

Determination of Uranium and Thorium in the Industrial Phosphoric Acid Using X-Ray Fluorescence Spectrometry with Wavelength Dispersive (WDXRF)

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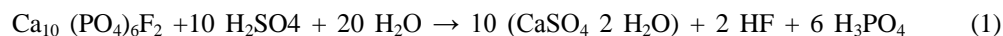
Abstract

The method of determination for uranium and thorium in the industrial phosphoric acid by wavelength-dispersive X-ray fluorescence spectrometry (WDXRF) responds positively to all the validation tests and can be adopted for the dosage for these elements. It is clear that the procedure of the proposed method is simple and requires less time to complete the analysis. The concentration for uranium and thorium in the Tunisian phosphoric acid is in the order of 22 ppm for uranium with a coefficient of variation of 0.77% and of about 4 ppm for thorium with a coefficient of variation of 1.37%.

Keywords: WDXRF, radioactive, uranium, thorium, analysis, validation

1. Introduction

Industrial Phosphoric acid is one of the most important products of the chemical industry, it is used in the manufacture of phosphate fertilizers; TSP: $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and DAP: $(\text{NH}_4)_2\text{HPO}_4$, feed livestock ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) and sequestering phosphate (sodium hexametaphosphate). The production of phosphoric acid is based on the chemical treatment of the rock phosphate with sulfuric acid, this process can be described by the following overall reaction of (Slack, 1968; Waggaman, 1969):



The sulfuric attack dissolved at the same time as apatite, almost all existing impurities in the soil. These consist of heavy metals, radionuclides and other natural elements (Becker, 1989). Some of these impurities can be recycled such as (U, Th, Y, Sc, rare earth ...) and could be recovered, and others that are penalizing for further use of acid such as (Cd, Cr, Pb, Mg ...), they must be eliminated or minimized.

In this work we focus on uranium and thorium and particularly to techniques for determining these elements. The methods currently used are:

- Gravimetry which consists in the precipitation of the uranyl ion with 2-hydroxy-1-naphthaldehyde, uranium is determined as U_3O_8 after calcining the precipitate at 850 °C. (Lopez et al., 1989) or the precipitation of the UO_2^{2+} ion, in the pH range 3–5, by a solution of *p*-aminobenzoic acid and pyridine in water. An amorphous yellow precipitate forms, which is easily filtered and has the composition $\text{UO}_2(\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{COO})_2 \cdot 2\text{Py} \cdot 2\text{H}_2\text{O}$. which is converted by calcination to U_3O_8 (Ripan and Sacelean, 1965). The uranium (VI) is precipitated quantitatively in the range of pH 5.0 to 7.5 with *N*-benzoyl-*o*-tolylhydroxylamine in the form of $\text{UO}_2(\text{C}_{14}\text{H}_{12}\text{O}_2\text{N})_2$ (Mrinal and Majumdar, 1970). The thorium, forms an insoluble complex with vanillin in the range of pH 4.0 to 6.2. Thorium (IV) can be determined gravimetrically and separated from cerium, uranium (VI) and trivalent rare earth. The precipitate obtained is converted into oxide ThO_2 by calcination and then weighed (Jain and Singh, 1962). Thorium (IV) make a precipitate with benzenephosphonic acid in the form $\text{Th}(\text{C}_6\text{H}_5\text{PO}_3)_2 \cdot 3\text{H}_2\text{O}$ at pH around 0.5. The precipitate containing three molecules of H_2O and it is stable between 140 °C and 180 °C. between 240 °C and 300 °C, the precipitate contains only two molecules of H_2O . $\text{Th}(\text{HPO}_4)_2$ is obtained anhydrous above 800 °C (Charles banks and Rodney Davis, 1955).

- Volumetry is used for dosing the uranium (VI) by carrying out a reduction using ferrous sulfate in phosphoric medium. The excess of Fe^{2+} is determined by the dichromate (Al Ammar and Basheer, 1993).

- The inductively coupled plasma coupled to mass spectrometry (ICP-MS) (Aydin and Soylak, 2007): the separation and concentration of thorium (IV) and uranium (VI) by solid phase extraction on Duolite XAD761 (resin adsorption). The chelates of thorium (IV) and uranium (VI) with 9-phenyl-3-fluorone formed and adsorbed on the XAD761 Duolite.

Thorium (IV) and uranium (VI) are quantitatively eluted with HCl 2 mol L⁻¹ and determined by inductively coupled plasma coupled to mass spectrometry (ICP-MS).

Another method to extract the uranium present in an aqueous phase; we have the extraction of the uranium using the D2EHPA and Synergistic D2EHPA-TOPO Mixture (Ali et al., 2012; Beltrami et al., 2013; Beltrami et al., 2014; Orabi et al., 2015), using a synergistic DOPPA-TOPO mixture (Krea and khalaf, 2013), using of DNPPA and bidentateoctyl(phenyl) CMPO (Mondal et al., 2014) and the adsorption method of the uranium (Hussein and Morsy, 2011; Morsy and Hussein, 2012; Ahmed et al., 2016)

- The spectrophotometric method; ion UO₂²⁺ make a chelate with meloxicam by the following reaction: 2 (meloxicam H) + UO₂²⁺ → UO₂(meloxicam)₂ + 2H⁺, the product is a yellow complex with an absorbance passes through a maximum at 398 nm (Lutfullah et al., 2008). Thorium, extract from a hydrochloric solution using the acid di (2-ethylhexyl) orthophosphoric, where the color is developed in the organic solution by adding an Arsenazo III solution and isopropanol, is determined by spectrophotometry with a maximum absorbance at 660 nm (Cerrai and Ghersini, 1967).

- The high resolution gamma spectrometry is used to determine the concentration of uranium and thorium in the surface soils, where soil samples are ground and sieved then stored for four weeks before analysis, it is carried for 18 hours (Tzortzis and Tsertos, 2004).

- The thin layer chromatography (Hodisan at al., 1998) is also used for the determination of uranium and thorium in presence of other metal ions using the iso-acid propyldithiophosphoric (PRDTP-i) in mobile phase as a complexing agent to differentiate between the species studied by modification of their retention time.

-The determination of the uranium isotope and thorium isotope is possible by coupling the ion chromatography and Inductively Coupled Plasma coupled to mass spectrometry IC-ICP-MS (Benkhedda et al., 2005; Zheng and Yamada, 2007; Rathore, 2008; Goodall and Lythgose, 1999; Betti, 1997), but the IC-ICP-MS has limitations due to the structure of the sample (capacity of the column, the acidity ...).

