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RESEARCH ARTICLE

Modification of Davies & Gray method for uranium determination in phosphoric acid solutions

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Abstract

The Davies-Gray method for uranium determination has been modified to facilitate the uranium determination in phosphoric acid solutions. In this concern, two phosphoric acid solutions, representing di-hydrate and high strength phosphoric acid, were prepared with different uranium concentrations. The concentration of uranium with the modified method was measured and compared with uranium determination with spectrophotometer method. The effect of different impurities in phosphoric acid such as; iron, fluoride, free sulfate, manganese, vanadium, and zinc on uranium concentration determination by the modified method were investigated. The obtained results clarify that, the modified method is applicable for uranium determination in both di-hydrate and high strength phosphoric acid in the range of ≥ 10 - 150 ppm uranium ion concentrations with high accuracy precision. The phosphoric acid impurities have almost no effect in uranium determination by using the modified method.

INTRODUCTION

Uranium recovery from unconventional resources has to take into account economic criteria and trends in the primary uranium market. Otherwise, it must be part of large-scale operations in which economies of scale partly compensate for the ore's low grade. The most abundant unconventional uranium resources are seawater and phosphate rock deposits **(1)**.

Phosphate rocks are a source of phosphorus – a vital element for plants. Phosphorus is one of the main raw materials used to make fertilizers and is also used in food supplements, drinks, and others industrial products. Phosphate deposits may be classified into two categories: igneous phosphate rocks (13%) and sedimentary phosphate rocks (87%) **(2)**.

Several studies have reported an average concentration of uranium close to 100 ppm in phosphate rocks **(3-4)**. However, the actual concentration can range between 23 and 220 ppm. In April 2011, UDEPO announced 7.8 Mt U for the uranium content in phosphate rocks deposits **(1)**. During the treatment of rock phosphate with sulfuric acid, about 80 – 90 % U_3O_8 of the total uranium content present in the rock matrix is solubilized **(5)**.

Phosphoric acid contains also other impurity elements at much higher concentration than uranium such as Fe^{+3} and /or Fe^{+2}, F^- and SO^{2-}_4 which influence the efficiency of the extraction process. The concentration of Fe is high and present in the range of 2.3 %; the uranium valence state is affected by the presence of Fe (II) which reduces U (VI) to U (IV) which is very important behavior during uranium recovery by solvent extraction technique **(6-7)**.

The high concentration of is F^- exerts a strong influence on the efficiency of uranium extraction process. Fluoride concentration in commercial phosphoric acid is relatively high averaging 1 wt %. Free sulfate ions are present in the acid since digestion of phosphate rocks to produce phosphoric acid by the wet method involves adding an excessive amount of concentrated sulfuric acid. Beside these elements, some trace elements which present in high concentration relative to the other and may affect the determination of uranium these elements are Mn and V which present in concentration range of about 840 and 46 ppm respectively **(6-7)**.

In the last few years, due to the rapid development observed in the means for getting a good use the atomic energy, analysis of radioactive minerals especially the determination of elements. Uranium and Thorium won a wide interest. The physical and chemical analyses of these elements have, in pace with the marked development in this field in general, the following deals with the methods used for uranium determination.

Various methods have been devised for the determination of uranium. In general, first step in any method is to free the uranium from its associated elements, interfering with the precision of the determinations, and then this is followed by the determination proper. Then the determination of uranium may occur using one of the following methods: Gravimetric **(8)**, Volumetric **(9)**, Colorimetric and Spectrophotometric **(10)**, Fluorometric **(11)**, Electronic or Radioactive **(12)**.

The DAVIES and GRAY **(13)** have reported a method for the determination of uranium which involves the reduction of uranium to U (IV) by excess Fe (II) in strong phosphoric-sulfamic acid, and excess Fe (II) is selectively oxidized by nitric acid in presence of Mo (VI) catalyst. Then the U (IV) is titrated by a dichromate solution or by cerium sulfate solution with a potentiometric titration using vanadyl as electrochemical enhancer. The overall process for the dichromate titration is seen below:

$$Cr_2O_7^{2-} + 3U^{4+} + 2H^+ = 2Cr^{3+} + 3UO_2^{2+} + H_2O$$

The high concentration of H_3PO_4 (4-9M) and the presence of impurities make it difficult to find a trustworthy, relatively fast analytical method for the low content uranium solutions. Uranium concentration is found between 0.005 - 0.2 g/1. In this concern, this paper aims to modify the method used by Davies & Gray/NBL for uranium determination in ortho phosphoric acid solutions namely 5 and 9 mol/L. Statistical analysis will be held on the obtained results using t-test and F-test (Anova) as well as application for commercial phosphoric acid.

2. EXPERIMENTAL:

2.1. Reagents:

The following reagents were required. All reagents were prepared from analytical reagent grade.

- Ferrous sulfate, 20 %, is prepared by dissolving 20 g of $FeSO_4.7H_2O$ in 50 ml then adds 2.5 ml H_2SO_4 and make up to volume in 100 ml volumetric Pyrex flask with distilled water.
- Potassium Bromide, 0.05 %, is prepared by dissolving 50 g of KBrin 100 ml and make up to volume in 1000 ml volumetric Pyrex flask with distilled water.
- Bromine water is prepared by adding 12.5 ml of Br_2 in 100 ml 0.05 % KBr then complete up to volume in 1000 ml volumetric Pyrex flask with 0.05 % KBr.
- Sulphosalicylic acid, 25 %, is prepared by dissolving 25 g of $C_7H_6O_6S.2H_2O$ in 10 ml distilled water and make up to volume in 100 ml volumetric Pyrex flask with distilled water.
- Sodium diphenylamine sulfonate, 0.2 %, is prepared by dissolving 0.2 g of $C_7H_6O_6S.2H_2O$ in 10 ml distilled water and make up to volume in 100 ml volumetric Pyrex flask with distilled water.
- Ammonium metavanadate, 8.4×10^{-4} M, is prepared by dissolving 0.0983 g of NH_4VO_3 in 500 ml distilled water then make up to volume in 1000 ml volumetric Pyrex flask with distilled water.

