JOURNAL OF RESEARCH of the National Bureau of Standards—C. Engineering and Instrumentation
Vol. 69C, No. 1, January–March 1965

Polarographic Analysis of Titanium (IV)—EDTA Complex: Application to Paint Pigments

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(August 3, 1964)

The Ti^{+4}-EDTA complex, buffered at pH 4.7, has been found to give polarographic waves suitable for the analysis of TiO_2 in paint pigments. A linear relationship between diffusion current and concentration of Ti^{+4} for the range 2.8×10^{-5} to 8.4×10^{-3} M has been observed. The pigments analyzed have been either in the dry form or extracted from whole paint. The method gives results in good agreement with the more complicated and time-consuming standard wet chemical method.

Standard methods for the analysis of TiO_2 in paint pigments involve rather tedious and time-consuming procedures and are also subject to several interfering ions, such as iron, chromium, and arsenic [3,6].[1] In searching for a faster, simpler method, and one which would be comparatively free of interferences, polarography was investigated. A study of the literature revealed that a variety of supporting electrolytes have been used, such as tartrate, citrate, oxalate, ethylenediaminetetraacetic acid (EDTA). These methods have been reviewed by Codell [2]. More recently, Banerjee, Budke, and Miller reported the use of a sulfuric acid-potassium persulfate medium for the determination of titanium in ores [1].

Sinyakova [5] and Pecsok and Maverick [4] studied the chemistry of the Ti-EDTA complex and found that reversible waves could be obtained over a fairly wide pH range. The latter authors suggested that this could be adapted to analytical uses.

This paper reports the development of a polarographic method, employing EDTA as the complexing agent, that results in a rapid, accurate analysis of TiO_2 in dry pigments or pigments extracted from paint.

1. Experimental Detail

1.1. Apparatus and Reagents

A Sargent Model XV Polarograph with a dropping mercury electrode and an H-cell were used. The cell was placed in a constant temperature bath maintained at 25.0±0.1 °C. Measurements of pH were made with a glass electrode pH meter.

Reagent grade titanium dioxide was used to determine the diffusion current constant (I_d). This standardization and calibration was checked with National Bureau of Standards Titanium Dioxide (Standard Sample No. 154).

1.2. Procedure

For pure samples of titanium dioxide a maximum of 0.2 g was weighed to 0.1 mg into a 100 ml beaker and 5.0 ml of concentrated H_2SO_4 and 1.0 g of $(NH_4)_2SO_4$ were added. The beaker was left uncovered, heated slowly at first and then rapidly, to fuming. After fuming for 5 min, the solution was cooled to room temperature and 15 ml of water was added very slowly with vigorous stirring. Two grams of the disodium salt of EDTA, dissolved in 15 ml of 7M NH_4OH, was then added to the sulfuric acid solution. The pH at this point was approximately 1.5 and 40 ml of 4M sodium acetate-acetic acid buffer was added to bring the pH to 4.7. The solution was diluted with water to a final volume of 250 ml. An aliquot was placed in the H-cell and purged with nitrogen for 10 min. A polarogram was then run. The graphical method described by Willard, Merritt, and Dean [7] was used to determine the wave heights.

The sulfuric-acid-insoluble components, such as white lead and silica, in titanium-containing pigments caused the formation of large aggregates which could not be adequately dispersed without prolonged heating. Therefore, it was necessary to modify the method for the preparation of solutions. After fuming for 5 min, the mixture was stirred thoroughly with a glass rod to break up any lumps of pigment. The mixture was then reheated to fuming for 1 min. The procedure for pure TiO_2 was then followed. It was found to be unnecessary to filter the mixture before running a polarogram.

2. Results and Discussion

2.1. Standardization

The data obtained for the analyses of reagent grade TiO_2 are shown in table 1. The I_d is independent of the concentration of titanium over the range 3×10^{-5} to 8×10^{-3} M. Although for the

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[1] Figures in brackets indicate the literature references at the end of this paper.

purposes of pigment analysis it would be unnecessary to deal with concentrations at the lower end of the range, the method was investigated to these further limits to assess its potential for use as a general method of analysis which would be valid over a rather large concentration range.

