2-(2-Thiazolylazo)-*p*-Cresol (TAC) as a Reagent for the Spectrophotometric Determination of Titanium (IV)

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Abstract. The reaction between titanium(IV) and 2-(2-thiazolylazo)-*p*-cresol-(TAC) in aqueous methanol media at apparent pH 4.0–5.6 results in a intensely coloured complex that is stable for at least 2 h. The combining ratio is 1 : 1 cation : TAC. Beer's law is obeyed up to 5.0 μg/ml titanium(IV) at 580 nm. The apparent molar absorptivity at 580 nm is $9.82.10^3$ l.mole^{-1}.cm^{-1} and the detection limit obtained was 5 ng/ml titanium(IV). A spectrophotometric method for the simultaneous determination of titanium and iron with TAC is proposed.

Key words: 2-(2-thiazolylazo)-*p*-cresol, titanium determination, simultaneous determination.

Hydrogen peroxide [1] is commonly used for the spectrophotometric determination of titanium. The method is simple and fairly selective, but not very sensitive (the apparent molar absorptivity is 700 l.mole^{-1}cm^{-1}). 2-(2-Thiazolylazo)-*p*-cresol (TAC) is an alternative, it reacts with titanium(IV), forming a 1 : 1 complex with an apparent molar absorptivity of $9.82.10^3$ l.mole^{-1}.cm^{-1} at 580 nm, in the presence of hydroxylammonium chloride. Iron(II) also reacts with TAC [2, 3] to give a complex with composition Fe(II)–(TAC)$_2$ and absorption peaks at 740, 580 and 520 nm. It is thus possible to determine titanium(IV) and iron(II) spectrophotometrically with TAC in a single sample.

TAC has also been used for the spectrophotometric determination of copper(II) [4], nickel [5], bismuth [6], and zirconium [7].

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Experimental

Reagents

TAC Solution: 0.1 g dissolved in 100 mL of methanol.

Standard titanium solution [8]: prepared by heating 0.20 g of titanium(IV) oxide with 8 ml of concentrated sulphuric acid and 3.2 g of ammonium sulphate until dissolved, cooling, and diluting to 1 litre with water.

Standard iron(II) solution: prepared by dissolving 0.176 g of iron(II) ammonium sulphate in 0.5% (v/v) sulphuric acid.

Buffer solution: prepared by mixing 2.0 M sodium acetate and 2.0 M acetic acid in appropriate ratio to give pH 5.

Stock solutions of others elements: prepared by dissolving suitable salts in water, 1% (v/v) nitric acid or 1% (v/v) hydrochloric acid.

Hydroxylammonium chloride solution: prepared by dissolving 10 g of the salt in 100 ml of water.

Procedure for Titanium in the Absence of Iron

Into a 25-ml standard flask, transfer a portion of solution containing up to 125 μg of titanium(IV). Add 2.5 ml of hydroxylammonium chloride solution, 8 ml of methanol, 2 ml of TAC solution and 5 ml of acetate buffer. Dilute to the mark with water, mix and after 5 min measure the absorbance at 580 nm in a 1-cm cell, using an appropriate blank. Prepare a calibration graph covering the range up to 125 μg of titanium per 25 ml.

Procedure for Iron in the Absence of Titanium

To a 25-ml standard flask containing up to 100 μg of iron, add 2.5 ml of hydroxylammonium chloride solution, 8 ml of methanol, 2 ml of TAC solution and 5 ml of acetate buffer. Dilute to the mark with water, mix, and measure the absorbance at 580 or 740 nm using a blank. Prepare a calibration graph covering the range up to 100 μg of iron per 25 ml.

Procedure for Determination of Both Titanium and Iron in Geological Matrices

Sample Decomposition. Weigh 0.2–0.3 g of sample (dried at 110°C), transfer it into a Teflon beaker, add a few ml of water, 1 ml of concentrated sulphuric acid and 10 ml of concentrated hydrofluoric acid, and heat on a hot-plate until white fumes appear. Cool, add 5–10 ml of concentrated hydrochloric acid and transfer the contents of the beaker to a 25-ml glass beaker. Heat until all the residue has dissolved, cool to room temperature, and transfer the solution into a convenient size of standard flask; make up to volume with demineralized water.

Analysis. Pipette a suitable volume of the sample solution into a 250-ml beaker, and heat it on a hot-plate almost to dryness. Cool, add 2.5 ml of hydroxylammonium chloride solution and transfer the solution to a 25-ml standard flask. Add 8 ml of methanol, 2 ml of TAC solution and 5 ml of acetate buffer. Measure the absorbances at 740 and 580 nm, against a reagent blank run through the whole procedure.

