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Determinations of Sb and Mo in Cairo's dust using high-resolution continuum source graphite furnace atomic absorption spectrometry and direct solid sample analysis

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HIGHLIGHTS

- Developed method for solid sampling analysis of Sb and Mo in dust was presented.
- The results were obtained from SS-HR-CS AAS.
- The pyrolysis and atomization temperatures were optimized.
- The average value of Sb is twenty times higher than the international screening level.
- Mo content is lower than screening level.

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ABSTRACT

The present work describes the determination of Sb and Mo in dust deposited on tree leaves using direct solid sample analysis. Nineteen air particulate samples were collected from different districts of Cairo and surrounding cities. Since some samples have been taken from places less exposed to the pollution factors, the present study allows the comparison of air quality between high and low polluted areas. High-resolution continuum source graphite furnace atomic absorption spectrometry has been investigated, using direct solid sample analysis. The optimum pyrolysis and atomization temperatures for Sb were found to be 800 °C and 1900 °C, and 1200 °C and 2650 °C, respectively for Mo. The limits of detection and quantification for both, Sb and Mo, were 15 μg g^{-1} and 50 ng g^{-1}, respectively. The characteristic mass at was found to be m_0 = 38 pg for Sb (217.582 nm) and m_0 = 28 pg for Mo (313.259 nm). The results obtained for three certified reference materials of urban particulate matter confirmed the validity of the investigated method. The content of Sb varied between 213 ± 1.3 μg g^{-1} and 1117 ± 230 μg g^{-1} with an average of 667 ± 339 μg g^{-1}. On the other hand, the Mo content varied from 113 ± 2.3 μg g^{-1} to 361 ± 51 μg g^{-1} and its average value equals 190 ± 62 μg g^{-1}.

1. Introduction

Air contamination in Greater Cairo and the surrounded districts is a problem of great interest as it is considered as one of the most polluted megacities around the world (United Nations Environment Programme, 1992). Greater Cairo is about 1000 years old, but parts of the metropolis date back to the time of the Pharaohs. It is the largest city in Africa and the Middle East and it includes Cairo, Giza and Kalubia provinces. The population of the Great Cairo urban agglomeration is more than 20 million. The monthly average temperature ranges from 14 °C in January to 29 °C in July, but the maximum day temperature can reach 45 °C in summer. It was recognized that the agricultural areas around Cairo decreased over the last years due to urban development. At the same time, industrial activities in Greater Cairo increased remarkably. Therefore, there are different major sources of air pollution, such as mobile sources (cars, trucks etc.), stationary sources (industry, power stations etc.), and open burning sources. This

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includes a wide variety of sources of air pollution coming from fossil fuels, such as sulfur dioxide (SO_2), nitrogen oxides (NO_x), carbon monoxide (CO), volatile organic compounds (VOCs) and air particulate matter (APM). In addition, there are extra air pollution sources coming from the production of steel and cement, desert dust and power plants.

The investigation of the aliphatic and aromatic fractions of road dust samples from Cairo was reported in the literature (Moharram and Sowelim, 1980; Mostafa et al., 2009). Several authors reported the determination of inorganic constitutes, mostly heavy metals, including Mo, in urban and rural road dust collected from road surface adjacent to the curb (Apeagyei et al., 2011; Hindy, 1980; Safar and Labib, 2010). Commonly, elemental analysis of air dust was carried out by means of spectroscopic techniques, namely Total Reflection X-ray Florescence (TXRF) spectroscopy (Cibin et al., 2008; Hallquist and Boman, 2004), line source Atomic Absorption Spectrometry (LS AAS) (Khairy et al., 2011), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Muránszky et al., 2011) or Inductively Coupled Plasma Optical Emission Spectroscopy (ICP OES) (Qiu et al., 2009). Each of these techniques has advantages and drawbacks, and their comparative benefits, in terms of analytical performance. However, the use of these techniques usually involves sample digestion procedures for total destruction of the matrix by chemical treatment. Sample dissolution is usually a tedious, time-consuming step that sometimes limits application of the analytical procedure in environmental studies and quality-control processes. In addition, hydrofluoric and perchloric acids would be essential for complete sample digestion, which results in spectral interferences in the final solution for most of the spectrometric techniques unless the solutions are strongly diluted.

