

Application of Titanometry to Titrations in Alkaline Medium. I. Determination of Dichromate and Cyanoferrate(III) Ions

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The formal redox potential Ti^{III}/Ti^{IV} was determined in the Na_2CO_3 medium over the pH range from 7.35 to 9.52 by using EDTA. It was found that the formate Ti^{III} complex in glycerine did not change its titre in air for 4 days. This solution was used as a volumetric reagent for the determination of $[Fe(CN)_6]^{3-}$ and $Cr_2O_7^{2-}$ ions in alkaline medium.

Because of their relatively high redox potential the Ti^{III} ions represent a volumetric reagent suitable for the estimation of several ions as well as organic substances in the medium of mineral acids. The value of this redox potential changes with acidity and concentration of titanium as reported by *Diethelm* and *Foerster* [1]. The study of the dependence of this redox potential on acidity in the presence of complex-forming substances was made by *Kolthoff* [2]. He found that the presence of complex-forming substances reacting with Ti^{III} resulted in a shift of potential to more negative values. Similar conclusions were drawn by *Syrokomskej et al.* [3]. By the use of complexone, *Čihalik* [4] succeeded in raising pH of solution (pH 6, $E_H^f = 0.31$ V) what brought about a decrease in redox potential.

This paper deals with the attempt to measure the formal redox potential Ti^{III}/Ti^{IV} at varying pH in Na_2CO_3 medium and in the presence of Na_2EDTA .

Since the main reason why titanometry is used in laboratories to a lesser extent is a small stability of aqueous solutions containing Ti^{III} compounds as well as their easy oxidability with air oxygen, the attempt was made to carry out the titrations in alkaline medium in the presence of air.

The possibility of using the known complexes of Ti^{III} with some organic ligands, especially oxalate complexes [5], formate complexes [6], and acetylaceton complexes [7], as titration reagents was studied. In particular, attention was paid to the statement of *Stähler* and *Bachzan* [6] that olive-green titanium(III) formates in anhydrous state are stable in air. This paper points out that an aqueous solution of titanium(III) formate may be stabilized by glycerine. Viscous solutions of glycerine were then diluted with dimethylformamide. The intense blue solutions thus obtained are stable in air and do not change their titre for 4 days. The solution has to be protected against light with a protective screen. The stability of this solution depends also on the quality of glycerine used. $K_2Cr_2O_7$ in alkaline medium was used as a standard for the determination of the titre of this solution.

The conditions were found for the determination of $Cr_2O_7^{2-}$ and $[Fe(CN)_6]^{3-}$ ions in ammoniacal buffer solution containing Na_2EDTA by using either the potentiometric

indication of end point or the visual indication with resazurin and resorufin. The error of determination did not exceed $\pm 1\%$. Both these indicators were put forward some time ago as titanometric indicators in acidic region [8] and resazurin was put forward as redox indicator for stannometric titrations in alkaline medium [9].

The formal redox potential Ti^{III}/Ti^{IV} varies from -654 to -966 mV against saturated calomel electrode in the pH range between 7.35–9.52 what allows to carry out titanometric titrations of many substances in alkaline medium using an inert nitrogen atmosphere and Na_2EDTA as a complex-forming reagent.

Experimental

Determination of formal redox potential Ti^{III}/Ti^{IV} in alkaline medium

An approximate 0.1 N- $TiCl_3$ in 0.3 N-HCl solution was prepared by diluting 15% solution of $TiCl_3$ (Lachema, Brno, anal. grade). The solution was held in an inert nitrogen atmosphere. An aqueous solution of 0.1 N- $K_3[Fe(CN)_6]$ was used as titration reagent. The alkaline medium was adjusted with the solution of Na_2CO_3 .

10 ml of 0.1 M- Na_2EDTA was added to 5 ml of a solution of 0.1 N- $TiCl_3$ so that the solution remained clear after the addition of Na_2CO_3 solution. Then the titration was carried out with the above volumetric reagents. The variation of potential was measured with a potentiometer "Radelkis" type OP-201/1 using a bright platinum indication electrode and a saturated calomel reference electrode. The measurements were made in a vessel with an inert atmosphere using nitrogen as inert gas. Table 1 provides the values of formal redox potentials Ti^{III}/Ti^{IV} against saturated calomel electrode as well as their dependence on pH which have been read from potentiometric curves. The temperature of the measurements was 23–24°C.

Table 1

pH	E^t	pH	E^t
7.35	-654	8.68	-795
7.52	-675	9.05	-875
8.16	-750	9.52	-936

Preparation of the volumetric solution of Ti^{III}

A solution of 0.1 N- Ti^{III} was prepared from 10–15% solution of $TiCl_3$ by adding 40–30 ml of this solution and 0.6 g of HCOOH into 170 ml of glycerine (anal. grade). After stirring an intense blue solution appeared and this solution was filled up with dimethylformamide in a volumetric flask to 250 ml. The solution was poured into a container of an automatic burette which was protected against light with a screen. The titration was carried out by means of a burette graduated by 0.02 ml in a medium of equimolar mixtures of NH_4OH and NH_4Cl using 0.1 M- $K_2Cr_2O_7$ as a standard. Since a turbidity appeared before end point, a solution of 0.1 M- Na_2EDTA was given into the titration solution as well. The working procedure involved an addition of 2 ml of 0.1 M- Na_2EDTA and 10 ml of ammoniacal buffer solution (pH 10.5) to 1–2 ml of standard.

