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Determination of plutonium in nitric acid solutions using energy dispersive L X-ray fluorescence with a low power X-ray generator

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ABSTRACT

This work presents the development of an in-line energy dispersive L X-ray fluorescence spectrometer set-up, with a low power X-ray generator and a secondary target, for the determination of plutonium concentration in nitric acid solutions. The intensity of the L X-rays from the internal conversion and gamma rays emitted by the daughter nuclei from plutonium is minimized and corrected, in order to eliminate the interferences with the L X-ray fluorescence spectrum. The matrix effects are then corrected by the Compton peak method. A calibration plot for plutonium solutions within the range 0.1–20 g L^{-1} is given.

1. Introduction

The energy dispersive X-ray fluorescence (EDXRF) spectrometry is used to quantify rapidly, simultaneously and by non-destructive assays, the transuranic elements (uranium, neptunium, plutonium, americium) in liquid wastes from the nuclear reprocessing plants. In the last 30 years, several configurations have been developed to determine in-line transuranic elements by excitation of K-lines from radionuclide sources or X-ray tube [1–4]. Only a few configurations have been developed by excitation of L-lines from radionuclides or X-ray tube, mainly with a wavelength-dispersive X-Ray fluorescence instrument: one is installed in a glove box at the Los Alamos National Laboratory leading to a sensitivity of around 2 ppm for uranium [5–8], another one was installed for in-line processes at AREVA La Hague [9] or CEA Marcoule in France. These devices use a specific detector and an X-ray generator of high power, requiring liquid cooling and a graphite monochromator for selecting the element which will be analyzed. Other configurations use HPGe detectors to measure self-induced X-ray fluorescence in spent nuclear fuel [10].

Advanced technology makes now possible a portable device for on-site analysis of the L X-rays transuranic elements by EDXRF without liquid cooling [11], in order to minimize as low as possible the amount of solid or liquid wastes. The purpose of this work is to develop, with an adjustable prototype, a new compact fluorescence L X-ray spectrometer and an analytical method to determine on a derivation duct, without dilution, the concentration value of plutonium within 0.1–20 g L^{-1} in nitric acid solution (10% HNO_3). In these solutions, the concentration values of uranium and americium are deliberately lower than the limit of detection of the spectrometer (~10 mg L^{-1} for a counting time of 300 s), so as not to interfere with the plutonium peaks.

2. Experimental

For the development of this spectrometer, two thallium standard solutions were firstly used to limit as low as possible the number of experiments with nuclear materials, and secondly, several plutonium solutions were prepared with ultra-pure plutonium standard. Then, these solutions were measured by our L X-ray fluorescence prototype spectrometer (Fig. 1).

2.1. Properties of plutonium standard

A solid plutonium standard was used to prepare plutonium solutions. This standard has a $^{239}_{94}Pu$ isotopic concentration higher than 90% and some radioactive impurities. The concentration values of uranium and americium were analyzed in September 2007 by inductively coupled plasma mass spectrometry and inductively coupled plasma atomic emission spectroscopy respectively, at

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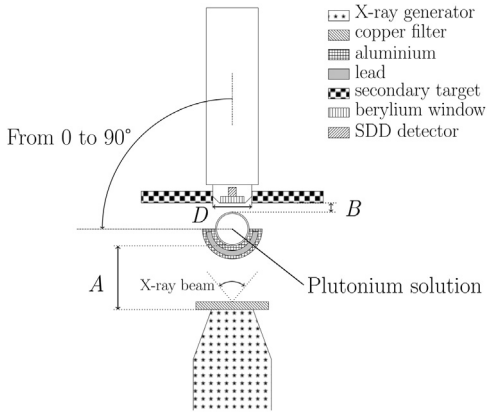

Fig. 1. Top view of the L X-ray fluorescence spectrometer used for the determination of plutonium in nitric acid solutions. *A*: distance from the X-ray generator to the sample. *B*: Distance from the secondary target to the sample. *D*: Diameter of the circular hole for the secondary target.

31 μg/g and 18 μg/g. These concentration values were then evaluated at the date of the experiments with an internal CEA evolution code of isotopic composition. The ^{241}AM concentration value (from the β^- decay of $^{241}_{94}$Pu with a half-life of 14.29 years), is evaluated at 33 μg/g. The total uranium concentration is evaluated at 200 μg/g.

2.2. Plutonium solution preparation

Plutonium solutions were prepared in a glovebox by using this solid standard Pu diluted in nitric acid solution and 18.2 MΩ cm deionized water. From this solution, five samples were prepared into 5 mL volumetric flasks in 10% HNO_3, containing respectively 19.98, 9.99, 4.99, 9.99 $\times 10^{-1}$ and 9.99 $\times 10^{-2}$ g L^{-1} of plutonium. Flasks are in polypropylene (PP, 1 mm thick, 90 mm high and diameter of 12 mm) and are moved out of the glovebox to be measured by XRF. Flasks were then put into a double flexible plastic shield made up of ethylene-vinyl acetate and ethylene-butyl acrylate (EVA/EBA), each one 0.3 mm thick and a width of 14 cm, in order to confine radioactive elements and to protect operators.

