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Talanta 69 (2006) 148–153
Talanta
www.elsevier.com/locate/talanta

An analytical application of the electrocatalysis of the iodate reduction at tungsten oxide films

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Received 4 August 2005; received in revised form 8 September 2005; accepted 8 September 2005

Abstract

Films of non-stoichiometric tungsten oxides have been deposited onto glassy carbon surfaces by electrodeposition from acidic W(VI) solutions and the chemical stability of these oxides was investigated by using the electrochemical quartz crystal microbalance. At these modified surfaces, rotating disc electrode voltammetric experiments indicated that iodate is electrocatalytically reduced in a mass-transport controlled process. The influence of the film thickness on the response to iodate was investigated and the results indicated a linear relationship between catalytic current and film thickness for relatively thin oxide layers. The modified electrode was employed successfully as an amperometric sensor for iodate in a flow injection apparatus. The linear response of the developed method is extended from 5 μmol L^{-1} to 5 mmol L^{-1} iodate with a limit of detection (signal-to-noise = 3) of 1.2 μmol L^{-1}. The repeatability of the method for 41 injections of a 1 mmol L^{-1} iodate solution was 0.8% and the throughput was determined as 123 h^{-1}. Interference from other oxidant anions such as nitrate and nitrite was not noticeable, whereas bromate and chlorate interfere at slight levels. The method was used in the determination of the iodate content in table salt samples.

Keywords: Electrochemical sensors; Iodate; Tungsten oxide; Flow injection; Amperometric detection; Salt samples

1. Introduction

A number of techniques and materials have been employed to modify the surface of solid electrodes [1]. We are particularly interested in the electrodeposition of transition metal oxides capable of mediating electron transfer from oxygenated anions. At sufficiently negative potentials, electrons and protons are injected into these films leading to non-stoichiometric oxides, which are very conductive materials [2]. The electrochromic and electrocatalytic features of tungsten and molybdenum oxides have been largely exploited in literature [2–5]. Accordingly, we have already studied the distinctive role of molybdenum oxide films towards the reduction of oxianions such as bromate and iodate, mechanistic and analytical aspects being reported [5].

Tungsten oxides constitute another class of material whose attachment to electrode surfaces has been described by at least two major procedures. The first one involves electrodeposition from W(VI) solutions [4,6] and the other one is based on thermal deposition [7–9]. By polarisation at adequate potentials, tungsten oxide films show electrochromic characteristics because of the formation of non-stoichiometric structures. The coloration/decoloration process has been ascribed to the insertion of monovalent ions into the film, as represented by the following equation^6:

$$WO_3 + x\,e^- + x\,M^+ \rightleftharpoons M_xWO_3 \qquad (1)$$

where M^+ is a monovalent ion (H^+, Na^+, Li^+) and x can very between 0 and 1.

The electrochromic properties of materials such as WO_3 have been extensively exploited in the development of display devices. Notwithstanding, only a few works have reported the use of these films in the fabrication of electrochemical sensors. The oxygen-transfer capability of these reduced tungsten oxide films have already been demonstrated by Kulesza and Faulkner by using bromate and chlorate as oxianions [10]. These authors have also incorporated platinum metal microparticles in thin film tungsten oxides and the effect of catalyst dispersion enhanced

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0039-9140/$ – see front matter
doi:10.1016/j.talanta.2005.09.010

the performance of the sensor compared to the bulk metal system [11,12]. A similar principle was used in a study involving the oxidation of HCOOH and $(COOH)_2$ at tungsten oxide surfaces [13,14]. Carboxylic acids were also determined by using FIA with potentiometric detection at tungsten oxide electrodes [15]. Recently, Casella and Contursi [16] have investigated the electroreduction of bromate, chlorite and nitrite at tungsten/tungsten oxide surfaces and the potential applicability of the modified surface has been suggested.

In the present communication we have reported results on the electrochemical behavior of iodate at glassy carbon surfaces modified by thin layers of tungsten oxides. The distinguished electrocatalytic feature of the immobilized material was used in the development of a flow injection method for the determination of iodate. We have a particular interest in this oxianion as the administration of iodine as KIO_3 in commercial table salt is a current practice in Brazil [17]. However, it is well-known that deficiency of iodine may induce hyperthyroidism [18] hence simple and cost-effective analytical methods for the determination of this anion are continuously desired.

