Talanta 130 (2014) 1–7

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

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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ARTICLE INFO

Article history:
Received 8 March 2014
Received in revised form
17 June 2014
Accepted 19 June 2014
Available online 27 June 2014

Keywords:
Field-flow fractionation
Rotating coiled column
Street dust
Nano- and submicron particles
Quantitative elemental analysis

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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http://dx.doi.org/10.1016/j.talanta.2014.06.040
0039-9140/

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 (Master-Flex 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