Spectrophotometric Determination of Uranium in Waste Water of Phosphoric Acid and Fertilizer Manufacturing Process

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In this study, waste water drains and produced phosphate fertilizers of conventional wet-process (hemihydrate) phosphoric acid and phosphate fertilizer plants were investigated to determine the average uranium contents in the active manufacturing period. The method chosen for the determination of uranium was an extension of an existing spectroanalytical method and was adopted for waste water analysis as described. The results show that average uranium contents (mg m$^{-3}$) in a three-month period are appreciable in the waste water channel of the $\text{H}_3\text{PO}_4$ unit, produce acid containing 28% $\text{P}_2\text{O}_5$ (20.75), $\text{H}_3\text{PO}_4$ unit, produce acid containing 54% $\text{P}_2\text{O}_5$ (35.69), NPK (Nitrogen, Phosphorus, Potassium fertilizer) process (23.94), DAP (diamonium phosphate fertilizer) process (58.26) and dilution with the factory’s other waste water streams which contain no uranium do not help to reduce the content to the EPA’s (Environmental Protection Agency) stated permittable U level (for underground waters 20 mg m$^{-3}$) in the sea discharge joint waste channel (34.01). The phosphate fertilizers such as composite NPK with 15% $\text{P}_2\text{O}_5$ were also found to contain appreciable amounts of uranium, 25.28 and 51.76 respectively (mg kg$^{-1}$).

Key words: Phosphate rocks, fertilizers, uranium, waste water, TOPO

Introduction

Phosphate rock is one of the essential raw materials of the wet-process phosphoric acid and phosphate fertilizer production process. It has long been recognised that trace metals and radionuclides in phosphate rock and the resulting fertilizer and acid product are an important environmental issue. Recently, most studies have concentrated on Cd and other heavy metal ions, however, very little information is available on the level of U in various raw or treated waters and waste waters. The processed phosphate rocks in many countries usually originate in Tunisia, Morocco, Jordan and Israel, and present appreciable amounts of uranium in the form of $\text{U}^{4+}$ and $\text{U}^{6+}$.

In our previous work, it was reported that various phosphate rocks shipped from Tunisia contain 34.2 mg kg$^{-1}$ uranium on average and a substantial amount of the radioactive material initially present passes to the produced phosphoric acid (24.5 mg kg$^{-1}$) and triple super phosphate fertilizer (77.6 mg kg$^{-1}$)$^1$. The distribution of the total uranium implies that some of the uranium is lost. This amount may be attributed
Spectrophotometric Determination of Uranium In Waste Water of Phosphoric..., A. UYANIK, et al.,

to disposing the radioactive material by waste water. In order to further studies, the uranium content of the various units and sea discharged joint channel of a phosphoric acid and fertilizer manufacturing process were determined. In addition to waste water, the uranium content of the new type of fertilizers manufactured other than those in our previous investigation were also determined.

The spectrophotometric method used was originally developed for solid sample analyses such as ores, phosphate rocks etc. and included an extraction step with TOPO (tri-octylphosphine oxide) in acidic media to eliminate the interfering matrix elements. For surface and well water analyses, direct spectrophotometric measurement without an extraction step was suggested. However no procedure was available for the analysis of such waste water samples. This paper is focused on 1) the slight changes and 2) application of an existing analytical procedure for determination of U in waste water samples. Experiments were carried out to obtain the correct acid concentration by the effect of nitric acid on TOPO by employing UV and FTIR spectroscopy.

