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A direct method for the determination of lead in beers by differential pulse polarography-anodic stripping voltammetry

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Abstract

In this paper, a fast procedure to determine lead in beers in situ was developed using Differential Pulse Polarography (DPP) and Anodic Stripping Voltammetry (ASV). Lead was deposited by reduction at -900 mV on the surface of the Static Mercury Drop Electrode (SMDE). Then, the preconcentrated metal was re-oxidized by scanning the potential from -900 to +100 mV, around -450 mV the signal belonging to lead was identified. The SMDE showed an excellent linear behavior at the concentration range, from 0.04975 to 0.4761 mg L^{-1} (r=0.9986). The limit of detection (LOD) found was 0.026 mgL^{-1} and the limit of quantification (LOQ) 0.087 mgL^{-1}, both of these values are under the maximum allowed concentration of lead (0.5 mg L^{-1}) in alcoholic beverages established by Mexican law NOM-142-SSA1-1995.

Keywords: Beer, Lead, ASV, DPP, Electrochemistry

1. Introduction

Beer is an alcoholic drink brewed mainly from malted barley, hops, yeast and water although other sources of fermentable carbohydrate (eg. maize, wheat, rice) and other natural ingredients may be added to create different styles and flavors [1].

Lead is a major chemical pollutant of the environment, thus, its concentration in vegetation in several countries has increased in recent decades due to anthropogenic activities. The great variation of Pb contents in plants is influenced by several factors, such as the presence of geochemical anomalies, pollution, seasonal variation, and genotype ability of its accumulation. The highest Pb contents (> 1 mg kg^{-1}) were observed in plants from Belgium, Hungary, Italy, Malta and Mexico [2].

Spectrophotometric and emission methods have been used to determinate lead in food. Limits of detection reported for these methods are 15 µg L^{-1}, 0.05 µg L^{-1} and 1.0 µg L^{-1} for Furnace Atomic Absorption Spectrometry (FAAS), Graphite Furnace Atomic Absorption Spectrometry (GFAS) and Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), respectively. To achieve these LOD, these methods require long sample treatments and expensive reagents to avoid spectral interferences [3]. There are a great number of articles [4-10] about heavy metals present in food, all of them use digestions methods (dry or wet) to destroy organic matter.

In this study, we used anodic stripping voltammetry-differential pulse polarography to achieve similar LOD like those of the spectroscopy methods for lead determination in beer, without the use of oxidant agents (H_2O_2), neither strong acids such as HNO_3 and $HClO_4$.

2. **Experimental**

2.1 *Instrument*

Voltammetric measurements were performed using an AUTOLAB PST050 Potentiostat and the MDE150 polarographic stand, both controlled by VoltaMaster4 software. The three electrode system consisted of the Static Mercury Drop Electrode (SMDE) as working electrode, silver chloride-silver (KCl 3 mol L^{-1}) electrode as reference and a platinum wire as counter electrode.

2.2 *Chemical reagents*

All reagents used in the preparation of the support electrolyte (KNO_3-HNO_3) were analytical grade reagents, provided from specialized distributors while standard solution (lead 10 ppm) was prepared from a certified stock solution Fluka Analytical (Pb 1000 ppm).

2.3 *Samples*

In this study eight beer samples were analyzed, they were classified in three groups, the first one was craft beers (three samples, S_1 to S_3), the second group included commercial beers (four samples, S_4 to S_7), and the last group was one imported beer (S_8), all beers were purchased from local supermarkets in San Luis Potosi.
The lead content in samples was determined by standard addition method, the result expressed in this paper is the average of three different measurements.

3. **Results and discussion**

3.1 Selection of best operational conditions for lead determination by ASV-DPP

After several attempts of digestion methods using different oxyacid mixtures (H_2O_2-HNO_3, HNO_3 only, H_2SO_4 only, H_2O_2-H_2SO_4), it is observed that the resulting solutions increases the residual current, which increased the value of detection limit for lead in this electrochemical method. Hence we decided to perform a direct measurement because the recovery found with direct method was higher than 90%; the only treatment needed was a mechanical degasification for 30 minutes. All parameters used to determine lead are described in **Table 1**.

3.2 Calibration curve

With the best operational conditions presented in Table 1, Figure 1 shows the calibration curve that ranges from 0.04975 to 0.4761 mg L^{-1}, which was performed using support electrolyte HNO_3-KNO_3 0.2 mol L^{-1}, data obtained from the calibration curve, is displayed in **Table 2**. The limit of detection (LOD) and limit of quantification (LOQ) were calculated according IUPAC, using three and ten times the standard deviation from the linear regression.

Table 1. Differential pulse polarography-anodic stripping voltammetry operational conditions.

Parameter	**Values**
Purge time	10 min
Purge time after standard addition	30 s
Volume of standard addition of Pb 10 mgL^{-1}	50 µL
Deposition potential	-900 mV
Deposition time	90 s
Support electrolyte volume	5 mL
Scan speed	4 mVs^{-1}
Equilibration time	15 s

3.3 Determination of lead in beer samples

After beer degasification, five mililiters of the sample were mixed with equal volume of support electrolyte. Nitrogen was bubbled for ten minutes in order to eliminate residual dissolved oxygen. Following best operational conditions described in Table 1, all samples were analyzed using DPP-ASV, lead was determined by standard addition method, to avoid matrix effects. The maximum allowed concentration (MPL) in alcoholic beverages established by Mexican law NOM-142-SSA1-1995 is 0.5 mg L^{-1}, while in other regions such as Ecuator the limit is 0.1 mg L^{-1} and to the Office International de la Vigne et du Vin [11] is 0.150 mg L^{-1}.

