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Selective Complexometric Determination of Titanium(IV) Using Sodium Potassium Tartrate or Ascorbic Acid as Masking Agent

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Abstract. A simple, rapid and accurate complexometric method is proposed for the determination of titanium(IV) where sodium potassium tartrate or ascorbic acid were used as masking agents. In the presence of diverse metal ions, titanium is first complexed with excess of EDTA and surplus EDTA is then titrated at pH 5–6 with zinc sulfate, xylenol orange being used as indicator. An excess of 5% aqueous sodium potassium tartrate is then added to displace the complexed EDTA from the Ti-EDTA complex quantitatively, which is titrated with zinc sulfate. Also, ascorbic acid may be used as the releasing agent. The methods work well in the range 1–53 mg of Ti(IV) for sodium potassium tartrate with relative errors $\pm 0.28\%$ and standard deviations ≤ 0.16 mg. For ascorbic acid the range is 1.00–30.00 mg of Ti(IV) with relative errors of $\pm 0.40\%$ and standard deviations of ≤ 0.05 mg

Key words: Complexometry; titanium determination; EDTA titration; sodium potassium tartrate; ascorbic acid; masking.

The analytical chemistry of titanium includes volumetric, gravimetric and colorimetric procedures. A complexometric method involving the back titration of the excess EDTA was reported [1] with pyrocatechol violet as indicator at pH 5.3–6.0 using standard copper sulfate titrant. The method of titration with iron, using a spectrophotometric endpoint [2] resulted in 0.7–1.5% low results. The failure of the procedure can be attributed to the formation of a hydrous oxide precipitate, which resulted in the release of EDTA from the Ti-EDTA complex. A more stable 1:1 compound is formed in the presence of hydrogen peroxide [3, 4], the reagent is used for the titrimetric determination of titanium [3–8].

This paper describes both sodium potassium tartrate and ascorbic acid as indirect masking agents for the complexometric determination of titanium(IV) at pH 5–6 under ordinary conditions.

Experimental

Reagents

All reagents used were of analytical or chemically pure grade.

Zinc Sulfate Solution (0.01M). Prepared by dissolving a known amount of zinc sulfate in distilled water and standardized by the quinaldate [9] method.

EDTA (0.01M). Prepared by dissolving the disodium salt of the compound in distilled water.

Titanium Sulfate Solution. Prepared from potassium titanyl oxalate and standardized using cupferron [10] gravimetrically.

Sodium Potassium Tartrate Solution. Used as a 5% solution in distilled water.

Ascorbic Acid Solution. Used as a 5% solution in distilled water.

Solutions of Foreign Ions. Solutions of various metal ions were prepared by dissolving calculated amounts of the metal nitrate/chloride in distilled water.

Xylenol Orange Indicator. Prepared by grinding 1 g of xylenol orange with 100 g of potassium nitrate crystals and used as such.

Procedure

Sodium Potassium Tartrate as Masking Agent. To an aliquot of a solution containing 1.06 mg to 53.00 mg of titanium(IV), an excess of 0.01M EDTA solutions was added and the pH was adjusted to 2–3 using diluted ammonia solution. The surplus EDTA was titrated against zinc sulfate solution at pH 5–6 (hexamine) to the sharp color change of the indicator (golden yellow to red). To this solution, an excess of 5% sodium potassium tartrate (1 ml for every 10 mg of Ti(IV)) was added. The contents were mixed well and the EDTA released was titrated with standard zinc sulfate solution. The second titer value corresponds to the titanium(IV) present.

$$1\ \text{ml}\ 0.01\ \text{M zinc sulfate} \equiv 0.48\ \text{mg of Ti(IV)}$$

Ascorbic Acid as Masking Agent. To an aliquot of a solution containing 1 mg to 30 mg of titanium(IV), an excess of 0.01M EDTA solution was added and the pH was adjusted to 2–3 using diluted ammonia solution. The surplus EDTA was titrated against zinc sulfate solution at pH 5–6 (hexamine) to the sharp color change of the indicator. To this solution an excess of 5% ascorbic acid was added, the contents were mixed well and the EDTA released was titrated with standard zinc sulfate solution. The second titer value corresponds to the titanium(IV) present.

