Method development for the determination of Cd, Cu, Ni and Pb in PM2.5 particles sampled in industrial and urban areas of Greater Cairo, Egypt, using high-resolution continuum source graphite furnace atomic absorption spectrometry

This is an author produced version of a paper published in:

Microchemical journal (ISSN: 0026-265X)

Citation for the published paper:

http://dx.doi.org/10.1016/j.microc.2013.10.009

Downloaded from: http://gup.ub.gu.se/publication/185675

Notice: This paper has been peer reviewed but does not include the final publisher proof-corrections or pagination. When citing this work, please refer to the original publication.
Method development for the determination of Cd, Cu, Ni and Pb in PM$_{2.5}$ particles sampled in industrial and urban areas of Greater Cairo, Egypt, using high-resolution continuum source graphite furnace atomic absorption spectrometry

Abdallah A. Shaltout$^{a,b,*}$, Johan Boman$^c$, Bernhard Welz$^d$, Ivan N.B. Castilho$^d$, Emad A. Al Ashkar$^a$, S.M. Gaita$^c$

$^a$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

$^c$Department of Chemistry and Molecular Biology, Atmospheric Science, University of Gothenburg, SE-412 96 Göteborg, Sweden

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

* Corresponding author; E-mail address: shaltout_a@hotmail.com (A.A. Shaltout)

Telefax: +202 3337 0931

Telephone: +202 3366 9974-2101
Abstract

Energy-dispersive X-ray fluorescence spectrometry (EDXRF) is not adequate for the determination of some potentially hazardous trace elements, such as Cd, Cu, Ni and Pb at low concentration in PM$_{2.5}$ atmospheric aerosol particles. Therefore, a method has been developed for the determination of these elements in atmospheric aerosol particles using high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS-GF-AAS) without using modifiers. The pyrolysis and atomization temperatures were optimized for this analysis. The samples were collected from industrial and urban areas of Greater Cairo, Egypt. Atmospheric aerosol particles, PM$_{2.5}$, have been collected on polycarbonate filters loaded by a cyclone sampler. The duration of the collection was 24 h at an air flow-rate of 3 L min$^{-1}$. Microwave-assisted acid digestion with ultra-pure nitric acid was used to dissolve the polycarbonate filters, including the atmospheric aerosol particles. For the validation of the methods, the results were compared with those obtained by total reflection X-ray fluorescence (TXRF) and inductively coupled plasma mass spectrometry (ICP-MS). Good agreement between the results of the different spectrometric techniques was found. The measured concentrations of Cd, Cu, Ni, and Pb were below the limits defined by international guidelines and national standards of ambient air quality.

Keywords: High-resolution continuum source graphite furnace atomic absorption spectrometry; Aerosol particle PM$_{2.5}$; Cd; Cu; Ni; Pb.
1. Introduction

The elemental analysis of the fine particulate matter, i.e. particles with aerodynamic diameter equal to or less than 2.5 µm (PM$_{2.5}$), has been in the focus of interest in the developed countries for quite some time. A major constituent of PM$_{2.5}$ is black carbon [1], which is also referred to as soot. It is produced by incomplete combustion of organic matter and always mixed with inorganic atmospheric constituents [2,3]. The knowledge of the composition of the inorganic atmospheric constituents is very important as it has an essential relation to health problems [4,5] and climate change [6-8]. In addition, it gives important information on their origin and also reveals whether they were emitted as primary or secondary particles. It is generally assumed that, the smaller the particle, the more harm it might cause, as it penetrates deeper into the lungs [9]. In addition, fine particulate matter have an effect on the radiation balance of the earth [10], because it scatters and absorbs most of the radiation in the visible region and it is therefore of great interest to measure its concentration in the ambient air. Furthermore, PM$_{2.5}$ has a long atmospheric residence time, which facilitates its transportation over long distances, covering thousands of kilometers. The bulk of these particles originates from anthropogenic emissions [11,12], both directly and as secondary formation in the atmosphere from gases, such as SO$_2$, NO$_x$ and volatile organic compounds. The local emission of fine particles can become an issue of regional and even global concern, since these particles are able to affect air quality in other countries through transnational and even transcontinental transport.

