



# Uranium enrichment measurements using the intensity ratios of self-fluorescence X-rays to 92<sup>\*</sup> keV gamma ray in UXK<sub>α</sub> spectral region

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## ABSTRACT

In this paper, the known multigroup γ-ray analysis method for uranium (MGAU) as one of the non-destructive γ-ray spectrometry methods has been applied to certified reference nuclear materials (depleted, natural and enriched uranium) containing <sup>235</sup>U isotope in the range of 0.32–4.51% atom <sup>235</sup>U. Its analysis gives incorrect results for the low component <sup>235</sup>U in depleted and natural uranium samples where the build-up of the decay products begins to interfere with the analysis. The results reveal that the build-up of decay products seems to be significant and thus the algorithms for the presence of decay products should be improved to resulting in the correct enrichment value. For instance, for the case of <sup>235</sup>U analysis in depleted uranium or natural ore samples, self-induced X-rays such as 94.6 keV and 98.4 keV lying in UXK<sub>α</sub> spectral region used by MGAU can be excluded from the calculation. Because the significant increases have been observed in the intensities of uranium self-induced X-rays due to γ-ray emissions with above 100 keV energy arising from decay products of <sup>238</sup>U and <sup>235</sup>U and these parents. Instead, the use of calibration curve to be made between the intensity ratios of self-fluorescence X-rays to 92<sup>\*</sup> keV γ-ray and the certified <sup>235</sup>U abundances is suggested for the determination of <sup>235</sup>U when higher amounts of decay products are detected in the γ-ray spectrum acquired for the MGAU analysis.

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## 1. Introduction

The determination of uranium enrichment in samples is a key measurement for product and process control in enrichment and fuel fabrication plants, technological process measurements, waste characterization, tracking of nuclear materials issued in illicit trafficking, and homeland security activities against terrorist threats and attacks, and it is also very important in internationally nuclear safeguards inspections to verify that uranium stock is being used for peaceful purposes. To carry out these inspections, the authorities are looking for rapid and more easy methods. These inspections must, of course, be, as far as possible, non-destructive, which favors γ-ray spectrometry over other methods like mass spectrometry. Moreover, it is desirable to get the accurate information in a short time of period without destroying the material in many nuclear applications [1]. Therefore, this aim requires a non-destructive detection and measurement technique such as γ-ray spectrometry. This technique also allows analysts or first responders in situ to measure, identify and find the location of the radiation sources and

radioactive materials. Among the different methods developed in the γ-ray spectrometry, the most widely employed and oldest one is that “uranium enrichment meter” principle which makes use of the 185.7 keV (57.7%) of <sup>235</sup>U full energy peak recorded either with NaI scintillation detector or with HPGe detectors [2–3]. This principle requires calibration of instrumentation with use of reference standard materials having at least two different enrichments by fixing the measurement conditions, and provided that the measured sample is identical to the standard materials [4]. Hence in routine field measurements the necessary calibrations are not always appropriate because of changes in geometry or container wall thickness. Therefore, the determination of relative abundances of uranium isotopes has recently been widely performed by γ-ray spectrometry utilizing either a set of uranium isotopic reference materials (SRMs) or a calibrated γ-ray detector using a set of radionuclide standards, or intrinsically calibrated Ge detector without use of any standards [5–8]. To overcome these difficulties and avoid the use of external standards, other methods based on self-calibration have been proposed [9]. More particularly X- and γ-ray spectrometry have been developed or are in progress for uranium enrichment measurements [10]. Especially, the introduction of MGAU method for non-destructive analysis of <sup>235</sup>U isotope characterization in depleted, natural or enriched uranium materials demonstrated the usefulness of intrinsically calibrated measurements for safeguards inspections. Additionally, MGAU method provides a very rapid

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assay (30–60 min in routine basis) results for isotopic abundances when used a suitable planar/coaxial Ge or a CdZnTe semiconductor detector. Because it is more practical to determine from the same spectrum both isotopic ratios and abundances of U and/or Pu bearing samples by using a portable multichannel analyzer (MCA) system equipped with a special high resolution Low Energy Ge (e.g., Canberra LEGe) detector or Safeguards Coaxial Ge detector (e.g., Ortec SGD-GEM). Such systems can give the analysts more accurate results from the lower part of a  $\gamma$ -ray spectrum (below 300 keV) utilizing multigroup analysis methodology (MGA) for determining U or Pu isotopic abundances. MGAU method was first formulated and established in 1994 [11], and since that time, a number of MGAU commercial program versions were released (V.1.0, V.2.2, 3.0, V.4.0) or as a MGA++ code suite and it has found a wide application in numerous fields as mentioned above. It is reported that MGAU method can be used to determine uranium enrichments of depleted to several tens of percent  $^{235}\text{U}$  atoms in samples, with both accuracies and precisions of 1–2% [7]. After testing the performance of MGAU method in different measurement conditions and with reference uranium samples having different physical and chemical forms, isotopic conditions, the adequacy of MGAU method was confirmed, however, the tests revealed also a number of major and minor deficiencies described in detail [12]. At the same time, the applicability of MGA method for depleted and natural uranium isotopic analysis in presence of some actinides in the samples was investigated, and it has been pointed out the remarkable contributions from the actinides to the uranium analytical peaks, thus leading to erroneous results being 6–25 times higher than their declared abundances for uranium isotopic analysis [13].

