

Sulphide Precipitation of Iron and its Effect on the Extraction of Uranium from Phosphoric Acid Medium

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Investigations on the removal of iron from phosphoric acid by precipitation method were carried out using pure and commercial sodium sulphides. The effect of iron on the extraction of uranium from phosphoric acid using a mixture of di-2-ethylhexyl phosphoric acid (HDEHP) and a commercial trioctyl phosphine oxide (CYANEX 921) in kerosene has been investigated. The influence of HDEHP, CYANEX 921, Fe(III), sulphide concentrations as well as temperature on the extraction of U(VI) from phosphoric acid were separately investigated. The results are compared and optimum conditions for monitoring the effect of iron and sulphide on the extraction of uranium from phosphoric acid are proposed.

1. Introduction

Phosphoric acid produced by Wet-Process contains small amounts of uranium together with many kinds of impurities, such as sulphate, fluorine compounds, iron, aluminum, magnesium, and calcium, as well as organic impurities.¹ The presence of such impurities in phosphoric acid adversely affects the process performance as well as the quality of produced acid. Further, the dissolved iron has a strong effect on increasing the acid viscosity and consequently decreasing the filtration rate. Iron also forms precipitates during concentration, clarification, and storage causing sludge problems accompanied by P₂O₅ losses. In addition, the P₂O₅ water-solubility of the fertilizers produced from high iron acids is low.²

The earliest known purification methods of phosphoric acid are based on the precipitation of sparingly soluble salts. Defluorination by Na₂SiF₆ or MgSiF₆·6H₂O precipitations are traditionally used methods.^{3,4} Some companies combine precipitation of barium sulphate with iron and the excess of barium for sulphate precipitation is removed from the acid using cationite.⁵ The precipitation of heavy metals as sulphides also constitutes one of the used methods.⁶ The degree of phosphoric acid purification was found to be higher when extraction technique with organic solvents is applied.⁷⁻¹¹ In this context, recovery of uranium from phosphoric acid by solvent extraction using synergic solvent, di-2-ethylhexyl phosphoric acid–trioctyl phosphine oxide (HDEHP–TOPO), diluted in kerosene was exceedingly investigated.¹²⁻¹⁸ Khorfan et al.¹⁹ showed that Al(III) and Ca(II) have a marked beneficial effect on uranium extraction from phosphoric acid medium, while Mg(II), Fe(III), and V(V) have a negligible effect. An increase in Fe(II) led to a decrease in the extraction of uranium from the same medium. Stas et al.²⁰ have established two mathematical models representing the effect of five parameters (uranium, iron, HDEHP concentration, P₂O₅%, and organic/aqueous ratio) on the selectivity and yield of U(VI) extraction, allowing the choice of the desired experimental conditions and estimation of the purity of the loaded solvent (U_{org}/Fe_{org}). These authors reported that the choice of high selectivity and yield is very difficult since factors that increase the ratio (U_{org}/Fe_{org}) decrease the yield of uranium extraction and vice versa.

Since Egyptian commercial phosphoric acid usually contains a significant amount of iron as Fe(III) (about 2.5 g/100 mL), its removal becomes of major interest as the presence of this ratio affects the extraction of uranium and hence the purification of the acid. The main objective of this investigation is to study the factors affecting the removal of iron as Fe(III) from phosphoric acid by precipitation and its effect on the extraction of uranium. In this context, the precipitation of iron was carried out with pure and commercial sodium sulphide in order to remove or decrease its concentration to the lowest possible value and assess the conditions for maximum extraction of uranium from phosphoric acid.

2. Experimental

2.1. Chemicals and Reagents. Uranyl nitrate was an (AR) Merck product. Orthophosphoric acid (85%) and ferric chloride were obtained from Adwic (Egypt). Pure sodium sulphide was supplied from Winlab (England), while its commercial form was a product of Solvay (Italy). HDEHP was a product of Union Carbide Corporation, USA and CYANEX 921, which is a commercial trioctylphosphine oxide containing 99% of the active substance,²¹ was kindly supplied by Cytec Inc., USA and used as received.