Experimental

Apparatus And Spectrophotometric Procedure. A Jenway Model 3010 pH meter with a glass electrode was used in the pH adjustments. The UV spectra of the solutions were taken at 200-600 nm wavelength range against reference cyclohexane and absorbance of the formed complex [uranyl(2-(5-bromo-2-pyridylazo)-5-diethyaminophenol)] for quantitative analysis was measured at 576 nm against blank solutions in 1 cm quartz cells with a Unicam Model UV2, UV-Visible Spectrometer. The FTIR spectra of TOPO solutions in cyclohexane were taken as liquid (0.05 mm thick) in KBr windows with a Unicam MATTSON 1000 FTIR spectrometer. Recorded background spectrum with cyclohexane were subtracted from the spectra of the samples. Samples for both UV and FTIR analyses were prepared by adding 20 ml of 0.1 M TOPO solution in cyclohexane as extracting agent to 40 ml distilled water containing 0.0 (neutral); 0.5; 1.0; 1.5; 2.0 and 3.0 M nitric acid concentrations respectively. Extracted phase for each acid concentration was taken for the analysis.

Reagents. The necessary solutions were prepared and used as described elsewhere.2,3 These solutions were:

Complexing Solution. 25 g of CyDTA as masking agent (1,2, cyclohexylene dinitrylo tetra acetic acid, Fluka), 5 g NaF and 65 g of sulphosalicylic acid were suspended in 800 mL water, neutralised to pH 7.85 with 40% sodium hydroxide and diluted to 1 L. One part of this solution was then diluted with an equal volume of water and the pH was adjusted with a pH meter to 8.35 with 40% sodium hydroxide and used as diluted complexing solution in the extraction step.

Buffer Solution. 149 g of triethanolamine was dissolved in 800 mL of water, the pH was adjusted to 8.35 with a pH meter by adding perchloric acid and allowed to stand overnight. The pH was re-adjusted to 8.35

Bromo-PADAP. 0.05 g of bromo-PADAP (2-(5-bromo-2-pyridylazo)-5-diethyaminophenol, Merck) was dissolved in 100 mL reagent-grade ethanol to obtain 0.05% (w/v) solution.

TOPO Solution. 19.3 g of TOPO (Merck) was dissolved in cyclohexane (Merck) and diluted to 500 mL to obtain 0.1 M solution.

Sampling. Waste water samples and phosphate fertilizers (NPK and DAP) were obtained from Samsun TÜGSAŞ Phosphoric Acid and Phosphate Fertilizer Plants. a) For waste water analyses, equal volume (500 ml) of everyday samples from the middle of each channel stream, b) for fertilizer analyses, randomly taken equal amounts (250 g) of samples from each batch were pooled and analysed at the end of each week for three months. Samples were collected in glass jars and kept for the analysis. In addition to these, processed
Spectrophotometric Determination of Uranium In Waste Water of Phosphoric..., A. UYANIK, et al.,

phosphate rocks (250 g) and phosphoric acids (500 ml) from various units were sampled by a similar method.

Procedures

Waste Water. A 100 mL portion of homogenized waste water sample was transferred into a flask and neutralized by adding 0.1 M NaOH solution and then acidified to 2M HNO\textsubscript{3} concentration by adding 5M HNO\textsubscript{3} solution. The residue (if any) was removed by filtering (Whatman filter paper No.40) and 5 mL 2\% (w/v) NaF and 2 mL 5\% (w/v) freshly prepared ascorbic acid solution were added.

Fertilizer. 1 g. ground and homogenized fertilizer sample was weighed and dissolved in 50 mL distilled water and the resulting solution was acidified to 2M HNO\textsubscript{3} concentration with 5M HNO\textsubscript{3} solution. The insolubles (very small) were removed by filtering (Whatman filter paper No.40) and 5 mL 2\% (w/v) NaF and 2 mL 5\% (w/v) freshly prepared ascorbic acid solution were added. The phosphate rocks and phosphoric acid samples (1 g each) were analysed by the procedure suggested\textsuperscript{2} without any change except twice extraction.

Extraction. Prepared sample solutions were extracted twice with 5 mL TOPO solution for 10 minutes in a 250 mL extraction flask and 2 ml extract was put into a 25 ml flask from the collected upper phase. On this portion, 1 ml diluted complexing solution, 3 ml 0.05\% (w/v) bromo-PADAP solution and 1 ml buffer solution (pH:8.35) were added and levelled by adding ethanol and was left for 30 minutes.

