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Detection and Evaluation of Uranium in different Minerals by Gamma Spectrometry and Laser Induced Breakdown Spectroscopy

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ABSTRACT

Analysis, detection and evaluation of source nuclear materials (e.g. uranium) in different minerals by sensitive techniques are a vital objective for uranium exploration, nuclear materials extraction, processing and verification. In this work, uranium in different geological formations was determined using gamma spectrometry and laser induced breakdown spectroscopy (LIBS). The investigated samples were collected from different regions distributed all over Egypt. The samples were then prepared for non-destructive analysis. A hyper pure germanium detector was used to measure the emitted gamma rays of uranium and its daughters in the samples. The concentrations of uranium in ppm (μg/g) in the investigated samples are given and discussed in this work. The highest uranium concentration (4354.9 ppm) was found in uranophane samples of Gattar rocks.

In Laser induced breakdown spectroscopy (LIBS) technique, plasma was formed by irradiating the rock surface with focused Q-switched Nd:Yag laser pulses of 7 ns pulse duration at the fundamental wavelength (1064 nm). Atoms and ions originating from the rock surface are excited and ionized in the laser produced hot plasma (~10 000K). The plasma emission spectral line is characteristic of the elements present in the plasma and allows identification of the uranium in the uranophane mineral. The strong atomic line at 424.2 nm is used for the qualitative identification of uranium. It can be mentioned that the elevated levels of uranium in some of the investigated uranophane samples are of great economic feasibility to be extracted.

Keywords : Gamma spectroscopy / Laser induced plasma / uranium minerals

INTRODUCTION

There are many destructive and non-destructive techniques to be used for the analysis of uranium. This work aims at using of γ-radiation and LIBS for the detection of uranium in different minerals selected from different areas in Egypt. Radio-analytical methods such as alpha spectrometry and mass spectrometry have traditionally been used for the determination of low-level natural radioisotopes. These methods are indispensable for detecting low nuclide concentrations, i.e. below 10^3 pg/g, at the cost of labor-intensive radiochemical processing of the sample[(1)]. In cases where low detection limits are not required, high-resolution gamma spectrometry provides the alternative of a non-destructive, multi-elemental, and less time consuming technique. Its feasibility has often been illustrated in the quantitative analysis of uranium, thorium and their decay products in environmental samples[(2)]. In LIBS technique, measurements can be carried out rapidly and on-line, thereby avoiding the long lag times associated with some other analytical techniques. In fact, elements can be identified in minutes once a reference database has been established and calibrations have been made. Because the laser beam is focused to a small spot (1–50μm), the technique provides spatial resolution of the sample composition for the evaluation of inhomogeneities. This method can also be adapted for remote analysis, which is particularly useful in radioactive environments[(3)]. On the other hand, most of destructive analytical procedures for the determination of uranium and thorium show difficulties with Egyptian iron rich silicate rocks[(4,5)] (e.g., hematitized granites).

DESCRIPTION OF THE INVESTIGATED SAMPLES

Seven Uranophane samples were collected in December 2002 from Gebel Gattar (height; 1965 m.), which is located in the Northern part of the Eastern desert, 35 km NW Hurghada city. The area is located between latitudes 27^0 12 30 and 27^0 21 59 and Longitudes 33^0 12 30 and 33^0 25 00 E. Gebel Gattar area has a rugged mountainous nature and is traversed by few major wadis[6].

Eleven rock samples were also collected from different areas distributed all over Egypt. All the collected samples were crushed, sieved, and packed in 100 ml containers for gamma ray analysis. The rock samples without any changes in their morphology were investigated by LIBS. The uranophane samples were palletized in the form of disc for LIBS investigation. Standard materials containing well-known concentration of uranium were used for quality control and calculation of the uranium concentration.

