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# Determination of thorium and uranium in nitrophosphate fertilizer solution by ion chromatography

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## Abstract

Different phosphate rocks contain various concentrations of thorium and uranium and the range of these concentrations can be significant. Digestion of phosphate rocks with concentrated nitric acid in a fertilizer production process leads to the dissolution of these metals in the resulting nitrophosphate solution. A direct method with a total analysis time of 10 min is described for the determination of thorium and uranium in nitrophosphate fertilizer solution. The method is based on cation-exchange chromatography coupled with spectrophotometric postcolumn detection with Arsenazo III at 660 nm. Elution is performed with a gradient concentration of hydrochloric acid or nitric acid and ammonium sulphate, utilizing a strong cation-exchange analytical column to perform the separation.

## 1. Introduction

Thorium and uranium are present in phosphate rocks at concentrations that can vary widely in different rocks depending on the mining location. Table 1 illustrates the concentrations of thorium and uranium in various phosphate rocks.

Dynamic ion-interaction chromatography has been used as a powerful tool in the determination of thorium and uranium [2] and in the presence of rare earths and/or transition metals [3,4]. A  $C_{18}$  column is usually used to perform the separation [5], with elution using hydroxyisobutyric acid (HIBA) with or without a sodium *n*-octanesulphonate (OSA) coating as the ion-interacting reagent (IIR). Usually postcolumn spectrophotometric detection with Arsenazo III is applied. Detailed investigations on the re-

tention behaviour of both cations have been carried out and it was concluded that a retention mechanism based on hydrophobic adsorption rather than cation exchange was operating [6,7].

Table 1  
Typical concentrations of thorium and uranium in phosphate rocks [1].

Phosphate rock	Th (ppm)	U (ppm)
Kola, Russia	22	2.8
North Carolina, USA	5	90
Florida, USA	40	120
Western region, USA	–	660
Palabora rock, S. Africa	90	9
BouCraa, Morocco	4	60
Khourigba, Morocco	8	100
Senegalese, Africa	–	190
Togolese, Africa	220	85
Tunisian, Africa	–	90
Israeli, Middle East	23	106
Jordanian, Middle East	4	60

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The ion interaction method of analysis offered excellent separations of the rare earths, thorium and uranium, where the anion ligand in the sample matrix is nitrate or chloride, but was less effective in the analysis of nitrophosphate fertilizer solutions. The main factor contributing to this decrease in efficiency was the phosphate ligand affinity for the thorium ion at the ion interaction method pH of ca. 4.0. In addition, the ion interaction method was unable to handle a large ratio of rare earths (RE) to thorium or uranium concentration. This ratio varies in the original phosphate rock used in the digestion stage of the fertilizer production process. A typical RE/Th and Re/U ratios are 350 and 2770, respectively. Moreover, the sample pH would have to be between 2.4 and 4.5 in order to achieve a quantitative recovery of both metals in the chromatographic run [8]. This pH range is unacceptable for samples containing phosphate and thorium owing to the very low solubility product values.

The determination of thorium and uranium by ion-exchange chromatography has also been reported, the elution of uranium being carried out first with hydrochloric acid, followed by thorium with the introduction of sulphate ligand. This method seems to involve an initial on-column removal of calcium ions, with uranium and thorium then being concentrated on the same column and subsequently injected separately. It also employs an analytical column which is no longer commercially available [9]. Moreover, another version of this method seems to have a different gradient programme, which was confusing [10].

The aim of this investigation was to develop a rapid and reliable method for the determination of thorium and uranium in nitrophosphate fertilizer solution. This investigation is connected with Norsk Hydro's continuous monitoring of the environmental aspects of nitrophosphate fertilizer production.

## 2. Theory

Uranium forms weaker cationic species than thorium with hydrochloric and nitric acids, in the

form of  $\text{UO}_2\text{Cl}^+$  and  $\text{UO}_2\text{NO}_3^+$ . When the chloride concentration of the eluent is increased, the concentration of the cationic species retained on the stationary phase decreases because the solution equilibrium is displaced to higher complex species [11]. In sulphuric acid media, uranium can form retainable complexes on a strong cation-exchange resin in the form of  $[\text{UO}_2(\text{HSO}_4)]^+$ . This hydrogensulphato complex of the uranyl ion cannot be formed from a neutral sulphate solution such as ammonium sulphate [12]. Uranium, in fact, is eluted very close to solvent front when the concentration of the sulphate ion is more than 0.1 M in the initial gradient programme.

