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Catalytic-adsorptive stripping voltammetric determination of ultra-trace iridium(III). Application to fresh- and sea-water

Clinio Locatelli[a,b,*]

[a] Department of Chemistry «G. Ciamician», University of Bologna, Via F. Selmi 2, I-40126 Bologna, Italy
[b] CIRSA (Centro Interdipartimentale di Ricerca per le Scienze Ambientali – Interdepartment Centre for Research in Environmental Sciences), Laboratory of Environmental Analytical Chemistry, University of Bologna, Via S. Alberto 163, I-48123 Ravenna, Italy

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ABSTRACT

An extremely sensitive stripping voltammetric procedure for ultra-trace determination of iridium(III) is reported. The method is based on the interfacial accumulation of the iridium(III)–CTAB complex onto the glassy carbon electrode, followed by the catalytic reduction of the adsorbed complex in the presence of bromate. $0.3\,\mathrm{mol\,L^{-1}}$ acetate buffer pH $4.7 + 6.9 \times 10^{-2}\,\mathrm{mol\,L^{-1}}$ $NaBrO_3 + 2.7 \times 10^{-5}\,\mathrm{mol\,L^{-1}}$ cetyltrimethylammonium bromide (CTAB) + $0.2\,\mathrm{mol\,L^{-1}}$ KCl was employed as the supporting electrolyte.

The analytical procedure was verified by the analysis of the standard reference materials: Sea Water BCR-CRM 403 and Fresh Water NIST-SRM 1643d.

The accuracy, expressed as relative error *e*%, was satisfactory, being lower than 6%, while precision as repeatability, expressed as relative standard deviation s_r%, was generally lower than 5%. The limit of detection was of the order of $2–3\,\mathrm{ng\,L^{-1}}$.

Once set up on the standard reference materials, the analytical procedure was transferred and applied to superficial water sampled in proximity to superhighway and in the Po river mouth area.

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1. Introduction

The amount of heavy metals in the environment continuously increases and accumulates owing to the anthropogenic activities [1].

However, in the last years, the problem relevant to the presence of platinum group metals (PGMs) in the environment is a topical subject of great interest. This is due to the fact that the PGMs concentration is significantly increasing with the more and more use of them in industrial catalysts production, autocatalytic converters, anticancer drugs, jewel production, photographic operations. In this contest, it is important to highlight that great attention has been addressed to platinum(II), palladium(II) and rhodium(III) [2 and therein references], less in the case of iridium(III), osmium(VIII) and ruthenium(III).

Among these, iridium(III) is an important geochemical marker in sedimentary environments [3].

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.

On the other hand, iridium is also one of the least abundant elements in the marine environment, so always escaping systematic study by environmental scientists. For this reason, few data are available for iridium(III) abundance in environment, especially in seawater [4,5], and consequently knowledge about its chemical speciation, distribution pattern and sorption–desorption behaviour in sea and superficial ecosystems is scarce.

Only in recent years, several papers regarding 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 these metals, spectroscopic techniques [6–16] are prevalently used, more rarely neutron activation analysis [17,18] and chromatography [19–21].

Voltammetric measurements are seldom employed [22,23], even if, in this field, it is important to point out the interesting work relevant to the electrochemical deposition of iridium oxide onto glassy carbon electrode [24].

For this reason, it seemed attractive and important to propose and set up a new extremely sensitive stripping voltammetric procedure for ultra-trace measurements of iridium(III) in environmental matrices, superficial water in particular, based on the coupling of catalytic and adsorption processes [25,26].

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[*] Correspondence address: Department of Chemistry «G. Ciamician», University of Bologna, Via F. Selmi 2, I-40126 Bologna, Italy. Fax: +39 051 209 94 56.
E-mail address: clinio.locatelli@unibo.it

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Table 1

Instrumental parameters for the determination of Ir(III) by square wave adsorptive-catalytic stripping voltammetry (SWAdCSV).[a] Supporting electrolyte: 0.3 mol L^{-1} acetate buffer pH 4.7 + 6.9 × 10^{-2} mol L^{-1} $NaBrO_3$ + 2.7 × 10^{-5} mol L^{-1} cetyltrimethylammonium bromide (CTAB) + 0.2 mol L^{-1} KCl.

