

A New Analytical Procedure for Quantitative Determination of Ti (IV) in Rocks and Sand Samples.

Dr. Jamal Younis Hamdo *

(Received 28 / 5 / 2009. Accepted 16 / 8 / 2009)

□ ABSTRACT □

A simple, selective and sensitive spectrophotometric method has been proposed for the determination of Ti(IV) using a newly synthesized 3- acetylpentane-2,4-dione (ACPD). The effect of pH, time of reaction and temperature were estimated. The stoichiometry of the complex was found to be 1:10 (metal:ligand).The effect of foreign ions in the determination of Ti(IV)) was investigated. Beer's law is obeyed for titanium concentration in the range (5 - 95 μ g/25 ml)at 400 nm.The molar absorptivity and Sandell's sensitivity of the coloured complex are $1.5 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, and $3.20 \times 10^{-3} \mu\text{g. cm}^{-2}$ respectively. The RSDs was below 3.5%. The proposed method has been successfully applied to determine of titanium in natural and standard samples.

Keywords: titanium(IV),3-acetylpentane-2,4-dione,analyticalreagent, spectrophotometry.

* Associated Professor, Department of Chemistry, Faculty of Science, Damascus University, Damascus-Syria.

طريقة تحليلية جديدة لتعيين Ti(IV) في العينات الصخرية والرملية

الدكتور جمال يونس حمدو*

(تاريخ الإيداع 28 / 5 / 2009. قُبل للنشر في 16 / 8 / 2009)

□ الملخص □

تعرض هذه الورقة البحثية طريقة تحليلية جديدة لتعيين التيتانيوم طيفياً باستخدام كاشف تحليلي جديد هو " 3- أسيتيل بنتان -4،2- ديون الذي يتفاعل مع Ti(IV) ويشكل معقداً بامتصاصية أعظمية عند الطول الموجي $\lambda_{max} = 400 \text{ nm}$. تتصف هذه الطريقة بالبساطة والانتقائية والحساسية العالية وسرعة التنفيذ. درس تأثير حموضة الوسط و كمية الكاشف التحليلي و زمن التفاعل ودرجة الحرارة ووجود أيونات التداخل في تعيين التيتانيوم وعينت الشروط المثلى للتعيين. وجد أن امتصاصية المعقد تخضع لقانون بير في مجال واسع من تركيز Ti(IV) (5 - 95 $\mu\text{g}/25 \text{ ml}$). كما وجد أن معامل الامتصاص المولي لهذا الكاشف يساوي $1.5 \times 10^4 \text{ L.mol}^{-1}\text{cm}^{-1}$ وأن حد الكشف يساوي 0.01 $\mu\text{g}/ \text{ml}$ ومعامل ساندل يساوي $3.20 \times 10^{-3} \mu\text{g} .\text{cm}^{-2}$ وأن الانحراف المعياري النسبي لا يتجاوز 3.5%. طبقت هذه الطريقة في تعيين Ti(IV) في بعض العينات المعيارية والطبيعية.

الكلمات المفتاحية: التيتانيوم (IV) ، 3 - أسيتيل بنتان -4،2-ديون ، كاشف تحليلي ، التحليل الطيفي .

* أستاذ مساعد - قسم الكيمياء - كلية العلوم - جامعة دمشق - دمشق - سورية.

Introduction:

Titanium has some unusual metallic characters. It is a lightweight, silver-gray metal. It has an excellent corrosion resistance and a high strength to weight ratio. It has very important and extensive uses in catalysts, paint pigments and corrosion inhibitors. It is valuable alloying agents and coexist in a number of industrially important alloys and steels. Alloys of this metal are used principally in missile, aircraft parts and filament material in electrical applications where lightweight, strength and ability to withstand extreme temperatures are important [1-4].

Because of its widespread use, the development of highly sensitive and selective spectrophotometric methods for titanium determination is essential. Various analytical techniques used for the determination of titanium in different types of matrices. Flame atomic-absorption spectrophotometry has unavoidable limitation, owing to the formation of highly stable oxide species in the flame, and atomic-absorption spectrometry with electro-thermal atomization generally involves expensive instrumentation, not available in all laboratories [5,6].

Spectrophotometric methods occupy special position due to their simplicity, less expensive instrumentation and high sensitivity.

