

FEASIBILITY STUDY OF CONTAMINANTS ANALYSIS IN URANIUM-CONTAINING MATERIALS BY LIBS SPECTROSCOPY

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Abstract

Uranium-containing samples are in the focus of analytical research for various reasons, for example with regards to nuclear safeguarding, quality management or nuclear forensic science. In our present contribution, we overview the challenges related to the analysis of contaminants in uranium-containing samples and the potential solution for overcoming them.

Introduction

Radioactive materials are very useful, since nuclear power plants provide electrical energy for hundreds of millions people, and they are also extensively applied for diagnostic and therapeutic purposes in medicine. Nevertheless, radioactive materials can mean serious threat too. The radiation emitted by these materials may initiate apoptosis and can severe the DNA, causing tissue deformations. In the current state of the international situation, the great destructive power of nuclear materials should also not be overlooked. Consequently, the regulation and qualification of radioactive materials is an important task. Uranium is one of the most commonly used fuel in nuclear reactors and bombs, thus its properties – including chemical purity - are tested very often.

Laser-induced breakdown spectroscopy (LIBS) is a modern, versatile trace analytical atomic spectroscopic technique, which is becoming increasingly popular in recent years for both quantitative and qualitative purposes. The light from a pulsed laser is focused onto the surface of a solid sample, where it ignites a microplasma. The analytical information can be retrieved from the optical emission of this microplasma. The use of this method usually require minimal or even no sample preparation and very little sample amount, furthermore the measurements can also be accomplished in a stand-off fashion, right in the field. All these characteristics make LIBS an ideal candidate for contaminants analysis in uranium-containing materials.

Discussion

Radioactive materials are typically analysed for three main causes by the methods of analytical atomic spectrometry.

Quality management is an essential part of manufacturing products, and this also goes for nuclear fuel grade uranium dioxide powder and pellets. The regulations of the international standards concerning their physical and chemical properties are very strict [1, 2]. Elemental impurities are also considered to be important, because they can effectively alter the physical properties (density, toughness, sinterability etc.) as well as nuclear properties of the powder and pellets. For example, the presence of a high concentration of boron or other neutron-capturing agents such as Gd, Eu, Dy, Sm and Cd can significantly lower the neutron flux

flowing through the uranium oxide, which in turn lowers the caloric value of the nuclear fuel. For this reason, the total boron equivalent concentration of these elements is not allowed to exceed 4 ppm. The maximum allowable concentration limits for other elements are usually in the 100-300 ppm range, but their cumulative concentration shall not exceed 1500 ppm.

Element	Maximum Concentration Limit of Uranium, µg/gU
Aluminum	250
Carbon	100
Calcium + magnesium	200
Chlorine	100
Chromium	200
Cobalt	100
Copper	250
Fluorine	100
Iron	250
Lead	250
Manganese	250
Molybdenum	250
Nickel	200
Nitrogen	200
Phosphorus	250
Silicon	300
Tantalum	250
Thorium ^A	10
Tin	250
Titanium	250
Tungsten	250
Vanadium	250
Zinc	250

^A Thorium is primarily of concern because of the reactor production of ²³³U.

Table 1. Traditional impurity limits in uranium dioxide according to [2]

Nuclear forensic investigations provide answers to questions concerning nuclear materials found outside of the regulatory control. One of such investigations is the elemental or isotopic “fingerprint-like” identification (assignment) of a “nuclear forensic signature” to a sample. This signature is characteristic for the ore, but the processing technology/facility employed will also impose its own signature onto the sample, the latter of which can then be used to identify the “manufacturer” and hence its legal status. This qualitative analytical application can allow the investigators to determine the origin of an unknown nuclear material [3].

In the case of **nuclear safeguards investigations** the analytes are ambient samples (soil, water, etc.). The average concentration of uranium in the Earth’s crust is low (only about 2-4 ppm), so if an elevated level of U concentration is found, it indicates either a leak from a nearby nuclear industry facility or the usage of nuclear weapons such as fission bombs or so called dirty bombs [4]. Due to their purpose, safeguards measurements deal with low concentrations and complex matrices [5].

Many atomic spectroscopy methods, such as graphite furnace atomic absorption spectrometry (GFAAS), spark- and arc atomic emission spectrometry, inductively coupled plasma atomic emission (ICP-AES) and mass spectrometry (ICP-MS), the latter two sometimes also combined with laser ablation sample introduction, were used in the literature for the above analyses. Unfortunately, none of these methods can be executed in the field, either because the instrumentation is bulky and costly, or because the instruments can only process liquid samples, so extensive sample preparation is needed prior to the spectroscopy measurements.

According to recent literature, LIBS has a great potential for becoming a quick, field-applicable, trace analytical technique for radioactive samples. For example, Campbell *et al.*

were able to discriminate different uranium oxides (UO_2 , U_3O_8 , UO_3) via the comparison of the relative intensity of some well-chosen uranium and oxygen lines [6]. Barefield *et al.* had shown that uranium and thorium can be detected by LIBS in their ores [7] and the same authors could also determine low concentrations of uranium in a glass matrix severe spectral interferences [8]. Russo *et al.* developed algorithms for spectral deconvolution of uranium isotopic spectral lines and demonstrated their usefulness in soil matrices for the fairly accurate determination of the $^{235}\text{U}/^{238}\text{U}$ isotope ratio [9]. LIBS limits of detection can also be adequate for even the most demanding technical/safeguards applications (in the sub-ppm range) [10].

It also has to be mentioned that since LIBS is an atomic emission spectrometry method, it generates line-rich spectra (it is not uncommon in complex matrices that the emission spectrum contains over 100,000 spectral lines!). If portable instrumentation with compact, conventional dispersive spectrometers are to be used for the analysis, one will face severe spectral interferences, especially in studies dealing with elements that have several isotopes. If isotope ratios are also to be determined, then the resolution of conventional spectrometers can cause problems, since atomic isotopic shifts are usually very small, on the order of pm only. In addition to this, the plasma is usually generated under atmospheric conditions (even is under a laser ablation chamber for safety reasons), which causes pressure-induced broadening of spectral lines [10].

At the moment it seems that there are two potential solutions to these problems. For isotope-resolving studies, laser ablation molecular isotopic spectrometry (LAMIS), introduced by Russo *et al.* [11], may be a solution. This approach uses LIBS experimental conditions favouring the formation/detection of molecular components and measures the molecular (e.g. oxide, fluoride) isotopic shifts instead of the atomic ones, because the former shift can be 100 times larger than the latter. The other possibility is to use advanced, compact, but high resolution spectrometer optical arrangements, such as the spatially heterodyne spectrometer (SHS) for LIBS. The first studies out in this research area [12, 13] are also promising and suggest that isotopic resolution will indeed be possible in the field by using LIBS spectrometry. At present, we are pursuing both of these approaches (LAMIS and SHS) in order to reach our goal of developing a LIBS-based method for the analysis of contaminants in uranium-containing materials.

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