Analysis of uranium ore concentrates for origin assessment

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Summary. In this study the most important analytical methodologies are presented for the nuclear forensic investigation of uranium ore concentrates (yellow cakes). These methodologies allow to measure characteristic parameters which may be source material or process inherited. By the combination of the various techniques (e.g. infrared spectrometry, impurity content, rare-earth pattern and U, Sr and Pb isotope ratio analysis by mass spectrometry), the possible provenances of the illicit material can be narrowed down to a few options and its declared origin can be verified. The methodologies serve for nuclear forensic investigations as well as for nuclear safeguards, checking the consistency of information.

1. Introduction

Currently one of the most important concerns in public about the use of nuclear energy is the possible diversion of nuclear materials for malicious purposes. The international safeguards system of the International Atomic Energy Agency (IAEA) aims the timely detection of diversion of such materials. Comprehensive safeguards agreements are designed to verify the correctness and completeness of States’ declarations. By this means it provides credible assurance in the absence of undeclared nuclear activities. According to the definition of the IAEA, fissionable materials (233U, 235U and 239Pu) and source materials (e.g. natural uranium and thorium or depleted uranium in metal, alloy or compound form) belong to the category of nuclear materials. Concentrates of natural uranium (generally called yellow cake) or thorium have a special role in this classification being an intermediate product between the naturally occurring ore and the feed in the next stage of the fuel cycle. Although the term source material shall not refer to the ore concentrate if it is used for non-nuclear processes, accountancy and verification do apply if they are to be used for nuclear purposes. Due to the open and free availability of technology to recover uranium or thorium from natural sources also by unconventional means (for instance as a by-product in fertilizer production) it is highly important to verify the origin of such materials [1].

Should uranium ore concentrate be diverted and at a later point in time detected and intercepted, the question on the origin of the material will be of primary importance. This will require a comprehensive and in-depth analysis of the material. Such nuclear forensic investigation, due to its complexity, involves a wide range of analytical techniques, including radiometric measurements (e.g. by gamma and alpha spectrometry), isotope ratio measurements (e.g. by thermal ionization mass spectrometry or inductively coupled plasma mass spectrometry (ICP-MS)), elemental analysis (e.g. by ICP-MS or laser induced breakdown spectroscopy) and structural analysis (e.g. scanning electron microscopy or infrared spectroscopy) [2–5]. These measurement techniques could give complementary pieces of information on the material with different capabilities and limitations.

The aim of the present study is to describe some of the most important techniques and their uses for the analysis of uranium ore concentrates (UOCs). The performance of the measured characteristics is also illustrated for a real confiscated yellow cake material (Fund-26). The main task was to perform nuclear forensic analysis on the material and to give assessment on the possible intended use and source of the material and to verify the statements about its origin.

2. Experimental

2.1 Investigated samples

In 2003 radioactive material was detected in a shipment of scrap metal in Rotterdam Harbour, the Netherlands. The shipment arrived from a dealer in Jordan. Part of the material was sent to Institute for Transuranium Elements (ITU) for analysis. External sources suggested that the items sampled originated from Iraq. Therefore, the samples were subjected to nuclear forensic analysis. The results were compared with those of the archive UOC samples of known origin in the ITU database and with data accessible in the open-source literature.

2.2 Analytical procedures

Infrared absorption measurements were performed on the solid material using the KBr pellet technique. The spec-
tra were recorded with a Fourier-transform infrared spectrometer (FT-IR) from Perkin–Elmer (Beaconsfield, England). 2–4 mg of the sample material was mixed with approximately 150 mg spectral grade KBr in an agate mortar and thoroughly ground and homogenized. The powder was pressed into a pellet with a hydraulic press.

The impurity determinations of the materials were carried out using an Element2 Inductively Coupled Plasma Mass Spectrometer, ICP-MS (Thermo Inc., Bremen, Germany). The dissolved samples were diluted to a uranium concentration of approximately 100 μg g⁻¹. The elemental composition was determined using matrix-matched external calibration applying Rh internal standard. The uranium concentration was determined after a successive gravimetric dilution of the dissolved material using external calibration.

The rare-earth (REE) elements were determined after chemical separation. The experimental details of the method and its validation are described in [6]. In short, the trivalent lanthanides were separated from the uranium matrix and other matrix components using extraction chromatography (TRU™ resin). The REE concentrations were determined in the aliquot using ICP-MS, and the lanthanide content of the original material can be calculated taking into account the weights of the sample material used for the separation, the weight of the aliquot after separation and the chemical recovery estimated by the analysis of a reference material measured parallel with the sample [6].

