



# Iridium and lead as vehicle emission pollutants: Their sequential voltammetric determination in vegetable environmental bio-monitors

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## ABSTRACT

The present work regards the sequential voltammetric determination of Ir(III) and Pb(II) in vegetable environmental matrices.

The analytical procedure was verified by the analysis of the standard reference materials: Tomato Leaves NIST-SRM 1573a and Olive Leaves BCR-CRM 062. Precision and accuracy, expressed as relative standard deviation and relative error, respectively, were generally lower than 6% in all cases, while the limits of detection for each element were lower than  $5.23 \mu\text{g kg}^{-1}$ .

Once set up on the standard reference materials, the analytical procedure was transferred and applied to laurel leaves sampled in three sites differently influenced by vehicle traffic.

A critical comparison with spectroscopic measurements is discussed.

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## 1. Introduction

The problem relevant to the presence in the environment of platinum group metals (PGMs), considered a new class of pollutants, is a topical subject of great interest and attention. This is due to the fact that the PGMs concentration is significantly increasing with more and more use in autocatalytic converters.

In fact, the use of autocatalytic converters, containing platinum group metals (PGMs), allows to obtain the decrease of pollutants in exhaust gases from motor vehicles, like lead, carbon monoxide, nitrogen oxides and unburned hydrocarbon, but, contemporaneously, it is the cause of a widespread distribution of fine particulate matter and dust originated from deterioration or abrasion of the bulk catalysts [1–3].

After the first massive use of Pt, Pd and Rh in the construction of autocatalytic converters, there has been a gradual reduction of these PGMs and a growing use of iridium as alloying with platinum, palladium and rhodium because of its extreme hardness and high resistance at very high temperatures.

Evidently this fact, considering the compelling use of autocatalytic converters has been the cause of an increasing concentration of such metal in the environment, vegetation, soil surfaces and superficial waters, especially in sites next to roadways at high traffic density, even if such concentrations are generally lower than  $0.1 \mu\text{g/L}$  in liquid

matrices (fresh and sea water) and lower than  $50 \mu\text{g/kg}$  in solid matrices (plant, soil and particulate matter) [4,5].

In the last decade, considering the toxicity of this element [6–10], the literature reports an increasing number of papers regarding the set-up of analytical procedures for the determination of iridium, employing, prevalently, spectroscopic techniques [11–16], more rarely neutron activation analysis [17] and chromatography [18,19]. Voltammetric measurements are seldom employed [20–23].

The present work is the continuation of the study relevant to the presence of PGMs in the environment [21–23]. It suggests a method for sequentially determining, by voltammetric technique, Ir(III) and Pb(II) in vegetable environmental matrices. Such a choice has been carried out since in perspective the vegetable matrices could be employed as biomonitors for the metal environmental pollution linked to the vehicle emissions.

## 2. Experimental

### 2.1. Apparatus

A Multipolarograph AMEL (Milan, Italy) Mod. 433 was employed for all the voltammetric scans, using a conventional three electrode measuring cell: a glassy carbon (GC) electrode (surface area:  $7.065 \text{ mm}^2$ , AMEL, Milan) as working electrode, an  $\text{Ag|AgCl|Cl}^-_{\text{satd}}$  electrode and a platinum wire as reference and auxiliary electrode, respectively.

The experimental conditions are reported in Table 1.

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**Table 1**

Instrumental parameters for the determination of Ir(III) and Pb(II) by Square Wave Adsorptive-Catalytic Stripping Voltammetry (SWAdCSV).<sup>a</sup> Supporting electrolyte: 0.35 mol L<sup>-1</sup> acetate buffer pH 4.8 + 7.5 × 10<sup>-2</sup> mol L<sup>-1</sup> NaBrO<sub>3</sub> + 0.15 mol L<sup>-1</sup> KCl + 4.3 × 10<sup>-5</sup> mol L<sup>-1</sup> cetyltrimethylammonium bromide (CTAB).

