, max. 0.0000005% Hg, GR, ISO, Merck), and 0.1 mL of solution containing 6–8 ppb ^{62}Ni, ^{76}Se, ^{149}Nd, ^{161}Dy and ^{174}Yb isotopes which were necessary to control completeness of digestion. The samples with acids were boiled until intensive white fumes appeared. Then the beakers were cooled, 3 mL deionized water was added to each of the beakers, and the samples were boiled down once again. After this, 2 mL HCl (Hydrochloric acid fuming 37% GR, ISO, Merck) and 0.2 mL 0.1 M H_3BO_3 solution were added to each sample, and they were boiled down to approximately 0.6 mL each. Then the samples were transferred to polyethylene beakers, diluted to 20 mL with deionized water, and 0.1 mL of 10 ppm In solution was added to each sample as an internal standard. For control, all the described procedures were also performed in three empty beakers.

The contents of B, Li, Be, Al, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th, and U in the samples were determined using an ICP-MS (X-7 ICP-MS Thermo Electron, USA). The measurements were made using the following parameters: a RF generator power of 1250 W; a PolyCon nebulizer; a plasma-forming Ar flow rate of 12 L min^{-1}; an auxiliary Ar flow rate of 0.9 L min^{-1}; an Ar flow rate into the nebulizer of 0.9 L min^{-1}; an analyzed sample flow rate of 0.8 mL min^{-1} and a resolution of 0.8 M. The contents of Li, Na, Mg, Al, P, S, K, Ca, V, Mn, Fe, Cu, Zn, Sr, and Ba were determined by ICP-AES (ICAP-61, Thermo Jarrell Ash, USA). The measurements were made using the following parameters: a RF generator power of 1200 W; an angular nebulizer; a plasma-forming Ar flow rate of 18 L min^{-1}; an auxiliary Ar flow rate of 0.9 L min^{-1}; an Ar flow rate into the nebulizer of 0.6 L min^{-1}; an analyzed sample flow rate of 1.5 mL min^{-1} and a plasma observation zone height of 14 mm. For Li, Al, V, Mn, Cu, Zn, Ba, which were determined both by ICP-AES and ICP-MS, average values were used. It should be noted that the data for these elements confirmed the accuracy of the results obtained by both methods. The results obtained for gabbro GSO 521-84P are in good agreement with the certified values.

3. Results and discussions

3.1. Fractionation and investigation of nano-, submicron, and micron particles of street dust samples

The design and operational parameters of the planetary centrifuge for the fractionation of street dust samples were chosen and optimized on the basis of the retention and elution of submicron standard samples of silica determined previously [16]. The original prototype of a planetary centrifuge equipped with a single-layer column with two symmetrical protrusions was applied to the fractionation of dust with water, a natural environmental solvent, being used as a carrier fluid (mobile phase). The recovery of nano-, submicron, and micron size fractions of dust samples was achieved by an increasing step gradient of the mobile phase flow rate at a constant column rotational speed (Fig. 2). The last fraction was eluted from the stationary column.

As is seen, four different fractions were separated from street dust sample no. 2. According to the data obtained by scanning electron microscopy (Fig. 3) these fractions contain <0.3, 0.3–1, 1–10, and 10–100 μm particles, correspondingly. Nearly all particles are of irregular shape except the finest fraction (<0.3 μm), in which one can see spherical and plate particles. It should be noted that this fraction might also contain somewhat larger organic

