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Titanium Determination under High-Sensitivity Conditions with 2-(5-Chloro-2-pyridylazo)-5-dimethylaminophenol. I

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The optimum working conditions for the complexing reactions between Ti(IV) and 2-(5-chloro-2-pyridylazo)-5-dimethylaminophenol (5.ClDMPAP) in aqueous alcoholic solutions were studied. When an ethanol solution of 5.ClDMPAP is added to a Ti(IV) aqueous solution, complex species, whose spectral and stoichiometric characteristics depend on pH, develop rapidly. The complex selected for the analytical work forms between pH 4.7 and 5.8 and has a 3 : 1 ligand-metal molar ratio. The complex fulfils Beer's law up to a Ti(IV) concentration of 0.7 ppm, working at $\lambda_{max}=580$ nm. The optimum concentration range (Ringbom) was between 0.05 and 0.7 ppm of Ti(IV). The molar absorptivity at $\lambda_{max}=580$ nm and Sandell index are 4.39×10^4 dm^3 mol^{-1} cm^{-1} and 0.0011 μg cm^{-2}, respectively. An absorptiometric method to determine Ti(IV) was developed and the proper ways to reduce interferences produced by some anions and cations are described. The method developed was applied to Ti(IV) determination in optical glass and ceramic materials.

The determination of small quantities of titanium is a very important fact when analyzing diverse materials such as glass, frits, ceramics, paints, sands, and natural water from nearby vanadium mines.

The atomic absorption technique, using flame as an atomization means, has not the sensitivity necessary for many cases. So, the searching of chromogenic reagents and the perfecting of techniques having analytical procedures with the proper sensitivity and selectivity for Ti(IV), is interesting. Reagents derived from phenylfluorone[1)] and the azo group (pyridylazo)[2)] and thiazolylazo[3)] yielded significant results. As to those reagents of the pyridylazo type, Shibata et al.[4)] proved that the presence of a dialkylamino group in a *p*-position with respect to the azo group and the existence of one halogen atom in the pyridine nucleus are highly important to attain a larger sensitivity in chromatic reactions. The reagent selected, 2-(5-chloro-2-pyridylazo)-5-dimethylaminophenol, fulfils both requirements. The general characteristics of this reagent and its use in zinc and vanadium determination have already been studied.[5,6)]

Experimental

Reagents. A 5.ClDMPAP solution was prepared by coupling *m*-dimethylaminophenol with sodium 5-chloro-2-pyridyldiazotate, according to the method described by Shibata et al.[7)] Purification was carried out by means of repeated cycles of dissolution-reprecipitation starting from ethanol-water mixtures. A 0.25% (w/v) solution from the pure material was prepared. Lower concentration solutions from the above one by dilution with ethanol, were prepared. All solutions were kept away from light. A 5×10^{-4} mol dm^{-3} solution can be kept unaltered for at least 25 d. The Ti(IV) solution was prepared according to that described by Roseman and Thornton.[8)] Its titer was determined by complexometric titration.[9)] To obtain reproducible results, the solution must be prepared daily. All the other chemicals were also of an analytical-reagent grade.

Apparatus. A Varian 634 UV-vis. spectrophotometer with 10 mm optical path cell to obtain the absorption spectra and absorbance measures was used. An Orion 701-A pH meter for pH measurements was used. Volumes in Ti(IV) complexometric titrations were obtained by means of an automatic Metrohm Dosimat E412P buret.

Results and Discussion

Influence of pH, Stoichiometry, and Conditions for Ti(IV) Absorptiometric Determination. The reaction between aqueous solutions of Ti(IV) and 5.ClDMPAP dissolved in ethanol produces, almost instantaneously and at different pH values, diverse complex species (Fig. 1). Table 1 shows the most important characteristics of the complexes. For the analytical work, the complex selected is the one formed quantitatively between pH 4.7 and 5.8 as it shows larger values of absorptivity and bathochromatic shift. Its formation starts at pH 4.3 and its maximum development is at the above pH range. As shown by the application of the method of continuous variations (Fig. 2) stoichiometry of the complex was 3:1 (5.ClDMPAP:Ti(IV)). The order in which the reagents are added is very important. First, the reaction between Ti(IV) and 5.ClDMPAP is promoted at low pH values (<2), and then a 5.0 pH buffer is added, so it is possible to work with the selected complex. According to the