E_i	+0.850
E_{ads}	+0.850
E_f	+0.300
t_{ads}	270
t_r	10
dE/dt	100
ΔE	50
τ	0.010
ν	0.100
η	10
r	600

[a] E_i, initial potential (V/Ag|AgCl|KCl(sat)); E_{ads}, adsorption potential (V/Ag|AgCl|KCl(sat)); E_f, final potential (V/Ag|AgCl|KCl(sat)); t_{ads}, electroadsorption time (s); t_r, delay time before the potential sweep (s); dE/dt, potential scan rate (mV s^{-1}); ΔE, step amplitude (mV); τ, sampling time (s); ν, wave period (s); η, wave increment (mV); r, stirring rate (r.p.m.).

2. Experimental

2.1. Apparatus

All square wave adsorptive-catalytic stripping voltammetric (SWAdCSV) scans were performed with a Multipolarograph AMEL (Milan, Italy) Mod. 433, assembling a conventional three electrode measuring cell having a glassy carbon electrode (GCE) (surface area: 7.065 mm^2, AMEL, Milan) as working electrode, an Ag|AgCl|KCl satd. electrode and a platinum wire as reference and auxiliary electrode, respectively.

0.3 mol L^{-1} acetate buffer pH 4.7 + 6.9 × 10^{-2} mol L^{-1} $NaBrO_3$ + 2.7 × 10^{-5} mol L^{-1} cetyltrimethylammonium bromide (CTAB) + 0.2 mol L^{-1} KCl was employed as the supporting electrolyte.

The experimental conditions are reported in Table 1.

Before the measurements, to avoid accidental contamination, the Teflon voltammetric cell was rinsed with suprapure concentrated 1:1 HNO_3 and then many times with Milli-Q water.

The solutions were thermostated at 20 ± 0.5 °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.

2.2. Reagents and reference solutions

All acids and chemicals were suprapure grade (Merck, Germany).

Acidic stock solutions of iridium(III) (1000 mg/L, Sigma–Aldrich, Germany) were employed in the preparation of reference solutions at varying concentrations, using, for diluting, water demineralized through a Milli-Q system.

Sea Water BCR-CRM 403 and Fresh Water NIST-SRM 1643d were employed as standard reference materials for optimising and setting up the analytical procedure.

2.3. Sampling and sample preparation

Superficial water samples (fresh and sea water) were taken with a portable suction pump made of stainless steel and pyrex glass, neither of which would yield contamination with iridium(III) to be determined. Model experiments exactly simulating the sampling procedure were performed with simulated fresh and sea water, to verify that the samples would not be contaminated by the sampling device. In the experimental conditions employed, the analyte concentration in these artificial samples was found to be lower than the relevant limits of detection.

To eliminate also the suspended matter fraction 0.22–0.45 μm, water samples were immediately filtered on the spot through 0.22 μm membranes and transferred into polyethylene bottles, previously soaked in 1:1 nitric acid for 48 h and rinsed many times with deionized water (Milli-Q).

The samples were cooled to 4 °C for transport, stored at this temperature and analysed within 72 h. Before voltammetric measurements the samples were kept at room temperature overnight.

2.4. Total analytical procedure

10 mL sample aliquots of 0.3 mol L^{-1} acetate buffer pH 4.7 + 6.9 × 10^{-2} mol L^{-1} $NaBrO_3$ + 2.7 × 10^{-5} mol L^{-1} cetyltrimethylammonium bromide (CTAB) + 0.2 mol L^{-1} KCl aqueous reference solution or of fresh and sea water, containing 0.3 mol L^{-1} acetate buffer pH 4.7 + 6.9 × 10^{-2} mol L^{-1} $NaBrO_3$ + 2.7 × 10^{-5} mol L^{-1} cetyltrimethylammonium bromide (CTAB) + 0.2 mol L^{-1} KCl were pipetted into the voltammetric cell and deaerated for 5 min by bubbling water saturated pure nitrogen.

The determination of Ir(III) was carried out by square wave adsorptive-catalytic stripping voltammetry (SWAdCSV).

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 standard reference material solutions.

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 iridium(III)-CTAB complex in the presence of bromate, following the scheme:

$$\text{Ir(III)–CTAB}_{\text{solution}} \rightarrow \text{Ir(III)–CTAB}_{\text{surface}} \quad \text{(accumulation)} \qquad (1)$$

$$\text{Ir(III)–CTAB}_{\text{surface}} + 3e^- \rightarrow \text{Ir(0)–CTAB}_{\text{surface}} \qquad (2)$$

$$2\text{Ir(0)–CTAB}_{\text{surface}} + \text{BrO}_3{}^- + 6\text{H}^+ \rightarrow 2\text{Ir(III)–CTAB}_{\text{surface}} + \text{Br}^- + 3\text{H}_2\text{O} + 6e^- \qquad (3)$$

A preliminary study was carried out employing the relevant aqueous reference solution (the blank concentration was lower than the respective limits of detection).