The combination of high charge and low hydrolysis makes thorium ion particularly retainable on cation-exchange resins from HCl and  $\text{HNO}_3$  at concentrations below about 1 M. Separations from other cations is thus facilitated, and trace amounts of thorium may be concentrated. Complexing agents such as citric acid, oxalic acid, hydrofluoric acid, carbonate and sulphate are necessary for its elution from the column [13]. This implies, that thorium forms weak cationic species with a sulphate ligand in the form of  $\text{ThSO}_4^{2+}$  [9]. The retention times of thorium decrease with increasing concentration of sulphate ion in the initial gradient programme.

## 3. Experimental

### 3.1. Instrumentation

A Dionex (Sunnyvale, CA, USA) 4000i eluent pump system with a 0.05-ml injection loop, a Gilson (Villiers-le-Bel, France) Model 221 auto-sampler and a Spectra-Physics (Santa Clara, CA, USA) were used. Data handling was performed with a Multichrom system (VG Instruments, UK). The analytical column was a dionex IonPac CS10 with strong cation-exchange functionality.

The postcolumn reagent was introduced (0.7 ml/min) via a low-volume T-mixer with a helium-pressurized delivery system. The length of the reaction coil between the mixing tee and the detector was 10 cm.

### 3.2. Reagents

The eluent and standard and sample solutions were prepared with pretreated water obtained via ion exchange and double distillation, followed by passage through Milli-Q water-purification system (Millipore, Waters Chromatography Division, Oslo, Norway).

Hydrochloric acid (2 *M*) or nitric acid (2 *M*), ammonium sulphate solution (2 *M*) and water were the separate eluents required for the analysis. The detection reagent Arsenazo III was 0.3 mM in 0.5 *M* glacial acetic acid. Detection was carried out at 660 nm. A reagent flow-rate of 0.7 ml/min was maintained.

Standard solutions (1 mg/ml) of thorium and uranium were obtained from Teknolab (Drøbak, Norway).

### 3.3. Sample preparation

Nitrophosphate fertilizer solution samples were diluted with water and made 0.25 *M* in hydrochloric acid or 0.25 *M* in nitric acid to prevent the precipitation of thorium phosphate. Typical mother liquor samples were diluted 1:25 or 1:50 depending on the concentration of the analytes.

## 4. Results and discussion

It was understood that an ideal method for the determination of thorium and uranium in nitrophosphate fertilizer solution would involve the detection of both metals at a relatively high acidity range (0.25–1.0 *M*) in order to minimize the complication of thorium phosphate precipitation. Arsenazo III offers this advantage, and is capable of forming coloured complexes with thorium and uranium at acid concentrations between 0.01 and 10 *M* HCl. In this high acid concentration range, the interferences from other metals are minimal, except those of zirconium, hafnium and the rare earths [14].

Therefore, a cation-exchange method that took advantage of the detection power of Arsenazo III was developed. The method also relies on the mass distribution ratios of both metals be-

tween a strong cation-exchange polymer and strong mineral acids. The potential interference in the determination of thorium and uranium in a nitrophosphate fertilizer solution arises from calcium, iron and, in some instances, rare earths, depending on the origin of the phosphate rock. The method developed can be applied with two different elution systems, as follows.

#### 4.1. HCl–(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> system

The mass distribution ratios for thorium, uranium and other potential interfering metals at different HCl concentrations are given in Table 2. Table 2 implies that an initial elution with HCl would separate uranium from thorium and would resolve uranium from calcium and iron(III). When the uranium ion has been totally eluted, the thorium ion can be eluted by the introduction of a sulphate ligand, as thorium has a much lower mass distribution ratio with sulphate [16].

Fig. 1 illustrates the selectivity of thorium and uranium for two different ligand systems. As seen from Table 2, thorium has a strong affinity for the sulphonated stationary phase when elution is carried out with 0.4 *M* HCl, while uranium has a much weaker affinity for the same stationary phase. Thorium, however, would lose this strong affinity when the sulphate ligand was introduced and therefore was eluted after the uranium ion.

