

‘Nuclear Forensic’ application of LA-MC-ICP-MS

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Abstract. Nuclear forensics is an evolving area of research, with new tools such as laser ablation multicollector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) offering rapid isotopic analyses of individual particles from nuclear materials. This paper compares the isotopic compositions ($^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$) of depleted uranium (DU) oxide particles that contaminate Colonie (NY, USA) with the tails assays from the Paducah gaseous diffusion plant (PGDP, KY, USA). $^{234}\text{U}/^{238}\text{U}$ was measured to verify that the Colonie DU originated from Paducah tails. The isotopic compositions of the Colonie DU particles can be explained by the inhomogeneous mixing of at least seven batches from PGDP tails.

1. Introduction

Lloyd *et al.* [1] demonstrated the novel and rapid application of laser ablation multicollector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) to analyse the isotopic compositions of a large number of individual microscopic uranium oxide particles (12 – 82 μm diameter). The particles of interest were isolated from soil and dust samples contaminated by emissions from the National Lead Industries (NLI) plant at Colonie (NY, USA). NLI produced uranium articles from 1958 to 1984, and burnt scrap metals in a furnace that vented several tonnes of uranium oxide particulates to the atmosphere [2, 3]. The morphologies and elemental compositions of the Colonie particles are described in Lloyd *et al.* [4]. Fission track identification (and qualitative isotopic analyses) of particles from a Colonie reservoir sediment core [5] have previously been reported by Lo *et al.* [6].

All of the Colonie particles analysed are from depleted uranium (DU), with $^{235}\text{U}/^{238}\text{U} < 2.4 \times 10^{-3}$ [1]. These are isotopically distinct from natural uranium, which has $^{235}\text{U}/^{238}\text{U} \text{ c. } 7.257 \times 10^{-3}$ [7, 8]. DU is the by-product or ‘tails’ from the artificial enrichment of the fissile isotope ^{235}U ; its characteristics and uses are detailed in Betti [9] and Blesie *et al.* [10]. Analysis of individual uranium oxide particles from Colonie revealed a range of discrete isotopic compositions, probably reflecting differences in the UF_4 feedstocks received by NLI. The UF_4 was probably supplied via Fernald, which National Lead also operated. It was speculated that the ^{236}U abundance in the NLI feedstocks increased towards 1979. Knowledge of the variability of DU isotopic compositions is important when assessing measurements from bulk environmental samples that comprise both this anthropogenic uranium and natural uranium, e.g. soils, dusts, vegetation, and urine. An understanding of the chronology of contamination could help constrain industrial and environmental processes relevant to this case-study.

The likely origin of the NLI feedstock was from the Paducah gaseous diffusion plant (PGDP, KY, USA), which produced U.S. low enriched uranium (LEU, 1 - 2 % ^{235}U) from natural and reprocessed uranium during the period that NLI handled uranium metals [11]. The origin of the NLI feedstocks is not identified in the available site documents. The two other enrichment plants that operated during the 1960’s and 1970’s were Oak Ridge (TN) and Portsmouth (OH), both of which produced enriched and highly enriched uranium (HEU), but information on their tails is not readily available [e.g. 12].

In the U.S., exceptional and otherwise uneconomic levels of ^{235}U depletion were reached in 1955/6, due to shortages of processed uranium feedstocks, the requirement for enriched uranium and for the continuous operation of recently commissioned gaseous diffusion plants [11].

The ^{235}U enrichment process also enriches ^{236}U , and especially the lighter ^{234}U isotope, in the product relative to the feed material. Uranium in secular equilibrium comprises $(5.495 \pm 0.014) \times 10^{-5} \text{ }^{234}\text{U}/^{238}\text{U}$

[calculated from decay constants in 13], but natural processes result in disequilibrium, ranging at least 0.5 – 14 times this value. Therefore ^{234}U is not a reliable indicator of anthropogenic contamination [14]. However, $^{234}\text{U}/^{238}\text{U}$ is characteristic of processing at each gaseous diffusion plant, and is therefore significant for nuclear forensics [11].

The range of $^{234}\text{U}/^{238}\text{U}$ reported for PGDP tails was $(5 - 18) \times 10^{-6}$. Because Paducah LEU fed the Portsmouth plant, ^{234}U and probably ^{236}U , are expected to be less abundant in the Portsmouth tails. Oak Ridge, which produced highly enriched uranium, can also be expected to have tails with low $^{234}\text{U}/^{238}\text{U}$; a tails assay reported in Rucker & Johnson Jr [15] was c. 4×10^{-6} .

