The Study on the Quantitative Analysis of the Uranium Oxides Samples using Handheld X-ray Fluorescence

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Abstract. Nuclear and other radioactive materials have been reported stolen or lose since the collapse of the Soviet Union in 1991. These materials can pose a potential threat to the general public as well as to the national infrastructure. The international community has held several meetings to determine appropriate, active responses to nuclear terrorism exploiting these materials, and has emphasized the importance of nuclear recognition as one of the primary means for nuclear security. In response to the governmental commitments, KINAC initiated a project to develop the preliminary characterization of unknown nuclear material out of regulatory control which helps to establish the national capability to make a grading of nuclear security events. This study it is investigated for the quantification possibility of Uranium oxides sample using HH-XRF as one of tools for the preliminary characterization.

KEYWORDS: Incident and Trafficking Database, Materials out of Regulatory Control, Nuclear Forensics, Handheld X-ray Fluorescence, Preliminary Characterization.

1 INTRODUCTION

According to the International Atomic Energy Agency(IAEA)'s Incident and Trafficking Database (ITDB), as of 31 December 2019, the ITDB contained a total of 3320 confirmed incidents reported by participating States since 1993. Of these 3320 confirmed incidents there are 254 incidents that involved a confirmed or likely act of trafficking or malicious use (Group Ⅰ), 828 incidents for which there is insufficient information to determine it is related to trafficking or malicious use (Group Ⅱ) and 2373 incidents that are not related to trafficking or malicious use (Group Ⅲ). These confirmed incidents can be divided by 3 type of material including Nuclear Material, Radioactive Source, Radioactively Contaminated Material. The number of incident related to Nuclear Material is 497, which corresponds to almost one of six [1].

Figure 1: Incidents reported by participating States from 1993 to 2019

(a) Categorization by Groups (b) Categorization by materials

These nuclear and other radioactive materials are defined as materials out of regulatory control (MORC) by IAEA, and regarded to pose a potential threat to the general public as well as to national security. In order to protect against these threats effectively, there have been the primary nuclear security related

international legal instruments such as the Convention on the Physical protection of Nuclear Material and its 2005 Amendment [2], the International Convention for the Suppression of Acts of Nuclear Terrorism [3], etc. In addition to these primary international instruments, IAEA has established a Nuclear Security Programme and instituted a Nuclear Security Series of publications to provide recommendations and guidance that States can use in establishing, implementing and maintaining their national nuclear security regimes. For the nuclear and other radioactive material out of regulatory control, IAEA nuclear security series No.15 were published for recommendations [4]. Especially, this recommendations suggest the State should adopt a graded approach to respond to the various possible nuclear security events and differing degrees of consequences and strive to develop its own national capability to quickly grade nuclear security events in the potential crime scene based on the involved nuclear or other radioactive material.

International community has successively held the nuclear security summits(NSSs) from 2010 to 2016 [5], in order to establish appropriate and active responses globally against nuclear terrorism exploiting these MORCs. Furthermore, it had emphasized the importance of nuclear forensics and illicit trafficking as one of primary means for nuclear security. After finishing the NSS at Hague, joint statement on countering nuclear smuggling and forensics in nuclear security was published. These joint statements were transferred to the IAEA Secretariat, then the Secretariat was circulated for the information of all IAEA member States as INFCIRC/917 and INFCIRC/918.

In response to the government commitments, Korea Institute of Nuclear Non-proliferation and Control (KINAC) had completed a R&D project to assess the current status of national nuclear forensics capability and identify the gap between the recommendations and current status [6]. As a following research, KINAC initiated another project to develop the preliminary characterization of unknown nuclear material out of regulatory control. It helps for the government to establish the national capability to make a grading of the nuclear security events.

Though several physical, chemical, elemental and radiological measurement devices can be utilized as a combination of methods and techniques for the preliminary characterization [7-8]. This study is focus to use the Handheld X-Ray fluorescence (HH-XRF) device for the elemental characteristic measurement. The reason why HH-XRF was selected for this study, while the XRF technique has been proposed for use in nuclear security in cases encountered out of regulatory control, most of applications focus on the desktop type in the laboratory which cannot utilize properly in time for grading the nuclear security events. Therefore, the handheld type of XRF devices with their mobility and convenience to use in field can be an alternative [9]. So, this paper describes about the feasibility study for HH-XRF application to the preliminary characterization.

2 MATERIALS AND METHODS

2.1 Measurements of Uranium Pellets with HH-XRF

The samples used in this study was the sintered Uranium dioxides (UO_2) pellets manufactured by Korea Electric Power Corporation Nuclear Fuel (KEPCO NF). KEPCO NF performs nuclear fuel fabrication as well as reactor core design as a representative public energy company. The material of interest, cylinder pellet, is the major chemical form conventionally used in the commercial nuclear fuel cycle, constituting the fuel rods in most nuclear power plants. The specification of the sample has 8.2 mm diameter and 9.8 mm height, 10.5 g/cm^3 density and 87.9 wt.% of Uranium content.

