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Determination of Cd, Pb and Ni by Square Wave Stripping Voltammetry in Particulate Matter Collected in Workplace Atmosphere of some Brazilian Industrial Foundries

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A concentração de Cd, Pb e Ni em material particulado atmosférico coletado no ambiente de trabalho de três fundições localizadas no município de Loanda, Paraná, Brasil, foram determinadas por voltametria de onda quadrada e ICP OES. Os resultados mostram que os trabalhadores estão sendo sistematicamente expostos a concentrações de Cd e Pb que são significativamente maiores do que o Limite de Concentração recomendado pela American Conference of Governmental Industrial Hygienists (ACGIH). Os resultados obtidos pelo método eletroanalítico não diferem significativamente dos resultados obtidos por ICP OES, indicando a potencialidade de sua aplicação no monitoramento destes ambientes com menores custos de implementação, operação e manutenção. Baseando-se nos resultados obtidos, alterações tecnológicas no processo de produção foram recomendadas, bem como a utilização de equipamentos de proteção individual no sentido de conservar a saúde e o bem estar dos trabalhadores, minimizando os danos ao ambiente externo.

The concentration of Cd, Pb and Ni in atmospheric particulate matter collected in the workplace of three foundries located in the municipality of Loanda, Paraná, Brazil, was determined by square wave voltammetry and ICP OES. The results show that workers are being systematically exposed to concentrations of Cd and Pb that are significantly above the Limit of Concentration recommended by the American Conference of Governmental Industrial Hygienists (ACGIH). Results obtained by the proposed electroanalytical method do not differ statistically from the results obtained by ICP OES, indicating its potential application to environmental monitoring at much lower cost of installation, operation and maintenance. According to the results obtained, technological changes in the production process were recommended, as well as the use of personal protective equipment in order to keep the health and well being of workers, minimizing damages to the external environment.

Keywords: foundries, heavy metals, particulate matter, voltammetry, exposure levels

Introduction

Atmospheric aerosols are solid or liquid particles smaller than 100 μm in diameter. Pollutant particles in the 0.001 to 10 μm range are commonly suspended near the sources of pollution, such as urban atmosphere, industrial plants, highways and power plants.[1] Atmospheric particulate matter generated from melting and pouring of brass in industrial foundries are a concern of occupational health to workers in these environments.[2,3] In foundry workplace environments the particulate matter is usually formed by condensation of metallic vapours, followed by oxidation reactions.[4-6] Because the smaller particles remain suspended in atmosphere, inhalation is the major path of contamination. Particulate matter in foundries have variable compositions, but Cd, Pb and Ni are elements of concern because they are minor components of most processed brasses.[7,8] Additionally, these metals have severe toxic and cumulative effects that have been extensively described in the literature.[4, 9-15]

Determination of metallic species in atmospheric particulate matter and aerosols (particle sizes ranging from 0.001 to 100 μm) is usually made by atomic spectrometric methods involving techniques such as flame and electro thermal atomic absorption (FAAS and ETAAS), inductively coupled plasma optical emission spectroscopy (ICP OES) and inductively coupled plasma mass spectrometry (ICP MS).[16-22] Although methods based on these techniques are robust and widely accepted around the world, the cost of acquisition, installation and maintenance of these instruments is high and may be even prohibitive for health control agencies in developing countries.

Electroanalytical techniques are known to be very sensitive and versatile, using low cost small size

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instruments that do not require special facilities such as laboratories with controlled atmosphere to reach detection limits as low as 10^{-10} mol L^{-1}.[23] The first report of determination of heavy metals such as Cd, Bi, Mn, Pb and Zn in particulate matter of industrial workplace environment was presented in 1947.[24] Heuman[25] determined Cd and Pb in air samples from Antarctica by differential pulse anodic stripping voltammetry. Nimmo and Fones[26] determined Cu, Cd, Co, and Ni in aerosols collected in cellulose acetate filters by cathodic adsorptive stripping voltammetry, validating their results by comparison with ETAAS. Quintal *et al.*[27] determined Cd, Cu, Pb and Zn by anodic stripping voltammetry in air samples from Yucatan, Mexico, collected in glass fibre filters during 24 hours, validating the proposed method by comparison with ETAAS. Cheng *et al.*[28] and Belostotsky *et al.*[29,30] determined Pb in air samples by anodic stripping voltammetry using a portable instrument able to collect, prepare and analyse the samples.