2. Experimental

2.1. Reagents

All reagents used were of analytical-reagent grade. A 54 mmol L^{-1} W(VI) solution was prepared from the dissolution of 0.50 g of metallic tungsten (Acros Organic) in 5 mL of 30% H_2O_2 solution (Merck). The remaining mixture was diluted in a volumetric flask with deionised water to 50 ml and stored for 15 days before use. After this period the pH of the pale yellow solution was 1.5 and its chemical stability was maintained for at least 3 months. Water used in the preparation of all solutions was processed through a water purification system (Nanopure Infinity, Barnstead).

2.2. Apparatus

Voltammetry was performed by using an EG&G 273A potentiostat connected to a 486 DX computer and a conventional three-compartment cell. The electrode assembly consisted of a glassy carbon disk (r = 1.5 mm) encapsulated in a Teflon cylinder as working electrode; a platinum wire as counter electrode and a Ag/AgCl (KCl saturated solution) electrode as reference. Rotating disk voltammetry was carried out using an AFCBP1 Pine Instrument Co. analytical rotator. The flow injection system consisted of a homemade electrochemical flow-through cell, an injection valve with loop volume 150 μL and a 50 mmol L^{-1} Na_2SO_4 solution (pH 2.5) as carrier electrolyte. Solutions were propelled by using a Reglo Analog MS-2/6 C Ismatec peristaltic pump. In electrochemical quartz crystal microbalance studies the working electrode was a 6 MHz AT-cut piezoelectric quartz crystal with diameter of 25 mm and a piezo active electrode area of 0.31 cm^2. Both electrode sides were previously evaporated with gold onto a chromium layer in order to improve the adherence of gold onto the quartz substrate. Frequency resonance shift was transformed in mass change using the Sauerbrey equation [19]:

$$\Delta f = -C_f \Delta m \qquad (2)$$

where the integral sensitivity constant, C_f (6.5×10^7 g cm^{-2} Hz^{-1}), was initially obtained by electrodeposition from a copper sulfate solution (0.5 mol L^{-1}) in an acidic medium (H_2SO_4, pH 1), and this value is in agreement with that obtained when the calibration was carried out with silver electrodeposition [20]. Experiments were carried out with a model PG 3901 Omnimeta potentiogalvanostat. Frequency shifts during the potential scan were measured by using a Stardford Research Systems instrument, model SR 620, connected to an oscillating circuitry (serial mode) and to a microcomputer for data acquisition.

2.3. Modification of the electrode surface

The typical procedure for electrodeposition of films of tungsten oxide onto the glassy carbon electrode surface involved consecutive potential scans at 50 mV s^{-1} between +0.5 and −0.8 V (17 potential cycles) in the W(VI) solution prepared as previously described. After the potential cycles the electrode was rinsed with deionised water to remove traces from the working solution. The modification process was concluded by transferring the modified electrode to the supporting electrolyte solution (50 mmol L^{-1} Na_2SO_4, pH 2.5) and cycling the potential consecutively (10 potential cycles) in the +0.5 to −0.8 V range. The influence of the film thickness on the current response for iodate was investigated by varying the number of potential cycles in the preparation of the modified electrode.

2.4. Volumetric determination of iodate

The iodate content in commercial salt samples was determined by using a classical procedure based on the quantitative reaction between the analite and excess iodide in acidic medium, the released triiodide being further titrated with a standard thiosulphate solution [21].

3. Results and discussion

3.1. Electrochemical deposition of tungsten oxides

At certain experimental conditions, the electrochemical reduction of W(VI) gives rise to the deposition of insoluble non-stoichiometric oxides at the working electrode surface, as reported in previous studies [2]. Accordingly, Fig. 1 (top) shows the result of 17 repetitive potential cycles in a W(VI) at pH 1.5, and the continuous current increase demonstrates the growth of a film oxide layer onto the electrode surface. Mass changes in the working electrode during the potential cycle can be observed by using the electrochemical quartz crystal microbalance. Fig. 1 (bottom) also indicates that the insoluble oxide is deposited during the scan towards more negative potentials. After this deposition step, the modified electrode was washed thoroughly with deionised water to remove traces of the W(VI) solution.

