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Colorimetric Determination of Titanium as Peroxomethylenediaminetetracarboxylate

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The system Ti-H_2O_2-methylenediaminetetracarboxylate generates a ternary complex that has strong absorption at 364 nm in acetate buffered medium (pH *ca.* 4.5). The quantifiable concentration at lower end for Ti at 0.4 ppm is sensitive enough to warrant its analysis in low ionic contents.

INTRODUCTION

The element titanium due to its industrial and commercial importance has been analyzed in a variety of samples by atomic absorption spectrophotometry[1] or molecular absorption spectrophotometry[2, 3]. Amongst the colorimetric reactions, the Ti-H_2O_2 reaction is better known and has been well explored, and it still remains an inexpensive and useful analytical method[2, 3]. The weak molar absorptivity of titano-peroxo complex (7×10^2 L $mole^{-1}$ cm^{-1}) has been enhanced through ternary complexation by addition of complexing ligands *e.g.* EDTA or CDTA to help improve the analytical sensitivity.[4–6] Several analytical applications incorporating Ti-peroxo complexation have been developed for titanium analysis in steels[7], minerals and alloys[8, 9] and plastics and food materials.[10, 11]

In our continued studies dealing with development of novel uses of colored reactions of analytical interest, newer ligands derived from polyaminocarboxylic acids are being examined for the quantification of common and uncommon elements. The present study explores the use of methylenediaminetetracarboxylic acid for Ti analysis. The primary objective of this study was to examine complexation behaviour of the new complexon toward Ti and compare the efficacy of the titano peroxomethylenediaminetetracarboxylate complex, if formed, with respect to other known titanium peroxo complexation reactions with ligands EDTA and CDTA.[5, 6]

EXPERIMENTAL

The reagents employed in this study were always prepared in deionized distilled water. The stock solution of the complexon, 1-methylenediaminetetracarboxylic acid, procured from Aldrich Chemicals, USA was prepared at 0.025 M, while for Taitanium its 1000 ppm atomic absorption standard was diluted to appropriate concentration when required. Other reagents required were of analytical grade purity or better. The analytical data were recorded on Cary-I, auto-recording UV-Vis spectrophotometer of 0.0001 AU sensitivity in conjunction with 1 cm matched quartz cells.

The titano-peroxomethylenediaminetetracarboxylate complex was developed in an aqueous system by addition of 5 mL of 3% H_2O_2 and 5 mL of acetic acid-sodium acetate buffer (1 M) followed by addition of 2.5 mL 0.025 M complexon to a titanium solution (8.35×10^{-4} M) in 25 mL volume. The solution was brought to boil and allowed to equilibrate for 5–10 min and then cooled to room temperature before completing the volume. The absorption spectrum of the system was followed in 200–800 nm range against a blank prepared similarly with buffer and hydrogen peroxide solution only. The systems titano-peroxo and titano-peroxomethylene-diaminetetracarboxylate were compared under identical experimental conditions. The experimental parameters (pH, ligand concentration, contact period) were established at the system λ_{max} of the species formed. The interference effects of common cations and anions were examined at equal or elevated concentrations compared to Ti concentration in the system under the optimized condition.

RESULTS AND DISCUSSION

The tetracarboxylic functionality of methylenediaminetetracarboxylic acid renders it similar to the well known ligands of parallel structure like EDTA or CDTA, which form strong 1 : 1 complexes with common and transition metal ions.[12] The complexation reactions of methylenediaminetetracarboxylic acid in this regard have been investigated with metal ions. In an identical pattern, formation of strong and stable 1 : 1 complexes has been observed in many a case.[12] Though Ti complexation reaction is not mentioned, yet it is presumed to follow the same course. In fact an analytical application of methylenediaminetetracarboxylic acid for simultaneous spectrophotometic determination of Cu and Co has been developed.[13] Hardly any other analytical use of this complexon is to be found in the literature. Since Ti-H_2O_2-EDTA and Ti-H_2O-CDTA systems absorbing in UV have been found effectivc in the characterization of Ti ion,[5, 6] it was thought to explore the Ti-H_2O_2-methylenediaminetetracarboxylate system and evaluate its analytical potential.

Some interesting features emerge from the interactions involving Ti, H_2O_2 and the new complexon. The experimental data show that in a direct Ti-complexon reaction, in an acetate buffer, no absorption peak occurs, and only an absorption is seen in 200–500 nm range. Interestingly the Ti-H_2O_2 system also in the acetate buffered medium behaves similarly .though has somewhat superior absorption compared to that of the Ti-methylenediaminetetracarboxylate species. However, when Ti-H_2O_2-complexon system is examined under similar conditions, not only the absorbance is enhanced still further, but the system is characterized by an absorption peak at 364 nm as seen in Fig. 1. The ternary Ti-peroxo-methyelene-diaminetetracarboxylate species is fully formed when the ligand concentration is about 3-fold or more in excess of the Ti concentration. The molar absorptivity of the complex is 1.13×10^3 L mole^{-1} cm^{-1}. The specific absorptivity (*i.e.* absor-