Linear calibration graphs were obtained for

Table 2  
Distribution ratio of metal ions between strong cation-exchange resin polymer and hydrochloric acid [15]

Cation	Concentration ( <i>M</i> )			
	0.1	0.2	0.5	1.0
UO <sub>2</sub> <sup>2+</sup>	5420	860	102	19.2
ZrO <sub>2</sub> <sup>2+</sup>	>10 <sup>5</sup>	>10 <sup>5</sup>	10 <sup>5</sup>	7250
Th <sup>4+</sup>	>10 <sup>5</sup>	>10 <sup>5</sup>	10 <sup>5</sup>	2049
La <sup>3+</sup> –Y <sup>3+</sup>	>10 <sup>5</sup>	10 <sup>5</sup>	2480–1460	264–144
Ca <sup>2+</sup>	3200	790	151	42.29
Fe <sup>3+</sup>	9000	4300	225	35.45

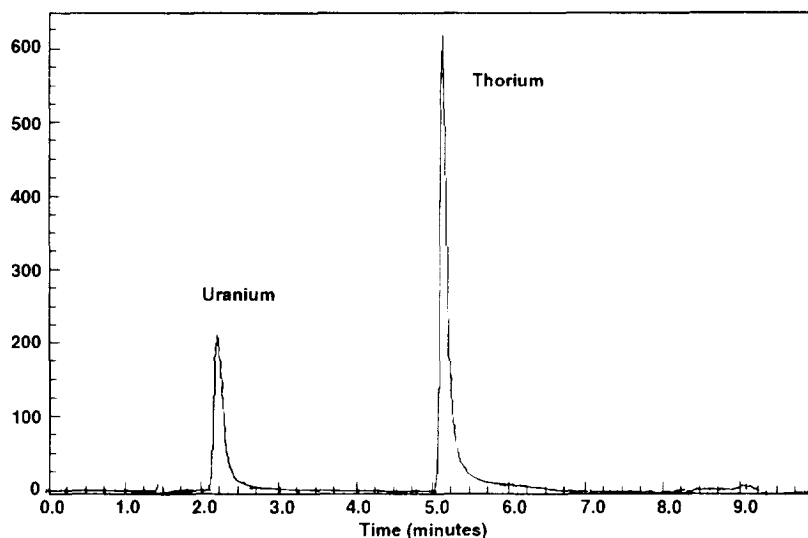


Fig. 1. Chromatogram of standard solution of thorium and uranium. Chromatographic conditions: Analytical column Ion Pac CS10. (Dionex Cop.). From 0.4 M HCl, 0.1 M  $(\text{NH}_4)_2\text{SO}_4$  to 0.4 M HCl, 1 M  $(\text{NH}_4)_2\text{SO}_4$  in 5 min; 2 ppm of each thorium and uranium; 0.05 ml injection volume; 0.1  $\mu\text{Vs}$  ( $10 \uparrow 4$ ) intensity. Eluent flow-rate 1 ml/min. Detection with Arsenazo III 0.2 mM in 0.5 M acetic acid at a flow-rate of 0.7 ml/min.

thorium and uranium in the concentration range 0.2–2.0 mg/l. The relative standard deviation with multiple injections ( $n = 10$ ) was calculated and found to be ca. 1% for uranium and 1.5% for thorium. These repeatability experiments were conducted on samples with uranium and thorium concentrations more than ten times the detection limits. Detection limits at three times the baseline noise for a 0.05-ml injection volume were 0.02 mg/l for uranium and 0.005 mg/l for thorium.

Two different mother liquor solutions [17] obtained directly from a fertilizer production line were investigated in detail. These solutions differed in the origin of the phosphate rock, namely 100% Kola from Russia and 100% BouCraa from Morocco. Fig. 2 shows the chromatograms of each mother liquor solution investigated.

The proposed method gave an excellent separation of calcium ion from uranium ion in the initial part of the analysis, which enabled the direct analytical procedure to be applied and made sample preconcentration and prior calcium removal unnecessary.