A literature survey revealed that over the years a variety of reagents of titanium such as hydrogen peroxide and diantipyrylmethan were applied [7-8]. The first has low sensitivity and the second has a low reaction rate and some foreign ions like iron(III) interfere seriously with both of them. Some of new azo derivatives from gallic acid were synthesized but their analytical performances were incompletely reported [9].

Some researchers developed highly selective spectrophotometric method for titanium in various mineral ores through precipitation Ti(IV) with some chromogenic reagents, then treatment the insoluble complexes with anionic surfactant to converse it to soluble complex [10], however there is not enough clear data about period of precipitation, and the complexity of the process using anionic surfactant during analysis.

On the other hand, some pretreatment, as liquid-liquid extraction have been proposed to enhance the sensitivity, but some significant interferences are observed [11-16].

In this paper, a newly synthesized 3-acetylpentane-2,4-dione (ACPD) is suggested as a chromogenic reagent for titanium. A rapid and simple method for spectrophotometric determination of titanium has been proposed and applied to the determination of this metal in rock, sand and standard samples of divers kinds. The distinct advantage of the proposed method is that the commonly associated metal ions, especially Zn, Pb, Ni, Al, W, Cr and Fe (using masking agent for Fe^{3+}) could be tolerated in considerable excess.

Experimental:

a) Apparatus

All absorbance measurements and absorption spectra were run by Spectro123-Labomed/USA using 1cm quartz cells. The pH value of solutions was controlled using an Orion pH-meter with combined glass electrode.

b) Reagents

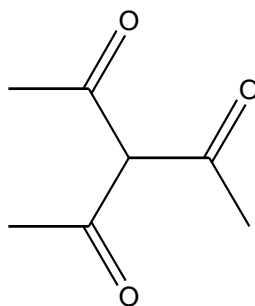
All chemicals used were of analytical grade, and distilled water was used throughout the study. A stock solution of titanium(IV) was prepared by fusing 0.3744 g of high-purity titanium oxide TiO_2 with potassium hydrogen sulphite. After completion of fusion, the residue was dissolved in 8 mL of concentrated sulphuric acid, diluted by distilled water to 1 L. The final solution of approximately $5.00 \times 10^{-3} \text{M}$ was standardized by an EDTA back-

titration procedure with bismuth and xylenol orange indicator, in presence of hydrogen peroxide. Other metal ion solutions were made from their salts or from the pure metals . The solutions were standardized and working solutions of lower concentration were obtained by dilution. $\text{NH}_3\text{-HAc}$ Buffer solutions were prepared by mixing 200 ml of 1.0 M acetic acid solution and 200 ml of 1.0 M ammonia solution, then, pH adjusted on to a suitable value by adding acetic acid or ammonia. The 3- acetylpentane-2,4-dione(ACPD) was synthesized and purified in the laboratory according to the method [17]. Solution of 2% ACPD was made by acetone-distillated water 1:1(v/v).

Results And Discussion:

The tautomeric properties of ACPD in its aqueous solutions were the base which accredits for using it as spectrophotometric reagent for titanium(IV). It has a high ability to form stable complexes with some transition ions in its Enole form. ACPD is accounted as a strong complex former because of presence of three high electro-negativity oxygen atoms in its structure which acts as a Lewis base while a transition ions act as an acid Lewis.

In order to achieve maximum sensitivity, the one-factor-at-a-time method was used to optimize the experimental parameters. The effect of several buffer solutions $\text{NH}_3\text{-HAc}$, HAc-NaAc , $\text{NH}_4\text{Cl-NH}_3$ and $\text{Na}_2\text{B}_4\text{O}_7\text{-HCl}$ were examined on the Ti(IV)- 3-acetylpentane-2,4-dione(ACPD) complex formation. The results indicated that color reaction in $\text{NH}_3\text{-HAc}$ buffer solution has the best sensitivity and was selected as medium for the subsequent experiments.