The Brazilian Ministry of Work and Employment, together with the Chemistry Institute and the Faculty of Pharmaceutical Sciences of the University of São Paulo, has developed a project at manufacturing facilities of stopcocks and faucet parts in the municipality of Loanda, Paraná State, Brazil, aiming the evaluation of the workplace quality. This paper presents the indoor concentrations of Cd, Pb and Ni in particulate matter (particle size > 0.8 μm)[16] collected in these industries. The utilisation of square wave anodic stripping voltammetry for determination of Cd and Pb, as well as the use of square wave cathodic adsorptive stripping voltammetry for determination of Ni was evaluated. The performance of the electroanalytical methods was compared with the method accepted by the National Institute of Organisation Safety Health (NIOSH),[16] based on the technique of ICP OES.

Experimental

Apparatus and reagents

Square wave voltammetry (SWV) measurements were performed with a 263 A potentiostat from EG&G (Princeton, NJ, USA) coupled to a 303 A model static mercury electrode also from EG&G. The electrochemical cell was completed with an Ag/AgCl reference electrode and a Pt wire as the auxiliary electrode. Data acquisition was performed with the model 270/250 Research Electrochemistry Software from EG&G using differential pulse mode of potential scanning and current sampling.

Determinations of Cd, Pb and Ni by ICP OES were made with a spectrometer from Spectro Analytical Instruments. A CEM MDS 2000 microwave furnace was used for sample digestion.

All solutions were prepared in deionized distilled water from a Milli-Q Plus system (Millipore). Analytical standard solutions were prepared by proper dilution of 1000 mg L^{-1} Titrisol (Merck) stock solutions ($CdCl_2$, $Ni(NO_3)_2$ and $Pb(NO_3)_2$). Analytical grade 10% (v/v) HNO_3 was used in the preparation of analytical solutions and dissolving the metal samples.

A 5.0 mol L^{-1} acetic acid/ammonium acetate buffer (pH 4.6) was prepared for proper pH conditioning in the voltammetric determination of Cd and Pb. For determination of Ni, a 0.50 mol L^{-1} H_3BO_3 solution neutralized to pH 8.0 with 2.0 mol L^{-1} NaOH was used to prepare the supporting electrolyte directly in the voltammetric cell. A 0.050 mol L^{-1} dimethylglioxime (DMG) solution in 95% ethanol was used as complexing reagent. All solutions were prepared from analytical grade reagents.

Sampling and sample digestion

Sampling of the particulate matter was made using portable individual pumps calibrated at a flow rate of 2.0 L min^{-1} to avoid filter saturation. These pumps are powered by rechargeable and sealed batteries, and have a system that enable to monitor and control flow rate variations of the aspirated air with precision of ± 5%. Flow rate calibrations were made before and after sampling using automatic Gillian calibrators. Using silicone tubes, the pumps were connected to plastic filter holders (Millipore system for aerosol sampling and analyses) containing mixed cellulose ester filters with diameter of 37 mm and pore size of 0.8 μm, so that the metallic particles are retained by filtration. The filters were positioned at a height of 1.6 m aiming to collect air samples as representative as possible of the air breathed by workers. Prior to the sampling, a pressure drop test was performed with the assembled filters using a manometer and all individual sampling pumps. Pressure variations within a range of ± 3% were accepted for sampling.

After the sampling instruments were mounted and tested, they were installed in two fixed sampling points close to the metal melting and pouring facilities. The two fixed points were located at each side of the electric furnace in which the brass is melted.