Since self-induced fluorescence X-rays such as 94.6 keV  $\text{UK}\alpha_2$  and 98.4 keV  $\text{UK}\alpha_1$  are used in URADOS and MGAU methods for the determination of uranium enrichment values, it is required to take into account the treatment of a very limited and complex  $\text{UXK}\alpha$  region [7,9,11]. Therefore, the aim of the present study is to investigate the effect of changes in the intensity ratios of self-induced fluorescence X-rays lying in  $\text{UXK}\alpha$  spectral region on uranium enrichment results obtained by MGAU. As pointed out in Ref. [7], a relation can be established between the known certified  $^{235}\text{U}$  enrichment values and both the intensity ratios of 94.6 keV  $\text{UK}\alpha_2$  fluorescence X-ray to the 92\* keV  $\gamma$ -ray and of the 98.4 keV  $\text{UK}\alpha_1$  fluorescence X-ray to the 92\* keV  $\gamma$ -ray from decay product  $^{234}\text{Th}$  of  $^{238}\text{U}$  parent, where the symbol (\*) denotes almost a real doublet (92.38 + 92.80 keV) peak with an average energy of  $\sim 92.6$  keV. To do this, a spectrum de-convolution process of the superimposed peaks lying in the  $\text{UXK}\alpha$  region is treated delicately by non-linear least squares fitting method employing a Gaussian function for  $\gamma$ -ray peaks and a pseudo-Voigt function for X-ray peaks.

## 2. Experimental

### 2.1. Materials and equipment

In this study, five uranium reference materials SRM series 969 consisting of nominal abundances of 0.32%, 0.72%, 1.96%, 2.98% and 4.51% atom  $^{235}\text{U}$ , and additionally two certified natural uranium ore materials containing 7.09 wt% uranium (BL-5) and 75.42 wt% uranium (CUP-2) with nominal  $^{235}\text{U}$  abundances of 0.72% atom  $^{235}\text{U}$  were used, as given in Table 1. Each of the SRM 969 samples contained 200.1  $\pm$  0.2 g of  $\text{U}_3\text{O}_8$  powder (density: 2.5 g  $\text{cm}^{-3}$ ) encased in Al cylinder containers with internal dimensions of 70 mm diameter  $\times$  20.8 mm height. The powdered-natural ore materials of 100  $\pm$  0.1 g for BL-5 and 25  $\pm$  0.1 g for CUP-2 were filled in plastic bottles (40 mm diameter) with a 1.5 mm thickness. Then, they were sealed tightly to ensure radioactive equilibrium attain between  $^{238}\text{U}$  and its decay products.

A portable  $\gamma$ -ray spectrometry (Canberra U-Pu Inspector 2000), based on digital signal processing MCA analyzer with a LEGe detector (Canberra GL0515R) was used. The detector has a planar Ge crystal with a 500  $\text{mm}^2$  active surface and a 15 mm thickness and its Al window is 0.5 mm in thickness. The detector has a measured resolution of 597 eV at 122 keV ( $^{57}\text{Co}$ ). It was calibrated to collect 4096 channel spectra with a gain of 0.07521 keV/channel, thus covering up to 308 keV energy. The data acquisition was carried out a commercially available gamma spectroscopy software (Canberra Genie 2000) and then analyzed with a MGAU software for uranium isotopic analysis. The measurements were performed with and without use of a 5 cm thick Pb shield against background radiations, especially for the reduction of  $\gamma$ -rays with low energies below 300 keV. In order to ensure good shapes of full energy peaks and to minimize peak count losses due to true coincidence summing effects, the measurements were performed at a distance of at least 10 cm between sample and detector window. The system dead time over all measurements were kept below 2.5% to avoid random coincidence corrections. The measurement periods were chosen as 10 min, 1 h, 14 h and 24 h to get better counting statistics of the  $\gamma$ -ray spectrum counts.

### 2.2. Multigroup $\gamma$ -ray analysis method

The multigroup  $\gamma$ -ray analysis method for uranium (MGAU) employs generally X- and  $\gamma$ -rays in the 80–130 keV region of a  $\gamma$ -ray spectrum taken from uranium without use of radionuclide standard sources or nuclear material standards. The descriptions of peak shapes, efficiencies, geometry, absorbing material effect and background subtraction considerations of the MGA methodology is described in detail [6,8]. In the principle of the MGA method, normalized “response functions” are constructed for each individual isotope based on available a priori information about energies and intensities of their X- and  $\gamma$ -rays. The method for the determination of the isotopic ratio is to measure basically the intensity of two or more peaks from  $\gamma$ -rays of similar energy (nearest energies) but arising from different isotopes. Since the  $\gamma$ -ray emission probabilities and half-lives of the isotopes are known, the isotopic ratios of two different atoms can be calculated if relative detection efficiencies for the peaks of interest can be estimated by the following relation:

$$\frac{N_1}{N_2} = \frac{I_1(E_1^i)\lambda_2 P_{\gamma_2}^j(E_2^j)\varepsilon_2(E_2^j)T_2(E_2^j)\Delta\Omega_2(E_2^j)}{I_2(E_2^j)\lambda_1 P_{\gamma_1}^i(E_1^i)\varepsilon_1(E_1^i)T_1(E_1^i)\Delta\Omega_1(E_1^i)} \quad (1)$$