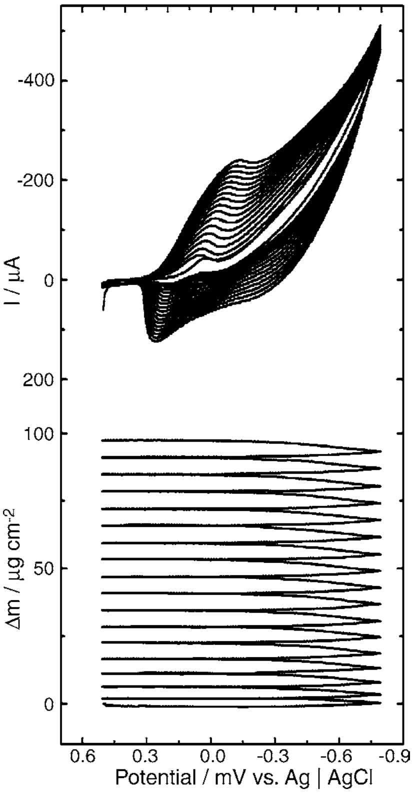


Fig. 1. Consecutive cyclic voltammograms for a 54 mmol L^{-1} W(VI) solution (pH 1.5) recorded with a Au disc electrode ($A = 0.31\ cm^2$) at 50 mV s^{-1} (top) and the respective mass increase during the deposition of tungsten oxide onto the electrode surface (bottom).

Fig. 2 shows the dependence of Δm as a function of charge density, the linear profile demonstrates the rigid behaviour of the film [22], i.e., the charge can be associated with the amount of deposited material, validating the use of the Sauerbrey equation (Eq. (2)).

The resulting modified electrode was then placed in an electrochemical cell containing only the supporting electrolyte and the voltammogram represented by curve C in Fig. 3 was obtained. The film showed broad cathodic and anodic peaks corresponding to the penetration and release of protons, respectively, according to the reaction shown in Eq. (1). A more detailed discussion on the electrochemical processes associated with this film may be found elsewhere [4]. It is noteworthy that cycling repeatedly the potential between the limits +0.5 and −0.8 V did not cause an appreciable decrease in the peak currents (less than 0.5% after 10 cycles), confirming the good chemical and electrochemical stability of the tungsten oxide film in the supporting electrolyte. On the other hand, a continuous current decrease was observed in voltammetric experiments recorded with the modified electrode immersed in Na_2SO_4 solutions at pH values higher than 4, probably because of chemical dissolution of the film, as discussed in a next section of this paper and reported in literature [6].

Investigations on the repeatability of the procedure employed in the deposition of tungsten oxides were performed by comparing voltammetric curves recorded with six different modified electrodes in the supporting electrolyte. Current measured at the cathodic peak potential (−0.2 V) did not vary more than 1%, demonstrating the excellent repeatability of the electrodeposition method. A linear relationship was obtained by plotting cathodic current peak values as a function of the number of potential cycles employed in the modification of the electrode surface (until 68 potential cycles), which is an indication of the low resistivity of the film and of its relatively high permeability to hydrogen-transport.

3.2. Electrocatalysis of the iodate reduction

Voltammogram corresponding to curve A in Fig. 3 demonstrates that iodate is electroinactive at a bare electrode surface. We have already proposed that at surfaces containing metallic oxides such as MoO_3, the oxygen-transfer reaction from the oxianion is facilitated when the electrode is polarised at sufficiently negative values [5]. This is a consequence of the formation of hydrogen Mo bronzes, very reactive toward catalytic reductions [23,24]. It should be emphasized that dissolved oxygen does not constitute a serious interfering species at the experimental conditions reported in Fig. 3 owing to the relatively high current levels. The influence of dissolved oxygen on amperometric