The isotopic analysis of U, Sr and Pb were performed with a Nu Plasma multi-collector ICP-MS instrument (Nu Instruments, UK). As uranium is present as a major component, no prior chemical separation was necessary. For the measurement the sample was diluted to a uranium concentration of approximately 100 ng g⁻¹. The measured isotope ratios were corrected for the mass bias using Russell’s formula. The Sr and Pb isotopic compositions were determined after sequential separation of the analytes. The details of the chemical separation and the measurements are discussed in detail elsewhere [7].

3. Results and discussion

3.1 Visual characterization

The bulk sample (referred to later as “Fund-26”) was a wet brownish yellow powder and was found on a filter bag inside a small steel filter housing (40 × 40 × 55 cm, gross weight 35 kg). The outside of the vessel was reported to be caked with dried mud, i.e. it apparently had been buried at some time. By its colour and the visible inhomogeneity (Fig. 1) it could be concluded that the material can only be a rough intermediate product. By its colour certain possible yellow cake compositions, for instance fully calcined uranium oxide can be excluded.

3.2 Infrared analysis

Infrared analysis of solid materials provides information on structural aspects of the material and thus allows conclusions on its composition. It can furthermore detect co-existing phases (if present), and is capable to estimate also

![Fig. 1. Scanning electron microscopy picture of the uranium ore concentrate sample (Fund-26) seized at Rotterdam Harbour.](image1)

![Fig. 2. The infrared absorption spectrum of the Fund-26 sample.](image2)

the uranium content by the intensity of the absorption of the characteristic uranium containing groups (e.g. UO₂²⁺). The infrared spectrum of the Fund-26 sample is shown in Fig. 2. The Fund-26 sample was found to be identical with the water-containing ammonium uranyl carbonate (AUC) spectrum reported in the literature [8]. The characteristic absorption bands can be assigned in the spectrum: the asymmetric stretching of the uranyl-group (ν₃) at 900 cm⁻¹, the U ← O link at 470 cm⁻¹, the ν₄ and ν₃ frequencies of the NH₄⁺-group at 1400 cm⁻¹ and 3200 cm⁻¹, respectively, the H₂O bending at 1625 cm⁻¹, and the ν₁ and ν₄ vibration bands of the CO₃²⁻ group at 1380 and 1525 cm⁻¹, respectively. Besides the composition of the material several impurities can also be detected in the spectrum: especially NO₃⁻ (having a sharp absorption peak at 1380 cm⁻¹) and a smaller band at 1120 cm⁻¹, which is characteristic to the sulphate group. These anions are usually introduced into the material during dissolution of ura-
nium from the ore body and purification. After precipitation of the product, the respective anions remain in the solid as anionic impurities. By the infrared analysis it can be concluded that the material is AUC, which was precipitated from a nitrate solution and carrying a smaller amount of sulphate. This AUC process was developed in the 1960’s and usually involves a precipitative re-extraction of uranyl nitrate from the organic phase [9]. By looking only the infrared spectrum the presence of other salts, such as (NH₄)₂(UO₂(CO₃)₂·(H₂O)₂ or (NH₄)₃(UO₂)₃(CO₃)₃·OH·(H₂O)₅, which are typically being formed in parallel with the AUC during the precipitation step, can not be excluded [9]. Most probably the source of the nitrate is from the solvent extract, while sulphate is the residual of the H₂SO₄ used for the dissolution of the ore or feed material. This scheme was also applied in Iraq at the Al Qaim facility, where the yellow cake was produced as a by-product from phosphorite ore by solvent extraction [10].

### 3.3 Uranium content and impurity results

The material, as expected from the visual characterization, contains high amount of impurities. Besides the high alkali and alkaline earth content, the elevated levels of Al (830 ppm), Cd (8.6 ppm), Cr (2300 ppm), Fe (9300 ppm), Ni (5600 ppm), Zn (630 ppm), P (3400 ppm) and V (12 ppm) were found. In the previous studies high-level phosphorous content was found to be a distinctive signature for UOCs produced from phosphorite ore [11]. The other above mentioned impurities present in this material (Al and various transition metals) are more applicable to compare them with those of a material produced with a similar method from the same feed material due to the elemental fractionation through all the metallurgical process (so-called comparative parameter). However, in this case, as the sample probably derives from the first steps of production, when this fractionation is less apparent, some conclusions can be drawn. The Tethyan phosphorites of Iraq are generally enriched in Cr, Ni, Cu, V and Zn [12] as well as in Cd and Ag [13]. As the confiscated material is in a crude form relatively well-preserving at least the order of magnitude of the major impurities, the results of the confiscated material are well in line with the declaration and statement.

The uranium content of the material was 32%. This value is significantly lower than the calculated uranium fraction of the stoichiometric composition of AUC (49.0%), even after taking into account the total impurity content, indicating the high moisture content.