Table 1. Characteristics of the Ti(IV)-5.ClDMPAP Complexes in Aqueous Alcoholic Solutions (55% v/v of Ethanol)

pH range of formation	5.ClDMPAP/Ti(IV) ratio	λ_{max}/nm	Absorptivity dm^3 mol^{-1} cm^{-1}
2.7—4.2	2/1	560	3.69×10^4
4.7—5.8	3/1	580	4.39×10^4
7.8—9.1	2/1	570	2.48×10^4

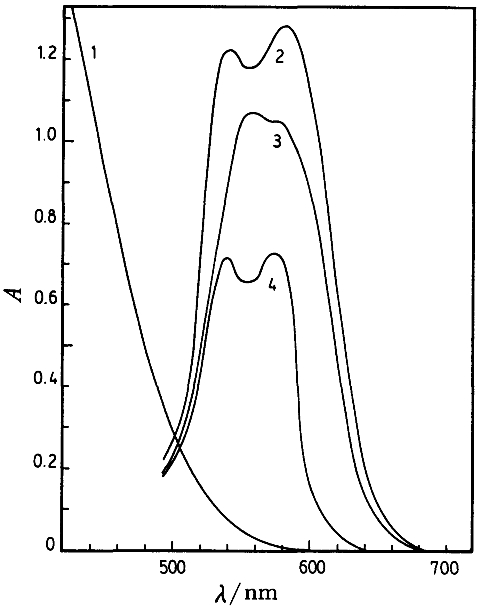

Fig. 1. Absorption spectra of the 5.CIDMPAP; Titanium-5.CIDMPAP complex in aqueous alcoholic solution.
$C_{reag}=1.2\times10^{-4}M$; $C_{Ti}=1.2\times10^{-5}M$; Ethanol-Water 55% (v/v). 1: 5.CIDMPAP vs. pure solvent as blank. 5.CIDMPAP-Ti(IV) complex vs. blank of reagent; 2: pH= 5.0; 3: pH=3.5; 4: pH=8.5.

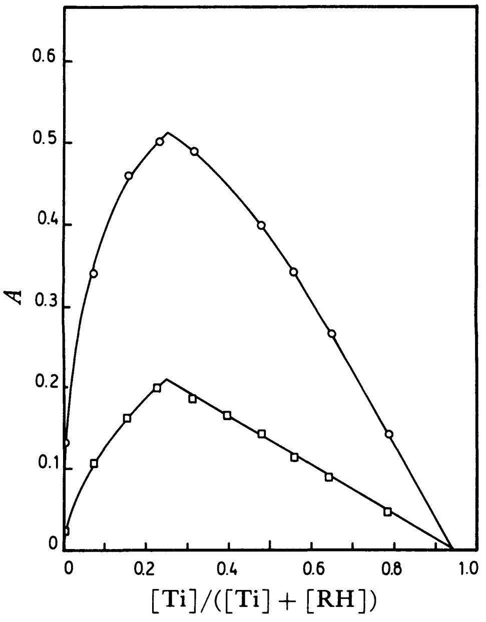

Fig. 2. Continuous variation method applied to the Ti(IV)-5.CIDMPAP complex.
$C_{reag}=C_{Ti}=1\times10^{-4}M$; pH=5.0. Ethanol-Water 55% (v/v).
Wavelength: ○ 580 nm; □ 600 nm.

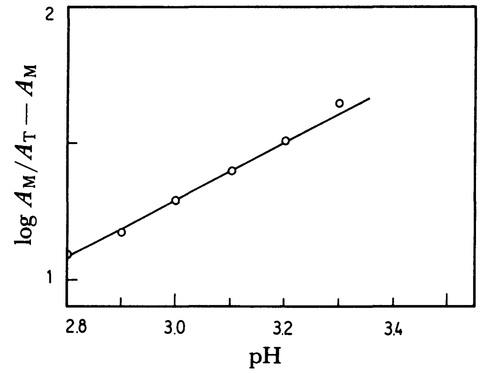

Fig. 3. Equilibrium shift method for determining hydrogen ions released during complexation.
$C_{Ti}=1.7\times10^{-5}M$; $C_{reag}=2.5\times10^{-4}M$; pH=variable; Wavelength 580 nm.
A_M=Absorbance read at unfavorable pH values for the complex formation.
A_T=Absorbance corresponding to a 3.4 pH solution and to a 1.7×10^{-5} M of the complex.

