



This item was submitted to Loughborough's Institutional Repository by the author and is made available under the following Creative Commons Licence conditions.

A yellow rectangular box containing the Creative Commons Attribution-NonCommercial-NoDerivs 2.5 license summary. At the top is the Creative Commons logo and the text 'creative commons COMMONS DEED'. Below this is the license title 'Attribution-NonCommercial-NoDerivs 2.5'. The text is organized into sections: 'You are free:' with a bullet point; 'Under the following conditions:' with three icons (BY, a crossed-out dollar sign, and an equals sign) and their descriptions; a list of two additional conditions; and a final statement about fair use and other rights. At the bottom, there is a link to the legal code and a disclaimer icon.

CC creative commons
COMMONS DEED

Attribution-NonCommercial-NoDerivs 2.5

You are free:

- to copy, distribute, display, and perform the work

Under the following conditions:

BY: **Attribution.** You must attribute the work in the manner specified by the author or licensor.

Noncommercial. You may not use this work for commercial purposes.

No Derivative Works. You may not alter, transform, or build upon this work.

- For any reuse or distribution, you must make clear to others the license terms of this work.
- Any of these conditions can be waived if you get permission from the copyright holder.

Your fair use and other rights are in no way affected by the above.

This is a human-readable summary of the [Legal Code \(the full license\)](#).

[Disclaimer](#)

For the full text of this licence, please go to:
<http://creativecommons.org/licenses/by-nc-nd/2.5/>

Spectrophotometric Determination of Uranium with Arsenazo-III in Perchloric Acid.

Authors: Muhammad Haleem Khan¹, Peter Warwick^{2*} and Nick Evans²

Affiliations: 1. Department of Chemistry, University of Azad Jammu & Kashmir, Muzaffarabad, Pakistan, 2. Department of Chemistry, Loughborough University, Loughborough, Leics, UK

* Author for correspondence. Fax 01509 223925: E-mail: p.warwick@lboro.ac.uk

Abstract

A short, sensitive and reliable spectrophotometric method, which has advantages over all known “wet chemistry” methods for uranium determination with regard to tolerance to common interferences, has been developed for the determination of uranium. Selectivity, molar absorptivity and the determination range of uranium have been enhanced by using 0.07 % arsenazo-III as a chromogenic reagent. The use of 3 mol dm⁻³ perchloric acid as a medium of determination was found to be excellent in terms of good solvent compatibility on dilution, destruction of organic contamination and simplicity of operation. The uranium-arsenazo-III complex formed instantly, and was found to be stable for more than 3 weeks with constant absorbance. Beer’s law was obeyed up to a uranium concentration of 16 µg g⁻¹, with

a molar absorptivity at 651 nm of $1.45 \times 10^5 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ at $24 \pm 2 \text{ }^\circ\text{C}$. Only phosphate and citrate at 70-fold excess over uranium interfere seriously, whereas other anions studied could be tolerated up to a 70 fold excess over uranium. Of the cations studied, only Mn(II), Co(II), Ni(II), Cu(II) and Cr(III) decreased the normal absorbance of the complex. Iron(III), Ce(III) and Y(III) enhanced the absorbance. Other cations studied did not affect the absorbance up to a 50 fold excess. The accuracy was checked by determining uranium from standard solutions in the range 10-50 $\mu\text{g g}^{-1}$. It was found to be accurate with a 96.0-98.6% recovery rate. The method has been successfully applied to standard reference materials and ore samples at $\mu\text{g g}^{-1}$ levels.

Keywords: Environmental Analysis; Uranium; Arsenazo-III; Spectrophotometric Method

Introduction

Uranium behaves differently from many other metals due to its variable oxidation state and tendency to form a wide variety of positive, neutral and negatively charged complexes, at approximately neutral pH. Unlike many other radioactive elements, its half life is commensurate with the age of the earth and, because of this, small amounts of uranium are found almost everywhere in the soil, rocks and water (Yemal'yanov and Yevstyukhin, 1969). The determination of uranium requires high

selectivity due to its strong association with other elements (Vinogradov, 1963; Aleksanddrova and Charykov, 1989). Several trace level wet chemistry analytical techniques have been reported for uranium determination, but most of these involve tedious and painstaking procedures (Slovak and Slovakova, 1978; Jaiswal et al, 1994).