2.2. Preparation of standard solutions:

U, Fe, F and SO_4 solutions were prepared by dissolution of certain weights of their salts in pure phosphoric acid solutions, phosphoric acid concentration of ≈ 5 and ≈ 9 mol L^{-1}, to obtain solutions containing different concentrations for each ion.

2.3. Experimental Procedure:

Uranium concentration was determined by a titration method using ammonium metavanadate method. In this method; 5 ml sample solution was taken in 250 ml conical flask then 15 ml of distilled water, 10 ml pure phosphoric acid and 2.5 ml ferrous sulfate were added. The solution was heated to ~ 70 ^{o}C then stand to cool at room temperature. After that, bromine water was added till a pale yellow color then two drops of sulphosalicylic acid was added. The solution was left for 3 minute. Finally, the titration was carried out against ammonium metavanadate until violet end point.

The uranium concentration in a sample will be determined based on the following relation:

$$U\ (g/\ l) = T \times V_1 \times 1000/V$$

Where, T is the titration intensity of NH_4VO_3 solution to uranium, (g U/ ml). V is the volume of sample solution, ml. V_1 is the volume of NH_4VO_3 solution consumed, ml.

The obtained results were statistically analyzed by the following equations:

$$\text{Mean}, M = \frac{\sum(X)}{N}$$

Where ∑ is Sum of, X is Individual data points, N is Sample size (number of data points)

$$\text{Standard deviation}, \sigma = \sqrt{\frac{\sum(X-M)^2}{N}}$$

Where ∑ = Sum of X = Individual data points
M = Mean of data points N = Sample size (number of data points)

$$\text{Relative standard deviation}, RSD = \frac{\sigma}{M}\ x\ 100$$

Where σ = Standard deviation M = Mean of data points

To examine the efficiency of the investigated method for uranium determination in ortho-phosphoric media, statistical analysis has been performed where T-Test is calculated first then the results confirmed by F-Test.

T-Test was calculated by the following equations:

Where, M_1 and M_2 are the mean of Set of U concentration at 9 and 5 mol L^{-1} respectively.

Where ∑ = Sum of, N = Sample size, D = difference between the two sets

Standard deviation, σ: $\sigma = \sqrt{\sum D_M - {}^{D}/_{n-1}}$

D = Difference between the two sets N = Sample size
D_m = Sum of difference of the two sets divided by sample points

Standard error of the mean, σ_M: $\text{Standard error of the mean}, \sigma_M = \frac{\sigma}{\sqrt{N}}$

Where σ = Standard deviation N = Sample size (number of data points

$$\mathbf{T} = \frac{X1-X2}{\sigma_M}$$

Where X1 and X2 are the U concentrations at 9 and 5 mol L^{-1} respectively.

To confirm the obtained results hypothesis testing methods included one way analysis of variance (ANOVA) followed by least significant differences test f-values of less than 0.05 and 0.01 were considered to indicate statistical significance. (***F*-test** is any statistical test in which the test statistic has an *F*-distribution under the null hypothesis. It is most often used when comparing statistical models that have been fitted to a data set, in order to identify the model that best fits the population from which the data were sampled. Exact "*F*-tests" mainly arise when the models have been fitted to the data using least squares) **(14)**.

$F_{\text{calculated}} > F_{\text{critical}}$, H_0 is rejected.

$F_{\text{calculated}} < F_{\text{critical}}$, H_0 cannot be rejected.

The f-test was calculated as presented in Table (1):

Table (1): Calculation of F-Test

Source of variance	Sum square	Degree of freedom	Mean sum square	F calculated
between	SSR	K- 1	$S_R^2 = SSR/K-1$	$F = \frac{S_R^2}{S_E^2}$
Ex. Error	SSE	K (n-1)	$S_E^{2=SSE/K(n-1)}$	
Total	SST	Nk-1		

3. RESULTS & DISCUSSION:

3.1. Description of the Method:

The automated determination of uranium according to the Davies and Gray method is described as the following; Uranium (VI) is reduced with iron (II) to uranium (IV) in a highly concentrated phosphoric acid medium (eq. 1). The excess of iron (II) is then oxidized to iron (III) with nitric acid in the presence of a molybdenum catalyst (eq. 2). The nitrous acid formed in this reaction is destroyed by sulfamic acid (eq. 3) and finally the uranium (IV) is titrated with potassium dichromate in the presence of a vanadium catalyst (eq. 4).

$$U^{6+} + 2Fe^{2+} \rightarrow U^{4+} + 2Fe^{3+} \ (1)$$

$$2Fe^{2+}HNO_3 + 2H^+ \rightarrow 2Fe^{3+} + HNO_2 + H_2O \ (2)$$

$$HNO_2 + NH_2HSO_3 \rightarrow N_2 + H_2SO_4 + H_2O \ (3)$$

$$3U^{4+} + 2Cr^{6+} \rightarrow 3U^{6+} + 2Cr^{3+} \ (4)$$

Description of the automated uranium determination based on the Modified Davies and Gray method is the same description based on Davies and Gray method, where it depends on iron (II) reduction in phosphoric acid as the following; Uranium (VI) is reduced with iron (II) to uranium (IV) in a highly concentrated phosphoric acid medium (eq. 5). The excess of iron (II) is then oxidized to iron (III) with bromine water (eq. 6). The produced brome in this reaction is reacted with 2-Hydroxy-5-sulfobenzoic acid (eq. 7) and finally the uranium (IV) is titrated with ammonium meta-vanadate (eq. 8).