Results and Discussion

EDTA reacts with Ti(IV) ion to form an unstable compound [10] which hydrolyzes at high pH. Polarographic studies of Pecsok and Maverick [11] suggested the formation of an oxygen containing titanium-EDTA complex at pH greater than 2; a more stable oxy compound is formed as TiO(EDTA) [12]. Tartrate is a selective masking agent, which forms a stable soluble complex. The tartrate ion in excess is able to displace EDTA quantitatively from the Ti-EDTA complex at room temperature. Ascorbic acid forms a 1:2 complex with titanium with a reported stability constant ($\log\beta$) of 24.8 [12]. Gaube et al. reported the titanyl ascorbate complex [13]. Ascorbic acid is able to replace the complexed EDTA quantitatively.

The amount of reagents required to decompose the Ti-EDTA complex was established by adding different volumes of 5% sodium potassium tartrate solution to a solution of 10.60 mg of titanium in the form of Ti-EDTA complex and determining the amount of titanium recovered; about 1.0 ± 0.1 ml of 5% sodium potassium tartrate was required (Fig. 1a). It is also established that about 9 ± 1 ml of 5% ascorbic acid was required for the release of 10.00 mg of titanium from its EDTA complex (Fig. 1b). An excess of the reagents has no adverse effect and the absence of any precipitate in the reaction mixture favors sharp end point.

Accuracy and Precision

The determination of titanium(IV) in titanium sulfate solution (Tables 1a & 1b) shows that accurate and reproducible results are obtainable with acceptable relative errors $\pm 0.28\%$, $\pm 0.40\%$ and standard deviations ≤ 0.16 mg, ≤ 0.05 mg, respectively, when sodium potassium tartrate and ascorbic acid were used as releasing agents. On comparing the computed value of the Students' t test (2.776 for 5% level of significance) with the tabulated value, it can be observed that there is no significant difference between the reference values and the value obtained by the proposed method.

Effect of Foreign Ions

Interference by foreign ions in the determination of titanium(IV) using sodium potassium tartrate as a masking agent was studied with aliquots containing 21.2 mg of titanium(IV) (Table 2). The presence of the following ions did not interfere within the concentration range studied: 75 mg of Zn(II), Co(II), Ni(II), Pb(II), Cu(II), Hg(II), Fe(III), Bi(III); 10 mg Pd(II), Mn(II); 40 mg of Ce(III), U(VI), V(IV); 30 mg of Cr(III), Tl(III), Al(III); 125 mg of acetate; 200 mg of nitrate, chloride, sulfate, borate, and phosphate. Severe interference occurred from Th(IV), Zr(IV), Sn(IV) and fluoride. The following ions did not interfere within the concentration range studied when ascorbic acid was used as the masking agent for the determination of 20.00 mg of Ti(IV): 100 mg of Zn(II), Co(II), Ni(II), Pb(II); 40 mg of Al(III), Bi(III),

