

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



Abdallah A. Shaltout^{a, b, *}, Bernhard Welz^{c, d}, Ivan N.B. Castilho^c

^a Spectroscopy Department, Physics Division, National Research Center, El Behooth Str., 12622 Dokki, Cairo, Egypt

^b Physics Department, Faculty of Science, Taif University, P.O. Box 888, 21974 Taif, Saudi Arabia

^c Departamento de Química, Universidade Federal de Santa Catarina, 88040-900 Florianópolis, SC, Brazil

^d Instituto Nacional de Ciência e Tecnologia do CNPq – INCT de Energia e Ambiente, Universidade Federal da Bahia, Salvador, BA, Brazil

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.

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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

* Corresponding author. Spectroscopy Department, Physics Division, National Research Center, El Behooth Str., 12622 Dokki, Cairo, Egypt. Tel.: +20 233669974 2101; fax: +20 233370931.

E-mail address: shaltout_a@hotmail.com (A.A. Shaltout).

includes a wide variety of sources of air pollution coming from fossil fuels, such as sulfur dioxide (SO₂), 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 constituents, 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; Shotyky 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 collect 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 contraAA 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

Table 2

Graphite furnace temperature program for the determination of Sb and Mo in solid dust samples and in aqueous calibration solutions.

	Temp./°C	Ramp/°C s ⁻¹	Hold time/s	Gas flow-rate/L min ⁻¹
(1) Drying	90	5	10	2.0
(2) Drying	130	7	10	2.0
(3) Pyrolysis	800 ^a , 1200 ^b	100 ^a , 300 ^b	15 ^a , 10 ^b	2.0
(4) Gas adaptation	800 ^a , 1200 ^b	0	5	0
(5) Atomization	1900 ^a , 2650 ^b	3000	8 ^a , 10 ^b	0
(6) Cleaning	2500 ^a , 2650 ^b	1500 ^a , 500 ^b	4	2.0

^a Sb.

^b Mo.

300 W, operating in a hot-spot mode, which emits a high-intensity spectral continuum over the entire spectral range from 190 to 900 nm. The spectrometer consists of a high-resolution double monochromator with a pre-dispersing prism and an echelle grating monochromator, both in Littrow mounting. The detector is a UV-sensitive charge-coupled device (CCD) array with 588 pixels, 200 of which are used for analytical purposes, which corresponds to a spectral environment of about 0.16 nm around the analytical line for Sb at 217.582 nm and about 0.35 nm around the line for Mo at 313.259 nm that becomes visible at high resolution. The spectrometer is computer controlled with specific software and allows access to arbitrary wavelength intervals within the entire spectral range. Due to the use of an internal neon lamp for dynamic wavelength stabilization, the achievable wavelength accuracy is about 0.1 pixel, corresponding to approximately 0.15–0.3 pm at wavelengths between 200 and 400 nm, respectively. Integrated absorbance (peak area) has been used exclusively for signal evaluation and quantification.

All experiments were carried out using pyrolytically coated solid sampling (SS) graphite tubes without dosing hole (Analytik Jena, Part No. 407-A81.303). Samples were weighted directly onto SS platforms (Analytik Jena, Part No. 407-152.023) using an M2P micro-balance (Sartorius, Göttingen, Germany, accuracy: 0.001 mg), and inserted into the graphite tubes using a pre-adjusted pair of tweezers, which is part of the SSA 5 manual SS accessory (Analytik Jena). Argon 99.996% (White Martins, São Paulo, Brazil) has been used as the purge and protective gas. The graphite furnace temperature program adopted for aqueous standards (calibration) and for solid samples for Mo (313.269 nm) and Sb (217.582 nm) is shown in Table 2.

