



Use of peak area instrumental datum as possibility to improve the analytical sensitivity in the sequential voltammetric determination of ultra-trace iridium and lead in vehicle emission particulate matter



Clinio Locatelli *

CIRSA (Centro Interdipartimentale di Ricerca per le Scienze Ambientali), Laboratory of Environmental Analytical Chemistry, University of Bologna, Via S. Alberto 163, I-48100 Ravenna, Italy

ARTICLE INFO

Article history:

Received 20 December 2012
Received in revised form 20 February 2013
Accepted 23 February 2013
Available online 5 March 2013

Keywords:

Iridium
Lead
Voltammetry
Peak area
Particulate matter
Spectroscopy

ABSTRACT

The possibility of using peak area instead of peak height is proposed for analytical sequential determination in particulate matter of iridium(III) and lead(II), elements linked to vehicle emissions.

In the case of species present at ultratrace concentration level or having low reversibility degree of the electrodic processes, the employment of peak area, instead of peak current, permits to achieve limits of detection lower even more of one order of magnitude.

The method is based on the voltammetric catalytic current of the Ir(III)–bromate and Pb(II)–bromate systems on glassy carbon (GC) electrode, using 0.25 mol L^{-1} acetate buffer pH 4.3 + $7.7 \times 10^{-2} \text{ mol L}^{-1}$ NaBrO_3 + 0.2 mol L^{-1} KCl [Pb(II)] and 0.25 mol L^{-1} acetate buffer pH 4.3 + $7.7 \times 10^{-2} \text{ mol L}^{-1}$ NaBrO_3 + 0.2 mol L^{-1} KCl + $3.5 \times 10^{-5} \text{ mol L}^{-1}$ cetyltrimethylammonium bromide (CTAB) [Ir(III)] as the supporting electrolytes.

For both elements, the accuracy, expressed as relative error e%, and the precision, expressed as relative standard deviation s%, were satisfactory, being, generally, lower than 6%.

To better validate the analytical procedure, a comparison with spectroscopic (electrothermal atomic absorption spectroscopy, ET-AAS) is also reported.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The peak area, i.e. the integration of the current–time transient stimulated by potential step, that represents the charge passed as a function of time $Q(t)$ [1], is less employed as instrumental datum in voltammetric quantitative analyses.

In our previous communications ([2] and references therein) a critical comparison on the use of peak area and peak current emphasised that, especially in the case of irreversible electrodic processes, certainly the use of the peak area instead of the peak current allows to achieve significant lower limits of detection, also more than one order of magnitude.

Such a possibility has been addressed to the problem of great interest relevant to the increasing presence of PGMs in environmental matrices, normally at ultratrace level concentration, and specifically in particulate matter (PM < 10 μm) owing to vehicle emissions [3–7].

These elements, widely used in the construction of autocatalytic converters, can be dangerous for the health of the population [8–10] by direct contact with the dust, by inhalation of fine particulate matter (aerodynamic diameter < 10 μm) and also through food and water.

In this context, it is important to highlight that great attention has been addressed to platinum(II), palladium(II) and rhodium(III) ([11] and references therein), less in the case of iridium(III), osmium(VIII) and ruthenium(III).

In the last decade, and always more frequently, iridium is employed as alloying (10–20% w/w) with platinum, palladium and rhodium in the manufacture of autocatalytic converters in order to withstand high temperature and high wear. Evidently this fact, considering their compelling use, is the cause of an increasing concentration of such metals in the environment.

Only in recent years, few papers concerning the set-up of analytical procedures for the determination of iridium(III) in matrices generally linked to the environment are reported in literature. Really, for the determination of this metal, spectroscopic techniques [12–17] are prevalently used, more rarely neutron activation analysis [18] and chromatography [19,20]. Voltammetric measurements are seldom employed [21,22]: no paper however aimed at determining iridium in airborne particulate matter, matrix which, evidently, shows to have also high concentrations of lead, metal, as well-known, strongly linked to vehicular traffic.

This paper is the continuation of a previous study concerning the determination of iridium(III) and lead(II) in plants used as bio-monitors [23], and aims to significantly improve the sensitivity of the voltammetric method, allowing to achieve limits of detection considerably lower, even more than one order of magnitude.

* Department of Chemistry “G. Ciamician”, University of Bologna, Via F. Selmi 2, I-40126 Bologna, Italy. Tel.: +39-051-209-94-50; fax: +39-051-209-94-56.

E-mail address: clinio.locatelli@unibo.it.

In fact, considering that: a) iridium(III) may show to have, in the supporting electrolytes usually employed for their voltammetric determination, inadequate reversibility degree of the electrodic process; b) the concentration is generally very low, especially in particulate matter, the present paper intends to pursue three main goals: 1) at first to optimize the instrumental and chemical parameters to obtain the best electrochemical response for iridium(III) and lead(II), carrying out a critical comparison on the use of peak area and peak height as instrumental datum, and, successively, 2) to highlight how the peak area as instrumental datum may be decidedly a good possibility to improve the sensitivity of the analytical procedure in the case of electrodic processes with low reversibility degree, especially when the metal concentration is too low, as in airborne particulate matter, i.e. close to the limits of detection. In fact in such a situation, the analytical determination could be critical, but possible if the peak area is used and impossible if the peak height is employed, and, last but not least, 3) to show, for the first time, that the Pb(II)–bromate catalytic system can be reasonably employed not only on mercury electrodes (hanging and film mercury electrode) [24], but also on solid electrodes, glassy carbon in the present case, even if, at the same concentration and in the same instrumental and chemical conditions, the relevant voltammetric signals, certainly well-defined, show to be lower than those obtained on hanging mercury drop electrode.