-The determination of thorium is possible by Energy dispersive X-ray fluorescence (EDXRF) (Mirashi et al., 2010), but we have problems of resolution and selectivity with (EDXRF).

-Other techniques such as the fluorimetry (Rathore, 2008; Sanjukta et al., 2008) The neutron activation analysis (Shinotsuka and Ebihara, 1997; Byrne and Benedik, 1988) and the alpha spectrometry (Hou and Roos, 2008; Saidou et al., 2008; Benedik et al., 2009; Jia et al., 2008) can be used for the determination of uranium and thorium, but these techniques require very long preparation of the sample (pre-concentration of the sample separation ...).

Although a variety of methods for the determination of uranium and thorium in different types of samples have been developed, there are several disadvantages for every method;

-The Precipitation methods: uranium and thorium have the same chemical properties, so they are difficult to separate, they precipitate together. We must then search the optimal conditions for selectivity. In addition the sensitivity of these gravimetric methods depends on a certain number of factors, the principal one being the interference, it is caused by the structure and concentration of the matrix elements (interference with the rare earth essentially).

-For colorimetric methods there are the stability problems for complexes and the problems of selectivity for the two elements (uranium and thorium).

- The inductively coupled plasma coupled to mass spectrometry (ICP-MS): the disadvantages of this method are the salinity of the matrix of samples processed and the isobaric interferences.

-The neutron activation analysis and the alpha spectrometry require a long process (counting and purification) and the use of a radioactive tracer.

- The gamma spectrometry, despite that it allows direct determination of uranium and thorium through their decay products, requires a long time to establish an equilibrium radiochemical decay products.

These methods require the use of many reagents and require multiple steps in preparations which causes a large error in measurement, in addition these methods require a very long time. Therefore it would be useful to have a simple, fast and accurate method for the determination of uranium and thorium in industrial phosphoric acid. The X-ray fluorescence spectrometry (XRF) is always an acceptable technique due to its acceptable precision and accuracy associated with its lower cost compared to the techniques mentioned above. We propose to perform the analysis of uranium and thorium in the industrial phosphoric acid by the wavelength-dispersive X-ray fluorescence spectrometry (WDXRF) with the use of the intensity of the line La (La1 and La2) for the determination of uranium and thorium. The X-ray fluorescence was used to determine traces of uranium and thorium in zircon, forming a tablet with 100 mg of zircon (Voldet, 1972), the author has determined the values in the range of 100 to 2000 ppm of uranium and 100 to 300 ppm of thorium in rocks zircon of Greenland. XRF is also used for the determination of thorium in the range of 0.1 to 1.2% of the plutonium in (Woltermanet al., 1974).

2. Experimental

2.1 Materials

2.1.1 Spectrometer

An X-ray fluorescence spectrometer (Magix 3kW, PW2403, PANalytical) was used for the determination of the uranium; it is a sequential spectrometer with wavelength-dispersive with a channel of measure based on a single goniometer covering the complete range of measure. It is equipped with an X-ray tube which is the X-ray source, the anode of the X-ray tube is in rhodium.

2.1.2 Scintillation Detector

It is constituted by a crystal of iodide of sodium in which the atoms of thallium are distributed in a homogeneous way (NaI; Tl), by a photocathode and by a tube photomultiplier.

It works by converting the X-ray in light which is then measured with a photomultiplier.

2.2 Sample Preparation

The samples of industrial phosphoric acid are analyzed directly without any prior preparation. Indeed, the industrial phosphoric acid is put in a cup (special sample holder for liquid) whose bottom is a polymer film and it is subjected directly to incident X-rays from the X-ray tube. In our case, it comes to an inverted optical. The X-ray tube is located under the sample. If the film broken during the analysis of the liquid, it can damage these parts. It is therefore necessary to adopt a sufficiently resistant film and make a compromise with the X-ray absorption and the presence of additives in the film (which allow the film to more resistant to some products). This problem does not arise in the case of direct optical.

For this problem, we used a film for liquid analysis by XRF which does not absorb X-rays and which has no effect or interference matrix which may influence our results.

This film is *X-Ray film MYLAR®*, diameter 63.5mm. We used a mass of 3 g with 0.1 mg of accuracy for industrial phosphoric acid sample. The analysis is made under helium (900 hPa pressure) to prevent boiling under the vacuum.

2.3 Measurement Conditions

Measurement conditions of uranium and thorium in industrial phosphoric acid using WDXRF are summarized as follows;

- Atmosphere: Helium (900 hPa pressure)
- Power: 60kV, 50 mA
- Crystal: LiF220
- Collimator: 150microns
- X-ray: U-L α 1 line of 13.631 keV energy and Th- L α 1 line of 12.986keV energy.

The WDXRF analysis of uranium and thorium in industrial phosphoric acid is shown in Figure 1.

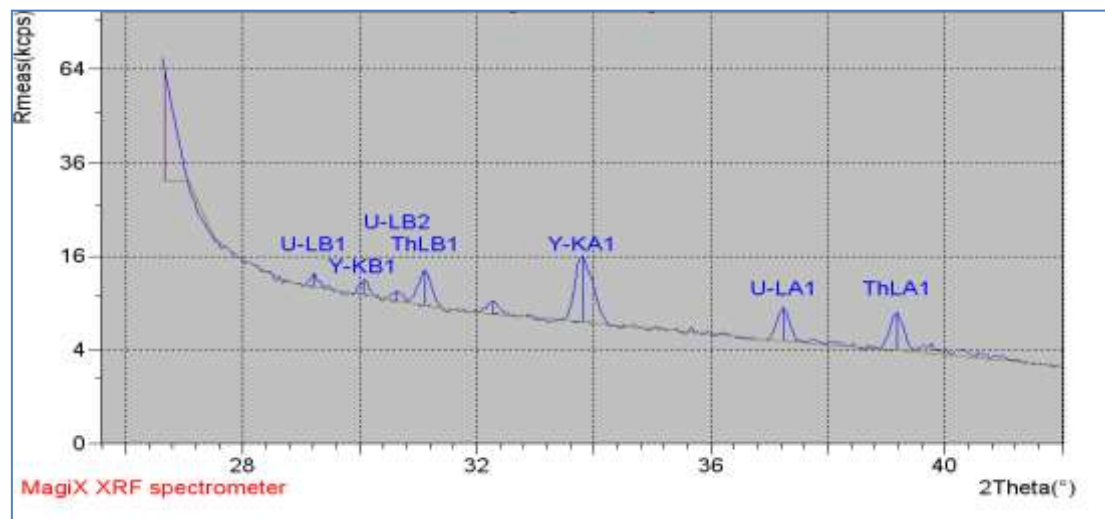


Figure 1. Detection of uranium and thorium peak using the crystal LiF220

- The experimental angle of the line of uranium: U-L α 1 (2θ) [noted U-LA1]: 37.247°

- The experimental angle of the line of thorium: Th- La1 (2θ) [noted Th-LA1] : 39.175°

3. Validation

The proposed method was validated by linearity, detection limit and quantification limit, specificity, fidelity (repeatability and reproducibility) and accuracy (AFNOR NF XPT 90-210, 1999; AFNOR NF ISO 5725-1, 1994).