A Bruker S1-Titan 600 handheld XRF analyser (Bruker, Billerica, MA, USA) was used for the experimental measurements. It consists of a fast silicon drift detector (SDD), an ultra-lean window, and an end window transmission type X-ray tube with the following specifications: maximum accelerating voltage 50 kV, 2 W, and rhodium (Rh) target. In this study, the spectrometer mode without any calibration was used, as shown in Figure 2, to achieve controlled measurement geometry.

Figure 2: Instruments for experimental measurements


A number of parameters can influence the beam profile irradiated into samples from the X-ray tube and resulting energy spectrum measured by the SDD. These parameters include accelerating electron voltage, current, measured time, and applied filters. The voltage and filters directly influence the incident X-ray beam in both energy distribution and intensity, while current and measuring time are proportional to the intensity at each energy interval.

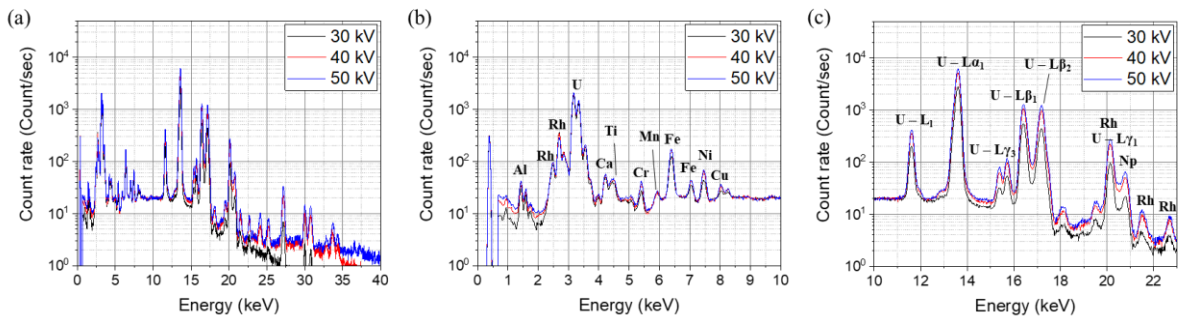
This study selected the no filter option, and accelerating electron voltages were set at three stages, while current and operating time were fixed at 35 μA and 60 sec in the real-time. Table 1 lists the parameter values and experimental settings.

Table 1: Experimental Parameters of Voltage, Current, Input Count Rate and Live Time by Sample

Voltage (kV)	Current (uA)	Input Count Rates (#/sec)	Live time (sec)
30	35	86,414	40.56
40	35	134,050	31.92
50	35	154,506	28.38

Figure 3 shows the measurement spectra of the UO_2 pellets at voltages of 30, 40, and 50 kV. Here, U $L\alpha_1$ and U $L\alpha_2$ lines (13.614, 13.438 keV) and U $L\beta_1$ and U $L\beta_2$ lines (17.220, 16.428 keV) by fluorescent X-rays were mainly produced. In addition, the peaks at 3.1 and 3.3 keV are determined as M lines of Uranium. Rayleigh and Compton peaks from Rh K and L lines as well as spectral artifacts under 10 keV are not apparent in the whole spectrum due to the relatively high intensities of Uranium's fluorescent X-rays.

Figure 3: Measured Energy Spectra from the UO_2 Sample



2.2 Evaluation on the Quantification of the Impurities in the Uranium Oxides

2.2.1 Composition of Uranium Oxides Certified Reference Materials

The samples used in this study are Certified Reference Material-123 (CRM-123) which were produced by New Brunswick Laboratory in United States. This CRM is an impurity standard intended for used in determining the non-volatile impurity content of Uranium fuel materials. Each unit of CRM 123(1-7) consists of six bottles containing normal Uranium oxide-U_3O_8 as matrix material, approximately 25 grams per bottle, to which eighteen selected elements have been added in varying concentrations. A seventh bottle, completing the unit, consists of matrix material alone.

