

## **RARE EARTHS IN URANIUM COMPOUNDS AND IMPORTANT EVIDENCES FOR NUCLEAR FORENSIC PURPOSES**

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### **ABSTRACT**

Nuclear forensics mainly focuses on the nuclear or radioactive material and aims to providing indication on the intended use, the history and even the origin of the material. Uranium compounds have isotopic or chemical characteristics that provide unambiguous information concerning their origin and production process. Rare earths elements (REE) are a set of sixteen chemical elements in the periodic table, specifically the fourteen Lanthanides in addition scandium and yttrium. These elements are often found together but in widely variable concentrations in uncommon varieties of igneous rocks. A large amount of uranium is in rare earths deposits, and may be extracted as a by-product. Accordingly, REE in uranium compounds can be used as an evidence of uranium origin. In this study, REE was determined in uranium compounds from different origin. Measurements were carried out using a High resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) Element 2, in low resolution mode (R-300).

### **1. INTRODUCTION**

At the beginning of the 1990's, the first incidents involving nuclear or other radioactive material were reported mainly in the Europe, with the breakdown of the Soviet Union. At that period, the International Atomic Energy Agency (IAEA) recorded more than 800 cases of illicit trafficking of nuclear or radioactive materials, reported from Germany, Czech Republic, Hungary and other central European countries.

Owing to such events, in 1995 the IAEA created a global database so-called IAEA Illicit Trafficking Database (ITDB), a system established to record and analyze incidents of illicit trafficking in nuclear and other radioactive material reported from 106 States participants currently [1]. The ITDB also includes incidents dating back to 1993. Accordingly, all these reports are focused on provide reliable information, previously unavailable, due to its dispersion [2]. Despite of the efforts on providing national policy makers, decision makers and technical managers with consolidated guidance for responding to incidents involving the interdiction of nuclear and other radioactive material, the numbers of incidents reported to the IAEA has increased over the past 18 years. . During all over these years, some real events became known worldwide; as topics of studies, these seizures were characterized for nuclear forensic purposes.

#### **1.1. Cases Studies**

In March 1992, the first seized nuclear material was intercepted in Augsburg, Germany and it consisted of 72 uranium pellets. The results of this material characterization were sufficient to attribute its intended use being fuel pellets for a Russian type graphite moderated reactor (RBMK),

with also a clue of the origin of the material being either Ulba Metallurgy Plant in Kazakhstan or Elektrostal in Russia [3]. In May 1994 in Tengen, Germany, the police found into a house 56g of radioactive material; the analyses showed that the radioactive powder contained 10 wt.% of Pu with a  $^{239}\text{Pu}$  enrichment of 99.75%. In August 1994, at Munich airport in Germany, three men were stopped carrying a suitcase containing 560g of Pu and U oxide powder and 210g of Li metal; the powder consisted of 64,9 wt.% of Pu and 21.7 wt.% of U [4]. In February 1997 two pieces of radioactively contaminated metal were found at the scrap metal yard in Karlsruhe, Germany. The elemental composition of the steel revealed its origin being either Eastern Europe or Russia [3].

In 1998 a nuclear fuel element was intercepted by the Italian law enforcement during an investigation on International nuclear material traffic. Specialists determined by high-resolution  $\gamma$ -spectrometry the composition of the nuclear materials which indicates being a fuel element of a reactor type Training Research Isotopes General Atomics (TRIGA) reactor illegally subtracted from Kinshasa (Zaire) nuclear plant and introduced in the international illegal market [5].

In July 2001, Pu was found in a urine control of an employee who had been working in a decommissioned reprocessing plant in Karlsruhe, Germany. Arrested and confessed guilt for stealing a plastic vial containing a liquid and a swipe cloth, also his car and apartment were contaminated; in addition, his girlfriend had incorporated Am and Cs [4]. The death of Alexander Litvinenko in 23 November 2006, former Russian spy, after a mysterious and painful illness was unveiled: poisoned with the radioactive isotope Polonium-210. After his poisoning discovery, small traces of radiation at several sites inspected were found as well as into the aircraft company, on which Litvinenko traveled between Moscow and London in October 2006. Litvinenko was the first known victim of a radiological murder [6]. In February 2007 in Lauenforde, Germany, 14 uranium pellets were found in a garden of a house; through the characterization of these seizure materials it was possible to identify their source: a German manufacture of nuclear fuel, operated by Siemens industry, where deviation would have occurred at a time when quality control rejected the capsules, which were produced in early 1991 [7].