This method is for the determination of uranium in situations where instrumental techniques are unavailable, or too expensive for routine use. However, it must be stated that ICP-MS and XRF, amongst others, are techniques that do not require tedious and painstaking procedures for sample preparation, and are robust in terms of accuracy, precision and selectivity (Van Loon et al, 1989; Gill, 1997; Meinrath et al, 1999; Ejniak et al, 2000).

The use of organic dyes for the spectrophotometric determination of actinides, including uranium, in various materials have been reported to be simple and selective, and have been widely investigated (Snell, 1978; Kantipuly and Westland, 1988; Khan et al, 1994; El Sweify and Kamel, 1997; Rohwer et al, 1997). Organic reagents largely based on azo-dyes have been used for the determination of uranium and other actinides (Strelow et al, 1976; Marczenko, 1986; Kuroda et al, 1990). Among these, the sodium salt of arsenazo-III has been reported to be more sensitive than other chromogenic reagents of this type, such as arsenazo-I and thorane, for the determination of uranium in various materials (Burger, 1973; Strelow et al, 1976;

Kuroda et al, 1990). The main advantage of this reagent lies in the high stability of its uranium complex which makes possible its analytical utilisation in strongly acidic media, where neither hydrolysis, nor the formation of polynuclear species, occur in the reaction (Savvin, 1961; Burger, 1973; Khan et al, 2001). The usefulness of the reactivity of arsenazo-III lies in the fact that metals whose complex formation depends on high pH, do not interfere with the determination of other elements such as Th, Zr, Pu and Np which give complexes in strongly acidic media (Strelow et al, 1976). In other words, by specifying the pH it is possible to use arsenazo-III very selectively. It is a commercial product, equally soluble in both water and dilute mineral acids (Strelow et al, 1976; Savvin, 1961; Burger, 1973; Khan et al, 1994; Khan et al, 2001).

In addition to the nature of the chromogenic reagent, the role of the medium of determination is also very important. Various lengthy and complicated procedures have been reported for the determination of uranium in organic and mineral acid media (Sharma and Eshwar, 1985; Amoli et al, 1999; Pranvera et al, 2000; Barakat and Abdel-Hamid, 2001; Starvin and Rao, 2004; Venkatesh and Maiti, 2004). Nitric acid, being an oxidizing agent, can easily decompose azo-dyes at room temperature (J. Korkisch et al, 1977; Khan et al, 1994). Arsenazo-III was found to be more stable in perchloric acid than in acids, such as nitric, which can cause oxidation. It has wide

applications in analytical work particularly for the elimination of organic interferences (Jyothi and Rao, 1990; Khan et al, 1994; Khan et al, 2002; Khan and Yasmin, 2003). It has some unique properties such as little oxidizing tendency at room temperature, stability on dilution and it can eliminate most of the volatile interfering anions easily (Khan et al, 1994; Khan et al, 2001). In the present study, which was designed to find a more convenient wet chemistry method for determining uranium, perchloric acid was successfully used as the medium of determination to enhance the uranium determination range, the stability of the metal complex and for the elimination of most of the interfering ions.

Experimental

A Shimadzu (Japan) model-1601 digital spectrophotometer equipped with a recording device was employed for the measurement of optical density. Analar grade disodium salt of arsenazo-III (2,7-bis(2-arsenophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonic acid) and perchloric acid (70-72%) purchased from E. Merck were used. A uranium standard solution (100 ppm (w/v)) was prepared from analytical reagent grade uranyl nitrate hexahydrate (Riedel-de-Haen, Switzerland) in 3 mol dm^{-3} HClO_4 . On the basis of the selectivity, sensitivity and reactivity of the reagent for tetravalent metal ions, U(VI) was first reduced to U(IV) by repeated treatment with ascorbic acid (Savvin, 1961), although the determination still works with U(VI).