The electrode reaction at pH 4.7 is [4]:

$$\mathrm{TiOY^{-2}+2H^{+}+e^{-}=TiY^{-}+H_2O}$$

where Y represents the EDTA ligand. This equation is, in fact, valid for values of pH from about 2.5 to 8. Below pH 2.5 the electrode reaction is $\mathrm{TiY}+e^{-}=\mathrm{TiY^{-}}$. From calculations using the reported values for the equilibrium constants the concentrations of $\mathrm{TiOY^{-2}}$ and $\mathrm{TiY^{-}}$ are equal at a pH of 2.4.

Table 1. *Polarographic analysis of titanium-EDTA complex using reagent grade* $\mathrm{TiO_2}$

	T(IV) concentration mmoles/liter	Diffusion current i_d(μA)	Diffusion current constant I_d[1]
1	0.02804	0.0786	1.454
2	.06003	.1692	1.462
3	1.532	4.312	1.460
4	2.944	8.323	1.466
5	2.959	8.320	1.458
6	5.842	16.620	1.476
7	5.872	16.616	1.468
8	5.907	16.750	1.471
9	6.824	19.218	1.461
10	6.859	19.213	1.453
11	8.145	23.159	1.475
12	8.190	23.15	1.466
13	8.225	23.386	1.475
14	8.270	23.376	1.466
15	8.446	23.924	1.465
Average			1.465
Standard deviation			0.007_3

[1] $I_d=i_d/Cm^{2/3}t^{1/6}$.
C=concentration in mmoles/liter.
m=drop mass in mg/sec.
t=drop time in seconds.

The electrode reaction taking place below pH 2.5 was not used as the basis of an analytical procedure because the solubility of EDTA in such acidic solutions is below that which will permit the preparation of clear solutions containing 2 g of the disodium salt. In addition, at pH 2.5, three forms of EDTA are present: $\mathrm{H_4Y}$, $\mathrm{H_2Y^{-2}}$ and primarily $\mathrm{H_3Y^{-}}$. Between pH 3.5 and 5.5, essentially the only form present is $\mathrm{H_2Y^{-2}}$. It is preferable that only one form of the ligand be involved in the complexation reaction. At pH 4.7, well defined, reversible polarographic waves are obtained which have low residual currents and flat plateau regions.

2.2. Effects of Supporting Electrolyte

The effect of sulfate ion concentration on the diffusion current (i_d) is shown in figure 1. With an excess of sulfate, added during the solution step, a wave appears at −0.7 V. versus the Saturated Calomel Electrode (S.C.E.), (curve C). This wave, attributed to a Ti-sulfate complex (curve A) [4], is formed at the expense of the Ti-EDTA complex and begins to appear at approximately 0.7 M $\mathrm{SO_4^{-2}}$. The addition of a large excess of EDTA does not achieve the complete removal of this wave. The Ti-EDTA reduction wave is shown in curve B. The effect of increasing sulfate concentration on the diffusion current of the Ti-EDTA complex is shown in figure 2. There is a linear decrease of i_d, and thus a decrease in the assay of titanium, with increase in the sulfate ion concentration and it is, therefore, necessary that the sulfate concentration be kept low and constant. In the routine preparation of solutions the concentration of sulfate can be sufficiently controlled to account for less than 0.1 percent change in the diffusion current. On the other hand, the Ti-EDTA diffusion current is