Brazil is one of the ITDB's member States; however, there are no official records of illicit trafficking of nuclear material in the country. Nevertheless, it is known worldwide a contamination by radioactive source elapsed from a theft in 1987. This tragic accident at the central region of Goiânia city resulted from the misuse of a strongly radioactive medical teletherapy source, caesium-137, not under radiation protection surveillance. Many individuals incurred external and internal exposure; the Comissão Nacional de Energia Nuclear (CNEN) monitored more than 112 000 persons, of whom 249 were contaminated either internally or externally. Of the 249 persons, 28 had radiation injuries, 20 were hospitalized and 4 taken to death [8].

Additionally, is the illegal extraction and transport, especially in the far northern Brazil, of geological radioactive materials, for example, torianita as well as the seizure of material fragments used as shielding for radioactive sources [9]. The main and most recent torianita's seizure at Amapá State dating back to 2004; since then every year the Federal Police have been seizing tons of this material in the region [10]. Recently, this mineral chemical signature was established by ensuring their identification in case of arrest anywhere in the world [11]. More recently, two cases occurred in Brazil in January 2010 portray the radioactive materials trafficking and illicit transportation. The first was the seizure made by the Amapá Civil Police, of 450 kg of pitchblende, a radioactive material with high content of uranium used in nuclear weapons [12]. The second case was the seizures made by the Federal Highway Police of plastics containing six gallons of Technetium-99m, illegally transported in a bus trunk from Foz do Iguaçu to Rio de Janeiro [13].

## 1.2. Chemical and Radiological Signatures

In the context of the forensic science, signatures stand for the characteristics of a given sample of nuclear or radioactive material that allows its distinction, or the identification of its origin. There are three types of signatures: chemical, physical and radiological. Chemical signatures can be related with their geological origin or their manufacturing process. Physical signatures are related with the handling, use or manufacturing process. Radiological signatures bring important information concerning to the origin, in case of minerals; use, in case of clinical instruments or nuclear reactors; and nuclear facilities, which are related to nuclear reactors, reprocessing plants and isotope enrichment plants. The uses of one of them, or all of them simultaneously, depend on the material type, as well as its chemical and physical form. Moreover, it depends on the evidences of radioactivity in the crime or seizure scene.

Quite of the research and development for nuclear forensic interpretation is based on the finding and understanding of these signatures. Through analytical techniques, physical, chemical, elemental and isotopic characteristics of the material can be determined. Physical characteristics include texture, size and shape of solid objects and the particle size distribution of powder samples. Chemical characteristics are associated with the exact chemical composition or the association of single molecular components. Elemental signatures are based on determination of major elements that can define the identity of nuclear material, and ultra-trace elements that may be indicative of the production process. Isotopic signatures come from the decay products of radioactive isotopes present in the material, capable of determining their age [2].

Rare earths elements (REE) are a set of seventeen chemical elements in the periodic table, specifically the fifteen Lanthanides in addition scandium and yttrium. These elements are often found together but in widely variable concentrations in uncommon varieties of igneous rocks. A large amount of uranium is in rare earths deposits, and may be extracted as a by-product. REE are also present in nuclear material (uranium and plutonium), which are formed in the reactor as a result of nuclear fission. In these materials, Lanthanides can be present in trace levels amount either as a contamination of the process or as residues from the raw material. Lanthanides measurements are used for the quality control and development of the nuclear fuel materials, or for the nuclear forensic investigation of found illicit nuclear materials. Accordingly, REE in uranium compounds can be used as an evidence of the uranium origin. The aim of this study is to determine eight rare earth elements as impurities in two uranium compounds from different origins, for nuclear forensics purposes. The REE chosen were Yttrium (Y), Lanthanum (La), Cerium (Ce), Praseodymium (Pr), Neodymium (Nd), Samarium (Sm), Gadolinium (Gd) and Erbium (Er).

## **2. EXPERIMENTAL**

### **2.1. Instrumentation**

The mass spectrometry analysis was carried out using a high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS), Finnigan MAT, Element 2 (Bremen, Germany, 1996). All measurements were carried out in low resolution mode (R=300). Prior to the sample analyses the instrument was tuned using a 10 ng.g<sup>-1</sup> multielement solution.