2.2. Procedure. Iron was spectrophotometrically determined using xylenol orange method.²² This method was modified to work in phosphoric acid medium and the effect of acid concentration on the absorbance of Fe(III) plotted in Figure 1 indicated that 0.03 M phosphoric acid is the optimum concentration for this method. The absorbance of the complex reached a maximum value at 550 nm after five minutes and was stable for two hours. U(VI) was measured at 665 nm by Arsenazo-III method.²³ Both methods gave no interference with each other. The precipitation of Fe(III) was carried out by adding the sodium sulphide solid to the phosphoric acid solution with continuous stirring followed by centrifugation and filtration to remove the precipitate. Unless otherwise stated, the aqueous phase contained 100 ppm U(VI) and/or 25 g/L Fe(III) in 5 M phosphoric acid. The extraction procedure was performed by shaking equal volumes of the aqueous and organic phases in stoppered glass tubes using thermostated shaking water bath.

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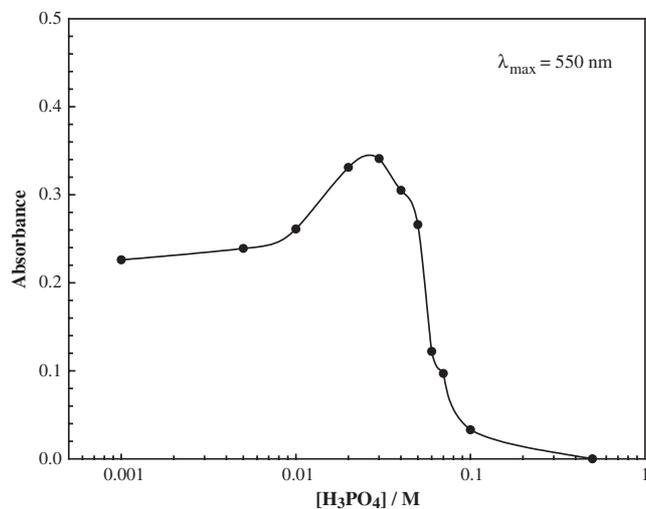


Figure 1. Effect of H_3PO_4 concentration on the absorbance of Fe(III) complex with xylenol orange indicator at $\lambda = 550$ nm.

3. Results and Discussion

3.1. Precipitation Process. Sodium sulphide leads to the precipitation of iron according to²⁴



In this concern, precipitation investigations were carried out using sodium sulphide in its pure and commercial forms. The results shown in Table 1 indicate that the precipitation percent of iron increases with increasing the sulphide concentration with higher values in favor of the pure form. The amount of sodium sulphide added seemed to be much more than the expected stoichiometric value which may be due to the partial consumption of sulphide in reaction with phosphoric acid. It was also found that sodium sulphide has almost no effect on the precipitation of U(VI) present in phosphoric acid within the used concentration range.

TABLE 1: Comparison between Pure and Commercial Sodium Sulphide in the Precipitation of 25 g/L Iron from 5 M Phosphoric Acid Medium

Na_2S / g/100 mL	Iron Precipitation / %	
	Pure Form	Commercial Form
5	15.8	8.2
10	27.6	19.0
15	-	28.8
20	57.6	48.8
25	73.5	62.8
30	-	67.2
35	81.8	72.8

3.1.1. Effect of Sodium Sulphide. The precipitation percent of Fe(III) plotted in Figure 2 as a relation among the amount of commercial sodium sulphide in g/100 mL, iron precipitation %, and $\text{P}_2\text{O}_5\%$ show that the precipitation percent of Fe(III) gradually increases with the addition of sodium sulphide reaching almost 75% precipitation with 35 g of sodium sulphide per 100 mL phosphoric acid solution. This amount of sulphide is equivalent to double the stoichiometric ratio necessary to precipitate the total amount of Fe(III) according to the above reaction (eq 1). More addition of sulphide caused the agglutination of the solution making the filtration very difficult and giving no significant enhancement in Fe(III) precipitation. On the other hand, the phosphoric acid concentration decreased from 5 M (30% P_2O_5) to about 3 M (18% P_2O_5)