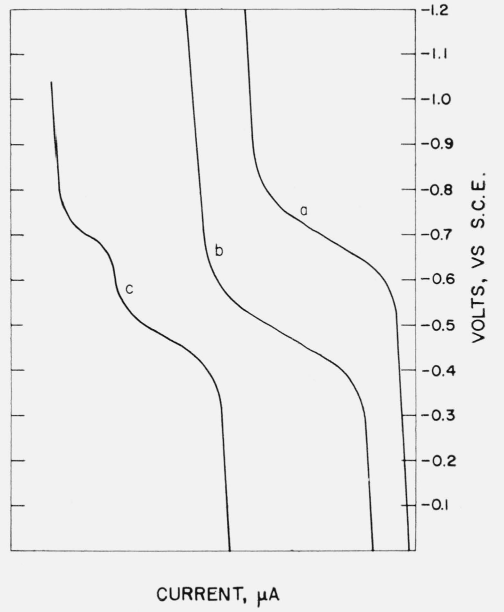

Figure 1. *Representative polarographic curves.*

a. $\mathrm{H_2SO_4}$ solution of Ti(IV)−no EDTA 0.4 M $\mathrm{SO_4^{-2}}$ pH=4.5.
b. Same as above but with EDTA pH=4.7.
c. Same as b., but with 1M $\mathrm{SO_4^{-2}}$.

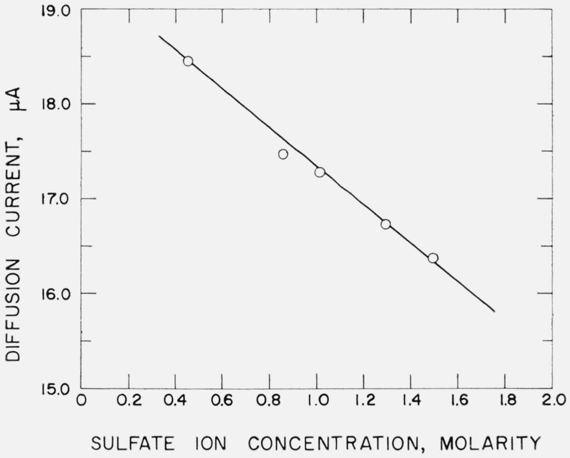

Figure 2. *Effect of sulfate ion concentration on the Ti(IV)−EDTA diffusion current.*

independent of the total concentration of EDTA over a range of 8 to 40 mM.

The order of addition of reagents has a pronounced effect upon the diffusion current. Addition of the buffer to the sulfuric acid solution prior to the addition of EDTA results in the formation of a different titanium complex which cannot be completely eliminated by the subsequent addition of EDTA.

2.3. Effect of Aging

Figure 3 illustrates the decrease of the diffusion current with time. About one week after the preparation of solutions a yellow color became noticeable and increased in intensity with time. Erratic results were obtained if solutions were left standing more than three days.

2.4. Effect of Temperature

The temperature dependency of the diffusion current was studied over the range of 20 to 30 °C. It was found that an increase of 1.4 percent in the diffusion current occurred for each degree rise in temperature.

2.5. Effect of Maximum Suppressor

No polarographic maxima were encountered in the analyses of the titanium-EDTA solutions and no maximum suppressors were used. When some other reducible cations are in solution, however, small maxima do occasionally occur. The effect of gelatin on the titanium-EDTA diffusion current was studied in the event that the simultaneous analysis of titanium and other cations might necessitate the presence of a maximum suppressor. The effect of gelatin on the diffusion current is shown in figure 4. Between 0.008 percent and 0.05 percent i_d decreases rapidly with increasing percentages of gelatin. Therefore, analyses should not be performed in this range. Lower percentages of gelatin are preferable if they succeed in eliminating maxima since maximum suppressors tend to change the values of the parameters in the Ilkovic equation, which is used to calculate I_d.

2.6. Interferences

A study was made of possible chemical interferences in the analysis. Weighed amounts of compounds were added in 1:1 molar ratios to the TiO_2 before dissolving in sulfuric acid. Al(III), Mg(II), Ca(II), Cr(III), Pb(II), Zn(II), and Fe(III) did not interfere in the analysis. Sb(III), however, did cause interference. In all of these determinations, it was necessary to have sufficient EDTA present to fully complex the foreign cations. For example, lead and zinc will compete for EDTA and, if those cations are added to a solution in which there is not sufficient EDTA available, the Ti-EDTA complex will dissociate so that the preferential lead and zinc complexes will form. In such cases, a titanium wave attributable to the Ti-sulfate complex appears which cannot be completely removed on the further addition of EDTA.