Arsenazo-III (0.07 % w/v) solution was prepared in $3 \text{ mol dm}^{-3} \text{ HClO}_4$. The Standard Reference Material, (SRM), which was in a matrix of sandy soil, was obtained from the New Brunswick Laboratory (NBL-49). Deionised water was used throughout the experimental work.

Uranium standard solutions containing $1\text{-}16 \mu\text{g g}^{-1}$ were taken in triplicate and heated slowly to near dryness. Reagent solution was added after cooling to room temperature. After thorough mixing, the optical density was measured at 651 nm against the reagent blank. For determination of uranium in SRM and local ore samples, a known weight, usually 1 g, was taken separately in duplicate in Teflon beakers and then decomposed by multiple treatment of 1:1 mixture of HNO_3 and HF for complete leaching (Korkisch et al, 1977). Uranium was then extracted from its nitrate solution by shaking with tributyl phosphate (TBP) in MIBK (Korkisch et al, 1977) and then determined spectrophotometrically.

Results and Discussion

Arsenazo-III in perchloric acid being a more sensitive reagent than, for example, arsenazo-I, forms a 1:1 complex with uranium in $3 \text{ mol dm}^{-3} \text{ HClO}_4$ having two absorption peaks for reagent and complex in the visible region from 340 – 700 nm. The absorption maxima of the complex was observed at 651 nm and that of reagent at

531 nm. This indicates a shift of the absorption band of the complex towards longer wavelength (Fig.1). The peaks are well separated due to the high analytical sensitivity and stability of the reagent in perchloric acid (Rohwer et al, 1997). The optical density of both was found to be at a maximum from 3 - 5 mol dm⁻³ HClO₄. The bluish colour of the complex develops instantaneously, and normal light and room temperature (24 ± 2 °C) do not affect the absorbance of the complex. Chromogenic solutions of different concentrations (0.01, 0.07, 0.1 % w/v) in 3 mol dm⁻³ HClO₄ were used for investigating the optimum concentration of the reagent necessary for complexation and maximum absorbance. An overlapping of absorbance was observed with 0.07 % and 0.1 % reagent solutions. A linear range for determination of metal complex was enhanced up to 16 µg g⁻¹ (Fig.2). The units of µg g⁻¹ were used to allow for the high density of the HClO₄ solution. However, reagent concentrations below 0.07 % (w/v) were found to be insufficient, and beyond that, a deviation from Beer's law was observed (Fig.2).

The tolerance for interfering ions on the spectrophotometric determination of uranium was examined individually by adding a relatively high concentration of these ions. It was observed that anionic concentrations greater than 70 fold and cationic concentrations greater than 50 fold excess over the uranium concentration as their sodium (NaNO₃) and potassium salts (KCl) decrease the normal absorbance of the

complex. The optical density in the absence of possible interfering anions was compared to the absorbance in the presence of foreign ions. The results are listed in table 1. This indicates that only phosphate and citrate seriously interfere with the determination, whereas volatile anionic interferences were minimised by the repeated slow heating with $3 \text{ mol dm}^{-3} \text{ HClO}_4$, prior to colour development. Serious interference by most of these anions were also reported for the various other methods developed in aqueous or organic media (Sharma and Eshwar, 1985). Among the cations tested, Mn(II), Co(II), Ni(II) and Cu(II) slightly decreased, and Cr(III) by 21%, the normal absorbance of the complex whereas, Ce(III) Fe(III) and Y(III) slightly enhanced the reference absorbance (Table 1). All other cations studied could be tolerated up to a 50 fold excess over the uranium concentration. The accuracy and precision of the method were also determined by measuring the concentration of standard uranium solutions in the range $10 - 50 \mu\text{g g}^{-1}$, after appropriate dilution if needed (Table 2). The results showed that the percentage recovery of uranium was quantitative with good precision (96.0 - 98.6%). The percentage deviation was found to be at a maximum (- 4.0%) at dilution ($10 \mu\text{g g}^{-1}$) whereas, the deviation decreased to -1.4%, when the concentration was increased to $50 \mu\text{g g}^{-1}$. This method for the determination of uranium has also been applied to an SRM sample using the procedure described above. The results based on the average of triplicate measurements are given in table 3. The findings are in good agreement with the

