Characterization of Liquid Waste in Isotope production and Research Facilities

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Abstract: In this work, an absolute method has been investigated to measure the $^{235}$U mass content in low and intermediate radioactive waste as a by-product in $^{90}$Mo production process, and at research labs. Destructive Assay (DA) using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was used to perform elemental analysis for the collected samples. Absolute Non Destructive Assay (NDA) methods in collaboration with general Monte-Carlo N-transport Code MCNP5 (MC) were employed to fully characterize the samples. ICP-OES was used to determine the sample composition and the Multi-Group Analysis software (MGAU) was also used for the determination of uranium enrichment. The obtained results from the absolute method were compared with those estimated based on MGAU and ICP-OES. An agreement between the two methods was found within an estimated maximum difference of about 3.5%.

Keywords: Low and intermediate radioactive waste, liquid waste characterization, Monte Carlo, Multi group gamma-ray analysis method (MGAU), Non-destructive method, Bulk measurements.

I. Introduction

Waste characterization for Nuclear Materials (NM) tracking (determination of uranium content and enrichment) is very important activity for both national and international nuclear safeguards. The aim is to verify that uranium stock is being used for peaceful purposes [1]. Radioactive wastes in radioisotope production and research facilities, in a wide range of concentrations of radioactive materials, and with a variety of physical and chemical forms [2, 3].

According to the International Atomic Energy Agency (IAEA) references [4, 5], Liquid Radioactive Waste (LRW) generated from Radioisotope Production Facility(RPF) based on the nuclear fission of Low Enriched Uranium (LEU) [3] are categorized as low and intermediate level radioactive waste. Fissile material (FM) concentration in LRW is not high; a specificity of those LRW is a content of salts which is up to hundreds of grams per liter. This fact makes the determination of FM concentration more difficult. NDA and DA [7] methods are used to measure and identify nuclear material for safeguard purposes. One of the most powerful tools available for NDA of NM is a gamma spectrometer, which includes an HPGe detector [8-11]. Efficiency of the detector depends mainly on the characteristics of the NM to be measured and the setup configuration. According to the dependency on physical standards to calibrate the measuring devices, these techniques may be classified as relative, semi-absolute or absolute ones. To obtain accurate results, standard NM with very similar characteristics to the verified samples has to be used in the calibration process. However, because suitable standards are not always available, sometimes an appropriate calibration curve could be constructed using MC calculations[8, 12, 13]. The use of MC simulation of a detector’s response to incident photons is becoming increasingly important [14]. It was used for efficiency calibration of detectors, either directly or through combination with experimental measurements [8, 14, 15, 16–24] since it contains a special tally, F8, which is specific for pulse height determination.

In this work, an NDA technique has been applied to characterize LRW samples collected from ESAC lab and RPF. A gamma spectrometer HPGe (ORTEC, Model: GMX60P4-83) was used to measure the most dominant gamma energy lines 185.71 keV and 1001.12 keV resulting from $^{235}$U and $^{240}$Pa daughter of $^{238}$U [25-27], HPGe

(CANBERRA, Model, GL0515R) with MGAU software was used to measure samples enrichment [28, 29]. MC method was used to calibrate the detector numerically.

The main purpose of this paper is to explore the possibilities of combining gamma counting with MC Calculations to improve absolute verification of liquid waste samples, also to quantify the uranium content in LRW samples. DA technique ICP-OES [30] was used to measure concentrations of elements present in the assayed samples in order to construct MC file.

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II. Material and method

2.1 Samples specification

Seven unknown LRW sample, two of them were collected from RPF (after cold commissioning) and five other LRW samples from ESAC-DA lab were also collected. The collected samples were placed in a cylindrical Plastic container. Bulk measurements for the assayed samples were presented in Table (1).

2.2 Method

2.2.1 Treatment

For the assayed samples the general equation for the net counting rates measured by HPGe is given as [8]:

\[ C_r = M_i S_a A_i \Omega_i \epsilon_i \] …………… (1)

Where \( C_r \) (s\(^{-1}\)) is the net count rate for the LRWSample, \( M_i \) (gm) is the mass of the measured isotope in the sample \( S_a \) (s\(^{-1}\) gm\(^{-1}\)) is the specific activity of a certain gamma energy line for the isotope, \( A_i \) is the total attenuation correction factor for sample configuration setup, \( \Omega_i \) is the fractional solid angle of the sample subtended by the detector, and \( \epsilon_i \) is the intrinsic full energy peak efficiency of the detector at a given gamma energy line.

The last three factors in Eq. (1) represent the absolute full energy peak efficiency of the detector (\( \epsilon_i \)) for sample configuration at a given gamma energy line. Thus the net count rate as a function of \( \epsilon_i \) could be given as

\[ C_r = M_i S_a \epsilon_i \] …………… (2)

The sample concentrations were measured using ICP-OES.

