

X-ray fluorescence-based method for the quantitative determination of uranium in the aqueous solutions

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Abstract. Currently, one of the important issues in the field of nuclear technology is providing special handling with respect to nuclear materials, due to their energy and commercial significance, as well as their potential radiation contamination threat. There is a necessity to have information about the full qualitative and quantitative composition of the sample as a part of special handling with nuclear materials. Spectrometric methods solve this problem effectively. One of these methods is the X-ray fluorescence analysis, which is fast, nondestructive and environmentally friendly with a high accuracy and reproducibility of the results. Development of uranium quantitative determination method in aqueous solutions to solve the problems of accounting and control of nuclear materials is the subject of research in this article. The development of the uranium concentration determination method in the aqueous solutions of uranyl nitrate $\text{UO}_2(\text{NO}_3)_2$ was carried out using Spectroscan MAKC-G – wavelength dispersive crystal diffraction XRF spectrometer.

1. Introduction

The significant efforts are made today in the world to provide special handling with respect to nuclear materials, as many of them have commercial and energy values. Also, there is a real threat of using nuclear materials for military or terrorist purposes. Moreover, the possibility of radiation contamination is of high importance. As it is known, special handling is aimed at providing the safety of nuclear materials and full information about them. It consists of three main components – the physical protection, accounting and control of nuclear materials [1].

From the system of accounting and control of nuclear materials point of view, it is always necessary to have full information about the qualitative and quantitative composition of a substance, as nuclear materials in any compound should be registered, starting from the minimum amount, and should be divided into categories. The issues concerning qualitative and quantitative composition of sample are resolved by spectrometric methods effectively. One of these methods is the X-ray fluorescence analysis, which is fast, nondestructive and environmentally friendly method with a high accuracy and results repeatability.

The subject of the research in this paper is to develop a method for determination of uranium concentration in the aqueous solutions to solve the problems of accounting and control of nuclear materials using MAKC-G analytical complex Spectroscan.

Spectroscan MAKC-G is a portable X-ray fluorescence wavelength dispersive crystal diffraction scanning spectrometer designed to determine the content of chemical elements from Ca to U of the substances in solids, liquids or powders, in solutions and thin films, deposits on filters.



2. The experimental evaluation of the method accuracy

With spectrometer Spectroscan MAKC-G standard multi-element sample was measured, in order to verify the settings and calibrations of device, as well as for accuracy evaluations.

With the qualitative analysis it was able to determine exactly the composition of the sample. Then, a quantitative analysis was made. The results are shown in table 1.

Table 1. The measurement results of the standard multi-element sample.

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Components	Abundance ratio, %					Average values
	Experimental values					
	1	2	3	4	5	
Ca	20.01	20.37	20.35	20.13	20.20	20.210±0.068
Ti	28.38	28.21	28.29	28.60	28.12	28.320±0.082
Cr	4.22	4.11	4.09	3.98	4.24	4.129±0.047
Fe	2.88	2.81	2.79	2.76	2.86	2.819±0.022
Ni	2.05	2.06	2.04	2.04	2.08	2.055±0.007
Zn	4.04	4.06	4.04	4.07	4.07	4.058±0.007
Sr	2.31	2.30	2.32	2.32	2.32	2.315±0.003
Pb	2.36	2.34	2.34	2.35	2.35	2.345±0.052
H*	0.07	0.07	0.07	0.07	0.07	—
C*	0.70	0.70	0.70	0.70	0.70	—
O*	32.98	32.98	32.98	32.98	32.98	—

* – filling component, cannot be measured using this XRF spectrometer

The results of the qualitative and quantitative analysis of the values correspond to the passport. The measurement error is introduced in the second decimal place.