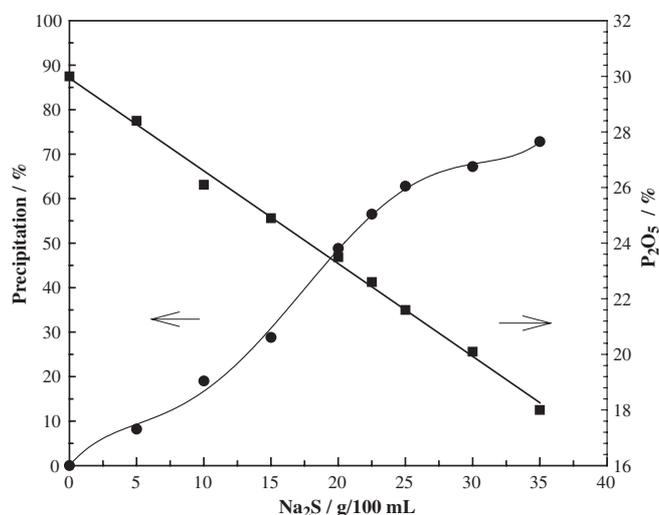


Figure 2. Effect of sodium sulphide on P_2O_5 and the precipitation percent of Fe(III) from 5 M phosphoric acid.

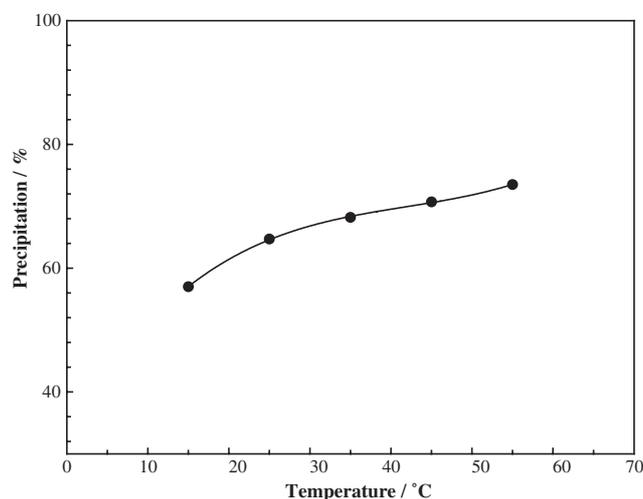


Figure 3. Effect of temperature on the precipitation of Fe(III) from 5 M H_3PO_4 by 25 g sodium sulphide per 100 mL H_3PO_4 .

upon addition of sulphide which may limit the use of large amounts of sulphide to remove Fe(III). This decrease in the acid concentration may be explained by the reaction between a part of phosphoric acid and sodium sulphide leading to formation of H_2S gas.²⁴

3.1.2. Effect of Time and Temperature. The effect of time on the precipitation of iron from phosphoric acid studied over the range of 1 – 60 minutes showed that ten minutes are quite sufficient for complete precipitation. The increase in temperature in the range of 15 – 55°C indicates that the temperature has a positive effect on the precipitation of Fe(III) from phosphoric acid, see Figure 3.

3.2. Extraction Process. A mixture of HDEHP and CYANEX 921 (total concentration 1.0 M) was used to investigate the extraction of U(VI) and Fe(III) from phosphoric acid. The extraction percent (%E) of U(VI) was found to increase with increasing the molar ratio of the above mixture up to 4:1 then decreases with further increase, as reported.^{20, 21} On the other hand, the extraction of Fe(III) did not exceed 1.4% with the same extractants as shown in Figure 4. This is in good agreement with the published data which show that, in absence of chloride, no extraction for Fe(III) takes place from nitric, sulphuric, perchloric, or phosphoric acid.²⁵ Therefore, the ratio 4:1 (HDEHP:CYANEX 921) was selected for extraction of U(VI) from 5 M H_3PO_4 in presence of Fe(III) ions.