where  $I_1$  and  $I_2$ : the measured peak intensity of isotope one and two (in cps),  $\lambda_1$  and  $\lambda_2$ : decay constant of isotope one and two (=0.693/half-life, in  $\text{s}^{-1}$ ),  $N_1$  and  $N_2$ : the number atoms of isotope one and two,  $P_{\gamma_1}$ : emission probability of  $\gamma$ -ray  $i$  from isotope one and  $P_{\gamma_2}$ : emission probability of  $\gamma$ -ray  $j$  from isotope two,  $\varepsilon_1$ : relative counting efficiency for  $\gamma$ -ray peak  $i$  with the energy  $E_1^i$  of isotope one,  $\varepsilon_2$ : relative counting efficiency for the  $\gamma$ -ray peak  $j$  with the energy  $E_2^j$  of isotope two,  $T_1$  and  $T_2$ :  $\gamma$ -rays  $i$  and  $j$  transmission factor to the detector,  $\Delta\Omega_1$  and  $\Delta\Omega_2$ : fractional solid angle of the detector [(1/4 $\pi$ ) $\Omega$ , solid angle in steradians], in which the symbols represent the isotope one as subscript (1) and the isotope two as subscript (2), respectively. Since the counting geometry or the counting efficiency is not reproducible, and the  $\gamma$ -ray attenuation by sample matrix effect or other absorbing materials such as container materials is not known for various samples, the MGA method provides a great advantage as a *standardless* analysis over other laborious spectroscopic methods. Because it practically makes use of the efficiency ratios that remove the need for reproducible geometry. Thus this property makes this method applicable to the samples in any arbitrary size, shape and composition. In order to obtain the isotopic ratio from Eq. (1), the MGA software uses

**Table 1**  
Certified isotopic compositions of standard reference materials.

Reference sample code <sup>a,b,c</sup>	Uranium amount (wt%)	Isotopic composition			
		atom%		mass%	
		<sup>235</sup> U/U	<sup>238</sup> U/U	<sup>235</sup> U/U	<sup>238</sup> U/U
SRM969-031	84.5 ± 0.3	0.3206 ± 0.0002	99.6627 ± 0.0004	0.3166 ± 0.0002	99.6668 ± 0.0004
BL-5	7.09 ± 0.03	0.7209 ± 0.0006	99.2738 ± 0.0010	0.7119 ± 0.0006 <sup>d</sup>	99.2828 ± 0.0010 <sup>d</sup>
CUP-2	75.42 ± 0.17	0.7209 ± 0.0006	99.2738 ± 0.0010	0.7119 ± 0.0006 <sup>d</sup>	99.2828 ± 0.0010 <sup>d</sup>
SRM969-071	84.5 ± 0.3	0.7209 ± 0.0005	99.2738 ± 0.0002	0.7119 ± 0.0005	99.2828 ± 0.0002
SRM969-194	84.5 ± 0.3	1.9664 ± 0.0014	98.0159 ± 0.0009	1.9420 ± 0.0014	98.0406 ± 0.0009
SRM969-295	84.5 ± 0.3	2.9857 ± 0.0021	96.9826 ± 0.0015	2.9492 ± 0.0021	97.0196 ± 0.0015
SRM969-446	84.5 ± 0.3	4.5168 ± 0.0032	95.4398 ± 0.0016	4.4623 ± 0.0032	95.4950 ± 0.0016

<sup>a</sup> Canadian Certified Reference Materials (CRM) were obtained from CANMET-Mining and Mineral Sciences, Canada.

<sup>b</sup> Standard Reference Materials (SRM 969) were obtained from New Brunswick Laboratory, Argonne, USA. The abundances <sup>234</sup>U/U and <sup>236</sup>U/U in SRM 969 are not given in this table since they are out of the scope of this study.

<sup>c</sup> The uncertainties quoted here are at 95% confidence level.

<sup>d</sup> The percentage values in mass were calculated approximately by multiplying a factor from the isotope content in atom% × (235/238).

the local intragroup relative efficiencies that can be determined by delineating intergroup efficiency known as intrinsic efficiency curve, which is determined by fitting observed peak intensities (divided by  $\gamma$ -ray emission probability) to a function in the form:  $\varepsilon(E_k^m) \propto I(E_k^m)/P_{\gamma,k}^m(E_k^m)$ , where  $m$  corresponds to the  $\gamma$ -ray  $i$  or the  $\gamma$ -ray  $j$ , and  $k=1, 2$  corresponds to isotope one (<sup>235</sup>U) and isotope two (<sup>238</sup>U), if the isotope <sup>234</sup>U with very low content is ignored for the simplicity. The X- and  $\gamma$ -ray peaks are very close in energy, e.g., in the 80–100 keV and 100–120 keV energy regions. Additionally, when the energies are nearly equal, the efficiency and  $\gamma$ -ray transmission or attenuation differences are also small. Therefore, a special iterative procedure in MGA method to separate contributions of <sup>235</sup>U and <sup>238</sup>U to the spectrum region of interest. In general,

the MGA method is greatly simplified by considering the following observations: (a) if two  $\gamma$ -rays energies in the same spectrum are close, then  $[\varepsilon_2 T_2]/[\varepsilon_1 T_1] \cong 1$ , (b) the fractional solid angle of detector is the same for both  $\gamma$ -rays originated from the isotopes,  $\Delta\Omega_1 = \Delta\Omega_2$ . Then, if the measured peak intensities can be determined extremely accurately, the isotopic ratio expressed in Eq. (1) can be obtained more precisely [14]. However, it is worth noting that the calculation methods for U and Pu isotopic analysis used in commercially available MGA codes differ from each other in at least some ways, e.g. (i) the technique for delineating the “intrinsic” efficiency curve and (ii) the use of most intense peaks in a  $\gamma$ -ray spectrum depending on U or Pu analysis procedures. For example, while the MGA software for Pu isotopic analysis uses the  $\gamma$ - and X-rays below 210 keV, the MGAU software for U isotopic analysis

**Table 2**  
The results for <sup>235</sup>U and <sup>238</sup>U abundances in depleted, natural and enriched uranium samples obtained by MGAU method.