3.1 Results and Discussion

3.1.1 Linearity, Detection Limit and Quantification Limit

The linearity of the proposed method was investigated by repeating the analysis ($n = 6$) at six concentration levels of 0, 20, 40, 60, 80 and 100 ppm for uranium and 0, 10, 20, 30, 40 and 50 ppm for thorium.

The intensity obtained at each concentration was plotted against the initial concentration of uranium and thorium and the linear regression equation was evaluated in the statistical treatment of calibration data. The characteristics of the regression were calculated using Microsoft ExcelTM. We have the following curves in figure 2 and in figure 3:

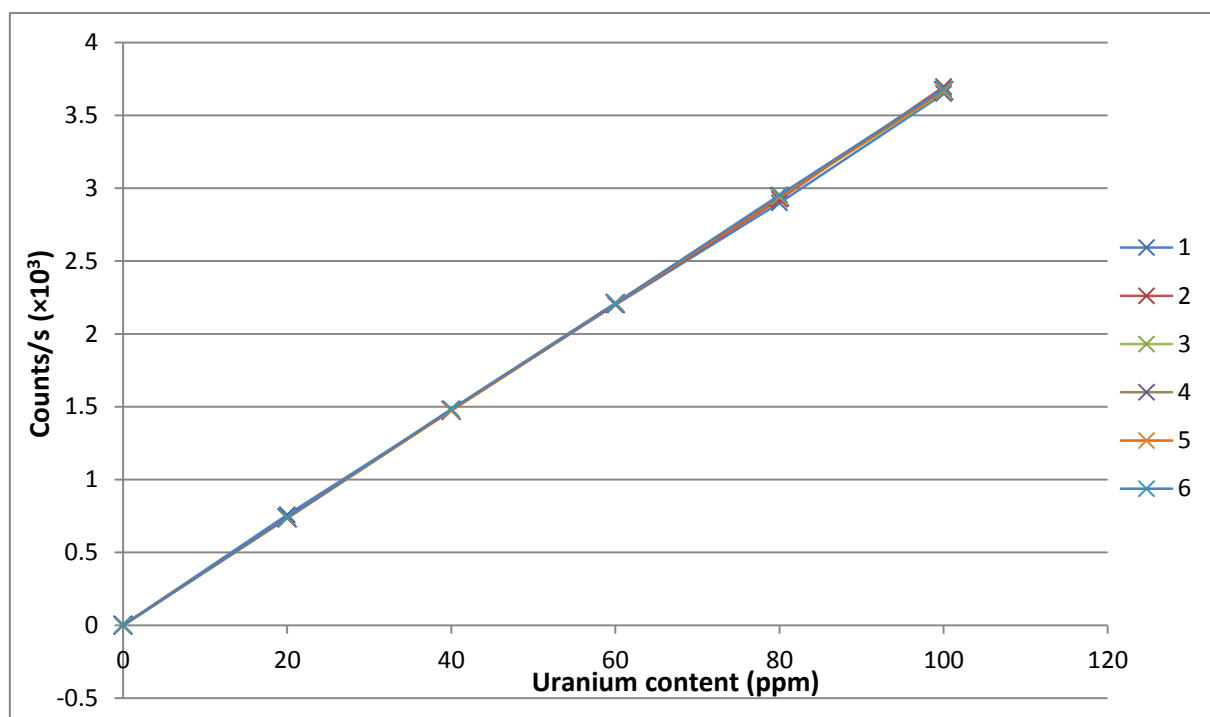


Figure 2. Calibration of the method for the determination of uranium

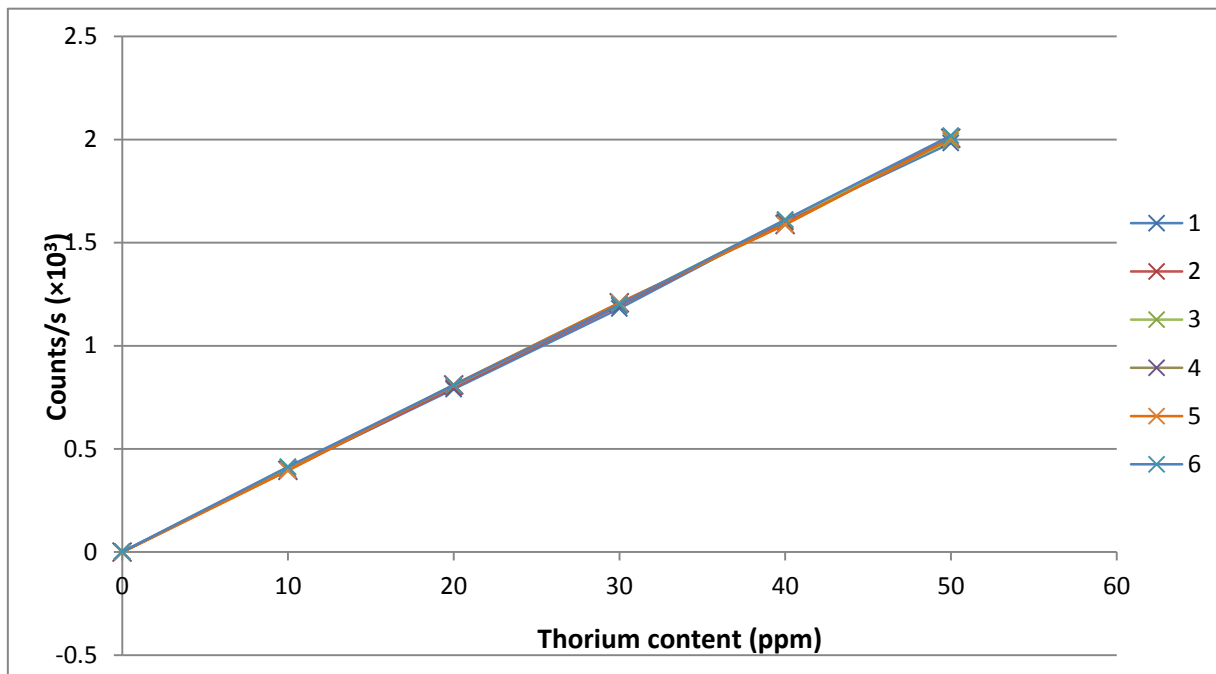


Figure 3. Calibration of the method for the determination of thorium

The measurement collected to perform the linearity can be used to calculate the sensitivity (b_1) and its standard deviation $S(b_1)$ and the blank value b_0 and its standard deviation $S(b_0)$.