3.2.1. Effect of Extractant. Plotting the distribution ratio values of U(VI) versus HDEHP concentrations in the range of 0.5 – 1.2 M or CYANEX 921 concentrations in the range of

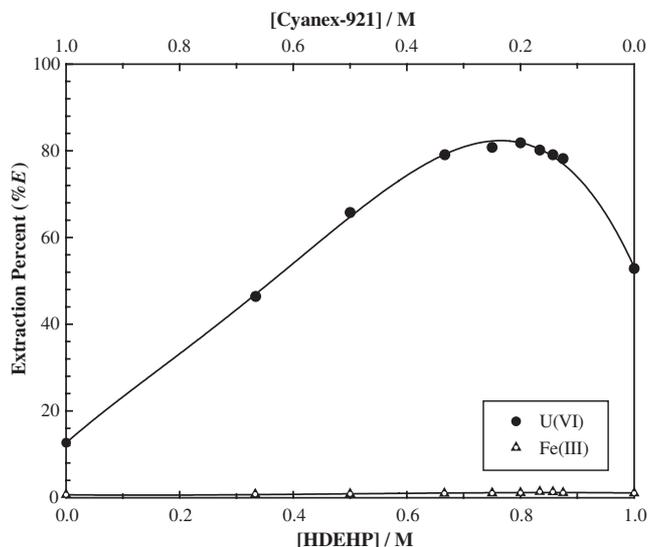


Figure 4. Effect of synergism of HDEHP and CYANEX 921 on the extraction of U(VI) and Fe(III) from 5 M H₃PO₄.

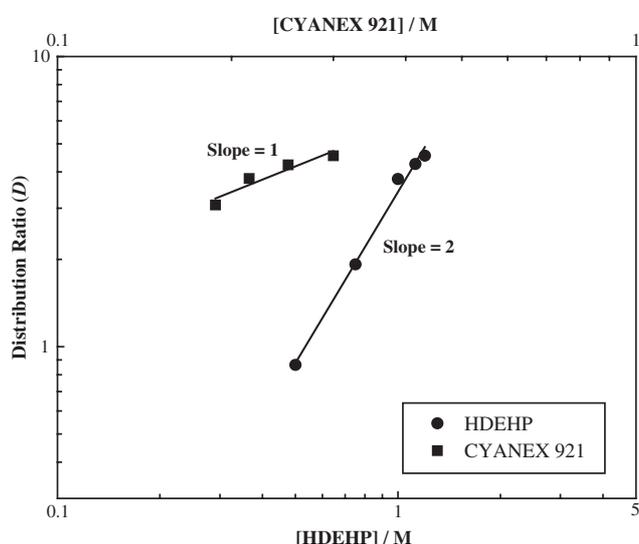


Figure 5. Effect of HDEHP or CYANEX 921 on the extraction of U(VI) from 5 M H₃PO₄.

0.18 – 0.3 M, Figure 5 gave linear relations with respective slopes of 2 and 1 suggesting the participation of one molecule of CYANEX 921 and two molecules of HDEHP in the extracted uranium species.

Based on the experimental results and considering that HDEHP is found as dimer in aliphatic diluents,²⁵ the extraction equilibrium is parallel with that reported²⁵ and may be given by



where HA and X denote HDEHP and CYANEX 921 molecules, respectively, and bars refer to the species in the organic phase.

The extraction constant of eq 2 is given by

$$K_{\text{ex}} = \frac{D[\text{H}^+]^2}{[(\overline{\text{HA}})_2]^2 [\overline{\text{X}}]}, \quad (3)$$

where D is the distribution ratio of U(VI) between organic and aqueous phases.

The calculation of K_{ex} at different $[\text{H}^+]$, $[\text{HA}]$, and $[\text{X}]$ using the previous equation gave an average value of $1920 \pm 53 \text{ M}^{-1}$.

3.2.2. Effect of Temperature. The increase in temperature in the range of 15 – 55°C was found to decrease the extraction of U(VI). The extraction constants, K_{ex} , of the extracted species

