

Rapid measurements of concentrations of natural uranium in process stream samples via gamma spectrometry at an extraction facility

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Received 19 January 2007; received in revised form 10 April 2007; accepted 10 April 2007

Available online 24 April 2007

Abstract

A new application of gamma spectrometry in the efficient measurement of natural uranium in the process stream at an extraction plant is described here. The inherent nuclear properties of uranium viz. emanation of characteristic gamma rays (185.7 keV) has been exploited for the determination of concentrations ranging from 5 to 450 g l⁻¹ by passive photon counting of 185.7 keV gamma rays from ²³⁵U isotope for a maximum of 3–10 min per sample. This technique is totally matrix independent unlike other instrumental analytical techniques like wavelength dispersive X-ray fluorescence spectrometry and UV–vis spectrophotometry. Solution samples of aqueous and organic phase can be directly counted without the requirement of sample preparation. A MINIM-based gamma spectrometer consisting of a multichannel pulse height analyzer and a 3 in. × 3 in. well-type NaI(Tl) scintillation detector with an approximately 2 in. thick lead shield has been employed for the measurements. The results are compared with those obtained by potentiometry and wavelength dispersive X-ray fluorescence spectrometry (WD-XRF). Relative standard deviation of 1–5% has been obtained depending upon the concentration of uranium, which is more than adequate for routine process control samples. This paper also discusses in detail the problems associated with the determination of high concentrations of uranium in using 63 and 93 keV gamma rays emanating from ²³⁴Th (*t*_{1/2} 24 days) the immediate daughter of ²³⁸U isotope in samples that have attained secular equilibrium and the limitations of these energies in the routine analysis of freshly extracted uranium.

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Keywords: Uranium; Gamma spectrometry; Process streams; Well-type NaI(Tl) scintillation detector

1. Introduction

Natural uranium dioxide pellets are the most widely used nuclear fuels in the pressurized heavy water nuclear power reactors (PHWR). The manufacturing process of uranium dioxide pellets involves various steps that include leaching of uranium from the ore using sulphuric acid [1], purification using anion exchange [2], precipitation as magnesium diuranate (MDU), purification through solvent extraction [3], precipitation of uranium as ammonium diuranate (ADU) [4], drying, calcination and reduction to uranium dioxide. In our uranium extraction plants, MDU is digested with nitric acid and uranium is extracted using TBP–kerosene mixture followed by precipitation using ammonia. The process flow sheet is given in Fig. 1.

Concentrations of uranium in the process stream samples provide essential information required for process monitoring, such as material input in UNF/UNS, extraction efficiency in UNE, effective stripping in UNPS/UNPE and over all material balance in LS and raffinate. Destructive techniques, such as gravimetry [5], volumetry [6], polarography [7], coulometry [8], X-ray fluorescence spectrometry [9] and spectrophotometry [10,11], etc. are available for the determination of uranium. Yet, each technique possesses some merits and demerits and cannot be applied without difficulty to all samples of process streams. Gravimetric methods, though highly precise, are time consuming. Volumetric methods consist of several steps and require varieties of chemicals. As a result these methods generate larger volumes of analytical effluents. While electroanalytical techniques are familiar alternative analytical methods, they are not preferred for routine analysis again owing to the multifunctional execution of procedural requirements and associated indispensable chemical consumption and effluent generation problems,

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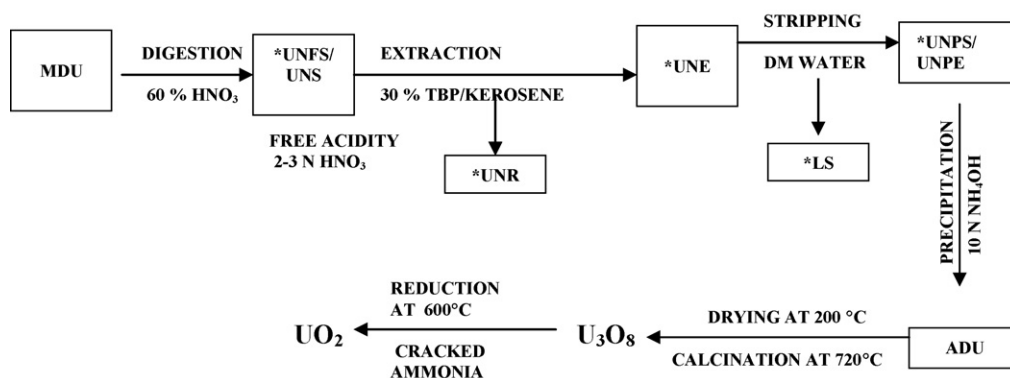