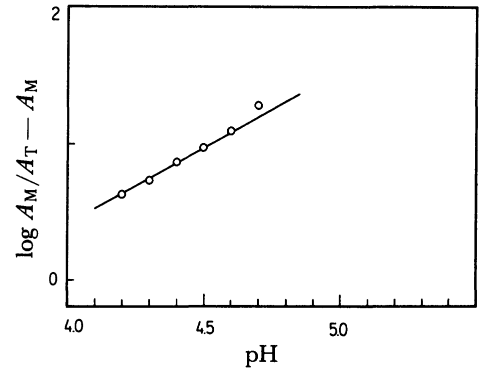

Fig. 4. Equilibrium shift method.
$C_{Ti}=1.4\times10^{-5}M$; $C_{reag}=2.2\times10^{-4}M$; pH=variable; Wavelength 580 nm.
A_M=Absorbance corresponding to a 4.8 pH solution and to a $1.4\times10^{-5}M$ of the complex.
A_T=Absorbance read at unfavorable pH values for the complex formation.

electrophoretic migration studies and the extraction with different solvents (benzene, chloroform, 3-methyl-1-butanol, and nitromethane) which have demonstrated the ionic nature of the chelates formed, and also assuming that $(Ti(OH)_2)^{2+}$ is the predominant species of Ti(IV),[10] the following reactions can be written:

$$(Ti(OH_2))^{2+} + 2RH \rightleftharpoons (Ti(OH)R_2)^+ + H_2O + H^+$$

$$(Ti(OH)R_2)^+ + RH \rightleftharpoons (TiR_3)^+OH^- + H^+.$$

The results obtained by applying the equilibrium shift method[11] (Figs. 3 and 4) have shown a release of one hydrogen-ion for each complexed Ti(IV)-ion in every chelation reaction. The above results sustain the proposed reactions. The equilibrium constant of the chelation reaction was studied by means of absorptiometric measurements;[12] the value obtained was 4.41×10^{15} at 25 °C. Table 2 shows experimental variables of Ti(IV) absorptiometric determination.

Influence of the Nature and Concentration of the Organic Solvent. Considering the poor solubility in water of 5.ClDMPAP and its Ti(IV) complexes, the

Table 2. Experimental Variables of Ti(IV) Absorptiometric Determination

pH Range	4.7—5.8
Solvent	Ethanol-water 55% (v/v)
Stoichiometry	3:1 (Reagent:metal)
Maximum absorption of complex	580 nm
Maximum absorption of reagent	440 nm
$\Delta\lambda$	140 nm
Stability of complex	At least 5 min
Beer's law-sensitivity acidity (pH)	5.0
Molar absorptivity	4.39×10^4 dm^3 mol^{-1} cm^{-1} (s=1228; $\mathrm{Cl}_{\alpha=0.05}^{42690-45270}$)
Optimum concentration range (Ringbom)	0.05—0.7 ppm
Sensitivity of sandell	0.0011 µg/cm^2
Beer's law fulfilment	Up to 0.7 ppm

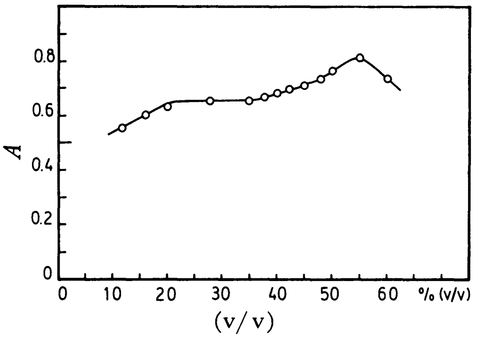

Fig. 5. Influence of the concentration of ethanol on the absorbance of Ti(IV)-5.ClDMPAP complex. pH=5.0; Wavelength 580 nm. Ethanol-Water % (v/v): variable.

addition of an organic solvent miscible in water is necessary. The influence of different solvents (methanol, ethanol, dioxane, acetone, and pyridine) was studied. Experimental results show that there are no changes in λ_{max} of the complex whichever the solvent used, but a maximum absorptivity is obtained when methanol or ethanol are used. The latter was selected for the work. The minimum ethanol concentration necessary to produce a maximum absorbance was 55% (v/v). It is also possible to work with a lower sensitivity by reducing ethanol percentage up to 30% (v/v) (Fig. 5) and no variations in the spectral characteristics or in the stoichiometric of the complex are observed.