3.1. Aqueous reference solutions

3.1.1. Reversibility degree of the electrodic processes

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

In the case of Adsorption Stripping Voltammetry, totally reversible electrodic processes, for small pulse height ($\Delta E < 200/n$ mV) as in the present work ($\Delta E = 50$ mV), the $w_{1/2}$ value, independently of concentration, is equal to 3.53 RT/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 [27a,28a].

The $w_{1/2}$ values reported in Table 2 show that, in the aqueous reference solutions and in the standard reference materials Ir(III) shows to have a fairly good reversibility.

Table 2

Experimental peak potentials, half peak widths and limits of detection in the aqueous reference solutions and in the standard reference materials solutions. The determined values are the mean of 5 independent determinations ± confidence interval at 95% probability level.

	Peak potential (E_p, V/Ag, AgCl, $Cl^-_{satd.}$)	Half peak width ($w_{1/2}$, mV)	Limit of detection (LOD, ng/L)[a]
0.3 mol L^{-1} acetate buffer pH 4.7 + 6.9 × 10^{-2} mol L^{-1} $NaBrO_3$ + 2.7 × 10^{-5} mol L^{-1} cetyltrimethylammonium bromide (CTAB) + 0.2 mol L^{-1} KCl	+0.603 ± 0.010	39 ± 2	2.3 ± 0.1
Sea Water BCR-CRM 403	+0.587 ± 0.015	47 ± 3	3.5 ± 0.1
Fresh Water NIST-SRM 1643d	+0.623 ± 0.015	43 ± 3	2.7 ± 0.2

[a] The limits of detection (LOD) (see Section 3.1.6) were obtained by the analytical calibration function of each element (K = 3, 95% confidence level).

3.1.2. Cyclic voltammetry of Ir(III)–CTAB in the presence of bromate

To prove the adsorptive-catalytic nature of the electrodic process of Ir(III)–CTAB in the presence of bromate, cyclic voltammetric measurements were carried out [27b,28b, 29] between +0.850 and +0.300 V/Ag, AgCl, $Cl^-_{satd.}$

One cathodic peak is observed at +0.561 V/Ag, AgCl, $Cl^-_{satd.}$ during the negative-going scan. The presence of a high cathodic peak at +0.577 V/Ag, AgCl, $Cl^-_{satd.}$ also in the reverse direction scan is certainly indicative of a catalytic process, as shown in Fig. 1, where the cyclic voltammograms of Ir(III)–CTAB in the presence (a) and in the absence (b) of bromate is reported. Moreover, when an accumulation period precedes the cyclic potential scans, the responses increase dramatically. Both these experimental observations show an enhancement by adsorption, but also that both forms of the complex, Ir(III)–CTAB and Ir(0)–CTAB [see adsorptive-catalytic scheme, Eq. (2)] remain adsorbed on the electrode surface.

Finally, it is also important to highlight that, in the absence of both CTAB and bromate, the Ir(III) cyclic voltammogram, at least at Ir(III) concentration of Fig. 1, does not show electrochemical signal.

In order to optimise the analytical procedure, and to obtain the best electrochemical response, the influence of the chemical conditions and of the different instrumental voltammetric parameters on peak current i_p have been investigated.