Standard Uranium Solutions. Aliquots of a volumetrically standardized stock solution of uranium, containing 100 \( \mu \text{g/mL} \) (as uranyl acetate) were diluted to 100 mL with water to obtain solutions containing 0.025-6.00 \( \mu \text{g/mL} \) uranium at 2M HNO\textsubscript{3} concentration. The same procedure including the extraction step were applied to the standard solutions and a calibration graph was constructed by measuring absorbances at 576 nm wavelength vs concentration \( y=0.1684x+0.0015, r^2=0.9998, \) reproducibility error=0.47\%, limit of detection=0.007 \( \mu \text{g/mL} \). Recovery studies were conducted by spiking the waste water and solid samples with 50 \( \mu \text{g} \) uranium standard and extracted by the procedure given above.

Results and discussion

1-Changes in the method: The suggested direct spectrophotometric determination of uranium in water samples produces reasonable results only when the sample is colourless, clear and its composition is not complex e.g. raw or treated surface, well and drinking waters. For the waste water analyses, a slight change is necessary due to the varying quality of the analysed samples. Extraction step with an extracting agent is employed to separate uranium from the matrix elements and other components in the solid sample analyses. Likely interfering matrix elements in uranium ore, phosphate rocks and phosphoric acid have been discussed in detail in previous papers. For example, it was pointed out by Johnson and Florence\textsuperscript{2} that ascorbic acid reduced the higher valency states of cerium, vanadium and iron, and prevented their extraction while floride complexed zirconium and thorium. Under the conditions some extraction of molibdenium occurred, but this element did not react with bromo-PADAP. It was also reported that no interference was observed from 20 mg of the following elements in the determination of 100 \( \mu \text{g} \) uranium: Al, As(V), AU(III), Ce(IV), Cr(III), Fe(III), Mo(VI), Nd, Pt(V), Sb(III), Sn(IV), Th, Ti(IV) and V(V). In addition 500 mg of phosphate, sulphate or chloride had no effect on uranium extraction. Although the concentration was lower than the solid samples, a similar matrix was present in waste waters, and therefore, a similar extraction step has to be applied to separate uranium from the main components of the waste water samples. For this purpose, a 0.001 to 0.1 M solution of TOPO in cyclohexane is used as an extracting agent which forms a stable \( \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TOPO} \) complex as described elsewhere\textsuperscript{4,5}. Complete extraction of uranium is not achieved.
from water samples unless the samples are acidified to a critical nitric acid concentration. First of all, this is partly due to the hydrolysis reaction at lower acid concentration:

\[ \text{UO}_2^2 + H_2O \leftrightarrow \text{UO}_2(OH)^+ + H^+ \quad K_h = 6.3 \times 10^{-5} \]

\[ \text{UO}_2^2 + H_2O \leftrightarrow \text{UO}_2(OH)^+ + H^+ \quad K_h = 6.3 \times 10^{-5} \]

Figure 1. Superimposed UV-VIS spectra of TOPO alone displaying the effect of HNO\textsubscript{3} concentration.

In addition, schoepite (UO\textsubscript{3}.2H\textsubscript{2}O) and several uranium phosphates are not very soluble, particularly at pH values above 7. Therefore, the analyst should be aware of these important considerations and take the necessary precautions during the pH adjustments. Otherwise, some loss of U may occur at higher pH during the waste water analyses if the excess of NaOH is added in the neutralization step. Secondly, it was found that the structure of TOPO in cyclohexane phase also changes by HNO\textsubscript{3} concentration present in the
aqueous phase and the extraction of uranium as uranyl ion into the organic phase is not achieved effectively.
The importance of the acid concentration for solid samples was mentioned in previous studies without clear spectrophotometric data and 1M HNO$_3$ concentration was suggested as the optimum experimental concentration. There is no agreement among the past reports about the optimum acidity of the extraction medium. For instance, White and Ross$^4$ reported that excess HNO$_3$ causes smaller recovery of uranium and extremely high extracton coefficients are obtained at 1M HNO$_3$ concentration. In contrast to this report, Florence & Farrar$^3$ reported that a 0.5-3M HNO$_3$ concentration could be used for >99% uranium recovery.