Reference sample code	Sample type	Counting time	Isotopic abundance <sup>a</sup>			
			Isotope <sup>235</sup> U		Isotope <sup>238</sup> U	
			MGAU measured ± unc. (%)	(%) [relative difference] <sup>b</sup>	MGAU measured ± unc. (%)	(%) [relative difference] <sup>b</sup>
SRM969-031	Depleted uranium	10 min	0.379 ± 0.153	18.22	99.618 ± 0.154	−0.04
		1 h	0.267 ± 0.069	−16.72	99.733 ± 0.070	0.07
		14 h	0.314 ± 0.018	−2.06	99.684 ± 0.018	0.02
		24 h	0.326 ± 0.014	1.68	99.672 ± 0.014	0.01
BL-5	Depleted uranium	10 min	0.942 ± 0.114	31.08	99.132 ± 0.133	−0.14
		1 h	0.921 ± 0.029	27.76	99.070 ± 0.030	−0.21
		14 h	0.912 ± 0.009	26.51	99.088 ± 0.095	−0.19
		24 h	0.911 ± 0.007	26.46	99.084 ± 0.072	−0.19
CUP-2	Natural uranium	10 min	0.770 ± 0.052	6.81	99.226 ± 0.052	−0.05
		1 h	0.751 ± 0.012	4.18	99.242 ± 0.013	−0.03
		14 h	0.752 ± 0.004	4.31	99.244 ± 0.004	−0.03
		24 h	0.762 ± 0.003	5.70	99.234 ± 0.003	−0.04
SRM969-071	Natural uranium	10 min	0.821 ± 0.124	13.89	99.179 ± 0.125	−0.10
		1 h	0.741 ± 0.051	2.79	99.252 ± 0.052	−0.02
		14 h	0.724 ± 0.015	0.43	99.272 ± 0.015	0.00
		24 h	0.707 ± 0.012	−1.93	99.289 ± 0.012	0.02
SRM969-194	Natural uranium	10 min	1.956 ± 0.116	−0.53	98.031 ± 0.118	0.02
		1 h	1.967 ± 0.048	0.03	98.021 ± 0.049	0.01
		14 h	1.954 ± 0.017	−0.63	98.032 ± 0.017	0.02
		24 h	1.961 ± 0.015	−0.27	98.026 ± 0.015	0.01
SRM969-295	Enriched uranium	10 min	2.779 ± 0.129	−6.92	97.195 ± 0.131	0.22
		1 h	2.950 ± 0.056	−1.20	97.031 ± 0.057	0.05
		14 h	2.980 ± 0.023	−0.19	96.999 ± 0.023	0.02
		24 h	2.983 ± 0.020	−0.09	96.996 ± 0.021	0.01
SRM969-446	Enriched uranium	10 min	4.473 ± 0.158	−0.97	95.506 ± 0.160	0.07
		1 h	4.431 ± 0.068	−1.90	95.540 ± 0.069	0.10
		14 h	4.468 ± 0.031	−1.08	95.507 ± 0.031	0.07
		24 h	4.507 ± 0.029	−0.22	95.466 ± 0.029	0.03

unc.: uncertainties are based on  $\pm 1\sigma$  confidence interval.

<sup>a</sup> The certified abundances for <sup>235</sup>U and <sup>238</sup>U are given in Table 1.

<sup>b</sup> The percentage relative bias (relative difference %) =  $100 \times (\text{measured}_{\text{MGAU}} - \text{certified})/\text{certified}$ .