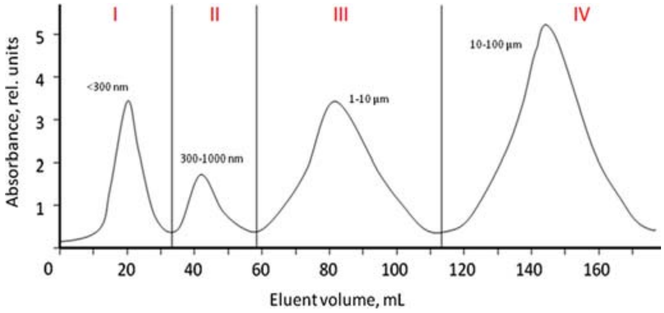
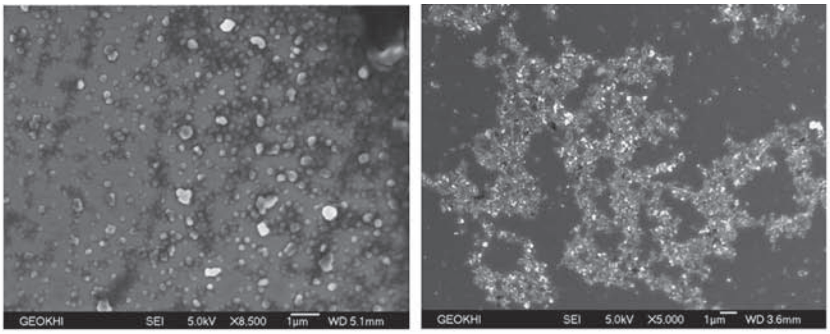
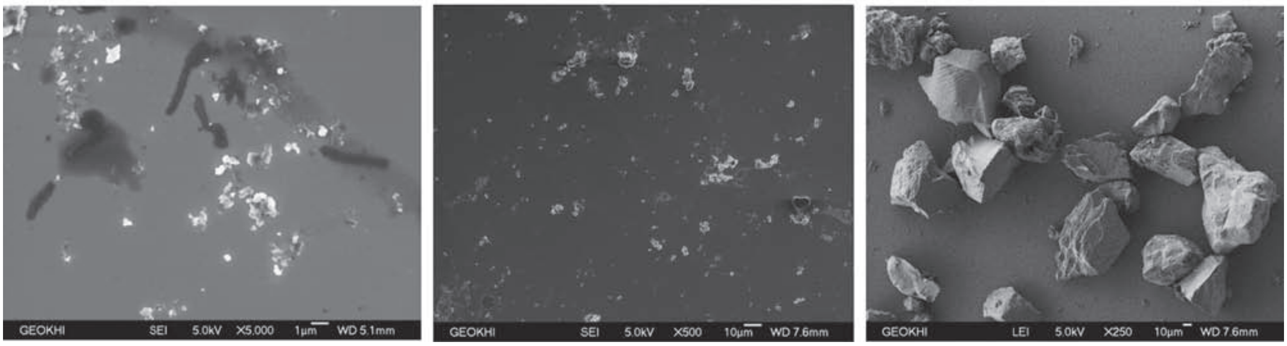


Fig. 2. Fractogram of street dust sample no. 2. Fractionation conditions: sample weight 100 mg; column rotation speed $\omega=800$ rpm; mobile phase (*bi-distilled water*) flow rate: I – 0.2 mL/min; II – 13 mL/min; III – 21 mL/min, and IV – 21 mL/min ($\omega=0$ rpm).



Fraction I (50-300 nm)



Fraction II (300-1000 nm) Fraction III (1-10 μm) Fraction IV (10-100 μm)

Fig. 3. Fractions of street dust sample no. 2 characterized by scanning electron microscopy.

Table 1
Concentration of elements in size fractions of street dust sample no. 2 as obtained by ICP-MS and ICP-AES ($n=4$, $1-\alpha=0.95$).