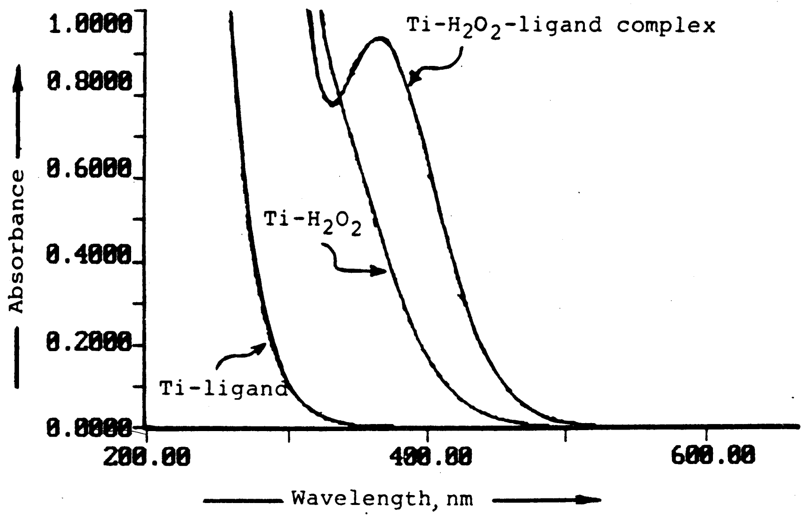

Fig. 1. Spectral behaviour of Ti species as peroxo-methylenediaminetetracarboxylate complexes: pH 4.5; Ti 8.35 × 10^{-3} M; ligand 2.5 × 10^{-3} M

bance for 1 μg/mL analyte) has been found to be 0.0236, while the sensitivity index (Sandell's sensitivity) observed is 0.0424 units. The empirical structure can be attributed similar to that seen with EDTA as $[TiO(H_2O_2)Y]^{2-}$ for such ternary complexes. The linear analytical response for Ti occurs in 0.40–40 ppm range under the described experimental conditions (Fig. 2). The analytical sensitivity at the lowest quantifiable concentration for Ti (0.4 ppm) is certainly superior to that of Ti-H_2O_2 reaction (2 ppm) or even Ti-H_2O_2-EDTA reaction (4 ppm) observed by the earlier authors.[6] The absorbance system has favorable reproducibility since even at 1 ppm Ti the relative standard deviation remains of the order of 5% ($\eta = 5$).

However, the pH control in 0.5–5.0 range is not critical but it is important to avoid absorbance variations if it is displaced toward alkaline condition, where absorption of the system decreases significantly particularly beyond pH 8.0 or so. The common ions (Na, Ca, Mg, Cr, Mn, Co, Ni, Cu, V, Cl^-, NO_3^- and SO_4^{2-}) at 5-fold excess over 10 ppm Ti did not offer any serious interference but for most of these positive errors exceeding 8–10% occcur when their concentrations exceed 25-fold excess over Ti.

The data show that Ti-H_2O_2-methylenediaminetetracarboxylic acid reaction can be regarded as a shade superior to the similar reactions examined with EDTA or CDTA. Comparative parameters (Table-1) are auto-demonstrative of the advantages in this case. Improved lower detection limit for Ti is very impressive with newer complexon and in part can also be attributed to more sensitive instrumentation available today compared to earlier years. Attempts were made to analyze Ti by this approach in natural aqueous systems (river waters and potable waters). However, none was detected, which is not surprising since natural absorbance of Ti in environmental waters (sea water or fresh water) rarely exceeds 1 μg/mL that is much lower than the detection limit of the method.[14] Interestingly

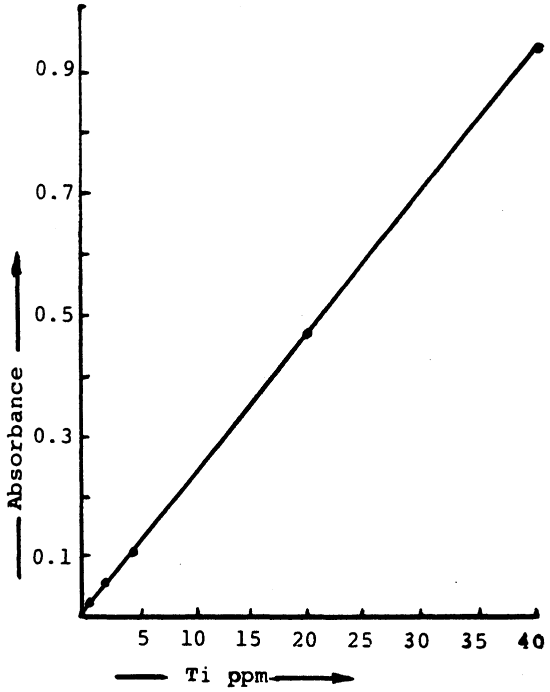

Fig. 2. Linear analytical response of Ti-H_2O_2 methylenediaminetetracarboxylate at 364 nm, pH 4.5

the analytical sensitivity of this reaction is superior to that of the sophisticated flame atomic absorption technique for Ti utilisable only in N_2O/C_2H_2 mode that offers a detection limit of 1.2 ppm[1]. In conclusion, for samples of low ionic contents this method is adaptable for μg analysis of Titanium.

TABLE-1
COMPARATIVE DATA ON Ti-PEROXO-COMPLEXON SPECIES

Ligand	λ_{max} nm	pH	$\varepsilon \times 10^2$ L mole^{-1} cm^{-1}	Analytical range (ppm)	Reference
EDTA	365	0.4–4.0	—	4–40	5
CDTA	370	0–5.0	8.26	1–60 (mg/sample)	6
Methylene- diamine-tetracaboxylic acid	364	0–5.0	11.30	0.4–40	This study

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