These standard deviations ($S(b_1)$ and $S(b_0)$) define as follows the limits of detection and quantification, based on the two definitions:

$$\text{The limit of detection: LD} = \frac{b_0 + 3.S(b_0)}{b_1} \tag{2}$$

$$\text{The limit of quantification: LQ} = \frac{b_0 + 10.S(b_0)}{b_1} \tag{3}$$

$$b_1 = \frac{SPE(x,y)}{SCE(x)} \tag{4}$$

$$b_0 = \bar{y} - b_1 \cdot \bar{x} \tag{5}$$

$$S(b_1) = \sqrt{\frac{s^2(e)}{SCE(x)}} \text{ standard deviation of the sensitivity } b_1 \tag{6}$$

$$S(b_0) = \sqrt{s^2(e) \left(\frac{1}{np} + \frac{\bar{x}^2}{SCE(x)} \right)} \text{ standard deviation of the blank } b_0 \tag{7}$$

$s^2(e)$: experimental variance of the regression.

$SCE(x)$: Sum of squared deviations for the variable x .

$SPE(x, y)$: Sum of the products of deviations for the variable x and y .

The results of the study linearity test are summarized in the following Table 1:

Table 1. Statistical results of the calibration

Designation	Observed value for uranium	Observed value for thorium
Number of levels(p)	6	6
Total number of measurements	36	36
sensitivity b_1	0.037 ppm	0.040 ppm
blank value b_0	0.006 ppm	0.002 ppm
Equation of linear regression	$Y=0.037X+0.006$	$Y=0.040X+0.002$
Correlation coefficient	0.9999	0.9998
Standard deviation of sensitivity $S(b_1)$	5.918×10^{-5}	8.235×10^{-5}
Standard deviation of the blank value $S(b_0)$	0.003	0.002
Detection limit (DL)	0.483 ppm	0.235 ppm
Quantification limit (QL)	1.168 ppm	0.671 ppm

The results of the test of evaluation of the linearity showed that the model of regression is considered acceptable for both for uranium and thorium and that the domain of linearity is validated.

3.2 The Specificity

To perform this test, we made 16 ($p=16$) standard additions on selected samples to cover the scope of the method. The regression line that passes from the points from the following equation is calculated:

$$r_i = C_0 + C_1 \cdot v_i \quad (8)$$

C_0 the intercept of the regression line.

C_1 the slope of the regression line.

v_i added content of uranium or thorium in the samples.

r_i observed content of uranium or thorium = content measured after addition - content measured before addition.

We carry a graph the values of v_i additions and observed values r_i and the straight recovery calculated and the line of slope 1 (equation $y = x$). The curves are shown in figure 4 for uranium and figure 5 for thorium.

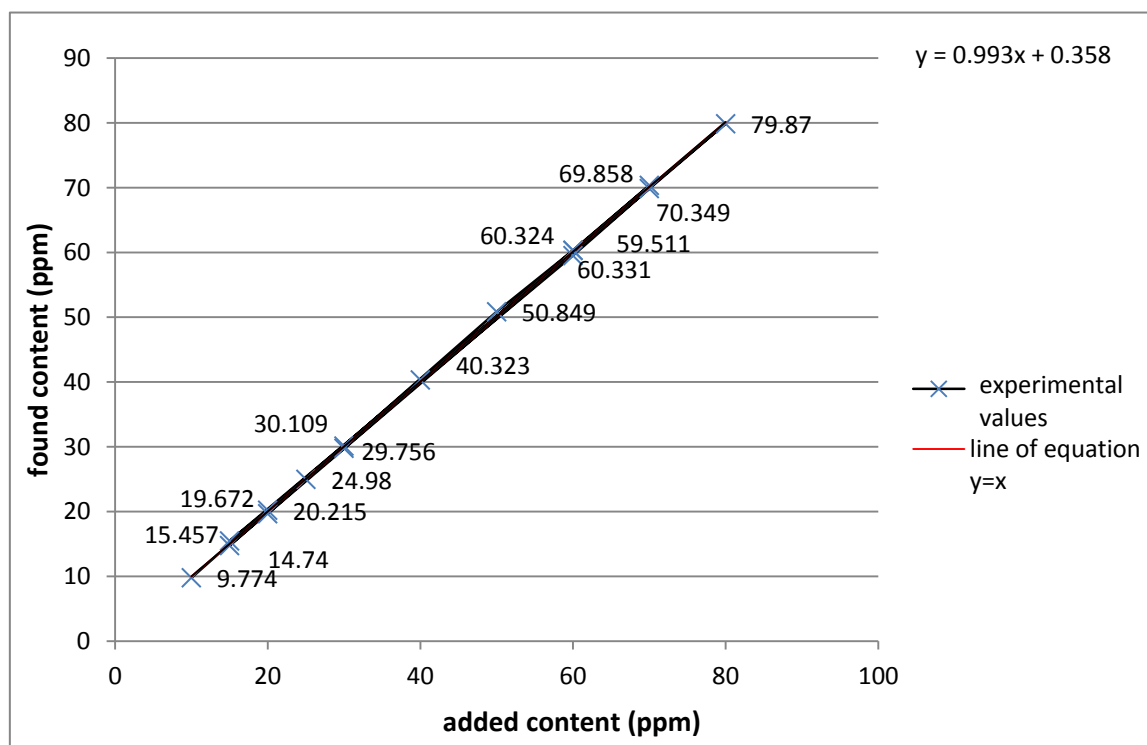


Figure 4. Study of the specificity of the method for the determination of uranium