2.3. Instrumentation

To decrease as low as possible the amount of solid or liquid nuclear wastes, the instrumentation requires compact devices without liquid cooling. If the plutonium detection limit is higher than 0.1 g L^{-1}, a low power X-ray generator cooled by thermal conduction could be used. The X-ray generator is a 50 kV MAGNUM Cabled (Moxtek, USA) made up of a tungsten filament, a silver target metal (Ag) and a beryllium window of 0.25 mm thick. The voltage can be adjusted from 10 to 50 kV and the beam current up to 200 μA; the maximum power for the X-ray production is 10 W. The X-ray generator is operated with a Moxtek FTC-200 Controller. Firstly, the X-ray generator parameters are adjusted during experiments at 50 kV and 50 μA. The fluorescence X-rays emitted from the sample are measured between 0.2 and 20 keV by a silicon drift detector (SDD) cooled with a Peltier module (Ketek, Germany) with a beryllium window of 8 μm thick and a detection area of 7 mm^2. The energy resolution at 5.8 keV is 148 eV and the shaping time of the detector amplifier is 2 μs. The analogue signal from the amplificator was converted into a digital signal by an analogue-to-digital converter (ADC, KeteK) and is analyzed through a multichannel analyzer with 4096 channels (MCA, Ketek) to generate the spectra with the MCDWIN software. The intensity of L X-rays was determined by a Gaussian fit.

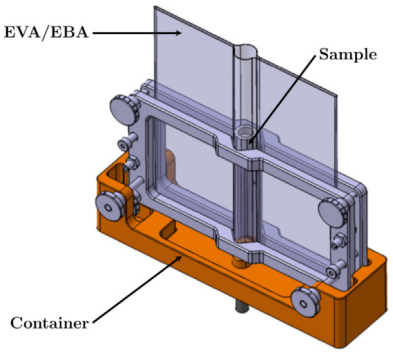

Fig. 2. Support used to analyze plutonium samples.

The distance *A* between the X-ray generator and the sample and the distance *B* between the secondary target and the sample are controlled through a graphical user interface and electric motors. The distance between the X-ray generator and the sample ranges from 12 to 40 mm and the distance between the secondary target and the sample varies within limits of 3 mm and 30 mm. The detector angular position ranges from 0° to 90°.

A big circular secondary target is placed in front of the detector (Section 3.1). Its characteristics are 50 mm in diameter and 2 mm thick. A circular aperture takes place at the centre of the secondary target so that X-rays emitted by the sample reaches the detector.

A lead half protection of 1.14 mm thick covered with a 0.7 mm thick aluminium sheet is used to stop the polychromatic radiations from the X-ray generator and to protect operators from the lead toxicity.

To analyze plutonium samples in a double plastic shield (EVA/EBA), an aluminium sample support has been designed with a container to maintain and protect the plastic shield, and to contain the solution in the case of vial leak (Fig. 2).

These instruments are in a lead box (50 cm $\times$ 50 cm $\times$ 65 cm) to protect operators from X-rays.

3. Determination of the optimum geometry

3.1. Requirements

The interpretation of X-rays spectra from plutonium samples must be carefully performed with portable EDXRF instruments, as the peak intensities are not necessarily correlated with the concentration values of the elements [12]. Daughter nuclei can be in excited states after alpha decays from $^{238}_{94}$Pu to $^{234}_{92}$U, from $^{239}_{94}$Pu to $^{235}_{92}$U, from $^{240}_{94}$Pu to $^{236}_{92}$U and from $^{242}_{94}$Pu to $^{238}_{92}$U. Two relaxation processes are then possible: either γ-rays are emitted with an energy generally higher than 50 keV [13], or X-rays from daughter nucleus are emitted from an internal conversion. Thus X-rays from internal conversion and γ-rays from de-excitation of the nuclear state are added to the characteristic X-rays from fluorescence. The use of the detector in the range 0.2–20 keV has the advantage to eliminate most of γ-rays, and avoid high saturation of the SDD detector. As an example, a low concentration of americium can saturate the detector because of two highly intense gamma peaks at 26.3 keV and 59.5 keV [5]. In the present case, the problem of L X-rays line analysis is mainly limited to the interference between X-rays from internal conversion and X-rays from fluorescence.

Two solutions are possible to correct the interference due to internal conversion and to correlate the peak intensities to the concentration values of elements. The first solution is to use a high powered X-ray source which requires in some cases a collimator in front of the detector [2,12,14]. The second solution is to perform a