In Greater Cairo, the largest city in Egypt and also in Africa, the air pollution problems due to the high levels of lead, sulfur dioxide and suspended particulate matter have led to many environmental problems. The origin of the air pollution in Greater
Cairo is multifold; burning of trash, poor dispersion factor due to the lack of rain, vehicle emissions (~4.5 million cars on the streets of Cairo), urban industrial operations, and its 15-20 million inhabitants. In addition, there are remarkable seasonal temperature changes ranging from 15-45 °C. It is estimated that 10,000 to 25,000 people per year die in Cairo due to air pollution-related diseases. Furthermore, Greater Cairo daily produces 10,000 tons of waste material without well-organized collection and management, resulting in illegal burning of the waste.

Previous studies on particulate matter (PM$_{2.5}$ and PM$_{10}$), polycyclic aromatic hydrocarbons (PAH) and volatile organic compounds (VOC) have been conducted in Greater Cairo [13-18]. Studies of PM$_{2.5}$ have been conducted not only in Greater Cairo but also in other developing countries (Vietnam, China, Pakistan, Tanzania, Kenya) [19-24] as well as in some European cities [25-28]. In none of these studies more recently introduced analytical techniques such as high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) have been used for quantitative elemental analysis of PM$_{2.5}$. Recently, fine aerosol particles (PM$_{2.5}$) have been collected from urban and industrial locations of Greater Cairo and analyzed using an energy dispersive X-ray fluorescence (EDXRF) spectrometer with Mo secondary target [29]. In this study the determination of Cd, Cu, Ni and Pb proved to be difficult due to the low intensities of the characteristic radiation of these elements, and their concentration in the collected aerosol particles was too low for an accurate determination.

Metals, such as Cd, Cu, Ni, and Pb might be toxic to human beings and it is therefore of interest to follow the eco-cycles of these metals as environmental hazards,
Once they are released into the atmosphere, biosphere and technosphere. In the present work, atmospheric aerosols from industrial and urban sites in Greater Cairo were sampled. The sample collection was carried out weekly for 24 h/sample during September and October 2010. The samples were analyzed for Cd, Cu, Ni and Pd using HR-CS GF AAS. For verification of the developed method, the results were compared with those obtained by total reflection X-ray fluorescence (TXRF) and inductively coupled plasma mass spectrometry (ICP-MS).

2. Experimental

2.1. Instrumentation

A Model contrAA 700 High-resolution continuum source atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) was used for the determination of Cd, Cu, Ni and Pb in the aerosol particles. The spectrometer consists of a pre-dispersing prism and an echelle grating monochromator, both in Littrow mounting. A xenon short-arc lamp with a nominal power of 300 W, operating in hot-spot mode, is used as the continuum radiation source. The detector is a UV-sensitive charge coupled device (CCD) array with 588 pixels, 200 of which are used for analytical purposes, whereas the rest is used for correction purposes. More details can be found in our previous work [32, 33].

For comparison, Total Reflection X-ray Fluorescence (TXRF) Spectrometry and inductively coupled plasma atomic mass spectrometry (ICP-MS) [34] were used. In TXRF a well-polished sample holder is used to hold the dried sample. The incidence angle of the well collimated exciting X-ray radiation is below 0.1 degrees and the radiation is totally reflected. The geometry allows a compact design resulting in low detection limits for many elements. For the TXRF analysis a S2 PICOFOX TXRF
spectrometer (Bruker AXS GmbH, Karlsruhe, Germany) was used. The radiation from an air-cooled X-ray tube is focused and monochromatized before exciting the elements in the digested sample. A Silicon Drift Detector is used for detecting the characteristic radiation of the elements in the sample. For quantification an internal standard is added. An ICP-MS ELAN 6000 (Perkin Elmer–SCIEX, Thornhill, Canada) was used for all comparison. A cross-flow nebulizer equipped with a Scott spray chamber was used. 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. 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

Deionized and further purified Milli-Q high purity water (Millipore, Bedford, MA, USA) was used throughout. Stock standard solutions for the elements under investigation, containing 1000 mg L$^{-1}$ were used (Merck, Darmstadt, Germany). Ultra-pure nitric acid (HNO$_3$, 65% m/v, Fluka, Sigma-Aldrich, Germany) was used for the digestion of the filters. Working standard solutions were prepared daily diluting the standards for HR-CS GF AAS and ICP-MS measurements. All other reagents were of analytical reagent grade. An internal standard (Ga) with a concentration of 5 mg L$^{-1}$ was used for the TXRF measurements.