### **2.2. Reagents and materials**

For the REE measurements external calibration standard solution used were prepared from a 1000 µg g<sup>-1</sup> standard solution (Spex<sup>®</sup>) by gravimetric dilution. The elements were chemically separated by ion exchange in columns in Hydrochloric acid medium. For the preparation of columns, 3g of dry cross-linked anion exchange resin Dowex<sup>®</sup> AG-1X8, 200-400mesh was cleansed with ultra-

pure water and  $0,4 \text{ mol L}^{-1}$  Suprapur grade Hydrochloric acid (HCl) (Merck) in ultrasound for 30min. The resin in water solution was placed in glass column (external diameter: 1,2cm and height: 13,5cm). The free column volume is approximately 0,8mL. Flow rate was  $0,225 \text{ mL min}^{-1}$ . For the sample and standards solution preparation Suprapur grade Hydrochloric and Nitric acids (Merck) were used, and further purified by sub-boiling destillation in quartz equipment.

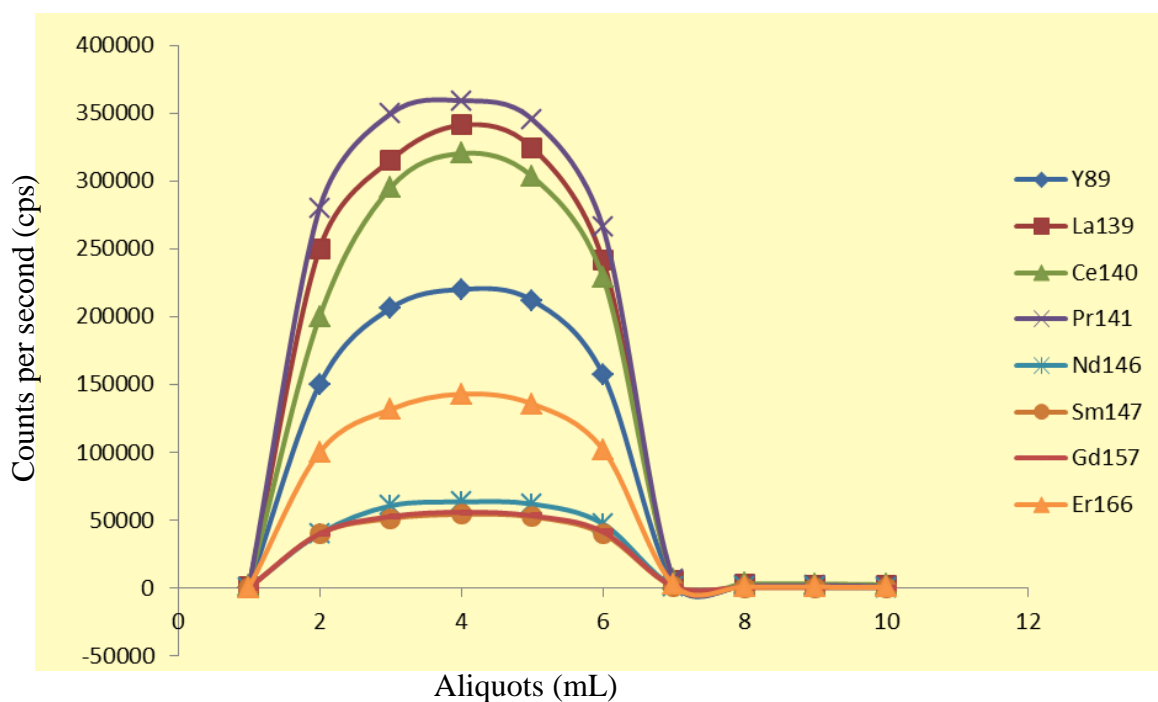
### 2.3 Methodology and Sample preparation for HR-ICP-MS analysis

