



Determination of rare earth elements in dust deposited on tree leaves from Greater Cairo using inductively coupled plasma mass spectrometry



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ARTICLE INFO

Article history:

Received 22 October 2012

Received in revised form

16 March 2013

Accepted 18 March 2013

Keywords:

ICP-MS

Dust deposited on tree leaves

Air pollution

Rare earth elements

ABSTRACT

This work aims at monitoring the rare earth elements (REEs) and Th in dust deposited on tree leaves collected inside and outside Greater Cairo (GC), Egypt. Inductively coupled plasma mass spectrometry (ICP-MS) was employed. The concentration of REEs in the collected dust samples was found to be in the range from 1 to 60 $\mu\text{g g}^{-1}$. The highest concentration of REEs was found in dust samples collected outside GC, in the middle of the Nile Delta. This would refer to the availability of black sands, due to desert wind occurrence during the sample collection, and anthropogenic activities. The limits of detection of the REEs ranged from 0.02 ng g^{-1} for Tm to 3 ng g^{-1} for Yb. There was an obvious variation in the concentration of REEs inside and outside GC due to variations of natural and anthropogenic sources. Strong correlations among all the REEs were found.

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1. Introduction

Urban atmospheric dusts were reported to adversely affect human's health (Harrison and Yin, 2000; Zhao et al., 2006). They contain a mixture of solid particles in the form of organic and inorganic pollutants (Warner, 1976; Godish, 2005). Anthropogenic, natural particulates and contaminants from an extensive range of urban and industrial sources are settling on the ground surface under the effect of atmospheric removal processes (dry and/or wet deposition). They are incorporated into the surface dusts or transferred to the surface of the soil. Tree leaves in urban areas have been reported as a good accumulator of atmospheric dusts (Moreno et al., 2003; Urbat et al., 2004). It can efficiently accumulate dusts due to their large surface area and waxy coating surface. Tree leaves in roadside and urban areas are commonly polluted by particulate matter (PM) mostly related to the traffic/motor vehicle emission, abrasion of tyres, brake linings as well as road surface cycling of dust in suspension due to vehicular movement and dispersion of

construction material (Gautam et al., 2005; Goddu et al., 2004; Prajapati et al., 2006). In addition, tree leaves allow the construction of sampling grids at different scales with high density of sampling points and spatial resolution, which are difficult to achieve in a monitoring station due to the wide distribution of trees. Thus, tree leaves can be used to determine the spatial and temporal distribution of atmospheric dusts (Urbat et al., 2004; Davila et al., 2006; Hanesch et al., 2003). An extensive research on atmospheric particles in urban environments is available (Jaradat et al., 2004; Al-Rajhi et al., 1996; Rodríguez-Navarro and Sebastián, 1996; El Shazly, 1990). Quantitative elemental analysis of dust deposited on street tree leaves can generate highly specific source information of great environmental importance because some of the elements are related to the development of respiratory and carcinogenic diseases (Green and Armstrong, 2003). However, there is a lack of rare earth elements (REEs) information in the airborne dust deposited on urban tree leaves, which could provide important information on environmental pollution in urban areas. The main anthropogenic activities that contribute to the presence of REEs are industrial activities, motorized vehicles, stoves, incinerators, aerosol sprays, leaky refrigerators, fumes from paint, varnish, and other solvents (Wang et al., 2009). Because of the

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widespread use of REEs, remarkable amounts of REEs are probably emitted into the atmosphere. One of the most advanced techniques typically employed for elemental analysis is inductively coupled plasma mass spectrometry (ICP-MS) (Zhang et al., 2007). During the last two decades, ICP-MS has proven to be the most powerful technique for the estimation of trace and ultra-trace elements concentrations, including REEs in a variety of samples (Nardi et al., 2009; He et al., 2005) which is largely due to its inherently high sensitivity and multielemental capability. REEs comprise a group of elements from La to Lu, which show very similar physical and chemical properties. Although the REEs are relatively abundant in the Earth's crust, they are typically dispersed and not often found in concentrated and economically exploitable forms. Due to small differences in ionic radii, fractionations between light REEs (from La to Gd) and heavy REEs (Tb–Lu) within the geochemical cycle may occur (Balaram and Rao, 2003).

The aim of this study is to evaluate REEs air pollution from natural sources as well as social–economical activities in the region of Greater Cairo (GC). We have chosen Greater Cairo as one of the highest populated urban areas worldwide. The present study is the first initiative about REEs pollution in dust deposited on urban tree leaves.

2. Materials and methods

2.1. Instrumentation

An ICP-MS ELAN 6000 (Perkin Elmer–SCIEX, Thornhill, Canada) was used for all measurements. Argon gas with minimum purity of 99.996% (White Martins, São Paulo, Brazil) was used as the plasma and nebulizer gas. A cross-flow nebulizer equipped with a Scott spray chamber was used in all measurements. A peristaltic pump from Ismatec (Glattbrugg, Switzerland) was used, at a typical solution flow rate of 1.3 mL min⁻¹. Nebulizer gas flow rate was maintained at 0.7 L min⁻¹, with a RF power of 1400 W. The instrument conditions were: auto lens mode on, 1400 hopping measure mode, dwell time of 15 ms, 40 sweeps/reading, 1 reading/replicate, 3 replicates. Platinum sampler and skimmer cones were used. An instrument performance check was carried out on a daily basis, in order to assure adequate sensitivity and low levels of oxide and doubly charged ions.