	Ir(III)	Pb(II)
$E_i$	+0.775	-0.450
$E_{ads}$	+0.775	-0.450
$E_f$	+0.500	-0.800
$t_a$	390	240
$t_r$	10	10
$dE/dt$	100	100
$\Delta E$	50	50
$\tau$	0.010	0.010
$\nu$	0.100	0.100
$\eta$	10	10
$r$	600	600

<sup>a</sup>  $E_i$ : initial potential (V/Ag|AgCl|Cl<sup>-</sup><sub>satd.</sub>);  $E_{ads}$ : adsorption potential (V/Ag|AgCl|Cl<sup>-</sup><sub>satd.</sub>);  $E_f$ : final potential (V/Ag|AgCl|Cl<sup>-</sup><sub>satd.</sub>);  $t_a$ : electroadsorption time (s);  $t_r$ : delay time before the potential sweep (s);  $dE/dt$ : potential scan rate (mV/s);  $\Delta E$ : step amplitude (mV);  $\tau$ : sampling time (s);  $\nu$ : wave period (s);  $\eta$ : wave increment (mV);  $r$ : stirring rate (r.p.m.).

Before the measurements, to avoid accidental contamination, the voltammetric cell was rinsed with suprapure concentrated 1:1 HNO<sub>3</sub> and then many times with Milli-Q water.

The solutions were thermostated at 20.5 °C and deaerated with water saturated pure nitrogen for 5 min prior to analysis, while a nitrogen blanket was maintained above the solutions during the experiments. The solutions were stirred with a Teflon-coated magnetic stirring bar in the purge step.

The atomic absorption spectrometry measurements were performed using a Perkin-Elmer Mod. A-Analyst 100 Atomic Absorption Spectrometer, equipped with a deuterium background corrector, Autosampler AS-72 and with HGA 800 graphite furnace. Single-element Lumina (Perkin-Elmer) hollow-cathode lamps were used. All measurements were carried out after the relative ashing and atomization curves had been studied for each element considered [24]. The experimental conditions are the following: wavelength (nm): 264.0 [Ir(III)], 283.3 [Pb(II)]; slit (nm): 0.2 [Ir(III)], 0.7 [Pb(II)]; dry temperature (°C): 100 [Ir(III)] and [Pb(II)]; charring temperature (°C): 1400 [Ir(III)], 875 [Pb(II)]; atomization temperature (°C): 2650 [Ir(III)], 1850 [Pb(II)]; sample volume injected: 20 µL, argon flow: 300 mL min<sup>-1</sup> at all steps except during atomization (60 mL min<sup>-1</sup>); for Pb(II), 0.2 mg (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> was employed as matrix modifier.

## 2.2. Reagents and reference solutions

All acids and chemicals were suprapure grade (Merck, Germany). Acidic stock solutions of iridium(III) and Pb(II) (1000 mg L<sup>-1</sup>, Sigma-Aldrich, Germany) were respectively employed in the preparation of reference solutions at varying concentrations for each element, using, for diluting, water demineralized through a Milli-Q system.

0.35 mol L<sup>-1</sup> acetate buffer pH 4.8 + 7.5 × 10<sup>-2</sup> mol L<sup>-1</sup> NaBrO<sub>3</sub> + 0.15 mol L<sup>-1</sup> KCl + 4.3 × 10<sup>-5</sup> mol L<sup>-1</sup> cetyltrimethylammonium bromide (CTAB) was employed as the supporting electrolyte.

## 2.3. Sampling and sample preparation

Laurel leaves were picked, accurately washed with Milli-Q deionized water and put in dry polyethylene bottles, previously washed with a solution of 20% suprapure HNO<sub>3</sub> for 72 h and finally rinsed many times with Milli-Q deionised water.

In order to eliminate, or at least to greatly minimize the interference related to the sampling procedure, the laurel leaves were picked in a homogeneous way on the whole circumference and throughout the height of the plants.

The samples, once dried at 40–45 °C for 96 h, were lyophilized and powdered by means of a corundum ball mill. Finally, they were dried at 50 °C for 48 h prior to the sample preparation.

