

# URANIUM in SURFACE SOILS: an EASY & QUICK ASSAY COMBINING X-RAY DIFFRACTION and X-RAY FLUORESCENCE QUALITATIVE DATA

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## Problem statement

Portugal has been a uranium-producer since the beginning of the last century. The uranium-rich area of Alto Alentejo, East-central Portugal, was identified more than fifty years ago [1]. The uranium-bearing mineralization occurs mostly in schistose rocks of the contact metamorphic aureole produced by intrusion of the Hercynian monzonitic granite of Alto Alentejo into the pre-Ordovician schist-greywacke complex forming deposits of vein and dissemination type.

The Nisa uranium-reservoir - situated at the sharp border of a large and arch-shaped granite pluton (fig. 1) - was identified in 1957 [2] but its exploitation was considered economically impracticable until recently. Its existence and the accumulated debris of these prospect efforts are a concern for local populations.

A study of the near-surface soils close to the Nisa reservoir (fig. 2), was therefore undertaken to assess the uranium retention by adsorption on clay components and its eventual release into the aquifer groundwater.

A combination of laboratory X-ray techniques (diffraction and fluorescence spectrometry) was designed as an attempt to very quickly appraise the presence of uranium in as-collected near-surface sediment samples. A description of the experimental methodology of this *easy & quick uranium assay* is presented.

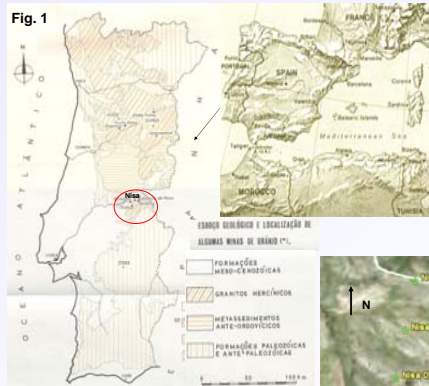


Table 1 - Identification and estimated relative proportion of mineral phases from soil samples collected in the Nisa region (fig. 3).

Soil nr.	Phase identification									
	Qz	Feld	Plag	Mosc	Illite	Kaol	Sme	12.3Å	6.4Å	Others
1	xxx	-	xx	-	x	-	x	x	x	C?
2	x	-	x	x	?	-	xx	?	x	C? G?
3	x	-	x	-	x	?	-	?	?	?
4	xx	x	-	xx	-	-	-	x	x	C?
5	xx	x	-	?	x	-	?	?	?	C?
6	xx	x	-	-	x	-	x	x	x	G
7	xxx	x	-	x	-	-	xx	x	?	G H?
8	xxx	x	-	-	x	-	x	x	x	C
9*	xx	x	-	x	-	-	xx	x	x	G? H?
10	xxx	x	-	-	x	-	xx	?	x	C
11	xxx	x	-	-	x	-	xx	-	?	?

Diagnose diffraction lines: Qz - Quartz, 3.33 and 4.26 Å; Feld - Feldspar 3.25 Å, single line; Plag - plagioclases, 3.2 - 3.15 Å, two lines; Mosc - Moscovite, 10 and 5 Å, intense and thin lines; Illite - 10 and 5 Å, broad lines; Kaol - Kaolinite, 7 Å; Sme - Smectites, 14.6 Å; Interstratified minerals, two lines, 6.2 and 12.3 Å; C - Calcite, 3.05 Å; G - Goethite, 4.18 Å; H - Hematite, 2.69 and 2.51 Å.

\* Soil sample containing uranium as detected by XRF-WDS ? , doubtful

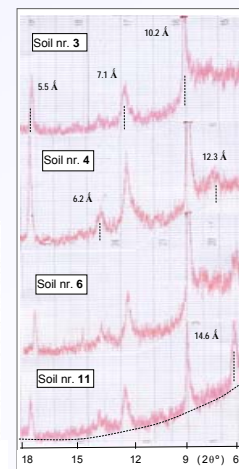


Fig. 10 - XRD spectra from some soil samples. Diagnosis lines of clay minerals are assigned (see Table 1).



Fig. 2

## Soil sampling

A soil profile was selected as a first approach to the study of uranium retention by surface soils in the Nisa area (fig. 3); this profile starts nearby a water course and extends to the north perpendicular to the reservoir (Mina de Nisa, assigned with an arrow). A total of eleven samples were collected at a depth of ~20cm (fig. 4).

Differences noticed in the soil colouring (figs. 4-7) were thereafter correlated with the mineralogical constitution.



Soil nr. 9



Soil nr. 11



Fig. 4



Fig. 5



Fig. 3



Fig. 8 - Sabugalite crystals [4]



Fig. 9 - Yellow phosphuranlyite in schistose rock (Monte do Tapadão, nearby Nisa).