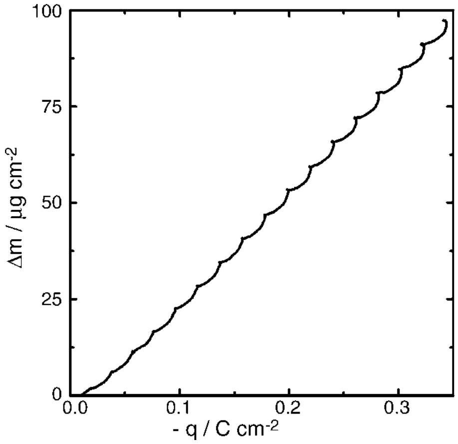


Fig. 2. Dependence of Δ*m* as a function of charge density during the electrodeposition of tungsten oxide (experimental conditions as in Fig. 1).

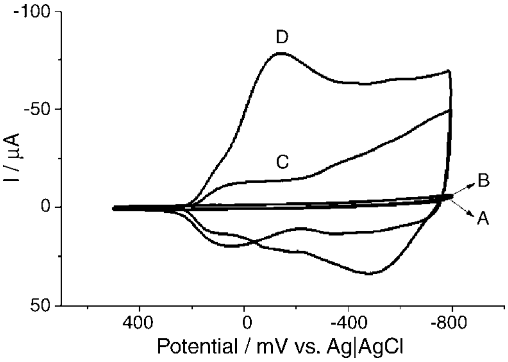
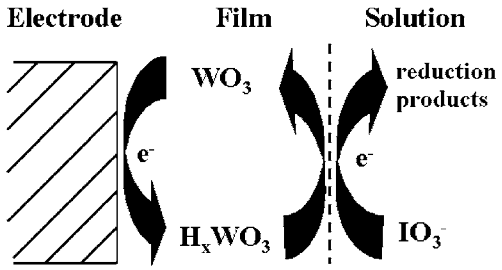


Fig. 3. Cyclic voltammograms recorded in a 50 mmol L^{-1} Na_2SO_4 solution (pH 2.5) before (A and C) and after (B and D) addition of iodate to give a final concentration = 2 mmol L^{-1}. Curves A and B: bare glassy carbon electrode; curves C and D: tungsten oxide modified electrode. Potential scan rate = 50 mV s^{-1}.

measurements at low iodate concentrations will be discussed in a later section.

Curve D in Fig. 3 demonstrates that tungsten oxide films can also act as efficient reductor materials when electrons are injected. The behaviour of iodate at the modified electrode indicates a remarkable current enhancement at the 0 V potential region, as a consequence of the chemical reduction of iodate by electrogenerated tungsten bronzes. The attenuation of the respective anodic component is also explained by this reaction, corroborating the existence of an electrocatalytical reaction as schematically proposed below:



Experiments to investigate the nature of the reduction products of iodate at the tungsten oxide cathode were not performed. Notwithstanding, from coulometric experiments we have already confirmed that iodide is generated during the cathodic reduction of iodate at surfaces containing molybdenum oxide coatings, hence it is likely that this anion is one of the reaction products [25].

The dynamics of the electrocatalysis associated with the iodate reduction was investigated by using rotating disc electrode voltammetry. Fig. 4 shows the voltammetric profile of the iodate reduction by changing the rotation rate of the electrode in a significantly large range. A plot of limiting current as a function of the square root of the rotation rate is seen in the inset of Fig. 4, which includes data for various concentrations of iodate. A set of straight lines with intercept near to zero was obtained, indicating that the overall electrode process is mass-transport controlled at the experimental conditions employed. This is a special feature of this oxide film in terms of electrocatalytic efficiency, as limiting current is solely governed by mass-transport of the analyte in the solution. Interestingly enough, Kulesza and Faulkner [4] have reported similar experiments by using bromate as an analyte but they found that the limiting current does not vary linearly with $\omega^{1/2}$. This suggests that the kinetic barrier involving the O-atom transfer from the oxianion to the bronze is significantly different from iodate to bromate, likely because of the higher polarisability of the iodine atom compared to bromine.

