*Review*

# Review of the Catalytic Voltammetric Determination of Titanium Traces

**Andrzej Bobrowski* and Jerzy Zarębski**

*Department of Building Materials Technology, Faculty of Materials Science and Ceramics,*
*AGH-University of Science and Technology, Al. Mickiewicza 30, 30-059 Kraków, Poland*

** Corresponding author: E-mail: gcbobrow@cyf-kr.edu.pl*
*Tel.: +48 126172451; fax: +48 126172452*

*Received: 01-03-2012*

## Abstract

Catalytic and catalytic adsorptive stripping voltammetry are some of the most sensitive analytical methods. A review of various catalytic and catalytic adsorptive systems of titanium and their use in voltammetric analysis is presented. The mechanisms of catalytic reactions are discussed in detail. In addition to a survey of literature (91 references), catalytic polarographic, voltammetric and catalytic adsorptive stripping voltammetric determination of titanium traces at liquid mercury and metallic films electrodes are discussed briefly. Moreover, the application of the redox systems Ti(IV)/Ti(III) for the indirect determination of voltammetrically inactive oxidizers participating in catalytic reactions (e.g. chlorates) and voltammetrically inactive ligands (e.g. organic acids and thiocyanates) is also presented.

**Keywords:** Titanium, Polarography, Catalytic adsorptive stripping voltammetry, Mercury, Thin films metallic electrodes.

## 1. Introduction

Titanium is an important element in many industrial branches, such as paper and pulp production, and an additive to stainless steel and light alloys essential for biomedicine, e.g. in orthopaedic and dental implants. The exact biological role of titanium is unclear, but it was found that tissues surrounding titanium implants contain high levels of this metal, potentially causing irritation. Its inertness and ability to be attractively coloured makes it a popular metal for use in body piercing.

The occurrence of titanium in the environment and its role in the metabolic processes of plants, animals and human is discussed by Kabata-Pendias and Mukherjee.[1]

Polarographic or voltammetric determination of titanium is generally based on the reduction of Ti(IV) to Ti(III).[2] In non-complexing acidic media, such as hydrochloric, perchloric and sulphuric acids, Ti(IV) gives fairly developed irreversible polarograms or voltammograms, with the exception of phosphoric acids, in which well-developed reversible polarograms were obtained.[3–5] Well-defined and reversible polarograms of Ti(IV) were observed both in strongly and moderately acidic solutions containing complexing agents (L), such as: organic acids,[6–9] complexones such as: NTA, EDTA,[10,11] DCTA,[12,13] HEDTA,[14] PDTA,[15] or phosphates and pyrophosphates.[16,17]

## 2. Catalytic Polarography and Voltammetry of Titanium

Many redox systems, either as Ti(IV)/Ti(III) aqua ions or Ti(IV)·L/Ti(III)·L (L being the ligand present in the supporting electrolyte), involve catalytic reactions of the first kind with oxidizing agents, such as hydroxylamine, bromate, chlorate and vanadium (IV), which leads to a significant enhancement of the Ti(IV) reduction current. These phenomena have been taken advantage of in order to increase the sensitivity of the determination of titanium, and of the indirect quantification of voltammetrically inactive oxidizers or voltammetrically inactive ligands.

The catalytic reaction between a complex of Ti(III).oxalate and hydroxylamine was first studied by Blazek and Koryta.[18,19] Extensive studies of the above catalytic reaction[20–22] showed that the product of the reaction between Ti(III) and $NH_2OH$ is the radical $\cdot NH_2$, which later reacts with $H_2C_2O_4$. This conclusion was confirmed by Calusaru, who used $D_2O$ and $ND_2OD$,[23–24] and Farnia et al., who added maleic acid to the solution. When combined with the $\cdot NH_2$ radical, maleic acid forms asparginic acid.[25]

The cyclic catalytic reaction occurs according to the following scheme:[18]

$$\text{Ti(IV)·oxalate} + e \rightleftarrows \text{Ti(III)·oxalate} \tag{1}$$

$$\text{Ti(III)·oxalate} + NH_2OH \rightarrow \text{Ti(IV)·oxalate} + NH_2^{\cdot} + OH^- \tag{2}$$

$$(COOH)_2 + 2\,NH_2^{\cdot} \xrightarrow{k} 2\,CO_2 + 2\,NH_3 \tag{3}$$

The redox system Ti(IV)/Ti(III)·EDTA induces a catalytic reaction with $BrO_3^-$ ions, resulting in a significant increase of the polarographic response. This fact was utilized in the determination of Ti traces.[26–29] Yamamoto et al. applied the above system for the DPP determination of Ti in carbon steel and Xerox paper.[30] In the Britton-Robinson buffer (pH 4.5), the polarographic response was proportional to the Ti concentration within the range of $10^{-8}$–$10^{-7}$ M. The suggested scheme of the catalytic reaction may be expressed by the following equations:[30]

$$\text{Ti(IV)·EDTA} + e^- \rightleftarrows \text{Ti(III)·EDTA} \tag{4}$$

$$6\text{Ti(III) EDTA} + 6H^+ + BrO_3^- \rightarrow 6\text{Ti(IV) EDTA} + Br^- + 3H_2O \tag{5}$$

The kinetics of the electrochemical reduction of the complexes of Ti(IV) and EDTA, HEDTA and DCTA, as well as the catalytic systems induced by these complexes with $ClO_3^-$ and $BrO_3^-$ ions were investigated by Kaneko.[31] The results of these studies indicate slow catalytic oxidation of Ti(III) complexes by $ClO_3^-$ ions and fast oxidation by $BrO_3^-$ ions.