3- acetylpentane-2,4-dione

a) Absorption Spectra of ACPD :

To 25 ml calibrated flask, a 2 ml of 2% ACPD solution was introduced to, then diluted to volume with buffer solution (pH 1-9), mixed well and after 5 minutes the absorbance of solution was measured at various wave lengths against acetone-water solution. It was found that λ_{max} was at 260 nm for all values of pH which indicates that there is one chromogenic group in the structure of this compound(ACPD).

b) Absorption Spectra of the Complex Ti(IV)- ACPD:

Study of absorption spectra of ACPD with Ti(IV) was carried out at various values of pH and wave lengths as follows : in to 25 ml calibrated flask, 4 ml 1×10^{-3} M of Ti(IV) solution and 2 ml of 2% ACPD solution were added ,then diluted to volume with buffer solution (pH 1-9), mixed well and after 5 minutes the absorbance of solution measured at wave length against blank prepared in a similar way but without Ti(IV). Results showed that constant maximum absorbance was obtained at pH 5 .Both increase and decrease of pH at this value gradually affects the stability and sensitivity of the complex.

At pH>5 a decrease of absorbance may be due to the hydrolysis of Ti(IV). At pH<5 a decrease of absorbance could be due to formation of a new cation resulting from reaction between hydrogen ions and the electron pairs in oxygen atoms. Absorption spectra of complex Ti-ACPD vs wave lengths at pH5 was studied in the same way. The maximum absorption was found to be at 400 nm.

c) Effects of the Reagent Concentration:

Under optimum conditions (pH5 and $\lambda_{\max}=400$ nm), the reagent concentration of ACPD, leading to maximum color stability was 10 times greater than the concentration of titanium ions.

d) Effect of Temperature and Time:

The effect of temperature on the reaction was studied at different temperatures under optimum conditions. The absorbance was stable between 25°C and 62°C then it dropped down gradually, which may be due to dissociation of the complex.

The effect of time on the reaction was observed from 1 min to 400 min under optimum conditions. Absorbance reaches a maximum value within 5 minutes at room temperature (25°C) and remains stable for at least 6 h.

e) Effect of Interfering Ions.

The effect of various foreign ions at $\mu\text{g mL}^{-1}$ levels on the determination of Ti(IV) was studied comparing with well known spectrophotometer reagents for Ti(IV) such as Diantipyrylmethane DAM [18], 2,2-Bichenoksalilu BCK [19] and triton305 TN [20]. The tolerance limits of interfering species were established at those concentrations that do not cause more than $\pm 2.5\%$ error in absorbance values of Ti(IV) at $1.0 \mu\text{g mL}^{-1}$ in the presence of foreign ions. Tolerance limits of foreign ions are listed in Table 1.

Table (1). Tolerance limits of foreign ions in the determination of titanium(IV)

Tolerance Ion	ACPD	DAM	BCK	TN
Zn(II)	1:200	Impossible	1:100	1:150
Pb(II)	1:155	--	1:100	1:100
Ni(II)	1:145	1:1	1:50	1:150
Cd(II)	1:110	1:1	1:100	--
Mg(II)	1:320	Impossible	--	1:100
Mn(II)	1:95	--	1:10	1:20
Cu(II)	1:15	1:10	--	1:20
Al(III)	1:100	1:10	1:1000	1:100
Ga(III)	1:20	1:1	--	--
Bi(III)	1:20	1:5	1:100	--
Rare Earth	1:25	1:1	--	--
Fe(III)	1:200 ¹	Impossible	--	Impossible
Cr(III)	1:100	1:5	1:5	1:100
Th(IV)	1:150	--	--	--
F ⁻	1:150	1:100	--	--

¹ Using F⁻ as masking agent.

I ⁻	1:100	1:10	--	--
WO ₄ ²⁻	1:320	1:2	1:100	1:20
Citric acid	1:140	--	--	--

Results showed that many inorganic ions except iron do not interfere in the determination of Ti(IV). It's important to note that, fluoride ions F⁻ don't interfere in the determination of Ti(IV) if it was less than 350 times of titanium in the sample. It gave us ability to obviate the effect of interfering iron ions. Thus F⁻ may be used as a masking agent to obviate the effect of iron ions interference.

f) Analytical Performance

The calibration graph was constructed under optimum conditions. A linear calibration graph was obtained for 5 µg to 95 µg Ti(IV) in a final volume of 25 mL. A negative deviation has been observed at higher concentration. The detection limit was found to be 0.01 µg mL⁻¹. The calibration graph has a correlation coefficient of 0.999. The molar absorptivity, and the Sandell's sensitivity of the method were found to be 1.5×10^4 L mol⁻¹ cm⁻¹ and 3.2 µg cm⁻², respectively. The reliability of the method was established by determination Ti(IV) in standard solutions of 8, 30, and 50 µg of T(IV) in a volume of 25 mL. Nine replicate determinations of each concentration gave relative standard deviations (RSD) and relative analytical error not exceeding 3.5% and 0.028 respectively.