Samples were collected by the method of consecutive and partial time sampling, that is, during three consecutive days, the atmosphere was collected for six hours, which correspond to 70% of the working day.[16] After the sampling was completed (at the end of the six hours period), the cartridges were disconnected from the pumps and their endings were properly sealed to avoid external contamination and stored for further digestion. Sampling was performed using this procedure in three foundries located in the municipality of Loanda, Paraná State, Brazil

For analysis, the cartridges were open, and the cellulose ester filters were transferred to 120 mL Teflon® flasks together with 5 mL of concentrated HNO_3. Sample digestion was performed in the CEM MDS 2000 microwave furnace following the parameters described in Table 1. The digested samples were filtered and transferred to 50.00 mL volumetric flasks, completing the volume with deionized water. In parallel, blank experiments of the acid and filters were performed to assess possible contaminations from the material utilised. To minimize these contaminations, the glassware was washed with 10% (v/v) HNO_3, followed by extensive washing with deionised water. Besides, an additional cleaning step was applied to the Teflon® digestion flasks, which were treated with 10 mL of 70% (v/v) HNO_3 using a digestion time of 10 min at pressure of 80 psi and 100% of the microwave potency, followed by exhaustive washing with deionised water.

Table 1. Microwave digestion parameters of particulate matter collected in mixed cellulose ester filters in presence of 5 mL of concentrated nitric acid

Parameter	Value
Power (%)	90
Pressure (psi)	80
Run time (min)	25
Pressure time (min)	8
FAN SPEED	100

Analyses of particulate matter

To perform the determination of Cd and Pb in the particulate matter, as well as in the blank of filter and reagents, 5.00 mL of the solution resulting from the microwave digestion were transferred to a voltammetric cell, partially neutralized with 10 mol L^{-1} NaOH and buffered with 40 μL of the 5.0 mol L^{-1} acetic acid/sodium acetate buffer (pH 4.6). This solution was deoxygenated by bubbling pre humidified N_2 for 60 s under stirring. Next, using a mercury drop with radius of 0.46 mm, the accumulation of both metal cations was performed for 60 s at –0.90 V *vs*. Ag/AgCl. After an equilibration time of 15 s, the potential was scanned from –0.90 to –0.20 V *vs*. Ag/AgCl using the square wave voltammetry technique with frequency of 10 Hz and pulse height of 25 mV. Using this experimental setup, a linear response was observed for Cd concentrations between 0.030 and 0.770 mg L^{-1}, and between 0.120 and 3.00 mg L^{-1} for Pb. Quantification of Cd and Pb was made by the standard addition method using a combined standard solution containing 5.0 mg L^{-1} Cd and 20.0 mg L^{-1} Pb. Cadmium and Pb concentrations in the solution samples were corrected for the impurities from reagents and filters, which were determined in parallel experiments using a similar procedure.

For determination of Ni a suitable volume of the solution resulting from the microwave digestion was neutralized with 10 mol L^{-1} NaOH solution until pH close to 8. An aliquot of 4.00 mL of this solution was transferred to the voltammetric cell containing 1.00 mL of supporting electrolyte (0.50 mol L^{-1} boric acid neutralized to pH 8.0) and 50 μL of 0.050 mol L^{-1} (DMG). This solution was deoxygenated by bubbling pre humidified N_2 for 60 s under stirring. Next, using a mercury drop with radius of 0.46 mm, the adsorption of the Ni-DMG complex was performed for 60 s at –0.80 V *vs*. Ag/AgCl. After an equilibration time of 15 s, the potential was scanned from –0.80 to –1.10 V *vs*. Ag/AgCl using the square wave voltammetry technique with frequency of 100 Hz and pulse height of 25 mV. For Ni concentrations between 20 and 65 μg L^{-1} the peak current was a linear function of the concentration. Quantification of Ni was made by the standard addition method using a standard 1.0 mg L^{-1} Ni solution. Nickel concentrations in the solution samples were corrected for the impurities from reagents and filters, which were determined in parallel experiments using a similar procedure.[31]

For evaluation of the electroanalytical method, all samples were also analysed by ICP OES[16] using external calibration with combined standard solutions containing the three metal cations at concentrations 0.01, 0.10, 1.0 and 10.0 mg L^{-1}. The wavelength used for determination of Cd, Pb and Ni were 226.502, 182.200 and 352.454 nm, respectively.

Detection and quantification limits of the voltammetric and ICP OES methods were computed, respectively, with the expressions: LDM = 3Sb/m and LQM = 10Sb/m, where Sb is the standard deviation of the blank and m is the slope of the calibration curve.[32] The limits of detection and quantification (L.O.D. and L.O.Q.) in samples were computed from L.D.M. and L.Q.M., based on the sampled volume of 0.672 m^3 day^{-1}, which corresponds to 70% (336 min) of a working day of 8 h (480 min), using the sampling flow rate of 2.0 L min^{-1}.