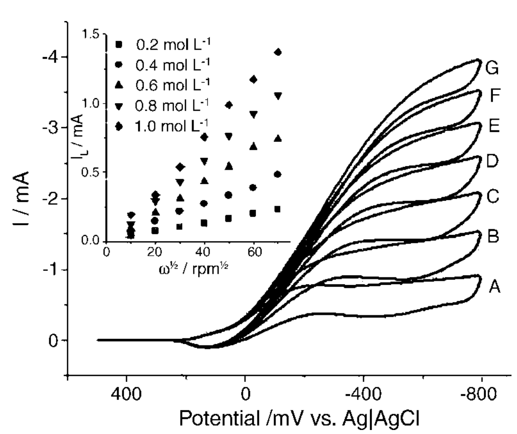


Fig. 4. Cyclic voltammograms recorded in a 50 mmol L^{-1} Na_2SO_4 + 2 mmol L^{-1} iodate solution (pH 2.5) with a tungsten oxide modified electrode at different rotation rates: 100, 400, 900, 1600, 2500, 3600 and 4900 rpm (A–G). Potential scan rate = 50 mV s^{-1}. The inset shows Levich plots for different iodate concentrations, limiting current values being measured at −800 mV.

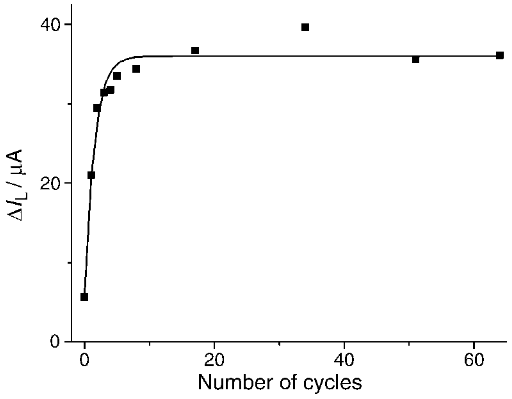


Fig. 5. Dependence of ΔI_L ($I_k - I_d$) on the number of cycles employed in the procedure of electrodeposition of tungsten oxides. I_k and I_d correspond to cathodic peak current values measured in the presence and absence of iodate (1 mmol L^{-1} iodate) for voltammograms recorded at 50 mV s^{-1}.

The effect of the film thickness on the iodate response was evaluated by measuring catalytic current values in experiments performed with continuously thicker films. Fig. 5 shows that current depends on film thickness at thinner films, which is a proof that iodate diffuses through the oxide layer. However, no further current enhancement was observed for thicker films, which may suggest that the modified electrode does not handle more material at these experimental conditions owing to a lack of iodate or some kinetic barrier such as the rate of the cross-exchange reaction between reduced tungsten oxides and the oxianion.

3.3. EQCM studies on the chemical stability of the film

A very important feature of modifier layers deposited at electrode surfaces, especially in terms of analytical applications, is the chemical stability of the sensor placed in contact with the supporting electrolyte or sample. As iodate is a strong oxidant at acidic conditions, some studies were then carried out aiming to investigate the influence of both pH and iodate on the stability of the oxide layer. Fig. 6 shows mass changes of the modified electrode during potential scans in 50 mmol L^{-1} Na_2SO_4 solutions at different pH values and no significant changes were noticed at low pH values, confirming results from voltammetric experiments. On the other hand, a continuous mass loss is seen at pH 4.7, which is likely explained due to a slow film dissolution process. Similar experiments involving the study of the chemical stability of the film were also carried out at alkaline conditions (pH 9.0). Analysis of curve D in Fig. 6 indicates that the film is instantaneously solubilised as the electrode is placed in contact with the supporting electrolyte,

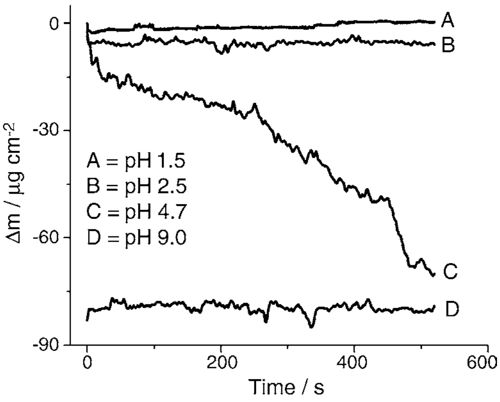


Fig. 6. Mass plot as a function of time for tungsten oxide films immersed in supporting electrolyte solutions (50 mmol L^{-1} Na_2SO_4) at various pH conditions.

