



**Measurement of Actinide Concentration in Solution Samples
from the NUCEF Reprocessing facility by X-ray and
Low Energy Gamma-ray Spectroscopy.**

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ABSTRACT

X-ray and low-energy gamma-ray spectroscopy has been used to measure actinide concentration within the back-end nuclear fuel reprocessing research facility at NUCEF. Research on advanced reprocessing techniques at NUCEF is based on the PARC refinement of the PUREX process which aims to recover Am and Cm from the highly active waste stream and to control and partition Np and Tc. It is hoped that the PARC process will mitigate the environmental impact of the wastes and improve the economy of reprocessing. The main actinides for which assay is required are U, Pu, Np and Am and knowledge of these concentrations will enable the following to be determined: i.) evaluation of the distribution of actinides throughout the reprocessing facility ii.) verification of the simulated actinide distribution from chemical kinetic simulations of the PARC process and iii.) assurance of safety and control over migrant radioactive species. The research presented here shows that passive measurement of x-rays and low-energy gamma-rays from solution samples provides an accurate and non-destructive means for assaying the concentration. The measurement technique is based on the use of the characteristic low energy gamma-rays and internal conversion x-ray emission from actinides (11keV to 22keV). The x-ray emission is a few orders of magnitude more intense than the characteristic gamma-ray emission and can be easily detected from solutions. The experimental system described here can be used for solution monitoring to a minimum concentration of typically 10⁻⁶ M for Pu, 10⁻¹⁰ M for Am and 10⁻⁶ M for Np.

1. INTRODUCTION

At JAERI, advanced reprocessing research is focused on the PARC (Partitioning Conundrum Key) refinement [1] of the PUREX process using a small scale reprocessing research facility at JAERI's Nuclear Fuel Cycle Safety Engineering Research Facility (NUCEF). The PARC process differs from conventional reprocessing in that Am and Cm are separated from the high level waste raffinate and Np is separated prior to U and Pu partitioning. Figure 1 shows a schematic diagram of the PARC process. The key measurement points at which monitoring of the actinide concentration are considered necessary are the Tc, Np, Pu and U product streams

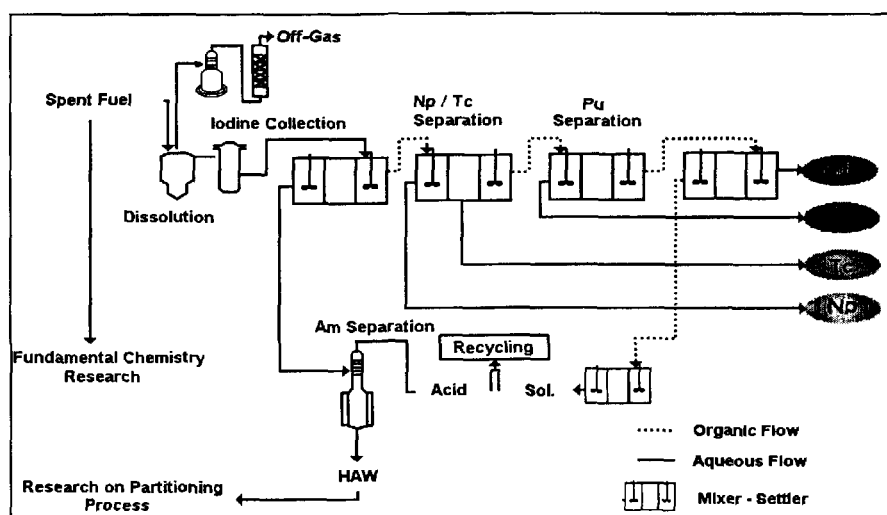


Figure 1. Flowsheet for PARC refinement of the PUREX process.

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The detection system has been developed as an off-line monitor using samples from the reprocessing facility transported to a fumehood, however it is envisaged that an on-line system could be developed based on the work described here.

2. PRINCIPAL OF MEASUREMENT TECHNIQUE

The technique is based on measuring x-ray and low energy gamma-ray emissions from the actinides. The most intense emission lines at low energy for Pu are the Uranium L x-ray lines that are a result of the alpha decay of Pu. For ^{238}Pu , the x-ray lines in the region 11keV to 23keV are 28,000 times more intense than the 43.47keV gamma-ray, see Table 1.