2.3. Reagents and certified reference materials

Deionized and further purified Milli-Q high purity water (Millipore, Bedford, MA, USA) was used throughout for preparation of calibration solutions. The Sb stock standard solution, containing 1269 mg L⁻¹ Sb, was prepared by diluting Sb₂O₃ (SPEX, Edison, NJ, USA) in 2 mol L⁻¹ HCl; the Mo stock solution containing 1000 mg L⁻¹ Mo was prepared from a Titrisol concentrate (Merck, Darmstadt, Germany). Working standard solutions of Sb and Mo were prepared daily diluting the standards for HR-CS GF AAS measurements. For the determination of Sb, Ru has been used as a permanent modifier whereas no modifier was necessary for the determination of Mo. A stock solution containing 1000 mg L⁻¹ Ru (Fluka, Buchs, Switzerland) has been used as provided for coating of the platform. Ten repetitive injections of 40 µL of the stock solution, each one followed by a five-step temperature program with previously optimized ramp and hold times (Araujo et al., 2009), have been used for coating the platform with a total of 400 µg of Ru modifier. The certified reference materials (CRM) BCR 176R, “Fly Ash” (European Commission, Community Bureau of Reference, Brussels, Belgium), NIST 1648, “Urban Particulate Matter” and NIST

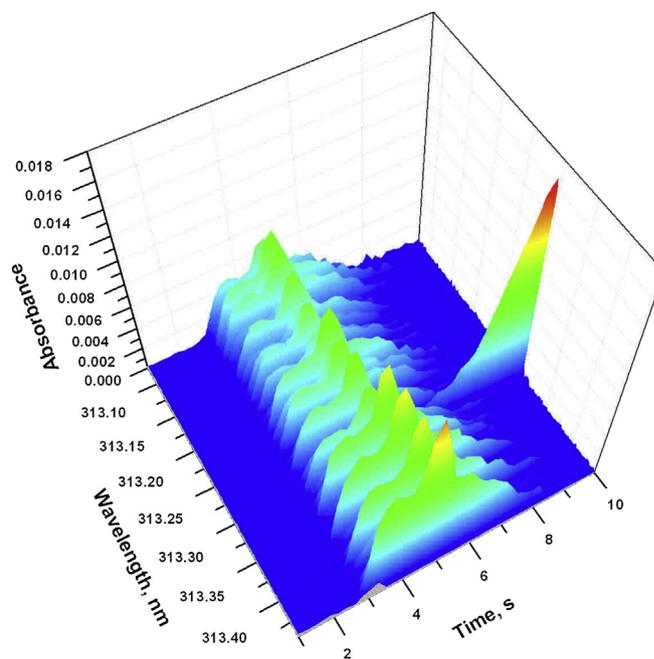


Fig. 1. Time- and wavelength-resolved absorbance spectrum for a dust fall sample in the vicinity of the Mo resonance line at 313.259 nm.

1649a, “Urban Dust” (National Institute for Standards and Technology, NIST, Gaithersburg, MD, USA), were used for validation purposes.

3. Results and discussion

3.1. Pyrolysis and atomization temperatures

The optimization of the pyrolysis and atomization temperatures has been carried out using an aqueous standard solution of 10 µg L⁻¹ of Sb and Mo and direct solid sample analysis with a sample mass of approximately 0.2 mg. It has been found that the pyrolysis and atomization temperatures of Sb and Mo for the solid dust fall samples were essentially identical with those determined for aqueous standard solutions without matrix effect (Araujo et al., 2009; Castilho et al., 2012a; Araujo et al., 2010). For Mo, the pyrolysis and atomization temperatures for the dust fall samples, using direct solid sample analysis were 1200 °C and 2650 °C, respectively. No modifier was necessary for the determination of Mo.

