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1 **Method development for the determination of Cd, Cu, Ni and**
2 **Pb in PM_{2.5} particles sampled in industrial and urban areas of**
3 **Greater Cairo, Egypt, using high-resolution continuum source**
4 **graphite furnace atomic absorption spectrometry**

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23 **Abstract**

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

41

42 **Keywords:** High-resolution continuum source graphite furnace atomic absorption
43 spectrometry; Aerosol particle PM_{2.5}; Cd; Cu; Ni; Pb.

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48 **1. Introduction**

49 The elemental analysis of the fine particulate matter, i.e. particles with
50 aerodynamic diameter equal to or less than 2.5 μm ($\text{PM}_{2.5}$), has been in the focus of
51 interest in the developed countries for quite some time. A major constituent of $\text{PM}_{2.5}$ is
52 black carbon [1], which is also referred to as soot. It is produced by incomplete
53 combustion of organic matter and always mixed with inorganic atmospheric
54 constituents [2,3]. The knowledge of the composition of the inorganic atmospheric
55 constituents is very important as it has an essential relation to health problems [4,5] and
56 climate change [6-8]. In addition, it gives important information on their origin and also
57 reveals whether they were emitted as primary or secondary particles. It is generally
58 assumed that, the smaller the particle, the more harm it might cause, as it penetrates
59 deeper into the lungs [9]. In addition, fine particulate matter have an effect on the
60 radiation balance of the earth [10], because it scatters and absorbs most of the radiation
61 in the visible region and it is therefore of great interest to measure its concentration in
62 the ambient air. Furthermore, $\text{PM}_{2.5}$ has a long atmospheric residence time, which
63 facilitates its transportation over long distances, covering thousands of kilometers. The
64 bulk of these particles originates from anthropogenic emissions [11,12], both directly
65 and as secondary formation in the atmosphere from gases, such as SO_2 , NO_x and
66 volatile organic compounds. The local emission of fine particles can become an issue of
67 regional and even global concern, since these particles are able to affect air quality in
68 other countries through transnational and even transcontinental transport.

69

70 In Greater Cairo, the largest city in Egypt and also in Africa, the air pollution
71 problems due to the high levels of lead, sulfur dioxide and suspended particulate matter
72 have led to many environmental problems. The origin of the air pollution in Greater

73 Cairo is multifold; burning of trash, poor dispersion factor due to the lack of rain,
74 vehicle emissions (~4.5 million cars on the streets of Cairo), urban industrial operations,
75 and its 15-20 million inhabitants. In addition, there are remarkable seasonal temperature
76 changes ranging from 15-45 °C. It is estimated that 10,000 to 25,000 people per year die
77 in Cairo due to air pollution-related diseases. Furthermore, Greater Cairo daily produces
78 10,000 tons of waste material without well-organized collection and management,
79 resulting in illegal burning of the waste.

80

81 Previous studies on particulate matter (PM_{2.5} and PM₁₀), polycyclic aromatic
82 hydrocarbons (PAH) and volatile organic compounds (VOC) have been conducted in
83 Greater Cairo [13-18]. Studies of PM_{2.5} have been conducted not only in Greater Cairo
84 but also in other developing countries (Vietnam, China, Pakistan, Tanzania, Kenya) [19-
85 24] as well as in some European cities [25-28]. In none of these studies more recently
86 introduced analytical techniques such as high-resolution continuum source graphite
87 furnace atomic absorption spectrometry (HR-CS GF AAS) have been used for
88 quantitative elemental analysis of PM_{2.5}. Recently, fine aerosol particles (PM_{2.5}) have
89 been collected from urban and industrial locations of Greater Cairo and analyzed using
90 an energy dispersive X-ray fluorescence (EDXRF) spectrometer with Mo secondary
91 target [29]. In this study the determination of Cd, Cu, Ni and Pb proved to be difficult
92 due to the low intensities of the characteristic radiation of these elements, and their
93 concentration in the collected aerosol particles was too low for an accurate
94 determination.

