Comparative study for measurement of environmental natural radioactivity in the crude phosphoric acid using nuclear and non-nuclear techniques

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ABSTRACT

The present work was attempts to develop rapid and accurate alternative analytical method for measuring naturally occurring radioactivity in the crude phosphoric acid (CPA). The measurements were achieved using nuclear method based on the non-destructive γ-ray measurements; and non-nuclear methods, including the ICP-OES and UV–vis colorimetric method. The results showed that, radionuclides of Th-234, Pa-234m (daughters of U-238) and U-235 were identified and quantified. The activity ratio of Th-234:U-235 was 21.0 ± 0.86. This value is significant because it is close and agrees with the reference naturally occurring activity ratio of 21.7 between U-238 and U-235. Total U in four different brands of the CPA (I–IV) was quantified using γ-emissions of its progeny (Th-234) for the aged samples only, or its natural isotope (U-235) for both fresh and aged samples. It was found that, the total U concentration in different four brands CPA (I–IV) of CPA using γ-emissions of Th-234 was 100.2, 68.7, 67.9 and 87.6 ppm for the brands I, II, III and IV, respectively with small coefficient of variance (CV,%) does not exceed 4%. For the same brands (I–IV) using γ-emissions of U-235 isotope, the total U concentration was 98.3, 75.5, 70.2 and 89.6 ppm, respectively with CV(%) below 5.3%. By ICP-OES method, U determination is negatively interfered with the phosphorous in all brands of CPA(I-IV). Alternative UV–vis spectrophotometry analytical method has been developed to detect the total U concentration using 10% oxalic acid as an efficient masking agent for Fe. By UV–vis method, the total U concentration in CPA brands was 102.3, 58, 56 and 73 ppm for I, II, III and IV brands, respectively with CV (%) less than 3.3%. Finally, it is concluded that the nondestructive γ-ray spectrometry may be the best choice for uranium measurement, especially in crude phosphoric acid (CPA) with relatively high P and Fe concentration.

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1. Introduction

Phosphoric acid (PA) can be produced using two different methods. One method is performed by direct reaction of ground phosphate rock (PR) with sulfuric acid, which also produces a lot of gypsum (calcium sulfate) as waste by-product. The second method is performed by burning elemental phosphorous and subsequent hydration of the phosphorous oxide. In most cases, the ore is digested by the H_2SO_4 to produce PA and calcium sulphate, known as phosphogypsum (PG) residue. The basic chemical reaction can be represented by Eq. (1) [1]:

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3PO_4 \tag{1}$$
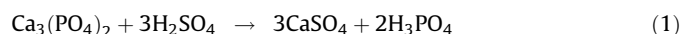
Each ton of P_2O_5 produced in the form of PA is accompanied by 4-6t of PG residue (dry weight). The impurities in the produced PA are removed by several techniques such as filtration, clarification, evaporation, solvent extraction, crystallization or ion exchange. The color of supper PA is either light green or black; depending on whether the ortho PA has been manufactured from calcined or uncalcined ore, respectively. Most green super PA is used for the manufacture of liquid ammonium fertilizer, a product containing 60% $(NH_4)_3PO_4$ and 40% H_2O. The high polymeric content allows the sequestration of other cationic metals, such as Fe, Al, Mg and Zn. The product is often used to carry these micronutrients to the recipient crops. Black super PA may either be sold as such for industrial uses or further processed by oxidation to produce green super PA [1].

In the view point of radioactivity, the naturally occurring uranium and its decay progenies present in phosphate ore are redistributed during the production of PA. Most of uranium,

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thorium or protactinium migrates to PA [2], while most of radium, lead or polonium enhanced in PG residues [3–5]. The activity concentration of U-238 varies over a wide range 0.14–2.6 Bq g^{-1}. The activity concentrations of U can also be determined from the uranium concentration by assuming that 1 g of U_3O_8 contains 12,347 Bq of U-238 [6].

The need for process control as well as the determination of material balance requires a sensitive and an accurate analysis for uranium in PA. Determination of U in the presence of different mineral impurities is a difficult analytical problem, especially as the U content being determined is much smaller than the content of impurities coming from the different minerals present and from the solutions used for their decomposition [7]. Many of analytical methods for U determination have already been published, but so far, none of them is universal enough to be directly applied to the determination of U in PA [7]. The previous methods used in determination of U are carried out by colorimetric method [8], volumetric titration method [9,10], wavelength-dispersive X-ray fluorescence spectrometry (WDXRF) method [11], ICP-MS [12], fission track analysis [13] and laser fluorimetry [14]. On the other hand, there are several nuclear spectroscopic techniques, including destructive methods such as liquid scintillation counting [15] and alpha particle spectrometry [16–18], nondestructive method using gamma ray spectrometry [19–21] and nuclear microscopy [22].

