Titanium Recovery from its Aqueous Media by 3-Acetylpentane-2,4-Dione as Reagent

J. Y. Hamdo

Department of Chemistry, Faculty of Sciences, Damascus University, Syria

ABSTRACT

3-acetylpentane-2,4-dione (AD) was synthesized and characterized using elemental analysis and IR spectroscopy, in order to examine it as an extractant for recovery of titanium from aqueous acidic media. Various factors, which affect recovery procedure as nature of acids, titanium concentration, acid concentration, type of diluents, and interfering ions, have been studied. It is shown to be a very effective extractant for titanium (IV) from perchloric acid medium, however, the time of extraction is very long (10 min). The extraction of titanium is independent of the initial metal ion concentration. Regarding competition among impurity metal ions, iron (III) seems to be the most competitive ion which could be avoided using fluoride ions as masking agent. The stripping of titanium was investigated using mixtures of 0.50 M NaF and 0.10 NaCl. The stripping procedure was very fast and the yield was 99.71%. The results of this investigation suggest that, it's highly recommended to use the synthesized compound as extractant for titanium ions from its acidic media.

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(AD)   ‒ 4 2 ‒
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0.10M   NaF   **0.50M   HCl**
.   **(   )**
AD   **.%99.71**
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1- Introduction

Efficient and selective separation of metal ions is gaining more importance because of the increasing demand for high purity products, and also for environmental concerns (Basudev *et al.,* 2007). There are various separation methods such as precipitation, diluent extraction, adsorption and ion exchange. Among them diluent extraction is a well-established technology, being used for the production of metals from relatively concentrated feed. However, industrial dilute effluents pose an important challenge, as diluent extraction technique is not cost effective for the separation of metals from the dilute solution (Kongolo *et al.,* 2003; Yabe *et al.,* 2003; Nafaa 2002; Dong 2003).

Being a strategic metal, titanium features innumerable commercial applications. Titanium and its alloys, due to their excellent characteristics as industrial materials, are used for various purposes in industry. In particular, titanium has been widely used in the aerospace industry, while titanium dioxide finds application as pigment in the paint industry. Moreover a larger-scale output of lower-cost titanium and titanium alloy products for use in automotive parts and buildings is increasing (Fontana, *et al.,* 2005).

Titanium ore can effectively be leached by H_2SO_4, HNO_3, HCl and mixed acid solutions. A preliminary study shows that in terms of titanium yield, the best result was obtained by $H_2SO_4+HNO_3$ (Giacoo, 2003).

A literature survey shows that, many reagents have been used for the extraction of titanium (IV) from aqueous solutions. It is recognized that neutral organo-phosphorous compounds are effective extractants for tetravalent metals, particularly for titanium (IV). Among these, tri-n-butyl phosphate (TBP), tri-octylphosphine oxide (TOPO) and Cyanex 923 (TRPO) have been used widely for the extraction of titanium (IV) from acidic chloride solutions (Allal *et al.,*1997; Sheng *et al.,* 1983; John-A *et al.,* 1999; Seyfi *et al.,* 2008). However, the use of TBP and TOPO leads to third phase formation when titanium (IV) is extracted from concentrated metal ion solutions (Basudev *et al.,* 2007; Seyfi *et al.,* 2008).

Organo-phosphorous acid derivatives such as dodecyl phosphoric acid (DPA) (Ritcey *et al.,* 1979), di-o-tolylphosphoric acid (DOTPA) (Islam *et al.,* 1985) and p-(1,1,3,3-tetramethylbutyl) phenyl phosphoric acid (PTPPA) (Mellah *et al.,* 1995), di (2-ethylhexyl) phosphoric acid (D2EHPA) (Biswas (A) *et al.,* 1998; Biswas (B) *et al.,* 2002; Rajeev *et al.,* 2002; Glauco *et al.,* 2008); have been used by