The abundance of ^{236}U in DU is highly variable. Reprocessed uranium is the source of the anthropogenic ^{236}U contamination that is typical of DU [e.g. 16]. PGDP received reprocessed uranium from 1953 – 1964, 1969, 1970, & 1972 – 1974; domestic (Hanford and Savannah River) and some foreign reactor tails accounted for up to 65 % of PGDP's annual inputs during that period [17]. A minority of the inputs to PGDP were from natural uranium. Recycling of reactor tails in the U.S.A. continued until 1976/7 [18]. The abundance of ^{236}U in recently produced DU is therefore expected to be lower.

A brief review of the literature presented in Lloyd *et al.* [1] shows that US and British munitions deployed in the Gulf War and Balkans conflicts have isotopic compositions that are not dissimilar to the Colonie particles. The DU in British munitions was also sourced from U.S. gaseous diffusion plants [19]. The isotopic compositions of PGDP tails were highly variable over time, and show the possible range for DU articles and wastes produced from these.

The present study compares the Colonie dataset [1] with the PGDP tails assays reported by Smith [17].

2. Methodology

The PGDP tails assays are stated to 4 significant figures for ^{235}U (wt. %), and 2 significant figures for ^{234}U and ^{236}U [17], without expression of uncertainty. The data cover random intervals from 1955 – 1982, with a gap from 1973 – 1976 when no assays were reported. The $^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ ratios from Colonie particles appear to be compatible with these.

In order to test the hypothesis that the DU used at NLI was from PGDP tails, $^{234}\text{U}/^{238}\text{U}$ was measured for a subset of the Colonie particles. Due to the arrangement of the particular multicollector array used by Lloyd *et al.* [1], it is not possible to measure both ^{234}U and ^{236}U simultaneously with ^{238}U . A different collector configuration was used in this study to measure $^{234}\text{U}/^{238}\text{U}$. Eighteen solutions were analysed, as these had previously been prepared. LA-MC-ICP-MS would otherwise be the preferred choice, requiring minimal sample preparation and thus offering greater productivity.

The sample preparation and analytical methodologies are detailed in Lloyd *et al.* [1], and are briefly described here. Microscopic uranium oxide spheres were picked from soils and dusts, and then dissolved in high purity concentrated HNO_3 and H_2O_2 . The solutions were diluted to c. 20 ng g^{-1} uranium in 2 % HNO_3 , and then analysed using MC-ICP-MS (VG Elemental Axiom). ^{238}U was measured on a Faraday cup (c. 1.2 V signal through a $10^{11} \Omega$ resistor), ^{234}U was measured on the axial continuous dynode secondary electron multiplier, using ion-counting mode. Mass-bias and detector linearity were corrected using a natural uranium solution (NBS SRM 950a). Peak jumping enabled the measurement of $^{235}\text{U}/^{238}\text{U}$ and these data are in good agreement with Lloyd *et al.* [1].

2. Results & discussion

The data from Lloyd *et al.* [1] are compared with the PGDP tails assays in Figure 1, with $^{236}\text{U}/^{238}\text{U}$ plotted against $^{235}\text{U}/^{238}\text{U}$. The $^{234}\text{U}/^{238}\text{U}$ data from this study are plotted in Figure 2, also against $^{235}\text{U}/^{238}\text{U}$.

The isotopic compositions of the Colonie particles can be explained by inhomogeneous mixing between batches of PGDP tails. The PGDP tails assays are reported for discrete dates; the isotopic compositions of tails tapped between these dates may vary. For example, evolution of the PGDP tails between 01/08/1967 and the next reported assay, 31/12/1968, could account for the spread of $^{236}\text{U}/^{238}\text{U}$ from the main cluster of Colonie particle compositions in Figure 1.

Several processes could effect mixing. Batches could have been mixed during the reduction of UF_6 to UF_4 , prior to supplying NLI. Possibly at Fernald (OH), which reduced uranium hexafluoride, including ^{236}U contaminated recycled uranium [18]. It is likely that feedstocks at NLI mixed during reduction of UF_4 to metal, through casting and machining operations, through collection and storage of wastes, and finally

during combustion in the NLI furnace.

The similarities of the ranges of isotopic compositions in particles from soils compared with those from dry dusts, suggests that wet chemistry in the terrestrial environment has not significantly driven isotopic mixing [1]. The majority of the analysed particles have primary ‘as-emitted’ morphologies [4], also suggesting minimal environmental mixing.