$$U^{6+} + 2Fe^{2+} \rightarrow U^{4+} + 2Fe^{3+} \ (5)$$

$$2Fe^{2+}Br_2 \rightarrow 2Fe^{3+} + 2Br^- \ (6)$$

$$2Br^- + HO_3SC_6H_3 - 2 - (OH)CO_2H.2H_2O \rightarrow Br_2C_6H_3CO_2H + H_2SO_4 + 2H_2O \ (7)$$

$$3U^{4+} + 2V^{5+} \rightarrow 3U^{6+} + 2V^{2+} \ (8)$$

3.2. Uranium determination in synthetic phosphoric acid:

In a wet process facility, phosphoric acid is produced by reacting sulfuric acid with naturally occurring phosphate rock. Wet process phosphoric acid normally contains 26 to 30 percent P_2O_5 (≈ 5 mol L^{-1} phosphoric acid). In most cases, the acid must be further concentrated to meet phosphate feed material specifications for fertilizer production. Depending on the types of fertilizer to be produced, phosphoric acid is usually concentrated to 40 to 50 percent P_2O_5 (≈ 9 mol L^{-1} phosphoric acid) by using 2 or 3 vacuum evaporators. Therefore, there are two types of feed phosphoric acid; di-hydrate phosphoric acid (≈ 5 mol L^{-1} phosphoric acid) and high strength phosphoric acid (≈ 9 mol L^{-1} phosphoric acid).

3.2.1. Effect of Uranium Concentration on uranium determination:

To determine uranium concentration in the feed phosphoric acid as mentioned above, two sets of uranium standard solutions of 5, 10, 20, 50, 75, 100, 150 ppm (≈ 5 and 9 mol L^{-1} phosphoric acid) were prepared. The obtained results are presented graphically in Figure 1 as a relation between uranium concentration and relative standard deviation. From the obtained results it is clear that the investigated method fit well with the initial uranium concentration at both ortho phosphoric acid concentrations, and the concentration of high strength phosphoric acid has no effect on the uranium determination. The obtained data clarify that this method is not accurate at concentration beyond 10 ppm according to the RSD calculated where it is acceptable when the result is less than 10 % and according to this value the method is good at concentration $\geq$ 10 ppm.

The obtained results were statistically tested using t-test, Table 5, which reveals that at freedom degree 6 and the at significance value of 0.05 and 0.01 (tabulated t value) which was 1.943 and 3.143 respectively. The calculated t (14.85) is greater than the tabulated one which clear that there is a significant difference between the uranium concentration and the investigated method fit well with the variances of uranium concentration at both concentration of ortho-phosphoric acid.

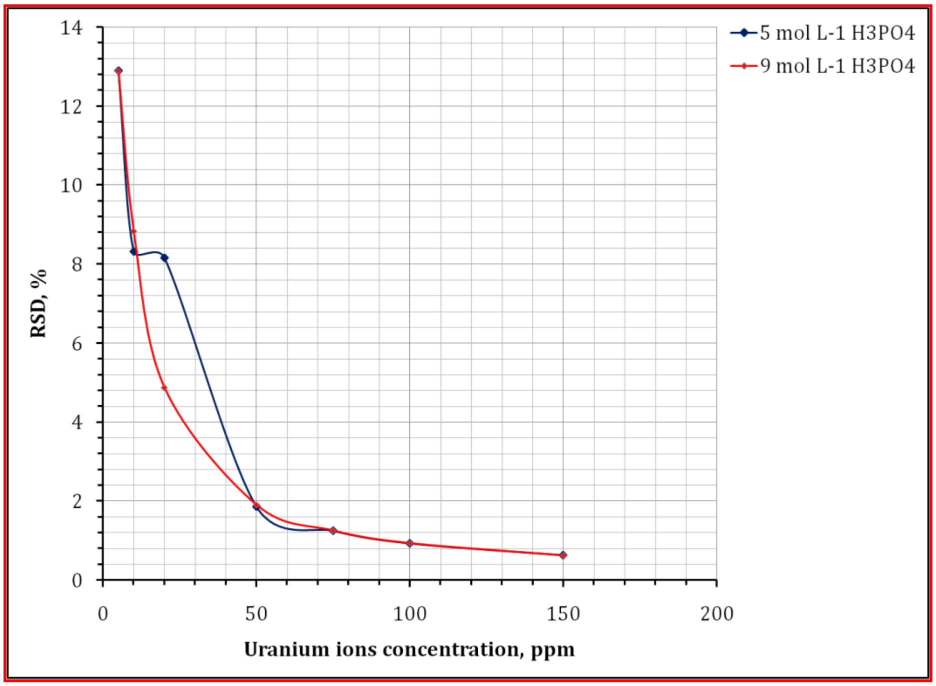

Figure (1): Relation between RSD and uranium concentration 5 and 9 mol l^{-1} phosphoric acid.