2.3. Sample collection and digestion

Atmospheric aerosols (PM$_{2.5}$) were collected from industrial and urban sites in Greater Cairo, Egypt, during September and October 2010. The urban site was situated
At the National Research Center, 3 km away from the center of Cairo whereas the industrial site was situated at Shobra El khema in the northwest of Greater Cairo. Atmospheric aerosols were collected on polycarbonate filters using a cyclone sampler (Casella CEL, Bedford, UK). The cyclone makes an air-stream move in a cyclonic orbit where larger particles are separated from the fine particles since their higher inertia prevents them from following the airflow. The polycarbonate filters have a diameter of 25 mm and a pore size of 0.4 µm. These filters have been used in previous studies and have a high particle collection efficiency and high purity [29-31]. The duration of the collection was 24 h with an air flow of 3 L min⁻¹. In order to avoid the influence of the traffic as a single source, the equipment (cyclone, flow meter, and the pump) was mounted at a height of 20 m, and more than 50 m from the nearest main road. The polycarbonate filters were weighted on a microbalance with µg determination limit (Sartorius CC50, Göttingen, Germany) before and after sampling to determine the mass concentrations. The polycarbonate filters including the atmospheric aerosols were dissolved with ultra-pure nitric acid using microwave-assisted acid digestion. Before the digestion, the PTFE vessels were soaked overnight in diluted nitric acid (10% m/v HNO₃) at room temperature followed by a cleaning program recommended by the manufacturer. For the digestion of air particulate filters, 5 mL of concentrated nitric acid (65% m/v) were added to each filter in the PTFE digestion vessels of the microwave system. The vessels were closed and introduced into the microwave oven and the digestion program given in Table 1 was used. In order to avoid foaming and splashing, the vessels were allowed to cool to room temperature after the end of the digestion program, opened carefully and the volume was made up to 12 mL with water. The digested samples of air particulate filters were used with the HR-CS GF AAS, TXRF and ICP-MS techniques.
Table 1. Microwave digestion program for the polycarbonate filters including the atmospheric aerosols.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td>200</td>
</tr>
<tr>
<td>Pressure, bar</td>
<td>40</td>
</tr>
<tr>
<td>Power, %</td>
<td>90</td>
</tr>
<tr>
<td>Ramp, min</td>
<td>5</td>
</tr>
<tr>
<td>Hold time, min</td>
<td>15</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1. Sample weight of PM$_{2.5}$

The mass concentrations of PM$_{2.5}$ ranged from 11 µg m$^{-3}$ to 71 µg m$^{-3}$ with an average of 33±18 µg m$^{-3}$ for the urban site, and it varied between 10 µg m$^{-3}$ and 14 µg m$^{-3}$ with an average of 12±2 µg m$^{-3}$ for the industrial site. The average mass concentrations were not comparable at the two sites and there are a wide range of mass concentrations of PM$_{2.5}$. The wide concentration range can be due to variations in the local climate, the variations in the amount of Saharan dust arriving at the sites and the experienced episodes of smoke from waste burning in the rice fields in the Nile delta north of Cairo during September to December [13, 35, 36]. An indication of the large-scale influence on air quality can be noticed from the PM$_{2.5}$ mass concentrations from the two locations. Although there is no legally binding limit for PM$_{2.5}$ in Egypt, the present average PM$_{2.5}$ concentrations at the industrial and the urban site is higher than the yearly mean standard, 25 µg m$^{-3}$, in the European commission’s environment quality standards for ambient air [37]. Table 2 illustrates the PM$_{2.5}$ mass concentrations from
other studies, mainly in the Mediterranean region and North-East Africa. The studies of 
PM$_{2.5}$ mass concentrations in Cairo [13,38] and in Beijing [39] shows high PM$_{2.5}$ mass 
concentrations compared with the present study. The PM$_{2.5}$ mass concentrations are in 
agreement with our previous study in Cairo [29] and comparable with other 
international studies from Beirut, Lebanon [40], Nairobi, Kenya [41], Athens, Greece 
[42] and Taif, Saudi Arabia [31], although, the present samples were only collected 
during September and October 2010.

Table 2, Comparison between the present concentration of PM$_{2.5}$ and published data 
from other studies.