In the case of Sb, the use of a modifier is typically required for GF AAS because of its volatility and the occurrence of double peaks in the absence of a modifier (Welz and Sperling, 1999). A mixture of palladium and magnesium nitrates is the modifier used most frequently for Sb (Welz and Sperling, 1999). However, as the manual addition of a modifier in solution over the solid sample on the SS platform complicates the process, only permanent modifiers thermally deposited onto the platform surface have been investigated in this study. The best sensitivity has been obtained with the iridium modifier, but the highest thermal stability of Sb has been provided by the ruthenium permanent modifier, so that the latter one has been chosen in the present work. The SS platform was therefore coated with 400 µg Ru as a permanent modifier. A pyrolysis temperature of 800 °C and an atomization temperature of 1900 °C have been employed for the determination of Sb by HR-CS GF AAS in the collected dust fall samples and in the aqueous standard solutions. Table 2 shows the optimized graphite furnace temperature program for Sb and Mo, which is close to the one

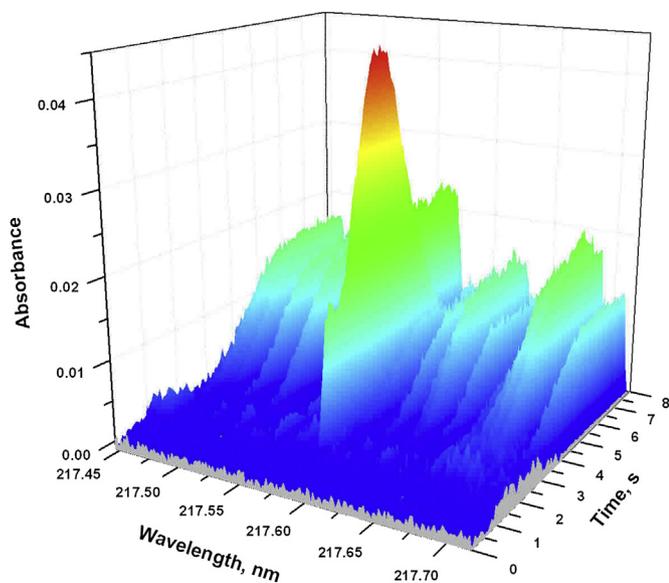


Fig. 2. Time- and wavelength-resolved absorbance spectrum for a dust fall sample in the vicinity of the Sb resonance line at 217.582 nm.

developed in previous work (Araujo et al., 2009; Castilho et al., 2012a; Araujo et al., 2010).

3.2. Quantitative analysis

For the determination of Mo, the primary resonance wavelength at 313.259 nm has been selected; the time- and wavelength-resolved absorbance spectrum in the vicinity of this line is shown in Fig. 1. In the case of Sb the most sensitive analytical line at 217.582 nm has been used as well; the time- and wavelength-resolved absorbance spectrum in the vicinity of this line is shown in Fig. 2 and the wavelength-resolved absorbance spectrum in Fig. 3. Significant structured background absorption could be observed for the dust fall samples under the optimized conditions; however, there was no spectral overlap between these structures and the analytical lines of Mo and Sb. Therefore, there is no spectral background correction required, besides the automatic correction for continuous background, and the Mo and Sb analyte signals showed a symmetric shape.

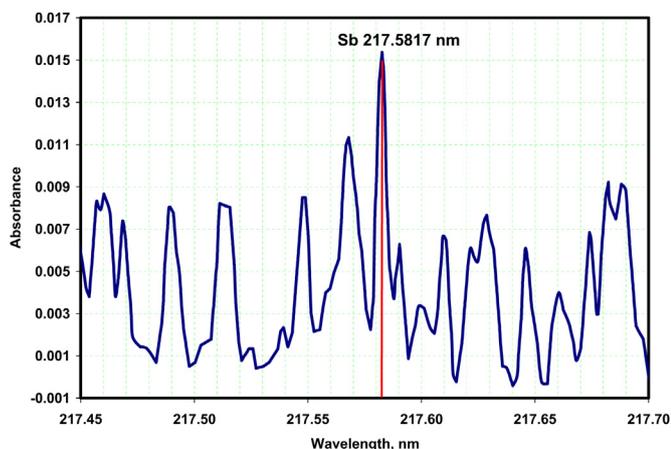


Fig. 3. Wavelength-resolved absorbance spectrum for a dust fall sample in the vicinity of the Sb resonance line at 217.582 nm.