#### 4.2. $\text{HNO}_3$ – $(\text{NH}_4)_2\text{SO}_4$ system

Similar chromatograms were obtained from the substitution of the initial HCl with  $\text{HNO}_3$ , as the mass distribution ratio in nitric acid medium is comparable to that in hydrochloric acid (Table 3). The application of this elution system on the same production line samples gave similar chromatograms (Fig. 3).

To demonstrate the accuracy of the method, two international standard samples, viz., different phosphate rocks obtained from different locations in the USA, were analysed and the results for uranium and thorium were compared. These standard samples were digested in hot concentrated nitric acid and analysed using the  $\text{HNO}_3$ – $(\text{NH}_4)_2\text{SO}_4$  elution system. Moreover, the analytical data obtained from this method were compared with data obtained by inductively coupled plasma mass spectrometry (ICP-MS). It can be seen from Table 4 that the results are in good agreement. The slightly lower results for thorium in the Western rock standard material may be due to incomplete dissolution of the

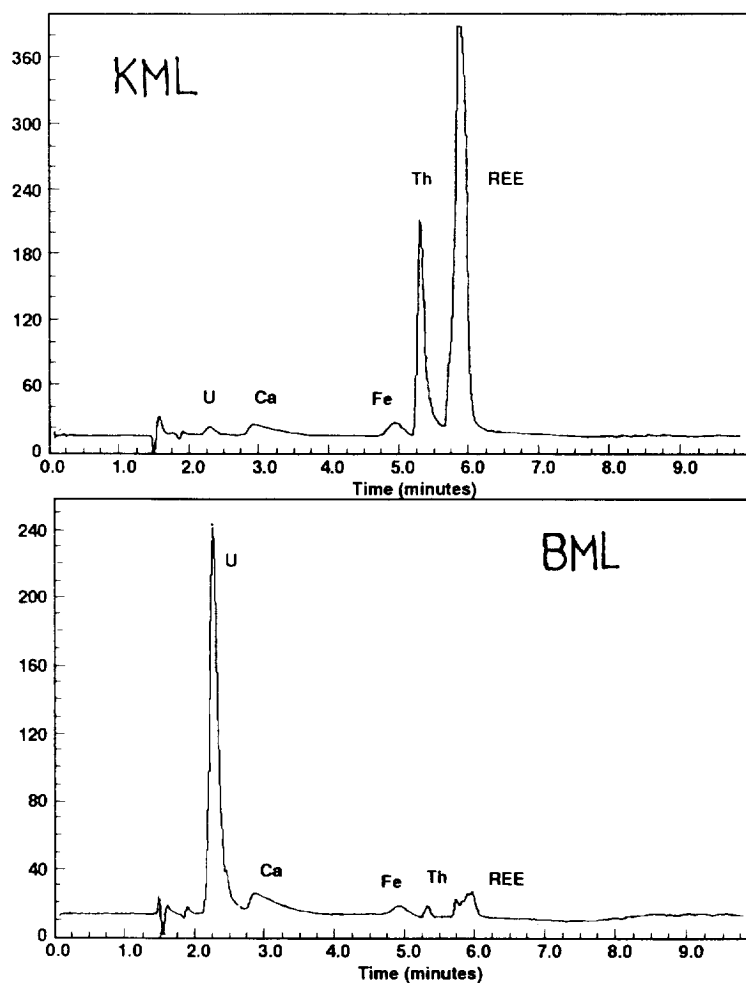


Fig. 2. Chromatograms of two different fertilizer solutions from production lines. KML = Kola Motherliquor, BML = BouCraa Motherliquor. Chromatographic conditions: 1/25 dilution factor with 0.25 M HCl; Other conditions as in Fig. 1.

Table 3  
Mass distribution ratio of cations between strong cation-exchange polymer and nitric acid [18]

Cation	Concentration (M)			
	0.1	0.2	0.5	1.0
ZrO <sup>2+</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	6500
Th <sup>4+</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	>10 <sup>4</sup>	1180
(Rare earths) <sup>3+</sup>	>10 <sup>3</sup>	>10 <sup>4</sup>	1870–1000	267–167
Ca <sup>2+</sup>	1450	480	113	35.3
Fe <sup>3+</sup>	>10	4100	362	74
UO <sub>2</sub> <sup>2+</sup>	659	262	69	24.4

apatite in hot nitric acid, owing to the presence of thorium fluoride, which is difficult to digest.

