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Uranium content in phosphate fertilizers commercially produced in Brazil

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Abstract

This work presents the results of the determination of uranium concentration in the most commonly used phosphate fertilizers employed in Brazilian agricultural land. The technique employed was the nuclear fission track registration in plastic foils of Makrofol KG (dry method), together with a discharge chamber system for track counting. Phosphate fertilizer samples and uranium standards were irradiated together with thermal neutrons in the 2 MW IEA-R1 research reactor of IPEN/SP. The uranium concentration in Brazilian phosphate fertilizers ranging from 5.17 to 54.3 ppm is in good agreement with the results reported in the literature for similar fertilizers produced in other countries.

Keywords: Uranium; Fission track; Fertilizer; Neutron irradiation

1. Introduction

Fertilizers usually employed in the agriculture contain traces of heavy metals, potassium and naturally occurring radionuclides, such as thorium and uranium and their decay products (Hamamo et al., 1995). In the case of fertilizers containing phosphate, high uranium concentrations (up to hundreds of ppm) have been reported in the literature (Qureshi et al., 2001; Barisic et al., 1992; Bolivar et al., 1995; Lal et al., 1985; Sam and Holm, 1995; Erdem et al., 1996; Guimond and Hardin, 1989; Hussein, 1994; Sharpley and Menzel, 1987; Al-Shawi and Dahl, 1995). Uranium presence is a consequence of the natural occurrence of this element in phosphate rocks usually employed as a source of phosphorous in phosphate fertilizer production.

Fertilizers containing phosphate have been used worldwide in increasing quantities in order to replenish natural nutrients, which are being continuously taken off from the soil due to farming activities and erosion problems. The fate of the uranium added to the agricultural soil by routine applications of phosphate fertilizers is not well known yet. However, continuous utilization of this type of fertilizer results in adsorption of a certain amount of minerals by plants, and therefore, this is a source of uranium in the human diet. This fact is of serious concern, because the daily intake of uranium with food (or even with water) may be considered as a chronic ingestion. An investigation of the uranium pathway from fertilizers to plants and to humans is, therefore, very important from the viewpoint of radiological protection of the general population. In order to undertake these studies, it is important to determine, with a reasonable level of confidence, the uranium concentration in the phosphate fertilizers that are being utilized in a particular agricultural soil. The technique of nuclear fission track registration (known as the solid-state nuclear track detector (SSNTD) technique) has demonstrated to be an excellent tool for this purpose (Lal et al., 1985; Qureshi et al., 2001; En et al., 1995). This investigation was undertaken with the aim of determining the uranium concentrations in the most commonly used Brazilian phosphate fertilizers using the

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SSNTD technique in the dry mode for sample analysis (dry method).

2. Experimental technique

For uranium concentration determination in fertilizer samples, the nuclear fission track registration technique was employed using a polycarbonate plastic commercially known as Makrofol KG (10 μm thickness) together with an automatic counting system consisting of a discharge chamber with aluminized mylar electrodes (Geraldo et al., 1979; Paschoa et al., 1990).

The experimental methodology has been developed with standard uranyl nitrate solutions whose concentrations ranged between 12 and 50 μg/l. This range corresponds approximately to the expected uranium concentrations in the fertilizer solutions (17–70 ppm by weight) (En et al., 1995), when the samples are prepared following the procedure adopted in this work (dissolution of ~35 mg dry weight of fertilizer in 50 ml of solution). The method consisted of depositing 5 μl of a uranium standard solution on the plastic detector surface followed by addition of 2 μl of a Cyastat detergent solution (1%, Cytec Industries Inc., West Paterson, NJ, USA) to reduce the droplet surface tension and to obtain a better homogeneity of drying aliquots. The droplets were carefully spread on the plastic foils to obtain large areas of deposition (around 7 cm^2) and allowed to evaporate under an infrared lamp. The resulting deposit of non-volatile constituents was covered with an extremely thin collodion film (pyroxylin, ether, alcohol) of about 20 $\mu g/cm^2$ thickness, for fixing the sample on the plastic detector. The plastic films containing the uranium standard and blank samples (the only chemical reagents) were rolled up together and fixed by a plastic tube holder as shown in Fig. 1. The set of plastic foils was placed into an aluminum rabbit (see Fig. 1), 22 mm in diameter and 70 mm in height, usually employed for neutron irradiation at the IPEN IEA-R1 (2 MW) pool-type research reactor. The aluminum rabbit, after soldering the cap on the open extremity, was placed near the reactor core for irradiation at a position where the thermal neutron flux was about 10^{13} n/cm^2 s. (Geraldo et al., 1992; Maidana et al., 1994).