To confirm the obtained results hypothesis testing methods included one way analysis of variance (ANOVA) followed by least significant differences test f-values of less than 0.05 and 0.01 were considered to indicate statistical significance. By comparing the obtained results of calculated value of f (Table 1) and the tabulated one at D.F (6 and

12), it is clear that the value of f calculated is bigger than the tabulated at 0.01 and 0.05 (5.42 and 3.29 respectively). This confirms the obtained t-test and the investigated methods fit well with the initial uranium concentration at 5 mol l^{-1} ortho phosphoric acid concentration. The same results were obtained to the 9 mol l^{-1} ortho phosphoric acid concentration. This means that the concentration of ortho phosphoric acid has no effect on the uranium concentration measurements using this method.

Table (1): F-test for the effect of uranium concentration on uranium determination using the investigated method.

Source of variation	D.F	SS	MSS	F
Between	6	297066	49510	6.234
Ex. Error	12	95308	7945.3	
Total	18			

3.2.2. Effect of impurities on uranium determination at uranium concentration of 100 ppm:

As the phosphoric acid is produced from phosphate rocks, it contains many impurities for example iron, fluoride, free sulfate and uranium. These impurities pass into wet phosphoric acid during rock acidulation. In the present work, the effect of iron, fluoride, free sulfate, manganese, vanadium and zinc ions concentration on the determination of uranium concentration in ≈ 5 mol L^{-1} phosphoric acid and ≈ 9 mol L^{-1} phosphoric acid were investigated at uranium concentration of 100 ppm.

3.2.2.1. Effect of iron ions on uranium determination:

The influence of iron ions concentration on the uranium determination on phosphoric acid solution was investigated by forming two sets of iron standard solutions of 0.5, 1, 2, 3 and 4 % in 5 and 9 mol L^{-1} ortho phosphoric acid with uranium concentration of 100 ppm. The obtained results are presented statistically analyzed in Table 2, and graphically in Figure 2 as a relation between uranium concentration and relative standard deviation.

The obtained results plotted in Table 2 reveal that the iron ions present in the both concentration of phosphoric acid had no effect on the uranium concentration and the RSD was less than 1at all uranium percent. This results were confirmed by t-test for iron ions which had been calculated at two value 0.05 and 0.01 at D.F 4 and the obtained results show that t-calculated < t-tabulated where t calculated was 0.263 while t-tabulated was 4.604, 3.747 at 0.05 and 0.01 respectively, which indicate that there is no significance difference between the treatment and the iron ions had no effect on the uranium concentration determination, similar results is obtained at ortho phosphoric concentration of 5 mol l^{-1}.

These results had been confirmed by the obtained value of f test where the calculated one is 2.01 (Table 2) which is less than the f-tabulated at 0.01and 0.05 (3.84 and 7.01 respectively). These results clear that the iron ions had no effect on the uranium concentration determination by the investigated methods.

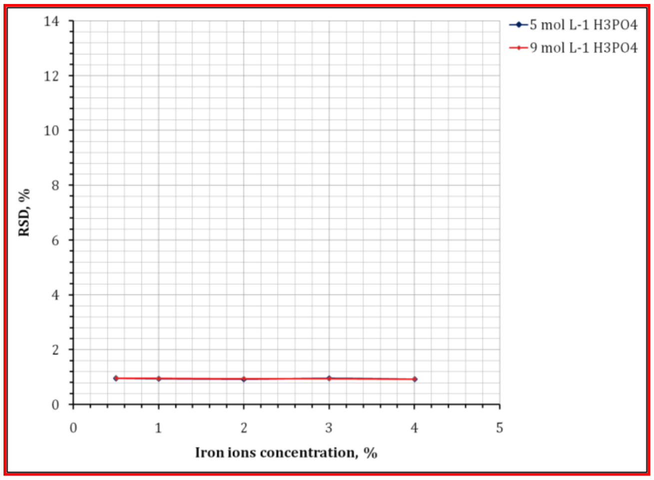

Figure (2): Relation between RSD and uranium concentration 5 and 9 mol l^{-1} phosphoric acid.

Table (2): F-test for effect of iron ions concentration on uranium concentration determination at 5 and 9 Mol L^{-1} ortho phosphoric acid concentrations.

Source of variation	D.F	SS	MSS	F
Between	4	18755848.5	4688962.1	2.010
Ex. Error	8	18655553.02	2331944.1	
Total	12			

3.2.2.2. Effect of Fluoride ions on uranium determination:

The effect of fluoride ions concentration on the uranium determination on phosphoric acid solution, was studied by forming two sets of fluoride standard solutions of 0.2, 0.5, 1, 1.5 (≈ 5 and 9 mol L^{-1} phosphoric acid, uranium 100 ppm). The obtained results are presented graphically in Figure 3 as a relation between uranium concentration and relative standard deviation and statistically analyzed in Table 3.