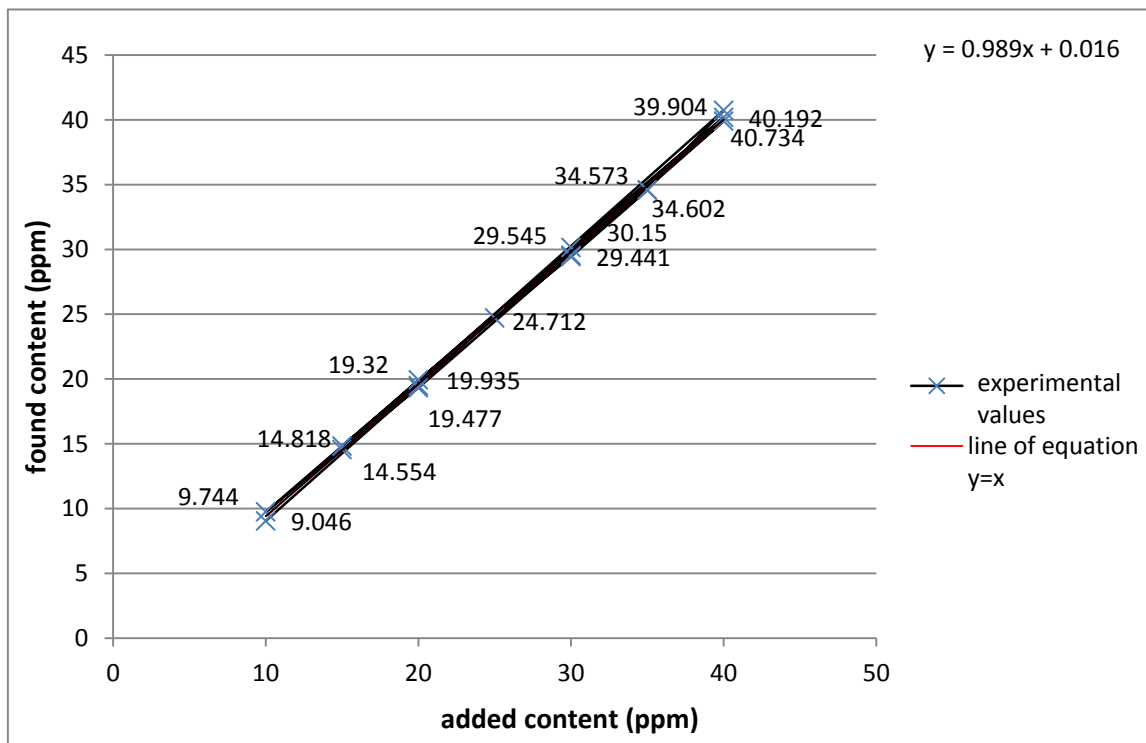


Figure 5. Study of the specificity of the method for the determination of thorium

3.3 Interpretation

To check if the slope of the regression line is equal to 1, a test is performed by calculating the t_{obs} which follows a Student distribution with $p-2$ degrees of freedom. t_{obs} is a criterion calculated to check the slope as it is described in the validation standard.

$$t_{obs} = \frac{|C_1 - 1|}{\sqrt{\frac{s^2(e)}{SCE(v)}}} = \frac{|C_1 - 1|}{s(C_1)} \tag{9}$$

$s^2(e)$: experimental variance of the regression.

$SCE(v)$: Sum of squared deviations for the variable v .

$s(C_1)$: standard deviation of the slope C_1

a) If t_{obs} is less than or equal to the critical value read from the Student table to the risk $1 - \alpha/2$ with $v = p - 2 = 14$ degrees of freedom, it is possible to conclude that the absence of interference and that the specificity is acceptable.

b) If t_{obs} is greater than the critical value, the method is not specific. In general, the risk of error α is taken to 1%.

t_{crit} value of a variable of Student to the risk $1 - \alpha/2$ with $v = p - 2$ degrees of freedom, the risk of error α is taken to 1% ($t_{crit} = 2.977$ from the Student table).

➤ We obtain $t_{obs \text{ for uranium}} = 0.788$ and $t_{obs \text{ for thorium}} = 2.046$

To check if the intercept is equal to 0, a test is performed by calculating the t'_{obs} which follows a Student distribution with $p-2$ degrees of freedom. t'_{obs} is a criterion calculated to check the intercept as it is described in the validation standard.

$$t'_{obs} = \frac{|C_0|}{s(C_0)} \tag{10}$$

$s(C_0)$: standard deviation of the intercept C_0

a) If t'_{obs} is less than or equal to the critical value read from the Student table to the risk $1 - \alpha/2$ with $p - 2$ degrees of freedom, it is possible to conclude that the intercept is not different from 0.

- b) If t'_{obs} is greater than the critical value, it is possible to conclude that the intercept is not equal to 0 and that the method is not specific. In general, the risk of error α is taken to 1%.
- We obtain t'_{obs} for uranium = 0.849 and t'_{obs} for thorium = 0.085
- $t_{obs} < t_{crit}$ it is possible to conclude that the absence of interference and that the specificity is acceptable for uranium and for thorium.
 - $t'_{obs} < t_{crit}$ it is possible to conclude that the intercept is not different from 0 for uranium and for thorium.
- The slope of the regression line for uranium and for thorium is equal to 1 and the intercept of the regression line for these two elements is equal to 0. It is thus possible to conclude that the absence of interference in the defined scope and the specificity for these two elements is acceptable.

3.4 The Fidelity (Repeatability and Reproducibility)

3.4.1 Repeatability

In the case of the study of the repeatability of the method of determination of uranium and thorium, 10 industrial phosphoric acid samples covering the scope were analyzed in triplicate repeatability conditions.

The internal repeatability variance of the alternative method $S_r^2(x)$ is equal to the sum $SCE_r(x)$ divided by the number of degrees of freedom appropriate.

$$S_r^2(x) = \frac{SCE_r(x)}{N-p} \quad (11)$$

With:

$$SCE_r(x) = \sum_{i=1}^p \sum_{j=1}^{n_j} (x_{ij} - \bar{x}_i)^2 \quad \text{Sum of squared intra-sample differences} \quad (12)$$

$$\bar{x}_i = \frac{\sum_{j=1}^{n_j} x_{ij}}{n_i} \quad \text{Average of the sample } i \quad (13)$$

$$N = \sum_{j=1}^p n_j \quad \text{Total number of measurements} \quad (14)$$

$$S_r(x) = \sqrt{S_r^2(x)} \quad \text{standard deviation of repeatability intra laboratory} \quad (15)$$

We can calculate the coefficient of variation of repeatability:

$$CV_r(\%) = \frac{S_r(x)}{\bar{x}} \times 100 \quad (16)$$

We obtain a value of standard deviation of repeatability intra-laboratory $S_r(x)$:

$$S_r(x)_{\text{for uranium}} = 0.147 \quad \text{and} \quad S_r(x)_{\text{for thorium}} = 0.042$$

and an average coefficient of variation of repeatability intra-laboratory CV_r : CV_r for uranium = 0.67 % and CV_r for thorium = 1.02 %.