Calibration curves were established using a blank and a series of standard solutions in the concentration range 25–4000 $\mu\text{g L}^{-1}$ (mass range: 0.5–80 ng) for Mo and 25–12,000 $\mu\text{g L}^{-1}$ (mass range: 0.5–240 ng) for Sb, respectively. Good correlation coefficients have been obtained with $R^2 = 0.997$ and 0.9995 for Mo and Sb respectively. The linear regression equations for Mo and Sb are $A_{\text{int}} = 0.0114m + 0.0127$ and $A_{\text{int}} = 0.0037m + 0.0041$, respectively, where A_{int} is the integrated absorbance summated over three pixels, and m is the analyte mass.

The results obtained for Mo and Sb in the collected dust fall samples are shown in Table 3. The precision, expressed as RSD, was in most of the cases better than 10%, which is quite acceptable for a routine determination of trace elements in the collected dust fall samples using direct solid sample analysis. Fig. 4 illustrates the distribution of Sb and Mo in the collected samples. It was found that the abundance of Sb and Mo in the collected dust fall samples is much higher than their abundances in the earth's crust, which is 1 $\mu\text{g g}^{-1}$ and 0.2 $\mu\text{g g}^{-1}$ for Mo and Sb respectively (Wedepohl, 1971). There are strong variations in the concentration of Sb for the collected dust fall samples. A remarkably high concentration of Sb was found in the majority of the samples, especially those collected from the different squares in Greater Cairo. According to the screening level of 31 $\mu\text{g g}^{-1}$ Sb of the USEPA (United States Environment, 2010), the concentration of Sb in the present work is up to 36-times higher than the screening level (Table 4). As an example, the concentrations of Sb are 1117 and 1073 $\mu\text{g g}^{-1}$ at Abassea square and Tahrir square, respectively. Other squares (Shobra El-Khema, Ramsis, Masr El-Gededa, Dokki and Sphenkis) as well as Haram Street location have also high concentrations of Sb, although less than Abassea and Tahrir squares.

The high concentration of Sb in most of the squares and some of the streets of Greater Cairo is most likely related to traffic, as brake linings or pads contain up to 7% of Sb_2O_3 and 1% of MoS_2 . Brake pads consist of backing material, such as steel fiber, glass fiber and ceramic fiber, combined by resin with carbon black as friction adjuster, brake noise adjuster and anticorrosive treatment. Because

Table 3

Quantitative determination of Sb and Mo in dust fall samples collected from Greater Cairo.

Samples ID	Measured values		Certified values		Sb:Mo
	Sb, $\mu\text{g g}^{-1}$	Mo, $\mu\text{g g}^{-1}$	Sb, $\mu\text{g g}^{-1}$	Mo, $\mu\text{g g}^{-1}$	
BCR 176R	430 ± 18		418 ± 18		
NIST SRM 1648	50 ± 5		45		
NIST SRM 1649a	35 ± 5	15 ± 1	29.9 ± 0.7	13.5 ± 0.9	2.2
AP#01	271 ± 37	207 ± 4			1.3
AP#02	213 ± 2	199 ± 18			1.1
AP#03	375 ± 73	186 ± 15			2.0
AP#04	526 ± 59	152 ± 50			3.5
AP#05	1117 ± 230	178 ± 8			6.3
AP#06	960 ± 90	173 ± 1			5.5
AP#07	442 ± 15	122 ± 10			3.6
AP#08	301 ± 31	132 ± 17			2.3
AP#09	609 ± 3	296 ± 18			2.1
AP#10	1040 ± 201	207 ± 6			5.0
AP#11	1073 ± 72	156 ± 18			6.9
AP#12	287 ± 36	229 ± 26			1.3
AP#13	897 ± 214	140 ± 50			6.4
AP#14	1089 ± 410	361 ± 51			3.0
AP#15	198 ± 16	185 ± 9			1.1
AP#16	992 ± 300	152 ± 38			6.5
AP#17	525 ± 56	162 ± 82			3.2
AP#18	831 ± 11	113 ± 2			7.4
AP#19	924 ± 56	263 ± 9			3.5
Average	667 ± 339	190 ± 62			3.5