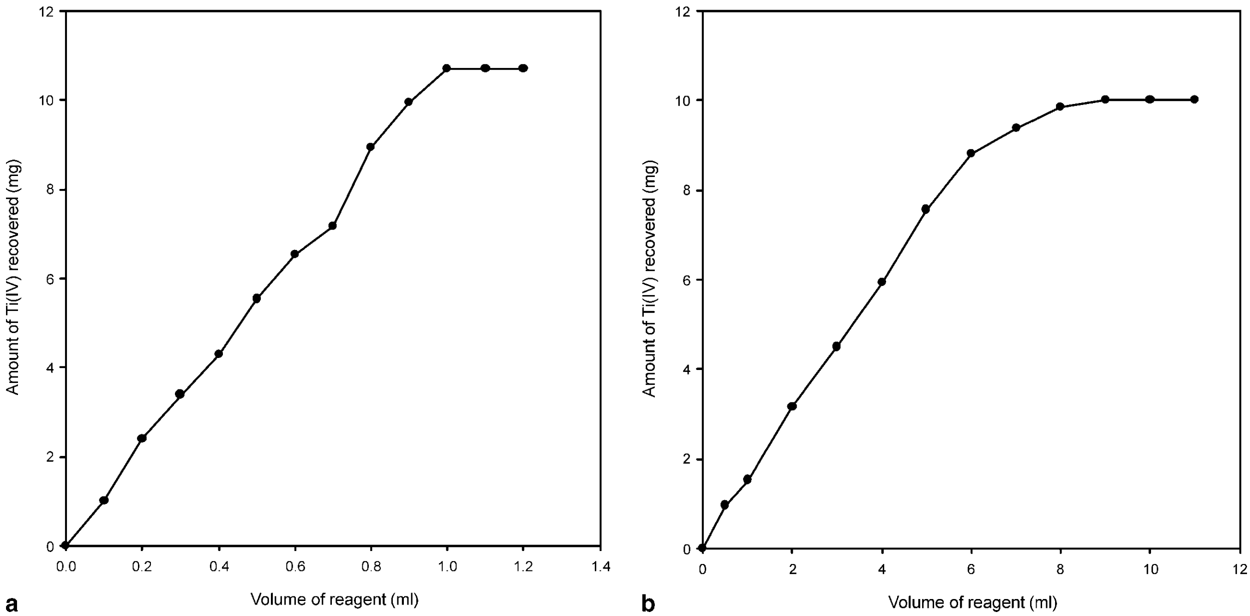

Fig. 1. (a) Effect of 5% sodium potassium tartrate on the release of 10.60 mg of Ti(IV). (b) Effect of 5% ascorbic acid on the release of 10.00 mg of Ti(IV)

Table 1a. Determination of titanium(IV) in titanium sulfate solution using sodium potassium tartrate as masking agent

Titanium present (mg)	Titanium found* (mg)	Relative error (%)	Standard deviation (mg)	Students' 't' value**
1.06	1.06	0.00	0.07	0.00
5.30	5.31	0.19	0.05	−0.45
10.60	10.57	−0.28	0.08	0.84
21.20	21.17	−0.14	0.11	0.61
31.80	31.78	−0.06	0.08	0.56
42.40	42.39	−0.02	0.10	0.22
53.00	52.93	−0.13	0.16	0.98

* Average of five determinations.
** Students' 't' test for 5% level of significance = 2.776.

Table 1b. Determination of titanium(IV) in titanium sulfate solution using ascorbic acid as masking agent

Titanium present (mg)	Titanium found* (mg)	Relative error (%)	Standard deviation (mg)	Students' 't' value**
1.00	1.00	0.00	0.05	0.00
5.00	5.02	0.40	0.03	1.49
7.50	7.52	0.27	0.02	2.24
15.00	14.99	−0.07	0.04	0.56
20.00	20.00	0.00	0.03	0.00
25.00	25.01	0.04	0.03	0.75
30.00	30.01	0.03	0.04	0.56

* Average of five determinations.
** Students' 't' test for 5% level of significance = 2.776.

20 mg Ce(III), Cr(III), V(IV), Zr(IV), 6 mg U(VI), Pt(IV), Fe(III), Mn(II); 100 mg of acetate, nitrate, sulfate, borate and phosphate. The ions Ag(I), Cu(II), Pd(II), Hg(II), Tl(III), Th(IV), Sn(IV), fluoride, Zr(IV) were found to interfere. The interference of Th(IV) can be obviated by the addition of sulfate (1%, 5 ml for 10 mg Th(IV)) prior to EDTA complexation as secondary masking agent. Interference by Tl(III) can be obviated by the addition of appropriate amounts of hydrazine sulfate, while the effect of Ag(I) can be nullified using potassium thiocyanate as secondary masking agent.

Analysis of Ti(IV) in Alloys

Titanium alloys usually contain a large number of elements [14]. Experiments were conducted with synthetic samples as well as with a sample of shape memory alloy. Synthetic mixtures of titanium with Ni, Cr and Fe were prepared according to their alloy compositions and the amount of titanium present in the mixture was determined by the proposed method. Experiments were also repeated for nitinol, Ni–Ti shape memory alloy (Shape Memory Applications Inc, California) with results in Table 3. Good recoveries were obtained.

