

Determination of Ti(IV) at low levels by voltammetry

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Abstract

Accurate and rapid determination of Ti(IV) at low or trace levels in HClO₄, HClO₄–NaClO₃, H₂SO₄, H₂C₂O₄, H₂C₂O₄–NaClO₃ and H₃PO₄ media can be done by voltammetry at the mercury drop electrode. New reliable procedures implementing square wave and differential pulse voltammetries are described. Kinetic peak currents resulting from slow complex formation are proportional to the analytical concentration of Ti(IV). Calibration lines, figures of merit and formulae for the calculation of concentrations are given. Limits of quantification are determined with an accuracy of about ±10% using standard solutions. In acid oxalate–chlorate medium, where a catalytic reduction of Ti(IV) occurs, the precision and sensitivity of differential pulse voltammetry compare very favourably with other modern microanalytical methods. The limit of quantification is 10^{−7} M. In the other media, this limit lies between 10^{−5} and 10^{−6} M.

An extremely simple mathematical formula for the contribution of the sphericity of the mercury drop on the peak current in square wave voltammetry in the case of slow charge-transfer reactions is incidentally given.

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1. Introduction

Current existing methods for the determination of Ti(IV): UV–visible spectrophotometry of the yellow–orange peroxide complex in acid solution with hydrogen peroxide, flame atomic absorption spectrometry and classical polarography have a typical sensitivity of the order of 2 mg L^{−1} (4 × 10^{−5} M) [1–4].

Ti(IV) species are reducible in acid media to the Ti(III) state. Well-formed voltammograms and accurate current readings are obtained only with the mercury drop electrode [2–4]. The investigation of the electrochemical kinetics of the Ti(IV)/Ti(III) couple in sulfuric acid and in acid oxalate media [5–8], enabled us to define and validate the experimental conditions for determining Ti(IV) at minor or trace levels by DC polarography, square wave voltammetry

(SWV) and differential pulse voltammetry (DPV) at the static mercury drop electrode (SMDE).

At low concentrations Ti(IV) species are monomers that would appear to have the Ti=O group [9]. In dilute HClO₄ the ionic forms Ti(OH)₃⁺ and Ti(OH)₂²⁺ should predominate rather than the titanyl ion TiO²⁺ [10]. Homogeneous slow reactions between titanyl complexes formed with HSO₄[−] [6] or C₂O₄^{2−} [5–7] ions affect the observed current. These complexes become more easily reducible with the increase in the concentration of ligand. When two species predominate, the electrochemical process is reduced to a simple CE mechanism.

Concentrated H₃PO₄ and non-complexing 0.05–0.2 M HClO₄ can be also used as supporting electrolyte for the determination of Ti(IV). In all media, the diffusion current is reached before the reduction of H⁺ begins.

Solutions of Ti(IV) in 0.1 M HClO₄ or H₂SO₄ are stable for several hours. When the acid concentration is higher than 0.5 M, no changes are observed in limiting or peak currents during several days. In oxalate medium of pH lower than 2, solutions of Ti(IV) are particularly stable.

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In H_3PO_4 lower than 1 M hydrolytic precipitation of Ti(IV) occurs. For H_3PO_4 concentrations greater than 2 M, solutions are stable for at least a day. Titanium (III) species are not suitable for analytical determinations because they are easily air oxidized.

The limits of quantification of Ti(IV), which will be given, relate to an accuracy of the order of $\pm 10\%$. In acid oxalate–chlorate media where a catalytic reduction of Ti(IV) occurs, the detection limit in DPV, which under optimal experimental conditions is in the neighbourhood of $1 \mu\text{g L}^{-1}$, compares with that in electrothermal atomic absorption spectrometry or in inductively coupled plasma-atomic emission spectrometry [1].

2. Experimental

Measurements were carried out at $25 \pm 0.2^\circ\text{C}$ with an EG&G Princeton Applied Research (PAR) model 263A potentiostat and with an EG&G PAR model 303A SMDE. The drop radius was 0.4 mm. A platinum wire was used as the auxiliary electrode and an outside KCl saturated calomel electrode (SCE) as the reference electrode. An inset tube, filled with the same solution as in the cell and closed with a vicor plug, was used in conjunction with a salt bridge of agar gel to connect the calomel electrode. For reasons of solubility, the agar gel was prepared for experiments in HClO_4 and H_3PO_4 with saturated NaCl, in H_2SO_4 with saturated KCl and in $\text{H}_2\text{C}_2\text{O}_4$ with 4 M NH_4NO_3 .

Removal of dissolved air in solution was performed with argon containing less than 5 ppm of O_2 .