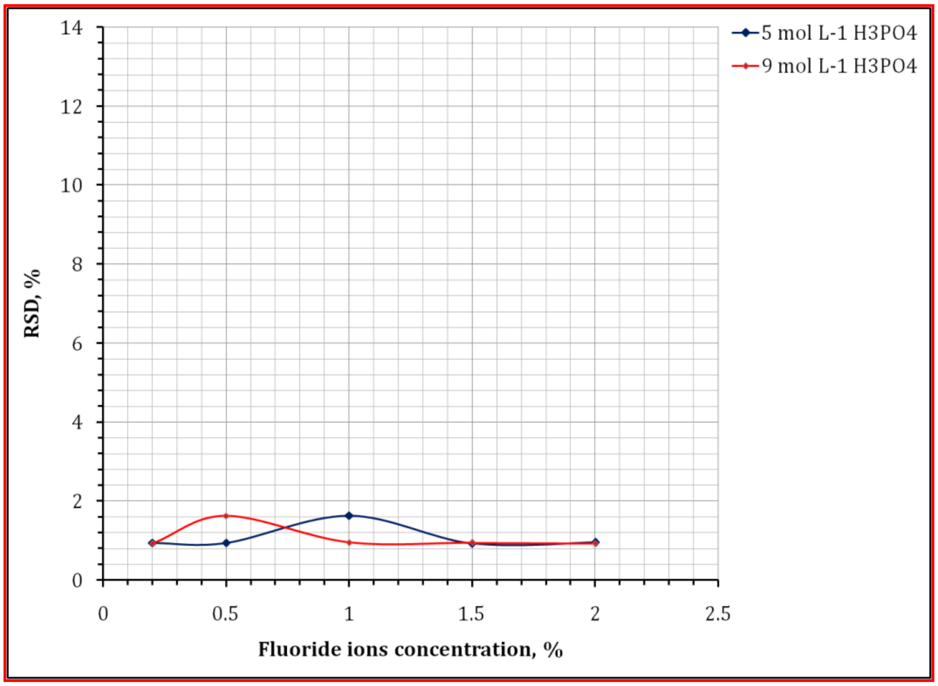

Figure (3): Relation between RSD and uranium concentration 5 and 9 mol l^{-1} phosphoric acid.

From the obtained results in Figure (2), it is clear that the F^- ions has no effect on the uranium determination at any concentration. These results were statistically analyzed by t-test. The t-test for Fluorin*e* ions has been calculated at two values 0.05 and 0.01 at D.F 4. The calculated t-test was 0.490 (Table 3) which is less than the tabulated t at 0.05 and 0.01 (4.604, 3.747 respectively). The prevailed results indicate that there is no significance difference between the treatment and the *Fluoride* ions had no effect on the uranium determination by this method. These results have been confirmed by f-test.

Table (3): F-test for effect of fluorine ions concentration on uranium determination at 5 and 9 Mol L^{-1} ortho phosphoric acid concentrations.

Source of variation	D.F	SS	MSS	F
Between	4	60636.2	15159.05	1.09
Ex. Error	8	111169.9	13896.2	
Total	12			

The value of f-tabulated at 0.01 is 3.84 and 0.05 is 7.01 where both are greater than the calculated f-test (1.09 Table 9). These results confirm the obtained results by t-test. Similar result is obtained at ortho phosphoric concentration of 5 mol l^{-1}.

3.2.2.3. Effect of free sulfate ions on uranium determination:

The influence of sulfate ions concentration on the uranium determination on phosphoric acid solution was investigated by forming two sets of sulfate standard solutions of 0.5, 1, 2, 3 and 4 g L^{-1} (≈ 5 and 9 mol L^{-1} phosphoric acid, uranium 100 ppm). The obtained results are presented statistically analyzed in Table 4 and graphically in Figure 4 as a relation between uranium concentration and relative standard deviation. From the obtained results in Figure 4, it is clear that the sulfate ions had no effect on the uranium determination and its RSD was less than 1 % which confirms the obtained results. The t-test for sulfate ions has been calculated at t D.F 4. The calculated t-test was 0.185 while the tabulated t at 0.05 was 4.604 and at 0.01 was 3.747. The obtained results indicate that there is no significance difference between the treatment and the sulfate ions had no effect on the uranium determination by this method.

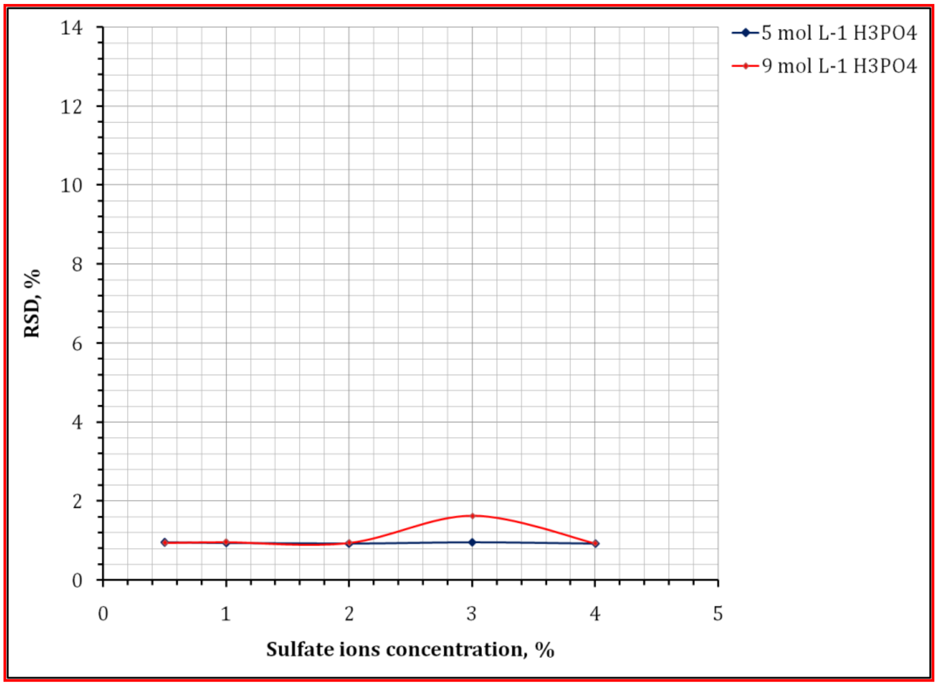

Figure (4): Relation between RSD and uranium concentration 5 and 9 mol l^{-1} phosphoric acid.