Results and Discussion

Figures of merit

Anodic stripping square wave voltammograms of mixtures of Cd and Pb with concentrations between 30 and 770 mg L^{-1} Cd and between 120 and 3090 μg L^{-1} Pb are shown in Figure 1. In solution, the L.D.M. were 0.40 and 1.8 μg L^{-1}, while the L.Q.M. were 1.2 and 5.8 μg L^{-1} for Cd and Pb, respectively. The peak current exhibited excellent linearity with the concentration of both metal cations (r > 0.999). The precision of Cd measurements were evaluated by 7 repetitive analyses at the concentration levels of 30 and 103 μg L^{-1}, resulting relative standard deviations (RSD) of 3.5 and 2.1%, respectively. The RSD for Pb were evaluated at the concentration levels of 120 and 414 mg L^{-1}, resulting values of 1.5 and 0.7%, respectively. Adsorptive stripping voltammograms obtained for Ni solutions with concentrations between 10 and 66 μg L^{-1} showed that peak currents were a linear function of Ni concentrations, as evidenced in Figure 2. The solution L.D.M and L.Q.M. for Ni were 0.17 and 0.58 μg L^{-1}, respectively. The RSD values at concentrations of 10 and 40 μg L^{-1} were 3.1 and 2.0 %, respectively.

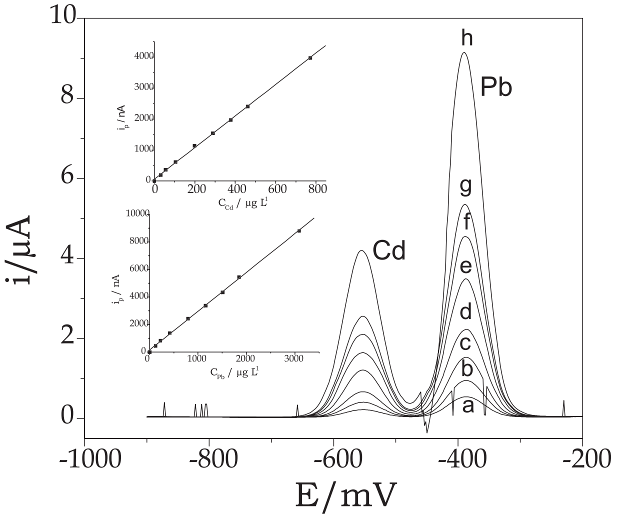

Figure 1. Square wave anodic voltammograms of Cd^{2+} and Pb^{2+} in medium of 0.040 mol L^{-1} acetic acid/sodium acetate buffer at pH 4.6, obtained after a deposition time of 60 s at –900 mV *vs*. Ag/AgCl. The square wave parameters were: frequency of 10 Hz and pulse height of 25 mV. Concentrations studied: 30 μg L^{-1} Cd and 120 μg L^{-1} Pb (a); 54.7 μg L^{-1} Cd and 218.9 μg L^{-1} Pb (b); 103.4 μg L^{-1} Cd and 413.8 μg L^{-1} Pb (c); 198.1 μg L^{-1} Cd and 792.3 μg L^{-1} Pb (d); 289.1 μg L^{-1} Cd and 1156 μg L^{-1} Pb (e); 376.7 μg L^{-1} Cd and 1507 μg L^{-1} Pb (f); 461.2 μg L^{-1} Cd and 1844 μg L^{-1} Pb (g); 770.2 μg L^{-1} Cd and 3089 μg L^{-1} Pb (h). The insert in this figure shows the analytical curves, which fitted the following linear equations: i_{pPb} = (2.82 ± 0.03)C_{Pb} + (142 ± 42), with r = 0.9996, and i_{pCd} = (5.09 ± 0.05)C_{Cd} + (64 ± 19), with r = 0.9996.