<table>
<thead>
<tr>
<th>References</th>
<th>Industrial, µg m$^{-3}$</th>
<th>Residential, µg m$^{-3}$</th>
<th>Year</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Present work</strong></td>
<td>12±2</td>
<td>33±18</td>
<td>2010</td>
<td>Cairo, Egypt</td>
</tr>
<tr>
<td>Shaltout et al [43]</td>
<td>47±15</td>
<td>46±31</td>
<td>2011</td>
<td>Taif, Saudi Arabia</td>
</tr>
<tr>
<td>Abu-Allaban et al [38]</td>
<td>216±11</td>
<td>62±3</td>
<td>2001</td>
<td>Cairo, Egypt</td>
</tr>
<tr>
<td>Saliba et al [40]</td>
<td>41</td>
<td>39</td>
<td>2003</td>
<td>Beirut, Lebanon</td>
</tr>
<tr>
<td>Götschi et al [42]</td>
<td></td>
<td>37±27</td>
<td>2002</td>
<td>Athens, Greece</td>
</tr>
<tr>
<td>Gatari et al [41]</td>
<td>30±9</td>
<td></td>
<td>2001</td>
<td>Nairobi, Kenya</td>
</tr>
<tr>
<td>Wang et al [39]</td>
<td></td>
<td>154±146</td>
<td>2001-2003</td>
<td>Beijing, China</td>
</tr>
<tr>
<td>Boman et al [29]</td>
<td>70±34</td>
<td>55±20</td>
<td>2010</td>
<td>Cairo, Egypt</td>
</tr>
</tbody>
</table>
3.2. Optimization of Pyrolysis and Atomization Temperatures

Aqueous standards of Cd, Cu, Ni and Pb were used to establish the optimum pyrolysis and atomization temperatures. The pyrolysis and atomization curves for the investigated analytes without the use of a chemical modifier are shown in Figure 1. The pyrolysis and atomization curves for Cd and Pb showed no significant difference in the maximum applicable pyrolysis temperature without analyte loss. In the case of Cu and Ni the highest pyrolysis temperatures without analyte loss were finally chosen in order to remove as much as possible of the residual matrix, and the lowest atomization temperatures for quantitative atomization were chosen in order to get the longest possible tube lifetime. Table 3 shows the optimized graphite furnace temperature program for the elements of interest. It has been found that higher sensitivity (integrated absorbance) is obtained in the absence of a chemical modifier than with modifiers (Ir, Ru, Pd). This is due to the fact that lower atomization temperatures can be used without a modifier, which results in a longer residence time of the atoms in the radiation beam, and hence a higher atom cloud density, at least for the more volatile elements [43].
Figure 1. Pyrolysis and atomization curves for aqueous standard solutions of Cd, Cu, Ni and Pb.

Table 3. The optimized graphite furnace program for Cd, Cu, Ni and Pb using HR-CS GF AAS.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Temp, °C</th>
<th>Ramp, °C s⁻¹</th>
<th>Hold time, s</th>
<th>Purge gas, L min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying 1</td>
<td>90</td>
<td>6</td>
<td>20</td>
<td>2.0</td>
</tr>
<tr>
<td>Drying 2</td>
<td>110</td>
<td>5</td>
<td>10</td>
<td>2.0</td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>600°, 1100°, 1300°, 700°</td>
<td>300°, 100°, 100°, 30°</td>
<td>10°, 30°, 20°</td>
<td>2.0</td>
</tr>
<tr>
<td>Gas Adaptation</td>
<td>600°, 1100°, 1300°, 700°</td>
<td>0</td>
<td>5</td>
<td>Stop</td>
</tr>
<tr>
<td>Atomization</td>
<td>1200°, 2000°, 2550°, 1700°</td>
<td>3000°, 1500°, 2000°</td>
<td>3°, 8°, 7°, 5°</td>
<td>Stop</td>
</tr>
<tr>
<td>Cleaning</td>
<td>2450°, 2650°</td>
<td>500</td>
<td>4</td>
<td>2.0</td>
</tr>
</tbody>
</table>

3.3. Analytical Figures of Merit

According to Table 4, the calibration curves for Cd, Cu, Ni and Pb showed reasonable linearity in the concentration range from 0.5-5 ng g⁻¹, 50-1000 ng g⁻¹, 10-100
ng g⁻¹ and 2.5-25 ng g⁻¹, respectively. The correlation coefficients were 0.997, 0.999, 0.999 and 0.997 for Cd, Cu, Ni and Pb, respectively. In the present work, the limits of detection (LOD) and quantification (LOQ) were determined as three times and ten times, respectively, the standard deviation of twenty consecutive measurements of the reagent blank. Table 4 shows the LOD and LOQ in ng g⁻¹ of Cd, Cu, Ni and Pb found in the APM samples. According to the obtained LOD and LOQ values, the suitability of the developed method for the determination heavy metals using HR-CS GF AAS without chemical modifiers becomes obvious. In our previous work [29,31], the accuracy of the method for analyzing PM₂.₅ was confirmed by using EDXRF setup. However, the digestion of the CRM of airborne particulate matter trapped on a filter is undesired in order to use it for further nondestructive analysis. The comparison with different spectroscopic techniques would be an alternative method.

