A NEW METHODOLOGY FOR DETERMINATION OF WATER OF CRYSTALLIZATION FOR URANYL NITRATE SAMPLES USING SCANNING ELECTRON MICROSCOPE, ENERGY DISPERSIVE X-RAY, AND MCNP-5

by

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The scanning electron microscope and its attached X-ray unit are valid tools for conducting surveys to determine whether or not the studied samples contain nuclear material. To verify their structure, ten solid uranyl nitrate specimens with various enrichment values (0.1 % to 1 %) were analyzed. The used samples have different numbers of hydrated water molecules; consequently, the properties of these materials in analytical chemistry and computational methods are not the same. Scanning electron microscope and energy dispersive X-ray are used in this work to visualize and analyze the sample of hexahydrate uranyl nitrate (natural 0.72 %). The specimen has been screened under optimal microscopy circumstances. In spite of the reliability of these tools, they are not accurate, particularly when carrying out complete qualitative and quantitative analysis. With the aid of the Monte Carlo code (MCNP-5), the approach presented here can resolve the limitations that tackle the microscope and X-ray testing. The suggested approach relates to the Monte Carlo calculations and X-ray elemental analysis. This relationship depends on the chemical composition of the material and was developed like software. The concentration and count rate calculation software has been established to determine the water of crystallization for uranyl nitrate samples.

Key words: uranyl nitrate, concentration, MCNP-5 code, crystallization water

INTRODUCTION

Water molecules existing inside crystals are called Water of crystallization or water of hydration [1]. This type of water lies in the crystal structure of a complex or a salt and is not bonded to the metal cation directly. The heating of the sample can cause this water to be removed and may also cause a loss of crystalline properties. Crystallization is found in many uranium and thorium compounds. One of the most widely used materials that have this property is uranyl nitrate. It is a crucial compound in the nuclear fuel cycle. It occurs in various hydration forms such as the hexahydrate [$UO_2(NO_3)_2.6H_2O$], and the trihydrate [$UO_2(NO_3)_2.3H^2O$] forms.

The hexahydrate form is considered the most popular uranium salt for commercial purposes. This form contains a small amount of impurity such as alkali therefore, it may require several cycles of purification. It is prepared by dissolving uranium oxides or hydroxides in an inorganic solvent (nitric acid) [2].

It is necessary to determine the chemical composition of uranium samples through measurements employing destructive assay (DA) technique. The change in the number of water molecules in a sample results in variation of the density of the material that leads to the modification of some material card entries in MCNP-5; therefore, this study aims to find a methodology for determining the number of water molecules, in certain compounds, that are more significant in nuclear safeguards.

A nuclear safeguard is an international approach implemented by the United Nations in order to assure peaceful applications of radiation. The most employed technique in safeguards is microscopy and X-ray analysis. A SEM and energy dispersive X-ray (EDX) play a role in locating particles, analyzing them, and measuring their micro size. The SEM can reveal information related to sample composition and its surface topography. The EDX uses a solid sample X-ray spectrum to obtain elemental chemical analysis [3]. All elements, including atomic numbers 4 (Be), and 92 (U) can be detected.

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Table 1. Description of the tested uranil nitrate NM samples used in the measurements

Sample ID	Chemical formula	Molecular mass [g mol^{-1}]	Mass [g]	Enrichment Range
UNH-6	$UO_2(NO_3)_2.6H2O$	502.1292	50	0.1-1%
UNH-4	$UO_2(NO_3)_2.4H2O$	466.0986		
UNH-2	$UO_2(NO_3)_2.2H2O$	430.0681		
UN	$UO_2(NO_3)_2$	394.0375		

The method described is based on a Monte Carlo N-Particle (MCNP) general-purpose code. This work explains a new method for determination of water of crystallization in uranyl nitrate samples using SEM, EDX, and MCNP-5, to resolve the shortage that faces SEM and EDX with MCNP simulation Code. The scarcity is partial qualitative and semi-quantitative analysis. In addition to this objective, concentration and count rate calculation (CCC) software is set up to promote the chemical composition obtaining. The measured commercial uranyl nitrate hexahydrate, used in this study, is located at key measurement point (KMP I) at the Egyptian nuclear and radiological regulatory authority (ENRRA).

EXPERIMENTAL SET-UP AND TECHNIQUES

Samples description

Ten tested uranyl nitrate samples with different enrichment values which ranged from 0.1 % to 1% in a solid phase, and a mass of 50 g, were studied. Detailed information on each sample is shown in tab. 1.