Calculation Method for Simultaneous Determination of Titanium and Iron

1. Method (a)

$$A_{740} = e_{740}^{Fe} \cdot b \cdot C^{Fe}$$

$$A_{580} = e_{580}^{Fe} \cdot b \cdot C^{Fe} + e_{580}^{Ti} \cdot b \cdot C^{Ti}$$

This method does not consider the weak absorption of the titanium-TAC complex at 740 nm.

2. Method (b)

$$A_{-740} = e_{740}^{Fe} \cdot b \cdot C^{Fe} + e_{740}^{Ti} \cdot b \cdot C^{Ti}$$

$$A_{-580} = e_{580}^{Fe} \cdot b \cdot C^{Fe} + e_{580}^{Ti} \cdot b \cdot C^{Ti}$$

This method consider the weak absorption of the titanium-TAC complex at 740 nm.

Results and Discussion

Solubility of TAC

TAC is only slightly soluble in water but readily soluble in aqueous media containing 20% or more methanol, ethanol, 2-propanol, acetone, dioxan or ethylene glycol. Methanol, ethanol and ethylene glycol are preferred as the absorbance of the titanium complex is higher in these media and remains stable for at least one hour.

Reaction Conditions

Maximal and constant absorbance is obtained for 50 μg of titanium(IV) with 0.70 ml of 0.1% TAC solution per 25 ml; so, 2.00 ml of TAC solution was selected as optimal.

The complex formation is greatly influenced by the pH, Table 1 shows that the best pH range is 4.0–5.6. The absorbance is somewhat dependent on the buffer concentration (shown in Table 2), it is necessary to use the same buffer concentration for all samples, standards and blanks.

The order of addition was studied and the results demonstrated that the complex was affected with it. The results showed (Table 3) that the reductant must be always added before the buffer.

A preliminary experiment showed that the Ti(IV)-TAC system is not stable in the absence of hydroxylammonium chloride (Table 4).

Table 5 shows that with titanium(IV) concentration of 2.0 μg/ml, the absorbance of the system is not affected by the presence of from 1 to 6 ml of a 10% solution of

Table 1. Effect of pH on complex formation. (Ti(IV): 2.00 μg/ml)

pH	Absorbance
3.00	0.047
3.46	0.105
3.78	0.364
4.00	0.382
4.56	0.402
5.13	0.396
5.64	0.383
5.81	0.372
6.23	0.366

Table 2. Effect of the concentration buffer on the TI(IV)-TAC system. (Ti(IV): 2.00 μg/ml; pH 5.0)

Buffer acetate concentration(M)	Absorbance at 580 nm
0.10	0.416
0.20	0.405
0.30	0.391
0.40	0.377
0.50	0.365

Table 3. Effect of order of addition or on the formation of the Ti(IV)-TAC complex. (Ti(IV): 2.00 μg/ml)

Order of addition	Absorbance
Titanium + Chloride[a] + Alcohol + TAC + Buffer + Water	0.405[b]
Titanium + Chloride + Buffer + Alcohol + TAC + Water	0.403
Titanium + Chloride + TAC + Alcohol + Buffer + Water	0.405
Titanium + Chloride + TAC + Buffer + Alcohol + Water	0.406
Titanium + TAC + Chloride + Buffer + Alcohol + Water	0.404
Titanium + Alcohol + Chloride + TAC + Buffer + Water	0.405
Titanium + Buffer + Chloride + TAC + Alcohol + Water	0.390
Titanium + TAC + Alcohol + Buffer + Chloride + Water	0.339
Titanium + TAC + Buffer + Chloride + Alcohol + Water	0.396
Titanium + Buffer + TAC + Alcohol + Chloride + Water	0.366

[a] Chloride = Hydroxylammonium chloride.
[b] Average of three determinations.

hydroxylammonium chloride in a 25 ml total of solution. A potentiometric titration revealed that the titanium(IV) is not reduced by the hydroxyammonium chloride, which suggest that this salt takes part in the complex formation. The Ti(IV)-TAC complex is not formed in the presence of other reducing agents such as hydrazine sulphate or ascorbic acid. A comparison of the spectra of titanium(IV)-TAC with and without hydroxylammonium chloride present shows that there is no difference between the positions of the absorbance maxima.