95

96 Metals, such as Cd, Cu, Ni, and Pb might be toxic to human beings and it is
97 therefore of interest to follow the eco-cycles of these metals as environmental hazards,

98 once they are released into the atmosphere, biosphere and technosphere. In the present
99 work, atmospheric aerosols from industrial and urban sites in Greater Cairo were
100 sampled. The sample collection was carried out weekly for 24 h/sample during
101 September and October 2010. The samples were analyzed for Cd, Cu, Ni and Pd using
102 HR-CS GF AAS. For verification of the developed method, the results were compared
103 with those obtained by total reflection X-ray fluorescence (TXRF) and inductively
104 coupled plasma mass spectrometry (ICP-MS).

105

106 **2. Experimental**

107 **2.1. Instrumentation**

108 A Model contrAA 700 High-resolution continuum source atomic absorption
109 spectrometer (Analytik Jena AG, Jena, Germany) was used for the determination of Cd,
110 Cu, Ni and Pb in the aerosol particles.. The spectrometer consists of a pre-dispersing
111 prism and an echelle grating monochromator, both in Littrow mounting. A xenon short-
112 arc lamp with a nominal power of 300 W, operating in hot-spot mode, is used as the
113 continuum radiation source. The detector is a UV-sensitive charge coupled device
114 (CCD) array with 588 pixels, 200 of which are used for analytical purposes, whereas the
115 rest is used for correction purposes. More details can be found in our previous work [32,
116 33]..

117 For comparison, Total Reflection X-ray Fluorescence (TXRF) Spectrometry and
118 inductively coupled plasma atomic mass spectrometry (ICP-MS) [34] were used. In
119 TXRF a well-polished sample holder is used to hold the dried sample. The incidence
120 angle of the well collimated exciting X-ray radiation is below 0.1 degrees and the
121 radiation is totally reflected. The geometry allows a compact design resulting in low
122 detection limits for many elements. For the TXRF analysis a S2 PICOFOX TXRF

123 spectrometer (Bruker AXS GmbH, Karlsruhe, Germany) was used. The radiation from
124 an air-cooled X-ray tube is focused and monochromatized before exciting the elements
125 in the digested sample. A Silicon Drift Detector is used for detecting the characteristic
126 radiation of the elements in the sample. For quantification an internal standard is added.
127 An ICP-MS ELAN 6000 (Perkin Elmer–SCIEX, Thornhill, Canada) was used for all
128 comparison. A cross-flow nebulizer equipped with a Scott spray chamber was used. A
129 peristaltic pump from Ismatec (Glattbrugg, Switzerland) was used, at a typical solution
130 flow rate of 1.3 mL min^{-1} . Nebulizer gas flow rate was maintained at 0.7 L min^{-1} with a
131 RF power of 1400 W. Platinum sampler and skimmer cones were used. An instrument
132 performance check was carried out on a daily basis, in order to assure adequate
133 sensitivity and low levels of oxide and doubly charged ions.

134

135 **2.2.Reagents**

136 Deionized and further purified Milli-Q high purity water (Millipore, Bedford,
137 MA, USA) was used throughout. Stock standard solutions for the elements under
138 investigation, containing 1000 mg L^{-1} were used (Merck, Darmstadt, Germany). Ultra-
139 pure nitric acid (HNO_3 , 65% m/v, Fluka, Sigma-Aldrich, Germany) was used for the
140 digestion of the filters. Working standard solutions were prepared daily diluting the
141 standards for HR-CS GF AAS and ICP-MS measurements. All other reagents were of
142 analytical reagent grade. An internal standard (Ga) with a concentration of 5 mg L^{-1} was
143 used for the TXRF measurements.

