Raman spectroscopy of uranium compounds and the use of multivariate analysis for visualization and classification

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A B S T R A C T

Raman spectroscopy was used on 95 samples comprising mainly of uranium ore concentrates as well as some UF_4 and UO_2 samples, in order to classify uranium compounds for nuclear forensic purposes, for the first time. This technique was selected as it is non-destructive and rapid. The spectra obtained from 9 different classes of chemical compounds were subjected to multivariate data analysis such as principal component analysis (PCA), partial least square-discriminant analysis (PLS-DA) and Fisher Discriminant Analysis (FDA). These classes were ammonium diuranate (ADU), sodium diuranate (SDU), ammonium uranyl carbonate (AUC), uranyl hydroxide (UH), UO_2, UO_3, UO_4, U_3O_8 and UF_4. Unsupervised PCA of full spectra shows fairly good distinction among the classes with some overlaps observed with ADU and UH. These overlaps are also reflected in the poorer specificities determined by PLS-DA. Higher values of sensitivities and specificities of remaining compounds were obtained. Supervised FDA based on reduced dataset of only 40 variables shows similar results to that of PCA but with closer clustering of ADU, UH, SDU, AUC. As a rapid and non-destructive technique, Raman spectroscopy is useful and complements existing techniques in multi-faceted nuclear forensics.

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1. Introduction

Nuclear forensics or *nuclear forensic science* is a discipline that has emerged from the need to tackle illicit trafficking of nuclear material, with a view to provide hints on the history of the material [1–3]. Nuclear forensics is not limited to the analysis of special nuclear material, but also involves radioactive materials since there are several applications for them. For instance, radioisotopes are widely used in medicine (treatment, diagnostic or sterilization of medical supplies) or industry (gauging or radiography).

Upon the confiscate of an unknown or lost radioactive material, the immediate tasks would be to understand the material, that is, '*What is it*?' Additionally, questions such as '*how and for what*

purpose was it produced?', '*Where was the material produced?*' and possibly '*How it got to the position where it was found?*' are more questions demanding a right answer.

The multi-disciplinary field tackles the questions by studying characteristic parameters of the nuclear material. These measurable parameters also referred as *signatures*, relate to the physical, chemical and isotopic characteristics of the material [4]. There is neither single methodology that could be applied to any found material, nor any single measurable parameter that would suffice in exclusive identification of the origin of the material. In this sense, the analysis of a combination of several characteristic parameters would elevate the confidence in nuclear forensic conclusions. This is the reason why, research is always carried out to look into prospective signatures of various nuclear materials (uranium and plutonium) at all stages of the nuclear fuel cycle.

In particular, this paper studies a group of compounds known as uranium ore concentrates (UOCs) and other uranium compounds such as UF_4 and UO_2. UOCs are products of uranium mining and milling processes at the early stages of the uranium fuel cycle. Uranium is leached from its ore, purified and subsequently

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concentrated. The concentrated uranium solution is then precipitated with a reagent, which can be ammonia/ammonium hydroxide, hydrogen peroxide, sodium hydroxide, ammonium carbonate or milk of magnesia. Products of ammonium diuranate, uranyl peroxide, sodium diuranate, ammonium uranyl carbonate and uranyl hydroxide are thus formed. Further drying and calcinations lead to the formation of UO_3 and U_3O_8. Although the colours of these powders range from yellow to orange, brown, green and black, they are collectively and colloquially known as yellow cakes [5]. These UOCs are further subjected to conversion processes where UF_4 and UO_2 (termed as non-UOC in this paper) are produced [6].

Various measurable parameters associated with yellow cakes have been identified as useful nuclear forensic signatures, such as analysis of uranium (major isotopes) [7,8], thorium [9], lead [10–12], strontium [11], sulphur [13] and neodymium [14] (minor isotopes), trace elements including rare-earth elements [7,10,12,15–17], non-volatile organics [18] and anionic impurities [17,19,20]. Spectroscopic techniques such as infrared [20], near infrared reflectance [21,22] and laser-induced breakdown spectroscopy have also been used to measure yellow cakes [23].

More recently, we have demonstrated the feasibility of using Raman spectroscopy as a tool for nuclear forensics purposes in the analysis of yellow cakes [24]. In fact, nuclear forensics has been applied to real cases of found or stolen UOCs [25–27] and therefore, the analytical scenario is real for this class of material, often traded in large quantities. Although Raman spectroscopy has been applied for the analysis of UOCs [28–33], the measurement of larger number of samples and different sample composition is necessary in evaluating its robustness as a signature for nuclear forensic purposes. To add further demonstration of Raman as a suitable nuclear forensic technique, it is applied in this study to 95 UOC and non-UOC samples of varying compositions with the goal of using different multivariate analysis for evaluation.