As can be seen from the superimposed UV spectra (see Figure 1) two absorption bands appear at 230 and 278 nm wavelengths in the UV spectrum of TOPO in cyclohexane. The absorption band observed at 278 nm is a shoulder band and becomes more apparent by adding HNO$_3$ to the aqueous phase and also shifts to a higher energy region. The absorption band which appears at 278 nm in neutral medium is observed more apparently at 269 nm at 0.5 M HNO$_3$ concentration. It shifted to a higher energy region and a band is observed at 259 nm at 1 M HNO$_3$ concentration. The band observed at 230 nm at neutral medium shifted to 237 nm (low energy) at 1 M HNO$_3$ concentration. It may be seen in Figure 2 that maximum absorbance was obtained at 2M HNO$_3$ and increasing the acid content over this concentration did not help to increase the absorbance values of the bands. When the behaviour of these bands are evaluated, the bands observed at neutral medium at 230 nm and 278 nm may be due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition respectively. Polarization of P=O bond occurs as complex forming and energy needed for the $n \rightarrow \pi^*$ transition is increased shifting to higher energy region, while the energy for the $\pi \rightarrow \pi^*$ transition is decreased (shifting to lower energy region). $\pi \rightarrow \pi^*$ transition is observed almost at the same wavelength (236 nm) on the spectrum of the solution extracted from 2M HNO$_3$ acidic solution, shifting to higher energy region is observed for n$\rightarrow$ $\pi^*$ transition (256 nm). This may indicate that TOPO is coordinated to the uranyl ion by the oxygen atom present in the structure of TOPO. The obtained spectra with uranium are almost identical to the reported spectra of different L$_1$-UO$_2$ complex except being in the higher energy region.

As can be seen from the superimposed UV spectra (see Figure 1) two absorption bands appear at 230 and 278 nm wavelengths in the UV spectrum of TOPO in cyclohexane. The absorption band observed at 278 nm is a shoulder band and becomes more apparent by adding HNO$_3$ to the aqueous phase and also shifts to a higher energy region. The absorption band which appears at 278 nm in neutral medium is observed more apparently at 269 nm at 0.5 M HNO$_3$ concentration. It shifted to a higher energy region and a band is observed at 259 nm at 1 M HNO$_3$ concentration. The band observed at 230 nm at neutral medium shifted to 237 nm (low energy) at 1 M HNO$_3$ concentration. It may be seen in Figure 2 that maximum absorbance was obtained at 2M HNO$_3$ and increasing the acid content over this concentration did not help to increase the absorbance values of the bands. When the behaviour of these bands are evaluated, the bands observed at neutral medium at 230 nm and 278 nm may be due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition respectively. Polarization of P=O bond occurs as complex forming and energy needed for the $n \rightarrow \pi^*$ transition is increased shifting to higher energy region, while the energy for the $\pi \rightarrow \pi^*$ transition is decreased (shifting to lower energy region). $\pi \rightarrow \pi^*$ transition is observed almost at the same wavelength (236 nm) on the spectrum of the solution extracted from 2M HNO$_3$ acidic solution, shifting to higher energy region is observed for n$\rightarrow$ $\pi^*$ transition (256 nm). This may indicate that TOPO is coordinated to the uranyl ion by the oxygen atom present in the structure of TOPO. The obtained spectra with uranium are almost identical to the reported spectra of different L$_1$-UO$_2$ complex except being in the higher energy region.