Table 1. X-ray and gamma-ray emissions from the actinides of interest.

| Nuclide | Half-life | L x-ray emission s / g | Gamma-ray / keV | γ emission s / g | Ratio x / γ emission |
|-------------------|-----------|---------------------------|--------------------|----------------------------|--------------------------------|
| ^{238}Pu | 87.8 y | 6.9×10^{10} | 43.47 | 2.5×10^6 | 28000 |
| ^{239}Pu | 24.1 ky | 9.6×10^7 | 51.62 | 4.8×10^5 | 200 |
| ^{240}Pu | 6.6 ky | 8.9×10^8 | 45.24 | 3.8×10^6 | 240 |
| ^{241}Pu | 14.4 y | 4.1×10^3 | 98.43 | 6.9×10^6 | 0.0006 |
| ^{242}Pu | 373.5 ky | 1.3×10^7 | 44.92 | 5.3×10^4 | 240 |
| ^{241}Am | 432.7 y | 5.0×10^{10} | 26.33 | 3.0×10^{10} | 1.65 |
| | | | 59.54 | 4.5×10^{10} | 1.1 |
| | | | 64.8 | 1.8×10^3 | 2.8×10^7 |
| ^{237}U | 6.8 d | 1.7×10^{15} | 26.33 | 5.9×10^{14} | 2.9 |
| | | | 59.54 | 9.9×10^{14} | 1.7 |
| | | | 64.8 | 3.1×10^{11} | 5.5×10^3 |
| ^{237}Np | 2.14 My | 1.4×10^7 | 29.38 | 3.4×10^6 | 4.0 |
| ^{234}Th | 24.1 d | 9.1×10^{13} | 63.3 | 3.9×10^{13} | 2.4 |

Detection of low energy photon emission implies that the thickness of the active detector can be kept to a minimum which has the advantage of ensuring that the detection efficiency for higher energy gamma-rays from fission products is significantly less than for the L series x-rays. This will hopefully improve the signal to noise ratio at low energy.

For assaying ^{237}Np , the gamma-ray emission at 29.4 keV is most suitable since it is free of interference from other gamma-ray emissions. ^{241}Am assay can be achieved using either the 26.3 keV or the 59.5 keV gamma-ray emissions although interference from ^{237}U needs to be accounted for should it be present. Fortunately, ^{237}U emission has been shown through calculations not to interfere with the measurements [2].

A disadvantage of utilising the U L x-ray emission for measuring Pu is that the energy of the x-rays are not dependent on the isotope since it is an atomic rather than nuclear transition. Thus in order to utilise the U L x-ray emission for the assay of Pu it is necessary to accurately determine the Pu isotopic composition by another means. Given that this is possible for all anticipated irradiated fuel reprocessing tests in NUCEF, the utilisation of x-ray emission is considered viable.

A disadvantage is that the difference in the energy of x-ray emission associated with the decay of the actinides is less than the resolution of a typical semiconductor detector and so the emission lines tend to overlap. Figure 2 shows the slight difference in the energy of the L x-ray emission for the main actinides of interest as measured by a Si(Li) detector. This problem can be overcome by relating the x-ray emission lines from the decay of Am and Np parents to characteristic gamma-ray emission, thus accounting for any x-ray emission not from the decay of Pu.

Two techniques are also proposed for assaying the uranium concentration. Firstly it is possible to use the gamma-ray emission at 63.3 keV from ^{234}Th , the daughter of ^{238}U . ^{234}Th is an active emitter due its short half-life however concentrations of ^{234}Th will be small due to the long half-life of its parent. The second technique relies on internal self absorption of gamma-rays within the liquid sample. It is possible to measure the relative change in peak heights of the 59.5 keV and 26.3 keV emission from ^{241}Am and provided that uranium is the most concentrated species, its concentration can be obtained. This latter technique can be used with either an external ^{241}Am source or the ^{241}Am within the sample liquid itself. Obviously the calibration for internal and external sources will be different and careful interpretation of the data is required.