several investigators but they are found to have very slow kinetics and to be less selective. Mixtures of extractants, seems to give faster kinetics (Kislik-A *et al.,* 1993). Critical reviews of published data on titanium (IV) extraction appeared in 1993 (Kislik-B *et al.,* 1993) and in 1999 (Sole, 1999). The review in particular, showed that titanium extraction passes through a minimum, depending on the acidity of aqueous phase (Kislik-A *et al.,* 1993). Moreover, mono-2-ethylhexyl phosphate (MEHPA) was found to be better and more selective than its counter part D2EHPA, because of its strong chelating capability and less sterically hindered sites (Sole,1999). Titanium extraction by EHEHPA has been studied (Fontan *et al.,* 2005; Jayachandran *et al.,* 1998; John-B *et al.,* 199;Sing *et al.,* 2002) in H_2SO_4, HCl and $HClO_4$ solutions. The kinetics of extraction was slow.

The Aim of The Work

This work aims to synthesis a new analytical compound "3-acetylpentane-2,4-dione (AD)" and evaluate the possibility of employing it as an extraction reagent for titanium (IV) from aqueous solutions. The distinct advantage of the proposed reagent is that low time extraction comparing with other reagents and the commonly associated metal ions, especially iron could be tolerated in considerable excess.

2- Experimental

2-1 Chemicals

All chemicals used were of analytical grade (supplied by Merck and BDH companies), and distilled water was used throughout the study. A stock solution of titanium (IV) was prepared by fusing 3.744g of high-purity titanium oxide TiO_2 with potassium hydrogen sulphite. After completion of fusion, the residue was dissolved in 80 mL of concentrated sulphuric acid, diluted by distilled water to 1L (Gunawardhana, 1983). The final solution of approximately 5.00×10^{-2}M was standardized by an EDTA back-titration procedure with bismuth and xylenol orange indicator, in presence of hydrogen peroxide (West,1969). The titanium concentrations used in this research varied from 0.003 M to 0.027M, according to the aim of the experiment. Other metal ion solutions (interference ions) at desired concentration were made from their salts or from the pure metals according to the known methods described in the literature (Korostleove, 1962). The organic solutions were prepared by dissolving carefully calculated

volume of AD into tested diluents. Concentration of AD in organic phase ranged between 0.02 M and 0.24 M according to the experiment. The effect of acid concentration was examined within the 0.5–8 M range.

The extractant "3-acetylpentane-2,4-dione" (AD) was synthesized and purified in the laboratory .

2-2 Apparatus:

All absorbance measurements and absorption spectra were run by Spectro123-Labomed/USA using 1cm quartz cells. The IR spectra was made using JASCO FT/IR-300 E Fourier Transform Infrared Spectrometer. The pH value of solutions was controlled using an Orion pH–meter with combined glass electrode. Elemental composition of synthesized compound was determined by using CHN elemental analyzer, perkin-elmer 2400.