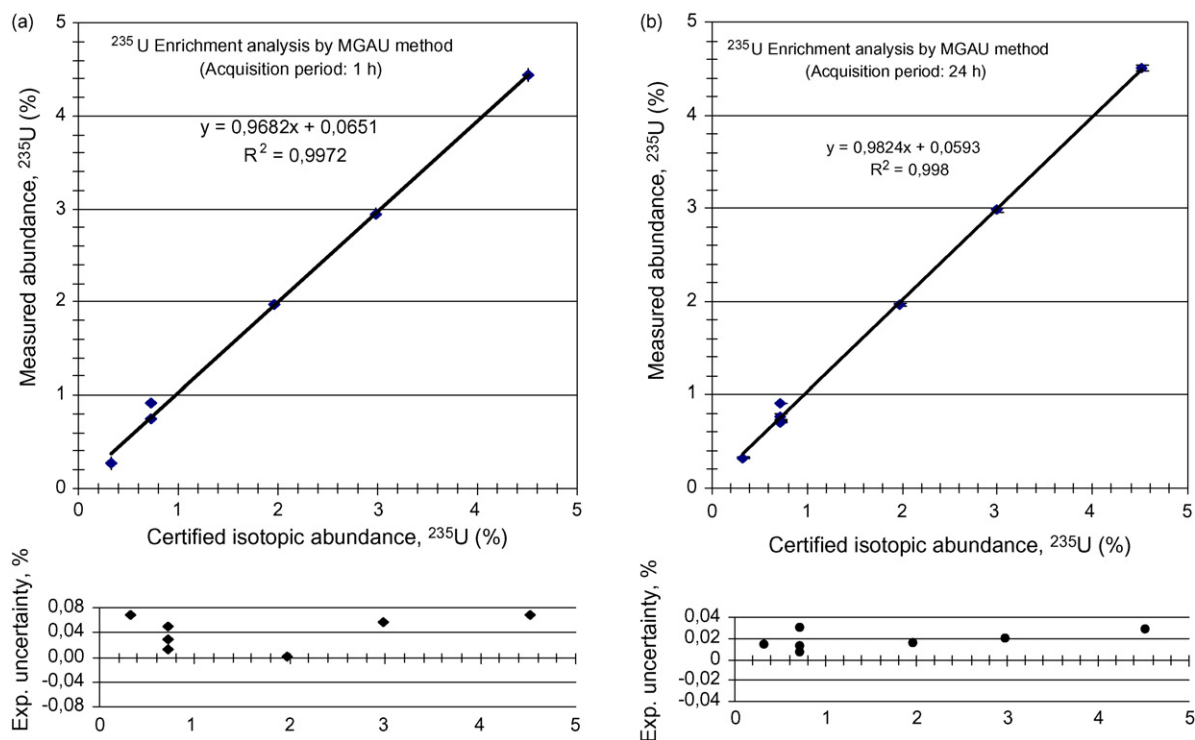


Fig. 1. Results for  $^{235}\text{U}$  abundance analysis by MGAU for certified uranium materials. (a) for 1 h counting period, (b) for 24 h counting period.

uses the energy region of 80–130 keV in the “intrinsic calibration” method.

### 3. Results and discussion

The results for  $^{238}\text{U}$  abundances in certified samples of depleted, natural and enriched uranium are given in Table 2, together with percentage relative biases from the certified values. The results for  $^{238}\text{U}$  abundance in the samples determined by MGAU are within uncertainty limits for a confidence interval of  $\pm 1\sigma$ . It has not been observed any remarkable difference between measured and certified isotopic abundance of  $^{238}\text{U}$ . That is, the measured abundances of  $^{238}\text{U}$  in all uranium samples are within 0.01–0.22% of those certified values and their precisions are also very high.

The results for  $^{235}\text{U}$  abundance obtained by MGAU are also given in Table 2. If the longer measurement period, say, more than 1 h up to 24 h employs for the data acquisition, it is evident that the measured abundances of  $^{235}\text{U}$  agree well only within 5% of the certified ones, except for depleted and natural uranium samples. When this measurement period compared to acceptable routinely safeguard verification analysis period of 30 min to 1 h employs, it is quite longer and the measured abundances of  $^{235}\text{U}$  in depleted and natural uranium are still inconsistent with those certified values. However, the experimental uncertainties in the determination of  $^{235}\text{U}$  are very low in which they are generally within the range of  $\pm(0.04\text{--}0.08\%)$  of the measured abundances in the certified materials ranging from 0.72% to 4.51% atom  $^{235}\text{U}$ , shown in Fig. 1(a) and (b) for the examples of 1 h and 24 h measurement periods, respectively. This indicates that the sufficient counting statistics for the uranium  $\gamma$ -ray spectra is accomplished for a measurement time being longer than 1 h.

On the other hand, the percentage relative biases between the measured and certified values of  $^{235}\text{U}$  isotope for enriched uranium materials remained below 2% of their certified values, thus MGAU method shows a good performance for enriched uranium materials

with higher measured precisions. In contrary, it is clearly seen in the examples in Fig. 2(a) and (b) that the percentage relative biases for the  $^{235}\text{U}$  contained in both depleted and natural uranium materials are higher than their certified isotopic abundances by 26.46% even if a relatively long measurement period, e.g., 24 h is chosen for testing.

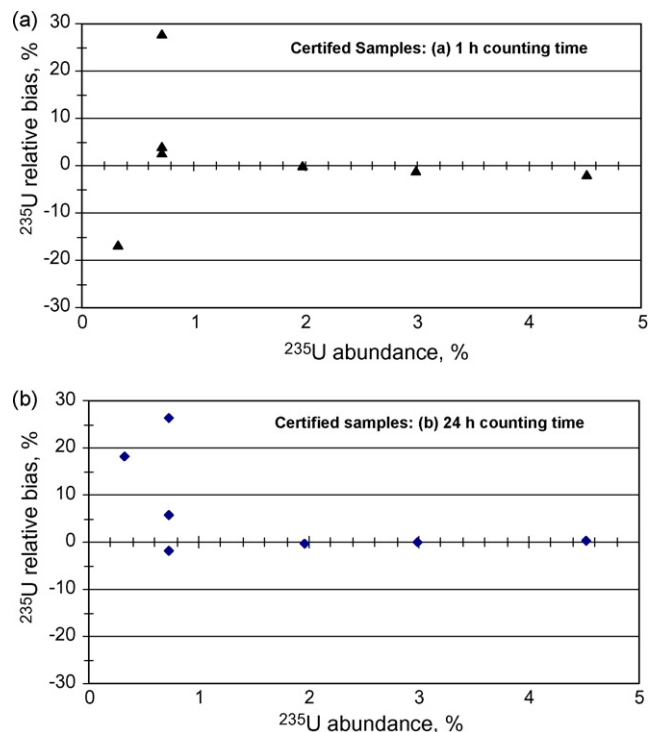


Fig. 2. Percentage relative biases on the determination of  $^{235}\text{U}$  in certified uranium materials containing from 0.32% to 4.51% atom  $^{235}\text{U}$ .