Accordingly, we conclude that as Ti(IV) : TAC ratio was found to be 1 : 1, a ternary Ti(IV) : TAC : $(NH_2OH)_x$ complex is formed, but the value of x could not

Table 4. Effect of the hydroxylammonium chloride [X] on the stability of the Ti(IV)-TAC system. (Ti(IV): 2.53 μg/m)

	Absorbance		
Time (min)	([X], 0%)	([X], 0.40%)	([X], 2.40%)
0	0.236	0.490	0.502
5	0.168	0.496	0.507
10	0.163	0.494	0.503
15	0.160	0.494	0.503
20	0.157	0.493	0.503
25	0.156	0.493	0.504
30	0.155	0.494	0.501
35	0.153	0.492	0.501
40	0.153	0.492	0.501
45	0.153	0.491	0.501
50	0.151	0.491	0.501
55	0.151	0.491	0.503
60	0.149	0.490	0.501

Table 5. Effect of the hydroxylammonium chloride concentration [X] on the Ti(IV)-TAC system. (Ti(IV): 2.00 μg/ml)

[X] (%)	Absorbance (580 nm)
0.50	0.380
1.00	0.404
2.00	0.403
3.00	0.402
4.00	0.404
5.00	0.405
6.00	0.405

be determined by the conventional methods, owing to the low stability of the system without this reactant. A $1:2:2:4$ Ti(IV):NH_2OH:Pyrocatechol Violet:Cetyl-trimethylammonium complex has been reported [9] which lends credence to this supposition.

Calibration Curve

The calibration curves were made under the conditions described above. The results are shown in Table 6.
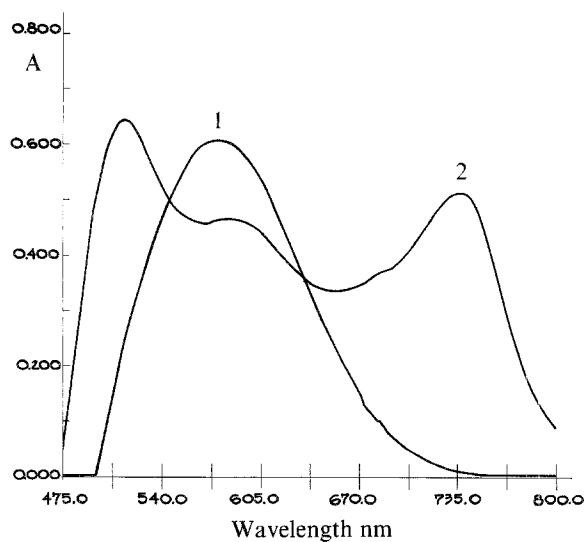
Interferences

The selectivity of the reaction was investigated by determining 12.5 μg of titanium in the presence of various amounts of other ions. The tolerance level for an ion was taken as the amount which caused a change of $\pm 2\%$ in the absorbance of the chelate. It was found that copper(II), nickel(II), iron(II), cobalt(II) and indium(III) interfere even at 1-μg level. Magnesium, calcium, barium, strotium, aluminium and thalluim-

Table 6. Characteristics of the Ti(IV)-TAC and Fe(II)-(TAC)$_2$ systems

System	λ(nm)	ε(pH 5.0) l.mole^{-1} cm^{-1}	Obedience to Beer's Law
Ti(IV)-TAC	580	$9.82.10^3$	0–125 μg
	740	$3.40.10^2$	—
Fe(II)-(TAC)$_2$	520	$1.51.10^4$	0–100 μg
	580	$1.08.10^4$	0–125 μg
	740	$1.18.10^4$	0–125 μg

λ = Absorption peak.
ε = Apparent absorption.

Fig. 1. Absorption spectra. *1* Ti(IV)-(TAC); *2* Fe(II)-(TAC)$_2$

(III) did not interfere even at 200 : 1 (w/w) ratio to titanium, but there was interference from vanadium(V) (260 μg), manganese(II) (650 μg), lanthanum (850 μg), cadmium (260 μg), lead (80 μg), yttrium (40 μg), gallium (30 μg), zirconium (40 μg), platinum(IV) (60 μg) and gold(III) (80 μg).

Table 7. Simultaneous determination of iron and titanium

Standard or sample[c]	No. of dets.	TiO_2 (%) present	TiO_2 (%) found[a]	TiO_2 (%) found[b]	Fe_2O_3 (%) present	Fe_2O_3 (%) found[a]	Fe_2O_3 (%) found[b]
Bauxite NBS	10	2.78	2.73 ± 0.04	2.74 ± 0.05	5.82	5.79 ± 0.09	5.79 ± 0.08
Clay1-IPT	4	0.24	0.26 ± 0.06	0.26 ± 0.05	1.94	2.01 ± 0.06	2.00 ± 0.05
Clay2-IPT	6	0.54	0.59 ± 0.06	0.60 ± 0.06	1.46	1.49 ± 0.11	1.47 ± 0.10
Clay3-IPT	4	1.04	1.11 ± 0.02	1.08 ± 0.02	1.28	1.32 ± 0.08	1.30 ± 0.09
Basalt	4	1.11	1.22 ± 0.17	1.23 ± 0.15	9.72	9.46 ± 0.06	9.45 ± 0.05
Granite	4	0.26	0.25 ± 0.02	0.25 ± 0.03	1.62	1.84 ± 0.10	1.85 ± 0.09
Clay4-IPT	4	1.40	1.45 ± 0.02	1.43 ± 0.02	1.56	1.57 ± 0.06	1.53 ± 0.06
Clay-BA	3	0.81	0.75 ± 0.08	0.74 ± 0.07	7.68	7.57 ± 0.06	7.57 ± 0.06
Bentonite-PB	3	1.18	1.26 ± 0.04	1.27 ± 0.03	9.21	9.48 ± 0.08	9.48 ± 0.08
Bauxite 1-MG	3	1.32	1.45 ± 0.04	1.44 ± 0.05	10.26	10.25 ± 0.08	10.26 ± 0.09
Bauxite 2-MG	3	1.19	1.16 ± 0.04	1.16 ± 0.05	9.44	9.28 ± 0.14	9.29 ± 0.13
Cement-BA	3	0.22	0.21 ± 0.02	0.22 ± 0.03	3.33	3.18 ± 0.12	3.16 ± 0.10