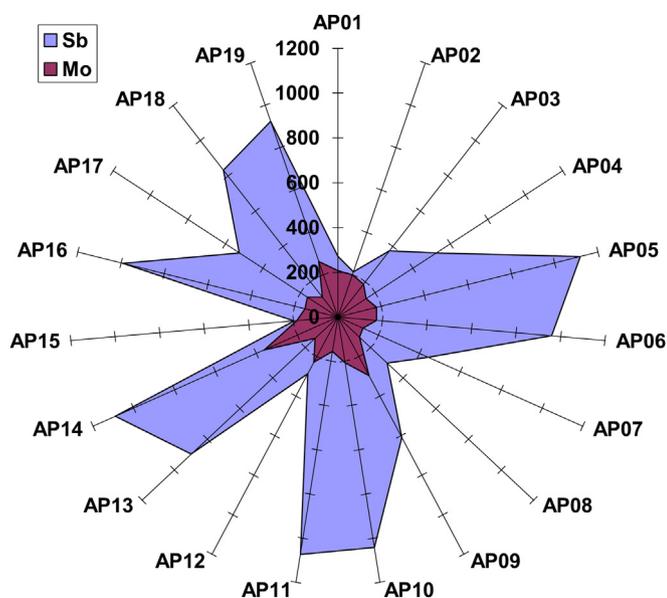


Fig. 4. Sb and Mo distribution in the dust fall samples collected from Greater Cairo.

the pad is heated by friction with the disk, the antimony sulfide must be treated for heat-resistant properties. The brake pads are typically exchanged only after 50,000–70,000 km; therefore, particles due to the brake pad wear are likely to be released into the atmosphere. Other application of Sb represents further anthropogenic sources such as Sb compounds in alloying material for lead and tin. Furthermore, Sb compounds are being used in chlorine- and bromine-containing fire retardants, the semiconductor industry, pigment, traditional cosmetics and antiprotozoan drugs.

Obviously, there might be other sources of Sb, natural processes whereas Sb is naturally found as the sulfide mineral stibnite (Sb_2S_3). Natural processes are unlikely to contribute significantly to the Sb content in road dust of a mega city, particularly not at major

Table 4

Comparison of the results (mean values) obtained in this work with published data about the content of Sb and Mo in air particulate matter (APM) collected on filter material and in road dust (RD); all values in $\mu\text{g g}^{-1}$.

Material	Sb	Mo	Sb:Mo	Reference
RD, Greater Cairo, Egypt	667	190	3.5	This work
RD, Luanda, Angola	3.4	2.0	1.7	(Ferreira-Baptista and De Miguel, 2005)
APM on filter, Buenos Aires, Argentina	262	186	1.4	(Castilho et al., 2012b)
RD, Hexi corridor, China	1.44	1.22	1.18	(Wang et al., 2010)
APM on filter, Casaccia, Italy	7.5	0.7	10.7	(Avino et al., 2008b)
APM on filter, Ladispoli, Italy	2.8	0.65	4.3	(Avino et al., 2008b)
APM on filter, Tokyo, Japan <2 μm	199	72	2.8	(Furuta et al., 2005)
APM on filter, Tokyo, Japan 2–11 μm	188	85	2.2	(Furuta et al., 2005)
APM on filter, Tokyo, Japan >11 μm	53	79	0.67	(Furuta et al., 2005)
RD, Buenos Aires, Argentina <37 μm	12	5.5	2.2	(Fujivara et al., 2011)
RD, Buenos Aires, Argentina 37–50 μm	9.95	4.3	2.3	(Fujivara et al., 2011)
RD, Buenos Aires, Argentina 50–75 μm	3.0	3.5	0.86	(Fujivara et al., 2011)
RD, Buenos Aires, Argentina 75–100 μm	3.34	2.9	1.1	(Fujivara et al., 2011)
Average ratio Sb:Mo			2.6	

