

## Spectrophotometric determination of uranium with arsenazo-III in perchloric acid

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### 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<sup>-3</sup> 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<sup>-1</sup>, with a molar absorptivity at 651 nm of 1.45 × 10<sup>5</sup> mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup> at 24 ± 2 °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 µg g<sup>-1</sup>. 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 µg g<sup>-1</sup> levels.

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### 1. 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; Aleksandrova and Charykov, 1989). Several trace level wet chemistry analytical techniques have been reported for uranium

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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 and Barefoot, 1989; Gill, 1997; Meinrath et al., 1999; Ejnik 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 et al., 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 (Savvin, 1961; Burger, 1973; Strelow et al., 1976; Khan et al., 1994, 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 (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, 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, 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.

## 2. 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  $3 \text{ mol dm}^{-3} \text{ HClO}_4$ . 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  $\text{HNO}_3$  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.

## 3. 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 to 700 nm. The absorption maxima of

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