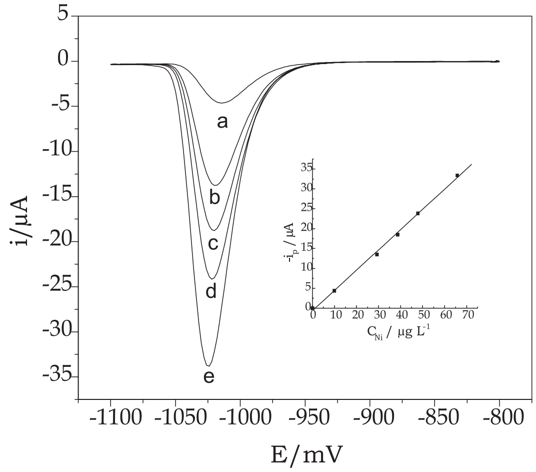

Figure 2. Square wave cathodic voltammograms of Ni^{2+} in 0.10 mol L^{-1} boric acid/sodium borate (pH 8.0) and 0.50 mmol L^{-1} DMG, obtained after an accumulation time of 60s at –800 mV *vs*. Ag/AgCl. Square wave parameters were: frequency of 100 Hz and pulse height of 25 mV. Concentrations studied: 9.95 (a); 29.27 (b); 38.65 (c); 47.85 (d) and 65.73 μg L^{-1} (e). The insert in this figure shows the analytical curve, which fitted the following linear equation: i_{pNi} = (0.51 ± 0.01)C_{Ni} – (0.6 ± 0.4), with r = 0.998.

Comparison with ICP OES

Based on the L.D.M and L.Q.M. values obtained in solution from the calibration curves, as well as on the flow rate of the sampling pump and the sampling time, it was possible to compute L.O.D and L.O.Q. in units of μg m^{-3} to perform the environmental evaluation. This computation also takes into account that each sample, after acid digestion, is diluted in a 50.00 mL volumetric flask. The L.O.D. and L.O.Q. values obtained by voltammetry were lower than the values obtained by ICP OES (Table 2), a fact that is explained by the pre-concentration step on the Hg electrode, as well as by the characteristics of the square wave voltammetry, which performs excellent discrimination between faradaic and capacitive currents.[23] Additionally, the net current read in square wave voltammetry results from the difference between anodic and cathodic currents (opposed signals), leading to a significant increase of the signal to noise ratio because of the reversibility of chemical systems studied in this work. Besides, the L.O.Q. values of both techniques were lower than the limits of concentration (LC) values recommended by ACGIH,[33] showing their appropriateness for monitoring the metal concentrations in the particulate matter present

Table 2. Values of L.O.D. and L.O.Q. for analyses of particulate matter in atmosphere considering a mean volume of 0.672 m^3 of air (volume sampled during 5.6 h flow rate of 2.0 L min^{-1}). For comparison purpose the concentration limit recommended by ACGIH (LC ACGIH)[33] is also shown

		Analytical Method			
Element	LC	ICP-OES		SWV	
	ACGIH	L.O.D.	L.O.Q.	L.O.D.	L.O.Q.
		(μg m^{-3})	(μg m^{-3})	(μg m^{-3})	(μg m^{-3})
Cd	2.0	0.08	0.28	0.03	0.09
Ni	50.0	2.32	7.72	0.01	0.04
Pb	50.0	2.05	6.83	0.13	0.43

Table 3. Comparison of arithmetic means of metal concentrations determined by ICP-OES and SWV

Sample	Concentrations obtained by both analytical methods					
	ICP OES			SWV		
	Cd (μg L^{-1})	Pb (μg L^{-1})	Ni (μg L^{-1})	Cd (μg L^{-1})	Pb (μg L^{-1})	Ni (μg L^{-1})
1	96±2	1.88±0.03	42±4	93±7	2.36±0.01	44±2
2	137±1	1.08±0.04	22±3	143±3	1.40±0.01	21.7±0.2
3	43±2	0.464±0.008	13±2	38±9	0.571±0.008	12.2±0.9
4	32.9±0.3	0.897±0.006	23±4	36±6	0.969±0.006	24±2
5	41.2±0.7	1.55±0.03	20±5	36±1	1.68±0.01	20.9±0.9
6	34±1	1.71±0.03	31±6	29±2	1.63±0.01	29±1

Results correspond to the average of three determinations by each method.

in the atmosphere of the foundries studied.