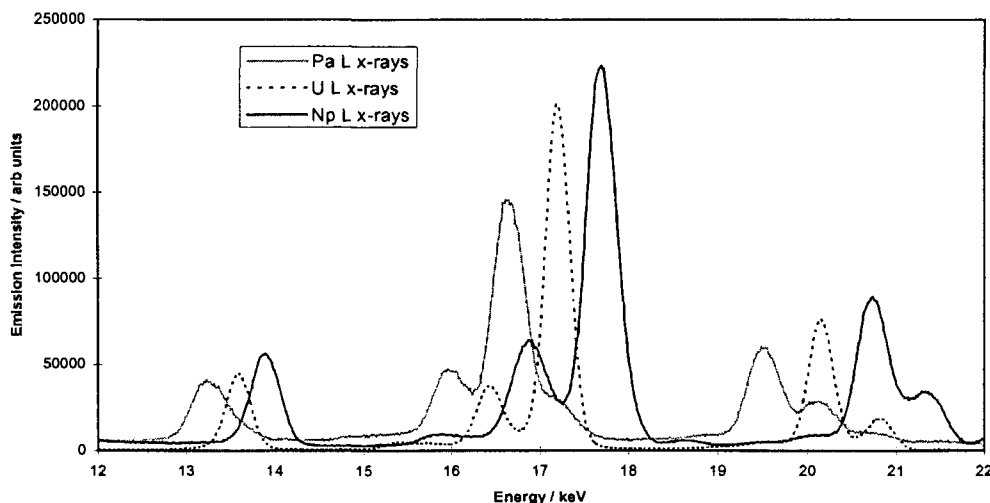


Figure 2. Energy of the x-ray emission resulting from the decay of ^{237}Np , Pu and ^{241}Am parents.

An example of an acquired Pu spectra from a sample with significant ^{241}Am grow-in is shown in Figure 3 using a Si(Li) detector. A procedure for separating the U L x-ray emission (from Pu decay) and the Np L x-ray emission (from ^{241}Am decay) has been reported by Nitsche [3] and Gatti [4]. The technique makes use of relating the Np L x-ray emission to a characteristic gamma-ray line of ^{241}Am such as 59.5 keV. Equation 1 outlines use of the technique.

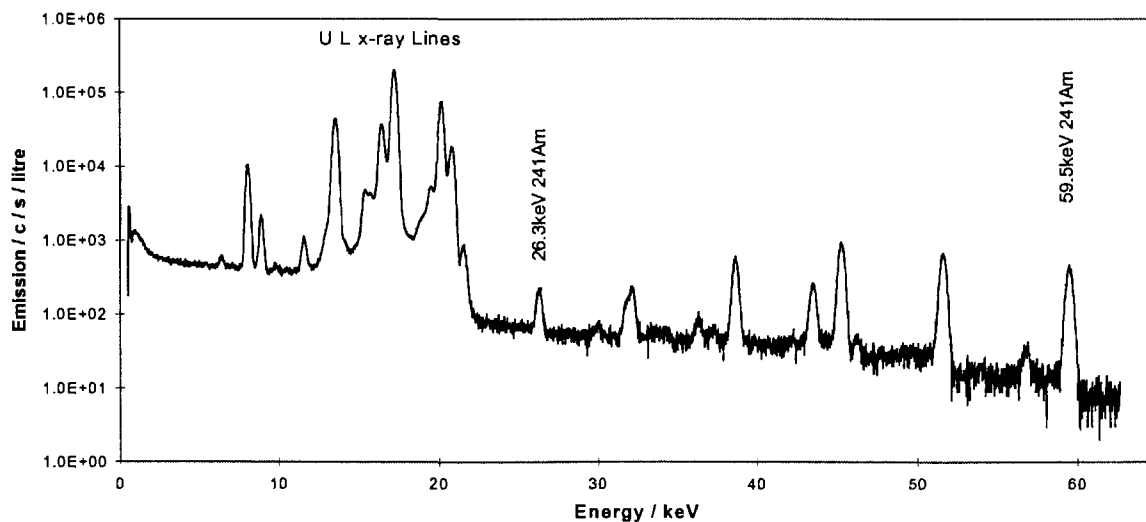


Figure 3. Example of a spectrum for a 6500 mg / litre Pu solution

$$C_{Pu} = C_{LX} - C_{\gamma} k \quad [1]$$

In Equation 1, the components are:

| | |
|--------------|---|
| C_{Pu} | is the L x-ray emission associated with the decay of Pu (the U L x-rays), |
| C_{LX} | is the total L x-ray emission (U L x-rays and the Np L x-rays from ^{241}Am), |
| C_{γ} | is the characteristic gamma-ray emission from the interfering actinide, e.g. 59.5 keV emission from ^{241}Am . |
| k | is a coefficient which relates C_{γ} to C_{LX} when no Pu is present. |

Here the total L x-ray emission region is the background corrected count rate within the energy range of 12.5 keV to 23.0 keV. The coefficient k must be obtained for a pure ^{241}Am sample which enables the 59.5 keV gamma-ray emission to be used as a measure of Np L x-ray emission. The coefficient is given by Equation 2 where C_{LX} and C_{γ} are the count rates from the L x-ray region and the 59.5 keV region, respectively.

$$k = \frac{C_{LX}}{C_{\gamma}} \quad [2]$$

A similar procedure can also be used to correct interference from ^{237}Np by using the 29 keV gamma-ray emission or indeed any other nuclide for which a characteristic gamma-ray emission line can be used for reference.

3. CALIBRATION MEASUREMENTS AND DATA INTERPRETATION

Measurement of the x-ray and gamma-ray emission from known U, Pu, Am and Np calibration samples has been conducted in a fumehood in the NUCEF facility using stock solution samples of 2 ml active volume in small glass vials. The detection system consists of a Series 7300 Canberra SiLi semiconductor detector (model type no. SL80175) 5 mm thick crystal with an active surface diameter of 80 mm² and a Be window of 1.0 mm thickness. The absolute efficiency of the detection system is approximately 0.2% below an energy of 30 keV.

Instrument calibration also requires a correction for self attenuation of x-rays and gamma-rays within the liquid sample. Since product streams will contain up to 200 grams / litre of uranium it is necessary to determine the attenuation of the L x-ray emission region as well as other important regions of interest. In order to quantify the self attenuation, solutions were created with varying concentrations of uranium between 0 and 200 grams / litre and fixed Pu content of 110 mg / litre. The Pu sample used was the same as described above, i.e. aged by 11 years with significant ^{241}Am grow-in.

By determining the ratio of the ^{241}Am 26.3 keV and 59.5 keV gamma-ray emissions, a measurement of the self attenuation within the sample can be determined, this procedure is described in further detail in reference 2.

The calibration data, corrected for self attenuation, are shown in Figure 4. The U L x-ray emission data for the assay of Pu have been corrected for interfering x-ray emission from the decay of ^{237}Np and ^{241}Am (Np L x-rays).