3. Preparation of uranyl nitrate aqueous solutions

The studies were conducted to measure aqueous solution of uranyl nitrate $\text{UO}_2(\text{NO}_3)_2$. This uranium connection was chosen for several reasons. Firstly, it is readily soluble in water and, therefore, it is safer to handle (as opposed to acid solutions). Secondly, uranyl nitrate is widely used at different stages of the nuclear fuel cycle, from the ore opening-up to the extraction separation of uranium and plutonium in spent nuclear fuel [2]. The step of prospecting and ore extraction is of particular interest, since the use of XRF analysis at this stage would greatly speed the process and replace longer, expensive and destructive chemical methods for qualitative and quantitative determination of the sample composition.

The process of sample preparation consists of several stages: mass calculation of uranyl nitrate dry powder to obtain the desired concentration of uranium in the solution; weighing of uranium powder using electronic scales with accuracy to three decimal places; dry uranyl nitrate dilution with water of 100 ml volume and mixing thoroughly; moving an aqueous solution into a special cell, which is supplied equipment to the spectrometer, with volume of 15 ml; the cell must be closed with the Mylar film and put through the adapter into the holder.

4. The experimental calibration curves

Several series of measurements of uranyl nitrate with concentration varying from 1 to 100 g/l. were made during the research. Measurement time is 8 minutes. The studies were conducted on two analyzing crystals – LiF(200) and C002. Characteristic lines of uranium were detected in the first and the second order of reflection on the analyzing crystal LiF(200) and in the second order on C002. In total, the five characteristic lines of the uranium, which are clearly visible in the measurement of all prepared solutions, have been selected for measurements. The calibration characteristics were obtained in the research result. These dependences are complex linear functions, which consist of two lines with transition between them, as it is shown in Figures 1 – 5.

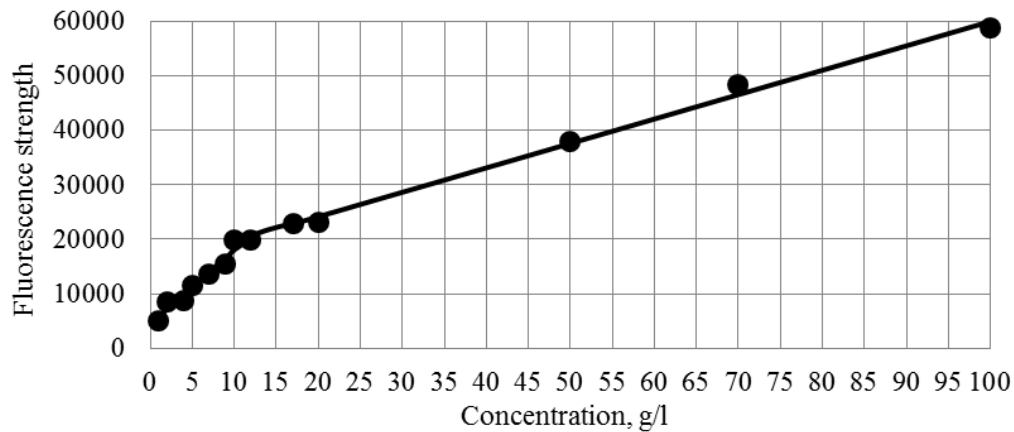


Figure 1. The calibration characteristic on a crystal LiF of 1 order reflection with a wavelength of 910 mA.