Measurements by SEM and EDX

The SEM utilized in this study is a JEOL JSM-6510LV model with resolution of 1 1 pÅ – 1 Å (1 Å = 10^{-10} m) [3]. The specimen was fixed inside the holder and was placed inside the apparatus evacuation chamber at working distance 10 mm (WD10 mm), voltage 30 kV, magnification value 200, and spot size 50 [4]. The previous conditions are related to the characteristics of the primary electron beam that generated from the filament and bombarded through the electron gun. In EDX analysis, detection limits are typically about 0.1 wt.%, although reduction can be achieved by using long counting times or better count rate (CR) using SDD detectors [5].

Monte Carlo modeling for the proposed system

The general Monte Carlo code (MCNP-5) was used to compute the absolute efficiency of the detector [6, 7]. The characteristics and specifications of the planar HPGe detector and tested NM were modeled [8], and 40 input files were created to run for these calculations. Also, there were 109 histories (number of photons) of 35 minutes running time used in these calculations. The specifications of the used laptop are 2.5 GHz Intel Core i7 processor. A tally card F8 is used to determine the pulse height of the detector and to calculate the absolute efficiency of the detector at 185.7 keV energy line [9].

Gamma calculations

High Purity Germanium detector (HPGe) [Canberra; model GL0515R with an active area of 540 mm^2, 1.5 cm height, and 122 keV FWHM at 540 eV] was used in the MCNP inputs. Multi-channel analyzer [inspector, Model IN2K], to collect the input energy pulses, the detector was adjusted at high voltage (2500V) [10-13]. A set of tested NM samples were used for executing the computational calculations. During these calculations, ten uranyl nitrate specimens with different water of crystallization that have various enrichment (Depleted, Natural and low enriched) were placed in a cylindrical bottle. The bottle was made from Polypropylene, contained 50 g of $UO_2(NO_3)_2$ and its dihydrate, tetra and hexahydrate forms.

The external diameter of the bottle was 13 mm while the internal one was 11 mm; as well, the fill height of the compact powder of all the samples was 42 mm. The specimen was placed facing the detector.

Concentration and count rate calculation software

The CCC software was built to facilitate obtaining of the chemical composition of the assayed uranyl nitrate sample. Although the detection limit of EDX measurement, at the hydrogen energy line, is not available and out of the detection range, the CCC software is the appropriate solution for this task.

The software was compiled by visual basic (version 6) that operated under windows. The CCC software is concerned with certain Uranyl nitrate compounds which have different amount of hydrated water. The CCC software is divided into two segments: one for EDX measurement and the other for HPGe detector measurement. In the first segment, by selecting the chemical composition form, the mass ra-

tios of each element are calculated at certain characteristic X-ray energy lines: at 0.392 KeV for nitrogen, 0.525 KeV for oxygen and 3.164 KeV for uranium. The second segment contains two variables obtained from fitting the data between the CR and the enrichment values. Each compound has different parameters depending on its chemical composition. By entering the enrichment value, the CR of U-235, at the energy line 185.7 KeV, is calculated.

Any compound has a molecular weight and a density that are considered important factors in MCNP code for getting the CR. As the CR changes, the density changes and vice versa. Finally, the number of hydrated water molecules is determined.

RESULTS AND DISCUSSION

SEM results

For qualitative analysis, it is of interest to look for uranium in samples and to obtain a rough estimation of the amount of each element within the sample. This can be done by identifying the peaks in the X-ray spectrum (fig. 1 shows the SEM image of the UNH-6 sample). For quantitative analysis, the proportion of each element is measured using areas under the X-ray peaks. Table 2 summarizes the theoretical and experimental calculations of uranyl nitrate hexahydrate.

Table 2 shows that the difference between the experimental and the theoretical calculations, due to elements such as hydrogen, has no chance of appearing as a peak in the EDX spectrum. Hence, quantifying nuclear samples that contain water of crystallization may be misleading.

Table 3 shows the theoretical calculations of the uranyl nitrate sample with different number of molecules of water of crystallization. The four elements (H, N, O, and U) have different mass percentages. Uranium is the most abundant element in all the samples, while hydrogen is the least. By increasing the amount of hydrated water, the ratio of hydrogen expressed in mass percentage increases.