One major common analytical problem during U measurements arises from the presence of high phosphate concentration which chemically suppressed the content of U and leads to underestimation of U concentration. The present work was undertaken to optimize the required conditions for accurate determination of the environmental radioactivity in the crude phosphoric acid samples. The optimized method was proposed based on the comparative study between colorimetric spectrophotometry and inductively coupled plasma-optical emission spectrometry (ICP-OES) as a non-nuclear techniques as well as nondestructive gamma ray spectrometry as a nuclear technique.

2. Experimental

2.1. Samples

In Egypt, phosphate rock (PR) was locally produced from El-Sobayea region (south east of Aswan) and digested by hot concentrated sulphuric acid (H_2SO_4) to produce several chemical products of economic interest. The prime out products include granulated and powdered single superphosphate (SSP, 17% P_2O_5), granulated triple superphosphate (TSP, 48% P_2O_5) and commercial phosphoric acid (CPA, 48–50% P_2O_5) [23]. Products of SSP and TSP used as solid fertilizers while the CPA have several applications. The CPA produced by the 'wet process' used in as liquid fertilizer to improve the agriculture production.

In this study, four different brands (I–IV) of the crude phosphoric acid (CPA) have been chosen for the investigation. Each one is produced at certain period and batch operation. For instance, CPA (IV) brand was produced in June 2014, whereas the other brands (I–III) of CPA were produced below 2014. The color of the CPA brands was green, brown, black and deep green. The color of the brands is attributed to the possible alteration in chemical constituents of the PR used in the batches through different interval times (2014 and below).

2.2. Non-destructive γ-ray spectrometry measurement

Duplicated samples weighing an accurately fifty grams (50 g) of each CPA brand were prepared. Each sample was packed in cylindrical polyethylene bottle (150-cm^3) and closed tightly. Then, the samples (two for each CPA brand) were stored for the radiometric assay based on two independent measurements using nondestructive γ-ray spectrometry. The first γ-measurement of samples was carried out immediately after production of the samples. In this concern, the total concentration of uranium in the CPA can be determined from the gamma emissions of its naturally occurring isotope of U-235 at the 143 keV (10.5%) and 185.7 keV (54%). Whereas, the second measurement was carried out after five months to establish the radioactive equilibrium between the U-238 and its γ-emission progenies; including Th-234 at the 63.3 keV (4.8%) and 92.6 keV (5.6%), and Pa-234m at the 1001.3 keV (0.84%), as given in Table 1.

The measurements were carried out by a low-background HPGe detector (Canberra, USA) with movable cylindrical Pb-shield. The operating high voltage and data acquisition were performed by software of GENIE-2000 provided by multichannel analyzer (8192 MCA) [24]. The energy calibration of the system was carried out using sealed point source containing; Co-60, Ba-133 and Cs-137 [25], whereas the efficiency calibration was done using capsulated certified reference (CRM) provided by the AQCS, IAEA, Vienna. The CRM contain known amount of the naturally occurring radionuclide's of uranium (56.9 ± 4.0 mg kg^{-1}), radium-226 (732.5 ± 54.5 Bq kg^{-1}) and thorium (17.8 ± 1.0 mg kg^{-1}) [26]. The obtained efficiency-energy calibration curve of the detection system is illustrated in Fig. 1.

Minimization of the coincidence-summing effect was described by elsewhere [27–30]. In this concern, the samples include brands of CPA, CRM of the IAEA-314 sediment and standard solution containing known amount of natural uranium (as nitrate salt) in 5 M phosphoric acid were measured at the same geometrical conditions (i.e., G ≈ 1), such as measuring time, sample-to-detector distance, sample weight and the same sample container. Therefore, correction factors were calculated and used to eliminate coincidence-summing influence for the measured brands of CPA (I–IV) within the low energy range (50–200 keV) by the measuring system calibrated by IAEA-314 sediment.

The activity concentration (A) of each detected radionuclide in the CPA was calculated using Eq. (2):

$$A(\text{Bq kg}^{-1}) = \frac{C_s - C_b}{\varepsilon \times P_\gamma \times W} \quad (2)$$

Table 1
The gamma energy lines of the naturally occurring radionuclide's.

Radionuclide	Decay series	Decay mode	γ-energy, keV	γ-emission probability, keV	Half-life, $t_{1/2}$
Th-234	U-238	β,γ	63.3	4.8	24.1 d
			92.6	5.6	
U-235	U-235	α,γ	143	10.5	7.1×10^8 y
			185.7	54	
Pa-234m	U-238	β,γ	1001.3	0.84	1.17 m

m: minute, d: day, y: year.