Fig. 1. Process flow sheet of extraction of natural uranium: MDU–Magnesium diuranate; UNFS–Uranyl nitrate feed solution/slurry; UNE–Uranyl nitrate extract; UNPS/UNPE–Pure/evaporated pure solution; LS–Lean solvent; UNR–Uranyl nitrate raffinate; ADU–Ammonium diuranate.

which are not desirable again. X-ray fluorescence techniques involve very high capital and operational maintenance cost on sophisticated instrumentation besides the disadvantage of strong matrix dependency. In these techniques linearity of counts with respect to concentration is observed only in the lower concentrations of uranium. As a result these techniques are limited to a very narrow dynamic range leading to several-fold dilution of samples to working range prior to analysis. In addition, if uranium is present in organic matrix as in the case of UNE and LS samples, the calibration standards also must be prepared in the identical matrix in order to obtain accurate results.

Earlier, in our laboratory a method based on the measurement of absorption of uranyl ions in visible region using UV–vis spectrophotometry was developed and communicated [12]. However, the technique requires sample dilution to the working range where high quantities of uranium are present. In samples containing very small quantities of uranium complexation of uranium using Arsenazo III in a strictly maintained acidity conditions is required. A lot of precaution had to be taken to avoid interference from the accompanying impurities in significant quantities causing bias in the results. In the case of organic samples, uranium had to be quantitatively stripped into aqueous medium prior to analysis. Thus this technique is a time consuming one besides being a destructive and effluent generating method. These limiting factors of the conventional techniques stressed the need for a routine nondestructive analytical method that is simple, rapid, sensitive, accurate and cost-effective.

We find that passive gamma spectrometry overcomes the impediments discussed in the foregone paragraphs and is quite desirable for the routine measurements of uranium in the process streams. Thus this technique stands as an excellent nondestructive analytical tool for this specific application. Reports on the gamma spectrometric measurements found in literature provide information regarding the application mainly for the determination of ^{235}U isotope content in the fuel pellets during production [13–19] and in spent fuel for the disposal of nuclear waste [20], both online and offline. Only the feasibility of the determination of the concentration of uranium by gamma spectrometry using high purity germanium (HPGe) detector [21,22] by monitoring the 1001 keV peak is available in literature. However, routine exploration for continuous monitoring of the process streams

in natural uranium extraction plants exploiting 185.7 keV photon counting using well-type NaI(Tl) detector has scarcely been reported.

Gamma photons with energies 63, 93, 143, 185.7, 776 and 1001 keV are significant in the spectrum of natural uranium decay series. The 185.7 keV gamma photons exhibit the maximum yield of 57% [23,24]. Although natural uranium consists of only 0.71% of ^{235}U content, owing to the very high yield of the 185.7 keV gamma photons considerable counts can be obtained in 3–5 min for uranium samples in the range of 5–450 g l⁻¹ using a multichannel gamma spectrometer equipped with a 3 in. × 3 in. well-type NaI(Tl) detector. The area under the peak of the 185.7 keV gamma rays are correlated to the concentration of uranium present in the sample and the content of uranium in the sample is determined from the calibration curves obtained with the standard solutions of uranium. The valuable advantage of this technique is found in that there is no matrix effect. Hence the calibration curves made using aqueous standards itself can be used conveniently for the determination of concentration of uranium in organic samples viz. UNE and LS. The nondestructive nature of the method offers the advantage of no effluent generation and thus eliminates the expenditure and labour involved in the recovery of uranium values from the analytical waste that accumulate in large quantities in the existing conventional methods of analysis.

The detailed account of the experimentation and the results are discussed in the foregoing pages of this paper. In order to ascertain the validity and establish the superiority of this technique, the results are compared with volumetry, WD-XRF, spectrophotometry and differential pulse voltametry. A systematic study has also been undertaken to study the feasibility of determination of concentrations of uranium using 63 and 93 keV gamma rays from ^{234}Th , the immediate daughter of ^{238}U and the results are discussed in detail.

2. Experimental

2.1. Reagents

A standard stock solution of 450 g l⁻¹ of uranium was prepared as follows: pure U₃O₈ powder from Uranium Oxide Plant was calcined at 850 °C in a muffle furnace for 4–5 h. After cool-

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