Element	Average content in the Earth crust (mg/kg)	Element concentration (mg/kg)				
		Initial sample (total content)	Fraction I ($m=0.1$ mg; 0.1 mass % of initial sample)	Fraction II ($m=0.2$ mg; 0.2 mass % of initial sample)	Fraction III ($m=2.1$ mg; 2.1 mass % of initial sample)	Fraction IV ($m=83.4$ mg; 83.4 mass % of initial sample)
P	930	830	2469 ± 504	893 ± 77	485 ± 129	750 ± 28
S	470	2400	6806 ± 197	2130 ± 635	3118 ± 427	2152 ± 611
Sc	10	5	147 ± 20	52 ± 13	17 ± 2	5 ± 1
Cr	83	53	316 ± 71	202 ± 15	52 ± 17	35 ± 6
Fe	46.5×10^3	21×10^3	$17.7 \times 10^3 \pm 0.56 \times 10^3$	$16.7 \times 10^3 \pm 2.1 \times 10^3$	$20.5 \times 10^3 \pm 3.6 \times 10^3$	$15.4 \times 10^3 \pm 4.2 \times 10^3$
Ni	58	39	297 ± 46	130 ± 21	36 ± 10	21 ± 4
Cu	47	71	105 ± 28	98 ± 4	44 ± 13	43 ± 12
Zn	83	388	2061 ± 475	663 ± 182	860 ± 34	235 ± 49
Cd	0.13	1	20 ± 2	5 ± 1	1 ± 0.3	-
Sn	2.5	5	109 ± 25	55 ± 5	12 ± 2	3 ± 1
Ba	650	480	856 ± 162	445 ± 54	217 ± 59	156 ± 25
Pb	16	75	125 ± 33	64 ± 20	57 ± 15	46 ± 8
Y	29	15	1 ± 0	4 ± 1	8 ± 3	12 ± 2
La	29	30	10 ± 4	12 ± 3	16 ± 5	40 ± 12
Ce	70	60	14 ± 4	22 ± 7	30 ± 10	81 ± 27
Pr	9	6	2 ± 1	3 ± 1	4 ± 1	10 ± 3
Nd	37	22	7 ± 2	11 ± 2	14 ± 4	32 ± 12
Sm	8	4	1 ± 1	2 ± 1	2 ± 1	6 ± 2

particles with lower density [16]. For street dust sample no. 5, the fractogram and micrographs are similar.

3.2. Elemental analysis of nano-, submicron, and micron size fractions of street dust samples

The separated fractions of street dust samples were filtered, dried, weighted, digested, and analyzed by ICP-MS and ICP-AES. It should be stressed that <0.3 and 0.3–1 μm size fractions contained only 0.1 and 0.2 mass% of the initial sample, respectively. However, reproducible analytical data were obtained (Tables 1 and 2). It should be also noted that the dissolution of the adsorbed target analytes in water (carrier fluid) might occur during the field-flow fraction procedure. However, even in the speciation analysis of soils, the water-soluble fraction is usually considered to be negligible [17]. The same is naturally true for street dust samples already “washed” by rain water.

The concentrations of elements in the size fractions of street dust sample no. 2 as obtained by ICP-MS and ICP-AES are presented in Table 1. The distribution of trace and major elements between separated fractions are clearly illustrated in Fig. 4. As is seen from the table and figure, the smaller the particle size, the

Table 2
Concentration of elements in size fractions of street dust sample no. 5 as obtained by ICP-MS and ICP-AES ($n=4$, $1-\alpha=0.95$).

Element	Average content in the Earth crust (mg/kg)	Element concentration (mg/kg)				
		Initial sample (total content)	Fraction I ($m=0.1$ mg; 0.1 mass % of initial sample)	Fraction II ($m=0.2$ mg; 0.2 mass % of initial sample)	Fraction III ($m=2.1$ mg; 2.1 mass % of initial sample)	Fraction IV ($m=83.4$ mg; 83.4 mass % of initial sample)
P	930	742	2145 ± 294	1493 ± 183	856 ± 126	726 ± 81
S	470	2900	4495 ± 354	3514 ± 865	2675 ± 198	1388 ± 379
Sc	10	5	109 ± 5	63 ± 14	18 ± 4	5 ± 1
Cr	83	79	188 ± 45	166 ± 45	102 ± 12	69 ± 12
Fe	46.5×10^3	33.6×10^3	$166 \times 10^3 \pm 3.7 \times 10^3$	$50.9 \times 10^3 \pm 11.1 \times 10^3$	$32.1 \times 10^3 \pm 2.8 \times 10^3$	$22.1 \times 10^3 \pm 4.6 \times 10^3$
Ni	58	54	110 ± 30	146 ± 28	48 ± 8	37 ± 5
Cu	47	172	284 ± 55	296 ± 68	155 ± 27	146 ± 24
Zn	83	322	406 ± 38	1058 ± 256	686 ± 28	304 ± 74
Cd	0.13	1	6 ± 1	4 ± 1	1 ± 0.3	1 ± 0.3
Sn	2.5	9	32 ± 6	50 ± 13	13 ± 3	8 ± 1
Ba	650	493	362 ± 96	540 ± 47	429 ± 26	174 ± 32
Pb	16	132	86 ± 7	294 ± 7	185 ± 42	138 ± 26
Y	29	15	13 ± 3	16 ± 2	12 ± 2	14 ± 1
La	29	21	9 ± 3	20 ± 3	28 ± 2	27 ± 7
Ce	70	52	17 ± 4	28 ± 1	39 ± 3	60 ± 14
Pr	9	5	1 ± 0	4 ± 1	6 ± 0	7 ± 2
Nd	37	19	9 ± 2	17 ± 3	25 ± 1	25 ± 4
Sm	8	4	4 ± 1	5 ± 1	3 ± 1	4 ± 1