The CR for energy line (185.7 keV), with accompanying uncertainties, σ_{CR}, at different enrichment values of the tested NM, are given in tables (4)-(7). Table 4 shows the relationship between the calculated CR using MCNP-5, tested NM enrichment and the mass of U-235. The value of absolute full-energy peak efficiency was calculated by MCNP-5, so the CR was obtained [13]. All the estimated uncertainties due to Monte Carlo calculations were less than 0.01 % [14]. It is clear that, by increasing the sample enrichment, the

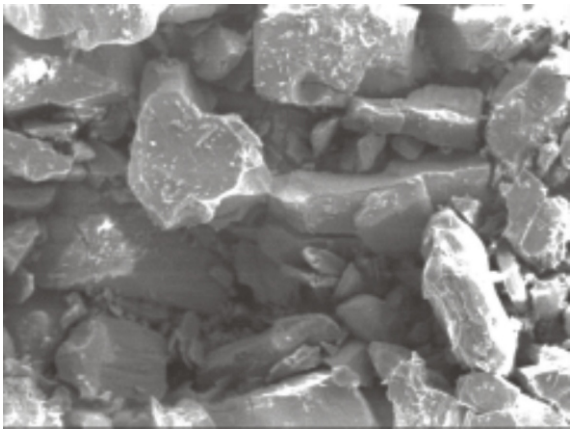

Figure 1. Uranyl nitrate hexahydrate SEM image at X200

Table 2. Theoretical and experimental calculation of uranyl nitrate hexahydrate

Sample	UNH-6 sample (experimental by EDX)							
Element	H	Error	N	Error	O	Error	U	Error
Mass [%]			2.81	0.004	45.59	0.0036	51.60	0.0039
Sample	UNH-6 sample (theoretical calculation)							
Element	H		N	O			U	
Mass [%]	2.408813		5.578925	44.6084			47.40387	

Table 3. Theoretical calculation of uranyl nitrate sample with different water of crystallization

Sample	UNH-4 sample (theoretical calculation)			
Element	H	N	O	U
Mass [%]	1.730013	6.01019	41.19149	51.06831
Sample	UNH-2 sample (theoretical calculation)			
Element	H	N	O	U
Mass [%]	0.9374759	6.513717	37.20206	55.34675
Sample	UN sample (theoretical calculation)			
Element	H	N	O	U
Mass [%]	0.4892316	6.798502	34.94571	57.76656

Table 4. Calculated CR of energy line 185.7 KeV due to ^{235}U isotopes with associated uncertainties for uranyl nitrate sample at different enrichment values (0.1-1 %)

Sample	Enrichment [%]	Count rate (σ_{CR}) [s^{-1}]	Mass of U [g]	Mass of ^{235}U [g]
1	0.1	0.0546 3.113 10^{-5}	30.203	0.01824
2	0.2	0.1092 6.225 10^{-5}		0.03648
3	0.3	0.1638 9.340 10^{-5}		0.05473
4	0.4	0.2184 12.455 10^{-5}		0.07298
5	0.5	0.2730 15.567 10^{-5}		0.09122
6	0.6	0.3276 18.682 10^{-5}		0.10947
7	0.7	0.3822 21.795 10^{-5}		0.12771
8	0.8	0.4368 24.909 10^{-5}		0.14596
9	0.9	0.4914 28.022 10^{-5}		0.16420
10	1	0.5459 ± 31.136 10^{-5}		0.18244

Table 5. Calculated CR of energy line 185.7 KeV due to ^{235}U isotopes with associated uncertainties for uranyl nitrate dihydrate sample at different enrichment values (0.1-1 %)

Sample	Enrichment [%]	Count rate (σ_{CR}) [s^{-1}]	Mass of U [g]	Mass of ^{235}U [g]
1	0.1	0.0444 2.534 10^{-5}	27.670	0.01530
2	0.2	0.0889 5.074 10^{-5}		0.03063
3	0.3	0.1334 7.611 10^{-5}		0.04594
4	0.4	0.1779 10.147 10^{-5}		0.06125
5	0.5	0.2224 12.683 10^{-5}		0.07656
6	0.6	0.2668 15.221 10^{-5}		0.09188
7	0.7	0.3113 17.757 10^{-5}		0.10719
8	0.8	0.3558 20.294 10^{-5}		0.12250
9	0.9	0.4002 22.830 10^{-5}		0.13781
10	1	0.4447 5.368 10^{-5}		0.15313

Table 6. Calculated CR of energy line 185.7 KeV due to ^{235}U isotopes with associated uncertainties for uranyl nitrate tetrahydrate sample at different enrichment values (0.1-1 %)

Sample	Enrichment [%]	Count rate (σ_{CR}) [s^{-1}]	Mass of U [g]	Mass of ^{235}U [g]
1	0.1	0.0369 2.102 10^{-5}	25.531	0.01304
2	0.2	0.0734 4.203 10^{-5}		0.02607
3	0.3	0.1105 6.304 10^{-5}		0.03911
4	0.4	0.1474 8.406 10^{-5}		0.05215
5	0.5	0.1842 10.506 10^{-5}		0.06518
6	0.6	0.2213 12.658 10^{-5}		0.07853
7	0.7	0.2579 14.711 10^{-5}		0.09126
8	0.8	0.2948 16.811 10^{-5}		0.10429
9	0.9	0.3316 18.913 10^{-5}		0.11733
10	1	0.3685 20.012 10^{-5}		0.13037

CR increases. The same trend is also remarked in tabs. (5)-(7).