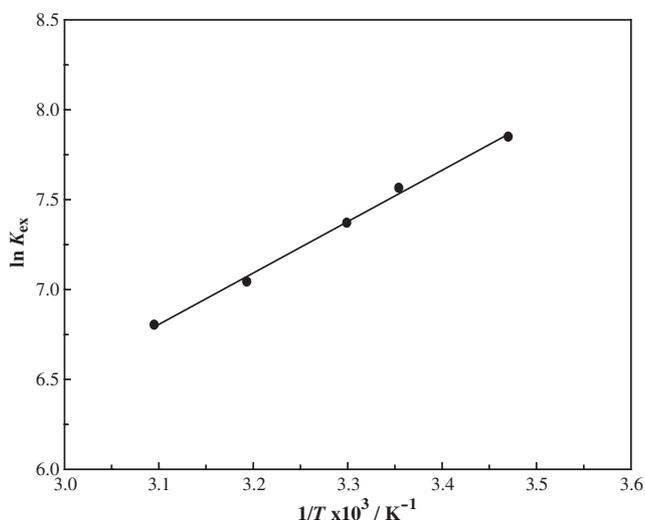
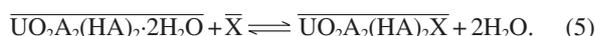
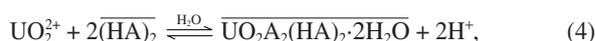


Figure 6. Effect of temperature on the extraction constant of U(VI) from 5 M H₃PO₄ by 0.8 M HDEHP + 0.2 M CYANEX 921 in kerosene.

calculated by applying eq 3 and plotted in Figure 6 as $\ln K_{\text{ex}}$ versus the reciprocal of the respective absolute temperatures, $1/T$, gave a straight linear relation with a positive slope from which the thermodynamic parameters were calculated by applying the common thermodynamic equations.²⁶

The enthalpy change (ΔH) and the entropy change (ΔS) values are $-23.65 \text{ kJ mol}^{-1}$ and $0.14 \text{ kJ mol}^{-1} \text{ K}^{-1}$, respectively. The U(VI)-HDEHP complex usually contains two hydrate water molecules when extracted and these are released when CYANEX 921 is added.²⁵ The release of water means that two reactant molecules (e.g., $\text{UO}_2\text{A}_2(\text{HA})_2 \cdot 2\text{H}_2\text{O}$ and X) may form three product molecules (e.g., $\text{UO}_2\text{A}_2(\text{HA})_2\text{X}$ and $2\text{H}_2\text{O}$), leading to a positive ΔS value. Since CYANEX 921 is more basic than H₂O, it is expected to form a stronger bond via an exothermic reaction (negative ΔH value). Hence, both enthalpy and entropy changes favor the extraction reaction, resulting in large values of $\ln K_{\text{ex}}$ (7.56 M^{-1} at 25°C). Therefore, the overall extraction equation (2) may be rewritten as follows,



3.2.3. Effect of Fe(III). The results of the effect of sodium sulphide given in section 3.1.1. indicate that the maximum possible amount of sodium sulphide which could be used for precipitation of Fe(III) from 5 M phosphoric acid did not remove it completely and more than 0.6 g/100 mL of Fe(III) are left in the acid. Therefore, it is important to study the effect of Fe(III) on the synergistic extraction of U(VI) from phosphoric acid by HDEHP- CYANEX 921 in kerosene. The addition of Fe(III) in the acid medium was found to decrease markedly the extraction of U(VI), and this decrease was nearly not affected by the increase in Fe(III) concentrations in the range 0.3 -2.6 g/100 mL as shown in Figure 7. This decrease in the extraction of U(VI) may be explained by the presence of excess sulphide ions (even in a small amount) which may retard the extraction of uranium, in addition to the possible reduction of U(VI) to U(IV) by sodium sulphide. To overcome this problem, hydrogen peroxide was used to oxidize the formed amount of U(IV) to the more extractable U(VI) and sulphide ions to sulphur. In this context, addition of 0.1 M H₂O₂ after addition of sodium sulphide was found to enhance the extraction of U(VI) to 74%. The increase in hydrogen peroxide concentration increased the extraction process which reached a maximum value of 88% with 0.3 M then remains constant with further addition, see Figure 8. The extraction of