144

145 **2.3.Sample collection and digestion**

146 Atmospheric aerosols ($\text{PM}_{2.5}$) were collected from industrial and urban sites in
147 Greater Cairo, Egypt, during September and October 2010. The urban site was situated

148 at the National Research Center, 3 km away from the center of Cairo whereas the
149 industrial site was situated at Shobra El khema in the northwest of Greater Cairo.
150 Atmospheric aerosols were collected on polycarbonate filters using a cyclone sampler
151 (Casella CEL, Bedford, UK). The cyclone makes an air-stream move in a cyclonic orbit
152 where larger particles are separated from the fine particles since their higher inertia
153 prevents them from following the airflow. The polycarbonate filters have a diameter of
154 25 mm and a pore size of 0.4 μm . These filters have been used in previous studies and
155 have a high particle collection efficiency and high purity [29-31]. The duration of the
156 collection was 24 h with an air flow of 3 L min^{-1} . In order to avoid the influence of the
157 traffic as a single source, the equipment (cyclone, flow meter, and the pump) was
158 mounted at a height of 20 m, and more than 50 m from the nearest main road. The
159 polycarbonate filters were weighted on a microbalance with μg determination limit
160 (Sartorius CC50, Göttingen, Germany) before and after sampling to determine the mass
161 concentrations. The polycarbonate filters including the atmospheric aerosols were
162 dissolved with ultra-pure nitric acid using microwave-assisted acid digestion. Before the
163 digestion, the PTFE vessels were soaked overnight in diluted nitric acid (10% m/v
164 HNO_3) at room temperature followed by a cleaning program recommended by the
165 manufacturer. For the digestion of air particulate filters, 5 mL of concentrated nitric acid
166 (65% m/v) were added to each filter in the PTFE digestion vessels of the microwave
167 system. The vessels were closed and introduced into the microwave oven and the
168 digestion program given in Table 1 was used. In order to avoid foaming and splashing,
169 the vessels were allowed to cool to room temperature after the end of the digestion
170 program, opened carefully and the volume was made up to 12 mL with water. The
171 digested samples of air particulate filters were used with the HR-CS GF AAS, TXRF
172 and ICP-MS techniques.

173 Table 1, Microwave digestion program for the polycarbonate filters including the
174 atmospheric aerosols.

Parameter	Value
Temperature, °C	200
Pressure, bar	40
Power, %	90
Ramp, min	5
Hold time, min	15

175

176 3. Results and Discussion

177 3.1. Sample weight of PM_{2.5}

178 The mass concentrations of PM_{2.5} ranged from 11 µg m⁻³ to 71 µg m⁻³ with an
179 average of 33±18 µg m⁻³ for the urban site, and it varied between 10 µg m⁻³ and 14 µg
180 m⁻³ with an average of 12±2 µg m⁻³ for the industrial site. The average mass
181 concentrations were not comparable at the two sites and there are a wide range of mass
182 concentrations of PM_{2.5}. The wide concentration range can be due to variations in the
183 local climate, the variations in the amount of Saharan dust arriving at the sites and the
184 experienced episodes of smoke from waste burning in the rice fields in the Nile delta
185 north of Cairo during September to December [13, 35, 36]. An indication of the large-
186 scale influence on air quality can be noticed from the PM_{2.5} mass concentrations from
187 the two locations. Although there is no legally binding limit for PM_{2.5} in Egypt, the
188 present average PM_{2.5} concentrations at the industrial and the urban site is higher than
189 the yearly mean standard, 25 µg m⁻³, in the European commission's environment quality
190 standards for ambient air [37]. Table 2 illustrates the PM_{2.5} mass concentrations from

191 other studies, mainly in the Mediterranean region and North-East Africa. The studies of
 192 PM_{2.5} mass concentrations in Cairo [13,38] and in Beijing [39] shows high PM_{2.5} mass
 193 concentrations compared with the present study. The PM_{2.5} mass concentrations are in
 194 agreement with our previous study in Cairo [29] and comparable with other
 195 international studies from Beirut, Lebanon [40], Nairobi, Kenya [41], Athens, Greece
 196 [42] and Taif, Saudi Arabia [31], although, the present samples were only collected
 197 during September and October 2010.