reference value of uranium within $\pm 2\%$ experimental error. Uranium has also been determined at $\mu\text{g g}^{-1}$ level in known local ore samples 'MCL 1-5 and HRCP 1-4' obtained from the mineral centre Lahore and the Hard Rock Centre Peshawar (Pakistan) after extraction using the procedure described with a precision of $\pm 0.7\%$. On the basis of precision and the quantitative recovery of uranium from SRM and local ores this method was shown to be reliable and accurate, and will be useful in the routine analysis of uranium at $\mu\text{g g}^{-1}$ level in ores and other materials.

References

- Aleksandrova, E.A., Charykov, A.K., 1989. Thorium Mixed Ligand Complexes of Morin as Analytical Form for Extraction-Photometric Determination of Thorium Microamounts. *Radiokhimiya*, 31, 96-101.
- Amoli, H., Salar, H., Rajabi, M., Mohanazadeh, F., 1999. Separation and Spectrophotometric Determination of Uranium in Caspian Sea Water. *J. Chem. Res.*, 9, 586-589.
- Barakat, M.F., Abdel-Hamid, M.M., 2001. Differential Estimation of U(VI) and U(IV) Ions in Aqueous Solutions by Arsenazo 1. *J. Radioanal. Nucl. Chem.*, 247, 159-163.
- Burger, K., 1973. *Organic Reagents in Metal Analysis*. Hungarian Academy of Science, Budapest.
- Ejnik, J.W., Carmichael, A.J., Hamilton, M.M., McDiarmid, M., Squibb, K., Boyd, P., Tardiff, W., 2000. Determination of the Isotopic Composition of Uranium in Urine by Inductively Coupled Plasma Mass Spectrometry. *Health Physics*, 78, 143-146.
- El Sweify, E.R., Kamel, F.H., Shabana, M.M., 1997. Use of Organic Dyes in Spectrophotometric Determination of Thorium and Uranium. *Arab J. Nucl. Sci. Appl.*, 30, 95.

- Gill, R., 1997. Modern Analytical Geochemistry. Addison Wesley Longman Ltd, London.
- Jaiswal, D.D., Dang, H.S., Pullat, V.R., Sharma, R.C., 1994. Spectrophotometric Determination of Uranium. Bull. Rad. Prot., 17, 44.
- Jyothi, A., Rao, G.N., 1990. Solvent Extraction Behaviour of Lanthanum(III), Cerium(III), Europium(III), Thorium(IV) and Uranium(VI) with 3-phenyl-4-benzoyl-5-isoxazolone. Talanta, 37, 431-433.
- Kantipuly, C.J., Westland A.D., 1988. Review of methods for the determination of lanthanides in geological samples. Talanta, 35, 1-13.
- Khan, M.H., Ali, A., Khan, N.N., 2001. Spectrophotometric Determination of Thorium with Disodium Salt of Arsenazo-III in Perchloric Acid. J. Radioanal. Nucl. Chem., 353-357.
- Khan, M.H., Ali, A., Mahmood, T., 2002. Determination of Essential and Toxic metals in Water and Foodstuffs of Muzaffarabad City by Atomic Absorption Spectroscopy. Pak. J. Anal. Chem., 3, 108-110.
- Khan, M.H., Hasany, S.M., Khan, M.A., 1994. J. Radioanal. Nucl. Chem., Spectrophotometric Determination of Micro Amounts of Thorium with Disodium Salt of 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)benzenearsonic acid (Thorin) as a Chromogenic Reagent. 188, 341-353.