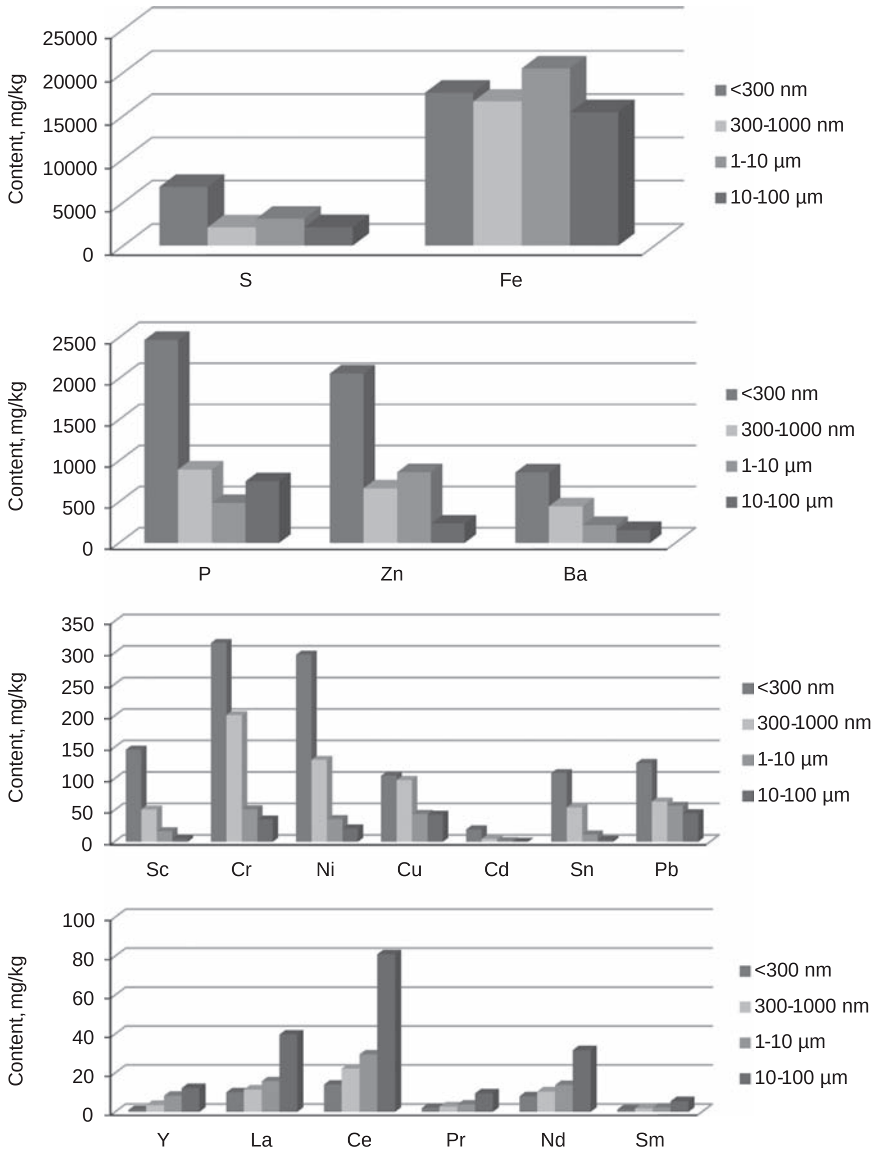


Fig. 4. Distribution of elements in different size fractions of street dust sample no. 2.