Table 2. Calibration curve data.

Parameter	Value
Calibration range (mg L^{-1})	0.04975 – 0.4761
Equation	y = 201.13(±7.96)x + 8.3837(± 0.56)
r^2	0.9972
r	0.9986
Limit of detection, LOD (mg L^{-1})	**0.026**
Limit of quantification, LOQ (mg L^{-1})	**0.087**
Recovery	95.51 ± 5.84%

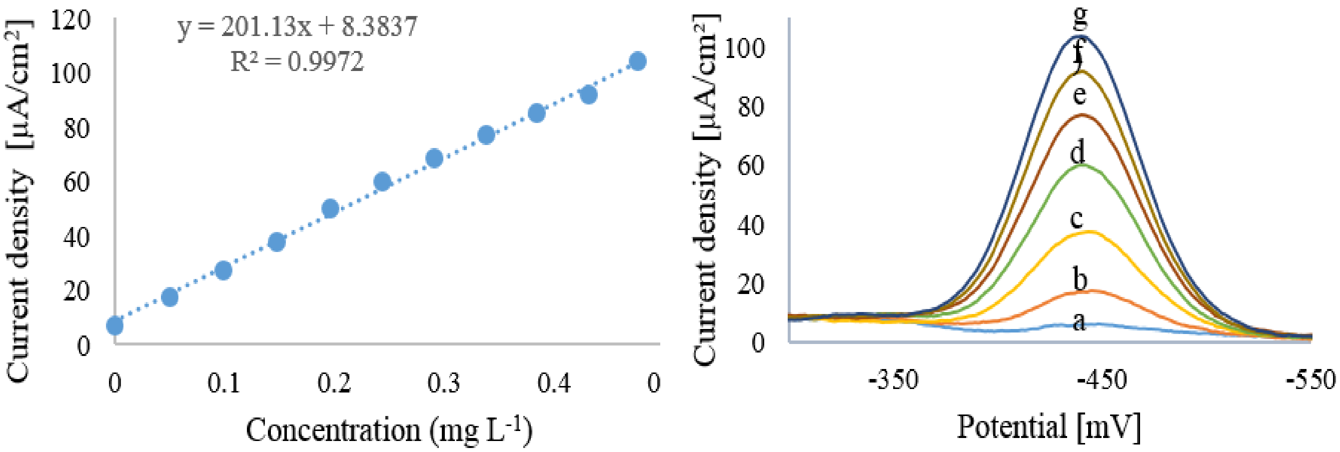

Figure 1. Calibration curve for lead in HNO_3-KNO_3 0.2 mol L^{-1} as supporting electrolyte. Potential was measured versus Ag-AgCl electrode (KCl 3 mol L^{-1}). Lead was ranged from 0.04975 mg L^{-1} to 0.4761 mg L^{-1}. a) residual current; b) 0.04975 mg L^{-1}; c) 0.1478 mg L^{-1}; d) 0.2439 mg L^{-1}; e) 0.3381 mg L^{-1}; f) 0.4306 mg L^{-1}; g) 0.4761 mg L^{-1}.

Table 3 shows the results obtained from lead determination using DPP-ASV. We used a procedure for significance testing [12] to prove that obtained results and the MPL were statistically different. This test uses t student model. The null hypothesis (H_0) is that 0.5 mg L^{-1} is equal to the obtained result of Lead in the beer, and the alternative hypothesis (H_1) is that both quantities are different (P = 5%). The t value was calculated with:

$$t_{calculated} = t_c = \left|\frac{\overline{(x} - 0.5)\sqrt{n}}{s}\right|$$

If $t_{calculated} > t_{tabulated}$, H_0 is not accepted and therefore H_1 is accepted. All these results were statistically different from 0.5 mg L^{-1}.

Beer samples were analyzed according to conditions in Table 1; these experiments showed that an *in situ* measurement is possible, the only treatment needed was mechanical degasification to eliminate carbon dioxide.

Table 3. Contents of lead in beers.

Group	Sample	Lead content (µg L^{-1})
Craft beers	S_1	13.2 ± 4.3
	S_2	66.4 ± 32.7
	S_3	15.6 ± 0.6
Commercial beers	S_4	9.7 ± 6.1
	S_5	13.4 ± 4.4
	S_6	9.8 ± 3.5
	S_7	33.9 ± 14.7
Imported beer	S_8	16.7 ± 1.6

Conclusions

In this study, a fast procedure was developed to determine lead content in beer by Anodic Stripping Voltammetry with Differencial Pulse Polarography. All beer samples displayed a low lead content, less than maximum allowed concentration (0.5 mgL^{-1}) stablished by mexican legislation.

It could be possible to apply this method to other beverages such as wines, sodas, juices and milk even though it is important to verify if it will be necessary to digest this kind of beverages in order to eliminate organic matter. In addition, this electrochemical method could be improved to become a good alternative against spectroscopic methods due to simpler operation, cheaper instrumentation and shorter analysis times. In addition, this electrochemical method does not need to use expensive reagents to eliminate interferences and digest the sample like in spectroscopic methods that have similar LOD.

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