The ion chromatographic method offers accurate analytical results and a simple sample preparation procedure compared with other instrumental methods.

## 5. Conclusion

Thorium and uranium can be determined directly and accurately in nitrophosphate sam-

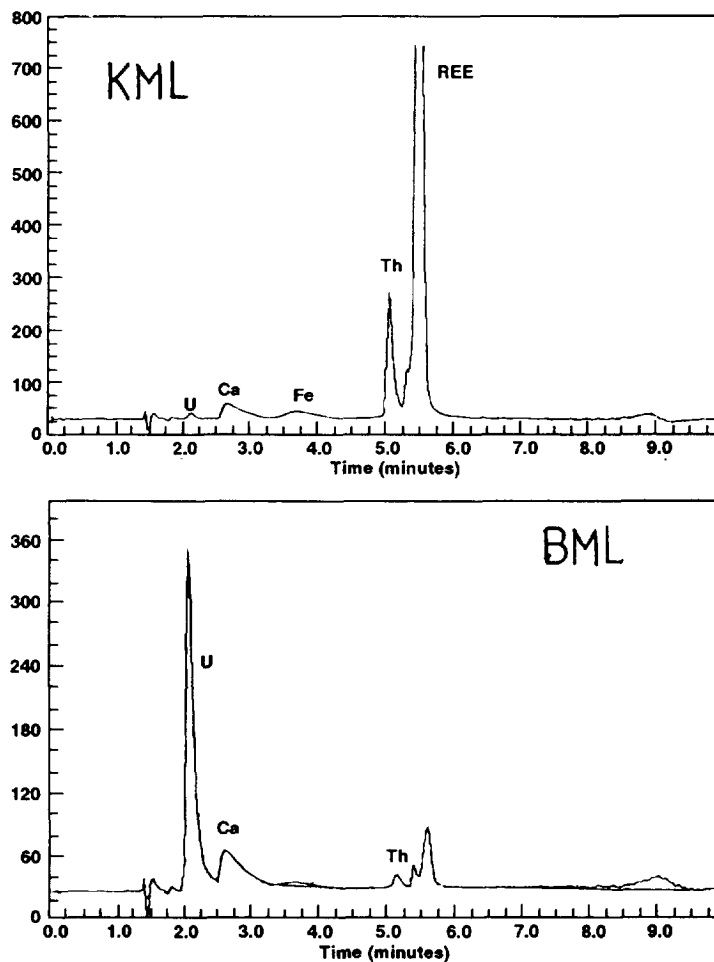


Fig. 3. Chromatograms of two different fertilizer solutions from production line. KML = Kola Motherliquo, BML = BouCraa Motherliquo. Chromatographic conditions: from 0.25 M HNO<sub>3</sub>, 0.1 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> to 0.25 M HNO<sub>3</sub>, 1 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> in 5 min. 1/25 dilution factor with 0.25 M HNO<sub>3</sub>. Other conditions as in Fig. 1.

Table 4  
Uranium and thorium concentrations in international standard materials

Standard material	Certified values	Found values	
		IC	ICP-MS
Florida rock 120b	U, 114.48 ppm Th, unavailable	U, 113.8 ppm Th, 9.2 ppm	
Western rock 694 NB	U, 141.4 ppm Th, unavailable	U, 135.7 ppm Th, 3.9 ppm	
Kola fertilizer solution		U, 2.44 mg/l Th, 17.1 mg/l	U, 2.57 mg/l Th, 16.5 mg/l
BouCraa fertilizer solution		U, 74.6 mg/l Th, 0.84 mg/l	U, 73.5 mg/l Th, 0.81 mg/l

ples obtained from a fertilizer process production line. Analysis can be carried out without sample preconcentration or calcium ion removal prior to the analytical procedure. The two different elution systems were described that resulted in similar chromatograms. The method takes advantage of the complexing power of Arsenazo III at high acidity and of the difference in selectivity of thorium and uranium ions with different ligand systems.

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