The catalytic reaction of the complex of Ti(IV) with 4-(2-Pyridylazo)resorcinol (PAR) and two oxidants – $H_2O_2$ and $BrO_3^-$ – present concurrently in the solution (Ti(IV)·PAR-$H_2O_2$-$BrO_3^-$) was utilized for the quantification of Ti in aluminium alloys and steel.[32] Botev et al. reported that the same redox system, Ti(IV)/Ti(III)·PAR also induces the catalytic reaction with V(IV) ions.[33] In the vast majority of works dealing with the application of catalytic systems for the voltammetric determination of Ti, the catalytic oxidation of Ti(III)-complexes by voltammetrically inactive $ClO_3^-$ ions is exploited the most frequently.[34]

Fast catalytic oxidation of Ti(III) ions by $ClO_3^-$ ions was observed in strongly acidic $HClO_4$ solutions.[35] The differential pulse polarography (DPP) catalytic peak of Ti(IV) in the solution containing $HClO_4$ and $NaClO_3$ was well-defined, but was overlapped by the background current from the discharge of hydrogen ions, especially at low concentrations of Ti(IV) ions.

The best developed catalytic polarograms and voltammograms, however, were observed in catalytic systems induced by the complexes of Ti(IV) with organic and inorganic ligands and $ClO_3^-$ ions as oxidizer.

In the first works on this subject, Koryta and Tenygl[36] and Koryta[37] found that the redox system Ti(IV)/ Ti(III)·oxalate induces a fast catalytic reaction with $ClO_3^-$ ions.

Since then, the catalytic system Ti(IV)/Ti(III)·oxalate-chlorate has been the subject of extensive studies by means of polarographic or voltammetric techniques, such as alternating current polarography (ACP),[38] DPP,[39] direct current polarography (DCP)[31] and square wave voltammetry (SWV).[35,40,41] The polarographic and voltammetric features of the catalytic system Ti(IV)/Ti(III)·oxalate-chlorate were compared with those of other catalytic systems induced by some selected ions.[42,43]

The reduction mechanism of Ti(IV)·oxalate was discussed in works[41,44] and the mechanism of catalytic reaction in the presence of chlorate ions is reported in detail in.[35,45]

Koryta and Tenygl reported that in the amperometric titration of $ClO_3^-$ with Ti(III) in an acidic solution of oxalic acid, one mole of $KClO_3$ consumes 5.5 moles of Ti(III).[36] Based on the above data the following scheme of catalytic reactions in the system comprising Ti(IV)/ Ti(III).oxalate + $ClO_3^-$ ions may be suggested. After electrochemical reduction of Ti(IV) at the surface of the working electrode,

$$\text{Ti(IV)·oxalate} + e \rightleftarrows \text{Ti(III)·oxalate} \tag{6}$$

the oxidation of Ti(III) occurs in two steps:

$$\text{I. } 6\,\text{Ti(III)·oxalate} + ClO_3^- + 6H^+ \xrightarrow{k} 6\,\text{Ti(IV)·oxalate} + Cl^- + 3\,H_2O \tag{7}$$

$$\text{II. } \text{Ti(III)·oxalate} + ClO_3^- + 2H^+ \xrightarrow{k} \text{Ti(IV)·oxalate} + ClO_2^{\cdot} + H_2O \tag{8}$$

It is most likely that the $ClO_2^{\cdot}$ radical reacts with the excess of oxalate. The occurrence of the radical $ClO_2^{\cdot}$ in the catalytic reaction induced by Ti(IV) L/Ti(III)·L was also confirmed by other authors.[46,47] The formation of radicals in catalytic reactions is often reported, e.g. in the system Fe(II)/Fe(III) + $H_2O_2$.[48]

In their extensive SWV studies,[35] Krulic et al. found that the overall process is more complicated and the catalytic reduction of Ti(IV) in oxalate–chlorate media is affected by the rate of the chemical reaction between the mono $Ti(OH)_2C_2O_4$ and the dioxalato $Ti(OH)_2(C_2O_4)_2^{-2}$ electroactive complexes of Ti(IV) which exist in solutions in the presence of small Ti(IV) concentrations. Both Ti(IV) complexes are reduced to the dioxalato complex of Ti(III), and the step responsible for the catalytic effect is the homogeneous oxidation of Ti(III)·dioxalate to Ti(IV)·dioxalate.

Fast catalytic reactions between chlorate and the complexes of Ti(IV) with other ligands, such as $H_2C_2O_4$ + $H_3PO_4$,[49] mandelic acid,[50–52] trihydroxyglutaric acid,[46] tartaric, malonic, citric and trihydroxyglutaric acids[47,53] and thiocyanate[54] have also been noted.

The above-mentioned catalytic systems of titanium and chlorate have frequently been applied in the analysis of titanium traces.

Due to the high value of the catalytic rate constant of the reoxidation of Ti(III) to Ti(IV), and in the presence of high concentrations of chlorate, catalytic currents of titanium are limited by the diffusion of Ti(IV) complexes to the electrode surface, and they are therefore proportional to titanium concentrations. Thus, well-defined voltammograms of catalytic systems of titanium were applied for the determination of titanium traces in steel,[53–55] pure phosphorus,[49] purified glass sands, quartz and concentrated fluoric acid,[56] polyolefin polymers,[28] solar-grade silicon,[57] water[5–52,58] and copper alloys.[59]

In the above mentioned examples of the application of the catalytic reactions induced by Ti(IV) complexes, the determination of titanium traces was performed in acidic supporting electrolytes, in which catalytic enhancement is relatively high, providing sensitive determination. The decrease of the acidity of the solution causes the decay of the catalytic amplification, as observed in the case of Ti(IV).oxalate – chlorate catalytic system. Less acidic supporting electrolytes can be, however, applied for simultaneous quantification of other ions, e.g. titanium and iron (Fig. 1). In Figure 1, the catalytic peak of Ti(IV) is well-separated from the diffusion peak of Fe(III) in a moderately acidic oxalate solution, and consequently both ions can be determined[35,56]. In strongly acidic solutions, the peak potential of Fe(III) ions shifts to more positive potentials and cannot be distinguished from the current of anodic dissolution of mercury.

In catalytic systems induced by the Ti(IV)/Ti(III) couple in solutions of strong non-complexing acids or in similar solutions containing ligands complexing titanium ions, faradic current is determined by the concentration of Ti(IV) ions and the concentration of oxidizers, e.g. $ClO_3^-$. The determination of low concentrations of titanium is performed in solutions with high concentrations of oxidizers; in these solutions catalytic reactions do not change their concentration in the vicinity of the electrode surface noticeably. In these conditions the only factor that influences the value of faradic current is the concentration of Ti(IV) ions, which is limited by the diffusion of these ions from the bulk of the solutions to the electrode surface. The analytical response, i.e. faradic current, is then proportional to the concentration of Ti(IV) ions, which enables their determination.