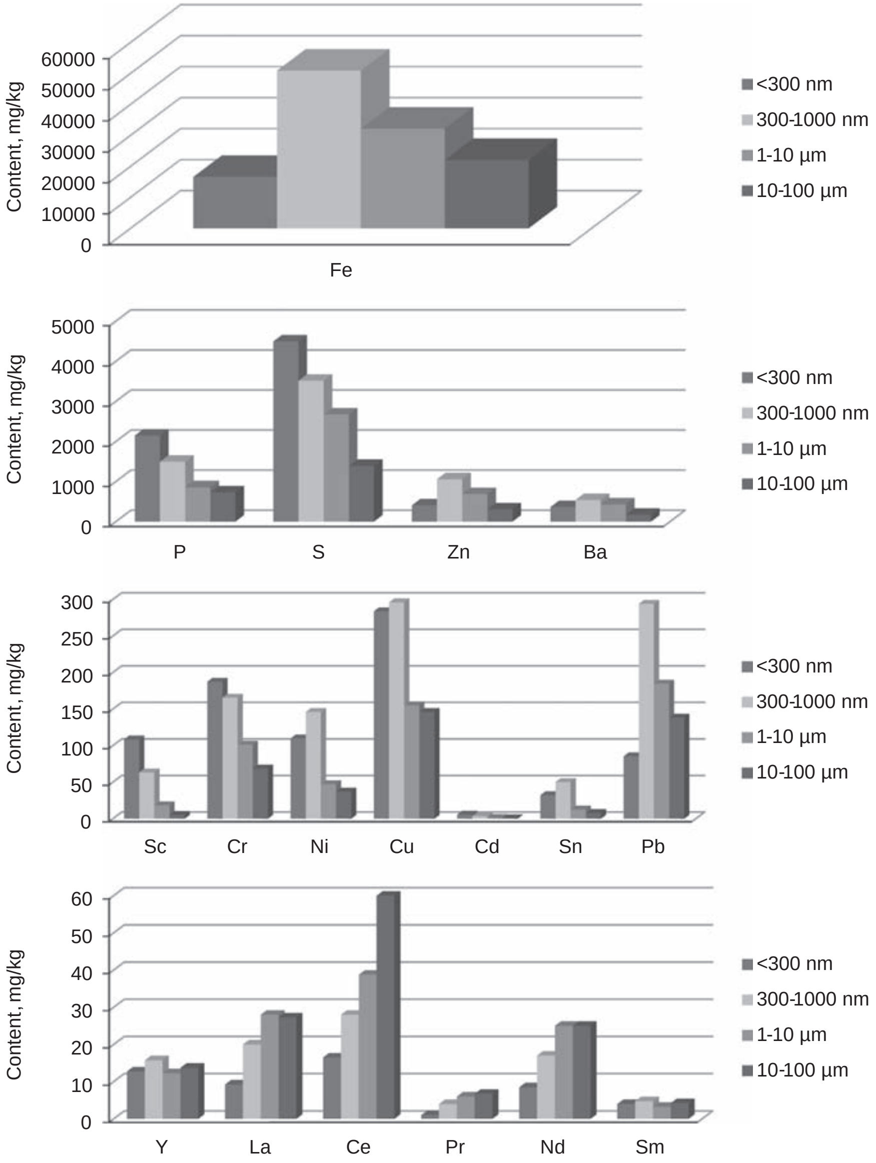


Fig. 5. Distribution of elements in different size fractions of street dust sample no. 5.