The f-test confirm the previous results by comparing the calculated f-test which had a value of 3.00 (Table 4) with the tabulated one at 0.01 and 0.05 (3.84 and 7.01 respectively). The obtained results indicated that there is no significance difference at both level and sulfate ions had no effect on uranium concentration by this method.

Table (4): F-test for effect of free sulfate ions concentration on uranium determination at 5 and 9 Mol L^{-1} ortho phosphoric acid concentrations.

Source of variation	D.F	SS	MSS	F
Between	4	60313.06	15078.28	3.00
Ex. Error	8	40206.9	5025.86	
Total	12			

3.2.2.4. Effect of Manganese ions on uranium determination:

The influence of manganese ions concentration on the uranium determination on phosphoric acid solution, was investigated by forming two sets of manganese standard solutions of 0.5, 1, 2, 3 4 g L^{-1} (≈ 5 and 9 mol L^{-1} phosphoric acid, uranium 100 µg ml^{-1}). The obtained results are graphically presented in Figure 5 as a relation between uranium concentration and relative standard deviation. From the results, it is clear that the manganese ions had no effect on the uranium determination and its RSD was in the range of 3 which is the permissible limit (10) which confirms the obtained results. The obtained results are statistically analyzed by using t-test, Table 5, where the calculated t at D.F 4 was 1.130969 while the tabulated t at 0.05 and 0.01 were 4.604 and 3.747 respectively. In addition, the obtained results confirm that there is no significance difference between the concentration of *manganese* ions and the uranium determination by this method.

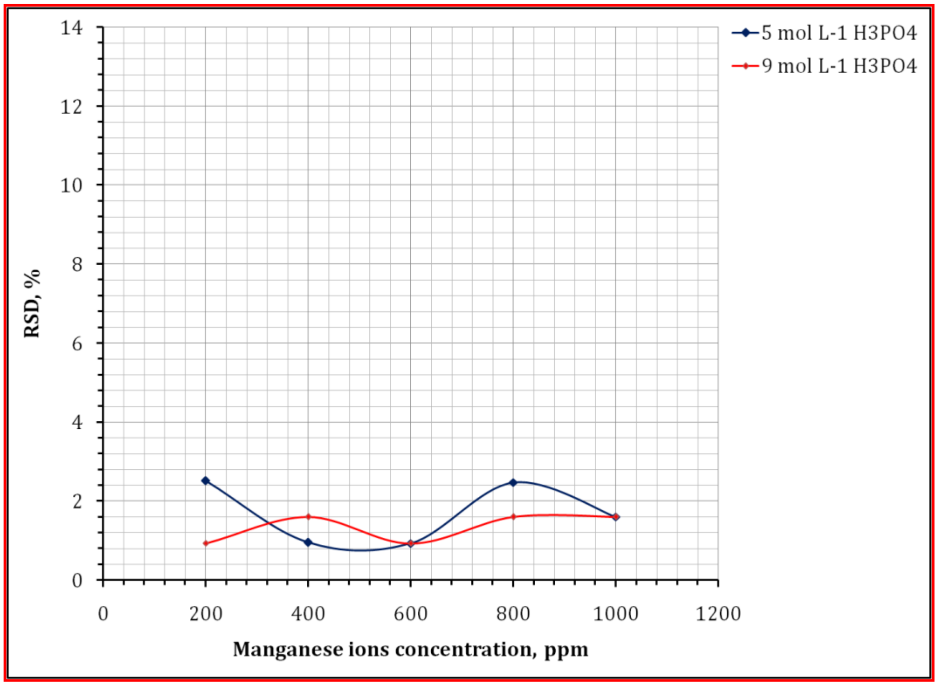

Figure (5): Relation between RSD and uranium concentration 5 and 9 mol l^{-1} phosphoric acid.

The f-test confirm the previous results by comparing the calculated f-test which had a value of 3.01 (Table 5) with the tabulated one at 0.01 and 0.05 (3.84 and 7.01 respectively). The obtained results indicated that there is no significance difference at any manganese concentration and there was no effect on uranium determination.

Table (5): F-test for effect of Manganese ions concentration on uranium determination at 5 and 9 Mol L^{-1} ortho phosphoric acid concentrations.

Source of variation	D.F	SS	MSS	F
Between	4	60467.2	15116.8	3.001
Ex. Error	8	40268.8	5033.6	
Total	12			

3.2.2.5. Effect of Vanadium ions on uranium determination:

The influence of vanadium ions concentration on the uranium determination on phosphoric acid solution was investigated by forming two sets of vanadium standard solutions of 0.5, 1, 2, 3, and 4 g L^{-1} (≈ 5 and 9 mol L^{-1} phosphoric acid, uranium 100 µg ml^{-1}). The obtained results are presented graphically in Figure 6 as a relation between uranium concentration and relative standard deviation. From the results, it is clear that the vanadium ions had no effect on the uranium determination and its RSD was less than 1 which is under the permissible level range. The obtained results are confirmed using t-test where the calculated t at D.F 4 was 1 while the tabulated t at 0.05 and 0.01 were 4.604 and 3.747 respectively. The obtained results indicate that there is no significance difference between the concentration vanadium *ions* in other words at any vanadium concentration there is no effect on the uranium determination by this method.