[a] Method (a), 95% confidence limit.
[b] Method (b), 95% confidence limit.
[c] The compositions are shown in Table 8.

Table 8. Composition of standards and samples analysed

Standard and sample	Al_2O_3 (%)	Fe_2O_3 (%)	TiO_2 (%)	SiO_2 (%)	CaO (%)	MgO (%)	Na_2O (%)	K_2O (%)
Bauxite NBS-USA[a]	55.00	5.82	2.78	6.01	0.29	0.02	0.02	0.01
Clay 1-IPT-SP[a]	38.40	1.94	0.24	45.10	0.07	0.14	0.01	0.85
Clay 2-IPT-SP[a]	35.90	1.46	0.54	48.00	0.06	0.24	0.01	0.91
Clay 3-IPT-SP[a]	29.10	1.28	1.04	55.80	0.09	0.20	0.01	0.29
Clay 4-IPT-SP[a]	45.00	1.56	1.40	30.70	0.07	0.13	0.06	1.26
Basalt[a]	15.48	9.72	1.11	56.14	7.54	4.36	2.75	2.07
Granite-[a]	15.06	1.62	0.26	71.80	1.21	0.50	3.79	4.78
Clay-BA[b]	16.36	7.68	0.81	—	3.26	3.15	0.56	2.56
Bentonite-PB[b]	20.72	9.21	1.18	—	0.48	2.47	0.51	1.18
Bauxite 1-MG[b]	53.25	10.26	1.32	—	0.06	0.05	0.20	0.29
Bauxite 2-MG[b]	61.47	9.44	1.19	—	0.04	0.05	0.06	0.03
Cement-BA[b]	3.67	3.33	0.22	—	53.10	1.81	0.23	0.48

[a] Standards.
[b] Samples (analysed by ICP in CEPED).
IPT Instituto de Pesquisa Tecnológica São Paulo; SP Brasil. CEPED Centro de Pesquisa e Desenvolvimento da Bahia Camaçari; Ba Brasil.

Sulphosalicylic acid, cyanide, bromide, chloride, glycine, borate, sulphate, iodide, thiosulphate and thiourea did not interfere at 1000 : 1 (w/w) ratio to titanium, but there was interference from EDTA (2.5 μg), NTA (2.5 μg), 1,10-phenanthroline (125 μg), sulphide (125 μg), tartrate (400 μg), citrate (400 μg), phosphate (400 μg) and fluoride (400 μg) in the amounts shown in the brackets.

Determination of Titanium and Iron

Although iron(II) interferes very strongly in the titanium determination, the reaction of Fe(II) with TAC yields a complex [composition Fe(II)-(TAC)$_2$] with absorption peaks at 740, 580 and 520 nm. Whereas the Ti-TAC complex has only one absorption peak, at 580 nm, and practically zero absorbance at 740 nm (Fig. 1).

Simultaneous determination of titanium and iron is therefore possible, by measuring the absorbances at 580 and 740 nm, and calculation based on the additive property of the absorbances. Ideally, a correction should be included for the slight absorbance of the Ti complex at 740 nm, but as shown in Table 7, this is not necessary for routine analyses.

Application

The method was applied to simultaneous determination of iron and titanium in various standards and samples (Table 8). The results (Table 7) indicate that the accuracy and precision for the proposed method are satisfactory. To obtain higher signals, 2-cm cuvettes were used. The method of calculation based on the measure of the absorbance at 740 nm for the iron and at 580 nm for the titanium and iron cannot be applied if the titanium amount is much higher than that of iron, in the sample.

Analysis of synthetic samples showed that the method can be used for samples with iron/titanium ratios in the range from 20 : 1 to 1 : 3.

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