squares and roads. From the anthropogenic sources point of view, Sb is increasingly being used in the semiconductor industry, in a wide variety of alloys, and as a flame retardant (Bogdanov et al., 1983). Industries such as smelters, coal-fired plants and refuse incinerators can release relatively high amounts of Sb into the air. It is well known that Sb compounds are used to make incombustible and thermally resistant plastic products. In addition, a lot of plastic products are treated with antimony sulfide for flame-proof properties. When these products are incinerated, Sb is enriched in the fly ash. When released to air, Sb can attach itself to very small particles and might stay in the air particulate matter and dust falls for many days and be transported over long distances. There is a possibility that antimony trioxide is produced during the process of heating, which is an abiding concern because antimony trioxide is known as being carcinogenic (International Agency for Research on Cancer, 1989).

In the case of Mo, there is a remarkable similarity in the concentration of this analyte in all the collected dust fall samples. According to the screening level of the USEPA of $390 \mu\text{g g}^{-1}$ (United States Environment, 2010), the average concentration of Mo in the present work of $190 \pm 62 \mu\text{g g}^{-1}$ and even the maximum value of $361 \mu\text{g g}^{-1}$ Mo is lower than the screening level (Table 3). Therefore, there appears to be no problem with the Mo concentration in the collected dust fall samples. However, natural and anthropogenic sources are responsible for Mo in dust fall samples. Naturally, Mo does not occur as a free metal on earth, but it is found in various oxidation states in minerals. Several metallurgical and chemical applications are based on Mo compounds due to its ability to withstand extreme temperatures without significantly expanding or softening.

According to Table 3, it is obvious that the average ratio between the two analytes is quite different in the dust fall samples, mostly because of the strong variation of the Sb content, which suggests that the source of the two elements might not be the same in all cases. Nevertheless, in average it comes close to a ratio of Sb:Mo ≈ 3.5 , and when the extreme ratios above 1:5 are excluded, the average comes to 2.3, which is close to the ratio of 2.2 in the NIST SRM 1649a (urban dust). A comparison of our results with values published by others might be of some interest as well. According to more recently published papers on the subject, which are compiled in Table 4, the ratios between the two analytes (Sb:Mo) range from 0.08 to 10.7, with an average of 2.6; however, when the three extreme values are excluded (not considering the results of the present work), the average comes to 2.1, again very close to the above-discussed values. It might therefore be assumed that a Sb:Mo ratio around 2 indicates that both elements are traffic-related, i.e., due to the wear of brake pads and linings, and quite a number of recently published reports come close to this value. Of course, the concentration of the two analytes in brake pads and linings might change from country to country and with time, as new compositions might be introduced without announcing the change in public; anyway, the exact composition of these materials is usually kept as a secret by the manufacturers. In cases where the ratio differs significantly from the above-mentioned ratio it might be assumed that other, most likely industrial sources, have a significant contribution to the Sb content in the collected dust or air particulate matter samples.

3.3. Enrichment factors

The concept of enrichment factors (EFs) was developed to drive the origin of elements in the atmosphere and precipitation (Reimann et al., 2005). Estimation of EFs may provide useful evidence of the source of elements in the aerosols and precipitation. It compares the relative concentrations of an analyte in the present

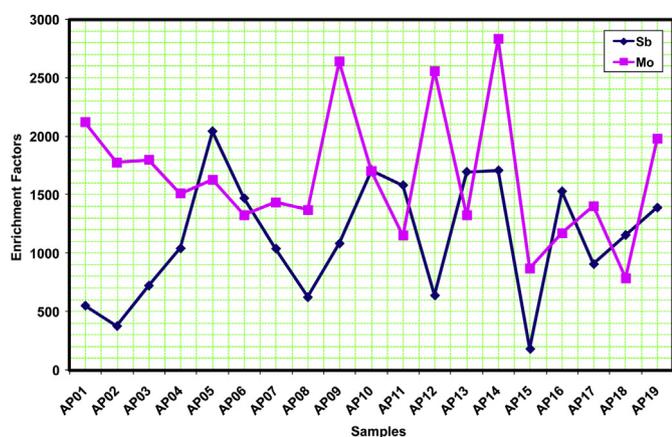


Fig. 5. Enrichment factor trends of Sb and Mo versus the collected samples.