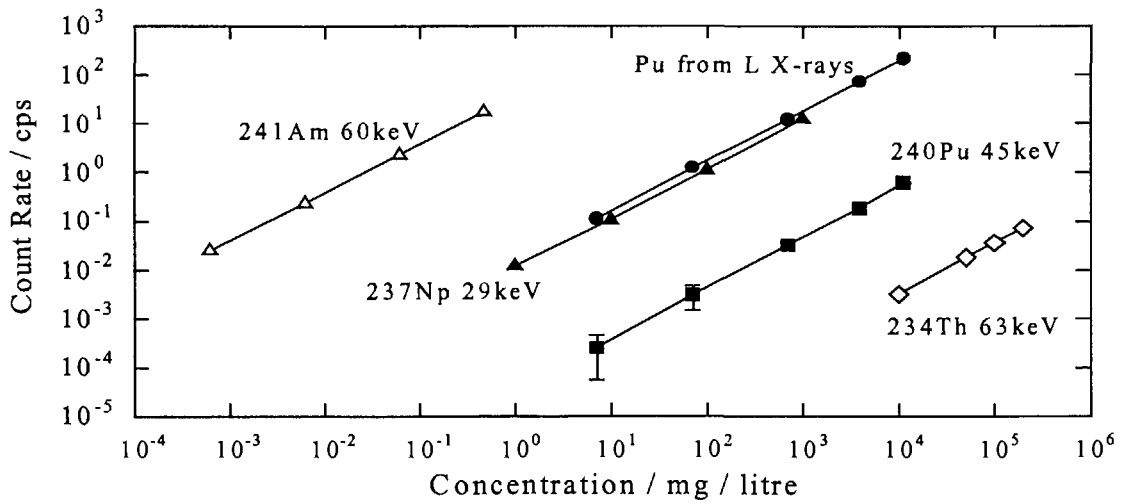


Figure 4. Calibration results for ^{241}Am , Pu, ^{237}Np and U. The data for ^{240}Pu shows the typical experimental errors (plotted for 2σ) associated with the calibration data.

4. NUCEF SIMULATED FEED SOLUTION MEASUREMENTS

Prior to full active phase commissioning of the reprocessing research facility in NUCEF, a simulated feed solution was fed through the facility and separated. This feed solution consisted of un-irradiated uranium combined with stock Pu solution, some non-radioactive fission product simulants as well as a small concentration of their radioactive tracer counterparts [5,6]. Figure 5 shows an energy spectrum of the simulated feed solution obtained with the Si(Li) detector and the composition of the feed is given in Table 2.

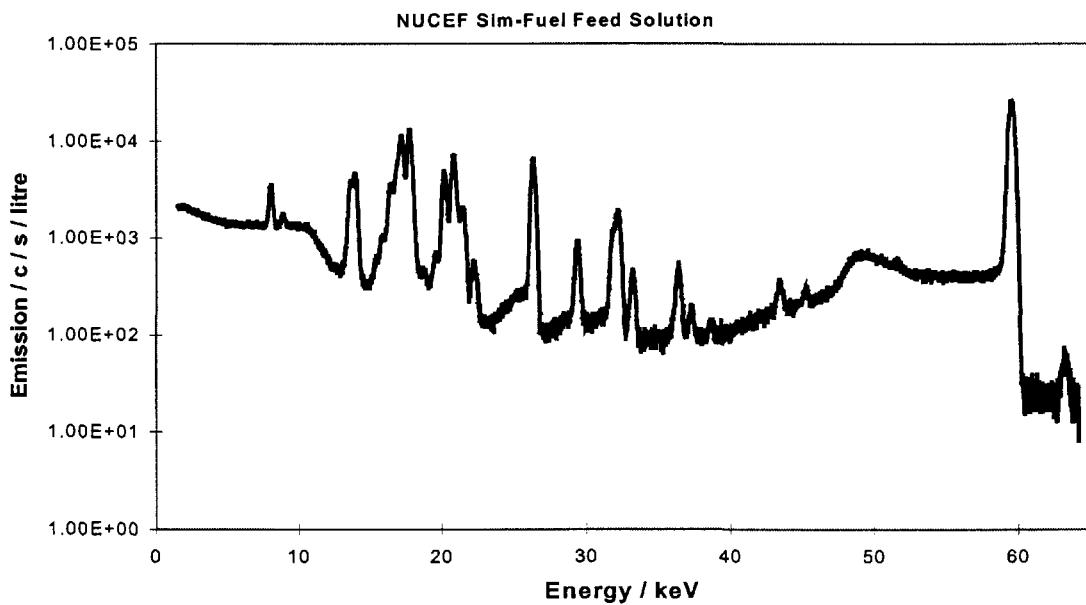


Figure 5. X-ray and low energy gamma-ray spectrum of the simulated feed solution to the NUCEF facility.