The uranium compounds chosen for the analysis were: one Uranium oxide,  $\text{U}_3\text{O}_8$ , from Argentina (Agência Brasileiro-Argentina de Contabilidade e Controle de Materiais Nucleares - ABACC) and one Uranium silicide,  $\text{U}_3\text{Si}_2$ , from French origin (Compagnie Pour L'Etude et La Realisation de Combustible Atomiques - CERCA). Approximately 500 mg of each sample was weighted into a Teflon vial and dissolved in 1,5 mL of concentrated ultra pure nitric acid ( $\text{HNO}_3$ ). After 30 min the samples were evaporated until almost complete dryness on a hot-plate at  $70 - 80^\circ\text{C}$ . Then, 1,5 mL of concentrate ultra pure HCl were added to the sample and evaporated until almost complete dryness on a hot-plate at  $70 - 80^\circ\text{C}$ . The last procedure was repeated and a final solution was obtained adding 10mL of  $10 \text{ mol L}^{-1}$  ultra pure HCl. The REE content of the sample final solution was separated by anion exchange. After gradual conditioning of the resin with 10mL of  $1 \text{ mol L}^{-1}$  HCl, 10mL of  $4 \text{ mol L}^{-1}$  HCl and 15mL of  $10 \text{ mol L}^{-1}$  HCl, the sample aliquot was loaded on the column. Finally the column was washed with 15mL of  $10 \text{ mol L}^{-1}$  HCl which were collected with the sample into a Falcon tube, obtaining a final solution of 25mL. Withdrew an aliquot of 4mL and diluted with ultra pure 2% (m/m)  $\text{HNO}_3$ , with a final solution of 20mL. After the gravimetric weighing of the final fraction and the gravimetric addition of In internal standard, the samples were analyzed by HR-ICP-MS using external calibration; the REE concentrations were determined using a calibration curve established by analysis of separately measured standards. It was analyzed three replicates for each sample.

The selectivity of the analytical methodology was evaluated adding known amount of REE and uranium ( $50 \text{ ng g}^{-1}$  Spex<sup>®</sup> standard solution of each rare earth and uranium) in 2%  $\text{HNO}_3$  solution, which was evaporated until almost complete dryness on a hot-plate at  $70 - 80^\circ\text{C}$ . Then, 1,5 mL of concentrate ultra pure HCl were added to the sample and evaporated until almost complete dryness on a hot-plate at  $70 - 80^\circ\text{C}$ . The last procedure was repeated and a final solution was obtained adding 10mL of  $10 \text{ mol L}^{-1}$  ultra pure HCl. The REE content of the sample final solution was separated by anion exchange with pre gradual conditioning of the resin, as described above. Aliquots were collected of 2 in 2mL, In internal standard was added and were analyzed by HR-ICP-MS using external calibration.

## 3. RESULTS AND DISCUSSION

Separation of uranium from other elements was done with uranium retention in anionic resin, as far as REE are not retained in anion exchange resin, Hydrochloric acid medium. The high retention of uranium (U) under these conditions is due to the formation of uranyl ion anionic complexes. In order to confirm the immediate elution of REE, the standard solution containing known amount of REE and uranium was prepared and its elution behavior on Dowex<sup>®</sup> resin was investigated. The test solution was loaded on the columns in  $10 \text{ mol L}^{-1}$  HCl and eluted with 15mL of the same reagent. The aliquots were collected separately and their REE contents were analyzed by HR-ICP-MS. The elution curves of the elements are showed in Fig. 1.



**Figure 1. Elution curves of REE. Quartz column, external diameter: 1,2cm. Height: 13,5cm. Free column volume: approximately 0,8mL. Flow rate: 0,225 mL min<sup>-1</sup>. 10 mol L<sup>-1</sup> HCl medium.**

As shown in Fig.1, all REE are eluted and under such circumstances uranium highly retains on the column, with only a very small portion in the load fraction.

Table 1 shows the limits of detection (LOD) of the method employed for REE determination.