3.4.2 Checking the Stability of Fidelity

It is performed by means of the test of Cochran to the risk error $\alpha = 1\%$. This test is to ensure if the fidelity is constant throughout the application domain.

$$C_{obs} = \frac{S_{\max}^2(x)}{\sum_{i=1}^p S_i^2(x)} \quad (17)$$

$S_{\max}^2(x)$ the maximum experimental variance.

$\sum_{i=1}^p S_i^2(x)$ the Sum of experimental variances.

C_{obs} this is a ratio calculated from the equation cited above to verify the stability of fidelity.

C_{crit} value of a variable of Cochran to the risk $\alpha=1\%$ with n number of distribution and number of sample p .

We compare C_{obs} with C_{crit} which is the critical value of the table of Cochran at the risk of error 1%. The

Statistical results of the verification of the stability of fidelity are presented in Table 2.

Table 2. Statistical results of the verification of the stability of fidelity

Designation	Observed value for uranium	Observed value for thorium
$S_{\max}^2(x)$	0.066	0.005
C_{obs}	0.108	0.097
Number of samples (p)	10	10
Number of replicates(n)	3	3
$C_{crit}(1\%)$	0.536	0.536

C_{obs} for uranium and for thorium is lower than the value of the table at the risk of error 1 %. It is possible to conclude that the fidelity in terms of repeatability intra-laboratory is constant in all the field of application for these two elements. The fidelity in terms of repeatability is acceptable.

3.4.3 Reproducibility

This test is used to calculate the intra-laboratory reproducibility of the method studied, that is to say his fidelity when repetitions are made by several operators or longer time intervals with respect to the method. A sample of industrial phosphoric acid was analyzed for 10 different days ($p=10$) with 3 replicates ($n=3$). The results are summarized in Table 3 for uranium and in Table 4 for thorium.

Table 3. Results of reproducibility test for uranium

Day	Replicates			Average	Variance	$S_r^2(x)$	$S_L^2(x)$	$S_R(x)$	$CV_R(\%)$
	1	2	3						
1	22.106	22.091	22.213	22.137	0.004				
2	22.189	22.205	22.218	22.204	0.001				
3	21.897	21.943	22.186	22.009	0.024				
4	22.435	22.376	22.528	22.446	0.006				
5	22.075	21.796	22.137	22.003	0.033	0.013	0.016	0.171	0.771
6	21.994	22.184	22.159	22.112	0.011				
7	22.221	22.307	22.213	22.247	0.003				
8	22.059	22.124	22.267	22.150	0.011				
9	21.987	22.379	22.224	22.197	0.039				
10	22.428	22.376	22.331	22.378	0.002				

Table 4. Results of reproducibility test for thorium

Day	Replicates			Average	Variance	$S_r^2(x)$	$S_L^2(x)$	$S_R(x)$	$CV_R(\%)$
	1	2	3						
1	4.03	4.152	4.094	4.092	0.004				
2	3.985	4.026	4.100	4.037	0.003				
3	4.082	4.117	4.142	4.113	0.001				
4	4.080	3.994	3.975	4.016	0.003				
5	4.128	4.147	4.109	4.128	0.001	0.002	0.001	0.056	1.371
6	4.044	4.105	4.086	4.078	0.001				
7	4.021	3.966	4.087	4.025	0.003				
8	4.093	4.140	4.115	4.116	0.001				
9	3.977	4.076	4.059	4.037	0.003				
10	4.124	4.033	4.083	4.080	0.002				

To calculate the variance of internal reproducibility, we rely on these formulas:

$$N' = N - \frac{\sum_{i=1}^p n_i^2}{N} \text{Corrected average number of repetitions} \quad (18)$$

$$S_L^2(x) = \frac{(p-1) \left(\frac{SCE_L(x)}{p-1} - S_r^2(x) \right)}{N'} \text{Variance inter-sample.} \quad (19)$$

$$S_R^2(x) = S_L^2(x) + S_r^2(x) \text{Variance of internal reproducibility.} \quad (20)$$

$$CV_R(\%) = \frac{S_R(x)}{\bar{x}} \times 100 \text{Coefficient of internal reproducibility.} \quad (21)$$

n_i : repetition number per day ($n=3$).

N : total number of measurements.

$SCE_L(x)$: Sum of squared inter-sample differences .

$S_F^2(x)$: variance internal repeatability.

$S_R(x)$: standard deviation of internal reproducibility.

➤ We obtain a value of coefficient of variation of reproducibility intra-laboratory CV_R :

$$CV_R \text{ for uranium} = 0.77 \% \text{ and } CV_R \text{ for thorium} = 1.37 \%$$

➤ Fidelity in terms of internal reproducibility is acceptable.

3.4.4 The Accuracy

In the case of the study of the accuracy of the method of determination of uranium and thorium in industrial phosphoric acid, 10 repetitions were performed on a NIST (National Institute of Standards and Technology) standards for uranium and thorium (the content of U is equal to 20 ppm and the content of Th is equal 10 ppm to). We obtained an average concentration of 19,865 ppm for uranium with a variance of 0.205 and 10.083 ppm for thorium with a variance of 0.095.

To evaluate the accuracy from a reference standard:

- Repeat by the same operator determining the analyte n test taken.
- Calculate the difference between the averages of n determination (\bar{x}) and the certified concentration of uranium and thorium in the reference standard (x_{SR}).
- Calculate the standard deviation of measurements obtained $S_R(x)$.

$$\bullet \text{ Calculate } t_{cal} = \frac{|\bar{x} - x_{SR}|}{\frac{S_R(x)}{\sqrt{n}}} \quad (22)$$

t_{cal} this is a ratio calculated from the equation cited above to verify the accuracy.

$t_{cal} = 2.083$ for uranium and for thorium is $t_{cal} = 2.747$

- Obtain $t_{crit} = t_{V,1-\frac{\alpha}{2}}$ from the Student table. ($t_{crit} = 3.355$)
- Compare t_{cal} to t_{crit}

The decision rule is as follows:

- If $t_{cal} > t_{crit}$: error accuracy is significant, it is possible to conclude that the method is not justified.
 - If $t_{cal} \leq t_{crit}$: error accuracy is not significant, it is possible to conclude that the method is justified.
- The value of t_{cal} for uranium and for thorium is less than the value of the Student table. It is possible to conclude that the accuracy error is not significant. The method is considered justified.
- After evaluating the criteria of linearity, specificity, limit of detection and quantification, accuracy and fidelity, the method is acceptable in the scope defined.