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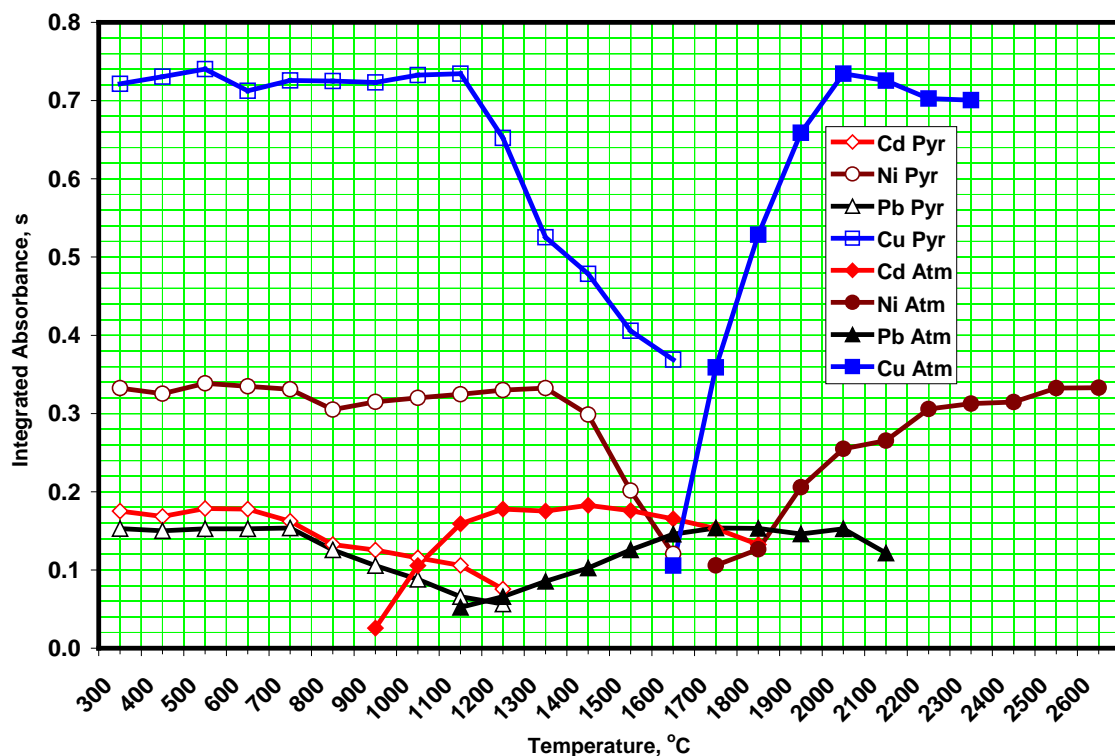
199 Table 2, Comparison between the present concentration of PM_{2.5} and published data
 200 from other studies.

References	Industrial, $\mu\text{g m}^{-3}$	Residential, $\mu\text{g m}^{-3}$	Year	Country
Present work	12±2	33±18	2010	Cairo, Egypt
Shaltout et al [43]	47±15	46±31	2011	Taif, Saudi Arabia
Abu-Allaban et al [38]	216±11	62±3	2001	Cairo, Egypt
Saliba et al [40]	41	39	2003	Beirut, Lebanon
Abu-Allaban et al [13]	150±80	78±48	1999, 2002	Cairo, Egypt
Götschi et al [42]		37±27	2002	Athens, Greece
Gatari et al [41]	30±9		2001	Nairobi, Kenya
Wang et al [39]		154±146	2001-2003	Beijing, China
Boman et al [29]	70±34	55±20	2010	Cairo, Egypt

201 **3.2. Optimization of Pyrolysis and Atomization Temperatures**

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

216



217
 218 Figure 1. Pyrolysis and atomization curves for aqueous standard solutions of Cd, Cu, Ni
 219 and Pb.