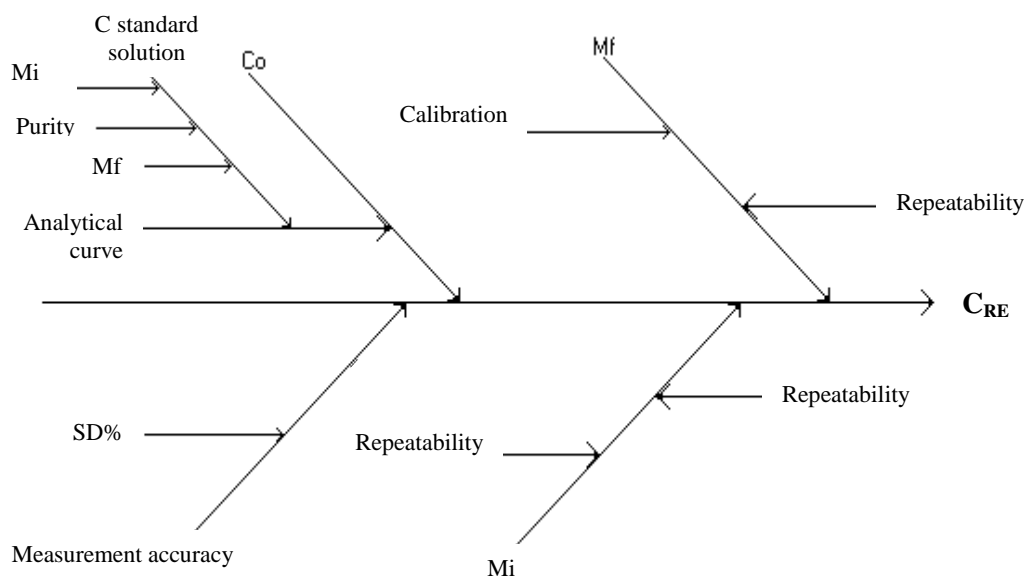
**Table 1. Limits of detection for REE analyzed by HR-ICP-MS with chemical separation**

Element	LOD (ng g <sup>-1</sup> )
Y	0,002
La	0,002
Ce	0,005
Pr	0,001
Nd	0,012
Sm	0,008
Gd	0,002
Er	0,0004

### 3.1 Analytical results with uncertainties associated

For several years the concept of measurement uncertainty has been discussed by experts. According to Eurochem / CITAC Guide the term measurement uncertainty can be defined as "a parameter associated with the measurement result that characterizes the dispersion of values that are reasonably attributed to the measurand." The uncertainty of the result may originate from various sources such as sampling, matrix effects and interference, environmental conditions, uncertainties of mass and volumetric equipment, reference values, approximations and assumptions incorporated in the method of measurement and procedure, and random variations. In this work the estimate of overall uncertainty was considered, which were discussed separately each source of uncertainty resulting in the contribution of each source. At the end the uncertainty of the method was obtained [14].

Fig.2 presents the cause and effect diagram that identifies the sources of uncertainty associated with the whole process of the method used in the REE determination.



**Fig. 2. Cause and effect diagram for each source of the method uncertainty**

Where  $C$  is the concentration,  $C_o$  is the HR-ICP-MS analyzed aliquot,  $M$  is the mass,  $M_i$  is the initial mass,  $M_f$  is the final mass,  $SD\%$  is the percentage standard deviation, and  $C_{RE}$  is the RE concentration.

The method was applied for the analyses of two uranium compounds from different origins in order to compare their REE profile, for nuclear forensic studies. The results presented on Table 2 clearly demonstrate the difference found on REE between the samples, evidencing that the uranium compounds under analyses have different origins.