The following equation is used to determine uranium isotopic mass content in the samples.

\[ M_i = C \times V \times E_i \] …………… (3)

Where \( M_i \) (gm) is the mass of a given isotope i, C concentration of uranium, V is the volume of the sample and \( E_i \) is the enrichment of the isotope.

2.2.2 Measuring devices

- **ICP-OES**, an iCAP 6000 ICP-OES from Thermo Fisher Scientific, UK, with ITEVA operating Software for full control of all instrument functions and data handling. This instrument is equipped with high performance solid state charge injection device camera, was used for the determination of uranium and interfering ions concentration.

- **Co-axial Photon Detector**, produced by (ORTEC #GMX60P4-83), and a digital signal processing data acquisition system (EG&G ORTEC TMDSPEC-plus) PC controlled by MAESTRO-32 software. the detector crystal dimensions were 66.9 mm in diameter and 73.1 mm in length and its performance characteristics were 60% relative efficiency, 2.3 keV energy resolution (full width at half maximum, FWHM) and 56:1 peak-to-Compton ratio at 1.33 MeV of \( ^{60}\text{Co} \) [33], was used for measuring Count rates.

- **A planar high resolution Ge-detector** [Canberra; model GL0515R with an active area of 540 mm\(^2\), 1.5 cm height and 540 eV FWHM at 122 keV], a cryostat [model 7905 SL-5] with 5 L liquid nitrogen dewar, was used to cool the detector, a portable Inspector Multi-channel Pulse-Height Analyzer [inspector, Model IN2K], for sorting and collecting the gamma-ray pulses coming from the main amplifier, an adjustable High Voltage Power Supply [HVPS], provides a negative voltage of 2000 V which necessary for the operation of the detector, The measuring system combined with the Canberra multi-group analysis software MGAU (version S507c) to estimate the \( ^{235}\text{U} \) enrichment.

- **A portable scintillation a NaI** (TI) assembly based on a Mini Multi Channel Analyzer model (MCA-166) with a NaI (TI) detector model (12S12-3.VDPA.003) and serial number (2518.05.09). As provided by the manufacturer, the detector has a NaI(Tl) crystal with dimensions (76.2 x 76.2 mm) and an Aluminum housing of 1mm was used for characterizing LLLW sample. The detector was placed inside a cylindrical lead shield with dimensions 43 cm height, 41 cm diameter.

- **Mico-Trans Spec (Micro-UF6)**, produced by (ORTEC, Model, Micro UF6, 7460), and a digital signal...
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processing data acquisition system (EG&G ORTEC TMDSPEC-plus) PC controlled by MAESTRO-32 software. The detector crystal dimensions were 50.7 mm in diameter and 30 mm in length, 1.99 keV energy resolution (full width at half maximum, FWHM) at 1.33 MeV of $^{60}$Co [33].

2.2.3 MCNP calculation

The co-axial HPGe was modeled using the MCNP5 code [32], since it contains a tally, F8, which is specific for detector pulse height determination. The absolute full energy peak efficiency of the detector at both 185.7 and 1001.1 keV gamma energies were calculated. Detector geometry was modeled according to information given by the manufacturer [33]. As shown in Fig.1. The drawing is not to scale just to emphasize different components of the detector. The detector dimensions, its Al-holder, Al-cap, dead layer and the distance from the detector crystal to the front of the detector cap are those of the manufacturer. Detailed characteristics of the samples were obtained from bulk measurements and ICP-OES measurements and used in the MC input file. Accurate results in the calculated efficiency of the simulated detector could be obtained if accurate model for the experiment is developed [8].

![Diagram of the detector model used for MC modeling](image)

Calculations were performed for the samples at six shifted positions horizontally and vertically from the detector center as shown in fig.2. and the average was calculated to avoid the error result from the description of the sample to detector position in MC input file (the position of the samples from the detector center was changed by 0.5 and -0.5 cm on x and y axes and 0.1 cm on z axis).

For most of the calculations, the number of histories was selected so as to keep the relative standard deviation due to MC calculations less than 2%. MC calculations were performed on a 2.66 GHz processor. The calculation times were about 15 min (10$^7$ histories).