The IR spectra of TOPO, TOPO with acid and TOPO-uranium complex taken in cyclohexane show differences and support the explanation given above (see Figure 3). The apparent changes are observed in the absorption of phosphoryl group (P=O). The band for stretching vibration of the phosphoryl group is observed at 1400-1050 cm$^{-1}$ region and its absorption frequency is highly affected by the total electronegativity of the bonded groups$^8,9$. Absorption frequency and intensity of the phosphoryl group is also affected by factors that weaken the P=O bond, such as hydrogen bonding, and changes the electronic dispersion. The absorption band for the phosphoryl group some times appears as a doublet in the spectrum and it shifts lower frequency in increased intensity by the effect of the hydrogen bond$^9,10$. In the FTIR spectra, it was observed that P=O absorption appears as a doublet and it shifts lower frequencies by complex forming (see arrows in Figure 3). While the absorptions of phosphoryl group of TOPO in cylohexane were observed at 1196 and 1179 cm$^{-1}$, following the uranium extraction and complex forming, they appeared at 1121 and 1113 cm$^{-1}$ frequencies. The results support the UV-VIS spectrophotometric observations. Absorption of phosphoryl group at lower frequencies shows a weaker P=O bonding which is only possible by complex forming. It is thought that TOPO is coordinated to uranyl ion by the oxygen atom present in the oxygen atom present in the structure of TOPO, therefore, the biggest change is to be expected in P=O vibrations. Actually, P=O vibration is highly affected by formation of hydrogen bonding and not only vibration frequency shifts lower but also band is broadened. IR absorption band of hydrogen bonded P=O is observed as a doublet and shifting to the lower frequency is about 50-100 cm$^{-1}$. Since complex formation
of the phosphoryl compounds is generally achieved through the free electron of the oxygen atom, a shift in the P=O vibration to the lower frequency is also observed. The magnitude of the observed frequency lowering for this effect is about $50 \text{ cm}^{-1}$. Since increased solvent polarity weakens the P=O bond, it shifts the phosphoryl group vibration frequency to lower frequencies. However, the effect of the polarity changes may not be more than $25 \text{ cm}^{-1}$.

\[
\begin{align*}
\text{TOPO, 1.5 M HNO}_3 + 25 \mu g U \\
\text{TOPO, 2.0 M HNO}_3 + 25 \mu g U \\
\text{TOPO, 2.0 M HNO}_3 + 50 \mu g U \\
\text{TOPO, 3.0 M HNO}_3 + 100 \mu g U
\end{align*}
\]

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{spectra.png}
\caption{Superimposed UV-VIS spectra of TOPO and TOPO+uranium solutions displaying the effect of HNO$_3$ concentration.}
\end{figure}

In the recovery studies, it was found that the extraction of 100 mL waste water sample once with a 5 mL extracting agent (proposed in the original method) at even 2M HNO$_3$ acid concentration is insufficient ($\sim 80\%$) for the complete extraction (calculated extraction coefficient: $K=128\pm5$) and twice extraction with 5 mL TOPO solutions at 10 minutes total extraction time resulted maximum recovery of present uranium ($\sim 98\%$). The result of the recovery studies performed by spiking the samples with a 50 $\mu$g of U are given in Table 1. White and Ross $^4$ discussed that the degree of extraction is slightly decreased when the aqueous/organic phase ratio is increased above 1. This may probably be the reason why twice extraction is needed in the experiments carried out in this laboratory. Since the amount of uranium present in waste
waters is low, therefore, sample volume taken for the analysis had to be increased. Prolonged extraction time also helps to complete the extraction to some extent. The extraction recovery also depends on the concentration of TOPO solution, extraction number and extraction time particularly in solutions in which aqueous/organic phase \( \gg 1 \). The reproducibility of the method was tested by 10 repeat determinations on aliquots of the standard uranyl acetate solutions (50 \( \mu \text{g of U} \)) and a relative standard deviation of \( \pm 1.73\% \) was obtained. The stability of the calibration standards was also tested and 4\% relative error was found in one week time span. Since the involved error was remarkable due to the deterioration of colour, freshly prepared standards were used whenever needed.