4. Conclusion

The present work has developed a method for the determination of uranium and thorium in the industrial phosphoric acid obtained with wet process. This method has been validated on Tunisian phosphoric acid used as a liquid concentrate without dilution. It offers several advantages in particular the speed of measurement, accuracy and low cost of operation. The proposed method has the advantage of not using reagents for the preparation of samples for analysis, the samples were analyzed directly without dilution or preparation which increases the accuracy of the analyzes. Moreover the relatively lower cost of the sensor for the wavelength dispersive X-ray fluorescence (WDXRF) offers a

major advantage compared to the energy dispersive analyzer (EDXRF) spectrometry, which has been frequently employed for determination of trace elements in phosphoric acid and the (WDXRF) analyzer has many advantages regarding resolution and selectivity over the (EDXRF). The application of the proposed method for the determination of uranium and thorium in industrial phosphoric acid shows that it contains more uranium than thorium (of about 22 ppm of uranium and 4 ppm of thorium).

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References

- AFNOR NF ISO 5725-1. (1994). Application of statistics. Accuracy (trueness and precision) of measurement methods and results. Part 1: general principles and definitions.
- AFNOR NF XP T 90-210. (1999). Water quality-Protocol for the evaluation of an alternative quantitative physico-chemical analysis method against a reference method.
- Ahmed, H., Orabi, Enass, M., El-Sheikh, W. H., Saleh, A. O., Youssef, M. Y., & El-Kady, Z. M. S. (2016). Potentiality of uranium adsorption from wet phosphoric acid using amine-impregnated cellulose, *Journal of Radiation Research and Applied Sciences*, 9, 193-206. <http://dx.doi.org/10.1016/j.jrras.2015.12.003>
- Al Ammar, A. S., & Basheer, H. M. (1993). Further development in the high-precision volumetric method for the determination of uranium in nuclear-grade uranium compounds. *Journal of Radioanalytical and Nuclear Chemistry*, 171(2), 435-441. <http://dx.doi.org/10.1007/BF02219867>
- Ali, H. F., Ali, M. M., Taha, M. H., & Ahmed, F. A. (2012). Uranium extraction mechanism from analytical grade phosphoric acid using D2EHPA and synergistic D2EHPA-TOPO mixture. *IJNESE*, 2(2), 57-61.
- Aydin, F. A., & Soylak, M. (2007). Solid phase extraction and preconcentration of uranium(VI) and thorium(IV) on Duolite XAD761 prior to their inductively coupled plasma mass spectrometric determination. *Talanta*, 72(1), 187-192. <http://dx.doi.org/10.1016/j.talanta.2006.10.013>
- BECKER, P. (1989). Phosphates and phosphoric acid: raw materials, Technology and economics of the wet process, Fertilizer Science Technology Ser (2nd ed.), 6, Marcel Dekker Inc, New York.
- Beltrami, D., Chagnes, A., Haddad, M., Varnek, A., Mokhtari, H., & Courtaud, B. (2013). Recovery of uranium (VI) from concentrated phosphoric acid by mixtures of new bis (1,3-dialkylxypropan-2-yl) phosphoric acids and tri-n-octylphosphine oxide. *Hydrometallurgy*, 140, 28-33. <http://dx.doi.org/10.1016/j.hydromet.2013.08.008>
- Beltrami, D., Chagnes, A., Haddad, M., Laureano, H., Mokhtari, H., & Courtaud, B. (2014). Studies on the selectivity of cetrimide for uranium extraction from wet process phosphoric acid. *Hydrometallurgy*, 207-214.
- Benedik, L., Vasile, M., Spasova, Y., & Watjen, U. (2009). Sequential determination of ²¹⁰Po and uranium radioisotopes in drinking water by alpha-particle spectrometry. *Applied Radiation and Isotopes*, 67(5), 770-775. <http://dx.doi.org/10.1016/j.apradiso.2009.01.033>
- Benkhedda, K., Epov, V., Evans, N., & Douglas, R. (2005). Flow-injection technique for determination of uranium and thorium isotopes in urine by inductively coupled plasma mass spectrometry. *Analytical and Bioanalytical Chemistry*, 381(8), 1596-1603. <http://dx.doi.org/10.1007/s00216-005-3147-y>
- Betti, M. (1997). Use of ion chromatography for the determination of fission products and actinides in nuclear applications. *Journal of Chromatography A*, 789(1-2), 369-379. [http://dx.doi.org/10.1016/S0021-9673\(97\)00784-X](http://dx.doi.org/10.1016/S0021-9673(97)00784-X)
- Byrne, A. R., & Benedik, L. (1988). Determination of uranium at trace levels by radiochemical neutron-activation analysis employing radioisotopic yield evaluation. *Talanta*, 35(3), 161-166. [http://dx.doi.org/10.1016/0039-9140\(88\)80058-4](http://dx.doi.org/10.1016/0039-9140(88)80058-4)
- Cerrai, E., & Ghersini, G. (1967). Spectrophotometric determination of thorium with arsenazo III in the organic phase after extraction with di-(2-ethylhexyl) orthophosphoric acid. *Analytica Chimica Acta.*, 37, 295-309. [http://dx.doi.org/10.1016/S0003-2670\(01\)80677-2](http://dx.doi.org/10.1016/S0003-2670(01)80677-2)
- Charles, B. V., & Rodney, D. J. (1955). Analytical applications of the reaction of thorium with benzenephosphonic acid. *Analytica Chimica Acta.*, 12, 418-431.
- Goodall, P., & Lythgoe, C. (1999). Rapid separation of uranium and plutonium by extraction chromatography for determination by thermal ionisation mass Spectrometry. *Analyst*, 124, 263-269. <http://dx.doi.org/10.1039/a809219b>
- Hussein, A., & Morsy, A. (2012). Uranium recovery from wet-process phosphoric acid by a commercial ceramic product. *Arabian Journal of Chemistry*. <http://dx.doi.org/10.1016/j.arabjc.2012.09.007>