![Diagram of the samples positions from the detector center used for MC modeling](image)
III. Experimental setup

3.1 Determinations of uranium and interfering ions concentrations by ICP-OES

An aliquot of an ICP multielements standard solution of (1000 mg/L) containing was used in the preparation of calibration solutions. The working standards were prepared by dilution of 1000 mg L⁻¹ certified solutions (AccuTrace™ Reference Standard, Plasma Emission Standard, 2-5% nitric acid). Micropipettes (DRAGON Ned, 100-1000 L) with disposable tips were used for pipetting solutions. A total of three standards were used for calibration with each metal ion and type I water (PURE LAB Prima Elga system) with purity of 18.2MΩ.cm at 250°C acidified with nitric acid was used as the calibration blank and also for cleaning all glasswares used. Calibration curve range from (0-10 mg L⁻¹) and the correlation coefficient range from (0.9997-0.9998). Approximately 10 ml withdrawn from each sample and measured three times. Samples were diluted to be within the range of calibration curve. Then the standard deviation was calculated.

3.2 Count rate measurements using Co-axial HPGe

The samples were placed above the detector as shown in Fig. 3. The axis of symmetry of each measured sample was adjusted to be in coincidence with the extended axis of symmetry of the detector. The measuring live time was selected such that statistical errors due to counting rates are always kept less than 1%, due to low count rates of the samples the measuring time was about two days.

3.3 Uranium mass estimation based on MGAU Measurements

The samples were placed in front of the detector, the samples-to-AL cap of the detector distances were approximately zero. The measuring time was set in such a way that enrichment error was about 2%, the measuring times ranging from 1.5-2 days.

3.4 Measurement of low liquid radioactive waste samples LLLW

LLLW sample was characterized using the techniques described in section 3.2 and 3.3 in addition to NaI(Tl) and micro UF₆ detectors were used to verify the results described as the following:

NaI (Tl) detector: The sample was placed just above the Al-cap of the detector. The axis of symmetry of the measured sample was to be coincidence with the extended axis of symmetry of the detector, while its plane was parallel to that axis. The measuring time for the background and sample was about 24 hours. Fig. 4 shows the different components and arrangement of the experimental setup.
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The Micro UF6 detector: LLLW sample was placed just above the Al-cap of the detector, the measuring time for the assayed sample was 72 hours. A background was collected with the same measuring time of the sample.

IV. Results and discussion

4.1 Uranium and interfering ions concentrations

Table 2 presents the measured uranium and interfering ions concentrations for all the samples. The listed values are those obtained via ICP-OES. The percentage relative uncertainties in the determined concentrations were ranging from 0.18 to 3.75. No uranium concentration was obtained for LLLW sample, this is may due to the uranium existence in the sample is below the detection limit.

<table>
<thead>
<tr>
<th>Sample Id</th>
<th>Concentration C x (% mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ILLW</td>
<td>5 ± 3.761</td>
</tr>
<tr>
<td>LLLW</td>
<td>1000 ± 0.2</td>
</tr>
<tr>
<td>ICPSTU2</td>
<td>890 ± 0.89</td>
</tr>
<tr>
<td>PRZ03</td>
<td>1567 ± 2</td>
</tr>
<tr>
<td>PRZ04</td>
<td>2617 ± 0.18</td>
</tr>
<tr>
<td>UNL02</td>
<td>455 ± 0.48</td>
</tr>
</tbody>
</table>

4.2 Measured count rates

Count rates of 185.7 and 1001.1 keV gamma rays relevant to $^{235}$U and $^{238}$U isotopes, respectively, were measured using the HPGe spectrometer. The measurements were performed as described previously in section 3.2. The count rates ($C_R$) with the associated percentage relative uncertainties ($σ_{CR}$) are given in Table 3.

<table>
<thead>
<tr>
<th>Sample Id</th>
<th>Count rate $C_R$ (% s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICPSTU2</td>
<td>3.37 ± 1.04</td>
</tr>
<tr>
<td>PRZ03</td>
<td>0.31 ± 4.19</td>
</tr>
<tr>
<td>PRZ04</td>
<td>0.56 ± 0.54</td>
</tr>
<tr>
<td>PRZ05</td>
<td>1.97 ± 0.35</td>
</tr>
<tr>
<td>UNL02</td>
<td>0.24 ± 2.39</td>
</tr>
<tr>
<td>ILLW</td>
<td>0.14 ± 0.45</td>
</tr>
<tr>
<td>LLLW</td>
<td>……</td>
</tr>
</tbody>
</table>

4.3 Estimation of Absolute Full Energy peak Efficiency of the detector using MC method

The absolute full energy peak efficiency of the detector at both 185.7 and 1001.1 keV gamma energies were calculated using the MCNP code. The results of calculations with the associated uncertainties are given in Table 4.