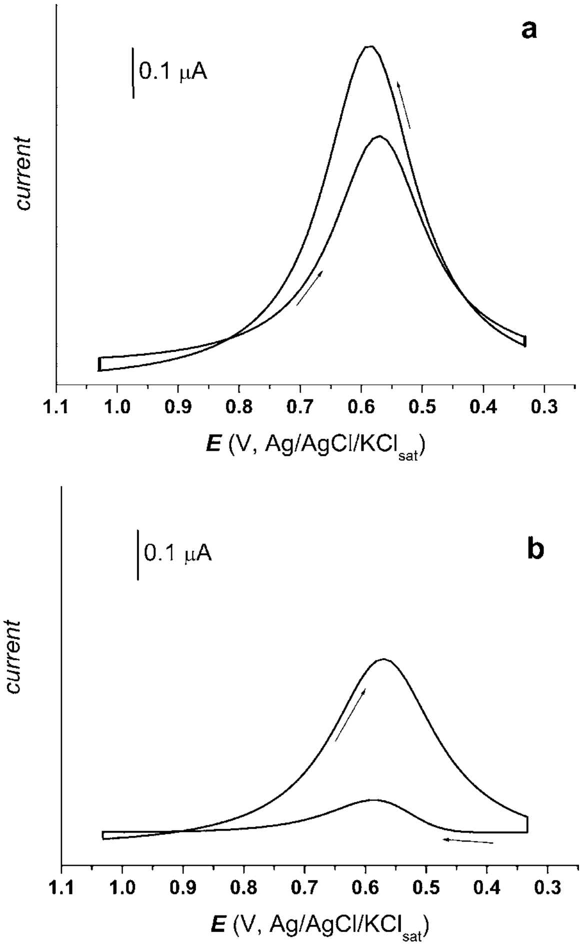

Fig. 1. Cyclic voltammograms of Ir(III)–CTAB in the presence (a) and in the absence (b) of 6.9 × 10^{-2} mol L^{-1} $NaBrO_3$. Potential scan rate 50 mV s^{-1}. Concentration: 596.0 ng L^{-1}. Supporting electrolyte: 0.3 mol L^{-1} acetate buffer pH 4.7 + 2.7 × 10^{-5} mol L^{-1} cetyltrimethylammonium bromide (CTAB) + 0.2 mol L^{-1} KCl.

3.1.3. Chemical conditions

3.1.3.1. Bromate concentration. Fig. 2 shows the relationship between Ir(III) peak current and bromate concentration. As the bromate concentration increases, the Ir(III) response increases linearly at first and then more slowly. In the experimental conditions employed, 6.9 × 10^{-2} mol L^{-1} BrO_3^- seems the best compromise.

3.1.3.2. CTAB concentration. The concentration of the ligand presents a similar effect on the stripping current. The Ir(III) signal *vs.* CTAB concentration shows to have an adsorption isotherm behaviour: the peak current increases rapidly with increasing CTAB up to 2.7 × 10^{-5} mol L^{-1} and then more slowly, keeping practically constant values (Fig. 3).

3.1.4. Instrumental voltammetric parameters

Particular attention was paid to electroadsorption time (t_{ads}) and to adsorption potential (E_{ads}).

As regard the wave amplitude (ΔE), in all cases, and till 100 mV, the peak current gives a linear relationship [$i_p = K(\Delta E)$].

The other parameters, like mercury drop size or delay before sweep, did not affect significantly (95% confidence level) the peak

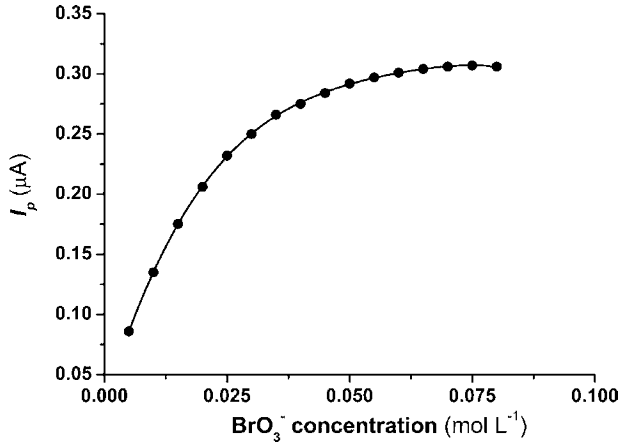

Fig. 2. Influence of BrO_3^- concentration on Ir(III) peak current. Concentration: 77.0 ng L^{-1}. Experimental conditions see Table 1. Supporting electrolyte: 0.3 mol L^{-1} acetate buffer pH 4.7 + n (0.5 × 10^{-2} < n < 8.0 × 10^{-2}) mol L^{-1} $NaBrO_3$ + 2.7 × 10^{-5} mol L^{-1} cetyltrimethylammonium bromide (CTAB) + 0.2 mol L^{-1} KCl.