Approximately 0.5 g, accurately weighed, was placed in a platinum crucible and dissolved in 4 mL 69% (m/m) HNO<sub>3</sub> + 3 mL 37% (m/m) HCl + 5 mL 98% (m/m) H<sub>2</sub>SO<sub>4</sub> at 130–150 °C. The mixture was evaporated to dryness and, after cooling, soluble salts were dissolved in 25 mL 0.35 mol L<sup>-1</sup> acetate buffer pH 4.8 + 7.5 × 10<sup>-2</sup> mol L<sup>-1</sup> NaBrO<sub>3</sub> + 0.15 mol L<sup>-1</sup> KCl + 4.3 × 10<sup>-5</sup> mol L<sup>-1</sup> cetyltrimethylammonium bromide (CTAB).

The solutions obtained were then diluted, if necessary, before spectroscopic measurements.

## 2.4. Total analytical procedure

10 mL sample aliquots of 0.35 mol L<sup>-1</sup> acetate buffer pH 4.8 + 7.5 × 10<sup>-2</sup> mol L<sup>-1</sup> NaBrO<sub>3</sub> + 0.15 mol L<sup>-1</sup> KCl + 4.3 × 10<sup>-5</sup> mol L<sup>-1</sup> cetyltrimethylammonium bromide (CTAB) aqueous reference solution or of solutions obtained in the mineralisation step of the standard reference material and of the laurel leaves, were pipetted into the voltammetric cell and deaerated for 5 min by bubbling water saturated pure nitrogen. The determination of Ir(III) and Pb(II) was carried out by Square Wave Adsorptive-Catalytic Stripping Voltammetry (SWAdCSV) [25] using a glassy carbon (GC) electrode as working electrode.

The voltammetric scans were carried out using the instrumental parameters listed in Table 1.

Table 2 shows the element peak potentials in the aqueous reference solutions and in the solutions obtained by digestion of the standard reference material and of laurel leaves.

## 3. Results and discussion

The procedure here proposed offers remarkable sensitivity, with detection limit at the picomolar level and relies on the dual current-magnifying effect of the stripping catalytic response of the adsorbed Ir(III)- and Pb(II)-CTAB complexes in the presence of bromate.

For both elements – Ir(III) and Pb(II) – the catalytic reactions occur at the surface of the working electrode when the reduced form of the depolarizer is oxidized to its previous voltammetric active form by an oxidizing agent in the layer of the solution close to the electrode surface, following the scheme of “catalytic systems of the first kind” described by Bobrowski and Zarebski [25]:

**Table 2**

Experimental peak potentials ( $E_p$ , V/Ag|AgCl|Cl<sup>-</sup><sub>satd.</sub>) in the aqueous reference solutions and in the solutions obtained by digestion of the standard reference materials and of laurel leaves. The determined values are the mean of 5 independent determinations ± confidence interval at 95% probability level.

Medium	Peak potential ( $E_p$ , V/Ag AgCl Cl <sup>-</sup> <sub>satd.</sub> )	
	Ir(VIII)	Pb(II)
Aqueous reference solutions <sup>a</sup>	+0.611 ± 0.010	-0.567 ± 0.010
Solution obtained by digestion of Standard reference material tomato leaves NIST-SRM 1573a	+0.643 ± 0.015	-0.609 ± 0.015
Solution obtained by digestion of standard reference material olive leaves BCR-CRM 062.	+0.637 ± 0.010	-0.623 ± 0.015
Solutions obtained by digestion of the laurel leaves	+0.629 ± 0.015	-0.613 ± 0.010

<sup>a</sup> 0.35 mol L<sup>-1</sup> acetate buffer pH 4.8 + 7.5 × 10<sup>-2</sup> mol L<sup>-1</sup> NaBrO<sub>3</sub> + 0.15 mol L<sup>-1</sup> KCl + 4.3 × 10<sup>-5</sup> mol L<sup>-1</sup> cetyltrimethylammonium bromide (CTAB).

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