Table 4, Figures of merit for the determination of Cd, Cu, Ni and Pb in PM₂.₅ samples after microwave-assisted acid digestion using HR-CS GF AAS

<table>
<thead>
<tr>
<th>Analyte</th>
<th>λ, nm</th>
<th>Linear Equation</th>
<th>$R^2$</th>
<th>LOD, µg L⁻¹</th>
<th>LOQ, µg L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>228.802</td>
<td>$A_{\text{int}} = 0.161m_{\text{Cd}} + 0.022$</td>
<td>0.997</td>
<td>0.03</td>
<td>0.096</td>
</tr>
<tr>
<td>Cu</td>
<td>216.509</td>
<td>$A_{\text{int}} = 0.0013m_{\text{Cu}} + 0.099$</td>
<td>0.999</td>
<td>11</td>
<td>33</td>
</tr>
<tr>
<td>Ni</td>
<td>232.003</td>
<td>$A_{\text{int}} = 0.0109m_{\text{Ni}} + 0.084$</td>
<td>0.999</td>
<td>0.94</td>
<td>2.8</td>
</tr>
<tr>
<td>Pb</td>
<td>217.005</td>
<td>$A_{\text{int}} = 0.0154m_{\text{Pb}} + 0.030$</td>
<td>0.997</td>
<td>0.27</td>
<td>0.82</td>
</tr>
</tbody>
</table>
3.4. Quantitative Analysis Results

There are several reasons for analyzing the aerosol particles with HR-CS-GF-AAS. In our previous work, quantitative elemental analysis of the aerosol particles was carried out using EDXRF with Mo as secondary target [29, 31, 34]. Quantitative results for Cd, Cu, Ni and Pb were difficult to obtain in the EDXRF analysis. As shown in Figure 2, Cu Kα and Ni Kβ1 are close to each other in energy, giving rise to higher LOD and LOQ with the relatively large peak widths obtained. There is also a spectral interference between Pb-Lα and As Kα at photon energy range of 10.5 keV, giving rise to an elevated LOD and LOQ for Pb. In addition, the characteristic radiation of Cd L lines (Lα1=3.134, Lα2=3.127, Lβ1=3.528, and Lβ2=3.717 keV) are overlapping with Ar lines (Kβ1=3.191, and Lβ2=3.71686 keV) and Ca Kα lines (Kα1=3.691, Kα2=3.688 keV). Since the analysis was carried out in ambient air and not in vacuum the Ar peak was high and the concentration of Ca in the aerosol samples is high, the LOD and LOQ of Cd was higher than the anticipated concentrations of Cd in the samples. Therefore, there is an essential need of an alternative, accurate technique for these elements. HR-CS GF AAS is one of the alternative techniques. Figures 3-5 illustrate examples of the time- and wavelength-resolved absorbance spectra of Cd (228.802 nm), Ni (233.003 nm) and Pb (217.001 nm) for some of the PM2.5 samples. Any continuous background absorption has been corrected automatically by the software of the instrument and does not appear in the absorbance spectra. The spectra of Cd and Cu do not show any other absorbance besides that of the analyte. This means that these elements could be equally determined using a conventional line-source atomic absorption spectrometer with deuterium background correction. In the case of Ni (Figure 4), however, there is a remarkable structured background around the absorbance signal of the elements of interest. The second absorption line at 232.036 nm close to the Ni line is due to iron, and the slight
shoulder that appears at the utmost right side of the spectrum is the wing of the secondary nickel line at 232.138 nm, which is slightly out of the spectral range [33]. In contrast, when conventional LS AAS with a deuterium background correction system is used, the atomic absorption due to iron would inevitably cause spectral interference, resulting in significant overcorrection. Zeeman-effect background correction could obviously deal better with these near-by absorption lines, although spectral interferences could not be excluded. Based on the calibration curves of Cd, Cu, Ni and Pb, quantitative analysis was carried out for the collected atmospheric aerosols using HR-CS GF AAS, the results of which are shown in Table 5. The high standard deviation in the results indicates that there were wide variations of all elements in the industrial and urban areas.