MATERIALS AND METHODS

1- Gamma Spectrometry

Gamma ray spectrometry is a powerful technique for determining qualitative and quantitative low-level natural and artificial radioactivity in environmental, nuclear materials and geological samples through their gamma- ray emission[7]. Gamma ray spectrometer equipped with hyper pure germanium detectors was used in this work. It consists of a hyper pure germanium detector (Tennelec Model) of a planar configuration with a high voltage power supply (negative polarity),a spectroscopy amplifier ,An analog –to-digital converter (ADC) and a 8192 multi-channel analyzer (MCA). The HPGe gamma ray spectrometer used has efficiency of 40% and a resolving power of 1.95 at 1332 keV of Co-60, a course and fine gain control of the spectroscopy amplifier; its differentiating and integrating time constants and all other parameters were adjusted before measurements. The best energy resolution and good linearity of the spectrometer were also selected.

2- Laser Induced Breakdown Spectroscopy (LIBS)

LIBS is a promising method which enables the elemental analysis of various rock samples in a small volume, based on atomic emission lines. When a powerful pulsed laser is focused on a surface, a tiny amount of the material is vaporized and through further photon absorption, it is heated until it ionizes[3]. This laser-induced plasma is a micro-source of light that can be analyzed by a spectrometer. The Nd: Yag laser is operated at the fundamental wavelength (1064nm). The target sample could be positioned and moved in all directions by micrometer screws with respect to the laser beam. The target could be rotated around an axis normal to the optical plane formed by the intersection between the laser beam and the optical axis of the spectrometer, thus allowing the laser to bombard the rock surface at variable angles[3]. The light emitted from the plasma was imaged 1:1 by a second quartz lens with focal length = 25 cm, into the entrance slit, typically a 20 μm-wide, of CM 112-cvi-sp (1/8 meter). The spectrometer has a grating with 1200 grooves per mm blazed at 250 nm, and a reciprocal linear dispersion of 0.63 nm/mm. The emission spectra were monitored by a CCD Camera Apogee (as given in figure 1). The obtained spectra consist of lines corresponding to the uranium element evaporated from the rock surface.

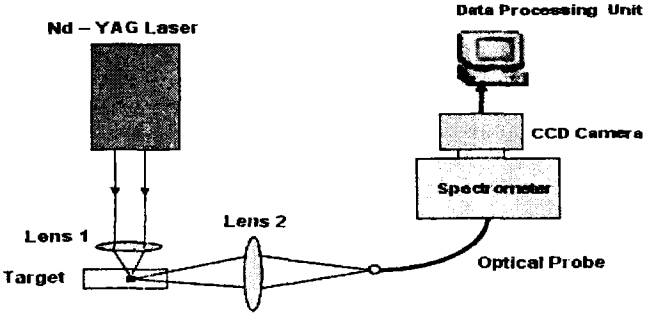

Fig.(1) LIBS Experimental Setup

RESULTS AND DISCUSSION

The results of the gamma spectrometric analysis of uranophane rock samples show that the uranium concentrations exhibited a remarkable variation (Figures 2,3 and Table 1). The uranium concentration in the analyzed rock samples ranged from 3.8 ppm to 4354.9 ppm.

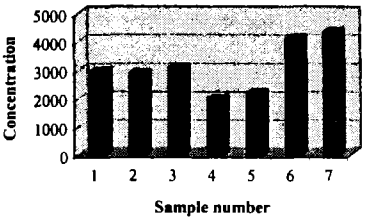

Figure (2) Variation of uranium concentration in different rocks samples (ppm)

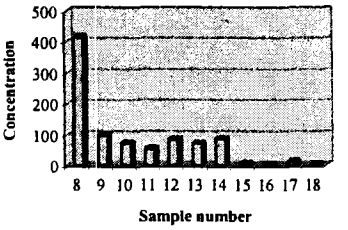

Figure (3) Variation of uranium concentration in different rocks samples (ppm)

Such remarkable variation reflects a lesser homogeneity than expected and may be indicative of a difference in the environment, which might have prevailed during the deposition. It is also possible that inhomogeneity might have been acquired post depositionally due to either water leaching or enrichment.