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

Stage	Temp, °C	Ramp, °C s ⁻¹	Hold time, s	Purge gas, L min ⁻¹
Drying 1	90	6	20	2.0
Drying 2	110	5	10	2.0
Pyrolysis	600 ^a , 1100 ^b , 1300 ^c , 700 ^d	300 ^{a,b,c} , 100 ^d	10 ^{a,b,c} , 30 ^d	2.0
Gas Adaptation	600 ^a , 1100 ^b , 1300 ^c , 700 ^d	0	5	Stop
Atomization	1200 ^a , 2000 ^b , 2550 ^c , 1700 ^d	3000 ^{a,c} , 1500 ^b , 2000 ^d	3 ^a , 4 ^b , 8 ^c , 7 ^d	Stop
Cleaning	2450 ^{a,b,d} , 2650 ^c	500	4	2.0

222 Cd^a, Cu^b, Ni^c, Pb^d

223

224 3.3. Analytical Figures of Merit

225 According to Table 4, the calibration curves for Cd, Cu, Ni and Pb showed
 226 reasonable linearity in the concentration range from 0.5-5 ng g⁻¹, 50-1000 ng g⁻¹, 10-100

227 ng g⁻¹ and 2.5-25 ng g⁻¹, respectively. The correlation coefficients were 0.997, 0.999,
 228 0.999 and 0.997 for Cd, Cu, Ni and Pb, respectively. In the present work, the limits of
 229 detection (LOD) and quantification (LOQ) were determined as three times and ten
 230 times, respectively, the standard deviation of twenty consecutive measurements of the
 231 reagent blank. Table 4 shows the LOD and LOQ in ng g⁻¹ of Cd, Cu, Ni and Pb found in
 232 the APM samples. According to the obtained LOD and LOQ values, the suitability of
 233 the developed method for the determination heavy metals using HR-CS GF AAS
 234 without chemical modifiers becomes obvious. In our previous work [29,31], the
 235 accuracy of the method for analyzing PM_{2.5} was confirmed by using EDXRF setup.
 236 However, the digestion of the CRM of airborne particulate matter trapped on a filter is
 237 undesired in order to use it for further nondestructive analysis. The comparison with
 238 different spectroscopic techniques would be an alternative method.

239

240 Table 4, Figures of merit for the determination of Cd, Cu, Ni and Pb in PM_{2.5} samples
 241 after microwave-assisted acid digestion using HR-CS GF AAS

Analyte	λ , nm	Linear Equation	R^2	LOD, $\mu\text{g L}^{-1}$	LOQ, $\mu\text{g L}^{-1}$
Cd	228.802	$A_{\text{int}} = 0.161m_{\text{Cd}} + 0.022$	0.997	0.03	0.096
Cu	216.509	$A_{\text{int}} = 0.0013m_{\text{Cu}} + 0.099$	0.999	11	33
Ni	232.003	$A_{\text{int}} = 0.0109m_{\text{Ni}} + 0.084$	0.999	0.94	2.8
Pb	217.005	$A_{\text{int}} = 0.0154m_{\text{Pb}} + 0.030$	0.997	0.27	0.82