2.3. Synthesis and characterization of AD

3-Acetylpentane-2,4-Dione was synthesized by reaction of acetyl acetone with acetyl chloride in benzene medium with mole ratio 1:1 in the presence of enough amount of KOH and 18-crown ether at room temperature for 3 hours. The reaction mixture was filtrated then purified by vacuum distillation to get transparent liquid, which doesn't dissolve in water but in mixture of water and acetone 1:1. The AD has molecular weight 142, density 0.95 g/mL at 25^0C. The scheme below illustrates the mechanism of the reaction:
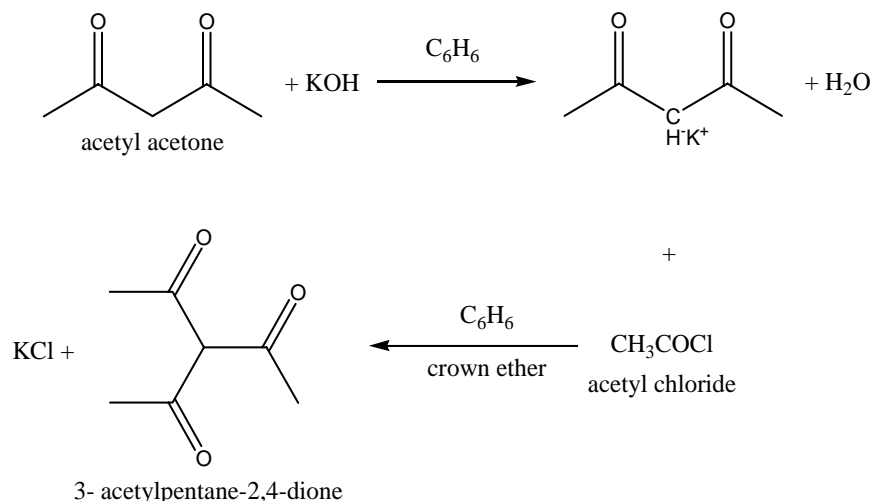
Characterization of reagent was done by elemental analysis (Table 1) and IR spectral analysis. As shown, there is a good theoretical and experimental agreements in elemental composition of synthesized reagent.

Table1. elemental analysis of AD, n=3 (where E_r,% is the relative error)

Elements	Calculated, theoretically,%	Calculated experimentally,%	E_r,%
H	7.04	7.25	2.98
C	59.15	60.64	2.52
O	33.81	32.11	-5.02

Our attention was confined on the part of the spectrum which shows absorption bands accepted to stretching and deformation vibrations for various functional groups and bonds in prepared compounds (Holler *et al.,* 2007)

- Absorption bands between 2800- 3000 cm^{-1} which describe stretching vibrations for $-CH_3$ and $-CH_2$ groups in compound.
- Absorption band at 1360 cm^{-1} which describes deformed vibration for $-CH_2$ group in compound.
- Absorption band at 1710 cm^{-1} which describes stretching vibrations for $-C=O$ group in compound.
- Absorption band at 1170 cm^{-1} which describes deformed vibration for $-C-H$ group in compound.

Joining the results of elemental analysis and IR spectra for prepared compound show a good agreement between theoretically and experimentally calculated results for ratios of elements. This agreement gives a big estimator that, the synthesized compound is the desired compound.

2-4 Extraction Procedures

20 mL of aqueous solutions of known concentration of titanium ions or titanium and interference ions (see paragraph 2-1) was taken in a 100 mL separatory funnel, and 20 ml of organic diluent of AD was added, then the mixture was shaken for a given time and the phases were allowed to separate. Phase separation occurred within 10 min. The organic layer was separated from aqueous layer. To ensure the complete recovery of the titanium, extraction was repeated with 5 ml of organic solution of reagent. For stripping process, the organic extract was shaken with mixed solution of 0.50 M NaF and 0.10 M NaCl at pH=3. The concentrations of titanium in the aqueous feed and strip solutions were determined spectrophotometrically by complexing

with hydrogen peroxide in acidic medium (West, 1969) whereas the metal ions in the organic phase was calculated by mass balance.

The distribution coefficient D was calculated as the ratio of the equilibrium concentration of Ti (IV) in the organic phase to that in the aqueous phase, while extraction percentage was calculated by the following equation (Saji *et al.,* 2003)

$$E\% = \frac{100\,D}{D + \dfrac{V_a}{V_o}}$$

Where: E% extraction percentage, V_O and V_a volumes of organic and aqueous phases respectively, D distribution coefficient.

All experiments were repeated on average five times and the accuracy determination of the metal concentration in the loaded phase was realized by mass balance and checked by complete stripping of the loaded organic phase followed by analysis of the stripped solution.

3- Results and Discussion

The tautomeric properties of AD 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. AD is accounted as a strong complex former because of the presence of three high electro-negativity oxygen atoms in its structure which acts as a Lwise base while transition ions act as an acid Lwise.