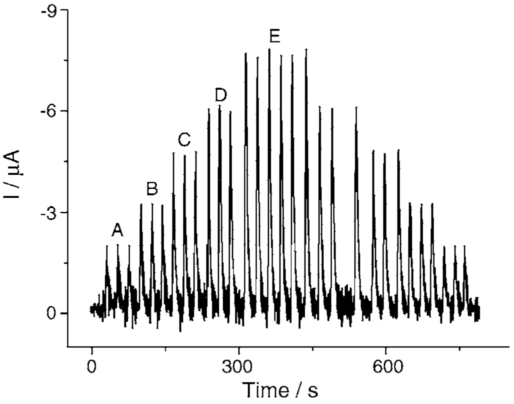


Fig. 7. FIA recordings for injections of iodate solutions at the following concentrations: 20, 40, 60, 80 and 100 µmol L^{-1} (A–E). $E = -0.2$ V.

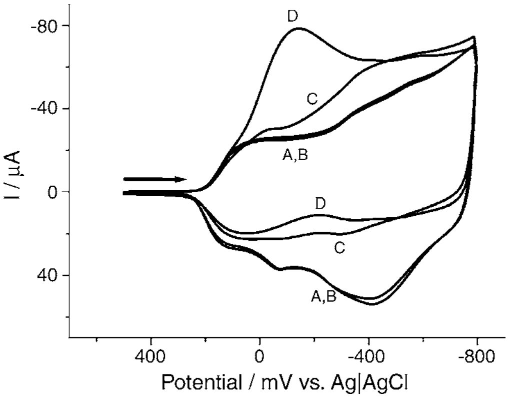


Fig. 8. Cyclic voltammograms recorded with a tungsten oxide modified electrode in a 50 mmol L^{-1} Na_2SO_4 solution (pH 2.5) before (A) and after independent addition of ClO_3^- (B), BrO_3^- (C) and IO_3^- (D) to give 2 mmol L^{-1} solutions of these oxianions. Scan rate = 50 mV s^{-1}.

this observation being in agreement with data in literature thatreports the dissolution of tungsten oxides to form tungstates [26]. EQCM experiments have also been performed in acidic medium (pH 2.5) containing iodate and the results resembled those reported in curves A and B in Fig. 6, suggesting that the film maintains its chemical integrity at these experimental conditions.

3.4. FIA amperometric determination of iodate

Based on results shown in Fig. 5, FIA experiments were carried out with glassy carbon electrodes modified with only 17 potential cycles. In order to find out the best compromise between sensitivity and minimization of the dissolved oxygen response, the operation potential was fixed at −0.2 V. At this experimental condition there was no need for deoxygenation of the supporting electrolyte, as demanded in a previous work where MoO_3 films were used as amperometric sensor for iodate determinations at −0.6 V [5]. As already mentioned, the pH of the supporting electrolyte (50 mmol L^{-1} Na_2SO_4 solution) should be maintained at a suitable range to avoid film loss due to continuous chemical dissolution. To this end, the pH of the carrier solution was fixed at 2.5. The repeatability of the procedure was established by a series of 41 injections of 1 mmol L^{-1} iodate solution and the standard deviation was found to be 0.8%, confirming the stability of the amperometric sensor at the chosen pH. Fig. 7 shows typical FIA recordings for injections of iodate solutions at the 20–100 µmol L^{-1} concentration range. Peak current values were found to be directly proportional to iodate concentration as attested by the straight line obtained ($I_{(\mu A)} = 0.035 + 0.071\ C_{(\mu mol\,L^{-1})}$, $r^2 = 0.9990$). The dynamic linear range was extended in the 5–5000 µmol L^{-1} iodate concentration range, the limit of detection was determined as 1.2 µmol L^{-1} (S/N = 3) and the analytical frequency was calculated as 123 injections h^{-1}.