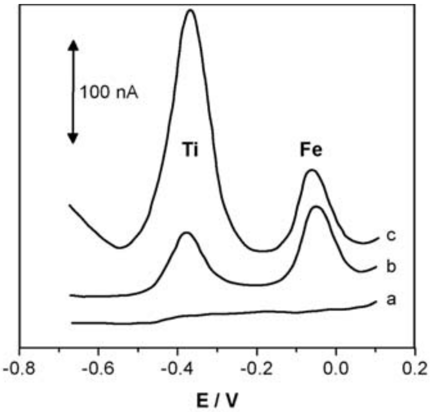


**Figure 1.** Differential pulse polarograms of Ti(IV) and Fe(III) in the solution of 0.05 M oxalate (pH 2.5): (a) supporting electrolyte, (b) 5 × $10^{-5}$ M Ti(IV) and Fe(III), (c) as (b) plus 0.05 M $KClO_3$ (authors' unpublished results)

When, however, the concentration of Ti(IV) is high compared to the concentration of $ClO_3^-$, the catalytic currents are limited by the diffusion of $ClO_3^-$ and are, therefore, proportional to the concentration of chlorate, which was first reported by Koryta and Tenygl.[36] The elaborated procedure of the indirect voltammetric determination of chlorate[36] was exploited for the quantification of chlorates in soil, air and natural waters.[50]

Another kind of catalysis induced by Ti(IV) ions, which found application in electroanalysis, is the reduction of Ti(IV) complexes in solutions containing a large excess of Ti(IV) over the concentration of the ligand. In these conditions, the formation of complexes of Ti(IV) ions with many other ligands resulted in the appearance of reversible polarographic or voltammetric curves at potentials more positive than that of non-complexed Ti(IV) ions. The reduction of Ti(IV), bound in the form of complexes, is not only reversible but also faster than the corresponding reduction of non-complexed Ti(IV) ions, as reported by Tribalat and Delafosse for the complex Ti(IV)-SCN.[60–61] This observation was confirmed by Turyan et al.[62,63]

It was later found that the redox system Ti(IV)/Ti(III)·SCN induces a catalytic reaction with chlorate and the scheme of this reaction is discussed in details by Turyan and Saksin.[54]

The catalytic polarographic waves of Ti(IV) with different ligands were applied for the determination of such compounds as citric acid, sulphosalicylic acid, pyrogallol, catechol and thiocyanate. The addition of chlorate resulted in the increase of the sensitivity and the precision of their determination.[64–66] This kind of catalysis, called ligand catalysis, was also observed in numerous cases for ions of other elements.[67,68]

An example of the volumetric catalytic reaction induced by Ti(IV) ions with polarographic detection is described by Li et al..[69] The Ti(IV) ions catalyze the oxidation of Brilliant Green by $JO_3^-$ ions and the product of this volumetric catalytic reaction was detected polarographically, making the indirect determination of titanium possible.

## 3. Catalytic Adsorptive Stripping Voltammetry of Titanium

The sensitivity of titanium determination was increased by means of adsorptive stripping voltammetric (AdSV) methods, which are based on the formation and accumulation of complexes of Ti(IV) with different ligands on the surface of working electrodes,[70–74] e.g. the hanging mercury drop electrode (HMDE) or the mercury film electrode (MFE).

Furthermore, some of these complexes may induce catalytic reactions which offer an additional increase in the sensitivity.

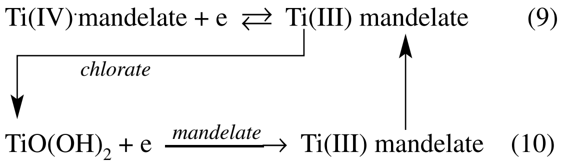
The final catalytic adsorptive voltammetric response is therefore the product of the double effect of interfacial accumulation and catalytic reaction:

$$I_F = [\text{adsorptive enrichment}] \times [\text{catalytic enhancement}]$$

Hence, the coupling of adsorptive accumulation and catalytic effects leads to extremely high values of the analytical signal, i.e. faradic current and, consequently, to very high sensitivity of the determination of a metal inducing catalytic reaction. Catalytic-adsorptive systems such as Ti(IV)-ligand-chlorate, in which such ligands as: mandelic acid,[71,75,76] pyrocatechol violet,[77] methylthymol blue, xylenol orange and calcein,[72] triphenylmethane dyes,[71] kalces, chromotropic acid and azo-compounds,[73] all of which form complexes with Ti(IV) ions, were used in the most sensitive methods of Ti(IV) determination and found application in its trace analysis.

Two other oxidants – bromate and cupferron – were also employed for catalytic-adsorptive stripping voltammetric (CAdSV) determination of Ti(IV) in the systems: Ti(IV)·mandelic acid – bromate[78] and Ti(IV)·cupferon.[79,80] The most important adsorptive catalytic voltammetric systems of Ti are collected in Table 1.