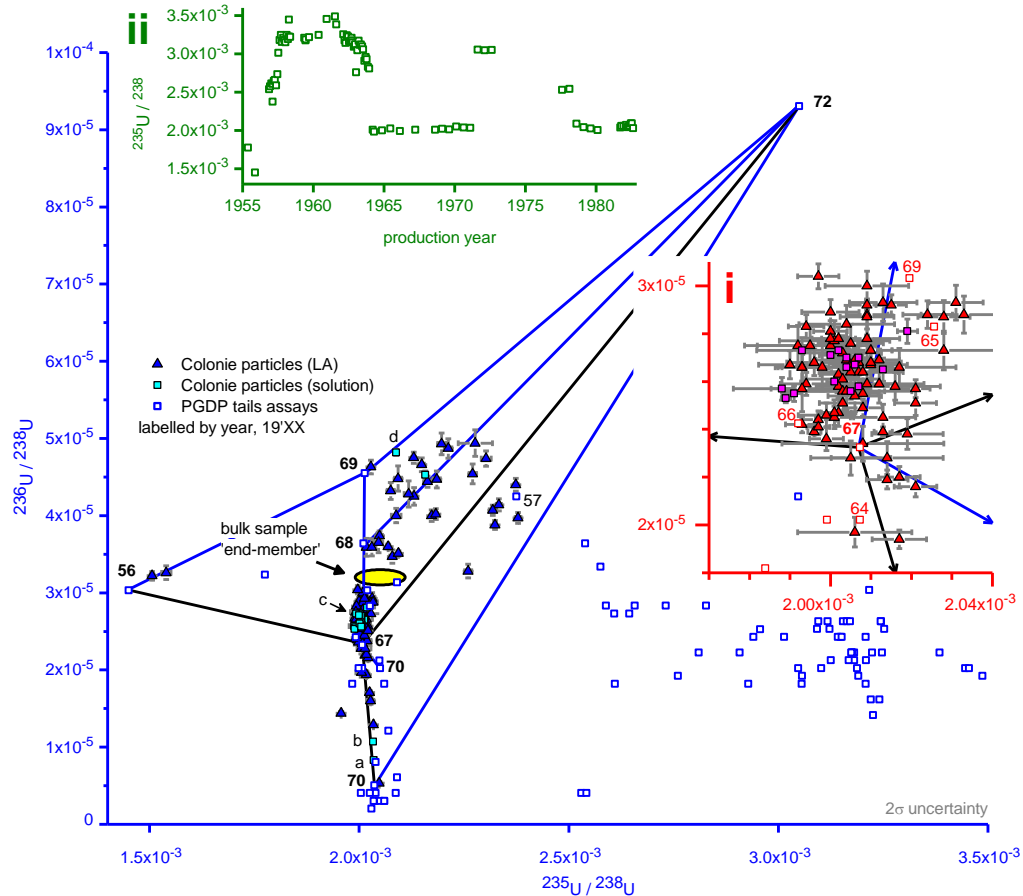


Figure 1. Plot of $^{236}\text{U}/^{238}\text{U}$ against $^{235}\text{U}/^{238}\text{U}$ for *Colonie* particles [1] and PGDP tails assays [17]. There appears to be good compatibility between select PGDP tails assays, which is confirmed by $^{234}\text{U}/^{238}\text{U}$ data presented in Figure 2. The mixing lines are discussed in the text. The average DU composition from bulk samples that aggregate these particles is plotted as an ellipse [3]. Three of the mixing lines are supported by $^{234}\text{U}/^{238}\text{U}$ data, plotted in Figure 2.

Inset i. Enlargement from the main clustered region, showing that the *Colonie* particles cluster towards higher ^{236}U than for the 1967 tails assay. This can be explained by evolution of the PGDP tails towards the next reported assay (31/12/1968).

Inset ii. Plot of all PGDP tails assays, $^{235}\text{U}/^{238}\text{U}$ against reporting date. This highlights the exceptionally low $^{235}\text{U}/^{238}\text{U}$ tails from 1956. The majority of the PGDP tails assays have $^{235}\text{U}/^{238}\text{U} > 2.5 \times 10^{-3}$; with one inferred exception, the *Colonie* particles are not compatible with these ($< 2.4 \times 10^{-3}$).