The accuracy of the electroanalytical determination of Cd, Pb and Ni was verified by comparison with ICP OES, which is the method recommended by NIOSH (Table 3).[16] The paired t-test was applied to results of Table 3, resulting experimental t values of 0.46, 2.14 and 0.20 for Cd, Pb and Ni, respectively. These results suggest that there is no evidence of systematic differences between the results obtained by the two methods. This statement is based on the fact that at 5 degrees of freedom and 95% of confidence interval the critical t is 2.57, a value that is larger than the experimental t values.[32]

Study of interferences

Interference of Cu and Zn on the voltammetric signal was investigated because these metals are the major components of the brass used in the foundries under study. Besides, possible interference of Cd, Pb and Ni in each other determination was also investigated. The concentrations of interfering species studied were based on the values determined by ICP OES, as well as on the proportion of metals found in the brass (Tables 4 and 5). Interference on Cd^{2+} and Pb^{2+} determination was studied using solutions of these cations with concentrations 100 and 400 μg L^{-1}, respectively, in medium of 0.040 mol L^{-1} acetic acid/sodium acetate buffer with pH 4.6. To study the interference on Ni determination, a 15 μg L^{-1} Ni^{2+} solution was used in medium of 0.050 mol L^{-1} boric acid/sodium borate (pH 8.0) in presence of 0.50 mmol L^{-1} DMG. Tables 4 and 5 show that the maximum interference on peak current was +6.8%, observed for Zn^{2+} on the determination of Cd^{2+}, when Zn^{2+} was present with a concentration 100 times larger than Cd^{2+}. These results indicate that the voltammetric method is very selective, even in presence of high concentration of foreigner species.

Table 4. Influence of interfering ions on peak currents of a solution containing Cd^{2+} and Pb^{2+} at concentrations 100 and 400 μg L^{-1}, respectively

Interfering cation	Ratio C_{int}/C_M^{a}		ΔI_p (%)	
	Cd^{2+}	Pb^{2+}	Cd^{2+}	Pb^{2+}
Cu^{2+}	10	2.5	-1.7	-0.4
	100	25	-0.4	-0.5
Ni^{2+}	0.15	0.01	-2.5	+0.1
	1	0.1	-1.8	+0.4
Zn^{2+}	10	2.5	+0.6	+0.3
	100	25	+6.8	-0.2

^{a}C_{int}=concentration of interfering ion; C_M= concentration of analyte; ΔI_p = variation of peak current in comparison to the value observed for pure Cd^{2+} and Pb^{2+} solutions.

Environmental evaluation

For evaluation of the environmental quality, it was assumed that the mean concentration of metals followed a log-normal distribution, resulting the Superior Limit of Confidence (SLC) for a confidence level of 95%, which is computed according to equation 1:

$$\ln(SLC) = M(\ln) + 0.5[DP(\ln)]^2 + t_{1/2(95\%)}[DP(\ln)/n^{1/2}] \quad (1)$$

where M(ln) is the arithmetic mean of the neperian logarithms of the metal concentrations, DP(ln) is the standard deviation of M(ln) for (n-1), n is the number of

Table 5. Influence of interfering ions on peak currents of a 15 μg L^{-1} Ni solution

Interfering ion	Ratio C_{int}/C_M^{a}	ΔI_p (%)
Cd^{2+}	0.3	+2.5
	13	-6.4
Cu^{2+}	67	0
	667	0
	3	-2.6
Pb^{2+}	47	+3.4
	133	-5.6
Zn^{2+}	67	0
	667	+4.5

^{a}C_{int}=concentration of interfering ion; C_M= concentration of analyte; ΔI_p = variation of peak current in comparison to the value observed for pure Cd^{2+} and Pb^{2+} solutions.

samples analysed and $t_{1/2}$ is the critical value of t (Student) for 95 % of two sided confidence interval and n-1 degrees of freedom.[33, 34]

This SLC is assumed as the representative value for comparison with the Limits of Concentration (LC) adopted by the American Conference of Governmental Industrial Hygienists (ACGIH), which are 2.0, 50.0 and 50.0 μg m^{-3} for Cd, Pb and Ni, respectively.[33] Figure 3 shows that the SLC for Ni are lower than the recommended LC of ACGIH for the three foundries studied. On the other hand, the SLC values for Cd and Pb are higher than the LC ACGIH recommended values, especially for Pb, indicating that workers are being exposed to dangerous concentrations of both metals. This requires corrective actions, such as improving the exhaustion efficiency in the workplace, and isolating the melting and pouring facilities in order to minimize the presence of particulate matter in the total environment of the foundry plant. Additionally, workers involved in the melting and moulding activities must use personal protective equipment.