Also a comparison between the spectrophotometric determination of titanium by the ACPD method and by other methods was carried out (table 2) [21]. The method is found to be both more sensitive and selective than most of the reported methods.

Table(2). Comparison between the ACPD Spectrophotometric Method and common known methods[21].

Reagent	Acidity	λ_{max} (nm)	Molar absorptivity (L.mol ⁻¹ .cm ⁻¹)	Interference ions
Hydrogen Peroxid	H ₂ SO ₄	410	0.7×10^3	Fe ³⁺ , V ⁵⁺ , U ⁶⁺ , Mo ⁶⁺ , C ₂ O ₄ ²⁻ , Citrate
Chromotroc Acid	pH 2.7-4.6	410	1.15×10^4	Fe ³⁺ , Zr ⁴⁺ , F ⁻ , Oxidants
Tiron	pH 4.3-9.6	390	1.59×10^4	Fe ³⁺ , Zr ⁴⁺ , V ⁵⁺ , U ⁶⁺ , Mo ⁶⁺ , Al ³⁺ , Cu ²⁺ , Rare Earth
Phenylfluorone	pH 9-10	460	--	Fe ³⁺ , Zr ⁴⁺ , V ⁵⁺ , U ⁶⁺ , Mo ⁶⁺ , Cr ⁶⁺ , W ⁶⁺ , Nd ⁵⁺ , Ta ⁵⁺
Gallic Acid	pH 4.5-5.3	400	9.0×10^3	Fe ³⁺ , W ⁶⁺ , V ⁵⁺ , Mo ⁶⁺
Diantipryl-methane	0.5M HCl	385	1.5×10^4	Fe ³⁺ , Zn ²⁺ , Cd ²⁺ , Hg ²⁺ , Sb ³⁺
Salicylfluorone	0.03-0.11M HCl	534	2.04×10^5	Fe ³⁺ , Ge ⁴⁺ , Sb ³⁺ , Mo ⁶⁺ , V ⁵⁺ , Ta ⁵⁺ , Sn ²⁺ , C ₂ O ₄ ²⁻ , Citrate
ACPD	pH 5	400	1.5×10^4	See table 1

g) Application of the Method:

The proposed method was successfully applied to the determination of Ti(IV) in rocks, sea sand and standard samples. The follow-up method for determination of Ti(IV) in one rock sample was carried out, while the other samples were analyzed in the same

manner. About 1.00g of accurately weighed, finely powdered rock sample was fused with potassium hydrogen sulphate (about 55 g) and diluted to 1L with concentrated hydrochloric acid and distilled water so as to maintain the final acid concentration of about 10 M of HCl. The result obtained were compared to those obtained by other common spectrophotometer reagents for titanium i.e hydrogen peroxide and diantipyryl methane (DAM) (Table3) . A good agreement could be seen among the results obtained using either of the three reagents.

Table(3). Comparative Determination of Titanium with H₂O₂, DAM, and ACPD Methods (as TiO₂), %

Sample	H ₂ O ₂	DAM	ACPD	RSD%
Rock sample	2.17±0.06	2.22±0.07	2.19±0.07	3.20
Sand sample1	7.22±0.22	7.12±0.25	7.09±0.19	2.67
Sand sample2	5.19±0.11	5.07±0.13	5.13±0.11	2.14
Standard sample 1	0.87±0.03	0.86±0.03	0.86±0.03	3.49
Standard sample 2	1.54±0.06	1.52±0.05	1.55±0.05	3.22

Conclusion:

The Suggested method for the determination of Ti(IV) spectrophotometry using ACPD as a complexing agent is a simple, inexpensive, rapid, and sensitive in comparison with previously reported methods. The additional advantage of this method in comparison with other instrumental methods is its simplicity, low cost, reliability and applicability to field determination of titanium. The new method has been successfully applied to the determination of titanium in real as well as in synthetic matrices.

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