<table>
<thead>
<tr>
<th>Sample Id</th>
<th>Absolute Full Energy Peak Efficiency $ε_a$ (% )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICPSTU2</td>
<td>2.237E-02±0.15</td>
</tr>
<tr>
<td>PRZ03</td>
<td>1.006E-01±0.068</td>
</tr>
<tr>
<td>PRZ04</td>
<td>1.226E-01±0.06</td>
</tr>
<tr>
<td>PRZ05</td>
<td>1.686E-01±0.05</td>
</tr>
<tr>
<td>UNL02</td>
<td>7.566E-02±0.08</td>
</tr>
<tr>
<td>ILLW</td>
<td>1.173E-01±0.00</td>
</tr>
<tr>
<td>LLLW</td>
<td>……</td>
</tr>
</tbody>
</table>

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4.4 $^{235}\text{U}$ Enrichment estimation

The measured enrichment of uranium samples using MGAU are given in Table 5 with the associated percentage relative uncertainties.

Table 5. Estimated enrichment based on MGAU measurements with the associated percentage relative uncertainties

<table>
<thead>
<tr>
<th>Sample Id</th>
<th>Estimated enrichment using MGAU E% ± (σ_E/E)%</th>
</tr>
</thead>
<tbody>
<tr>
<td>ICPSTU2</td>
<td>0.715 ± 3.916</td>
</tr>
<tr>
<td>PRZ03</td>
<td>0.395 ± 4.810</td>
</tr>
<tr>
<td>PRZ04</td>
<td>0.355 ± 4.776</td>
</tr>
<tr>
<td>PRZ05</td>
<td>0.536 ± 3.358</td>
</tr>
<tr>
<td>UNL02</td>
<td>0.566 ± 3.710</td>
</tr>
<tr>
<td>ILLW</td>
<td>......</td>
</tr>
</tbody>
</table>

The uncertainty in the measured enrichment of each sample of uranium using MGAU is mainly due to the random error of the measurements (less than 5%).

Fig. 5 shows the estimated $^{235}\text{U}$-enrichment values with their uncertainties. The percentage relative uncertainties in the estimated enrichment for absolute and MGAU-based methods were found to have maximum values of 4.4 and 4.78%, and minimum 0.9% and 3.7% respectively. While the relative differences between the $^{235}\text{U}$ enrichment estimated using the two methods range between 0.7% to 3.5%. It is clear that the estimated enrichment using both methods is in agreement within the uncertainties.

Fig. 5. $^{235}\text{U}$-enrichment estimated by absolute method (based on MCNP5 calculations) in comparison with that obtained results based on MGAU.

For ILLW sample, enrichment can’t be measured either by MGAU due to low count rates of the sample or by MC since there is no count rate for 1001.12 keV which is used for $^{238}\text{U}$ calculation.

4.5 Uranium-isotopic mass contents $^{235}\text{U}$ and $^{238}\text{U}$

To show the agreement between the two methods, the estimated masses with the uncertainties respectively (error bars) are illustrated in Fig. 6 and Fig. 7 for $^{235}\text{U}$- and $^{238}\text{U}$-isotopes, respectively. It is clear from the figures the agreement between the two methods with the accuracy and precision.

Fig. 6 shows the estimated $^{235}\text{U}$-mass content values with their uncertainties. The shaded column represent the mass calculated in accordance to equation (3) [based on ICP-OES results (table 2) and MGAU results (table 5)], and the white one is the uranium mass obtained via absolute method. It is clear that the estimated masses using both methods are in agreement within the uncertainties.

Fig. 7 shows the estimated $^{238}\text{U}$-mass content values with their uncertainties. The shaded column represent the mass calculated in accordance to equation (3) [based on ICP-OES results (table 2) and MGAU results (table 5)], and the white one is the uranium mass obtained via absolute method. It is clear that the estimated masses using both methods are in agreement within the uncertainties.
4.6 LLLW Sample

No uranium content was obtained for LLLW sample, this is may be due to the uranium existence in the sample is below the detection limit.

V. Conclusion

In this study the uranium mass content and enrichment have been measured in uranium bearing samples collected from different locations. The $^{235}$U and $^{238}$U mass contents in low and intermediate radioactive waste, as a by-product in $^{99}$Mo production process and at research labs have been investigated. The samples were characterized using DA technique to estimate the total uranium mass content, then, NDA measurement were performed to estimate uranium isotopic mass content and enrichment. For ILLW sample, the enrichment could not be measured either by MGAU due to low count rates or absolute measurements due to the absence of any recognized count rate at 1001.12 keV gamma energy line which is used for $^{238}$U mass calculation. The used DA and NDA measurement could not detect any uranium in the LLLW sample; this is may be due to the relatively very low level concentration of uranium in it. Otherwise, an agreement between the used methods was
found within an estimated maximum difference of about 3.5%. The low concentration of uranium in LLLW sample (below the detection limit of the used devices) indicates that such LRW could be discarded in such a way that no safeguards obligation are required.

References