The end point was estimated potentiometrically. The solution thus prepared did not change its titre for 4 days. Afterwards a change in colour (solution became grey) as well as in titre was observed as obvious from Table 2.

Table 2
Temporal stability of the Ti^{III} solution in the medium of Na_2CO_3
pH 10–10.8

t [hours]	Consumption [ml]	Added 0.1 N- $\text{K}_2\text{Cr}_2\text{O}_7$ [ml]	f
0.0	4.724	1	0.2123
23.33	4.770	1	0.2096
26.33	4.772	1	0.2096
30.33	4.717	1	0.2123
47.33	4.772	1	0.2096
59.48	4.744	1	0.2110
62.33	4.746	1	0.2107
79.51	4.759	1	0.2105
84.33	4.761	1	0.2101
87.33	4.772	1	0.2096
107.33	5.250	1	0.1905
152.33	5.727	1	0.1748

Table 3
Determination of $\text{Cr}_2\text{O}_7^{2-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ ions

Added [mg]	Indication of end point	pH	Found [mg]	Error [%]
$[\text{Fe}(\text{CN})_6]^{3-}$				
21.195	resazurin: colour change	10.70	21.308	+0.53
21.195	blue—red—colourless	10.66	20.983	—1.00
21.195	resorufin: colour change	10.57	21.308	+0.53
21.195	red—colourless	10.55	21.308	+0.53
21.195	potentiometrically	10.69	21.295	+0.47
21.195		10.50	21.195	0.00
$\text{Cr}_2\text{O}_7^{2-}$				
3.599	resazurin: colour change	10.55	3.631	+0.89
3.599	blue—red—colourless	10.58	3.631	+0.89
3.599	resorufin: colour change	10.58	3.631	+0.89
3.599	red—colourless	10.60	3.631	+0.89
3.599	potentiometrically	10.55	3.622	+0.64
3.599		10.50	3.615	+0.44

Determination of chromates and ferricyanides

The determination of $\text{Cr}_2\text{O}_7^{2-}$ and $[\text{Fe}(\text{CN})_6]^{3-}$ ions was carried out in equimolar mixtures of NH_4OH and NH_4Cl . The end point was fixed either potentiometrically or visually using resazurin and resorufin as indicators, which were applied because of their relatively good stability in alkaline medium. 0.5% aqueous solutions of sodium salts of resazurin and resorufin were used. The hydrolysis of Ti^{IV} was hindered by 0.1 M solution of Na_2EDTA .

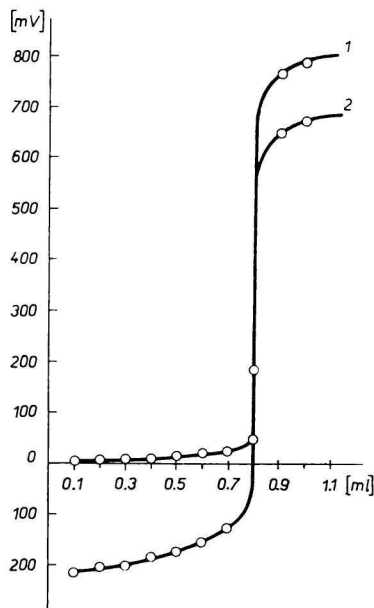


Fig. 1. Potentiometric titration curves for the solutions of $[\text{Fe}(\text{CN})_6]^{3-}$ and $\text{Cr}_2\text{O}_7^{2-}$ ions. 1. titration of 1 ml of 0.1 N- $\text{K}_2\text{Cr}_2\text{O}_7$; 2. titration of 1 ml of 0.1 N- $\text{K}_3[\text{Fe}(\text{CN})_6]$. Titrations were carried out after adding 2 ml of 0.1 M chelator 3 and 10 ml of NH_4OH — NH_4Cl buffer solution.

The solution of titrated ion, 2 ml of 0.1 M- Na_2EDTA and 1–2 drops of indicator solution containing 0.1% of sodium salt of resazurin or resorufin in water were put into 10 ml of buffer containing NH_4OH and NH_4Cl and the titration was performed under constant stirring up to colour change. The plot of potentiometric titration is presented in Fig. 1. The results of all determinations are given in Table 3. 1 ml of 0.1 N- Ti^{III} solution corresponds to 21.195 mg of $[\text{Fe}(\text{CN})_6]^{3-}$ or 3.599 mg of $\text{Cr}_2\text{O}_7^{2-}$.

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