![Figure 3. Superimposed FTIR spectra of TOPO and TOPO+uranium solutions displaying the effect of HNO\(_3\) concentration.](image)

281
Spectrophotometric Determination of Uranium In Waste Water of Phosphoric..., A. UYANIK, et al.,

Table 1. Recovery of 50 µg uranium added to various analysis samples

<table>
<thead>
<tr>
<th>Spiked samples</th>
<th>First extraction</th>
<th>Second extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste water</td>
<td>79.3±1.5</td>
<td>97.3±0.7</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>78.7±3.1</td>
<td>96.9±2.5</td>
</tr>
<tr>
<td>Phosphate rock*</td>
<td>74.7±4.7</td>
<td>96.0±1.0</td>
</tr>
<tr>
<td>Fertilizer (NPK)*</td>
<td>80.7±0.6</td>
<td>97.3±1.5</td>
</tr>
<tr>
<td>Fertilizer (DAP)*</td>
<td>81.3±2.5</td>
<td>98.5±1.5</td>
</tr>
<tr>
<td>Overall average</td>
<td>78.9±2.6</td>
<td>97.2±0.9</td>
</tr>
</tbody>
</table>

* Small amount of insolubles filtered out before the extraction

1-Application of the method. The average uranium content of the phosphate rocks (shipped from Algeria and Tunisia), phosphoric acids (28% and 54% P$_2$O$_5$) and fertilizers (NPK, DAP) analysed are given in Table 2 and the average uranium content of the waste water channels are given in Table 3. The uranium content of the analysed samples naturally vary from one batch of the processed phosphate rock to another. The detailed analysis of the phosphoric acids, fertilizers and waste waters from each batch of the used phosphate rock is very difficult in a continuous process and is not actually necessary from the environmental point of view. Although it is very important, controlling uranium in waste water channels seems impractical and may not be the main goal of a plant, since it represents only a small portion of the investigated problem. It may be seen from Table 2 that appreciable amounts of uranium present in the processed phosphate rocks pass into the produced phosphoric acids and then to fertilizers. Composite fertilizer (NPK) contains less P$_2$O$_5$ than DAP fertilizer and this results in the uranium content of DAP being much more than in NPK. Therefore, control and effective removal of the present uranium must be taken into consideration during the phosphoric acid production process.

Table 2. Uranium contents of the materials employed and produced in the Phosphoric acid and fertilizer process in three months period

<table>
<thead>
<tr>
<th>Material</th>
<th>Highest (n=2)</th>
<th>Lowest (n=2)</th>
<th>Average (n=10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPK fertilizer</td>
<td>27.30±3.30</td>
<td>21.52±0.23</td>
<td>25.28±2.09</td>
</tr>
<tr>
<td>DAP fertilizer</td>
<td>59.65±0.44</td>
<td>36.60±0.14</td>
<td>51.76±4.37</td>
</tr>
<tr>
<td>Phosphate Rock (Tunisia)</td>
<td>40.29±0.21</td>
<td>36.75±0.30</td>
<td>38.84±1.24</td>
</tr>
<tr>
<td>Phosphate rock (Algeria)</td>
<td>35.75±0.08</td>
<td>28.90±0.38</td>
<td>31.97±2.33</td>
</tr>
<tr>
<td>H$_3$PO$_4$ Unit I (28%)</td>
<td>20.42±0.27</td>
<td>17.68±0.79</td>
<td>18.81±0.94</td>
</tr>
<tr>
<td>H$_3$PO$_4$ Unit II (28%)</td>
<td>45.80±3.01</td>
<td>32.24±0.22</td>
<td>40.19±3.40</td>
</tr>
<tr>
<td>Concentrated H$_3$PO$_4$ (54%)</td>
<td>52.64±0.45</td>
<td>49.91±2.10</td>
<td>50.78±1.06</td>
</tr>
<tr>
<td>Phosphogypsum Unit I</td>
<td>5.62±1.04</td>
<td>3.25±0.59</td>
<td>4.58±0.64</td>
</tr>
<tr>
<td>Phosphogypsum unit II</td>
<td>6.50±0.98</td>
<td>4.38±0.52</td>
<td>5.37±0.68</td>
</tr>
</tbody>
</table>

282
Table 3. Uranium contents of the waste water drains of various units of the investigated phosphoric acid and fertilizer process in three months period