A set of nine uranium standards and three blank foils were prepared, stacked and irradiated for a time period of 3 min. This irradiation time was chosen in order to allow control of possible radiation damage in the Makrofol foils. Three Makrofol KG foils (30 μm total thickness) were used to separate each one of the 12 sample foils to avoid the contribution of the fission fragments produced by neighboring samples. This shielding thickness is much higher than the expected range of about 20 μm for the fission fragments in Makrofol plastic (Tipier et al., 1974).

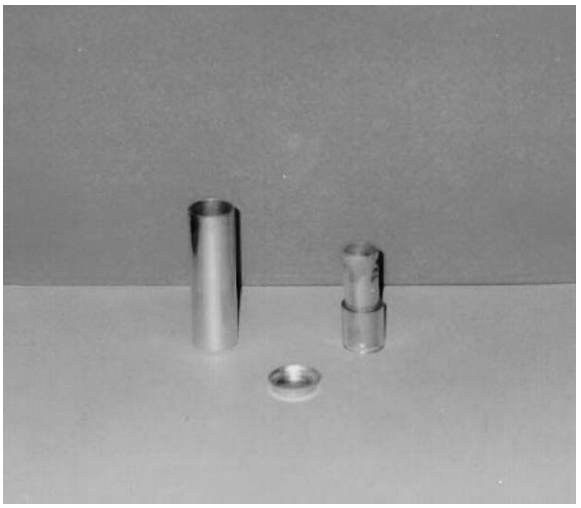

Fig. 1. Irradiation aluminum rabbit, aluminum cap, and a set of Makrofol KG foils containing sample deposits.

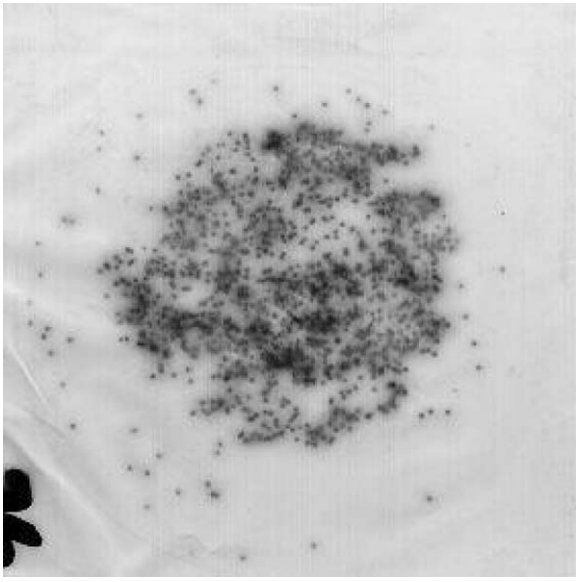

Fig. 2. Etched tracks in Makrofol KG detector with the record of uranium from a large (around 7 cm^2) evaporated droplet after counting in a discharge chamber.

After the irradiations, chemical etching of the plastic detectors was carried out at 60°C for 12 min in a mechanically stirred 35% (w) KOH solution. The etched fission tracks were counted in an automatic discharge chamber using aluminized mylar foils as electrodes (Geraldo et al., 1979; Paschoa et al., 1990). For the scanning conditions adopted in this work (1300 V prespark and 550 V operating voltage), a counting reproducibility was about 0.2%. Fig. 2 presents, as an

illustration, an area of about 7 cm^2 of the Makrofol foil after fission track counting in the discharge chamber. With a discharge chamber, large deposit areas are important for a better counting statistics, considering the counting saturation at approximately 1100 tracks/cm^2 (Geraldo et al., 1979; Paschoa et al., 1990).