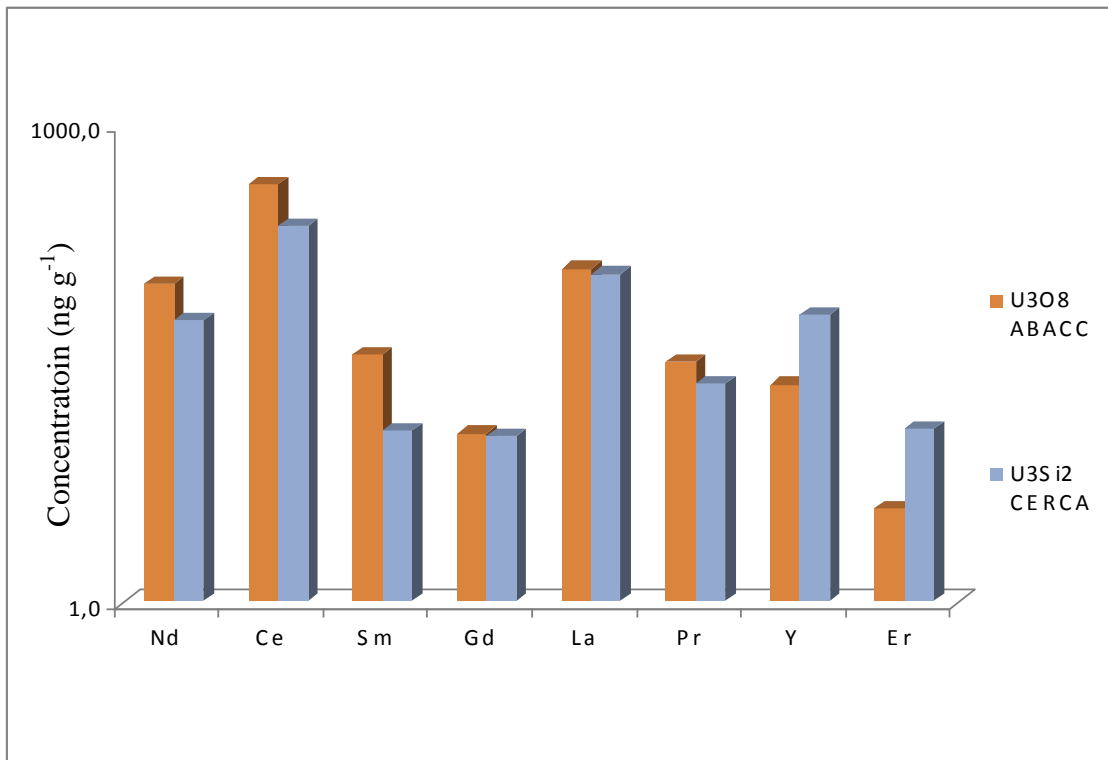
**Table 2. Rare earth impurities in uranium compounds associated with expanded uncertainty U(C)<sup>a</sup>**

Element	U <sub>3</sub> O <sub>8</sub> ABACC ng g <sup>-1</sup>	U <sub>3</sub> Si <sub>2</sub> CERCA ng g <sup>-1</sup>
Y	23,3 ± 11,0	64,8 ± 10,5
La	125,9 ± 14,0	116,6 ± 14,1
Ce	425,9 ± 30,8	235,0 ± 32,5
Pr	32,3 ± 2,2	0,29 ± 0,12
Nd	101,5 ± 8,35	58,9 ± 8,66
Sm	36,3 ± 3,9	12,0 ± 4,2
Gd	11,5 ± 0,9	12,09 ± 0,44
Er	3,9 ± 1,1	12,29 ± 1,01

a. Resulting product of the combined uncertainty by a coverage factor  $k = 2$  for a confidence level of approximately 95%.

For the REE analyzed, the expanded uncertainty level more suitable for measurements taken met around 6% ranging up to 16%. Conversely, four elements presented an uncertainty greater than 20%, such as Er and Y uranium oxide from ABACC with 28% and 47% of expanded uncertainty, respectively. For the Pr uranium silicide from CERCA presented 41% of expanded uncertainty; its concentration was found in picogram per gram level. The higher uncertainty source contribution for these cases was found in the HR-ICP-MS measure precision; due to the reduced number of counts per second obtained from the HR-ICP-MS for some REE, it was obtained a high percentage of standard deviation measures.

The results found were also plotted on a histogram, as showed in Fig.3. The REE Sm, Y and Er presented the greatest differences in terms of concentration between the two uranium compounds.



**Fig. 3. REE histogram for the two uranium compounds analyzed by HR-ICP-MS**

#### 4. CONCLUSIONS

The method used for the determination of Rare Earth Element (REE), involving chemical separation of REE anion exchange resin followed by HR-ICP-MS analysis, has great advantage over direct measurement of the analyte especially when analyzing REE in difficult matrixes at trace-level. For instance, if possible interferences are present at high level or in radioactive materials (e.g. U ores, spent fuels). As Dowex<sup>®</sup> resin chloride form highly retains uranium and other metals in concentrate Hydrochloric acid medium, the REE are completely eluted on the first fraction. To increase the measurements precision the use of isotopic dilution technique could prove more advantageous over the method employed in this study, with calibration curve. However, as the separation and distinction of RRE were possible for two samples from different origins, the presented method has potential application also in the field of nuclear forensics, where REE prototype can be used for the origin assessment of unknown samples.

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