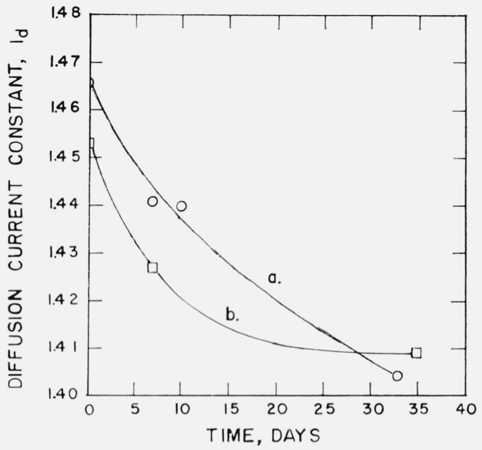

FIGURE 3. *Effect of time on the Ti(IV)–EDTA diffusion current constant.*

a. 0.1652 g. TiO_2/250 ml.
b. 0.1370 g TiO_2/250 ml.

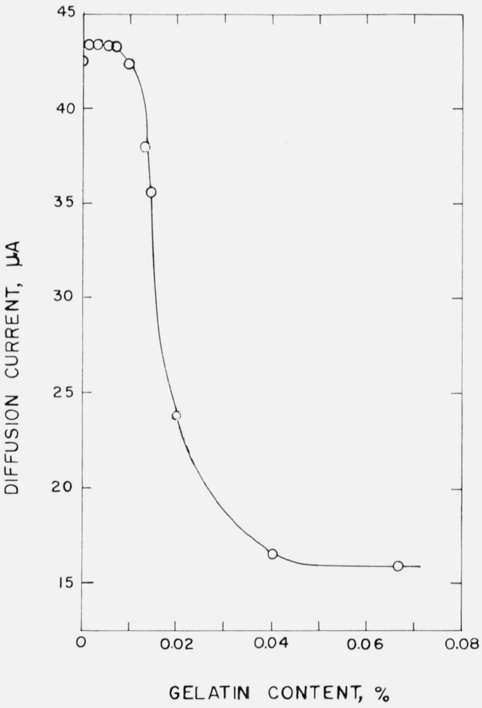

FIGURE 4. *Effect of gelatin on the Ti(IV)–EDTA diffusion current.*

2.7. Analysis of Pigments

Table 2 presents data on the analysis of pure TiO_2 as well as several pigments extracted from paint and a synthetic pigment extracted from a mixture of white lead, zinc oxide, titanium dioxide and bodied linseed oil. The standard method referred to in the table utilizes the Jones reductor method for the titanium analysis [3]. The precision and accuracy of the polarographic method is seen to be comparable to the standard volumetric method. In addition, the polarographic method is considerably faster, less subject to interferences and requires smaller sample weights.

TABLE 2. TiO_2 *Assay of NBS standard and paint pigments*

Sample	Titanium dioxide content		Difference in methods
	% by Volumetric method	% by polarographic method	
1 Reagent grade	99.46±0.30 [4]	(1)	
2 NBS std.[5]	98.58±0.14	98.57±0.06	−0.01
3 Synthetic pigment	22.71±0.19	22.61±0.19	−0.10
4 TT-P-102 [3]	13.27±0.25	13.41±0.22	+0.14
5 TT-P-115	13.84±0.16	13.40±0.10	−0.44
6 TT-P-115 [2]	$13.5_6 \pm 0.2_2$		−0.16
7 TT-P-25	8.62±0.11	8.54±0.09	−0.08
8 TT-P-21	3.87±0.30	3.78±0.15	−0.09
Average omitting run 5			0.10

[1] Reagent Grade TiO_2 used as standard material.

[2] Analysis of same pigment used in Run 5 by spectrophotometric method (Beckman D. U. Spectrophotometer) to check large difference between volumetric and polarographic results.

[3] Sample numbers refer to Federal Specification of the original paint from which pigment was extracted.

[4] Average of at least four determinations on all samples; precision is expressed as standard deviation.

[5] Standard Sample No. 154 certified as 98.7 percent TiO_2.

The authors express their appreciation to George Marinenko and John K. Taylor of the National Bureau of Standards for their help and encouragement throughout the course of this work.

3. References

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(Paper 69C1–187)