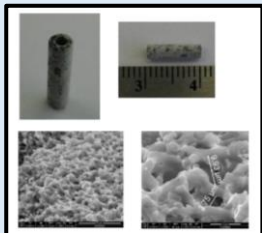


## ABSTRACT

- The work described here relies on **organic compounds** used in the nuclear cycle (extractants, diluents and specific additives) to provide a valuable information about the origin and process of nuclear materials.
- When used in headspace mode, MONOTRAP is an efficient method to capture trace-level volatile and semi-volatile organic markers from small amounts (10 – 100 mg) of uranium ore concentrates (UOCs).



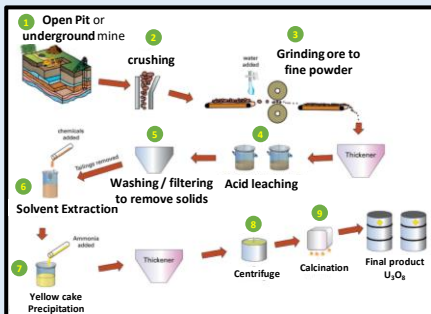
Photos and SEM of MONOTRAPs

- MONOTRAP is easy to implement in the field for control of nuclear material in the context of nuclear safeguards, without any contact with the radioactive samples, avoiding radiological contamination controls.
- When combined with the high-resolution power and mass accuracy of a GC/Q-TOF mass analyzer, using both electron impact and chemical ionization and a comprehensive search against our “in-house” spectral database of “non-proliferation” organic chemical markers: **this new method has**

**the potential to facilitate the identification of nuclear production processes and thus to verify the correctness and the completeness of the declarations made by the States about their nuclear material and activities.**

## BACKGROUND / INTRODUCTION

- Uranium is usually recovered from ores by hydrometallurgical processes that includes grinding, leaching, and purification in organic solvents and diluents



Simplified uranium extraction process

## HIGH RESOLUTION MASS SPECTROMETRY INSTRUMENTATION AT THE CEA FOR NUCLEAR SAFEGUARDS

- The main interest of HRMS lies in their capacity to measure the masses of the organic molecules in a precise and accurate way
- It is then possible to trace the accurate mass to their raw molecular formula and thus, most often, to the identity of the targeted analytes

# Molecular expertise at the CEA for nuclear safeguard: does organic matter?

Maxime C. BRIDOUX

CEA/DAM/DIF

[maxime.bridoux@cea.fr](mailto:maxime.bridoux@cea.fr)

Françoise LEPRINCE and Françoise ZIELINSKI

## MAIN CONTENT

- For a nominal mass ( $m/z$ ) of 28, using a low-resolution mass spectrometer (i.e. a simple quadrupole), it is not possible to differentiate between carbon monoxide (CO) nitrogen ( $N_2$ ) molecules since both molecular structures all have the same nominal mass (e.g. 28 amu).
- In contrast, using a high-resolution mass spectrometer ( $R_s \sim 15\,000$ ) it is easy to distinguish the molecules  $^{12}C^{16}O$  (red peak) and  $^{14}N_2$  (blue peak) since they have exact masses equal to 27.99491 and 28.00614 amu respectively.

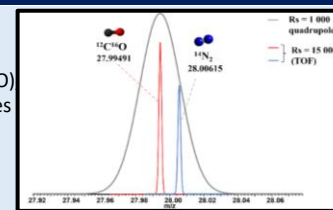
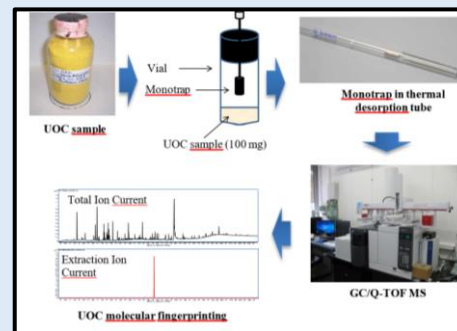


Illustration of the advantage of a high resolution TOF instrument over a low resolution instrument such as a single quadrupole.

## MOLECULAR FINGERPRINTING OF URANIUM ORE CONCENTRATES

- Approximately **100 mg** of UOCs are weighted and transferred into a glass vial in a disposable glove bag. A volume of 1  $\mu$ L of a mixture of 3 internal standards is spiked directly into the UOC samples. The MonoTrap device is then inserted in the headspace of the vial and the vial is placed onto a heated plate at 175°C for 11 hours. This step transfers the volatile and semi-volatile compounds onto the MonoTrap.

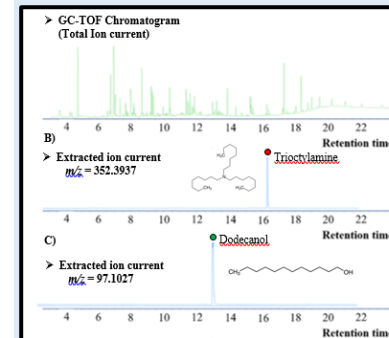


MonoTraps are used for headspace sampling of UOCs, transferred into thermal desorption tubes and analyzed by thermal desorption GC/Q-TOF MS

optimized beforehand. The chromatographic analysis is performed with a constant helium flow rate (1 mL/min) on a HP5MS column

## APPLICATION TO A UOC SAMPLE OF KNOWN ORIGIN

- The sample considered is a mining concentrate from the **Rössing plant in Namibia**. This plant exploits open-pit granite deposits.



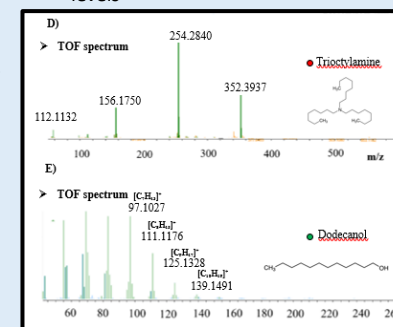
GC/Q-TOF chromatogram of a UOC sample from the Rössing plant.

- The process is based on the extraction of uranium in sulfuric acid, purification on an ion exchange resin of Duolite a de-extraction step by diluted sulfuric acid and a solvent extraction step in a mixture of 7 vol. % **Alamine 336 / 3% isodecanol** in a **Shellsol 2325** type petroleum diluent.

- The headspace MonoTrap extraction of UOC samples, followed by their GC/Q-TOF thermal desorption analysis and by a comprehensive search against our “in-house” database revealed the detection of trioctylamine and dodecanol at trace levels

- The extracted ion current (EIC) at  $m/z$  value 352.3937 (deprotonated molecular ion  $[M-H]^+$  of trioctylamine ( $[(CH_3(CH_2)_7]_3N$ )) results in a single chromatographic peak that eluted at the exact same retention time as trioctylamine pure standard.

- The combination of i) exact mass on both molecular ion and fragments, ii) same retention time as a pure standard and iii) spectral library match with our database **makes a definitive positive identification for both the extractant trioctylamine and of the additive dodecanol**



Q/TOF-MS spectrum of trioctylamine and of dodecanol.

## CONCLUSION

- When used in headspace mode, Monolithic Material Sorptive Extraction showed to be an efficient method to capture trace-level volatile and semi-volatile organic markers from small amounts (10 – 100 mg) of UOCs.
- This sampling methodology is easy to implement in the field for control of nuclear material in the context of nuclear safeguards, without any contact with the radioactive species, avoiding the need for radiological contamination controls.