## Uranium in the Nisa region

Previous studies on the Nisa deposit [3-5] have shown that the main uranium mineralization belongs to the Autunite group - general formula  $A(UO_2)_2(XO_4)_2 \cdot 8-12 H_2O$ , where A = Ba, Ca, Cu, Fe<sup>2+</sup>, Mg, Mn, Na, H<sup>+</sup>Al, and X = P, As, V. The uranyl phosphate minerals **Autunite**,  $Ca(UO_2)_2(PO_4)_2 \cdot 10-12 H_2O$ , **Torbernite**,  $Cu(UO_2)_2(PO_4)_2 \cdot 8-12 H_2O$ , **Salecite**,  $Mg(UO_2)_2(PO_4)_2 \cdot 10 H_2O$ , **Uranocircite**,  $Ba(UO_2)_2(PO_4)_2 \cdot 12 H_2O$ , and **Sabugalite**,  $HAl(UO_2)_2(PO_4)_2 \cdot 16 H_2O$  were found, along with **Phosphuranlyite**,  $Ca(UO_2)_2(PO_4)_2(OH)_2 \cdot 6H_2O$  and **Pitchblende** (~UO<sub>2</sub>, amorphous).

Specific uranium minerals were not identified in samples collected along the first soil profile but small crystal aggregates of sabugalite (fig. 8) were quite commonly seen in fragments of granitic rock and phosphuranlyite was assigned in schistose rocks during a latter field campaign (fig. 9).

## Uranium retention by soil minerals

It is widely recognized that clay minerals play an important environmental role in retaining hazardous metals, being even used in the remediation of contaminated soils [6].

Following uranium oxidation and further release from carrier minerals, the formation of *linear uranyl ions*  $[UO_2]^{2+}$  is recognized as responsible for the behaviour of this element in soils. The mobility of this linear cation may be strongly restricted by adsorption on the surface of clay minerals, particularly montmorillonite [7] and kaolinite [8], either by outer-sphere adsorption occurring onto the basal planes or by inner-sphere fixation on the edges of the clay layer at the amphoteric ligand sites [9]. In the latter case, carbonate anions play an important catalytic role [10].

As mentioned before, the eventual release of uranium into the aquifer groundwater in the Nisa region is a concern for the population in general. However, the fact that soils from this region proved to be rich in smectite-type clays - potentially capable of efficiently adsorb uranyl ions - is a very positive result that anticipates a low U-content in groundwaters [11].

## Experimental: easy & quick X-ray test

An easy-and-quick test was successfully implemented to ascertain the presence of uranium by combining two X-ray laboratory techniques: *diffraction* (XRD) to identify the component mineral phases and roughly estimate their relative proportion, and *fluorescence spectrometry* in wavelength dispersive mode (XRF-WDS) to make certain of uranium presence and roughly evaluate its content by comparison with selected chemical components of the soil.

Soil samples were first dried at 40C and the fraction <150µm was thereafter irradiated. A Philips powder diffractometer with Bragg-Brentano geometry, equipped with a large-anode copper tube and a graphite crystal monochromator, was used to collect XRD spectra (fig. 10) covering the angular 2θ region interesting to identify clay minerals (5-18°). Table 1 summarizes the mineralogical data so obtained.

Uranium occurrence in soil samples was assessed by XRF-WDS using a Philips PW1400 spectrometer equipped with a rhodium tube and a LiF200 analysing crystal. The angular region 21-28° (2θ) was chosen for the analysis because it covers the Kα lines from elements common in soils of granitic origin (Rb, Sr, Y, Zr) and the La lines from U (26.14°) and Th (27.47°) plus some Lβ lines, therefore enabling a quick comparison of relative levels of concentration (fig. 11). Soil nr. 9 (collected near the Nisa reservoir) was the only one from the eleven test samples where uranium was detected.

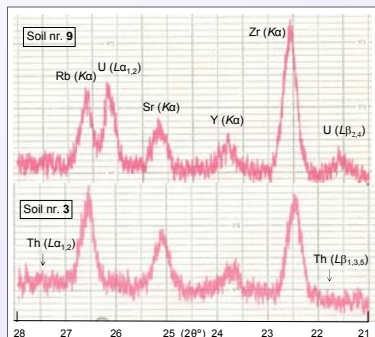


Fig. 11 - XRF spectra showing the presence of U in soil nr. 9, while soil nr. 3 is free from U being representative of all the other ten samples.

## Final comments

Through the described *easy&quick test* the presence of U in soils is rapidly assessed and a prompt chemical mapping can be performed. Obtained results compared quite well to the data of certified time-consuming analytical tests of uranium in litter on performed on these soil samples: 353 µg/L for soil nr. 9 and less than 50µg/L for the other samples. The test is now being applied to analyse more than one thousand soil samples collected according to a suitable mesh with the aim of demarcating actual areas of potential risk in the Nisa region.

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