dust to that in earth's crust. In the present work, the following equation was used to calculate the EF;

$$EF = \frac{(E_{el}/E_{REEs})_{\text{dust fall}}}{(E_{el}/E_{REEs})_{\text{earth's crust}}} \quad (1)$$

where E_{el} is the concentration of the element under investigation, and E_{REEs} is the total concentration of the rare earth elements. The total concentration of the rare earth elements of the dust fall was taken from our previous work (Shaltout et al., 2013) whereas the reference values of the earth's crust were taken from reference (Wedepohl, 1995). The sum of the rare earth elements was selected because it is rarely enter the atmospheric aerosol from anthropogenic sources. This was suggested as a suitable reference quantity (Bargagli et al., 1995; Bergamaschi et al., 2005). As shown from Fig. 5, the enrichment factors of Sb and Mo are highly enriched which could be referred to the different anthropogenic sources. The obtained results are in a good agreements with the literature whereas, Sb and Mo are considered as a highly enriched elements ($EF > 100$) (Berg et al., 1994).

3.4. Sensitivity and limit of detection

The limit of detection (LOD) has been calculated as three times the standard deviation of 10 measurements of a blank divided by the slope of the calibration curve; in SS-GF AAS the blank measurements are usually carried out according to the "zero mass response" technique (Kurfürst and Kurfürst, 1998), introducing the platform without sample, but with the modifier, as it is practically impossible to find a blank dust sample without analyte. The limit of quantification (LOQ) is based on the same measurements, using 10 times the standard deviation of the blank readings. The LOD and LOQ were determined as 15 and $50 \mu\text{g g}^{-1}$ for both, Mo (313.259 nm) and Sb (217.582 nm), based on a sample mass of 0.2 mg introduced into the furnace. A larger sample mass could obviously be introduced, resulting in even lower LOD and LOQ; however this was not found necessary for the present investigation. The characteristic mass (m_0), defined as the mass of the analyte that produces an integrated absorbance of 0.0044 s, has been determined as 38 μg for Sb and 28 μg for Mo.

3.5. Accuracy of the method

To confirm the validity of the analytical procedures, standard reference materials of airborne particulate matter were measured. Three certified reference materials (CRM), BCR 176R (City Waste

Incineration Ash), NIST SRM 1648 (Urban Particulate Matter) and NIST SRM 1649a (Urban Dust) have been analyzed, and the analytical results are listed in Table 3. Unfortunately only one of the CRM had a certified value for Mo; however, all the found values were in a good agreement with the certified values at a 95% confidence interval. This shows that direct solid sample analysis HR-CS GF AAS with calibration against aqueous standards can be used for this kind of determination.

4. Conclusion

A simple, fast and reliable procedure for the determination of Mo and Sb in dust deposited on tree leaves from Greater Cairo has been developed using high-resolution continuum source graphite furnace atomic absorption spectrometry and direct solid sample analysis. A clear advantage of direct solid sampling is that the method does not require any toxic or corrosive acids and does not produce any hazardous waste; in addition, the method is fast, as it does not require any sample preparation. Calibration could be carried out against aqueous standards, which further simplifies the procedure. Based on the measurement of the certified reference materials, there is a good agreement with the certified values at a 95% confidence interval. It was found that the concentration of Sb is more than one order of magnitude higher than the screening level of the USEPA, whereas the average concentration of Mo is below the screening level. It might be assumed that many more elements could be determined in road dust or similar samples using the same technique.

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