Figure 4: Six Bottles for the CRM-123 (1-7)

Table 2: Certificate of Analysis for the CRM-123 (1-7)

	123-1	123-2	123-3	123-4	123-5	123-6	123-7
Element	Micrograms of Impurity Element per gram of Uranium (as metal)						
Al	205.1	98.4	49.1	21.6	11.1	5.6	<2
Ca	218	107	52.2	24.1	12.6	7.9	4.1
Fe	212.2	109.7	58.5	27.2	17.5	12.2	7.9
Ni	200	100.1	52.1	21.3	11.3	6.3	2
Si	245	120.2	56.5	24.2	14.8	10.9	8
Na	390.9	174	79.5	42.4	24.2	14.5	4
Zn	222	112	52.7	20.4	11.7	6.1	0.3
Zr	256	134	60	20	13	<10	<10
Cr	105.9	54.9	23.1	12.9	7.6	4.3	2.3
Mg	102.3	50.8	20.3	11.1	5.5	2.9	1.8
Mo	97.7	48.9	20.6	10.1	5	2.3	0
Cu	52.8	25.6	10.8	5.9	2.6	1.17	0.2
Pb	43.9	22.8	9.5	4.9	2.8	1.3	0.4
Mn	51.9	27.4	11.8	5.6	3.1	1.2	0.27
Sn	48	23.7	9.5	5.9	2.8	1.3	0.2
V	50.5	25	9.4	4.9	2.7	1	0.2
B	6	2.3	1.07	0.51	0.28	0.11	<0.07
Cd	5.3	2.4	1.1	0.48	0.28	0.12	<0.02

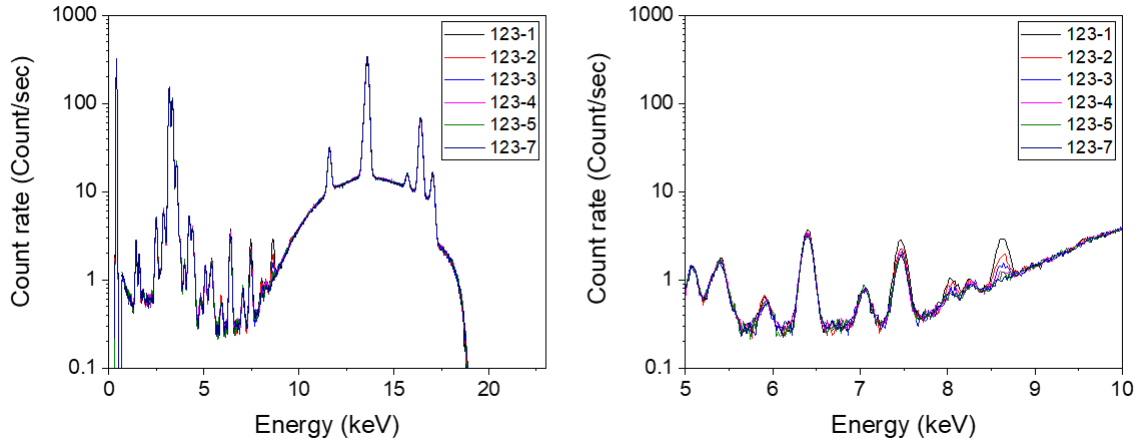
2.2.2 Measured spectrum

The samples were divided into 5 grams each from the entire CRM-123 bottles for measuring using HH-XRF, then the moved to the XRF sample cup and sealed by thin film.

Figure 5: Measured energy spectra from CRM-123(1-7)

These samples were measured with 19 kV accelerating electron voltages, 80 micro Ampere of current and no filter option. The results are described in Figure 6.