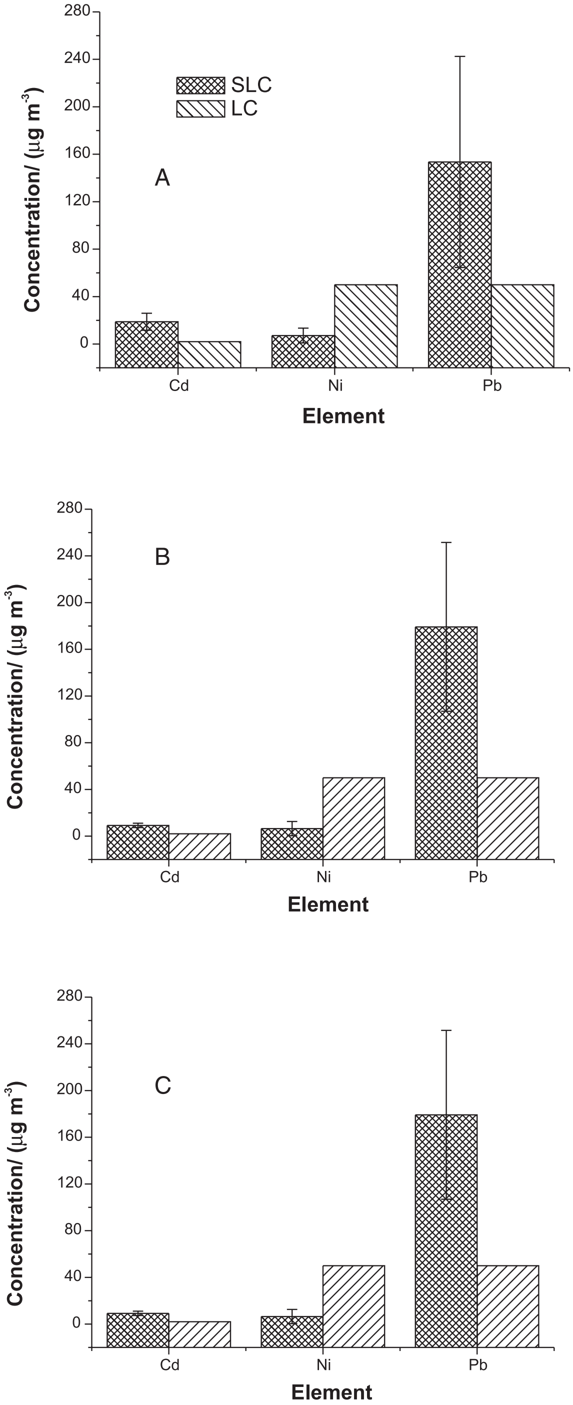

Figure 3. Mean Superior Limits of Concentration (SLC) for the three foundries studied in comparison with the Concentration Limits of ACGIH (LC).[33] Results of SLC correspond of mean values of 24 samples collected in each foundry.

Conclusions

The results show that the square wave voltammetry method is suitable to determine concentrations of Cd, Pb and Ni in atmospheric particulate matter collected in the workplace of foundries. The results obtained by this method were not statistically different from the results obtained by ICP OES. An advantage of the electroanalytical method is the low cost of equipment and maintenance, as well as the higher sensitivity, since the accumulation time on the working electrode can be increased if necessary, that is, the pre concentration is performed directly in the voltammetric cell. Additionally, voltammetric equipments can be miniaturized and used on site, providing real time data on the environmental quality of the workplace atmosphere. On the other hand, the ICP OES technique is very fast and is suitable to perform simultaneous analysis of all cations studied.

The results obtained by both methods show that workers in the foundries evaluated are being systematically exposed to concentration levels of Cd and Pb higher than the maximum concentrations recommended by ACGIH. These results indicate that corrective actions are necessary in order to minimize the leaking of particulate matter to the atmosphere, as well as to emphasize the need for use of personal protective equipments by the workers.

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