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Review article

An overview of spectrometric techniques and sample preparation for the determination of impurities in uranium nuclear fuel grade

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ABSTRACT

This review is focused on the impurities determination in uranium nuclear fuel grade matrix with the use of spectrometric methods. It is known that uranium is the major element and material for the sustainable use in the nuclear energy. The optimized use of this technology involves the improvement of several processes to power generation. With regard of fuel reliability, the chemical characterization combined with environmental protection is particularly important in the uranium production cycle or in the nuclear fuel cycle, subject to an increasing number of international conventions and protocols. The performance of nuclear fuel in reactors depends mainly on the chemical composition of its impurities and its estimation is important from the point of view of neutron economy. Among the instrumental analytical techniques commonly used for the determination of elemental impurities in uranium compounds spectrometric techniques are commonly used, such as; FAAS, GFAAS, ICP OES and ICP-MS. Usually, it is necessary in a previous uranium separation and preconcentration of the impurities for elemental determination. Thus, the aim of this review is to give an overview of the main process using sample preparation, separation and preconcentration of analytes for the instrumental determination.

Contents

1. Introduction

Over the past 50 years as the nuclear energy option, and especially its applications in health, industry, engineering and environment had a significant development and represent an important advance in the population quality life, especially with the use and development of new radiopharmaceuticals and radioisotopes [1–3]. The main element known used in nuclear power generation is uranium, often found in the oceans at an average concentration of 1.3 parts per billion (ppb) is a element of great commercial interest due do their applications in nuclear field [3,4].

There are several areas around the world where the concentration of uranium in the ground is sufficiently high that extraction of it for use as nuclear fuel is economically feasible. Such “economic concentrations” are called “ore.” When mined, it yields a mixed uranium oxide product, (U_3O_8). Uranite or pitchblende is the commonest uranium mineral used to produce the nuclear fuel. For many years from

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the 1940s, all of the uranium that was mined was used in the production of nuclear weapons, but this ceased in mid of the 1970s. Today the only substantial use for uranium is as fuel in nuclear reactors, mostly for electricity generation [3–5]. As nuclear power is the main use of uranium, heat from nuclear fission can also be used for industrial processes. It is also used for marine propulsion (mostly naval), whereas research reactors are important ways for making radioisotopes [3].

The largest uranium resources, the amount known to be economically recoverable from ore bodies, are naturally relative to costs and prices. They are also dependent on the intensity of past exploration effort, and are basically a statement about what is known rather than what is present in the earth's crust. The resources of metal minerals are a small fraction of what is present. With Australia has a substantial part of the world's uranium, followed by Kazakhstan and Canada [3,4]. The Brazilian uranium reserves are 300,000 tons and are among of the six largest in the world this gives the country strategic security with regard to the energy supply in nuclear field.

Uranium is a slightly radioactive metal that occurs throughout the earth's crust. Has an atomic number of 92 and its metallic silver in color. It is about 500-times more abundant than gold, 40-times as silver and about as common as tin, tungsten, and molybdenum. It occurs in most rocks in concentrations of 2–4 ppm, for example, at about 4 ppm in granite, which makes up 60% of the earth's crust. In rocks and ore, this element is not found in the metallic state but generally occurs in minerals such as carnotite, uraninite, and pitchblende. In the environment it occurs naturally as three radioactive isotopes: ^{238}U (99.27%), ^{235}U (0.72%) and ^{234}U (0.005%), but other isotopes can be synthesized. Uranium is an element that naturally presents various oxidation states (namely +2, +3, +4, +5 and +6), but uranium appears mostly in its hexavalent form. In fertilizers, uranium concentration can be as high as 400 ppm (0.04%), and some coal deposits contain uranium at concentrations >100 ppm (0.01%) [3–7].

According to the most optimistic scenarios of the Nuclear Energy Agency (NEA), an agency of the OECD, the participation of nuclear power in the energetic generation on planet can reach 22% to 2050 due to increased demand in countries like China and India. Thus, in this period, there is a forecast about 1400 operating reactors producing four times the amount of nuclear energy generated today [7].