3-1 Nature of Acids and Extraction Equilibrium

Sole (1999) in her review, reports on the very slow kinetics for the extraction of titanium by organo-phosphorous extractants. Saji and Reddy (2003) observed that by using EHEHPA, extraction equilibrium was attained within 90 min in HCl, while Sing and Dhadke (2002) observed a short equilibrium time (3 min) in $HClO_4$. Fontana *et al.,* (2005) by using EHEHPA with mixed acid solutions as aqueous phase, the extraction rate of titanium from nitrate and chloride media requires 60 min to reach equilibrium, while the kinetics is much slower in the sulphate medium and required 120 min to attain equilibrium while increasing concentration of EHEHPA using the nitrate and chloride media, the extraction rate achieved within 30 min, while from the sulphate medium it is achieved in 60 min showing a positive effect of the extractant concentration on the

kinetics. Seyfi (2008) observed that by using TBP extraction stage from sulfate and nitrate solutions was reached within 50 min.

For the present investigation, 0.012 M Ti (IV) at 4 M acid (sulphuric, nitric, hydrochloric and percloric) as aqueous phase and 0.24 M. AD in carbon tetrachloride were used. The extraction rate of titanium from nitrate, chloride, sulphate media requires 55, 42, 33 min respectively to reach equilibrium, and moreover not completed extraction whereas percentage of extraction didn't exceed 30% in any case, while the extraction was very fast in the perclorate medium and required 10 min to attain equilibrium and the percentage of extraction was $99.71 \pm 0.42\%$. Depending on these results, the mentioned above acids media except percloric were avoided in the next study and the last one, acid was used as a medium for extraction of titanium. From these data, it was seen that titanium extraction from a perclorata medium presents higher distribution coefficient values than other medium. It may be due to the difference in the activity of Ti (IV) in these media and ion-pairing nature of these anions (Fontana *et al.,* 2005).

3-2 The Effect of Titanium Concentration

About 4M aqueous solutions of $HClO_4$ with different concentrations of titanium (0.003-0.027M) were equilibrated separately with 0.24M AD in carbon tetrachloride. The results showed that distribution coefficients in used acidic media are not influenced by the initial titanium concentration. However, this statement can only be valid when the acidity and concentration of AD remain constant and when the extractant concentration is 20 times greater than the concentration of titanium ions. Fontana *et al.,* (2005) and Biswas and Begum (1998), noticed similar behavior for the extraction of titanium using D2EHPA.

3-3 The effect of Extractant concentration

The influence of AD concentration was studied by extracting the fixed amount of titanium ions with varying amount of AD (0.06-0.36 M). The results are taken as the mean of five values and conditions were taken as follow: Aqueous phase Ti^{4+} = 0.012 M, C_{HClO4} = 4 M, and phase ratio: 1.

It has been observed that (fig.1) 0.24 M of AD is adequate for the quantitative extraction of the mentioned concentration of titanium (IV). The lower concentration of AD gives lower percentage extraction while a large excess of the reagent can be used without any benefit .
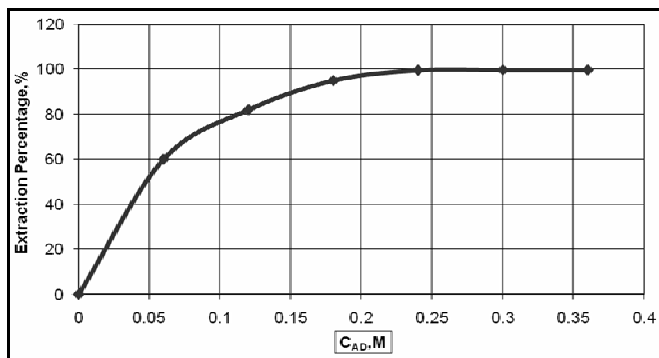
Fig.1 The effect of extractant concentration on the extraction percentage of Ti (IV).