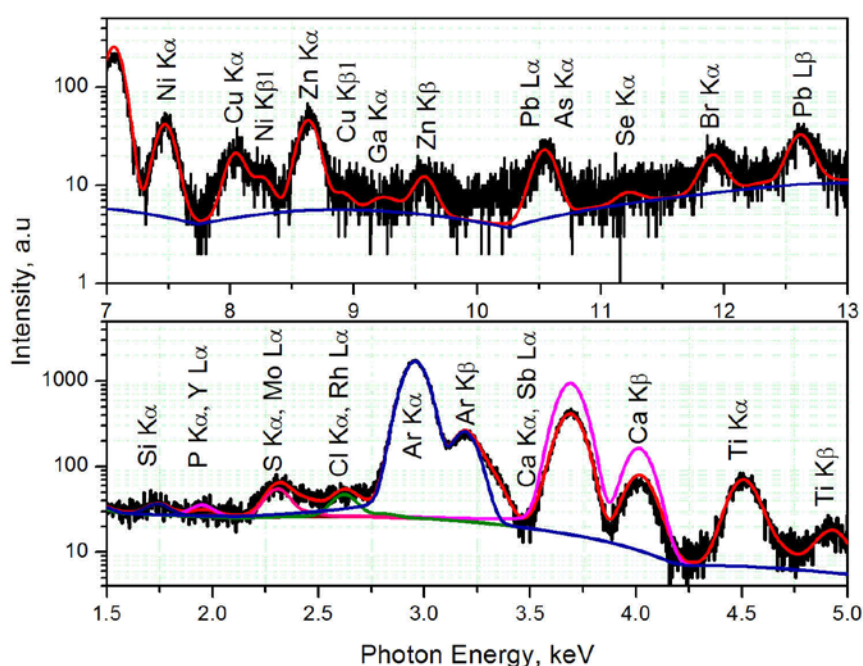
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244 3.4. Quantitative Analysis Results

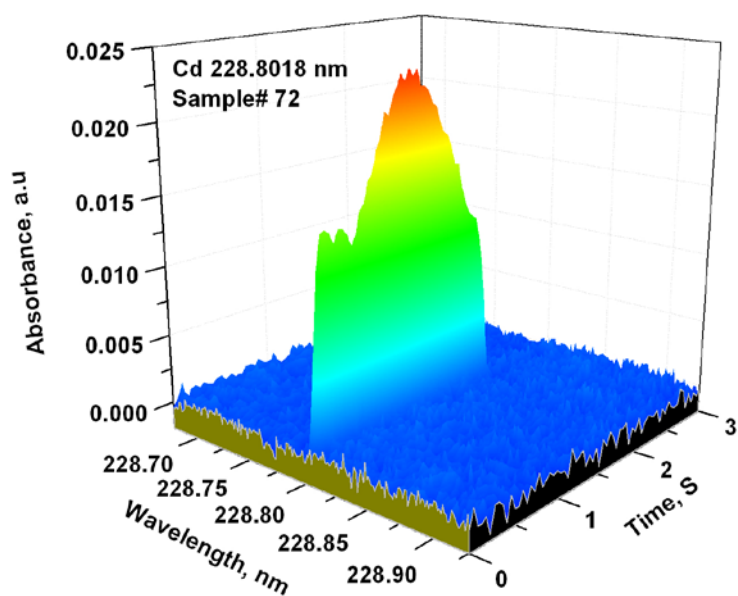
245 There are several reasons for analyzing the aerosol particles with HR-CS-GF-
246 AAS. In our previous work, quantitative elemental analysis of the aerosol particles was
247 carried out using EDXRF with Mo as secondary target [29, 31, 34]. Quantitative results
248 for Cd, Cu, Ni and Pb were difficult to obtain in the EDXRF analysis. As shown in
249 [Figure 2](#), Cu $K\alpha$ and Ni $K_{\beta 1}$ are close to each other in energy, giving rise to higher LOD
250 and LOQ with the relatively large peak widths obtained. There is also a spectral
251 interference between Pb- L_{α} and As K_{α} at photon energy range of 10.5 keV, giving rise
252 to an elevated LOD and LOQ for Pb. In addition, the characteristic radiation of Cd L
253 lines ($L_{\alpha 1}=3.134$, $L_{\alpha 2}=3.127$, $L_{\beta 1}=3.528$, and $L_{\beta 2}=3.717$ keV) are overlapping with Ar
254 lines ($K_{\beta 1}=3.191$, and $L_{\beta 2}=3.71686$ keV) and Ca K_{α} lines ($K_{\alpha 1}=3.691$, $K_{\alpha 2}=3.688$ keV).
255 Since the analysis was carried out in ambient air and not in vacuum the Ar peak was
256 high and the concentration of Ca in the aerosol samples is high, the LOD and LOQ of
257 Cd was higher than the anticipated concentrations of Cd in the samples. Therefore, there
258 is an essential need of an alternative, accurate technique for these elements. HR-CS GF
259 AAS is one of the alternative techniques. [Figures 3-5](#) illustrate examples of the time-
260 and wavelength-resolved absorbance spectra of Cd (228.802 nm), Ni (233.003 nm) and
261 Pb (217.001 nm) for some of the $PM_{2.5}$ samples. Any continuous background absorption
262 has been corrected automatically by the software of the instrument and does not appear
263 in the absorbance spectra. The spectra of Cd and Cu do not show any other absorbance
264 besides that of the analyte. This means that these elements could be equally determined
265 using a conventional line-source atomic absorption spectrometer with deuterium
266 background correction. In the case of Ni ([Figure 4](#)), however, there is a remarkable
267 structured background around the absorbance signal of the elements of interest. The
268 second absorption line at 232.036 nm close to the Ni line is due to iron, and the slight