Reagent Concentration. To evaluate this variable, a saturation curve was plotted (Fig. 6) at pH 5.0. The Ti(IV) concentration was kept constant 2.4×10^{-5} mol dm^{-3} and the one belonging to 5.ClDMPAP was modified between 2.0×10^{-6} and 1.2×10^{-3} mol dm^{-3}. Absorbance was read at λ_{max}=580 nm and ethanol concentration remained in 55% (v/v). The absorbance of the complex's solutions reached a maximum value for a 15:1 ligand-metal ratio and they remained unaltered for proportions of up to 50:1. On the other hand, the graph shows that the complex formed has a relatively high stability and that, at the same time, proves stoichiometry already established. The complex's solutions at pH 5.0, keeping a 20:1 ligand: metal molar ratio, show no changes in their spectral curves and absorptivity at λ_{max}=580 nm for, at least, 5 minutes.

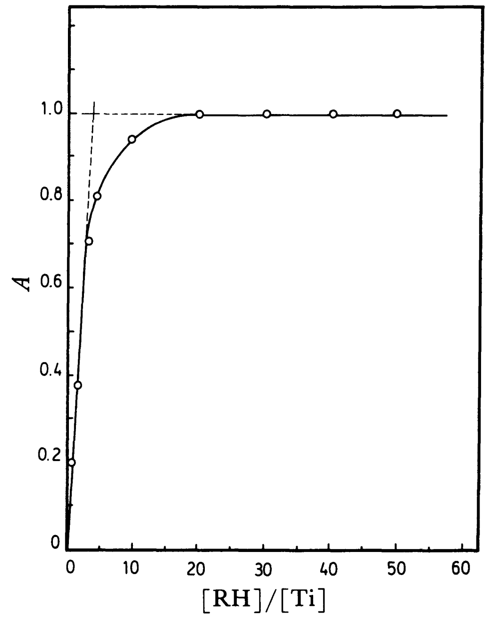

Fig. 6. Saturation curve.
pH=5.0; Ethanol-Water 55% (v/v); C_{Ti}=constant=2.4×10^{-5} M. Wavelength 580 nm.

Effect of Foreign Ions. Under the experimental conditions required for the 5.ClDMPAP complexation with Ti(IV), the reagent also reacts with other metal ions. This is the case for other reagents of this type and thus there occur more or less severe spectral interferences that cannot be controlled by masking. Interferers are Fe(III), Cu(II), Ni(II), Co(II), W(VI), Nb(V), Ta(V), and V(V). The Zn(II), Mn(II), Mo(VI), and Cr(VI) ions are tolerated in a 10:1 molar ratio (foreign ion:Ti(IV)). For Al(III) and Mg(II), the ratio tolerated is 50:1; for Na(I) and K(I), it is 1000:1. Besides, the tolerances for different anions, especially those from strong acids used to dissolve samples and other anions and compounds added as possible masking agents, were delimited. If a maximum 2% error is admitted, the hydrogen phtalate, bromide, perchlorate, sulfate, thiosulfate, and iodide ions may be present in a 2000:1 ratio in front of Ti(IV), whereas thiourea and sulfamic

Table 3. Tolerances for Some Common Cations

Ion	Ion–Ti(IV) tolerated molar ratio	Ion–Ti(IV) tolerated mass ratio	Notes[a)]
Cd(II)	10	26	b)
Co(II)	10	13	b)
Ni(II)	10	13	b)
Mn(II)	20	25	b)
Pb(II)	25	119	b)
Zn(II)	50	75	b)
Mo(VI)	100	220	b)
Cr(VI)	100	119	b)
UO_2(II)	10	58	b)
Fe(III)	5	6	c)
Zr(IV)	10	21	d)
Hf(IV)	10	41	d)

a) Ti(IV) taken: 0.55 ppm. b) Previous extraction with 8-quinolinol 0.1 mol dm^{-3} in chloroform with no masking agents present. (V_o=V_w), at pH 1.5. Probable interferences by Ca(II), Sr(II), Ba(II), La(III), Na(I), and K(I) are also solvent by this method. c) Previous double extraction with 8-quinolinol 0.1 mol dm^{-3} in chloroform with EDTA 0.1 mol dm^{-3} present as masking agent. (V_o=V_w), at pH 8.2. This method is also useful to solve interferences by Co(II) and Ni(II) and it increases the tolerances for Zn(II), Mn(II), Mo(II), Al(III), and Mg(II). d) Previous extraction with 8-quinolinol 0.1 mol dm^{-3} in chloroform with oxalate 0.1 mol dm^{-3} present as masking agent. (V_o=V_w), at pH 8.2.