3- 4 The Effect of Perchloric Acid Concentration

It is important to study thoroughly the effect of Percloric acid concentrations on the extraction of titanium. The extraction percentage of Ti (IV) vs. C_{HClO4} plots for 0.012 M Ti (IV) and 0.24 M..AD in carbon tetrachloride systems are given in Fig. 2. Higher percentage extraction is observed at 4M $HClO_4$ and more; lower extraction at lower concentration of $HClO_4$ (<4M) slightly depends upon a cation exchange mechanism, while at 4 M and more it is due to a solvation mechanism with perchlorate ions incorporated into the complex indicating the presence of mononuclear species as reported elsewhere for D2EHPA and EHEHPA (Fontana *et al.,* 2005; Rajeev *et al.,* 2002) respectively.
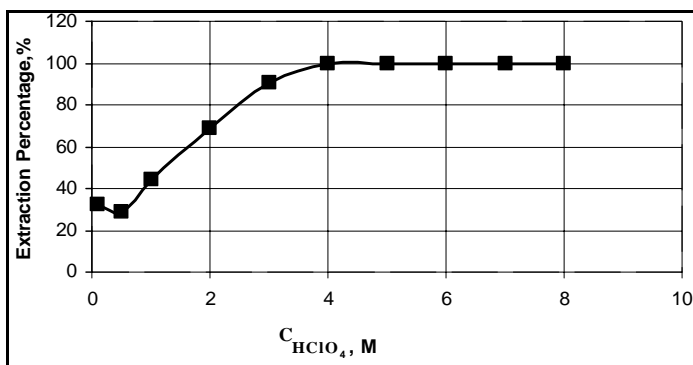

Fig. 2. The Effect of the acidity of the aqueous phase on the extraction percentage of Ti (IV) with AD.

3-5- The Effect of Diluents

Various diluents, such as toluene, chloroform, carbon tetrachloride, benzene, and kerosene, have been employed for the extraction of Ti (IV). Amongst the diluents tested, carbon tetrachloride was found to give the best results. So carbon tetrachloride was preferred as the diluent for AD, as it provided better phase separation (Table 2). The results are taken as the mean of five values and conditions was taken as follow: Aqueous phase Ti^{4+}= 0.012 M, C_{HClO4} = 4 M, C_{AD} = 0.24 M and phase ratio: 1:1.

Table 2. The Effect of diluents on the extraction percentage of Ti (IV) with AD, $C_{Ti(IV)}$ = constant.

Diluent	Extraction Percentage, %	E_r,%
Carbon tetrachloride	99.71	**-0.29**
Chloroform	94.55	**-5.45**
Toluene	93.41	**-6.59**
Benzene	92.86	**-7.14**
Kerosene	87.44	**-12.56**

3-6- The Effect of Interfering Ions

The effect of various diverse ions on the extraction of Ti (IV) was studied with AD in carbon tetrachloride. The tolerance limit of individual foreign ions was set so that the reduction of the percentage extraction was not more than ±2.5 %. Only EDTA, thiocyanate and oxalate interfere seriously with the extraction of Ti (IV) by the proposed extractnt . (Table 3).

Table3. The Effect of various interfering ions on the extraction of Ti (IV)

Interfere ions	Interfere ratio Ti (IV): Interfere ion
Alkali and earth akkli ions,	Don't interfere
Zn^{2+}, Ni^{2+}, Cd^{2+}, Mg^{2+}, Mn^{2+}, Cu^{2+},	1:25
Al^{3+}, Ga^{3+}, Bi^{3+}, Cr^{3+}, Th^{3+}, Pb^{2+}, Rare Earth ions	1:16
Fe^{3+}	1:5
F^-, Cl^-, Br^-, I^-, SO_3^{2-}, SO_4^{2-},	1:20
EDTA, thiocynate and oxalate	Impossible

Based on the metal extraction percentage obtained with synthetic leaching solutions, selective titanium extraction can be done efficiently at 4M acid concentration (Table 3). In particular many ions do not interfere in any case, while others are slightly interfered. Iron (III) seems to be the most competitive ion, reaching in some cases 20% extraction in perchloric acid. It's important to note that, fluoride ions F^- don't interfere in the extraction of Ti (IV) if it was less than 20 time of titanium in the sample. It gave us the 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.

