

ANALYSIS OF PHOSPHORIC ACID

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ABSTRACT

In the processes for recovery of uranium as a by product of phosphoric acid production the following ions are effective: Fe^{2+} , Fe^{3+} , PO_4^{3-} , Al^{3+} , F^- , Ca^{2+} , SO_4^{2-} . On the other hand, $\text{Fe}^{2+}/\text{Fe}^{3+}$, $\text{U}^{4+}/\text{U}^{6+}$ ratios and total oxidant consumption of the acid are also very important factors. In this study the above mentioned variables were determined in phosphoric acid samples obtained from Samsun Fertilizer Plant of Turkish Nitrogen Industries Corporation.

ÖZET

Fosforik asitten yan ürün olarak uranyum kazanılması için uygulanan proseslerde Fe^{+2} , Fe^{+3} , PO_4^{-3} , F^- , SO_4^{-2} , Ca^{+2} , U^{+4} , U^{+6} iyonları etkili olmaktadır. Bunun yanında $\text{Fe}^{2+}/\text{Fe}^{3+}$, $\text{U}^{4+}/\text{U}^{6+}$ oranları ile asidin toplam yükseltgen ihtiyacı önemli kriterler olarak davranmaktadırlar. Bu çalışmada Azot Sanayi T.A.Ş. Samsun Gübre Fabrikasından temin edilen fosforik asit örneklerinde, yukarıda belirtilen tayinler yapılmıştır.

INTRODUCTION

Today, uranium is produced mainly from its minerals. Besides its minerals, phosphoric acid is the most promising and feasible source of uranium. The acid composition plays an important role in all processes for recovery of uranium from phosphoric acid /1,2/. For example, the increase of phosphate concentration in the DEHPA/TOPO process decreases efficiency of uranium extraction. Total Fe, especially the ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ plays a determining role in the redox potential of the medium in both extraction and Stripping steps. The ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$ affects the ratio of $\text{U}^{4+}/\text{U}^{6+}$ and precautions should be taken in uranium extraction and stripping steps. Silicate, sulphate and calcium ions

may cause precipitation in the medium and some economical and technological difficulties arise in the processes. The fluoride ion plays a catalyzing role in reducing U^{6+} to U^{4+} in extraction step, which is not desired. Aluminum behaves as a masking agent by forming a complex with fluoride ion. During the pretreatment of the acid for extraction, the amount of the reagent necessary for the adjustment of redox potential of the medium should be determined.

The spectrophotometric, volumetric and gravimetric methods were applied for the determination of the mentioned species.

The samples were supplied by the Samsun Fertilizer Plant of Turkish Nitrogen Industries Corporation. First of all, the samples were filtered through the gouch crucible and the filtrates were analysed after three times filtration through whatman 42 filter paper.

METHODS

I. Determination of Phosphate.

A. Spectrophotometric Method /3-7/

This method is applied for concentrated uranium compounds and solutions. It is based on measurement of absorbance of the complex that is formed by phosphate ions and ammonium molybdate after reaction by hydroquinone, at 650 nm. The error is less than 3 % within 0.2-0.7 absorbance range.

B. Volumetric Method /8/.

The method utilizes the reactions of H_3PO_4 with NaOH as a mono and dibasic acids at pH 4.4 and 9.7. The first titration point is at pH of 4.4 and the second is at pH of 9.7. The percentage of H_3PO_4 is calculated in terms of difference of NaOH amount consumed between the first and second end points. If the amount of the interfering ions is too high, especially in presence of HCl, the end points should be taken as pH 3.6 and 8.4.

This method is used in order to process phosphoric acid in the fertilizer manufacturing industry.

II. Determination of Aluminum /3.4/.

This method is based on precipitation of aluminum with 8-hydroxy quinoline (oxine). The precipitate is dissolved in chloroform. Absorbance of this solution

is measured with a spectrophotometer. The error is less than 2% within 0.2-0.5 absorbance range.

III. Determination of Calcium (Volumetric Method) /3-5/.

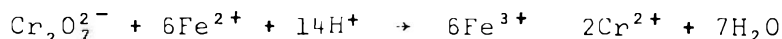
Calcium is precipitated at pH 5 as oxalate. The precipitate is dissolved in H_2SO_4 . The solution is titrated with 0.1 N KMnO_4 , and the end point is determined by the bromophenol blue indicator. The error is less than 1% within the concentration range of 10-50 mg Ca.

IV. Determination of Iron (Spectrophotometric Method) /3-7/.

The method is based on the reduction of Fe^{3+} to Fe^{2+} with hydroxylamine and formation of a complex with orthophenantroline and the measurement of the absorbance at 525 nm. The error is less than 2% within 0.2-0.7 absorbance range.

V. Determination of Fe^{2+} (Volumetric Method) /3-5,7/.

This method is based on oxidation of Fe^{2+} to Fe^{3+} by potassium dicromate. The reaction can be represented by the equation.



(1 ml of 0.025 N $\text{K}_2\text{Cr}_2\text{O}_7$ is equivalent to 1.396 mg of Fe^{2+})

VI. Determination of Sulphate (Gravimetric Method) /3-5,7/

The method is based on the precipitation of sulphate ions by BaCl_2 as BaSO_4 . The error is less than 2% within 20-200 mg SO_4^{2-} range.