Yokoi and van den Berg were the first to combine the adsorptive properties of the Ti(IV).mandelic acid complex with the catalytic enhancement of the voltammetric response, which resulted in a significant increase in the sensitivity of Ti determination.[75,76] They suggested the following scheme of the catalytic reactions:



$$\text{Ti(IV)·mandelate} + e \rightleftarrows \text{Ti(III) mandelate} \qquad (9)$$

$$\text{TiO(OH)}_2 + e \xrightarrow{\text{mandelate}} \text{Ti(III) mandelate} \qquad (10)$$

It was hypothesized by the cited authors that Ti(IV)·mandelate is not regenerated because of the slow rate of complexation and the participation of $TiO(OH)_2$ in the catalytic cycle. The introduction of the above-mentioned catalytic system – Ti(IV)·mandelic acid-chlorate[76] – to analytical practice made it possible to significantly decrease the detection limit of the voltammetric determination of titanium traces. It was observed that the sensitivity of the CAdSV determination of Ti was ca. 20 times higher after the addition of $5 \times 10^{-2}$ M $ClO_3^-$, which allowed the quantification of Ti(IV) traces in sea water in the presence of $2 \times 10^{-7}$ M Cu(II), As(V), Ni(II), V(V), Fe(III), Al(III), Sb(V) and $1 \times 10^{-7}$ M Cd(II), Co(II), Cr(III), Ga(IV), Mn(II), Pb(II) and W(VI). The above-mentioned method was also employed for the Ti determination in pure chemical reagents,[81] animal tissues,[82] raw materials and silica glass samples.[71]

Moreover, Yokoi and van den Berg also elaborated the CAdSV procedure for the simultaneous determination of Ti(IV) and Mo(V) in the same supporting electrolyte containing mandelic acid and chlorate.[75] The same approach was then utilized for the determination of Ti(IV) and Mo(V) in brine, either in static conditions[83] or in a flow injection system.[84] It was shown in the paper[71] that in the solution of mandelic acid and chlorate, titanium can be simultaneously determined with molybdenum in silica glass samples (Fig. 2).

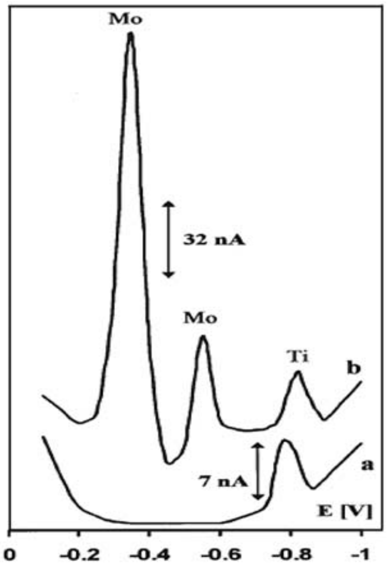


**Figure 2.** DP AdSV curves of Ti and Mo in a solution containing mandelic acid without (a) and with (b) an addition of $4 \times 10^{-3}$ M chlorate ions. Accumulation time 90 s, accumulation potential –0.15 V (reprinted with kind permission from Springer Science+Business Media: Fresenius Journal of Analytical Chemistry, *Analytical control of silica glass production. Voltammetric determination of titanium and iron in raw materials and silica glass samples,* 367(2000):764, M. Gawryś, J. Golimowski, *Fig. 2 in the above article*).

An interesting catalytic adsorptive system of Ti with cupferron was elucidated by Ye and Yang.[80] The most interesting aspect of this system is the double role played by cupferron, which acts both as a ligand and an oxidant.

The determination of titanium ultratraces by means of CAdSV in the catalytic adsorptive system: Ti(IV)·pyrocatechol violet-chlorate was described by Vukomanovic and Van Loon.[77] The procedure was applied in the analysis of sea water.

Gawryś and Golimowski found that the catalytic adsorptive stripping determination of titanium(IV) can also be carried out in the solutions containing such complexing ligands as methylthymol blue, xylenol orange and calcein, in the presence of chlorate.[72,73] The addition of chlorate into the solution increased the sensitivity of the determination by more than one order of magnitude. Another advantage of the above procedures over the other voltammetric procedures was high selectivity. The methods were applied for the determination of titanium in crystalline quartz and silica glass samples.[72]

The complexation of titanium by the salicylfluorone ligand (SAF) has also enabled the determination of its traces in a formic buffer solution containing chlorate by means of linear sweep catalytic adsorptive stripping voltammetry.[85] The electrode reaction of Ti(IV)-SAF adsorbed on the surface of the electrode was found to be irreversible. The dependence of the Ti peak current on the concentration of Ti was found to be linear in the range from $1.2\ 10^{-9}$ to $1.6 \times 10^{-7}$ M. The method has been applied to a sample of human hair.

The selected examples of the application of CAdSV for titanium determination are presented in Table 1.

## 4. Catalytic Voltammetry of Titanium at Films or Solid Electrodes

In the past, catalytic systems were widely used in many voltammetric procedures which relied on the use of liquid mercury electrodes. In many cases, the voltammetric methods employing the mercury electrodes made it possible to determine extremely low concentrations of some metals at the $10^{-11}$ – $10^{-10}$ M level, thanks to the catalytic amplification of the voltammetric response. Recently, a new type of environmentally friendly metal film electrodes, less toxic and easily employed in on-site analysis or in automatic flow analyzers, were introduced to the electroanalytical practice, namely, the bismuth film electrodes (BiFE) generated in-situ or ex-situ on different carbon supports. These electrodes proved to be useful in the ca-

**Table 1.** Examples of catalytic systems applied in adsorptive stripping voltammetry of titanium.

| **Ligand** | **Oxidizing agent** | **pH** | **Working electrode/ Voltammetric mode** | **$E_p$(V) application** | **LOD,** | **Refs.** |
|---|---|---|---|---|---|---|
| mandelic acid | $ClO_3^-$ | 3.3 | HMDE/LSV, DPV | –0.90 | $7 \times 10^{-12}$ M (60 s),<br>$1 \times 10^{-12}$ M (600 s)<br>see water | 75,76 |
| mandelic acid | $ClO_3^-$ | 3.3 | HMDE/DPV | –0.90 | $5 \times 10^{-9}$ M (240 s)<br>high purity chemical reagents | 81 |
| mandelic acid | $ClO_3^-$ | 3.5 | μ-HgFE/AuSWV | –0.90 | $2 \times 10^{-9}$ M (20 s)<br>mice tissue | 82 |
| mandelic acid | $ClO_3^-$ | 3.3 | HMDE/HMDE in FIS* DPV | –0.90 | $3 \times 10^{-8}$ M (40 s)<br>brine | 83,84 |
| mandelic acid | $BrO_3^-$ | 3.3–3.4 | HMDE/DPV | –0.80 | $6 \times 10^{-9}$ M (30 s)<br>crystalline quartz,<br>silica glass | 71 |
| pyrocatechol | $ClO_3^-$ | 4.9 | HMDE/LSV | | $1 \times 10^{-11}$ M (30 s)<br>sea water | 77 |
| cupferron | cupferron | | HMDE/LSV | | $1.25 \times 10^{-9}$ M (3 min) | 80 |
| methylthymol blue | $ClO_3^-$ | 2.6 | HMDE/DPV | –0.55 | $1.1 \times 10^{-9}$ M (30 s)<br>crystalline quartz,<br>silica glass | 72 |
| xylenol orange | $ClO_3^-$ | 2.6 | HMDE/DPV | –0.55 | $4.1 \times 10^{-10}$ M (30 s)<br>crystalline quartz,<br>silica glass | 72 |
| calcein | $ClO_3^-$ | 2.6 | HMDE/DPV | –0.70 | $1.2 \times 10^{-10}$ M (60 s)<br>crystalline quartz,<br>silica glass | 72 |
| salicylfluorone | $ClO_3^-$ | 3.5 | HMDE/LSV | | $6.0 \times 10^{-10}$ M<br>human hair | 85 |