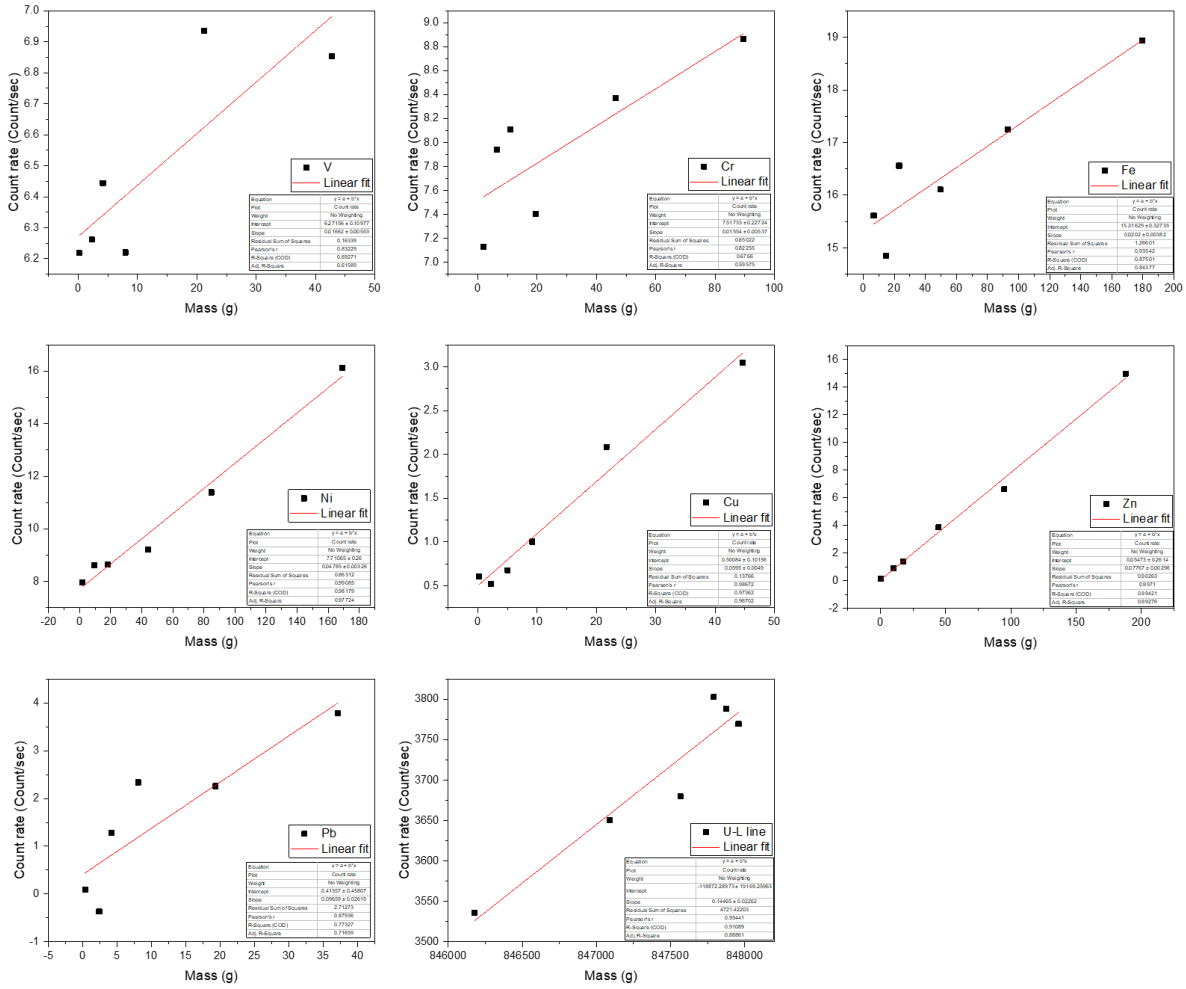
Figure 6: Measured energy spectra from CRM-123(1-7)



2.2.3 Evaluation on the linearity for Quantification

The linearity between each element's mass included in the CRMs and the corresponding fluorescence intensities are compared, and linear regression analysis was conducted with figure 6. As a result of this, seven elements (V, Cr, Fe, Ni, Cu, Zn, Pb) showed to have enough linearity for the calibration of content. In addition, Uranium element also determined that it has 0.91 for the determination of coefficient, it means to have enough linearity for the calibration of content.

Figure 6: Linear regression analysis for the major and trace element of the sample



2.3 Limit of Detections

Limit of detection (LOD) for the seven impurities were calculated using the equation (1). It was assumed that CRM 123-7 which has lowest concentrations was a blank sample, and the results are shown as Table 3.

$$LOD = 3.3 \times \frac{\sigma \text{ of blank sample}}{\text{Slope}} \quad (1)$$

Table 3: Limit of Detection for the 7 Elements to have the linearity

	V	Cr	Fe	Ni	Cu	Zn	Pb
LOD (ppm)	30.17	34.62	39.35	11.76	6.58	11.65	30.13

In case of Nickel and Zinc, their LOD represented to have lower concentrations than CRM 123-4. Iron and Copper are represented to have lower concentrations than CRM 123-3. Since these LOD represent very low concentrations which can be utilized for impurities of the high purity Uranium oxides powder except for Vanadium, it is determined that those LOD can be used for quantification of nuclear material

in the process of fuel fabrication plant. While it can be able to quantify for high concentration of Uranium with high linearity and sensitivity, but additional experiments should be in place for low concentration of Uranium.

3 CONCLUSION

This paper investigated whether Uranium oxides samples can be quantified using HH-XRF. First of all, the pellets, made of sintered Uranium dioxides powder, were measured by HH-XRF. Uranium's fluorescent X-rays were clearly observed in the spectrum. Secondly, Uranium Oxides CRM-123(1-7) were prepared and measured by HH-XRF. The results showed that there are 7 elements to have linearity and it can be used for the quantification of impurities in the normal Uranium oxide-U_3O_8 as matrix material. Using these experimental data, LOD for the 7 elements were calculated. In addition, Uranium elements also showed that there is linearity in the high concentration. However, it is determined that it needs to have additional experiments for the low concentration.

4 ACKNOWLEDGEMENTS

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