In radiation spectroscopy, it is important to produce mathematical calibration curves for radiation detectors. The validity of the proposed model is checked using sets of nuclear material standards [15]. Figures 2(a)-2(d), show the relationship between the CR and enrichment for tested NM samples. The fitting calibration curve is obtained for all the samples [16]. The CR overall uncertainty, σ_{CR} has been produced from statistical uncertainties of the activity and efficiency values calculated by MCNP code [17, 18].

The two parameters in the second part of CCC software are obtained by fitting the data between the CR and enrichment. The analyst can make use of the following flow chart to demonstrate the process used by CCC software. The process consists of five steps needed to determine the number of hydrated water molecules. It begins with preparing the sample, then scanning it using SEM then EDX analysis to determine uranium concentration and ends with calculating the CR and comparing it with that produced from the software.

Table 7. Calculated CR of energy line 185.7 KeV due to ^{235}U isotopes with associated uncertainties for uranyl nitrate hexahydrate sample at different enrichment values (0.1-1%)

Sample	Enrichment [%]	Count rate (σ_{CR}) [s^{-1}]	Mass of U [g]	Mass of ^{235}U [g]
1	0.1	0.0309 1.766 10^{-5}	23.699	0.01123
2	0.2	0.0619 3.532 10^{-5}		0.02246
3	0.3	0.0929 5.298 10^{-5}		0.03369
4	0.4	0.1239 7.065 10^{-5}		0.04493
5	0.5	0.1548 8.831 10^{-5}		0.05616
6	0.6	0.1858 10.590 10^{-5}		0.06739
7	0.7	0.2168 12.360 10^{-5}		0.07863
8	0.8	0.2477 14.130 10^{-5}		0.08986
9	0.9	0.2787 15.890 10^{-5}		0.10109
10	1	0.3088 17.610 10^{-5}		0.1120