*FIS – flow injection system

talytic voltammetric determination of the selected elements,[86] including titanium.

To minimize the amount of toxic mercury, the HMDE was also replaced by a mercury film electrode deposited on the gold microdisc support[82]. The CAdSV signal of Ti in the presence of mandelic acid and chlorate increased linearly up to $2 \times 10^{-6}$ M. The procedure was used for the determination of Ti in mice tissue.

The utilization of the interdigitated microelectrode array[87] in the solution containing oxalate and $NH_2OH$ made it possible to determine Ti(IV) by means of catalytic voltammetry. The method was applied for the voltammetric determination of Ti in plastic bags.

An attempt was also made to replace the hazardous mercury with working electrodes built of environmentally friendly materials. For this purpose, an ex-situ pre-plated BiFE was adopted by the authors of this paper for the catalytic voltammetric determination of titanium in the system with Ti(IV)/Ti(III), oxalate and chlorate ions.[88] It has been shown that a BiFE suitable for the above purpose was obtained when the supporting GC electrode was plated with bismuth in a solution containing 0.02 M $Bi(NO_3)_3$, 0.5 M LiBr and 1 M HCl,[89] using a single cycle of linearly swept potential starting from –0.25 V to –0.8 V and back to –0.25 V at a scan rate of 25 mV/s. Since the catalytic effect was equal to 4, the sensitivity of the method was high (Fig. 3) and the titanium signal was linear in the range from $2 \times 10^{-8}$ to $1 \times 10^{-6}$ M Ti(IV).

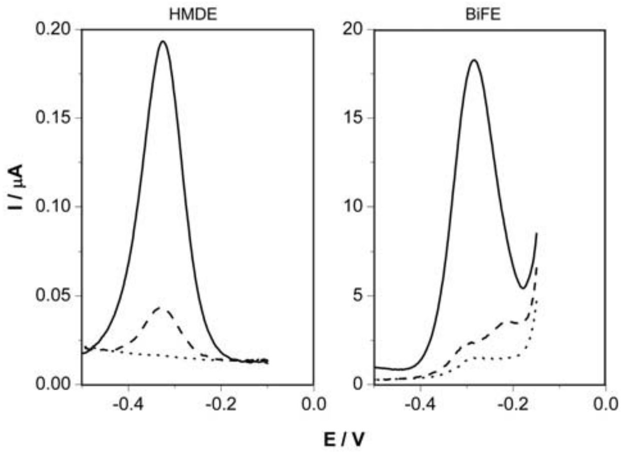


**Figure 3.** Differential pulse voltammograms of a solution containing: (dotted line) $1 \times 10^{-7}$M Ti(IV) and 0.02 M $H_2SO_4$; (dashed line) $1 \times 10^{-7}$M Ti(IV), 0.02 M $H_2SO_4$ and 0.02 M oxalic acid, (solid line) $1 \times 10^{-7}$M Ti(IV), 0.02 M $H_2SO_4$, 0.02 M oxalic acid and 0.05 M $KClO_3$. *Left: HMDE, right: BiFE* (authors' unpublished results)

Another method entails the adsorptive accumulation of the mandelic complex of titanium (IV), coupled with the catalytic reoxidation of Ti(III). mandelic complex in the presence of $KClO_3$, performed at the surface of the BiFE[90] prepared ex-situ in an acidic bismuth bromide solution.[89] The principles of this method are illustrated in Figure 4.

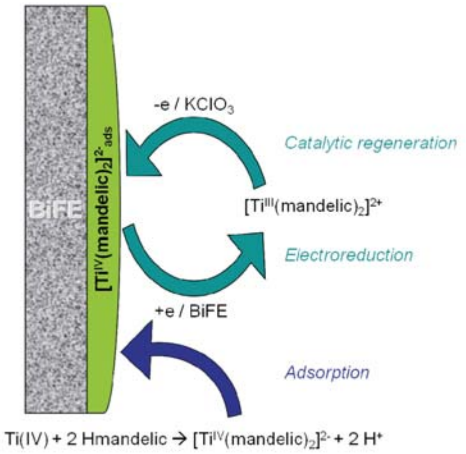


**Figure 4.** The illustration of the electrochemical processes occurring at the surface of the BiFE for the catalytic adsorptive voltammetric system Ti(IV)/Ti(III)-mandelic acid and $KClO_3$.