2. Experimental

2.1. Apparatus

Voltammetric scans were performed with a Multipolarograph AMEL (Milan, Italy) Mod. 433, assembling a conventional three electrode measuring cell having a glassy carbon (GC) electrode (surface area: 7.065 mm², AMEL, Milan) as working electrode, an Ag|AgCl|Cl⁻_{satd.} electrode and a platinum wire as reference and auxiliary electrodes, respectively.

0.25 mol L⁻¹ acetate buffer pH 4.3 + 7.7 × 10⁻² mol L⁻¹ NaBrO₃ + 0.2 mol L⁻¹ KCl and 0.25 mol L⁻¹ acetate buffer pH 4.3 + 7.7 × 10⁻² mol L⁻¹ NaBrO₃ + 0.2 mol L⁻¹ KCl + 3.5 × 10⁻⁵ mol L⁻¹ cetyltrimethylammonium bromide (CTAB) were employed as the supporting electrolytes for the sequential determination of Pb(II) and Ir(III), respectively (for optimization of the supporting electrolyte composition, see Section 3.1.2.1, subsection 3.1.2.1.2, “Chemical Conditions”).

Before the measurements, to avoid accidental contamination, the Teflon voltammetric cell was rinsed with suprapure concentrated 1:1 HNO₃ and then many times with Milli-Q water.

The solutions were thermostated at 200.5 °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 electrothermal atomic absorption spectrometry (ET-AAS) 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 hollow-cathode lamps were used. All measurements were carried out after the relative ashing and atomization curves had been studied for each element considered [25].

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): 1450 [Ir(III)], 850 [Pb(II)]; atomization temperature (°C): 2650 [Ir(III)], 1800 [Pb(II)]; sample volume injected: 20 µL, argon flow: 300 mL min⁻¹ at all steps except during atomization (60 mL min⁻¹); for Pb(II), 0.2 mg (NH₄)₂PO₄ was employed as matrix modifier.

2.2. Reagents and reference solutions

All acids and chemicals were of suprapure grade (Merck, Germany). Acidic stock solutions of iridium(III) and lead(II) (1000 mg L⁻¹, 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.

Mintek-Sarm-7 was employed as standard reference material for optimizing and setting up the analytical procedure.

2.3. Total analytical procedure

The total analytical procedure consists in carrying out two steps in succession:

- 1) 10 mL sample aliquots of 0.25 mol L⁻¹ acetate buffer pH 4.3 + 7.7 × 10⁻² mol L⁻¹ NaBrO₃ + 0.2 mol L⁻¹ KCl aqueous reference solution or of solutions obtained in the mineralisation step of the standard reference material and of the filters (see Section 4), were pipetted into the voltammetric cell and deaerated for 5 min by bubbling water saturated pure nitrogen. The determination of Pb(II) was carried out by Differential Pulse Catalytic Voltammetry (DPCV).
- 2) Successively, in the same voltammetric cell, 1.0 mL of 3.85 × 10⁻⁴ mol L⁻¹ CTAB (final CTAB concentration 3.5 × 10⁻⁵ mol L⁻¹) was added for the determination of Ir(III) by Differential Pulse Adsorptive-Catalytic Stripping Voltammetry (DPAdCSV).

3. Results and discussion

3.1. Aqueous reference solutions

When an ideal supporting electrolyte is employed, the metals sought must give well shaped and well separated waves, so that they can be determined simultaneously. Generally the choice of the supporting electrolyte is bound to the kind of matrix to analyse, but, in such supporting electrolytes, the metals investigated do not always show to have good reversibility of the electrodic processes, so influencing and reducing the analytical sensitivity.

In fact, the reversibility of the electrodic process influences the voltammetric signal, since the peak current decreases with increase of the irreversibility.

Really, as previously reported in literature [2,26], it happens that the peak height decreases, but simultaneously the voltammetric peak widens out, keeping its area practically constant. Evidently, such experimental situation affects the analytical sensitivity of the calibration curves – higher if the peak area is employed – so allowing lower limits of detection to be achieved.

3.1.1. Reversibility degree of the electrodic processes

In absence of heterogeneous rate constant K_s relevant to the electrodic processes at GC electrode of Ir(III) and Pb(II) in acetate buffer medium, only a qualitative indication about the reversibility of each electrode process has been evaluated by measuring the half peak width values $w_{1/2}$.

It is well-known that, in the case of differential pulse voltammetry [1,27–30], totally reversible electrodic processes, for small pulse height [31] as in the present work, show to have $w_{1/2}$ value, independently of concentration, equal to 3.53RT/nF mV, which at 25 °C is equal to 90.6/n mV, where n is the number of electrons involved in the electrodic process.

The $w_{1/2}$ values reported in Table 1, obtained in aqueous reference solutions and in the solutions obtained by digestion of the standard reference material and of the filters, show the fairly good reversibility of the Ir(III)–Ir(0) and the quasi-reversibility of the Pb(II)–Pb(0) electrodic processes.

Download English Version:

<https://daneshyari.com/en/article/7643496>

Download Persian Version:

<https://daneshyari.com/article/7643496>

[Daneshyari.com](https://daneshyari.com)