MONITORING OF URINE BY EXTRACTION CHROMATOGRAPHY WITH TRI-N-OCTYLPHOSPHINE OXIDE SUPPORTED ON A POLYPROPYLENE COLUMN

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ABSTRACT

Monitoring of personnel working with 20% enriched uranium implies development of techniques for excreta analysis, mainly for urine, with very low detection limits.

The method described allows the determination of 20% enriched uranium after extraction in tri-n-octylphosphine oxide (TOPO), 0.5 M in toluene, supported on polypropylene capillary columns [1]. Alpha activity is later measured in a low background liquid scintillation equipment [2] and the fluorescence in a fluorimeter [3], with detection limits, for 500 mL of urine, of 15.0 ± 4.0 mBq L^{-1} and $5x10^{-2} \pm 10^{-2}$ μg L^{-1}.

INTRODUCTION

The control of 20% enriched uranium in the orine of workers requires periodic analysis of a large number of samples from different areas. Since the radiological risk is very important, it is necessary to rely on a technique able to detect levels well below the values established in the monitoring of natural uranium and adapted to the perfomance of a large number of determinations. Kel-F colums in reversed phase partition chromatography were used to purify urine [4], as well as extraction with organic compounds such as tributylphosphate (TBP) or bis-2-ethylhexylphosphoric acid (HDEHP) [5], with adjustment of the media prior to measurement.

The microcapillary chromatographic technique using TOPO as the supported phase is very adequate to concentrate uranium since this selective reagent, in permanent contact with the solution, enhances the extraction of uranium through a stable complex formed. As elution with toluene is performed instead of stripping, losses are minimized so that the efficiency in the application of the sample, regulates the efficiency of the column. The eluate is a purified solution, 160 times more concentrated than the original sample. Fluorimetry and gross alpha activity by low background liquid scintillation are performed on different aliquots.

REAGENTS AND EQUIPMENT

Nitric acid, Cicarelli pa.
Hydrogen peroxide, Douglas pa.

Tri-n-octylphosphine oxide, Mallinckrodt A.R..
Ethyl alcohol pa.
Toluene scintillation grade
Naphthalene scintillation grade
PPO scintillation grade
Sodium fluoride, Merck pa.
Calcium ortophosphate dibasic solution (100 mg mL^{-1})
Ammonium hydroxide, Merck pa.
Polypropylene PR-125
Jarrell Ash 26000 Fluorimeter
Platinum dishes
Fussion furnace, 1300 °C
Beckman LS-3150 T Liquid Scintillation, equipped with a low background system.

EXPERIMENTAL

Mineralization of organic matter

10 mL of concentrated nitric acid and 3 mL of calcium ortophosphate dibasic solution are added to 800 mL of urine in a beaker. The solution is left at 60 °C for one hour. Ammonium hydroxide is slowly added while stirring up to pH = 10. The precipitate is digested overnight, centrifuged and the supernatant discarded. The solid is mineralized to white ashes on a hot plate with 1:1 nitric acid and hydrogen peroxide. The ashes are dissolved in 80 mL of 1M nitric acid and hydrolyzed for one hour at near boiling temperature.

Setting the chromatographic column

The chromatographic column, 5 m long, is coiled downwards on a cylindric plastic support 50 mm diameter. The microcapillar of 1.2 mm of internal diameter is imbibed with 300 µL of a 0.5 M solution of TOPO in toluene. The column is previously washed with ethyl alcohol and vacuum dried.

Loading and elution

The cooled hydrolyzed liquid is poured through the column, previously treated with 1 mL of 1 M nitric acid, at a rate of 20 drops per minute and the contents are eluted into a liquid scintillation vial with 5 mL of toluene. Three 200 µL aliquots are used for fluorimetry and 5 mL of a scintillation cocktail containing 10 g of PPO and 160 g of naphthalene in 1000 mL of toluene are added to the remaining solution into the vial and it is measured by low background liquid scintillation. A blank of urine and a recovery test are run together with the urines and measured in the same conditions.

RESULTS

The following considerations were taken during the standardization of the technique:

Pyrophosphates formation

The pyrophosphates formed during mineralization tend to compete with TOPO for the uranium, resulting in very widespread recovery values . To avoid this interference an acid hydrolysis

is performed during one hour.

Urine volumes

Volumes of urine ranging from 200 to 2000 mL were processed, with no influence in recovery values. Volumes of 1 M nitric acid used to solubilize the ashes varied accordingly, since 10 mL of 1 M nitric acid are needed for every 100 mL of urine. 800 mL of urine are adequate regarding both detection limits and amount of sample to be requested.

Capillary length

Capillary tubes 1, 3 and 5 m long were used. Recoveries were poor in the first case, improved in the second case but were not reproducible. Columns 5 m long proved to be optimum regarding high recoveries and reproducibility.

TOPO concentration

Recoveries did not change in the 0.5 to 1.0 M concentration range and a 0.5 M value was adopted. Since the minimum amount of extractant needed to imbed the whole column was 300 µL, this was the volume chosen.

Percolation rate

There were no significative changes in recovery values for flow rates ranging from 20 to 40 drops per minute, but recoveries were very low for rates over 50 drops per minute.

CONCLUSIONS

Since the concentration factor is high enough to detect very low uranium levels, this technique is suitable for controlling personnel working with different uranium compounds. Besides, it is very convenient when dealing with many samples in different matrixes, because measurements are done inmediately after elution, requiring only the addition of the scintillation mixture.

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