For the composition of the supporting electrolyte optimal for titanium determination, i.e. 0.1 M NaCl (pH 3), 0.004 M mandelic acid and 0.045 M $KClO_3$, the catalytic adsorptive peak of titanium recorded after 60 s of accumulation at –0.25 V in DPV mode was observed at –0.75 V vs. Ag/AgCl/3M KCl electrode. The linear range covered almost two orders of magnitude from $1 \times 10^{-9}$ to $5 \times 10^{-8}$ M Ti.[90]

The performance of another type of bismuth film electrodes (BiFEs) plated ex situ from 0.17 M Bi(III) in 1.0 M $HClO_4$ for catalytic adsorptive stripping voltammetry of Ti(IV) had also been demonstrated.[91] The BiFEs were prepared by plating bismuth on a glassy carbon support at deposition potentials of –0.3 V and –1.0 V, for two charges: 10 mC or 25 mC. The morphology of the deposits was evaluated and its influence on the Ti(IV) voltammetric responses in the presence of 0.004 M mandelic acid and 0.045 M $KClO_3$ was discussed.[91]

## 5. Summary

Due to the low solubility of titanium compounds, mostly $TiO_2$, their influence on the metabolic processes in living organisms, including plants and animals, seems to not be significant. Titanium dioxide is often used in medicaments, e.g. pills, as the inert feeler which is not assimilated in the alimentary canal. There are, however, cases in which the presence of titanium may considerably influence the properties of the product, such as glasses, making them non-transparent for UV-irradiation. In these cases the determination of titanium, even in trace amounts, is necessary. Among the analytical methods that enable the determination of titanium, voltammetry offers many advantages such as high sensitivity, wide range of applicability, accuracy, simplicity of analytical procedures, low cost of instrumentation and reagents. Due to the above-mentioned advantages, voltammetry is very often applied in the determination of many compounds and elements, including titanium.

The fundamental reaction in voltammetric methods of titanium detection is the reduction of Ti(IV) ions, present in the solution as hydrated ions or complexed with various ligands, to Ti(III) at the surface of the working electrode. The reduction of Ti(IV) ions with the participation of one electron results in an analytical signal (i.e. faradic current) that is rather low, offering moderate sensitivity of the quantification of titanium.

In the solutions without ligands the reduction of Ti(IV) ions is irreversible, resulting in fairly developed voltammetric signals of titanium observed at highly negative potentials close to that of hydrogen ion deposition. Moreover, the presence of other ions may interfere in the determination titanium.

Reversible reduction of Ti(IV) complexes causes well developed voltammetric curves to appear at more positive potentials, which enables to avoid possible interferences from other elements. The sensitivity of the determination of titanium in the case of the reversible reduction of Ti(IV) complexes is higher, but does not significantly exceed that for irreversible reduction.

A great increase in the sensitivity of titanium determination was achieved by utilizing stripping procedures or/and catalytic phenomena. These approaches led to the elaboration of extremely sensitive voltammetric method, which may be used to determine very low amounts of titanium.

Another field of application of the catalytic properties of redox systems Ti(IV)/Ti(III) is the indirect determination of oxidizers participating in catalytic reactions, e.g. chlorates, which are voltammetrically inactive and difficult to detect by means of other analytical methods. In these cases catalytic voltammetry offers simple, inexpensive, and time- and reagent-saving procedures.

The voltammetric properties of Ti(IV) complexes may be also applied for indirect determination of voltammetrically inactive ligands, e.g. organic acids and thiocyanates, recording the reversible pre-waves of these complexes preceding the irreversible wave of hydrated Ti(IV) ions. This kind of catalytic phenomenon is called ligand catalysis.

In a prevalent number of voltammetric procedures of titanium detection mercury working electrodes are used; these electrodes offer the highest sensitivity, reproducibility and accuracy of the determination. However, due to toxicity of mercury and the difficulty in recycling it, novel voltammetric procedures are being elaborated, with the aim of limiting the use of this metal as the electrode material or even entirely replacing mercury with other metallic materials. In one such attempts a thin mercury film deposited on a gold microdisc was applied for titanium determination.[82]

So far, only a few attempts at the exploitation of new non-mercury electrodes for the determination of titanium have been made.

When using bismuth film electrodes deposited on glassy carbon supports for titanium determination, well developed and sensitive catalytic or catalytic adsorptive stripping voltammetric curves were observed; however, the sensitivity of the method was lower and the detection limit was higher than that obtained by means of mercury electrodes.

An extensive investigation of the properties and performance of the new metallic film sensors suggests that the progress in their design may lead to electrodes that are comparable to mercury electrodes in terms of performance as far as the determination of metal/Ti traces is concerned.

Finally, it should be emphasized that, by coupling the very efficient adsorptive accumulation of electroactive titanium species on the electrode surface with the catalytic reaction, catalytic voltammetry and in particular catalytic adsorptive stripping voltammetry provide a significant amplification of the analytical response, resulting in high sensitivity, a considerable decrease in the detection limit, and an improved selectivity of the determination.

# 6. Perspectives

Further investigations and the elaboration of the voltammetric procedures of the determination of titanium traces should proceed in two directions:

1. Searching for new, efficient adsorptive-catalytic titanium systems, i.e. new ligands forming such complexes with Ti that would have strong adsorptive properties and induce catalytic reactions providing a high increase of the Ti voltammetric analytical signal. These catalytic systems of Ti could be applied for the determination of ultratrace amounts of Ti, which cannot be quantified by means of current voltammetric catalytic or adsorptive-catalytic procedures. This includes cases in which due to the low solubility of titanium compounds (geological samples, tissue fluids coming in contact with titanium implants, etc.), Ti concentration is lower than the limit of detection of hitherto applied voltammetric methods.
2. Elaboration of new mercury-free working electrodes with voltammetric characteristics similar to those of mercury, which would simplify the analytical procedures of Ti determination (metal film, screen-printed electrodes, etc.).

# 7. Acknowledgements

Financial support from the Polish National Science Centre (Project 2011/01/B/ST8/07794) is gratefully acknowledged.

