DETERMINATION OF THE URANIUM CONTENT IN BRAZILIAN FERTILIZERS

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ABSTRACT

In this work it was performed a study of the uranium content in some of the main commercially available Brazilian fertilizers. The technique employed was the fission track registration in Makrofol KG together with a discharge chamber system for fission track counting. After prepared in the form of uranyl nitrate, the samples were deposited on the plastic foils (dry method) and irradiated near the core of the IPEN IEA-R1 (2MW) research reactor. The results obtained are compared with values reported in the literature for similar samples.

I. INTRODUCTION

As is well documented in literature [1-5], uranium is an important trace constituent (tens of ppm) in phosphate rocks which are usually employed as phosphorous source in the fertilizer production. During continuous application of this type of fertilizer in agriculture, a certain amount of minerals are absorved by plants and thus, the uranium comes to be an usual element in the human alimentary dietary. This is preocupating because the daily intake of uranium through food and/or water may be regarded as a chronic ingestion and thus, the investigation of the pathway uranium (fertilizers) to plants and to human is particularly important concerning the radiological protection of the general population. The present investigation was undertaken in order to evaluate the uranium content in some Brazilian fertilizers produced by phosphate materials and which are being extensively applied in the national agriculture.

II. EXPERIMENTAL TECHNIQUE

Six different fertilizer samples and one phosphate rock sample, listed in table 1, were acquired directely from the manufactorers. They were grinded properly and sieved through a 70 mesh siev. In order to obtain a solution in the form of uranyl nitrate, around 20 mg of each powder sample was treated with nitric acid (4M) and evaporated to

dryness. The final residue was taken up in 2% nitric acid and made up to 50 mL. A reagent blank was run simultaneously with the sample. Standard solutions of uranyl nitrate, containning known quantities of uranium, were also prepared, following the same procedure of the samples. Using a calibrated micropipet, 10 µL droplet of the sample solution was deposited on clear Makrofol KG sheet (10 µm thickness) and allowed to evaporate under infra-red lamp, inside a glove box to protect against laboratory contaminated air. Together with the sample 5 μ L of a 1% cyastat solution (wetting agent) was deposited in order to reduce the droplet surface tension and consequentely, to obtain more homogeneous deposits [6]. During the deposition, the droplet was carefully scattered by the micropipet in such way that large deposit areas, around 6 cm^2 , were obtained at the end of the evaporation process. This is very important when using discharge chambers for automatic counting of fission fragment tracks due to the chamber counting saturation at approximately 1100 tracks/cm² [7]. After evaporation of the solution, two other Makrofol KG sheets were used as cover (total thickness of 20 µm) in order to separate them during the irradiation. The range of fission fragments in Makrofol KG has been experimentaly determined in this work and the value found was around 15 µm. Sets of 10 piled up samples and standard uranium deposits were placed inside aluminum cylinders (rabbit), 22 mm diameter and 70 mm high, usually employed for material irradiations. The aluminum rabbit was sealed by soldering a cap at the open extremity and possible air leaking has been checked with a solution of glycerin at 150 °C. The

rabbits were placed near the core of the IPEN IEA-R1 reactor, a 2 MW pool type research reactor, at a position (EIRA 24B, shelf 5) where the thermal neutron flux is around 10^{13} n/cm².s [8]. An irradiation time of 3 minutes was chosen for all studied materials, in order to control possible radiation damages in the Makrofol KG foils [7]. After the irradiation, the plastic detectors were etched in a KOH (35%) solution at 60 °C for 10 minutes and the resulting amplified fission tracks were counted in an automatic discharge chamber.

III. RESULTS AND DISCUSSION

In order to verify the relationship between uranium content and fission track density, samples of standard solutions, with uranium concentration ranging from 1.0 to 8.0 μ gU/L were used for obtaining a calibration curve. As can be seen in Figure 1, the best curve fitted to the experimental data points, using least squares methods [9], was a straight line y = a + bx, which coefficients are: $a = 189 \pm 28$ and $b = 131 \pm 7$. In this qualitative study it was not taking into consideration the background contribution because the results were not employed for uranium determinations in the unknown samples.

The uranium content for each sample was calculated comparing the results obtained with those of an uranium standard solution irradiated simultaneously. The values found are presented in Table 1. The total uncertainties for the experimental data were obtained by summing in quadrature the following error contributions: sample track counting statistics (0.3 - 6.4%), uranium standard counting statistics (1.1 - 12.7%), sample mass (0.05%), solution volume (0.2%), counting reproductibility (1.5%) and blank sample (3.3%).



Figure 1. Variation of the Track Density with Uranium Concentration.