Fertilizer samples with various nitrogen, phosphorous and potassium (N, P, K) concentrations were acquired directly from Brazilian manufacturers. They were ground properly and sieved to pass through a 70 mesh sieve. In order to obtain a solution in the form of uranyl nitrate, similar to the uranium standard solutions, a known mass (about 35 mg) of each powder sample was treated with nitric acid (4 M) and evaporated to dryness on a thermal plate. The resulting residue was dissolved in 2% nitric acid, and the solution was diluted to a total volume of 50 ml. A reagent blank was run simultaneously with the fertilizer sample for background correction. All the phosphate fertilizer sample deposits on the Makrofol KG foils were prepared in the same way as described for the standard uranium solutions. Results are reported as the concentration of U in the original solid.

Table 1
Results of uranium quantitation in Brazilian phosphate fertilizers using the nuclear fission registration technique

Fertilizer manufacturer	N, P, K composition (%)	Uranium concentration (ppm)
Nitrobras	10, 10, 10	28.45±0.60
Nitrobras	04, 14, 08	29.50±0.25
Manah	13, 13, 28	19.34±0.74
Manah	04, 30, 20	26.10±0.55
Ultrafertil	06, 30, 24	22.26±0.78
Ultraverde	10, 10, 10	30.60±0.42
Serrana	04, 14, 08	54.3±2.3
Mitsui	04, 14, 08	34.29±0.79
Fertibras	10, 10, 10	20.81±0.45
Nutrisafra	04, 14, 08	38.57±0.85
Fertiliza	02, 20, 20	15.72±0.34
Heringer	03, 15, 15	5.17±0.27

3. Results and discussion

In order to verify the relationship between uranium concentration and fission track density in the present technique, standard samples with uranium concentrations between 17 and 70 ppm were irradiated together with the blank deposits. The results obtained in 12 irradiations show an excellent linearity of the dependence of the fission track density on uranium concentration ($\chi^2 \sim 1$) (Geraldo and Smith, 1990). This calibration curve can be used for determining uranium concentration in any fertilizer sample prepared in the form of uranyl nitrate, at least within the concentration range studied and in the absence of precipitation of other dissolved species, which could attenuate the fission fragments. Samples with uranium concentrations above or below this interval can be analyzed by using deposits with sample mass respectively lower or higher than the one employed in this work ($\sim$35 mg). The detection limit attained with this technique was 0.80 μg/l (blank deposit), which corresponds to a uranium concentration in the ppb region.

In order to take into account potential fluctuations of reactor flux in time during the irradiation and spatially across the irradiation container, determination of the uranium concentration for each fertilizer sample involved normalization of the results to those produced by three deposits of a standard solution irradiated simultaneously; one of these deposits was in the center, and the two others were at the edges of the detector foils set. The obtained values are listed in Table 1. Only the standard deviation of the weighted mean of the replicates obtained for each sample was taken into consideration in calculations of the overall uncertainties in the concentrations.

The range of the uranium concentrations determined in this work is compared with the values reported in the literature for similar fertilizers in Table 2. As can be seen, our results are in reasonable agreement with those obtained by the other authors. The highest uranium concentration found in the Brazilian phosphate fertilizer is, however, much lower than those reported from the other countries, except from India.

Table 2
Comparison of the intervals of uranium concentrations in phosphate fertilizers produced in different countries

Country	Uranium concentration (ppm)	Method of determination	Reference
USA	8.9–221.0	γ-Ray spectrometry	Hamamo et al. (1995)
Germany	3.2–185.5	γ-Ray spectrometry	Pfister et al. (1976)
Uzbekistan	11–70	Fission track	Al-Shawi and Dahl (1995)
India	15.9–35.8	Fission track	Lal et al. (1985)
Croatia	66–127	γ-Ray spectrometry	Barisic et al. (1992)
Yugoslavia	58.9–162.0	Spectrophotometry	Vucic and Ilic (1989)
Brazil	5.17–54.3	Fission track	This work

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