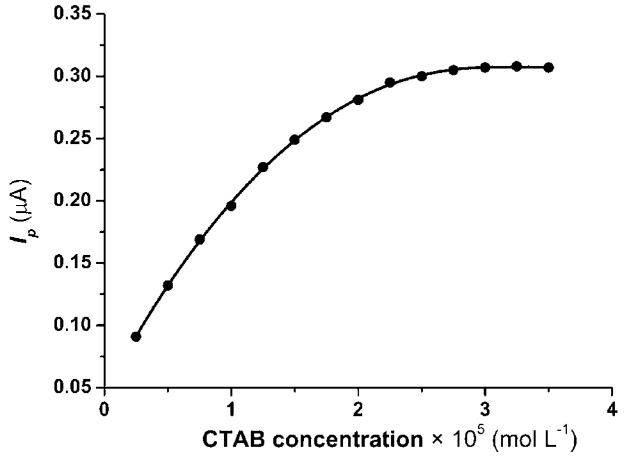

Fig. 3. Relationship between cetyltrimethylammonium bromide (CTAB) concentration and Ir(III) peak current. Concentration: 77.0 ng L^{-1}. Experimental conditions see Table 1. Supporting electrolyte: 0.3 mol L^{-1} acetate buffer pH 4.7 + 6.9 × 10^{-2} mol L^{-1} $NaBrO_3 + n$ $(0.25 \times 10^{-5} < n < 3.50 \times 10^{-5})$ mol L^{-1} cetyltrimethylammonium bromide (CTAB) + 0.2 mol L^{-1} KCl.

shape and, consequently, the peak current. The stirring rate was the highest allowed (600 rpm).

3.1.4.1. Electroadsorption time t_{ads}. Ir(III) peak current *vs.* electroadsorption time shows an adsorption isotherm behaviour, increasing linearly with electroadsorption time till 8–9 min.

Then the choice of the optimum value in this time range is strictly linked to the analyte concentration to determine.

3.1.4.2. Adsorption potential E_{ads}. The dependence of the stripping current on the adsorption potential is reported in Fig. 4 Only slight variations in the response are observed, with optimal values around +0.850 V/Ag, AgCl, $Cl^{-}_{satd.}$

3.1.5. Analytical calibration functions

Using instrumental experimental conditions of Table 1, the analytical calibration functions of each individual element were determined in the aqueous reference solutions.

In the range of concentrations investigated (<LOD – 250 ng L^{-1}), a linear i_p *vs.* metal concentration relationship was found for each single element.

In all cases the correlation coefficients were good ($r^2 > 0.9989$).

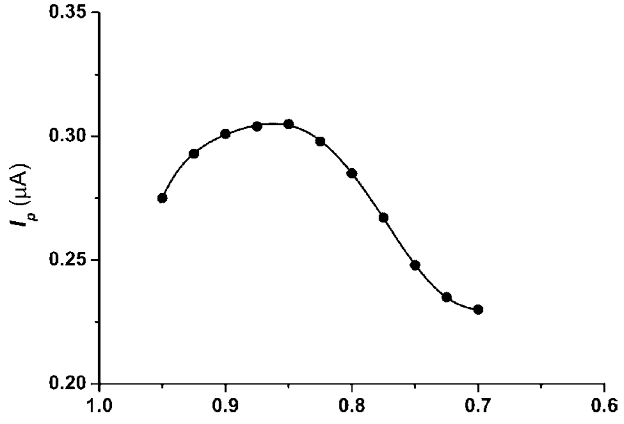

Fig. 4. Variation of Ir(III) peak current with adsorption potential. Concentration: 77.0 ng L^{-1}. Experimental conditions see Table 1. Supporting electrolyte: 0.3 mol L^{-1} acetate buffer pH 4.7 + 6.9 × 10^{-2} mol L^{-1} $NaBrO_3$ + 2.7 × 10^{-5} mol L^{-1} cetyltrimethylammonium bromide (CTAB) + 0.2 mol L^{-1} KCl.

Table 3
Accuracy and precision of the analytical procedure. The determined values are the mean of 5 independent determinations ± confidence interval at 95% probability level. Concentration: ng/L. In all cases the spiked-sample concentration was 69.0 ng L^{-1}.

standard reference material	Determined value	*e* (%)	s_r (%)
Sea Water BCR-CRM 403	73 ± 4	+5.8	5.0
Fresh Water NIST-SRM 1643d	65 ± 4	−5.8	4.7

3.1.6. Limits of detection

Using the experimental conditions of Table 1, the limit of detection (LOD) in the aqueous reference solution (Table 2) was obtained by the equation LOD = $K\ s_{y/x}/b$ [30], where $s_{y/x}$ and b are the estimated standard deviation and the slope of the analytical calibration function of each element, respectively, with a 95% (K = 3) confidence level [31].