- Khan, M.H., Yasmin, N., 2003. Study of Metallic Pollutants in Water and Food Items of an Industrial City by Atomic Absorption Spectrophotometry. *Pak. J. Bio. Sci.*, 6(14), 1276-1281.
- Korkisch, J., Steffan, I., Arrhenius, G., Fisk, M., Frazer J., 1977. Chemical Analysis of Manganese Nodules : Part II. Determination of Uranium and Thorium after Anion-Exchange Separation. *Anal. Chim. Acta*, 90, 151.
- Kuroda, R., Kurosaki, M., Hayashibe Y., Ishimaru, S., 1990. Simultaneous Determination of Uranium and Thorium with Arsenazo III by Second-Derivative Spectrophotometry. *Talanta*, 37, 619-624.
- Marczenko, Z., 1986. Separation and Spectrophotometric Determination of Elements. Ellis Horwood, Chichester.
- Meinrath, G., Volke, P., Helling, C., Dudel, E.G., Merkel, B.J., 1999. Determination and interpretation of environmental water samples contaminated by uranium mining activities. *Fres. J Anal Chem*, 364, 191-202.
- Pranvera, L., Alqi, C., Safet, D., Filip, L., 2000. Determination of Uranium by Spectrophotometric method with Arsenazo-III. *Asian J. Chem.*, 12, 732-738.
- Rohwer, H., Rheeder, N., Hosten, E., 1997. Interactions of uranium and thorium with arsenazo III in an aqueous medium. *Anal. Chim. Acta*, 341, 263-268.
- Savvin, S.B., 1961. Analytical use of arsenazo III: Determination of Thorium, Zirconium, Uranium and Rare Earth Elements. *Talanta*, 8, 673.

- Sharma, C.D., Eshwar, M.C., 1985. Rapid Spectrophotometric Determination of Thorium(IV) with 1-(2'-thiazolylazo)-2-naphthol. *J. Radioanal. Nucl. Chem.*, 91, 323-328.
- Slovak, Z., Slovakova, S., 1978. Optimization of the Spectrophotometric Determination of Uranium(VI) with Arsenazo III in Strongly Acidic Solutions. *Fresenius Z. Anal. Chem.*, 292, 43-44.
- Snell, F.D., 1978. *Photometric and Fluorometric Methods of Analysis*. John Wiley & Sons, New York.
- Starvin, A.M., Rao, T.P., 2004. Solid Phase Extractive Preconcentration of Uranium(VI) onto Diarylazobisphenol Modified Activated Carbon. *Talanta*, 63, 225-232.
- Strelow, F.W.E., Kokot, M.L., Van der Walt, T.N., Bhaga, B., 1976. Rationalized Determination of Uranium in Rocks for Geochemical Prospecting using Separation by Ion Exchange Chromatography and Spectrophotometry with Arsenazo(III). *J. S. Afr. Chem. I*, 29, 97-104.
- Van Loon, J.C., Barefoot, R.R., 1989 *Analytical Methods for Geochemical Exploration* Academic Press, Inc., London.
- Venkatesh, K., Maiti, B., 2004. Preconcentration and Separation of Uranium from Thorium by Solid Phase Extraction with XAD-4 Modified with Organic Reagents. *Sepr. Sci. Tech.*, 39, 1779-1789.

Vinogradov, A.P., 1963. Basic Characteristics of the Geochemistry of Uranium.

Academy of Science, USSR.

Yemal'yanov, V.S., Yevstyukhin A.I., 1969. The Metallurgy of Nuclear Fuel.

Atomizdat, Moscow.

Figure Captions:

Fig. 1. Absorption spectra of (a) Arsenazo-III (0.07% w/v) in $3 \text{ mol dm}^{-3} \text{ HClO}_4$; (b) uranium-arsenazo-III complex.