Table 2. Composition of the simulant feed solution used in the NUCEF tests.

| Element / substance | Concentration |
|---------------------|---------------|
| Nitric Acid | 2.9 M |
| Nitrous Acid | 0.00116 M |
| U | 250 g / l |
| Pu | 2.68 g / l |
| Tc | 11 mg / l |
| Np | 137 mg / l |
| I | 2.1 mg / l |
| Ru | 960 mg / l |
| Zr | 1.47 g / l |
| Sr | 340 mg / l |
| Mo | 1.20 g / l |
| Ce | 870 mg / l |
| Ba | 580 mg / l |
| Pd | 520 mg / l |
| Cs | 1.0 g / l |
| La | 436 mg / l |
| Others | 570 mg / l |

It is important to note that the samples assayed in this work do not contain the intensely radioactive fission products that will be present during dissolution of actual irradiated spent fuel. Furthermore, the presence of the fission products will most likely result in the inability to assay the feed solution and highly active waste stream or indeed any stream prior to primary fission product decontamination.

The results for measurements of each flowstream are shown in Tables 3 to 6 for Np, Am, Pu and U together with comparisons obtained by previous techniques based on gamma-ray spectroscopy of tracers or chemical titration, described in further detail in reference 2. The errors quoted are to one standard deviation.

Table 3. Results for measurements of Np concentration.

| Product Stream | Previous 277.6 keV ²³⁹ Np measurement mg / litre | 29.4 keV ²³⁷ Np measurement mg / litre |
|----------------|--|--|
| Feed Solution | 137.5 ± 18.5 | 149.2 ± 5.4 |
| Tc Product | 13.9 ± 1.9 | 16.0 ± 0.5 |
| Np product | 62.6 ± 8.4 | 68.2 ± 2.2 |
| Pu product | 17.8 ± 2.4 | 14.2 ± 1.4 |
| U product | 9.1 ± 1.2 | - |

Table 4. Results for measurements of the Am concentration.

| Product Stream | Previous measurement [7] mg / litre | 59.5 keV ²⁴¹ Am measurement mg / litre |
|----------------|--|--|
| Feed Solution | 1.5 | 1.63 ± 0.05 |
| HAW | 0.85 ± 0.11 | 0.69 ± 0.02 |
| Tc Product | - | 0.0014 ± 0.0005 |
| Np product | - | 0.0047 ± 0.0015 |
| Pu product | 0.0049 ± 0.0024 | 0.011 ± 0.007 |
| U product | 0.0013 ± 0.0008 | 0.0013 ± 0.0005 |

Table 5. Results for measurements of the Pu concentration.

| Product Stream | L x-ray measurement mg / litre | Previous ²⁴⁰ Pu 45.4 keV measurement mg / litre |
|----------------|-----------------------------------|--|
| Feed Solution | 3780 ± 756 | 2618 ± 497 |
| Tc Product | 80.4 ± 3.2 | 85.4 ± 13.7 |
| Np product | 263.4 ± 8.4 | 274.0 ± 19.2 |
| Pu product | 653.4 ± 20.9 | 653.0 ± 131 |
| U product | 85.0 ± 2.7 | 76.0 ± 17.5 |

Table 6. Results for measurements of the Uranium concentration.

| Product Stream | Titration measurement g / litre | 63.3 keV ²³⁴ Th measurement g / litre | 26.3 keV / 59.5 keV ratio measurement g / litre |
|----------------|------------------------------------|---|---|
| Feed Solution | 250 | 242 ± 29 | 264 ± 13 |
| Tc Product | 9.9 ± 1.8 | 5.6 ± 1.9 | 5.6 ± 0.5 |
| Np product | 8.1 ± 1.9 | 7.0 ± 2.5 | 8.5 ± 0.5 |
| Pu product | - | - | - |
| U product | 41.1 ± 7.5 | 35.7 ± 4.2 | 42 ± 6 % |

6. CONCLUSIONS AND DISCUSSION

The results given confirm the suitability of using x-ray and low energy gamma-ray emission to assay the concentrations of actinides in reprocessing streams. However further work is required to determine the effect of gamma-ray emissions from reprocessed irradiated fuel which has not yet been measured using the instrumentation described here.

It is anticipated that the work described here will aid the development of actinide monitoring systems that will be incorporated in-line within advanced reprocessing facilities. It is unfortunately impossible to back-fit an in-line monitoring system into the NUCEF reprocessing facility due to the commencement of hot experiments and the limited space available for shielding around the detectors. However, it is certainly viable to use an instrumentation system based on the method described above with a flowcell arrangement for continuously monitoring a product flowstream.

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