# 8. References

1. A. Kabata-Pendias, A.B. Mukherjee, *Trace Elements from Soil to Human;* Springer, Berlin, **2007.**

2. I. M. Kolthof, J. J. Lingane, *Polarography*; Interscience Pulisher, New York, London, **1952,** Vol. 2, p.442**.**
3. J. J. Lingane, J. M. Kennedy, *Anal. Chim. Acta* **1956**, *15*, 294–300.
4. G. M. Habashy, *Collect. Czech. Chem. Commun*. **1956,** *21*, 3166–3172.
5. N. Fatouros, D. Krulic, N. Larabi, *J. Electroanal. Chem.* **2004,** *568*, 55–64.
6. D. F. Adams, *Anal. Chem*. **1948**, *20*, 891–895.
7. V. Vandenbosh, *Bull. Soc. Chim. Belg*. **1949**, *58*, 532–536.
8. R. Pecsok, *J. Amer. Chem. Soc*. **1951**, *73*, 1304–1308.
9. Z. Kowalski, J. Zarębski, *Chem. Anal. (Warsaw)* **1967**, *12*, 1237–1249 and **1968**, *13*, 55–63.
10. S. I. Siniakova, *J. Anal. Chem. (USSR)* **1953**, *8*, 333–339.
11. R. Pecsok, E. F. Maverick, *J. Amer. Chem. Soc*. **1954,** *76*, 358–362.
12. R. Pribil, Z. Roubal, E. Svatek, *Chem. Listy* **1952**, *46*, 396–400.
13. J. Zarębski, *Chem. Anal. (Warsaw)* **1974**, *19*, 981–989.
14. J-F. Wei, M. Qian, *Anal. Lett*. **1994**, *27*, 2551–2568.
15. L. Hernandez, A. Zapardiel, J. A. Perez-Lopez, I.E. Bermejo, *Anal. Chim. Acta* **1987**, *198*, 239–244.
16. M. Kawahara, H. Mochizuki , R. Kajiyama, *Bunseki Kagaku (Japan Analyst)* **1959**, *8*, 25–30.
17. D. I. Kurbatov, *J. Anal. Chem. (USSR)* **1959,** *14*, 743–744.
18. A. Blazek, J. Koryta, *Chem. Listy*, **1953**, *47*, 26–32.
19. A. Blazek, J. Koryta, *Collect. Czech. Chem. Commun*. **1953**, *18*, 326–336.
20. J. H. Christie, G. Lauer, *Anal. Chem*. **1964**, *36*, 2037–2038.
21. J. M. Saveant, E. Vianello, *Electrochim. Acta* **1964**, *10*, 905–920.
22. P. J. Lingane, J.H. Christie, *J. Electroanal. Chem*. **1967**, *13*, 227–235.
23. A. Calusaru, *Isotopenpraxis* **1968**, *10*, 401–404.
24. A. Calusaru, *Uspiekhi Khim*. **1976**, *48*, 221–240.
25. G. Farnia, G. Sandoma, E. Vianello, *J. Electroanal. Chem*. **1978**, *88*, 147–149.
26. W. F. Toropova, R. S. Zabbatova, *J. Anal. Chem. (USSR)* **1970**, *25*, 1059–1062.
27. H. Kaneko, K. Kaneko, *Bunseki Kagaku (Japan Analyst)* **1979**, *28*, 27–773.
28. N. Diwan, A. P. Joshi, *J. Indian Chem. Soc*. **1989**, *66*, 839–840.
29. P. V. C. Rao, V. J. Koshy, *Talanta* **1994**, *41*, 1911–1915.
30. Y. Yamamoto, K. Hasebe, T. Kambara, *Anal. Chem*. **1983**, *55*, 1942–1946.
31. H. Kaneko, *J. Electroanal. Chem*. **1984**, *169*, 221–231.
32. C. Zhang, G. Lou, P. Gao, *Lihua Jianyan, Huaxue Fence* **1984**, *24*, 267–269.
33. J. Botev, N. Elenkova, Ch. Sheytanov, *Dokl. Bolg. A. N.* **1966**, *16*, 1059–1061.
34. A. Bobrowski, J. Zarębski, *Electroanalysis* **2000**, *12*, 1177–1186 and refs therein.
35. D. Krulic, N. Fatouros, N. Larabi, E. Mahe, *J. Electroanal. Chem.* **2007**, *601*, 220–228.
36. J. Koryta, J. Tenygl, *Collect. Czech. Chem. Commun*. **1954**, *19*, 839–841.
37. J. Koryta, *Collect. Czech. Chem. Commun*. **1955**, *20*, 1125–1130.
38. D. E. Smith, *Anal. Chem*. **1963**, *35*, 610–614.
39. M. H. Kim, R. L. Birke, *Anal. Chem*. **1983**, *55*, 522–527.
40. J. Zeng, R.A. Osteryoung, *Anal. Chem*. **1986**, *58*, 2766–2771.
41. D. Krulic, N. Larabi, N. Fatouros, *J. Electroanal. Chem.* **2005**, *579*, 239–242.
42. J. Zarębski, *Chem. Anal. (Warsaw)* **1985**, *30*, 699–716.
43. J. Zarębski, *Chem. Anal. (Warsaw)* **1987**, *32*, 65–76.
44. N. Fatouros, D. Krulic, N. Larabi, *J. Electroanal. Chem.* **2003**, *549*, 81–90.
45. D. Krulic, N. Larabi, N. Fatouros, *J. Electroanal. Chem***.** **2005**, *579*, 243–247.
46. E. G. Tschikryzova, S. Ya. Mashinskya, *J. Anal. Chem. (USSR)* **1971**, *26*, 1105–1110.
47. E. G. Tschikryzova, S. Ya. Mashinskya, *J. Anal. Chem. (USSR)* **1972**, *27*, 1960–1965.
48. Z. Pospisil, *Chem. Listy*, **1953**, *47*, 33–42.
49. N. K. Ignatova, P. M. Zaytsev, M. Yu. Gornostayeva, *J. Anal. Chem. (USSR)* **1978**, *33*, 2140–2143.
50. E. G. Tschikryzova, S. Ya. Mashinskya, S. A. Sobina, S. M. Bardin-Stein, N. A. Romanov, L. Ya. Cheyfetz, *J. Anal. Chem. (USSR)* **1982**, *37*, 1996–2001.
51. L.Ya. Cheyfetz, A. W. Tscherevik, A. E. Wasyukov, L. F. Kabanenko, *J. Anal. Chem. (USSR)* **1987**, *42*, 450–455.
52. L. Ya. Cheyfetz, P. M. Zaytsev, *J. Anal. Chem. (USSR)* **1989**, *44*, 986–995.
53. E. G. Tschikryzova, S. Ya. Mashinskya, *Zav. Lab*. **1974**, *40*, 1442–1443.
54. Ya. I. Turyan, E. S. Saksin, *Electrokhim*. **1971**,*7*, 86–90.
55. D. Ferri, P. L. Buldini, *Analyst* **1982**, *107*, 1375–1379.
56. J. Zarębski, J. Heyrovsky *Memorial Congress on Polarography*, Prague, 1980, Proceedings II, p. 192.
57. P. L. Buldini, D. Ferri, F. Zignani, *Fresenius Z. Anal. Chem.* **198**3, *314*, 660–664.
58. B. J. Basu, S. R. Rajagopalan, D. K. Padma, *Indian J. Chem. Sect. A*. **1995**, *34*, 320–322.
59. S. Ya. Mashinskaya, E. G. Tschikryzova, I. I. Wataman, W. N. Baskin, *Zav. Lab*. **1984**, *50*, 11–12.
60. S. Tribalat, D. Delafosse, *Anal. Chim. Acta* **1958**, *19*, 74–89.
61. S. Tribalat, *J. Electroanal. Chem*. **1960**, *1*, 443–452.
62. Ya. I. Turyan, E. W. Sahsin, *Electrokhim*. **1970**, *6*, 961–966.
63. Ya. I Turyan, P. M. Zaitsev, Z.W. Zaitseva, *Electrokhim*. **1973**,*9*, 1143–1146.
64. Ya. I Turyan, E. W. Sahsin, *J. Anal. Chem. (USSR*) **1970**, *25*, 998–1003.
65. E. W. Sahsin, Ya. I. Turyan, *J. Anal. Chem. (USSR)* **1970**, *25*, 2362–2367.
66. E. W. Sahsin, Ya. I. Turyan, *Electrokhim*. **1972**, *8*, 1150–1152.
67. Ya. I. Turyan, *Uspiekhi Khim*. **1973**, *42*, 969–986.
68. Ya. I. Turyan, O. E. Rubinski and P. M. Zaitsev, *Poljarografitcheskaya Katalimetriia*, Chimija, Moscow, **1998**.
69. L. J. Li, A. B. Wang, P. G. He, Y. Z. Fang, *Indian J. Chem. Sect. A: Inorg. Bioinorg. Phys. Teor. Anal. Chem.* **2000**, *39*, 541–544.