2. Experimental

2.1. Investigated samples

2.1.1. Industrial yellow cakes
There were a total of 89 industrial UOCs investigated in this study. These samples of UOCs represent a large number of the world's uranium mines. All the samples are in powder form and were pressed into pellet using hydraulic press 3630 X-Press (SPEX Industries Inc., USA) to ease handling and to avoid possible contamination. A pressure of approximately 74 MPa was applied to the samples.

2.1.2. Laboratory synthesized yellow cakes
Six additional yellow cakes were prepared in our laboratory. The compounds were synthesized under controlled conditions by precipitation from chemically pure uranium nitrate solutions with various reagents. The details can be found elsewhere [24]. The synthesized compounds are sodium diuranate, ammonium diuranate, uranyl peroxide, uranyl hydroxide and two samples of ammonium uranyl carbonate. Five samples were dried at 105 °C while one of the two ammonium uranyl carbonate samples was dried at room temperature.

In total, the given/assumed composition (from the industry) or known composition (from laboratory) of all the 95 samples are distributed as ammonium diuranate – ADU (35), ammonium uranyl carbonate – AUC (4), sodium diuranate – SDU (6), U_3O_8 (13), uranium hydroxide – UH (20), UF_4 (3), UO_2 (2), UO_3 (4) and uranium peroxide – UO_4 (8). In addition, the assumed compositions were verified or modified based on our infrared data published recently [20].

2.2. Instrumentation

2.2.1. Raman spectrometer
Senterra bench-top model of Raman spectrometer from Bruker® (Germany) was used for the measurements of the ore concentrates. Measurement with silicon was done daily prior to measurements to ensure that the sensitivity of the instrument does not change significantly on the different days of measurement. Calibration of wavenumbers is done automatically by the instrument with neon.

Two different frequency lasers, 785 and 532 nm are available with Senterra. The former permits largely the measurements of all samples, while the latter is not favourable as the higher energy causes much fluorescence and sample degradation due to the heat induced from the laser. Laser power of 10 mW or 25 mW is mostly used on the samples. For calcined samples (darkly coloured samples), 10 mW has to be used as the use of 25 mW will lead to the instantaneous formation of oxide, thus changing the real composition of the sample. Integration times are typically 10 s and are increased for samples that yield weaker signal. The selected spectral range is 1560–90 cm^{-1} as no peaks are observed outside this region.

2.2.2. Infrared spectrometer
Fourier Transform Infrared (FT-IR) measurements were performed using Perkin Elmer System 2000 spectrometer (from Perkin Elmer Ltd., Beaconsfield, UK) with the spectra range of 400–4000 cm^{-1} and 2 cm^{-1} resolution. The full details can be found elsewhere [20].

2.3. Multivariate data evaluation

A PLS Toolbox version 7.5.2 (Eigenvectors Research, Inc., USA) for Matlab version 8.1 (The Matworks Inc., Natick, MA, USA) software was used for multivariate data analysis; in particular principal component analysis (PCA), partial least square discriminant analysis (PLS-DA) and Fisher Discriminant Analysis (FDA) were applied on Raman spectra.

2.3.1. Principal component analysis
PCA is a central part in multivariate explorative data analysis. High dimensional and collinear datasets are reduced in dimensionality to reveal latent and relevant information in data [33]. In this study, an exploratory analysis based on PCA, was applied on Raman spectra and, as internal cross validation, the random subsets cross validation method was applied using a data split of 9 and 20 as number of interactions.

Before applying the algorithm, the spectral range included in the evaluation was reduced from 1560–90 cm^{-1} to 1150–120 cm^{-1} to exclude regions where there are no peaks, arising from molecular vibrations. Pre-processing includes baseline correction, normalization and smoothing (Savitzky–Golay). The spectra obtained by Raman spectroscopy give information about the molecular composition and impurities, therefore the sample compositions were selected as labels.

2.3.2. Partial least square discriminant analysis
A sample classification was performed by PLS-DA. The PLS-DA is considered a supervised class-modelling method in which prior knowledge of the classes of the samples test is required. The PLS-DA is based on Partial Least Square Regression (PLSR). The X matrix is the PCA scores while the Y matrix is constructed on columns of binary numbers where 1 represents the sample member of a class and 0 if it is not a member. The sample membership of a class is then modelled and predicted as a 0 or 1 within a threshold limit of usually 0.5. Diagnostic plots of different