In the case of voltammetric technique, since the analytical calibration functions were determined by standard addition method, it was possible to obtain the LODs directly also in the standard reference materials (Table 2).

3.2. Standard reference materials

The method set up in aqueous reference solutions was applied to standard reference materials Sea Water BCR-CRM 403 (from Institute for Reference Materials and Measurements, European Commission, Joint Research Centre, Belgium) and Fresh Water NIST-SRM 1643d (from National Institute of Standards and Technology, Gaithersburg, MD, USA) in order to confirm and verify the applicability of the analytical procedure, determining its accuracy and precision (Table 3).

In both standard reference materials, the Ir(III) concentration, in the experimental conditions employed, was lower than its limit of detection.

However it is important to highlight that, to test accuracy and precision of the analytical procedure, the metal concentrations listed in Table 3 have been spiked in the above standard reference materials.

This may seem an anomalous procedure, but, in our opinion, it resulted to be the only way, considering that Standard Water (fresh and sea water) Reference Materials containing certified concentrations of Ir(III) were not available.

In the experimental conditions employed, precision as repeatability [30], expressed as relative standard deviation (s_r %) on five independent determinations, was satisfactory, being, in all cases, lower than 5%, while accuracy, expressed as relative error (*e*%) was generally lower than 6% (Table 3).

Fig. 5 shows the square wave adsorptive-catalytic stripping voltammogram of Ir(III) in the standard reference material Fresh Water NIST-SRM 1643d.

3.3. Practical applications

Once set up the procedure for the voltammetric determination of Ir(III), the method was transferred to fresh- and sea water sampled in three sites, one in proximity to superhighway (site A, fresh water), and two inside the Po river mouth area, the former near a heavily trafficked way (site B, fresh water) and the latter in a bay (Goro Bay) directly connected with the Adriatic Sea (site C, sea water, salinity 2.9%), and sufficiently far from vehicle traffic.

The experimental results, obtained using the instrumental parameters of Table 1 [(concentration: ng/L): 23.7 ± 0.9 (site A); 6.9 ± 0.2 (site A); <LOD (site C)] show that the analytical procedure proposed is certainly applicable and transferable without problems to superficial water matrices.

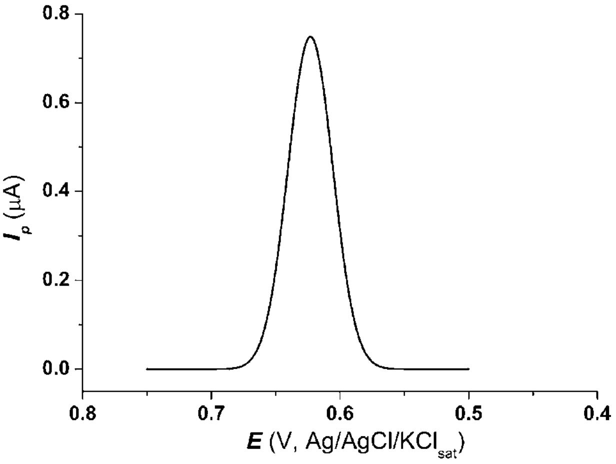

Fig. 5. Square wave adsorptive-catalytic stripping voltammogram of Ir(III) in Fresh Water NIST-SRM 1643d Standard Reference Material. Concentration: 159.0 ng L^{-1} (spiked). Experimental conditions: see Table 1.

Finally, it is important to emphasize that, with regard to Ir(III) concentration in superficial waters, comparison of the results reported in this paper with those relevant to the different sampling sites may be very difficult, perhaps impossible, owing to the lack of the literature data.

4. Conclusions

- Voltammetry is certainly a valid analytical technique, simple and suitable for multicomponent metal determinations in complex matrices. In fact it shows good precision, accuracy, selectivity, presenting also high sensitivity, so allowing to obtain very low limits of detection.
- Moreover, such a technique may be certainly a good alternative to spectroscopy, which, considering the very low metal concentration to determine, needs too expensive equipment like inductively coupled plasma (ICP) or better inductively coupled plasma/mass spectrometry (ICP/MS), since electrothermal atomic absorption spectrometry shows to have inadequate limits of detection to determine the very low Ir(III) concentrations in environmental matrices [32]. In fact, the great advantage in using voltammetry is certainly the equipment, but also the running cost: very low in the case of voltammetry, extremely high in the case of ICP and ICP/MS, also 25–30 times higher in the case of ICP/MS.

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