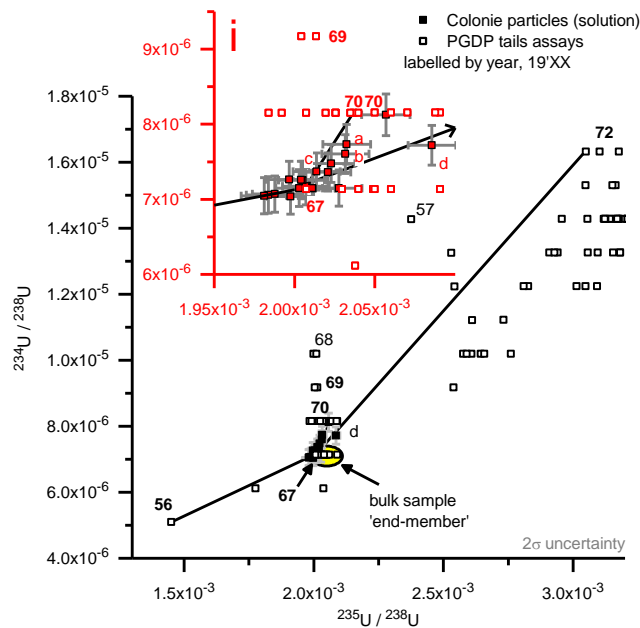


Figure 2 (and inset i). Plot of $^{234}\text{U}/^{238}\text{U}$ against $^{235}\text{U}/^{238}\text{U}$ from individual *Colonie* particles, compared with the PGDP tails assays [17]. Three mixing lines have been drawn through the data, connecting three tails assays to 01/08/1967. Particles labelled **a**, **b** and **c** are compatible with mixing towards a low $^{236}\text{U}/^{238}\text{U}$ batch from 31/12/1970 (see Figure 1). The particle labelled **d** does not show good compatibility with the PGDP tails assays, having low ^{234}U and high ^{236}U abundance. The average DU composition from bulk samples that aggregate these particles is plotted as an ellipse [3].

The following observations are made from data presented in Figures 1 and 2:

- i. From the $^{234}/^{238}\text{U}$ dataset, presented in Figure 2, the *Colonie* particle data appear to cluster around the PGDP tails assay from 01/08/1967 ($7.1 \times 10^{-6} \text{ }^{234}\text{U}/^{238}\text{U}$ and $2.007 \times 10^{-3} \text{ }^{235}\text{U}/^{238}\text{U}$). The mean of the *Colonie* particles' ratios are $(7.3 \pm 0.1) \times 10^{-6} \text{ }^{234}\text{U}/^{238}\text{U}$ and $(2.02 \pm 0.01) \times 10^{-3} \text{ }^{235}\text{U}/^{238}\text{U}$. From bulk soil samples that aggregate these particles, the average DU composition was $(7.1 \pm 0.3) \times 10^{-6} \text{ }^{234}\text{U}/^{238}\text{U}$ and $(2.05 \pm 0.06) \times 10^{-3} \text{ }^{235}\text{U}/^{238}\text{U}$ [3]. This provides strong evidence that PGDP tails from 1967 dominated the NLI feedstocks. Thus, it can be inferred that the majority of the NLI contamination occurred during or after 1967.
- ii. In Figure 1, the *Colonie* particles cluster above the tails assay from 01/08/1967, spreading towards higher $^{236}\text{U}/^{238}\text{U}$ reported for 31/12/1968. A smaller cluster of *Colonie* particles plots close to the 31/12/1968 composition. A single *Colonie* particle plots close to PGDP tails from 31/12/1969. Thus, there is some evidence that NLI feedstocks originated from PGDP tails that evolved through 1967 – 1969. The isotopic composition of four particles collected by air filters more than ten years later, plot in this region [20].
- iii. There is a tail from the main clustered region of Figure 1 towards low $^{236}\text{U}/^{238}\text{U}$, with little $^{235}\text{U}/^{238}\text{U}$ variation. There are a number of candidate 'batches' in $^{236}\text{U}/^{238}\text{U}$ against $^{235}\text{U}/^{238}\text{U}$ space, with which the main cluster could form a mixing line. The particles labelled **a**, **b**, and **c** are also plotted in Figure 2 for $^{234}\text{U}/^{238}\text{U}$ against $^{235}\text{U}/^{238}\text{U}$. When $^{234}\text{U}/^{238}\text{U}$ is considered, the composition from 31/12/1970 is the only compatible low $^{236}\text{U}/^{238}\text{U}$ candidate. However for $^{234}\text{U}/^{238}\text{U}$, the mixing line is shifted toward the composition from 30/06/1970. Additionally, there is evidence of a discrete mixing line departing from the cluster towards 30/06/1970 in Figure 1i (supported by a single data point in Figure 2). Thus, there appears to be evolution between the periodic tails assays. This probably reflects differences in the inputs to the PGDP; in 1970 the majority of these were tails from Oak Ridge, Portsmouth and Hanford sites.
- iv. There is a spread from the main clustered region of Figure 1 towards higher $^{236}\text{U}/^{238}\text{U}$ and higher $^{235}\text{U}/^{238}\text{U}$. This is best explained by mixing between each of the previously identified isotopic