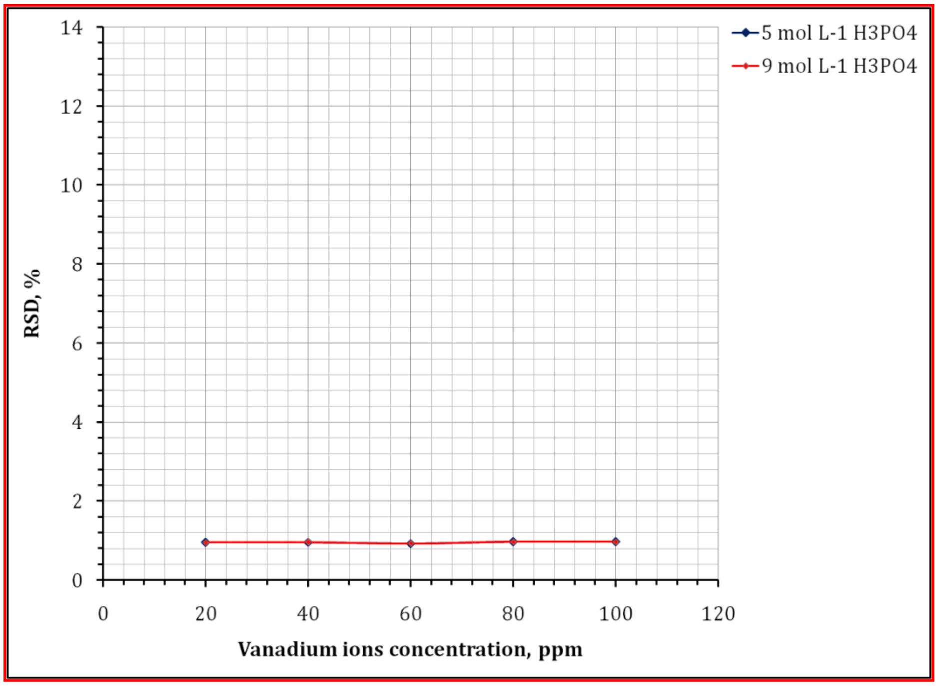

Figure (6): Relation between RSD and uranium concentration 5 and 9 mol l^{-1} phosphoric acid.

The f-test confirm the previous results by comparing the calculated one which had a value of 3.001 (Table 6) with the tabulated one at 0.01 and 0.05 (3.84 and 7.01 respectively). The obtained results indicated that there is no significance difference at both level vanadium ions and there is no effect on uranium concentration determination by this method.

Table (6): F-test for effect of Vanadium ions concentration on uranium determination at 5 and 9 Mol L^{-1} ortho phosphoric acid concentrations.

Source of variation	D.F	SS	MSS	F
Between	4	58548.8	14637.2	3.001
Ex. Error	8	39021.9	4877.735	
Total	12			

2.2.2.6. Effect of Zinc ions on uranium determination:

The influence of zinc ions concentration on the uranium determination on phosphoric acid solution was investigated by forming two sets of zinc standard solutions of 0.5, 1, 2, 3 and 4 g L^{-1} (≈ 5 and 9 mol L^{-1} phosphoric acid, uranium 100 µg ml^{-1}). The obtained results are presented graphically in Figure 7 as a relation between uranium concentration and relative standard deviation. From the results in, it is clear that the zinc ions had no effect on the uranium determination and its RSD was less than 2 which is under the permissible level range. The value of t-test at D.F 4 was 0.112 while the tabulated one at 0.05 and 0.01 were 4.604 and 3.747. The obtained results show that the value of calculated t is small than the tabulated one which gives an indication that there is no significance difference between both treatment.

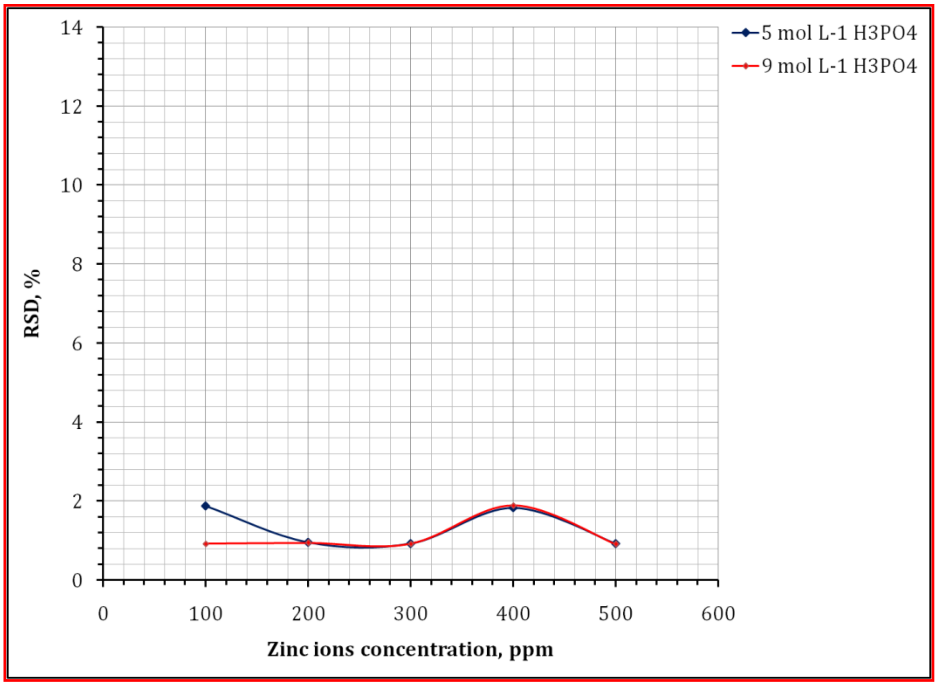

Figure (7): Relation between RSD and uranium concentration 5 and 9 mol l^{-1} phosphoric acid.