<table>
<thead>
<tr>
<th>Waste Unit</th>
<th>Highest (n=2)</th>
<th>Lowest (n=2)</th>
<th>Average (n=10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₃PO₄ Unit I</td>
<td>60.80±0.84</td>
<td>15.48±1.23</td>
<td>35.69±13.86</td>
</tr>
<tr>
<td>H₃PO₄ Unit II</td>
<td>32.24±0.26</td>
<td>10.95±0.97</td>
<td>20.75±5.73</td>
</tr>
<tr>
<td>NPK process</td>
<td>25.03±2.01</td>
<td>22.00±1.25</td>
<td>23.94±1.11</td>
</tr>
<tr>
<td>DAP process</td>
<td>113.02±2.58</td>
<td>45.00±1.90</td>
<td>58.26±25.43</td>
</tr>
<tr>
<td>Sea Discharged Joint Channel</td>
<td>65.28±3.05</td>
<td>28.21±2.54</td>
<td>34.01±12.60</td>
</tr>
<tr>
<td>H₂SO₄ Unit</td>
<td>under range</td>
<td>under range</td>
<td>under range</td>
</tr>
</tbody>
</table>

3-Environmental point of view. The present results indicate that controlling uranium in the waste water drains of the phosphoric acid and fertilizer production process is very important from environmental and radioactive waste disposal point of view. EPA has stated that the permissible uranium level is 20 mg m⁻³ for ground waters (surface waters not specified in concentration unit)¹¹. No information has been found in the EPA resources related to the allowable limit concentrations of uranium stated as μg/L in waste water and fertilizers¹²,¹³. They are generally stated as total β and α radiation dose, pCi/L (picoCurie/L). Since the radioactivity levels of the samples were not measured in this study, a reliable comparison with the EPA’s values is not available because all radionuclides present and formed in the waste water support the total emitted radiation. All investigated waste water streams including sea discharged joint waste channel contain more uranium than the specified ground water uranium level. However, the expected sea concentration of uranium will remarkably be lower than the waste water concentration of uranium due to the sea dilution. Since the factory has been working and discharging waste for 20 years in the region, emitted radiation of the total radionuclides and the concentration of uranium (if possible with the other radioactive species) in sea water, sea sediments and close ground water reserves must be investigated to make a clear assessment about the actual radiation dose and uranium level. It is factually wrong to believe or to claim that no harm has ever proven from very low-dose radiation. On the contrary. Existing human evidence shows cancer induction by radiation at and near the lowest possible dose and dose rate with respect to cell nuclei. By any reasonable standard of scientific proof, such evidence demonstrates that there is no safe dose or dose rate below which dangers disappear. There is no threshold dose. Serious, lethal effects from minimal radiation doses are not “hypothetical,” “just theoretical,” or “imaginary.”¹⁴

The investigated problem is not a unique local problem and most plants using similar processes in the world may suffer from the same pollution problem. Despite the increasing interest in commercial phosphate rocks and phosphoric acid as a future source of uranium, the economical recovery of uranium from the process is not foreseen in the near future in developing countries for it is very difficult and costly. If the present uranium is removed from the produced phosphoric acid, a scant and invaluable industrial material will be recovered, the residues on the filter cake will be reduced so that in the waste water channels, and sea discharge joint channel. Produced fertilizers will contain minute amounts of uranium. Otherwise, in addition to the sea pollution, another which seems more important in the long term is that soil pollution will appear in the fertile agricultural areas due to high amounts of uranium in the phosphate fertilizers used. Various studies on the use of uranium containing fertilizers have been carried out in the countries where those type of fertilizers are widely used. It has been reported that sandy soils, fertilized by a phosphate fertilizer for a long period, decrease the quantity of the uranium only by erosion in the rage of 25-60% and the rest is
accumulated. Other types of soil (e.g., clayey, humus, limy) are likely to hold more uranium than the sandy soils. One of the important results that may be obtained from this study is that necessary precautions should be taken into consideration sooner, otherwise a radioactivity problem due to soil pollution will face developing countries in the near future.

References