Interference studies were focused on other oxidant anions able to deliver oxygen atoms to reduced tungsten oxide species. Nitrate and nitrite have no effect on the determination of iodate. On the other hand, upon adding bromate and chlorate at similar concentrations of iodate the peak current increased 13 and 2%, respectively (Fig. 8). This is a clear indication of the effect of the polarisability of the central atom on the ability of the species to transfer oxygen atoms.

3.5. Determination of iodate in commercial salt samples

The proposed method was successfully applied to determine the iodate concentration in salt samples. To minimise capacitive effects caused by the high salt concentration in the samples, NaCl was also added to the carrier electrolyte. At the appropriate experimental conditions established, the amount of iodate contained in four commercial salt samples was determined using the standard addition method. Table 1 shows the results obtained,

Table 1
Iodate content in salt samples determined by the proposed FIA amperometric procedure and by the conventional method (iodometry)[21]

Samples	Iodometric (mg iodine/kg salt)	Amperometric (mg iodine/kg salt)	Relative error (%)
1	68 ± 2	69 ± 1	+1.5
2	54 ± 2	53 ± 1	−1.9
3	47 ± 2	45 ± 1	−4.3
4	51 ± 1	52 ± 1	+2.0

Values are reported as percentage of iodine in the sample (mg iodine/kg sample).

Table 2
Limit of detection values for various methods reported in literature for iodate determination

Technique	Detection limit (S/N = 3) (μg iodate L^{-1})
Ion chromatography [27]	500
Ion chromatography [28]	86
IC–ICP-MS [29]	0.045
Spectrophotometry [30]	8
Spectrophotometry [31]	50
Cappilary electrophoresis [32]	5
Cappilary electrophoresis [33]	10
Amperometry [9]	1050
Amperometry[a]	210

[a] This work.

as well as the ones found by using the recommended method from literature [21]. The good agreement between results confirms the suitability of the method to measure the iodate content in this kind of sample, with a satisfactory limit of detection, good repeatability and high throughput. Also, data demonstrate that all samples contain iodate at a concentration level within the limits established by the Brazilian legislation (40–100 mg iodine/kg salt) [17].

Table 2 shows a list of various recent methods reported in literature for determining iodate. It is clearly seen that the limit of detection of the proposed method is not as good as the other ones. However, very expensive instrumentation is required in some cases. Also, most of these methods are not suitable for routine analysis and some of them are based on indirect reactions where species with some appropriate chemical characteristic for monitoring have to be produced. Therefore, strategies involving the use of amperometry are welcome for measuring the iodate content in table salt samples as the proposed procedure attends the demands of the legislation, is simple, cost-effectiveness and possesses a high analytical frequency. Nevertheless, it should be pointed out that the limit of detection could be significantly reduced by performing the amperometric measurements at more negative potential values, where the sensitivity is much higher. This would demand a more sophisticated manifold to minimize the influence of dissolved oxygen, as reported in a previous study [5].

4. Conclusions

The cathodic reduction of iodate is facilitated at electrodes surfaces covered by a layer of tungsten oxide. The linearity of the I_L versus $\omega^{1/2}$ plot is maintained over a relatively large iodate concentration range, assuring the use of this modified electrode as an amperometric sensor. At optimised experimental conditions the proposed FIA method was found to work properly in the determination of the iodate content in commercial salt samples. Analytical figures of merit are better to those reported in a previous work, where glassy carbon electrodes modified with molybdenum oxides were used as amperometric sensors for iodate [5] (see Table 2). Furthermore, by using tungsten oxides signals can be measured at a potential region where dissolved oxygen does not interfere, minimizing additional steps involving the need for deoxygenation of both carrier electrolyte and samples.

Acknowledgements

The authors would like to thank CNPq (Conselho Nacional de Pesquisa e Desenvolvimento Tecnológico) and FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) for the financial support. We also acknowledge Dr. Susana I.C. Torresi and Dr. Luis Kosminsky for the helpful suggestions.