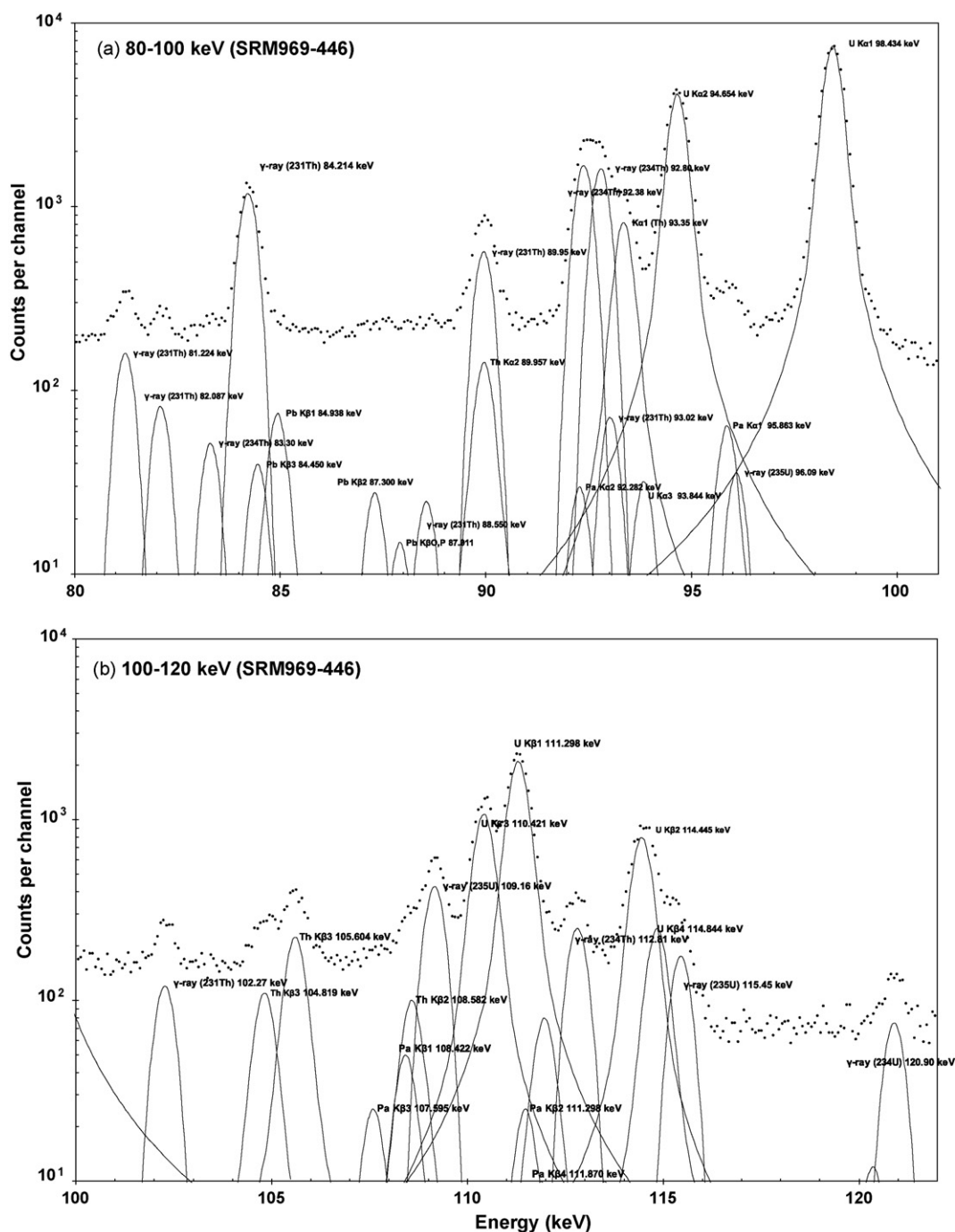


Fig. 3. (a and b) A typical fitting of the X- and  $\gamma$ -ray peaks in UXK $_{\alpha}$  and UXK $_{\beta}$  region of enriched uranium spectrum.

This limitation for depleted and natural uranium is mainly due to the low  $^{235}\text{U}$  component, in relation to those of  $^{238}\text{U}$  and uranium self-induced X-ray fluorescence, in the analyzed spectrum [15]. Particularly, the results obtained from depleted and natural uranium imply that the self-fluorescence X-ray peaks lying in spectral regions of UXK $_{\alpha}$  and UXK $_{\beta}$  of an uranium spectrum analyzed by MGAU can seriously be affected due to the contributions of emissions with the energy of above 100 keV from decay products of  $^{235}\text{U}$  and  $^{238}\text{U}$ . To demonstrate this, the increases in the intensities of self-induced X-rays such as 94.6 keV (28.3%) and 98.4 keV (45.8%) of uranium have been determined. For this, a non-linear least squares fitting procedure has been applied to fit the observed counts in the 80–100 keV UXK $_{\alpha}$  region shown in Fig. 3(a) and those

in the 100–120 keV UXK $_{\beta}$  region shown in Fig. 3(b) of the measured uranium  $\gamma$ -ray spectrum by adjusting the fit parameters.

As previously described in Ref. [13], the measured data were used to describe the peak line shapes in the de-convolution treatment of the X-rays and  $\gamma$ -ray peaks in the energy regions chosen in each spectrum, with a Gaussian function,  $G(E)$  for  $\gamma$ -ray peak and a pseudo-Voigt function for X-rays,  $V_p(E)$  consisting of an overall function, which is a weighted sum of Gaussian function,  $G(E)$  and Lorentzian function,  $L(E)$ . Then, a linear background  $B(E)$  function was added to both them as follows:

$$V_p = kG(E) + (1 - k)L(E) + B(E) \quad (2)$$

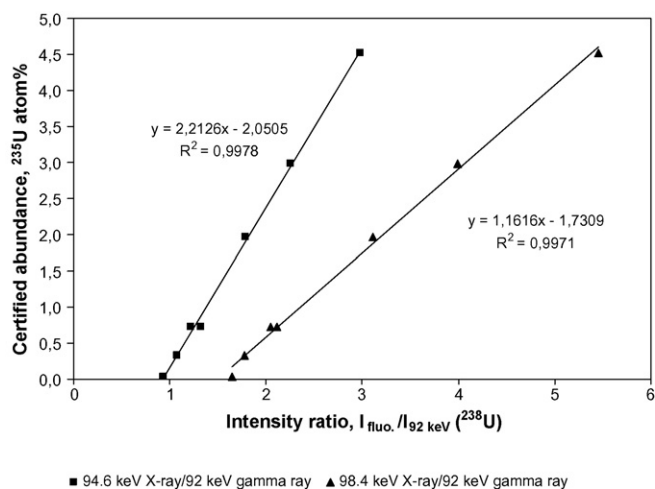


Fig. 4. Intensity ratios of the 94.6 keV X-ray to  $92^+$  keV  $\gamma$ -ray and the 98.4 keV X-ray to  $92^+$  keV  $\gamma$ -ray plotted versus certified  $^{235}\text{U}$  abundance.

where  $k$  is a weighting factor, taken as 0.57 in a pseudo-Voigt function [16,17]. The same full-width at half maximum,  $\sigma = \text{FWHM}$  is chosen for both  $G(E)$  and  $L(E)$  functions:

$$G(E) = I_{\max} \left[ -\ln 2 \left( \frac{E - E_0}{\sigma/2} \right)^2 \right] \quad (3)$$

$$L(E) = \frac{I_{\max}}{1 + [(E - E_0)/(\sigma/2)]^2} \quad (4)$$

where  $I_{\max}$  is the height of the peak and  $E_0$  is the centroid energy of the peak. In the fitting procedure, while the Gaussian function  $G(E)$  fits the top of the peak, the Lorentzian function  $L(E)$  fits the tail of the peak described by a pseudo-Voigt function. No additional terms such as short and long tailing and/or a step-wise function for background were added to the fitting functions to characterize the line shapes of individual peaks. This choice of functions allowed to reduce the number of fit parameters as much as possible.

After the fitting process, the peak intensity of  $92^+$  keV  $\gamma$ -ray for  $^{238}\text{U}$  from both the 92.4 keV and 92.8 keV  $\gamma$ -rays of  $^{234}\text{Th}$  ( $^{238}\text{U}$ ) is determined more accurately by using a simple weighted average employing the four data sets [18–21], given in Table 3.

In order to obtain the mean intensity of the  $92^+$  keV  $\gamma$ -ray, the following equation was used:

$$I_{92^+ \text{ keV}}(i) = \frac{P_{\gamma 1} I_1 + P_{\gamma 2} I_2}{P_{\gamma 1} + P_{\gamma 2}} \quad (5)$$

where  $i = 1, 2, 3, 4$  denotes individual data set for different emission probabilities,  $I_1$  is the peak intensity for the 92.4 keV  $\gamma$ -ray and  $I_2$  is the peak intensity for the 92.8 keV  $\gamma$ -ray, obtained after fitting procedure.

The final intensity for the  $92^+$  keV  $\gamma$ -ray peak,  $I(^{238}\text{U})$  is calculated from arithmetic mean of these four weighted values,  $I_{92^+ \text{ keV}}(i)$  and they are given in Table 4 for each kind of uranium.

Subsequently, the intensity ratios of 94.6 keV self-fluorescence X-ray to  $92^+$  keV  $\gamma$ -ray, and of 98.4 keV self-fluorescence X-ray to  $92^+$  keV  $\gamma$ -ray are determined from the fitted net counts for each peak. The intensity ratios of 94.6 keV fluorescence X-ray to  $92^+$  keV  $\gamma$ -ray and of 98.4 keV fluorescence X-ray to  $92^+$  keV  $\gamma$ -ray are plotted to those  $^{235}\text{U}$  certified abundances of the reference materials as shown in Fig. 4.

These plots show the good linear relations between the increasing intensity ratios of the uranium self-fluorescence X-rays versus the  $^{235}\text{U}$  abundance in uranium materials with regression coefficients,  $R^2 \geq 0.99$ . This linear relation seen in Fig. 4 implies that if a calibration curve is made for these self-fluorescence X-rays using

Table 3  
Nuclear data sets for the  $92^+$  keV  $\gamma$ -rays and self-fluorescence X-rays lying in  $\text{UXK}_{\alpha}$  energy region of uranium spectrum.

Origin	Energy (keV)	Data set no. 1, Ref. [9]		Data set no. 2, Ref. [19]		Data set no. 3, Ref. [20]		Data set no. 4, Ref. [21]	
		Energy (keV)	$\gamma$ -Ray emission probability (%)	Energy (keV)	$\gamma$ -Ray emission probability <sup>a</sup> (%)	Energy (keV)	$\gamma$ -Ray emission probability (%)	Energy (keV)	$\gamma$ -Ray emission probability (%)
$\gamma$ -Ray ( $^{238}\text{U}/^{234}\text{Th}$ )	92.4	92.367	2.52 ± 0.06	92.359	2.621	92.38	2.81 ± 0.15	92.38	2.81 ± 0.24
$\gamma$ -Ray ( $^{238}\text{U}/^{234}\text{Th}$ )	92.8	92.793	2.50 ± 0.06	92.784	2.648	92.80	2.77 ± 0.15	92.80	2.77 ± 0.24
Self-fluo. X-ray $\text{K}\alpha_2$	94.6	94.654	61.2 ± 0.2 <sup>b</sup>	94.652	62.5 <sup>b</sup>	94.654	28.3 ± 0.6	94.654	28.2 ± 0.6
Self-fluo. X-ray $\text{U K}\alpha_1$	98.4	98.435	100 <sup>b</sup>	98.434	100 <sup>b</sup>	98.434	45.8 ± 0.9	98.434	45.1 ± 0.9

<sup>a</sup> No uncertainties quoted.