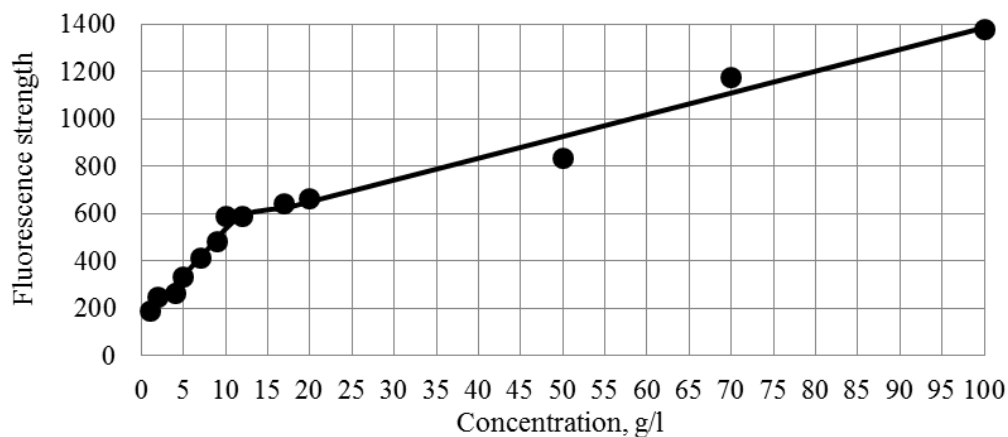


Figure 2. The calibration characteristic on a crystal LiF of 2 order reflection with a wavelength of 720 mA.

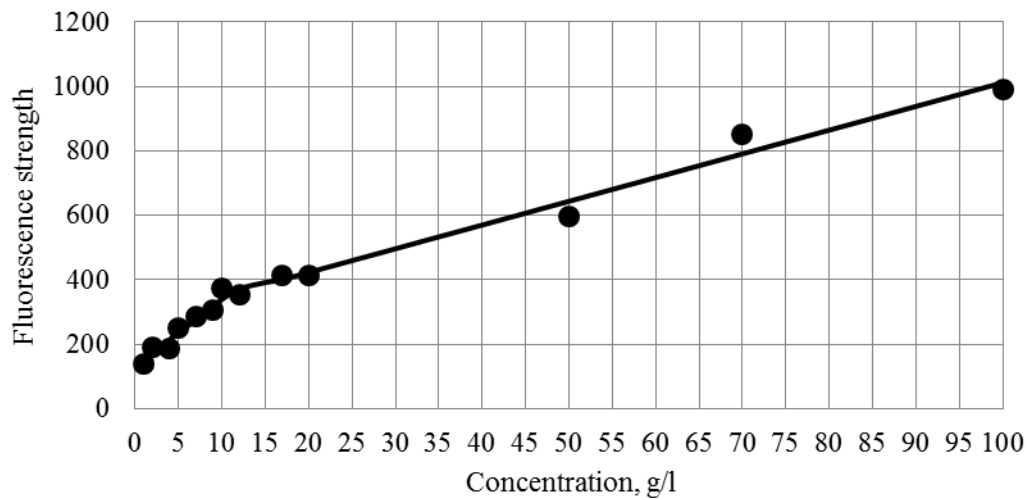


Figure 3. The calibration characteristic on a crystal LiF of 2 order reflection with a wavelength of 754 mA.

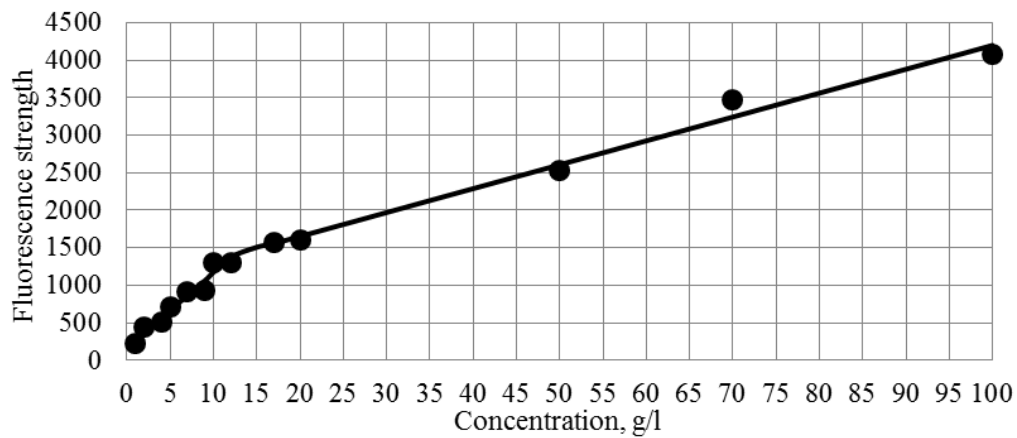


Figure 4. The calibration characteristic on a crystal LiF of 2 order reflection with a wavelength of 910 mA.