References

[1] R.C. Murray, in: A.J. Bard (Ed.), Electroanalytical Chemistry: A Series of Advances, vol. 13, first ed., Marcel Dekker Inc., New York, 1984, p. 191.
[2] A. Guerfi, L.H. Dao, J. Electrochem. Soc. 136 (1989) 2435.
[3] P. Delichere, P. Falaras, A. Hugot-Le Goff, Thin Solid Films 161 (1988) 47.
[4] P.J. Kulesza, L.R. Faulkner, J. Am. Chem. Soc. 110 (1988) 4905.
[5] L. Kosminsky, M. Bertotti, Electroanalysis 11 (1999) 623.
[6] S.I.C. de Torresi, A. Gorenstein, R.M. Torresi, M.V. Vásquez, J. Electroanal. Chem. 318 (1991) 131.
[7] B. Reichman, A.J. Bard, J. Electrochem. Soc. 126 (1979) 2133.
[8] K.D. Lee, Thin Solid Films 302 (1997) 84.
[9] M. Regragui, M. Addou, A. Outzourhit, J.C. Bernéde, E. El Idrissi, E. Benseddik, A. Kachouane, Thin Solids Films 358 (2000) 40.
[10] P.J. Kulesza, L.R. Faulkner, Colloids Surf. 41 (1989) 123.
[11] P.J. Kulesza, L.R. Faulkner, J. Electroanal. Chem. 259 (1989) 81.
[12] P.J. Kulesza, W. Lu, L.R. Faulkner, J. Electroanal. Chem. 336 (1992) 35.
[13] C. Bock, B. MacDougall, Electrochim. Acta 47 (2002) 3361.
[14] C. Bock, A. Smith, B. MacDougall, Electrochim. Acta 48 (2002) 57.
[15] Z. Chen, P.W. Alexander, Anal. Chim. Acta 332 (1996) 187.
[16] I.G. Casella, M. Contursi, Electrochim. Acta 50 (2005) 4146.
[17] National Agency of Sanitary Surveillance (ANVISA). JT Edict No 218, of 24 March 1999.
[18] J.B. Stanbury, A.E. Ermans, P. Bourdoux, C. Todd, E. Oken, R. Tonglet, G. Vidor, L.E. Braverman, G. Medeiros-Neto, Thyroid 8 (1998) 83.
[19] G. Sauerbrey, Z. Phys. 178 (1964) 457.
[20] C. Gabrielli, M. Keddam, R.M. Torresi, J. Electrochem. Soc. 138 (1991) 2657.
[21] J. Basset, R.C. Denney, G.H. Jeffery, J. Mendham, Vogel—Textbook of Quantitative Chemical Analysis, 5th Edition, Longman Scientific & Technical, Graint Britain, 1989, p. 384.
[22] D. Ye, D. Bélanger, J. Phys. Chem. 100 (1996) 15848.
[23] L. Kosminsky, R.C. Matos, M.H. Tabacniks, M. Bertotti, Electroanalysis 15 (2003) 733.
[24] A.C. Pereira, T.L. Ferreira, L. Kosminsky, R.C. Matos, M. Bertotti, P.K. Kiyohara, M.H. Tabacniks, M.C.A. Fantini, Chem. Mat. 16 (2004) 2662.
[25] L. Kosminsky, M. Bertotti, J. Electroanal. Chem. 471 (1999) 37.
[26] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, third ed., Wiley, England, 1972, p. 947.
[27] S.D. Kumar, B. Maiti, P.K. Mathur, Talanta 53 (2001) 701.
[28] Y. Kitamaki, T. Takeuchi, Anal. Sci. 20 (2004) 1399.
[29] T. Eickhorst, A. Seubert, J. Chromatogr. A 1050 (2004) 103.
[30] Z. Xie, J. Zhao, Talanta 63 (2004) 339.
[31] A.A. Ensafi, M.A. Chamjangali, Spectroc. Acta A 59 (2003) 2897.
[32] K. Yokota, K. Fukushi, S. Takeda, S. Wakida, J. Chromatogr. A 1035 (2004) 145.
[33] Z. Huang, K. Ito, A.R. Timerbaev, Anal. Bioanal. Chem. 378 (2004) 1836.