269 shoulder that appears at the utmost right side of the spectrum is the wing of the
 270 secondary nickel line at 232.138 nm, which is slightly out of the spectral range [33]. In
 271 contrast, when conventional LS AAS with a deuterium background correction system is
 272 used, the atomic absorption due to iron would inevitably cause spectral interference,
 273 resulting in significant overcorrection. Zeeman-effect background correction could
 274 obviously deal better with these near-by absorption lines, although spectral interferences
 275 could not be excluded. Based on the calibration curves of Cd, Cu, Ni and Pb,
 276 quantitative analysis was carried out for the collected atmospheric aerosols using HR-
 277 CS GF AAS, the results of which are shown in Table 5. The high standard deviation in
 278 the results indicates that there were wide variations of all elements in the industrial and
 279 urban areas.



280

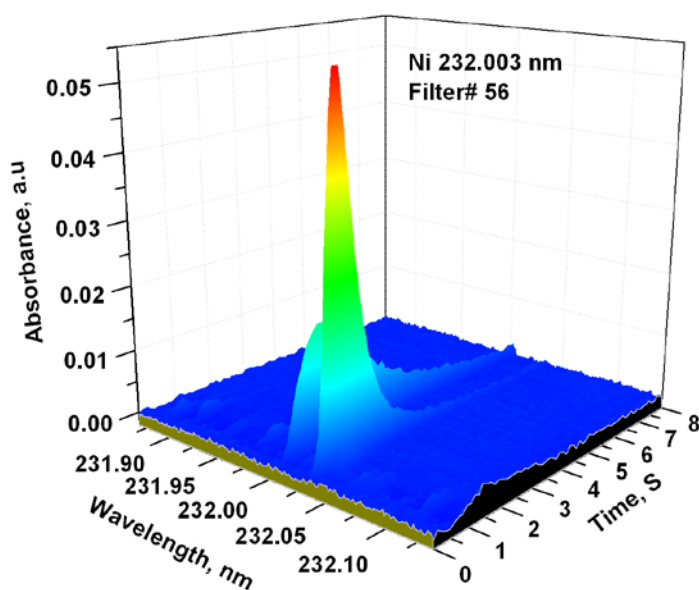
281 Figure 2, EDXRF spectra of the aerosol particles collected on polycarbonate filters