### 3.4 Uranium isotope ratio results

The ²³⁵U/²³⁸U and ²³⁴U/²³⁸U ratios measured by MC-ICP-MS were (7.253 ± 0.013) × 10⁻³ and (5.502 ± 0.066) × 10⁻⁵, respectively, identical with those of the natural uranium isotopic composition. Traces of anthropogenic ²³⁶U content (²³⁶U/²³⁸U) ratio is approximately (1.4 ± 0.2) × 10⁻⁷ were detected by the Nu Plasma MC-ICP-MS measurement indicating the presence of previous neutron irradiation and reprocessing activity. The typical abundance sensitivity of the instrument using the deceleration filter at m/z = 236 for the ²³⁶U/²³⁸U ratio is about 10⁻⁸, and the hydride contribution, which was minimized using an Aridus desolvation unit, is below 5 × 10⁻⁵. This result has been verified also by a thermal ionization mass spectrometric measurement (TIMS) using modified total evaporation method (Triton, Thermo Inc. Bremen, Germany). The measured ²³⁶U/²³⁸U ratio is (1.545 ± 0.002) × 10⁻⁷.

### 3.5 Rare-earth elemental analysis

The rare-earth elemental (REE) pattern was found to be an important signature to determine the ore-type used as source for the production of uranium ore concentrate, since the REE pattern is invariant in most hydrometallurgical processes [11]. The REE pattern of the confiscated material is shown in Fig. 3. The pattern is a flat, shale-like pattern without Ce or Eu anomaly. This pattern was previously found in UOCs produced from certain sandstone-type deposits and in reworked sedimentary phosphorites [11]. Although it could not be verified with a comparison sample, according to the literature the Iraqi phosphate beds are a sequence of limestone, marl, shale and siltstone, and it included syngenetic deposition of phosphate under reducing condition [12, 13]. This can explain the shape of the flat pattern and the lack of Ce anomaly. The typical REE patterns of some phosphorites from the Middle East and the Phosphoria formation together with the typical pattern of a continental “old” phosphorite (Khubsugul) are also shown in Fig. 3 [14–16]. The marine sedimentary Tethyan phosphorite deposits of the Middle East are characterized either by seawater-like pattern (e.g. phosphorite from Israel in Fig. 3) or shale-like flat pattern (e.g. Egypt sample). Clearly the REE pattern of Fund-26 has a similar pattern to this latter group.

### 3.6 Strontium and lead isotope ratio measurements

The measured ⁸⁷Sr/⁸⁶Sr isotope ratio in the confiscated samples in comparison with those of other UOCs from the ITU database is shown in Fig. 4 [7]. In the previous study the Sr isotope ratio was always found to be low (approximately 0.708) in phosphorite-based materials. This is due to the fact that this value is determined by the Sr/Rb ratio in the mineral, which is always very high in phosphorite due to the

![Fig. 3. Normalized REE pattern of the various phosphorites and the Fund-26 sample [14–16].](image)
2.1 than 2 composition indicating a young uranium ore deposit (less distinguishable from the natural representative lead isotopic signatures), e.g., the Paleocene Akashat deposit, which was mostly used for the alimentary Tethyan deposits in the Middle East, including the Mulberry samples (both are phosphorite ores) are low compared to the other uranium ore deposits. The value measured for Fund-26 compares well to these two samples.

The Pb isotopic composition in the Fund-26 (the 204Pb, 206Pb, 207Pb and 208Pb are 1.357 ± 0.005, 25.91 ± 0.21, 21.03 ± 0.11 and 51.70 ± 0.13, respectively) was indistinguishable from the natural representative lead isotopic composition indicating a young uranium ore deposit (less than 2 × 109 years) [7]. This is valid for all the marine sedimentary Tethyan deposits in the Middle East, including the Paleocene Akashat deposit, which was mostly used for the uranium production in Iraq [12].

4. Conclusions

Nuclear forensic methods are highly important tools to verify the declared origin of uranium ore concentrates. Moreover, they can be applied to narrow down or identify the origin of unknown uranium ore concentrates intercepted from illicit trafficking. Most of the methods can be applied using comparative signatures, i.e. requiring a comparison sample or a database (containing information on samples of known origin). Some signatures, however, e.g. REE pattern, Pb dating of the ore used for production) are of predictive nature, thus they provide information on the provenance of the uranium ore concentrate without the need for a direct comparison. Using the measurement results in conjunction with open-source literature information (e.g. from geology or uranium metallurgy) the possible origin can be narrowed down to relatively few possibilities. However, measurement of as many parameters as possible is necessary. For the Fund-26 material the investigated parameters corroborate information on the presumed origin. Other parameters (e.g. oxygen and neodymium isotope ratio measurement, analysis of trace-level organic residual) can be used for additional verification of the results.

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