2.2. Reagents and samples

Deionized water with a resistance of 18.2 MΩ cm was obtained from a Milli-Q system (Millipore, Bedford, USA) and used throughout. Working and calibration solutions were prepared daily by proper dilution from a 10 mg L⁻¹ multi REEs stock standard solution. All other reagents used were of analytical reagent grade. Nitric acid (65%, Merck, Darmstadt, Germany) was submitted twice to sub-boiling distillation in a quartz apparatus (Kürner Analysetechnik, Rosenheim, Germany). Hydrofluoric acid (40% Riedel-de Haën, Germany) was equally distilled in a PTFE system (Kürner Analysetechnik). Analytical-reagent grade H₃BO₃ (CAQ-Casa da Química, São Paulo, Brazil) was used as supplied. Dust deposited from ambient air on leaves of street trees of Greater Cairo (GC) were brushed out from leaf surface and dried. Each sample was collected from the upper leaf surfaces of *Ficus nitida* trees at central and peripheral branches, 2 m above the ground. The dust samples were stored in unused standard plastic bags, transferred to a desiccator soon after collection, and kept for analysis. Nineteen dust samples (from AP01 to AP19) were collected from different locations inside and outside GC in the period from 1th to 31th July, 2010. The sampling sites were selected from areas with variable (expected) pollution levels, according to car traffic, population density and industrial activities. Therefore, the dust samples were collected near economical and industrial units, as well as the main roads. The certified reference material (CRM) "urban particulate matter" (NIST 1648, National Institute of Standard and Technology, Gaithersburg, USA) was used to attest the accuracy of the analytical procedure.

2.3. Analytical procedure

Sample digestion represents the most critical step in most analytical methods for routine determination of chemical elements. Microwave digestion was found suitable for the determination of the REEs in dust samples (Kulkarni et al., 2007). Dust samples were digested using an Analytik Jena microwave digestion system (TOPwave, PM60, Analytik Jena AG, Jena, Germany). Prior to digestion, the PTFE vessels were soaked overnight in diluted nitric acid (HNO₃, 10% v/v) at room temperature, followed by microwave-assisted heating using concentrated HNO₃. The temperature program is shown in Table 1s. For digestion, 5 mL of concentrated HNO₃ and 2 mL of HF were added to mass aliquots containing approximately 250 mg of the

dust samples in the PTFE digestion vessel of the microwave system. The vessels were closed and carefully stirred for 5 min in an ultrasonic bath (Model 28X, DENTSPLY International, USA). The closed vessels were then removed from the ultrasonic bath and left to stand at atmospheric pressure for 30 min. Finally, the vessels were introduced inside the microwave oven and submitted to the digestion program shown in Table 1s. In order to avoid foaming and splashing at the end of the digestion program, the vessels were cooled for one hour to room temperature and opened carefully. Prior to ICP-MS analysis, excess fluoride ions were eliminated by adding boric acid and heating the resulting solution to 110 °C in a hot plate (Sucharová and Suchara, 2006). The resulting solutions were transferred to polypropylene bottles and diluted up to 40 mL with deionized water. Procedural blanks, submitted to the same steps described above for the dust samples, were analysed in parallel to each sample.

Calibration curves of REEs and Th were prepared from a multi-element standard solution in concentrations ranging from 5 to 250 µg L⁻¹. The suitable isotope for each element was used. The solutions of the digested samples were diluted 100 times prior to analysis, in order to cope with the maximum tolerable level of dissolved solids in ICP-MS. The REEs are in the mass region from ¹³⁹La to ¹⁷⁵Lu, which is virtually free from interferences except from oxides of other REEs. Potential isobaric interferences from oxides were either negligible due to the low concentration of REEs in the samples or corrected by application of correction equations in the software.

2.4. Statistical analysis

Statistical analysis plays an important role, considering that the deposited dust samples were collected in different locations. This is very important in order to detect the hidden structure and association of rare earth elements in the quantitative analysis data set, in an attempt to explain the influence of latent factors on the data distribution (Shaltout et al., 2011, Shaltout et al., 2012a,b). Based on the statistical point of view, Pearson's correlation coefficients were found as the most suitable. Correlation analysis was applied for different elements and locations in order to obtain information about the dispersion and the similarity between the samples. Pearson's correlation coefficients were calculated to examine the relationship between the quantitative analysis results at different locations and different elements. A Student *t* test at a 95% level of confidence was calculated when comparing certified and measured samples.

3. Results and discussion

3.1. Analytical figures of merit and quality assurance

The limits of detection (LODs) were determined as three times the standard deviation of the 20 consecutive measurements of the reagent blanks multiplied by the dilution factor used for sample preparation (Table 2s). The LODs ranged from 0.02 ng g⁻¹ for Tm to 3 ng g⁻¹ for Yb. The LOD values clearly illustrate the ability of the present ICP-MS setup for the determination of very low concentrations of REEs in the dust samples. The calibration curves for the REEs showed excellent linearity in the concentration range from 5 to 250 ng g⁻¹, with correlation coefficient ranging from $R^2 = 0.999$ to $R^2 = 1$.

Precision and accuracy of the quantitative analysis using ICP-MS were assured through repeated analysis of a standard reference material (NIST 1648–urban particulate matter), subjected to the same protocol adopted for the dust samples. A comparison with the available certified values is shown (Table 3s). Average values and the standard deviations of five replicates were taken for each determination under the optimized operational conditions. No significant differences at a 95% confidence level were observed between certified and measured values by applying the paired *t* test, and the null hypothesis would be acceptable. This demonstrates the accuracy of the proposed method using ICP-MS for the determination of REEs in dust samples collected over leaf surfaces.

3.2. Quantitative analysis of REEs in dust samples deposited on leaf surfaces

With the exception of Tb, the average concentration of REEs outside GC was higher than inside GC (Table 1). This suggests further anthropogenic and natural sources outside GC such as

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