Uranium Concentracion (µgU/L)

TABLE 1. Uranium Content in Brazilian Fertilizers

| Type of Fertilizer (N,P,K) | Uranium (ppm) | |
|----------------------------|------------------|--|
| Dimy (10,10,10) | 19.15 ± 0.98 | |
| Dimy (04,14,08) | 21.52 ± 0.88 | |
| Nitrobras (10,10,10) | 27.4 ± 1.0 | |
| Nitrobras (04,14,08) | 16.1 ± 1.1 | |
| Fertimix (06,30,24) | 32.2 ± 1.6 | |
| Manah (04,30,20) | 25.3 ± 1.2 | |
| Phosphate Rock | 64.5 ± 2.1 | |

In Table 2 the present data are compared with the experimental results reported in the literature by other authors, for samples similar to the ones studied in this work. As can be seen, the calculated values for the uranium content in Brazilian fertilizers are in good agreement with the results obtained in ref. [2] (India) and ref. [10] (Uzbekistan). However, the values of uranium content reported for the samples analysed in ref. [3] (Croatia) as well as in refs. [1,4] (USA) are about twice higher than those of the present work. This can possibly be accounted for a higher uranium contents of the phosphate rocks from USA and Croatia when compared with those from Brazil, India and Uzbekistan, as can be observed in Table 2.

 TABLE 2. Variation Intervals of the Uranium Content in Fertilizers and Phosphate Rocks

| Samples | Uranium(ppm) | Refs. | Local |
|-----------------|---------------|-------|------------|
| | Content Range | | |
| Superphosphates | 15.9 to 35.8 | [2] | India |
| P-Fertilizers | 32 to 62 | [3] | Croatia |
| P-Fertilizers | 11 to 70 | [10] | Uzbekistan |
| P-Fertilizers | 16.1 to 32.2 | This | Brazil |
| | | Work | |
| P-Fertilizers | 30 to 200 | [1,4] | USA |
| Phosphate Rocks | 77 to 101 | [3] | Croatia |
| Phosphate Rocks | 80 to 105 | [5] | Spain |
| Phosphate Rocks | 64.5 | This | Brazil |
| | | Work | |
| Phosphate Rocks | 08 to 399 | [1] | USA |

REFERENCES:

[1] Menzel, R. G., Uranium, Radium and Thorium Content in Phosphate Rocks and Their Possible Radiation Hazard, Journal Agric. Food Chem. vol. 16, p 231-234, 1968.

[2] Lal, N., Sharma, P. K., Sharma, Y. P. and Nagpaul, K.K., **Determinatio of Uranium in Fertilizers Using Fission Track Method**, Fertilizer Research vol. 6, p 85-89, 1985.

[3] Barisic, D., Lulic, S. and Miletic, P.,Radium and Thorium in Phosphate Fertilizers and Their Impact on the Radioactivity of Waters, Water Research vol. 26, p 607-611, 1992. [4] Sharpley, A., N., and Menzel, R. G., **The Impact of Soil and Fertilizer Phosphorous on the Environment,** Advances in Agronomy, vol. 41, p 297-324, 1987.

[5] Bolivar, J.P., Garcia-Tenorio, R. and Garcia-Leon., Fluxes and Distribution of Natural Radionuclides in the Production and Use of Fertilizers, Applied Radiation and Isotopes, vol. 46, p 717-718, 1995.

[6] Wyllie, H., A., Johnson, E., P. and Lowenthal, G., C., A Procedure for Stirring Aliquots of Radioactive Solutions
When Making Thin 4p Counting Sources, Journal Applied Radiation and Isotopes, vol. 21, p497-499, 1970.

[7] Geraldo, L., P., Mafra, O., Y. and Cesar, M., F., **Determination of the Uranium Concentration in Water Samples by the Fission Track Registration Technique,** Journal Radioanalytical Chemistry, vol. 49, p 115-126, 1979.

[8] Geraldo, L., P., Dias, M., S. and Koskinas, M., F., Average Neutron Cross Section Measurements in U-235 Fission Spectrum for Some Threshold Reactions, Radiochimica Acta, vol. 57, p 63-67, 1992.

[9] Geraldo, L., P. and Smith, D., L., Covariance Analysis and Fitting of Germanium Gamma- Ray Detector Efficiency Calibration Data, Nuclear Instruments and Methods, vol. A290, p 499-508, 1990.

[10] En, Z., Jumaev, N. and Usmanova, M., M., **Application** of Fission Track Detection Technique for Determination of Uranium in Liquids, Radiation Measurements, vol. 25, p 389-390, 1995.