Table 4. Results in the Determination of TiO_2 in Samples

Sample	Found % (w/w) in this method	Found % (w/w) in standard method[17)]	Error/%
Optical glass type Athermal-50	0.66 (s=0.019), Cl 0.64—0.68, α=0.05	0.67 (s=0.018), Cl 0.65—0.69, α=0.05	1.5

Table 5. Results in the Determination of TiO_2 in Samples

Sample	Composition % (w/w)		Found % (w/w)	Error/%
Glass soda-lime flat (NBS N^0 621)	SiO_2	80.800	0.0118 (s=0.002; $Cl^{0.010-0.014}_{\alpha=0.05}$)	1.6
	Al_2O_3	2.300		
	Fe_2O_3	0.029		
	TiO_2	0.012		
	ZrO_2	0.030		
	CaO	0.020		
	MgO	0.020		
Ceramic material soda-feldspar (BCS N^0 375)	SiO_2	67.10	0.375 (s=0.016; $Cl^{0.358-0.392}_{\alpha=0.05}$)	1.3
	Al_2O_3	19.80		
	Fe_2O_3	0.12		
	CaO	0.89		
	TiO_2	0.38		
	MgO	0.05		
	K_2O	0.79		
	Na_2O	10.40		

acid may exist in a 5000:1 molar ratio. The acetate ion may be present in a 10000:1 molar ratio. The tolerance for oxalate and fluoride were 10:1; for ascorbic acid, 50:1. Tartrate, phosphate, citrate, EDTA, and CDTA also interfere. In order to attain a larger selectivity, the behavior of several reagents (cupferron,[13)] 8-quinolinol,[14)] diethyldithiocarbamate[15)]) that allow Ti(IV) separation by means of liquid-liquid extraction was studied. The extraction procedure using 8-quinolinol and chloroform as solvent, together with pH regulation and the presence of complexing agents, proved to be the most efficient method to separate several interferes.

Method Using 8-Quinolinol and Chloroform. Into a decanting flask, pour 5 cm^3 of solution having between 0.25 and 3.5 ppm of Ti(IV) and the foreign ion under analysis. Then add 5 cm^3 of 8-quinolinol 0.1 mol dm^{-3} in chloroform and stir it vigorously during 5 min; separate the organic phase, put it dry into a porcelain crucible on sand bath and melt it with 0.4 g of potassium hydrogensulfate. Cool it, take it with water and pour it into a 25 cm^3 flask; then add 2 cm^3 of reagent, 6 cm^3 of ethanol, 1 cm^3 of sodium hydroxide 1 mol dm^{-3}, 4 cm^3 of buffer (acetic/acetate) of pH 5.0 and bring it to gauging. Read the solution absorbance at λ_{max}=580 nm against a reference prepared as usual. By the above method, tolerances shown in Table 3 are attained (the maximum admissible error was set in 2%).

The characteristics of interferences by Nb(V), Ta(V), V(V), and Cu(II) made it necessary a new methodology, still under development, which yielded significant results.

Applications. The methodology developed was applied to two kinds of samples:

1. Optical glass: samples: Athermal 50 and Soda-Lime Flat (NBS N° 620). The method applied is as follows: In a platinum crucible, weigh one amount of crushed glass sample having no more than 1mg of TiO_2. Then add 10 cm^3 of sulfuric acid 1:1 and 15 cm^3 of hydrofluoric acid. Evaporate on sand bath until sulfuric acid white fumes appear. Let it get cold and take with 15—20 cm^3 of distilled water. Pour it into a 150 cm^3 flask and heat it until salt dissolution. Pour it into a 100 cm^3 flask (filter in case barium sulfate is present) and bring it up to gauging. Take 2 cm^3 of the filtrate; add 1 cm^3 of solution 0.2 mol dm^{-3} of sodium oxalate and adjust pH at 3.9 in 5 cm^3 as final volume; proceed with the method as above described. Results obtained for Athermal 50 optical glass contrasted against the hydrogen peroxide method[16,17] (Table 4).
2. Ceramic material:sample: Soda Feldspar (BCS N° 375). The method was the same as the one described for glass samples. Results are shown in Table 5.

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