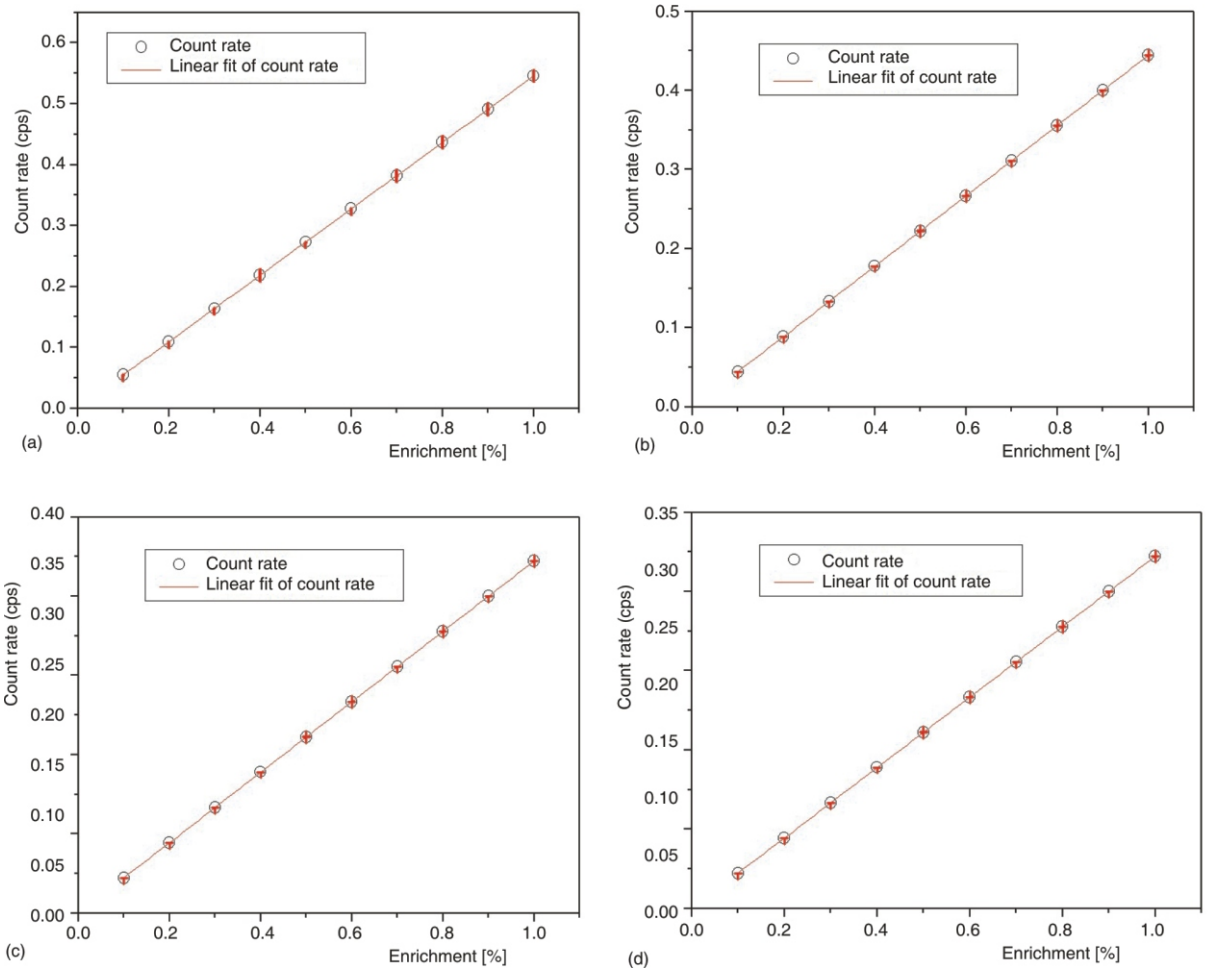

Figure 2 (a-d). The relation between CR and enrichment for uranyl nitrate sample, the dihydrate form, the tetrahydrate and the hexahydrate, respectively; cps means counts per second

CONCLUSIONS

Among safeguard assay techniques, SEM and EDX have advantages as they can quickly identify any unknown material to reveal its composition for nuclear safeguards inspections. However, it also has some limitations, particularly when qualifying elements of lower atomic numbers ($Z < 4$), as well as, they provide us with a semi-quantitative spectrum. There is no potential for elements such as hydrogen to appear as a peak in the EDX spectrum. Therefore, it is not accurate to quantify nuclear samples containing hydration water. The application for assessing concentration and count intensity is appropriate and reliable for evaluating the uranyl nitrate degree of crystallization. The proposed methodology in

this study correlates between the EDX measurements and CR calculated from MCNP-5. This correlation is accomplished using proposed uranyl nitrate samples with different enrichment values that differ in the degree of hydration. The methodology proves that it can overcome EDX limitations and can be considered an additional tool for covering all elements in the periodic table.

AUTHORS' CONTRIBUTIONS

The idea of the work was suggested by the authors during a scientific meeting of the team. Relationship building, implementation, the work of codes, writing, and revising the paper were achieved through joint and equal efforts of the three authors.

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НОВА МЕТОДОЛОГИЈА ОДРЂИВАЊА КРИСТАЛИЗАЦИЈЕ ВОДЕ ЗА УЗОРКЕ УРАНИЛ НИТРАТА ПРИМЕНОМ СКЕНИРАЈУЋЕГ ЕЛЕКТРОНСКОГ МИКРОСКОПА, ЕНЕРГЕТСКЕ ДИСПЕРЗИЈЕ Х-ЗРАЧЕЊА И MCNP5 ПРОГРАМА

Скенирајући електронски микроскоп и прикључени рендген-апарат представљају валидан алат за утврђивање присуства нуклеарних материјала у испитиваним узорцима. Ради верификације њихових структура, анализирано је десет чврстих узорака уранил нитрата са различитим вредностима обогаћења (од 0.1 % до 1 %). Коришћени узорци имају различит удео хидриране воде, те стога својства ових материјала у рачунарским и методама аналитичке хемије нису иста. Скенирајући електронски микроскоп и енергетска дисперзија Х-зрачења примењени су у овом раду како би се визуализовали и анализирали узорци хексакидрат уранил нитрата (природни 0.72 %). Узорак је скениран под оптималним условима микроскопа. Упркос поузданости ових уређаја, они ипак нису довољно тачни, нарочито када се спроводи комплетна квалитативна и квантитативна анализа. Уз помоћ Монте Карло програмског пакета (MCNP5), поступак који је приказану овом раду може решити ограничења микроскопа и тестирања Х-зрачењем. Предложена метода односи се на Монте Карло прорачуне и елементалну анализу Х-зрачењем. Веза зависи од хемијског састава материјала и развијеног програмског пакета. Програмски пакет за прорачун концентрације и броја импулса остварен је како би се одредила вода кристализације за узорке уранил нитрата.

Кључне речи: уранил нитрат, концентрација, програмски пакет MCNP5, кристализација воде