70. M. G. Paneli, A. Voulgaropoulos, *Electroanalysis* **1993**, *5*, 355–373 and refs therein.
71. M. Gawrys, J. Golimowski, *Fresenius J. Anal. Chem.* **2000**, *367*, 763–765 and refs therein.
72. M. Gawrys, J. Golimowski, *Anal. Chim. Acta* **2001**, *427*, 55–61.
73. M. Gawrys, J. Golimowski, *Electroanalysis* **2003**, *15*, 1017–1022.
74. J. Wang, J. S. Mahmoud, *J. Electroanal. Chem.*, **1986**, *208*, 383–394.
75. K. Yokoi, C. M. G. van den Berg, *Anal. Chim. Acta* **1991**, *245*, 167–176.
76. K. Yokoi, C. M. G. van den Berg, *Anal. Chim. Acta* **1992**, *257*, 293–299.
77. D. V.Vukomanovic, G. W. van Loon, *Fresenius J. Anal. Chem.* **1994**, *350*, 352–358.
78. M. H. Xu, Z. Zhang, Z. Liu, *Fenxi Xuaxue* **1989**, *17*, 254–247.
79. V. Gemmer-Colos, R. Neeb, *Naturwiss.* **1986**, *73*, 498–499.
80. B. X.Ye, S. X. Yang, *Talanta* **1994**, *41*, 537–540.
81. R. Naumann, W. Schmidt, G. Höhl, *Fresenius J. Anal. Chem.* **1992**, *343*, 746.
82. M. do Carmo Pereira, M. de Lourdes Pereira, *Electroanalysis* **1999**, *11*, 1207–750.
83. A. Romanus, H. Müller, D. Kirsh, *Fresenius J. Anal. Chem.* **1991**, *340*, 363–370.
84. A. Romanus, H. Müller, D. Kirsh, *Fresenius J. Anal. Chem.* **1991**, *340*, 371–376.
85. X. Zhang, L. Wang, D. Shen, *J Indian Chem Soc.* **2000**, *77*, 421–423.
86. A. Bobrowski, J. Zarębski, *Curr. Anal. Chem.* **2008,** *4*, 191–201 and refs. therein.
87. P. Tomcik, P. Jencusova, M. Krajcikova, D. Bustin, A. Manova, M. Cakrt, *J. Electroanal. Chem.* **2006**, *593*, –171.
88. A. Bobrowski, A. Krolicka, K. Pacan, J. Zarębski, *Electroanalysis* **2009**, *21*, 2415–2419.
89. A. Krolicka, A. Bobrowski, *Electrochem. Comm.* **2004**, *6,* 99–104.
90. A. Gorczyca, A. Krolicka, A. Bobrowski, Book of abstracts of YISAC 2006 : *13th Young Investigators' Seminar on Analytical Chemistry*, Zagreb, Croatia, **2006**, p. 15.
91. A. Bobrowski, A. Krolicka, J. Zarębski, *Electroanalysis* **2010**, *21*, 1421–1427.

## Povzetek

Katalitska ter katalitska adsorpcijska inverzna (stripping) voltametrija sta dve od najbolj občutljivih analiznih metod. Predstavljen je pregled različnih katalitskih in katalitskih adsorpcijskih sistemov za titan ter njihova uporaba v voltametrijski analizi. Podrobno razpravljamo o mehanizmih katalitskih reakcij. Poleg tega na kratko pregledamo literaturo (91 referenc), katalitsko polarografsko, voltametrijsko in katalitsko adsorpcijsko inverzno voltametrijsko določitev sledov titana na kapalni živosrebrovi in kovinskih filmskih elektrodah. Prav tako predstavimo uporabo redoks sistema Ti(IV)/Ti(III) za posredno določitev voltametrijsko neaktivnih oksidantov, ki sodelujejo v katalitskih reakcijah (npr. klorati) in voltametrijsko neaktivnih ligandov (npr. organskih kislin in tiocianatov).