Fig. 2. Relationship between absorbance of uranium-arsenazo-III complex as a function of metal ion and reagent concentration, at 0.07% and 0.1% arsenazo-III (O), at 0.01% arsenazo-III(●)

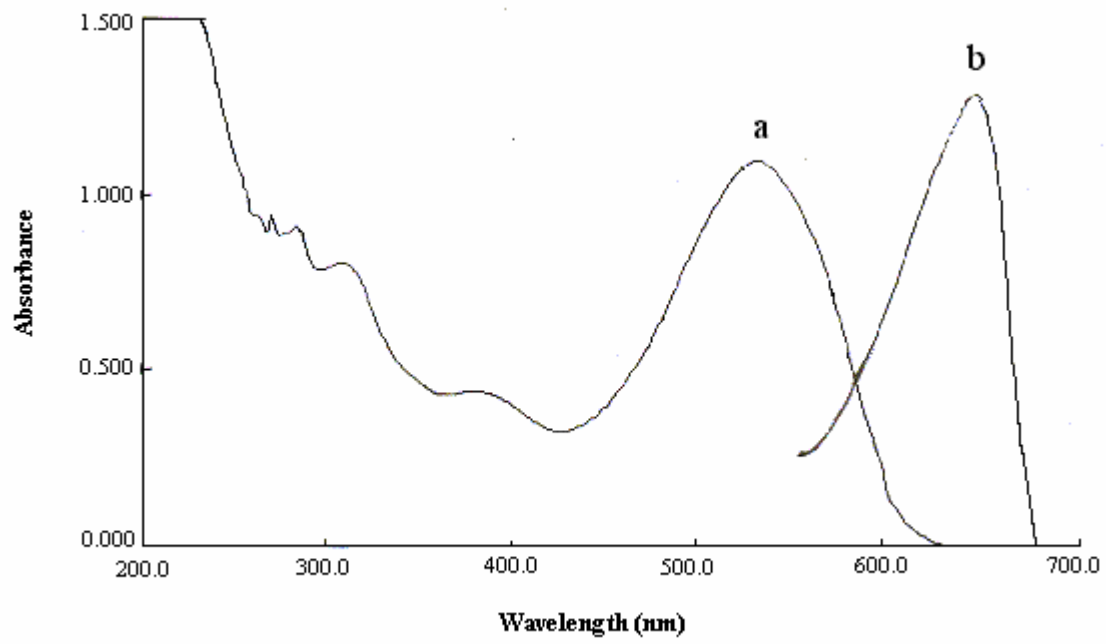


Figure 1

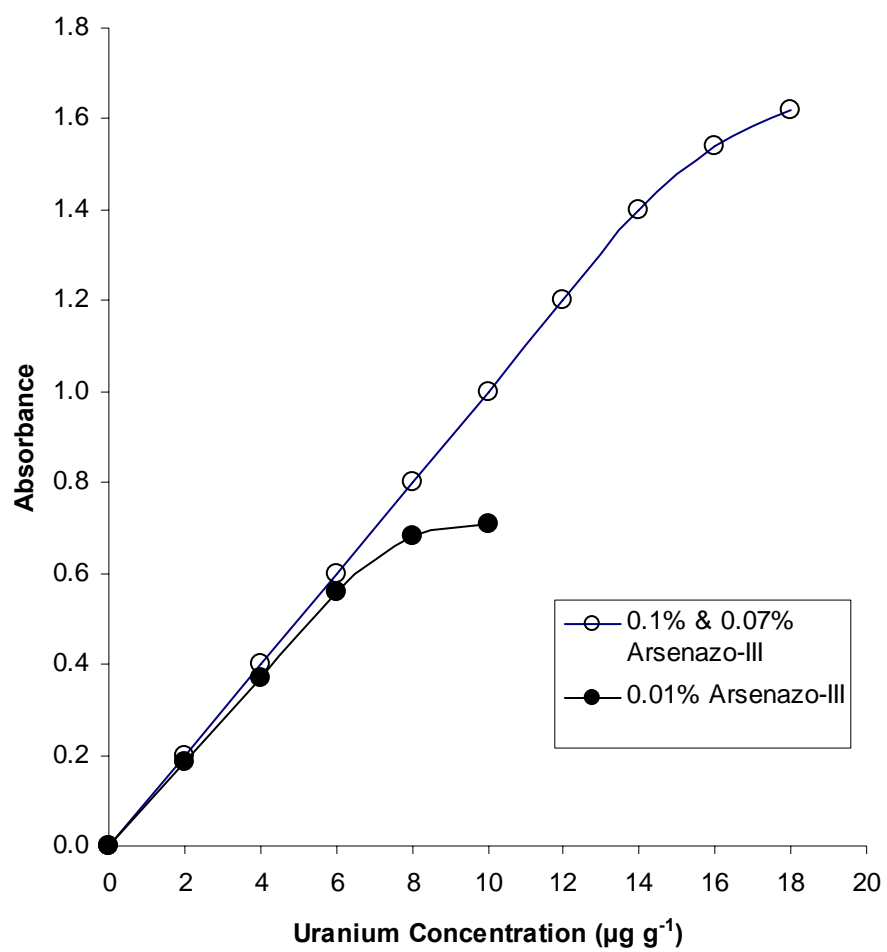


Figure 2

Table 1. Influence of interfering ions in the determination of uranium.

Anions	Absorbance	± % Deviation	Cations	Absorbance	± % Deviation ^f
Nil	0.620 ^b		Nil	0.620 ^b	
Phosphate ^a	0.280	-54.8	Ce(III) ^e	0.710	+14.5
Fluoride ^a	0.596	-3.8	Y(III) ^c	0.695	+12.0
Nitrate ^a	0.622	+0.32	Al(III) ^c	0.635	+2.4
Acetate ^a	0.605	-2.4	Cr(III) ^c	0.490	-20.96
Citrate ^a	0.46	-25.8	Fe(III) ^e	0.700	+12.9
Sulfide ^a	0.610	-1.6	Co(II) ^e	0.567	-8.5
Thiocyanate ^d	0.615	-0.8	Mg(II) ^c	0.614	-0.9
Oxalate ^a	0.618	-0.32	Pb(II) ^c	0.632	+1.9
Cyanide ^d	0.608	-1.9	Zn(II) ^e	0.628	+1.2
Ascorbate ^a	0.627	+1.1	Cu(II) ^e	0.610	-1.6
			Mn(II) ^c	0.595	-4.0