Table 2. Determination of titanium(IV) in presence of diverse ions

Diverse ion	Using sodium potassium tartrate				Using ascorbic acid			
	Diverse ion taken (mg)	Ti(IV) taken (mg)	Ti(IV) found# (mg)	Relative error (%)	Diverse ion taken (mg)	Ti(IV) taken (mg)	Ti(IV) found# (mg)	Relative error (%)
Ag(I)*	–	–	–	–	5	20.00	19.98	−0.10
Zn(II)	75	21.20	21.28	0.37	100	20.00	19.98	−0.10
Ni(II)	75	21.20	21.12	−0.38	100	20.00	19.96	−0.20
Co(II)	75	21.20	21.24	0.19	100	20.00	19.99	−0.05
Pb(II)	75	21.20	21.14	−0.28	6	20.00	19.97	−0.15
Pd(II)	10	21.20	21.23	0.14	–	–	–	–
Cu(II)	75	21.20	21.32	0.57	–	–	–	–
Hg(II)	75	21.20	21.21	0.05	–	–	–	–
Mn(II)	10	21.20	21.27	0.33	6	20.00	19.98	−0.10
Fe(III)	75	21.20	21.31	0.52	6	20.00	19.96	−0.20
Al(III)	30	21.20	21.28	0.37	–	–	–	–
Bi(III)	75	21.20	21.03	−0.80	40	20.00	19.98	−0.10
Ce(III)	40	21.20	21.34	0.66	20	20.00	20.00	0.00
Cr(III)	30	21.20	21.05	−0.71	20	20.00	19.98	−0.10
Tl(III)*	30	21.20	21.28	0.37	5	20.00	19.98	−0.10
Th(IV)*	10	21.20	21.23	0.14	–	–	–	–
V(IV)	40	21.20	21.17	−0.14	20	20.00	19.96	−0.20
Pt(IV)	–	–	–	–	6	20.00	19.97	−0.15
U(VI)	40	21.20	21.33	0.61	50	20.00	19.97	−0.15
CH_3COO^-	125	21.20	21.24	0.19	100	20.00	19.98	−0.10
NO_3^-	200	21.20	21.25	0.24	100	20.00	19.96	−0.20
Cl^-	200	21.20	21.13	−0.33	–	–	–	–
SO_4^{-2}	200	21.20	21.18	−0.09	100	20.00	19.96	−0.20
BO_3^{-3}	200	21.20	21.24	0.19	100	20.00	19.98	−0.10
PO_4^{-3}	200	21.20	21.21	0.05	100	20.00	19.97	−0.15

* Masked with secondary masking agents (see text).
# Average of 3 determinations.

Table 3. Determination of titanium in solutions of alloy composition

Alloy composition	Composition weight (%)	Using sodium potassium tartrate		Using ascorbic acid	
		Ti(IV) found# (%)	Relative error (%)	Ti(IV) found# (%)	Relative error (%)
Titanium Beta-CEZ (Cr + Fe + Ti)	2.00 + 1.00 + 82.00	81.42	−0.70	81.93	−0.09
Ni + Ti	55.00 + 45.00	44.68	−0.71	44.87	−0.29
Nitinol (Ni + Ti)	56.00 + 43.80	43.53	−0.62	43.61	−0.43

Average of three determinations.

Conclusions

1) A new method for the determination of titanium(IV) using a masking technique is reported.
2) The method is simple and rapid as it does not require heating, and also does not require standardization of EDTA.
3) The reagents sodium potassium tartrate and ascorbic acid are readily available.
4) The reagents do not form any precipitate either with zinc sulfate, the titrant or with titanium, the metal ion to be determined under the experimental conditions.
5) The low effect of foreign ions on the accuracy and precision of the method reveals that the method may be suitable for the determination of titanium in its alloys, mixtures, and complexes.

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