compositions with PGDP tails from 31/12/1972. Inhomogeneous, 3-way mixing can account for the compositions that fall within the triangles delimited by the previously identified mixing lines.

- v. Two of the 115 particles analysed by Lloyd *et al.* [1] are isotopically similar to the tails assay from 01/04/1956, with an exceptionally low $^{235}\text{U}/^{238}\text{U}$ ratio. These particles uniquely could have been emitted at the beginning of NLI's operations at Colonie. There is evidence of slight mixing with the isotopic composition from 31/12/1969. $^{234}\text{U}/^{238}\text{U}$ data are not available for these particles.
- vi. PGDP tails assays that are compatible with the Colonie particles, but not specifically required to explain their range of isotopic compositions, were reported from 01/07/1957, 01/08/1964, 01/11/1965, 01/07/1966 and 30/06/1969.
- vii. Tails produced between April 1957 and May 1964 can be excluded due to their high $^{235}\text{U}/^{238}\text{U}$ ratios. There is little justification to include tails produced after 1972.
- viii. The particle labelled **d** in Figures 1 and 2 cannot be explained from the PGDP tails assays dataset, having low ^{234}U with high ^{236}U . It is possible that the periodic tails assays do not represent the full range of DU produced from PGDP, or that on occasion NLI sourced feedstocks from other plants.

Thus, a total of seven PGDP tails batches supplied the majority of the NLI feedstocks (similar to tails assays from: 01/04/1956, 01/08/1967, 31/12/1968, 31/12/1969, 30/06/1970, 31/12/1970 and 31/12/1972). The isotopic signatures of these tails do not follow a simple 'evolution', as was previously speculated in Lloyd *et al.* [1]. It can be inferred that the 01/08/1967 batch contributed significantly to the NLI emissions, and that the majority of the contamination was therefore emitted from NLI site after 1967. The majority of the contamination footprint appears to have been emplaced by 1979 [3].

Latest generation MC-ICP-MS instruments are available with configurations that allow for all of the uranium isotopes to be simultaneously measured on discrete dynode type secondary electron multipliers. These offer better linearity and stability characteristics when compared with continuous dynode secondary electron multipliers. Options are also available for abundance-sensitivity filters for both ^{236}U and ^{234}U . In addition to this, the NEPTUNE *Plus* with Jet Interface option (Thermo Scientific, Bremen, Germany) can achieve sample utilization efficiencies of c. 4 % (solution through to ion detection) [21]. Amplifiers with 10^{12} and 10^{13} ohm feedback resistors also improve signal to noise ratios for small ion beams on Faraday cups [22]. The combination of these developments greatly improves the capabilities of MC-ICP-MS for nuclear forensic applications.

3. Conclusions

The Colonie DU particles show a spread of isotopic compositions ($^{235}\text{U}/^{238}\text{U}$ & $^{236}\text{U}/^{238}\text{U}$) compatible with the tails from the Paducah gaseous diffusion plant. Assuming that DU tails from the other US enrichment plants had disparate $^{234}\text{U}/^{238}\text{U}$, the NLI feedstocks most likely originated from Paducah. There is evidence of mixing between at least seven batches of feedstocks with discrete isotopic signatures. The majority of the NLI contamination appears to originate from tails produced from 1967 – 1969. This knowledge helps constrain the timing of emissions, and subsequent environmental processes that have dispersed this contaminant. The acquisition of a large and precise dataset that can now be convincingly related to a specific enrichment plant, further supports the advantages of LA-MC-ICP-MS for nuclear forensics. In addition to $^{235}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$, $^{234}\text{U}/^{238}\text{U}$ data is useful for source identification.

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