282

283 Figure 3, Time- and wavelength-resolved absorption spectrum of Cd 228.802 nm in

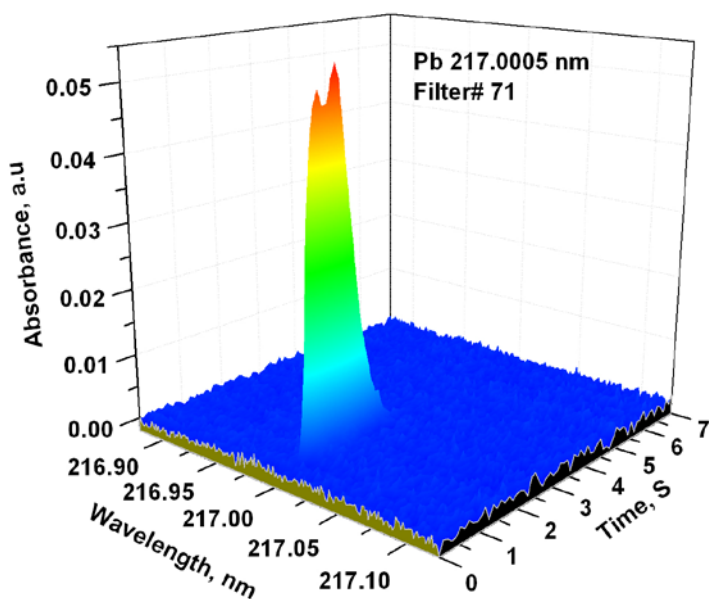
284 PM_{2.5} (Filter #72) without chemical modifier using HR-CS GF AAS.



285

286 Figure 4, Time- and wavelength-resolved absorption spectrum of Ni 232.003 nm in

287 PM_{2.5} (Filter #56) without chemical modifier using HR-CS GF AAS.



288

289 Figure 5, Time- and wavelength-resolved absorption spectrum of Pb 217.001 nm in
 290 PM_{2.5} (Filter #71) without chemical modifier using HR-CS GF AAS.

291 As shown in Table 5, the concentrations of Cd, Cu, Ni and Pb in the urban area
 292 are higher than in the industrial area. Therefore, it would be expected that the industrial
 293 activities are not the main source of these elements. To determine if this tendency is
 294 temporary or not, more sampling for a longer period of time is needed. Anthropogenic
 295 activities, such as the heavy flow of traffic in the urban area could be one of the reasons
 296 for the higher concentration of these elements. In order to validate the developed
 297 methods, table 5 shows a comparison of the three different spectroscopic techniques for
 298 determination Cd, Cu, Ni and Pb in the collected PM_{2.5} samples. There is good
 299 agreement between the three different techniques indicating the validity of the
 300 developed method using HR-CS GF AAS. However, the concentration of Ni in the
 301 industrial site by HR-CS-GF-AAS is clearly lower than the value obtained by ICP-MS.
 302 This is due to the continuous background around Ni line at 233.003 nm and the low
 303 concentration of Ni in the present samples. Furthermore, the comparison confirms that

304 the concentrations of Cd, Cu, Ni and Pb in an urban area are higher than those in the
 305 industrial area. Finally, the elements Cd, Cu, and Pb in the atmospheric aerosol samples
 306 seem to be below the limit of the air quality of the European Union [37], with the
 307 possible exception of Ni. The average concentration of Ni in the urban area is higher
 308 than the air quality standard of the European Union whereas the concentrations of Ni in
 309 the industrial area seem to be below the AQS. Sampling for longer time periods,
 310 including the different seasons, is needed in order to confirm the accurate
 311 concentrations of the elements.

312 Table 5 Comparison of the three different spectroscopic techniques for determination
 313 Cd, Cu, Ni and Pb in PM_{2.5} samples. Concentrations and one standard deviation are
 314 given in ng/m³.

Analyte	HR-CS-GF-AAS		ICP-MS		TXRF		AQS*
	Industrial	Urban	Industrial	Urban	Industrial	Urban	
Cd	0.50±0.24	4.0±1.8	0.45±0.34	3.6±1.1	-	-	5
Cu	73.4±0.7	123±81	80.1±7.7	130±36		132±129	-
Ni	<2.8	38±15	9.0±2.9	41±13		42±0	20
Pb	23.8±3.7	55±13	19±5	91±50	22	71	500

315 *AQS: EU Air Quality Standards [37]

316

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 320 Links program.

321

322 **Conclusion**

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

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