The f-test confirm the previous results by comparing the calculated f-test which had a value of 3.002 (Table7) with the tabulated one at 0.01 and 0.05 (3.84 and 7.01 respectively). The obtained results indicated that there is no significance difference at any level of zinc ions concentration and there was no effect on uranium concentration by this method.

Table (7): F-test for effect of Vanadium ions concentration on uranium determination at 5 and 9 Mol L^{-1} ortho phosphoric acid concentrations.

Source of variation	D.F	SS	MSS	F
Between	4	61749.9	15437.45	3.002
Ex. Error	8	41143.5	5142.6	
Total	12			

3.3. Uranium determination in commercial phosphoric acid samples:

Based on the results obtained from uranium determination in synthetic phosphoric acid, uranium was determined in different commercial phosphoric acid samples, representing dihydrate and high strength phosphoric acid, with different uranium concentrations by of Davies & Gray/NBL Modification method. In this concern, different concentrations of uranium standard were added to commercial phosphoric acid samples and then the total uranium concentration was and the original uranium concentration is determined.

The uranium concentration in commercial phosphoric acid was determined, with two different acid concentration, first one with concentration range of 28 – 30 % P_2O_5 (≈ 5 mol L^{-1}), while the second range from 42 to 45 % P_2O_5 (≈ 9 mol L^{-1}) by adding different uranium standard concentration, 10, 20, 30 and 40 mg L^{-1} to phosphoric acid sample. The obtained results are graphically plotted in Figure 8 as a relation between uranium standard concentration addition and uranium concentration measured.

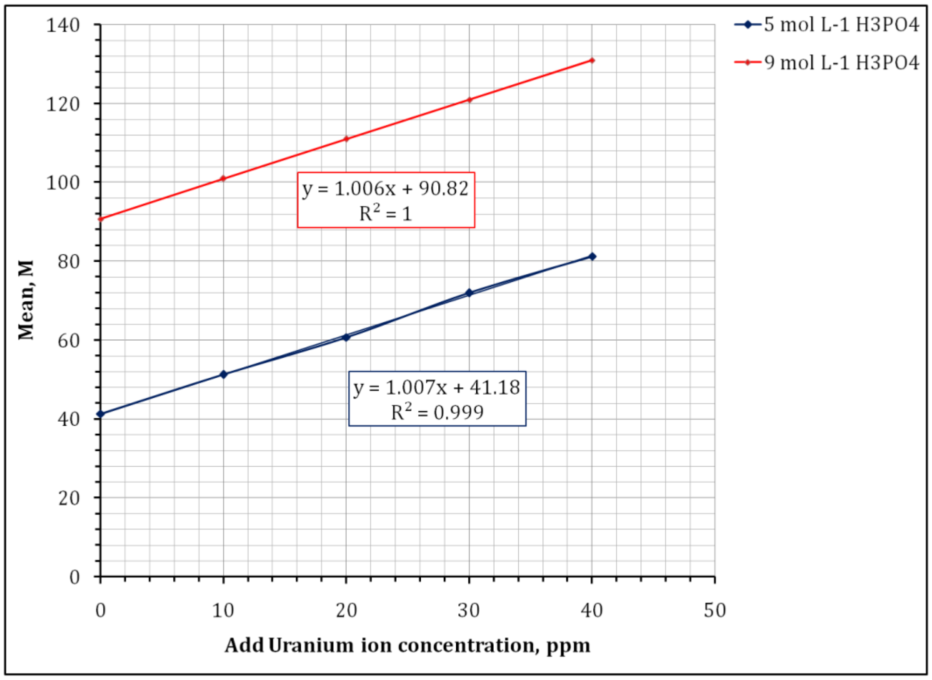

Figure (8): Uranium concentration determination in commercial phosphoric acid samples.

The results obtained from Figure (8) clarify that the uranium concentration in the original sample is 41.0 ppm which almost the same results obtained from direct uranium determination in original sample, 41.3 ppm, without uranium standard addition. The obtained result was confirmed by f-test (Tables 8 and 9) which indicate that the addition of uranium to the pregnant solution do not affect the efficiency of the method for uranium determination, where the calculated f was 3.0 while the tabulated one at degree of freedom (4 and 8), and significance 0.01 and 0.05 was3.84 and 7.01 respectively which is higher than the calculated one. This means that, the Davies & Gray/NBL Modification method is applicable to measure uranium in dihydrate phosphoric acid samples at both acid concentrations.

Table (8): F-test analysis for effect of uranium ions addition on uranium determination at 28 – 30 % P_2O_5 (≈ 5 mol L^{-1}) concentration.

Source of variation	D.F	SS	MSS	F
Between	4	20745.1	5186.27	3.01
Ex. Error	8	13822.9	1727.87	
Total	12			

Table (9): F-test analysis for effect of uranium ions addition on uranium determination at 42 – 45 % P_2O_5 (≈ 9 mol L^{-1}) concentration.

Source of variation	D.F	SS	MSS	F
Between	4	69044.3	17261.1	3.039
Ex. Error	8	45425.1	1727.87	
Total	12			

4. **CONCLUSION:**

The Davies-Gray method was modified for uranium determination in phosphoric acid. The concentration of uranium with the modified method was measured and compared with uranium determination with spectrophotometer method. The effect of different impurities in phosphoric acid such as; iron, fluoride, free sulfate, manganese, vanadium, and zinc on uranium concentration determination by the modified method were investigated. The obtained results clarify that, the modified method is applicable for uranium determination in both di-hydrate and high strength phosphoric acid in the range of ≥ 10 - 150 ppm uranium ion concentrations with high accuracy precision. The phosphoric acid impurities have almost no effect in uranium determination by using the modified method.

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