VII. Determination of Silicon (Gravimetric Method) /3-5/

In this method, silicon is precipitated as SiO_2 and weighed. HF is added to this residue and solution is evaporated to remove silicon as SiF_4 and weighed. From the difference in weight the amount of silicon is calculated. The error is less than 5% within 4-12 g/l SiO_2 range.

VIII. Determination of Total Oxidant Consumption (Volumetric Method) /3/.

This method is based on oxidation of Fe^{2+} and U^{4+}

by $K_2Cr_2O_7$. Excess of dichromate is titrated with iron ammonium sulphate solution with sodium diphenyl ammonium sulphonate indicator. The amount of total oxidant consumed is calculated from the consumption of iron ammonium sulphate. The error is less than 1%.

Total oxidant consumption value can also be expressed in terms of the weight of H_2O_2 , 1 g-eq. $H_2O_2 = 17.01$ g.

IX. Determination of Ratios of Fe^{2+}/Fe^{3+} and U^{4+}/U^{6+}

Fe^{2+}/Fe^{3+} and U^{4+}/U^{6+} ratios are calculated after determination of total U, Fe, Fe^{2+} and total oxidant consumption in H_3PO_4 sample by using the equations given below:

$$Fe = Fe^{2+} + Fe^{3+}$$

$$U = U^{4+} + U^{6+}$$

Total oxidant consumption = $Fe^{2+} + U^{4+}$. Fe^{3+} , U^{4+} , U^{6+} amounts are calculated from these equations.

X. Determination of Fluoride (Volumetric Method) /3-5/.

Fluoride is separated from the sample in presence of silica, as fluosilicic acid by steam distillation at $135 \pm 1^\circ C$ or $180 \pm 1^\circ C$. The fluosilicic acid is hydrolyzed with NaOH. Then, free fluoride is titrated with thorium nitrate by using of sodium alizarine sulphonate as an indicator. The error is less than 3% within concentration range of 6-15 mg F^- . The distillation apparatus is shown in Fig.1.

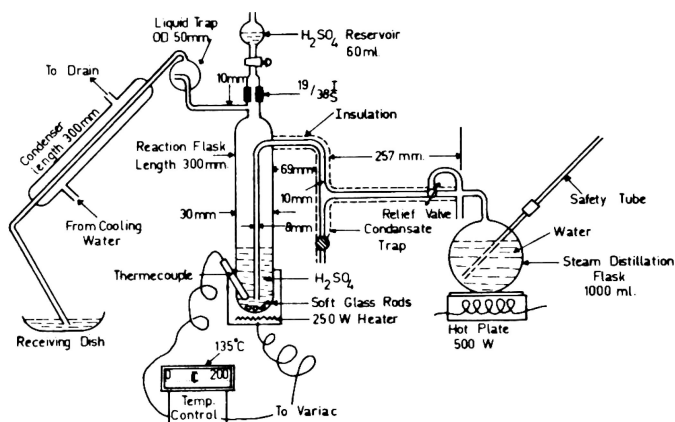


Fig.1. Fluoride distillation apparatus.

RESULTS AND DISCUSSION

Two different samples of phosphoric acid which were obtained from Samsun Fertilizer Plant of Turkish Nitrogen Industries Corporation were analyzed and the results are given in Table-1. Fluoride determination is not satisfactory and results are not included in the table.

TABLE-1. Analysis of commercial phosphoric acid samples.

Constituent	Concentration (g/l)	
	Sample I	Sample II
H ₃ PO ₄ (a)	3.85 ± 0.16 (M)	3.84 ± 0.08 (M)
H ₃ PO ₄ (b)	-	3.99 (M)
Fe ₂ O ₃	2.21 ± 0.20	2.08 ± 0.11
Fe(II)	0.0168 ± 0.0012	0.0148 ± 0.001
Fe(III)	1.54	1.46
CaO	-	1.38 ± 0.09
Al ₂ O ₃	-	2.96 ± 0.06
SiO ₂	4.38 ^c ± 0.8	2.42 ± 0.5
SO ₄ ²⁻	56.83 ^c ± 1.5	22.22 ± 0.54
TOC ^d	7.230 × 10 ⁻⁴	6.053 × 10 ⁻⁴
H ₂ O ₂ ^e	0.0122	0.0102
U ₃ O ₈	0.083	0.049
U (IV)	0.0503	0.0405
U (VI)	0.0197	0.00144

a: Spectrophotometric method

b: Volumetric method

c: H₃PO₄ sample is not filtered

d: TOC, total oxidant consumption, g.eq/l,

e: Total H₂O₂ requirement

Generally, there is a similarity between the results of analyses of the different acid samples taken from Samsun Fertilizer Plant. Ca and Al were not analyzed in the first acid sample. The amounts of silicate and sulphate in the first sample are analyzed as received while the second sample was filtered before the analysis. When the composition of the two acid samples are compared, it is apparent that there are differences between them. This shows that the composition of phosphoric acid depends on the composition of the phosphate rocks and the process applied. Therefore, before the uranium recovery process is applied, analysis of phosphoric acid must be completed and necessary precautions should be taken.

The methods mentioned in this study has been applied to phosphoric acid analyses. These methods are problem-free, interferences are minimized and give very small error. The only disadvantage is that more time is required compared to the techniques such as atomic absorption and X-ray fluorescence spectrophotometry.

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