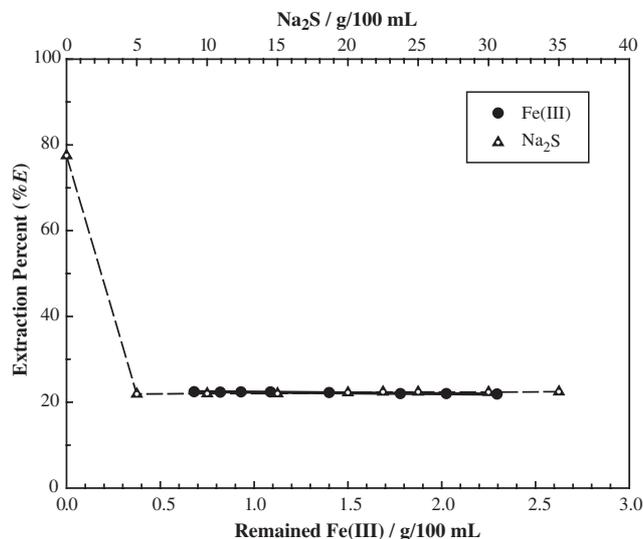


Figure 7. Effect of Fe(III) and sodium sulphide concentrations on the extraction of U(VI) from 5 M H_3PO_4 by 0.8 M HDEHP + 0.2 M CYANEX 921 in kerosene.

both Fe(III) and U(VI) from 5 M phosphoric acid solution without addition of sodium sulphide (only H_2O_2) was also carried out for comparison and found to be 12.5% and 56%, respectively. This marked decrease in the percent of U(VI) extraction shows the importance of removal of Fe(III) by precipitation followed by addition of H_2O_2 prior to the extraction process to avoid its coextraction and its suppressive effect.

3.3. Application on Commercial Phosphoric Acid. The applicability of the proposed method for the removal of Fe(III) from commercial phosphoric acid was tested on a pretreated acid (green acid). In this concern, 10 mL of the acid was heated to 50°C and 2.5 g of sodium sulphide was added with continuous stirring. After centrifugation and filtration, the solution was treated by 0.4 mL H_2O_2 and shaken with equal volume of HDEHP–CYANEX 921 mixture (of ratio 4:1) in kerosene at 25°C. The two phases were separated and the amounts of Fe(III) and U(VI) were determined. It was found that iron extraction percent remains as low as obtained previously with the pure phosphoric acid, while the extraction percent of uranium decreased from 83% to about 66%. This decrease may be explained by the possibility of extraction of other ions usually found in the commercial acid such as Co, Ni, Mn, Cd, Zn, and Pb which may compete with uranium in the extraction process.

4. Conclusions

Sodium sulphide was found to be useful for precipitation of Fe(III) from phosphoric acid medium and the pure form gave better results compared with the commercial one. Ten minutes were found to be quite sufficient for complete precipitation and the temperature increases the precipitation percent. The synergic mixture of HDEHP and CYANEX 921 in kerosene used for the extraction of U(VI) from phosphoric acid showed poor extraction of Fe(III). The extraction of U(VI) from phosphoric acid by HDEHP–CYANEX 921 mixture in the ratio 4:1 decreased with temperature. The marked decrease in the extraction percent of U(VI) due to the presence of excess sulphide ions was effectively overcome by addition of hydrogen peroxide, which leads to the oxidation of U(IV) to the extractable U(VI) form and sulphide to sulphur.

Application of the proposed precipitation method for removal of Fe(III) on a commercial green phosphoric acid gave satisfactory results.

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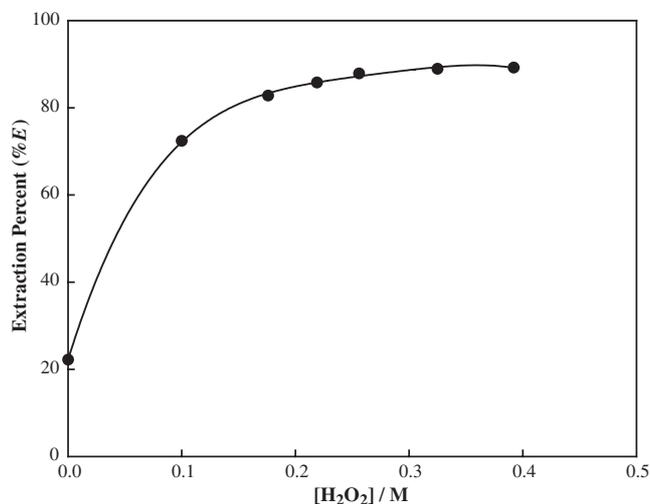


Figure 8. Effect of H_2O_2 concentration on the extraction of U(VI) from 5 M H_3PO_4 by 0.8 M HDEHP + 0.2 M CYANEX 921 in kerosene after precipitation of iron by Na_2S .