higher the content of trace elements that may be of anthropogenic origin (Sc, Cr, Ni, Cu, Cd, Zn, Sn, Pb). For example, the content of Ni in <0.3, 0.3–1, 1–10, and 10–100 μm fractions is 297 ± 46, 130 ± 21, 36 ± 10, and 21 ± 4 mg/kg, correspondingly. In general, the content of Sc, Ni, Cd, and Sn in the finest fraction (<0.3 μm) is 15–30 times higher than their content in the coarse fraction (10–100 μm), or in the bulk sample. Such a dramatic concentration of anthropogenic trace elements in the finest dust fraction might be attributed to an active source of contamination near the sampling site. This may be explained as follows. When the pollution is “fresh”, contaminants can be predominantly associated with the finest particles deposited from the air. In the aging process, such particles may aggregate and the peak content of contaminants may correspond to somewhat larger particles. Also a gradual dissolution of metal compounds of anthropogenic origin (in particular, metal oxides) followed by their re-sorption may occur. Soil particles, which are larger than atmospherically deposited ones, usually have an increased sorption capacity and hence preferentially bind dissolved compounds [17]. This might be another reason for the re-distribution of metals in the course of aging.

It should be stressed that the concentrations of Sc, Cr, Ni, Cu, Cd, Sn, in the bulk sample and in the coarse fraction are comparable to the average element contents in major types of magmatic rocks in Earth crust [18]. Hence, the total contents of enumerated elements indicate no considerable anthropogenic contamination.

For rare earth elements (La, Ce, Pr, Nd, Sm), in contrary, higher concentrations were found in large particles (10–100 μm). This is expected since rare earth elements are most likely of natural sources and may therefore be present in coarse particles of soil minerals. Sc is an exception and its behavior is of special interest. Sc and other rare earth elements under study are characterized by similar physicochemical properties. However, the distribution of Sc between dust size fractions looks like that of the conventional widespread heavy metal contaminants. Such results may be evidence of Sc contamination in the sampling area. It should be noted that Sc is known to be used in alloys with Al and Ti used for example in aircraft parts. This might be a reason for the increased concentration. Since the highest concentration was found in the finest fraction, the geological origin does not seem to be significant, however the anthropogenic origin is more likely via high-temperature processes. The assumption made is not supported by the existing data of environmental monitoring in Moscow. In general, due to the low toxicity of Sc there is little relevant data on the contamination of soils by this element. Nevertheless, Sc is known to be bound to soil minerals more strongly than other rare earth elements [19]. Hence, without a source of contamination its distribution between dust size fractions would have been different to that observed.

The distribution of elements in size fractions of street dust sample no. 5 is presented in Table 2 and Fig. 5. In general, similar trends are observed for sample nos. 2 and 5, except for the finest (<0.3 μm) fraction. The content of Ni, Cu, Sn, and Pb in this fraction is lower than in the next submicron fraction (0.3–1 μm). This might be attributed to somewhat aged pollution and aggregation of particles.

The results obtained are in agreement with an assumption that the accumulation of elements (e.g., heavy metals) in the finer dust fractions is higher when elements have an anthropogenic origin [1,20,21]. However, the finest dust fractions (<0.3 μm and 0.3–1 μm) have been separated, weighed, and analyzed for the first time. Hence, the evaluation of general regularities of trace and major elements associated with nano- and submicron dust particles necessities in-depth research.

4. Conclusions

Nowadays, the application of analytical chemistry methods to the exposure assessment of environmental contaminants has attracted increased attention [22]. In the present work nano-, submicron, and micron particles of street dust samples were successfully separated, characterized, weighted, and analyzed. Though the finest fractions contain less that 0.5 mass% of the bulk sample, reproducible analytical results were obtained. It has been demonstrated that dramatically elevated concentrations of anthropogenic trace elements (Cr, Ni, Cu, Cd, Zn, Sn, Pb) can be found in the <0.3 and 0.3–1 μm size fractions. Due to their increased mobility and ability to penetrate into the deepest alveolar area of the lungs, these particles need special consideration.

For the first time evidence has been collected which shows that the sampling area may be subjected to Sc contamination. It would have been impossible to make such a conclusion on the basis of the analysis of bulk samples since total contents of Sc in soil and street dusts are both very low. Besides, Sc compounds have low physicochemical mobility and solubility and hence the intensity of their entry into soil is rather low.

The proposed approach to the fractionation of nano- and submicron particles in the analysis of particulate environmental samples provides a unique opportunity to resolve relevant tasks of environmental analytical chemistry and monitoring, geochemistry, and soil science. It should be further extended to dust, ash, and soil samples of different nature with various histories of contamination.

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