For this reason, alternative analytical techniques for direct solid sample analysis are of great interest. Neutron activation analysis (NAA) is one of the potential candidate techniques that do not require previous destruction of the sample and it was used for direct dust sample analysis (Chutke et al., 1994; Avino et al., 2008a); however, this technique is not available in most laboratories. Laser-induced breakdown spectroscopy (LIBS) has also been used as a powerful technique for investigating direct solid sample analysis (Asgill and Hahn, 2009). The technique is considered essentially non-destructive and sample preparation is minimized. However the quantitative determination of Sb and Mo in dust fall with LIBS and NAA is not an easy task due to the low analyte concentrations. Sb and Mo were considered as one of the main sources of dust fall resulting from the social economical activities, motor vehicle traffic, particularly from brake and tire wear. Sb and Mo and many of their compounds are toxic, bio-accumulative and persistent in the environment, and their behavior and transport depend on their chemical forms (Ariza et al., 2000; Müller et al., 2007; Shotyk et al., 2005).

The aim of this study was to develop a fast, simple and reliable method for the determination of Sb and Mo in dust samples collected from nineteen sites inside and outside Greater Cairo, using a minimum of sample preparation. High-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) with direct solid sample analysis (SS) was found an attractive alternative for Sb and Mo determination in air particulate matter. The advantageous features of HR-CS SS-GF AAS are simplicity, speed, reliability and sensitivity, and the possibility of performing analyses directly on solid samples without any sample preparation or usage of reagents. In addition, there is no need for prior crushing, grinding or milling, as the dust samples already exist in the form of fine powder. Therefore there is no problem of contamination arising from the grinding material or reagents.

Table 1
Locations of the dust samples collected for this study.

Location	Nr	
15 May City, Outostrad Road	AP#01	Urban
15 May City, Garden	AP#02	Urban
Al Maasara-Outostrad Road	AP#03	Urban
Saker Kouriesh	AP#04	Urban
Abassea Square	AP#05	Urban
Masr El Gededa	AP#06	Urban
Helwan	AP#07	Urban-Industrial
Helwan Metro Station	AP#08	Urban-Industrial
Torra El Balad Metro Station	AP#09	Urban-Industrial
Ramsis Square	AP#10	Urban
Tahrir Square	AP#11	Urban
Ataba Square	AP#12	Urban
Dokki Square	AP#13	Urban
Sphenkis Square	AP#14	Urban
Astobary	AP#15	Rural
Sadat City	AP#16	Industrial
Giza Square	AP#17	Urban
Harram Street	AP#18	Urban
Shobra El-khema	AP#19	Industrial

2. Experimental

2.1. Sample collection and sampling sites

The samples collected in this study represent dust deposited from ambient air on leaves of the street trees (leave dust). Each sample was gently brushed out and collected from the evergreen upper leaf surfaces of *F. nitida* trees at central and peripheral branches, 2 m above the ground. The collected samples were kept in auto sealable polyethylene bags, manually homogenized and stored in desiccators. For each sample, tens of leaves at the same height were used. The selection of *F. nitida* trees comes from its widespread in Cairo's streets and the possibility to collected a few grams of the dust samples from its upper leaf surfaces. In addition, the dust deposited in leaves represents the normal distribution of the dust from ambient air. Furthermore, the leaves of the *F. nitida* trees are not waxy and it is easy to collect all the particulate matter from its upper surfaces. Therefore, there is no missing to the particulate matter.

Dust samples were collected from sixteen different locations in Greater Cairo and two locations in the surrounding provinces. The deposited dust samples were collected during July 2010. At each site, dust deposited on leaves of the street trees was collected using of a sweeping tool, put in plastic bags and then transferred to the laboratory. The sampling sites were selected from areas with different pollution levels according to the traffic density and industrial activities. In addition, some deposited dust samples were collected near the economical units, which produce gaseous pollutants; others were taken near the roads which had different traffic intensities and the other samples were collected close to farming areas and far away from the sources of pollution. Therefore, there is a possibility to make a comparative analysis between heavy metal air pollution in those places. Table 1 illustrates the details of the locations where the dust samples have been collected.

2.2. High-resolution continuum source atomic absorption spectrometry

A high-resolution continuum source atomic absorption spectrometer, Model contrAA 700 (Analytik Jena AG, Jena, Germany) with two separate sampling compartments for flame and graphite tube atomizers have been used throughout this work. Only the latter atomizer has been used in this work. The instrument is equipped with a xenon short-arc lamp with a nominal power of