3-7- Stripping evaluations

The effect of stripping agents and their concentration on titanium recovery from a loaded organic phase consisting of 0.24 M AD and 0.012M Ti (IV) has been investigated. A single stage experiment with various concentrations of sulphuric, hydrochloric and perchloric acids show that, the maximum percentage of titanium stripping was found to be about 30 % because of the strong Ti–AD complex in organic phase. Jayachandran and Dhadke (1998); Sing and Dhadke (2002) reported that a mixture of H_2O_2 and sulphuric acid produces quantitative stripping of titanium as $Ti(OH)_4(H_2O_2)SO_4$.). Fontana et al., (2005) showed that increasing concentration of H_2O_2, the stripping of titanium increases to 80%. An interesting breakthrough was achieved by Seyfi (2008) throughout using sodium carbonate as a stripping agent. The stripping of titanium was very fast and the yield was 100%.

In our investigation, Ti (IV) was stripped with a simple solution consisting of mixtures of 0.50 M NaF and 0.10 NaCl. The pH was adjusted to be 3 with HCl, generating TiF_6^{2-} anions. The organic/aqueous phase ratio was 1:1 (vol./vol.). The stripping of titanium was very fast and the yield was 99.80 % $\pm$ 0.30 (Fig3). The time required for the complete stripping was only 12 min. Probably, the titanium- floride complex is much more stable in its aqueous medium than the titanium-AD complexe in organic medium. It's interesting to mention that, stripping agents used by Fontana et al., (2005); Seyfi (2008) (sodium carbonate and a mixture of H_2O_2 and sulphuric acid) were proved in our investigation for comparing with our suggested agent. Results show that a sensible differences in their efficient as stripping agents for titanium.
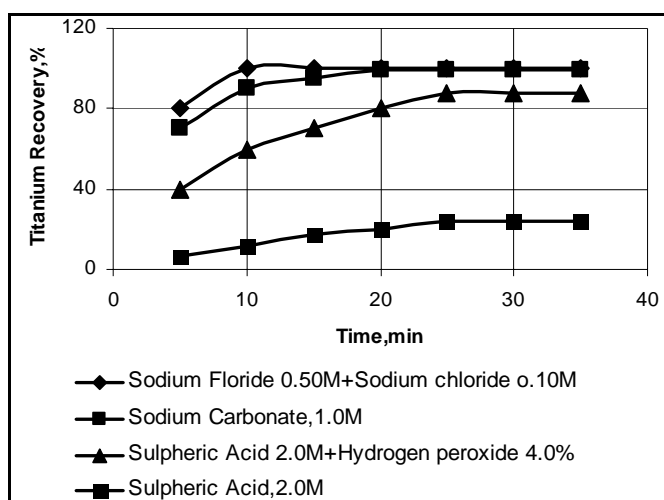
Fig.3.Rate of stripping of titanium from AD using different stripping agents.

Conclusion

The above results of the extraction experiments with 3- Acetylpentane-2,4- Dione lead to the following conclusions:

1. Liquid–liquid extraction of titanium (IV) was investigated in order to examine the effect of different factors, on the recovery by AD.

2. It is shown to be a very effective extractant for titanium (IV) from perchloric acid, however, the time of extraction is very high, (10 min), comparing with literature data.

3. The extraction of titanium is independent of the initial metal ion concentration indicating the presence of mononuclear species.

4. The stripping of titanium by sodium fluoride and sodium chloride is complete and fast.

5. Regarding competition among impurity metal ions, iron (III) seems to be the most competitive ion which could be avoided using fluoride ion as masking agent.

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