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References

- (1) J. R. Wazer, *Phosphorus and its Compounds*, Interscience Publishers, Inc. New York (1961).
- (2) H. El-Shall and E. A. Abdel-Aal, Publication No. 01-154-171, Florida Institute of Phosphate Research, University of Florida (2001).
- (3) A. V. Slack, *Phosphoric Acid*, M. Dekker (Ed.), New York (1968).
- (4) D. Goldstein, *Phosphoric Acid Purification*, (FMC Corp.), Patent USA No. 3819810 (1974).
- (5) K. Beltz, K. Frankenfeld, and K. Gotzman, *Verfahren zur Entfernung von Eisen aus Phosphorsäure*, Patent West Germany No. 2047261 (1975).
- (6) K. Hirayama, C. Kimura, and J. Minagawa, *Phosphoric Acid Refining using Hydrogen Sulphide*, Patent Japan No. 49-37038 (1974).
- (7) I. L. Bradford and B. F. Ore, *Extraction Process for Purification of Phosphoric Acid*, Patent USA No. 4053564 (1977).
- (8) P. T. Chiang and J. D. Nikerson, *Solvent Extraction of H_3PO_4* , Patent USA No. 3867511 (1975).
- (9) M. Takahara, *Production of Phosphoric Acid of High Purity*, Patent USA No. 3917805 (1975).
- (10) T. A. Williams, *Purification of Phosphoric Acid*, Patent UK No. 1436114 (1976).
- (11) T. A. Williams and F. M. Cussons, *Purification of Phosphoric Acid*, Patent UK No. 1436113 (1976).
- (12) F. T. Bunus, V. C. Domocos, and P. Dumitrescu, *J. Inorg. Nucl. Chem.* **40**(1), 117 (1978).
- (13) F. Bunus and I. Miu, Proceedings of a Technical Committee Meeting, Vienna, **266**, 207 (1995).
- (14) F. Bunus and I. Miu, Proceedings of a Technical Committee Meeting, Vienna, **343**, 221 (1997).
- (15) F. J. Hurst, Nuclear Fuel Cycle Information Workshop, 22 Oak Ridge National Lab. USA (1983).
- (16) A. K. Al-Matar and K. M. Rawajfeh, *Pure and Applied Sciences*, **22B**(6), 1459 (1995).
- (17) S. Khorfan, Y. Koudsi, A. Dahdouh, and H. Shlweit, Proceedings of the International Conference on Uranium Extraction, **217**, 42 (1996).
- (18) K. M. Rawajfeh and A. K. Al-Matar, *Hydrometallurgy*, **56**, 309 (2000).
- (19) S. Khorfan, Y. Koudsi, and W. Rafool, *J. Radioanal. Nucl.*

- Chem. **250**(1), 147 (2001).
- (20) J. Stas, A. Dahdouh, H. Shlewit, and S. Khorfan, *Hydrometallurgy*, **65**, 23 (2002).
- (21) E. Dziwisni, and J. Szymanowski, *Solv. Extr. Ion Exch.* **16**(6), 1515 (1998).
- (22) K. L. Cheng, *Talanta*, **3**, 147 (1959).
- (23) Z. Marczenko, *Spectrophotometric Determination of Elements*, Ellis Horwood Ltd. Poland (1976).
- (24) G. Svehla, *Vogel's Qualitative Inorganic Analysis*, 7th Ed. Thomson Press India Ltd. (1996).
- (25) A. K. De, S. M. Khopkar, and R. A. Chalmers, *Solvent Extraction of Metals*, Van Nostrand Reinhold Company, London (1970).
- (26) J. Rydberg, C. Musikas, and G. Choppin, *Principles and Practices of Solvent Extraction*, Marcel Dekker, Inc. USA (1992).