			Ni(II) ^e	0.570	-8.0
			Ba(II) ^c	0.627	+1.1
			Sr(II) ^e	0.622	+0.3
			Ca(II) ^c	0.618	-0.3
			Na(I) ^c	0.620	0.00

^a as sodium salt, ^b reference value, ^c as nitrate, ^d as potassium salt, ^e as chloride ^f based on 3 replicates

Table 2. Accuracy of analytical method based on added/found concentration of uranium using 0.07% w/v arsenazo-III in 3 mol dm⁻³ HClO₄

Uranium (Added) ($\mu\text{g g}^{-1}$)	Uranium (Found*) ($\mu\text{g g}^{-1}$)	Recovery (%)	\pm Deviation (%)
10	9.6	96.0	- 4.0
20	19.4	97.0	- 3.0
30	29.3	97.7	- 2.3
40	39.2	98.0	- 2.0
50	49.3	98.6	-1.4

* Determinations are based on mean of 3 measurements.

Table 3. Determination of uranium in Standard Reference Material (concentration in percentage)

SRM sample code	Reference value ($\mu\text{g g}^{-1}$)	Measured value* ($\mu\text{g g}^{-1}$)	\pm %Deviation
NBL-49	0.046	0.045 \pm 0.001	-2.17

* Measurements are based on the mean of 3 determinations.