Figure 2, EDXRF spectra of the aerosol particles collected on polycarbonate filters
Figure 3, Time- and wavelength-resolved absorption spectrum of Cd 228.802 nm in PM$_{2.5}$ (Filter #72) without chemical modifier using HR-CS GF AAS.

Figure 4, Time- and wavelength-resolved absorption spectrum of Ni 232.003 nm in PM$_{2.5}$ (Filter #56) without chemical modifier using HR-CS GF AAS.
Figure 5, Time- and wavelength-resolved absorption spectrum of Pb 217.001 nm in PM$_{2.5}$ (Filter #71) without chemical modifier using HR-CS GF AAS.

As shown in Table 5, the concentrations of Cd, Cu, Ni and Pb in the urban area are higher than in the industrial area. Therefore, it would be expected that the industrial activities are not the main source of these elements. To determine if this tendency is temporary or not, more sampling for a longer period of time is needed. Anthropogenic activities, such as the heavy flow of traffic in the urban area could be one of the reasons for the higher concentration of these elements. In order to validate the developed methods, Table 5 shows a comparison of the three different spectroscopic techniques for determination Cd, Cu, Ni and Pb in the collected PM$_{2.5}$ samples. There is good agreement between the three different techniques indicating the validity of the developed method using HR-CS GF AAS. However, the concentration of Ni in the industrial site by HR-CS-GF-AAS is clearly lower than the value obtained by ICP-MS. This is due to the continuous background around Ni line at 233.003 nm and the low concentration of Ni in the present samples. Furthermore, the comparison confirms that
the concentrations of Cd, Cu, Ni and Pb in an urban area are higher than those in the industrial area. Finally, the elements Cd, Cu, and Pb in the atmospheric aerosol samples seem to be below the limit of the air quality of the European Union [37], with the possible exception of Ni. The average concentration of Ni in the urban area is higher than the air quality standard of the European Union whereas the concentrations of Ni in the industrial area seem to be below the AQS. Sampling for longer time periods, including the different seasons, is needed in order to confirm the accurate concentrations of the elements.

Table 5 Comparison of the three different spectroscopic techniques for determination Cd, Cu, Ni and Pb in PM$_{2.5}$ samples. Concentrations and one standard deviation are given in ng/m$^3$.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>HR-CS-GF-AAS</th>
<th>ICP-MS</th>
<th>TXRF</th>
<th>AQS*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Industrial</td>
<td>Urban</td>
<td>Industrial</td>
<td>Urban</td>
</tr>
<tr>
<td>Cd</td>
<td>0.50±0.24</td>
<td>4.0±1.8</td>
<td>0.45±0.34</td>
<td>3.6±1.1</td>
</tr>
<tr>
<td>Cu</td>
<td>73.4±0.7</td>
<td>123±81</td>
<td>80.1±7.7</td>
<td>130±36</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt;2.8</td>
<td>38±15</td>
<td>9.0±2.9</td>
<td>41±13</td>
</tr>
<tr>
<td>Pb</td>
<td>23.8±3.7</td>
<td>55±13</td>
<td>19±5</td>
<td>91±50</td>
</tr>
</tbody>
</table>

*AQS: EU Air Quality Standards [37]

Acknowledgements

This work was supported by the Swedish International Development Agency (SIDA) and the Swedish Research Council (VR) under the auspices of the Swedish Research Links program.
Conclusion

Due to the difficulty to detect Cd, Cu, Ni and Pb at low concentration with the EDXRF technique, a simple and reliable procedure for the determination of these analytes in PM$_{2.5}$ collected from industrial and urban sites in Greater Cairo has been developed using HR-CS GF AAS without the use of chemical modifiers. The collected atmospheric aerosols were completely digested using microwave-assisted acid digestion. Calibration has been carried out using aqueous standards of the elements of interest. In order to validate the developed methods, TXRF and ICP-MS were used for quantitative analysis of the sample under investigation. The comparison confirms the validity of the developed method. In our future work, longer sampling periods for the PM$_{2.5}$ atmospheric aerosol particles will be considered particularly for the determination of Cd and Ni.

References


[40]. N. A. Saliba, F. El Jam, G. El Tayar, W. Obeid, M. Roumie, Origin and variability of particulate matter (PM$_{10}$ and PM$_{2.5}$) mass concentrations over an Eastern Mediterranean city, Atmospheric Research 97 (2010) 106-114.