Uranium is the major element and material basis for the sustainable use of nuclear energy. The optimized use of this technology involves the improvement of processes from mining and milling to power generation, which is achieved today's by advanced fuel design and core operational strategies and more demanding for example “Burn up” extended time residence even longer, higher thermal rates, also satisfy the appropriate safety margins. With regard to of fuel reliability, the chemical characterization combined with environmental protection is particularly important in the uranium production cycle, or better in the nuclear fuel cycle, subject to an increasing number of international conventions and protocols [8].

The performance of nuclear fuel in reactors depends mainly on the chemical composition of its impurities. The determination of these impurities is carried out mainly from the neutron economy point of view. During the different production stages and manufacturing of the Fuel Element (FE), the material may be contaminated with impurities from contact with a wide variety of metallic and nonmetallic compounds used in the process [8–10].

There is a need for e efficiency improvement and complementarily between the analytical techniques employed, especially with the recent development of the uranium silicide (U_3Si_2) and uranium-molybdenum alloy (U-Mo) technology in chemical characterization of fuel element [10,11].

Initially, in a short time, we intend to produce and qualify the U_3Si_2 based fuel with 4.8 $gU.cm^{-3}$, considered the most advanced commercial fuel today [12].

For proper reactor operation it is necessary to be made a strict quality control of these impurities in the energy matrix before it is placed in a nuclear reactor [13].

The presence of microconstituents, especially those elements with high cross section, including lithium, causes thermal neutrons absorption, reducing the nuclear fuel efficiency. Other impurities of lower cross section, however, at higher concentrations as the other alkali metals, alkaline earth and transition metals, can prejudice the efficiency of nuclear fuel, for example, reducing the fuel density. Alkali metals such as calcium and magnesium and also iron tends to form oxides preferentially affecting the oxygen/metal ratio in fuel matrix [6,11,14,15].

Thus, trace elements concentration, impurities or microconstituents that may be present or that can be tolerated is very specific and depends on the different types of fuel materials. The presence of Fe, Co and Ni give a contamination indication that occurred during the manufacturing process or the wear and tear of equipment. The control Cd content is important from the neutron economy point of view. Alkali metals, alkaline earth, some rare earths elements, manganese and cobalt, among others, is also activated in the radionuclides producing process after irradiation in the reactor [9,15,16].

The presence of common elements such as B, Cd, Hf and some rare earths such as Sm, I, Gd and Dy in the fuel reactor, even at ultratraces level is harmful to their efficient operation. The impurities metallic concentrations in the fuel must be below the maximum permitted level specified for obtaining the necessary density of “pellets” and also to reduce the loss of the high neutrons absorption. Quantitative determination of elements in nuclear uranium matrix is needed before their use as nuclear fuel. About 35 trace elements were listed in the specifications issued by ASTM C 787 for UF_6, requiring six or more techniques to determine all these impurities [17].

Several techniques have been applied in the elemental determination on uranium compounds and among them spectrometric methods are most used, since many elements can be estimated simultaneously in a short time using a small sample amount. Each method has advantages and shortcomings relative to non-spectral or spectral interference, precision, accuracy, cost (acquire, operation and support), sample type (solid or liquid) and apparatus employed in the analysis. The applicability of the method must also be taken into consideration whether each detection technique is overly complex or requires extensive and laborious separation or preconcentration steps [18].

Among the instrumental analytical techniques commonly used for the determination alkali and alkali earth metals in uranium compounds spectrometric techniques are commonly used, such as flame photometry and inductively coupled plasma optical emission spectrometry. Usually, it is necessary for a previous uranium separation by solvent extraction, precipitation, ion exchange chromatography, distillation and electrolysis [18]. The main problem in the use emission techniques is the spectral interference in the complex uranium emission spectrum. This approach use a fractional distillation technique with carriers to circumvent this problem, however, this methodology can be applied only for some elements such as Cd, Co, Cr, Cu, Fe, Mn, Ni, among others. The emission spectrometer with inductively coupled plasma source (ICP OES) is not able to determine most interest elements, without first to proceed to a preliminary uranium chemical separation, because of the large and complex spectral interference [18].

Ion chromatography can act as an alternative method to complement the currently applied techniques because of its versatility, ease of automation fast separation, selectivity and sensitivity. It is a multielement technique and has been widely used to analyze nuclear fuels, both in the final product as in process materials. Transition metal ions can be analyzed by ion chromatography using chelation, by reverse-phase chromatography and cation/anion ion chromatography [15,19]. For the transition metals cationic species separation it must be done through the complexation of metal ions in the mobile