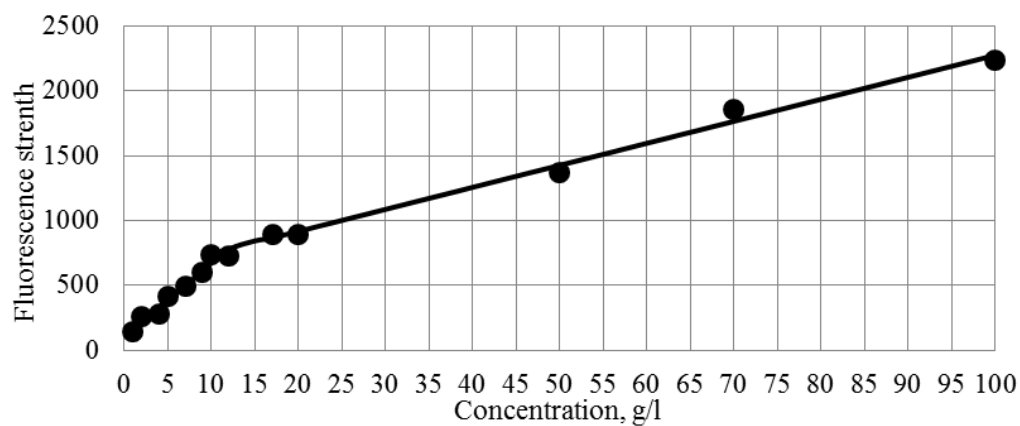


Figure 5. The calibration characteristic on a crystal C002 of 2 order reflection with a wavelength of 910 mA.

5. Analysis and testing of the method

Taking into account the dependencies between the concentrations of uranium in solution and fluorescence strength, it can be seen that a kink between two straight falls on a point with a value of 15 g/l, both on the analyzing crystal LiF and on the pyrolytic graphite in all investigated orders of reflection. Decomposition of calibration curves in two lines is due to effects of fluorescence quenching and self-shielding in the samples.

The studies were conducted with aqueous solutions of uranyl nitrate, and, as it is known, the water includes oxygen, which is the most prominent dynamic fluorescence quenching agent and is able to quench the fluorescence of almost all known fluorophores. With the decrease of uranium concentration in the solution the fluorescence strength decreases, but the concentration of oxygen on the contrary increases, consequently, the influence of the dynamic fluorescence quenching process increases. It is also important to note that even conducting rapid measurement (which was used in the work), the sample is heating. The dynamic quenching depends on diffusion, which, in turn, depends on the temperature. The increasing temperature increases diffusion coefficient. In addition, the quenching rate constant increases as a result of increasing temperature.

Moreover, the self-shielding effect influences on the results of measurements, because with increasing concentrations of uranium in solution, its solubility decreases and the probability of radiation's absorption in sample increases [3, 4].

Possibility of using the developed method was tested on the two standard samples, which have uranium concentrations 60 and 40 g/l. The maximum error in determining the uranium concentration was 2%.

6. Conclusion

During the research, by measuring the standard multi-elements sample it has been proved that the measurement results obtained by this XRF spectrometer have a high precision. Also, the possible use of this spectrometer to determine the elemental composition of the samples and quantitative determination of uranium in accounting and control of nuclear materials was proved.

Within the framework of the objectives a series of the experiments to determine the interconnection between the various uranium concentrations in aqueous solutions and their secondary radiation. As a result, the method for the quantitative determination of uranium in an aqueous solution has been developed and, later, successfully tested using analytical complex Spectroscan MAKC-G. The measurement error doesn't exceed 2 %.

The using of this method at different stages of the nuclear fuel cycle will simplify main manufacturing processes and will make them faster and cheaper. Also, it should be noted that this method does not depend on the chemical compounds of uranium. It is only necessary for the compound to be able to dissolve in water.

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