- Hodisan, T., Curtui, M., Cobzac, S., Cimpoiu, C., & Haiduc, I. (1998). The limit of detection improvement in TLC determination of uranium and thorium in the presence of other metal ions. *Journal of Radioanalytical and Nuclear Chemistry*, 238(1), 179–183. <http://dx.doi.org/10.1007/BF02385377>
- Hou, X., & Roos, P. (2008). Critical comparison of radiometric and mass spectrometric methods for the determination of radionuclides in environmental, biological and nuclear waste samples. *Analytica Chimica Acta*, 608(2), 105–139. <http://dx.doi.org/10.1016/j.aca.2007.12.012>
- Jain, B. D., & Singh, J. J. (1962). Separation and gravimetric determination of thorium and cerium (IV) with vanillin. *Analytica Chimica Acta*, 27, 359–362. [http://dx.doi.org/10.1016/S0003-2670\(00\)88516-5](http://dx.doi.org/10.1016/S0003-2670(00)88516-5)
- Jia, G., Torri, G., Ocone, R., Di Lullo, A., De Angelis, A., & Boschetto, R. (2008). Determination of thorium isotopes in mineral and environmental water and soil samples by α -spectrometry and the fate of thorium in water. *Applied Radiation and Isotopes*, 66(10), 1478–1487. <http://dx.doi.org/10.1016/j.apradiso.2008.03.015>
- Krea, M., & Khalaf, H. (2000). Liquid-liquid extraction of uranium and lanthanides from phosphoric acid using a synergistic DOPPA-TOPO mixture. *Hydrometallurgy*, 58(3), 215–225. [http://dx.doi.org/10.1016/S0304-386X\(00\)00129-8](http://dx.doi.org/10.1016/S0304-386X(00)00129-8)
- Lopez-de-Alba, P. L., Gonzalez, S., & Gomez, L. J. (1989). Gravimetric determination of uranyl ion with 2-hydroxy-1-naphthaldehyde/2H-1N/. *Journal of Radioanalytical and Nuclear Chemistry*, 136(3), 203–210. <http://dx.doi.org/10.1007/BF02164120>
- Lutfullah, N. A. M., Rahman, N., & Najmul, H. A. S. (2008). Optimized and validated spectrophotometric method for the determination of uranium(VI) via complexation with meloxicam. *Journal of Hazardous Materials*, 155(1-2), 261–268. <http://dx.doi.org/10.1016/j.jhazmat.2007.11.055>
- Mirashi, N. N., Sangita, D., Sanjay, K. S., Satyajeet, C., Misra, N. L., & Aggarwal, S. K. (2010). Energy dispersive X-Ray fluorescence determination of thorium in phosphoric acid solutions. *Spectrochimica Acta Part B*, 65, 579–582. <http://dx.doi.org/10.1016/j.sab.2010.05.006>
- Mondal, S., Singh, D., Anitha, M., Sharma, J., Hubli, R., & Singh, H. (2014). New synergistic solvent mixture of DNPPA and bidentate octyl(phenyl) CMPO for enhanced extraction of uranium (VI) from phosphoric acid medium. *Hydrometallurgy*, 147–148, 95–102. <http://dx.doi.org/10.1016/j.hydromet.2014.04.023>
- Morsy, A., & Hussein, A. (2011). Adsorption of uranium from crude phosphoric acid using activated carbon, *Journal of Radioanalytical and Nuclear Chemistry*, 288, 341–346. <http://dx.doi.org/10.1007/s10967-011-0980-7>
- Mrinal, K. D., & Majumdar, A. K. (1970). N-benzoyl-o-tolylhydroxylamine as a gravimetric reagent for uranium (VI). *Analytica Chimica Acta*, 50, 243–247.
- Orabi, A., El-Sheikh, E., Mowafy, A., Abdel-Khalek, M., & El Kady, M. (2015). Studies on the selectivity of cetrinide for uranium extraction from wet process phosphoric acid, *International Journal of Mineral Processing*, 137, 26–33. <http://dx.doi.org/10.1016/j.minpro.2015.02.012>
- Rathore, D. P. S. (2008). Advances in technologies for the measurement of uranium in diverse matrices. *Talanta*, 77(1), 9–20. <http://dx.doi.org/10.1016/j.talanta.2008.06.019>
- Ripan, R., & Sacelean, V. (1965). Une nouvelle méthode pour le dosage gravimétrique de l'uranium. *Talanta*, 12, 69–72.
- Saidou, B. F., Laedermann, J. P., Kwato N. M. G., & Froidevaux, P. (2008). A comparison of alpha and gamma spectrometry for environmental natural radioactivity surveys. *Applied Radiation and Isotopes*, 66(2), 215–222. <http://dx.doi.org/10.1016/j.apradiso.2007.07.034>
- Sanjukta, K. A., Niyoti, S. S., Pandey, S., Sounderajan, S., & Enkateswaran, G. V. (2008). Direct determination of uranium in seawater by laser fluorimetry. *Talanta*, 77(1), 422–426. <http://dx.doi.org/10.1016/j.talanta.2008.07.002>
- Shinotsuka, K., & Ebihara, M. (1997). Precise determination of rare earth elements, thorium and uranium in chondritic meteorites by inductively coupled plasma mass spectrometry—a comparative study with radiochemical neutron activation analysis. *Analytica Chimica Acta*, 338(3), 237–246. [http://dx.doi.org/10.1016/S0003-2670\(96\)00528-4](http://dx.doi.org/10.1016/S0003-2670(96)00528-4)
- Slack, A. V. (1968). Phosphoric Acid, Marcel Dekker, New York.
- Tzortzis, M., & Tsertos, H. (2004). Determination of thorium, uranium and potassium elemental concentrations in surface soils in Cyprus. *Journal of Environmental Radioactivity*, 77(3), 325–338. <http://dx.doi.org/10.1016/j.jenvrad.2004.03.014>

- Voldet, P. (1972). Dosage de traces d'uranium, de thorium et de plomb par fluorescence-x. études sur des "zircons" synthétiques et application à quelques zircons naturels du Groenland. *Analytica Chimica Acta*, 62, 297–304.
- Waggaman, W. H. (1969). Phosphoric acid and phosphatic fertilizers, Hafner Publishing Company, New York & London.
- Woltermann, H. A., Eckstein, R. R., Redding, P. L., & Tomes, S. A. (1974). Determination of thorium in plutonium by X-ray spectrometry. *Journal of Nuclear Materials*, 54(1), 117-120. [http://dx.doi.org/10.1016/0022-3115\(74\)90082-8](http://dx.doi.org/10.1016/0022-3115(74)90082-8)
- Zheng, J., & Yamada, M. (2006). Determination of U isotope ratios in sediments using ICP-QMS after sample cleanup with anion-exchange and extraction chromatography. *Talanta*, 68(3), 932–939. <http://dx.doi.org/10.1016/j.talanta.2005.06.065>

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