Stock solutions of Ti(IV) in H_2SO_4 were prepared with TiO_2 99.9% from Merck. Dissolution of the oxide was obtained in 14 M H_2SO_4 by brief boiling at about 200°C . Titanium (IV) oxysulfate–sulfuric acid complex hydrate 99.99% from Sigma–Aldrich was also used. The later was dissolved in acids by being heated at about 60°C in a water bath. Some solutions were prepared with very soluble $\text{Ti}(\text{NO}_3)_4$ 99.9%+ from Sigma–Aldrich and $(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$ “pure” from Acros organics. Concentrations of Ti(IV) were determined by the direct comparison method using a Prolabo TiCl_4 A.A.S. standard. All other chemicals were of analytical grade purity.

It will be considered that both waveforms in SWV and in DPV result from the superimposition of a potential step of height $|\Delta E|$ and of duration Δt on the steps of height $|\Delta E_s|$ and of duration Δt_s of a potential staircase. The ratio $r = \Delta t/\Delta t_s$ is 0.5 in SWV and lower or equal to 0.5 in DPV. All experiments were performed with ΔE and ΔE_s of the same sign. It is pointed out that in the PAR software “pulse height” corresponds to $|\Delta E|/2$.

For Ti(IV) concentrations lower than 5×10^{-5} M, the signal-to-noise ratio in DPV performed with a pulse duration Δt of the order of 40 ms and a step duration Δt_s three times higher or more, is much better than in the corresponding SWV. Apparently, this peculiar behaviour is caused by a more efficient reduction of the capacitive contribution and of stray couplings.

3. Results and discussion

3.1. Perchloric acid medium

3.1.1. DC polarography

Apart from some introductory remarks for the reduction of Ti(IV) in HClO_4 given in one of our previous works [6] there are no other bibliographical data.

In HClO_4 higher than 0.5 M the limiting diffusion current of Ti(IV) in DC polarography is masked by the current of the proton discharge. In 0.1 M HClO_4 , the reduction of Ti(IV) at the SMDE produces a well-defined irreversible wave. The waves of equal height presented in Fig. 1 were obtained by dividing the current by the analytical concentration of Ti(IV), c^* , which was 8×10^{-5} M and 2×10^{-3} M. This figure shows that the limiting diffusion current is directly proportional to c^* and that the apparent cathodic charge transfer coefficient, α , is smaller for the highest concentration. The half-wave potential is -0.732 V vs. the SCE for $c^* = 8 \times 10^{-5}$ M and shifts to -0.756 V for $c^* = 2 \times 10^{-3}$ M. In 0.1 M HClO_4 , from the limiting diffusion current at the SMDE the mean diffusion coefficient of Ti(IV), $4.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, was calculated using the well-known equation:

$$I_d = -FADc^*[1/(\pi Dt)^{1/2} + 1/r_0] \quad (1)$$

The limit of the polarographic quantification of Ti(IV) in 0.1 M HClO_4 is slightly lower than 10^{-4} M. We notice that in 5×10^{-5} M solution of Ti(IV), the limiting diffusion current is no longer observed.

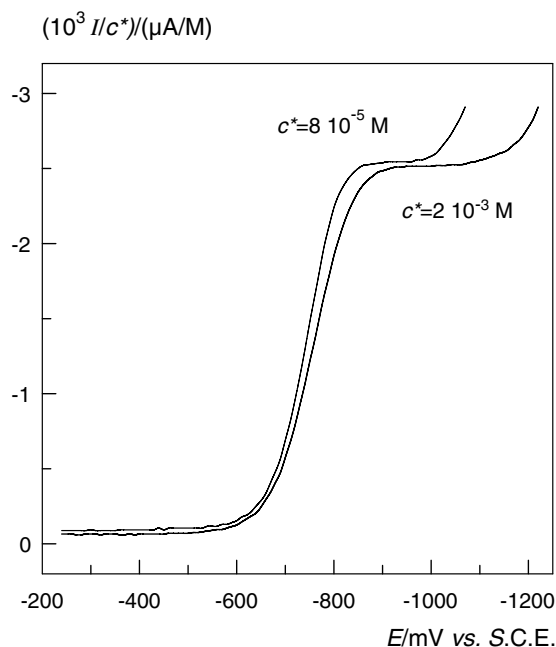


Fig. 1. The ratio of the polarographic current I in 0.1 M HClO_4 to the analytical molar concentration c^* of Ti(IV) is plotted as a function of the potential E . The values of c^* are indicated near the curves. Conditions: Drop time 1 s, radius of the SMDE $r_0 = 0.4$ mm, temperature $\theta = 25^\circ\text{C}$.

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