The possibility of oxidation of U(IV) to U(VI) to form the more mobile uranyl compound (UO_2)—followed by leaching would eventually result in lowering the initially higher U content . This situation could be also facilitated by the radioactive decay of U(VI)[8]. The post-depositional environment of uranium in the younger pink granites at Gattar II North Eastern desert, Egypt is more favor. Geological exploration in this area shows relatively high alteration products where considerable hematization resulted in an iron content ranging from 3-7%. Iron had been liberated from iron sulphide mineral whose oxidation gives sulphate iron in acid solution[9,10]. Sulphate, like carbonate (CO_2/P_2O_8), forms complex compounds with uranyl ion[9,10]. The sulphate complexes are not so stable as those with carbonate but are sufficiently stable to increase the solubility of U(VI) mark ably[9]. This indicates that the uranyl sulphate dissolved in water would have a few percent of its uranium available as uranyl ion[9,10].

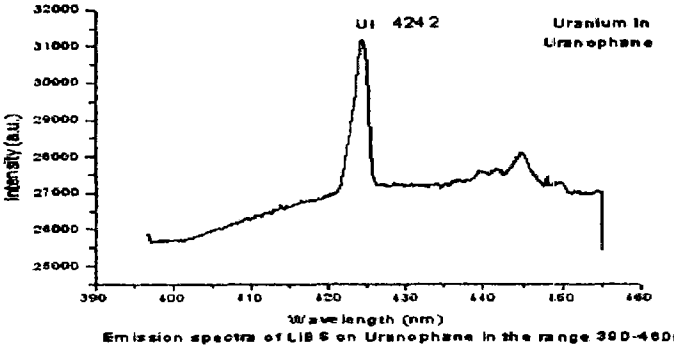

Figure (4) The Emission Spectrum of LIBS on Uranophane Rock

The spatial distribution of uranium plasma produced by applying the LIBS technique on uranophane rock surface was studied. It was found that as the distance from the target varies in mm, the spectral line intensity changes. The figure (4) shows the spectral line intensity of uranium at wavelength 424.2 nm (424.2 nm) in the range 390-460 nm.. The value between brackets is the literature value. The uranium element in all the investigated uranophane samples was also detected by LIBS at the same wavelength (424.2 nm). The high uranium content in the investigated uranophane samples shows the

economic importance of such ore. Extraction of uranium from such complexes will be of great economic feasibility. The same result has been recently published[11]. As a matter of fact, uranium concentration of 500 ppm is economically feasible to be extracted[12].

Table 1 The Gamma Spectrometry Results of the Analyzed Rock Samples

Sample Site	Serial No.	Site Description	U Concentration (ppm)
Gattar 1	1	Northern part of the Eastern desert	2958.7
Gattar 2	2	Northern part of the Eastern desert	2887.5
Gattar 3	3	Northern part of the Eastern desert	3088.8
Gattar 4	4	Northern part of the Eastern desert	4116.8
Gattar(R1)	5	Northern part of the Eastern desert	1977.1
Gattar(R2)	6	Northern part of the Eastern desert	2190.8
Uranophane	7	Northern part of the Eastern desert	4354.9
Monazite	8	Rosetta	415.8
Zircon	9	Rosetta	74.3
Zirconium	10	Rosetta	99.1
Routile	11	Rosetts	56
Phosphate	12	Assuit	85.4
Phosphate	13	Abu-Zaabal	73.2
Phosphate	14	Kafr El Zeit	87.8
Manganeese	15	Um Bogma, Sinai	7.1
Manganeese	16	South Egypt	6.1
Illiminite	17	Rsetta	14.7
Granite	18	Aswan	3.8

CONCLUSION

Based on the non-destructive Gamma and LIBS assay, it can be concluded that the investigated minerals contain uranium with wide variation and high concentration: from 3.8 ppm to 4354.9 ppm. This means that some of the analyzed samples especially Gattar granite (uranophane) are of economic concern. The economic feasibility study concerning extraction of uranium from Gattar (uranophane) rock is highly recommended. The techniques used are sensitive enough to detect uranium in different minerals with high accuracy.

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