<sup>b</sup> Self-fluorescence % relative intensity.

**Table 4**  
The fitted peak intensities of uranium self-fluorescence X-rays and 92<sup>+</sup> keV  $\gamma$ -rays of <sup>234</sup>Th and their intensity ratios.

Reference sample code	Sample type	$\gamma$ -Ray intensity (cps)		Self-fluorescence X-ray intensity (cps)		Ratio of peak intensities <sup>a</sup>	
		92.4 keV $\gamma$ -ray <sup>234</sup> Th( <sup>238</sup> U) $I_1$	92.8 keV $\gamma$ -ray <sup>234</sup> Th( <sup>238</sup> U) $I_2$	94.6 keV UK $\alpha_2$ $I_{\text{flu}}$	98.4 keV UK $\alpha_1$ $I_{\text{flu}}$	94.6 keV/92 <sup>+</sup> keV $I_{\text{flu}}/I(^{238}\text{U})$	98.4 keV/92 <sup>+</sup> keV $I_{\text{flu}}/I(^{238}\text{U})$
SRM969-031	Depleted uranium	0.2957	0.2905	0.3172	0.5204	1.0798	1.7716
BL-5		0.6654	0.6866	0.8882	1.4216	1.3191	2.1113
CUP-2	Natural uranium	1.7111	1.6900	1.5860	2.7924	0.9312	1.6395
SRM969-071		0.2852	0.2852	0.3489	0.5839	1.2234	2.0473
SRM969-194		0.2588	0.2324	0.4441	0.7743	1.7842	3.1108
SRM969-295	Enriched uranium	0.2509	0.2350	0.5519	0.9773	2.2532	3.9899
SRM969-446		0.2482	0.2377	0.7296	1.3327	2.9869	5.4559

The symbol (\*) means that this energy is a doublet: (92.4 + 92.8 keV).

<sup>a</sup> The mean intensities calculated from the weighted intensities of  $I_1$  (92.4 keV) and  $I_2$  (92.8 keV) by using Eq. (5) for the  $\gamma$ -ray emission probabilities  $P_{\gamma 1}$  and  $P_{\gamma 2}$  taken from Data Sets No. 1–4 given in Table 3.

the intensity ratios of the 94.6 keV X-ray to 92<sup>+</sup> keV  $\gamma$ -ray and the 98.4 keV X-ray to 92<sup>+</sup> keV  $\gamma$ -ray plotted versus certified <sup>235</sup>U abundance, then the unknown enrichment value can easily be estimated. Such a calibration curve taken into account the fluorescence X-rays can be useful to determine the <sup>235</sup>U abundance especially when the samples have higher amounts of decay products for case of natural uranium ore materials. It is clearly seen in Fig. 4 that the intensities of uranium self-induced X-rays for both the 94.6 keV and 98.4 keV have been increased substantially due to the contributions from X- and  $\gamma$ -rays with energy above 100 keV arising from the decay products of <sup>235</sup>U and <sup>238</sup>U, and themselves. However, the increases in the intensity ratios of the uranium fluorescence X-rays to 92<sup>+</sup> keV  $\gamma$ -ray are higher than those expected in natural uranium ore samples such as BL-5 and CUP-2. This is the reason that they have higher amounts of the decay products in the ore materials than those of the processed uranium such as U<sub>3</sub>O<sub>8</sub>. Hence the MGAU analysis program gives incorrect results for <sup>235</sup>U abundance in uranium ore samples such as BL-5 and CUP-2 as is seen in Table 2, where the build-up of the decay products begins to interfere with the analysis. On the other hand, it might be expected the variations in the self-fluorescence X-ray peak intensities which may also depend on sample matrix and matrix form (liquid, powder), density, size, chemical composition of sample and its container, etc. But these probable effects of the material characteristics on the self-induced X-rays have not been investigated in this study due to out of the scope and lack of varieties of uranium samples in a different forms.

#### 4. Conclusion

In case of <sup>235</sup>U isotopic analysis in depleted or natural uranium samples, the build-up of decay products seems to be significant and the algorithms for analysis such as MGAU and URADOS for the presence of decay products should be improved to resulting in a correct enrichment value. For instance, self-induced X-rays such as 94.6 keV and 98.4 keV lying in UXK $\alpha$  spectral region used by MGAU program can be excluded either from the calculation procedure or from the increases in the peak areas of self-fluorescence X-rays can be compared with the results for <sup>235</sup>U enrichment determination by means of a known calibration curve of using self-fluorescence X-rays. When depleted or natural uranium samples are measured, the significant increases have been observed in the intensities of uranium self-induced X-rays due to  $\gamma$ -ray emissions with above 100 keV energy arising from decay products of <sup>238</sup>U and <sup>235</sup>U and themselves, thus resulting in erroneous abundances for <sup>235</sup>U. In case higher amounts of decay products are detected in the  $\gamma$ -ray spectrum acquired for the MGAU analysis, it is suggested that a calibration curve be made between the intensity ratios of self-fluorescence X-rays to 92<sup>+</sup> keV  $\gamma$ -ray and certified <sup>235</sup>U abundances for the determination of <sup>235</sup>U enrichment.

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