# HIGH RESOLUTION $\gamma$- AND X-RAY SPECTROMETRY OF RADIOACTIVE MINERALS (*)

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*ABSTRACT* — Gamma ray-spectrometry has been used in qualitative and quantitative analysis of uranium ores. However till recently only NaI(Tl) detectors were used and due to the complexity of the spectra this was a great limitation. In this work we used Ge(Li) an Ge (hyperpure) detectors and so it was possible to show that the method was applicable to the measurement of uranium concentration as low as 0,02 %. On the other hand it was possible to detect the presence of other non radioactive elements through the analysis of their characteristic X-rays produced by autofluorescence.

## 1 — INTRODUCTION

In recent years the search for minerals of uranium and thorium has been pursued with great effort and even the detection of these radioactive elements in mineral ores with low concentration is assuming special relevance. It is then obvious that the use of the most advanced techniques of nuclear spectrometry will play an important role in this field.

Some years ago [1 − 6] the use of $\gamma$-spectrometry with NaI(Tl) detectors made possible the identification of certain groups of elements of the radioactive families. However the measurement of the concentration of several of these elements was dependent on proving the existence of radioactive equilibrium. In fact the low resolution of the

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NaI(Tl) detectors did not enable the unambiguous identification of uranium and thorium $\gamma$-rays.

Nowadays the introduction of the Ge(Li) detectors in this field [7] has changed the situation since it became easier to verify whether or not the radioactive equilibrium is present. Nevertheless the great complexity of the $\gamma$-ray spectrum in the range of energy below 120 keV calls for the use of Ge (hyperpure) detectors. These have the advantage of a high resolution in the range 10 to 120 keV together with a good efficiency and an almost transparency for $\gamma$-rays of higher energies. On the other hand the presence of these high energy $\gamma$-rays will induce the production of X-rays by autofluorescence. The detection of the X-rays can then be used as another technique to identify the elements present in the mineral ore. Furthermore this last technique makes possible the search for the other non radioactive elements. This by itself can be of great help to establish the chemical composition of the mineral ore.

## 2 — $\gamma$-RAY SPECTROMETRY

In figure 1 we show a $\gamma$-ray spectrum of a sample of an uranium ore from the mine of Cunha Baixa, Nelas (Portugal), obtained with a coaxial Ge(Li) detector with 25 $cm^3$ of active volume. It is possible to see several peaks corresponding to transitions with energies between about 150 keV and 2200 keV. The resolution (2 keV for the 662 keV peak) enabled us to separate several transitions corresponding to the decays of $^{226}$Ra, $^{214}$Po and $^{214}$Bi. The first of these elements belongs to the group III of Rosholt [8] and the last two to the group IV.

As it is well known these groups were defined in such a way that each one started with a long lived element except the group IV which contains the $^{222}$Rn. On the other hand all the elements in the same group of Rosholt are in radioactive equilibrium and have radiochemical and geochemical affinities. So group I contains the elements of the uranium-radium series from $^{238}$U till $^{234}$U; groups II and III contain only one element each, $^{230}$Th and $^{226}$Ra respectively; group IV contains the elements from $^{222}$Rn till $^{210}$Tl and finally to group V belong the elements from $^{210}$Pb till $^{206}$Pb.

The study of the decay scheme of all the nuclei of the uranium family shows that for the group I the $\gamma$-rays have energies equal to or less than 93.5 keV. In groups II and V we only observe one γ-ray in each namely the 67.8 keV corresponding to the decay of $^{230}$Th and the 46.5 keV from the decay of $^{210}$Pb. These low energy γ-rays can all be seen with a Ge(Li) detector but the measurements made from the spectrum are spoilt by the presence of X-rays.

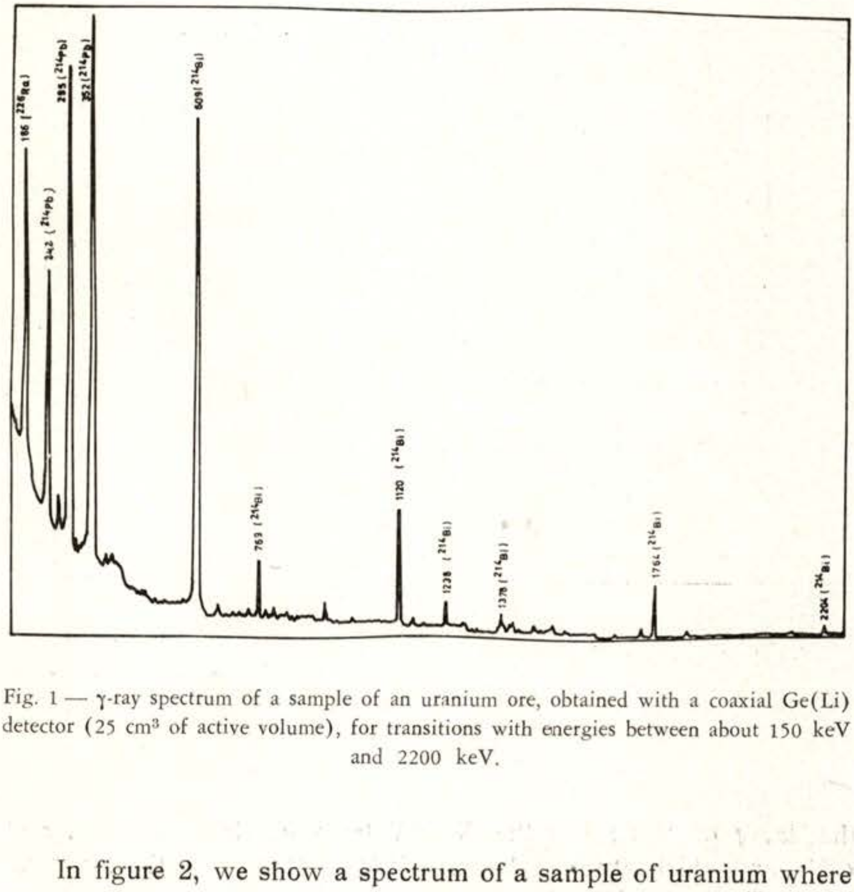

Fig. 1 — γ-ray spectrum of a sample of an uranium ore, obtained with a coaxial Ge(Li) detector (25 cm$^3$ of active volume), for transitions with energies between about 150 keV and 2200 keV.

In figure 2, we show a spectrum of a sample of uranium where it is possible to see transitions from 40 keV to 600 keV. Besides the peaks already present in the previous figure it is now possible to identify the 46.5 keV, 67.8 keV and 93.5 keV transitions mentioned above. We will see below the advantage of using a Ge (hyperpure) detector in these measurements.

Recently Mubarakmand et al. [9] used the direct γ-ray spectrometry in the measurement of absolute concentrations in uranium ores. They have claimed that this method is accurate for uranium concentrations above 0.1%. However their measurements were based on the study of the 93.5 keV transitions and as we have shown in figures 1 and 2 a large contribution to the 93.5 keV peak is due to X-rays and Compton background. Furthermore if in the sample there is $^{232}$Th and its daugther nuclei the 84.4 keV transition from the decay of $^{228}$Th and the 99 keV transition from the decay of $^{228}$Ac are sufficiently near the 93.5 keV peak to mask the measurements. These problems led us to review the study of the γ-spectrum of radioactive minerals. Our aim is twofold:

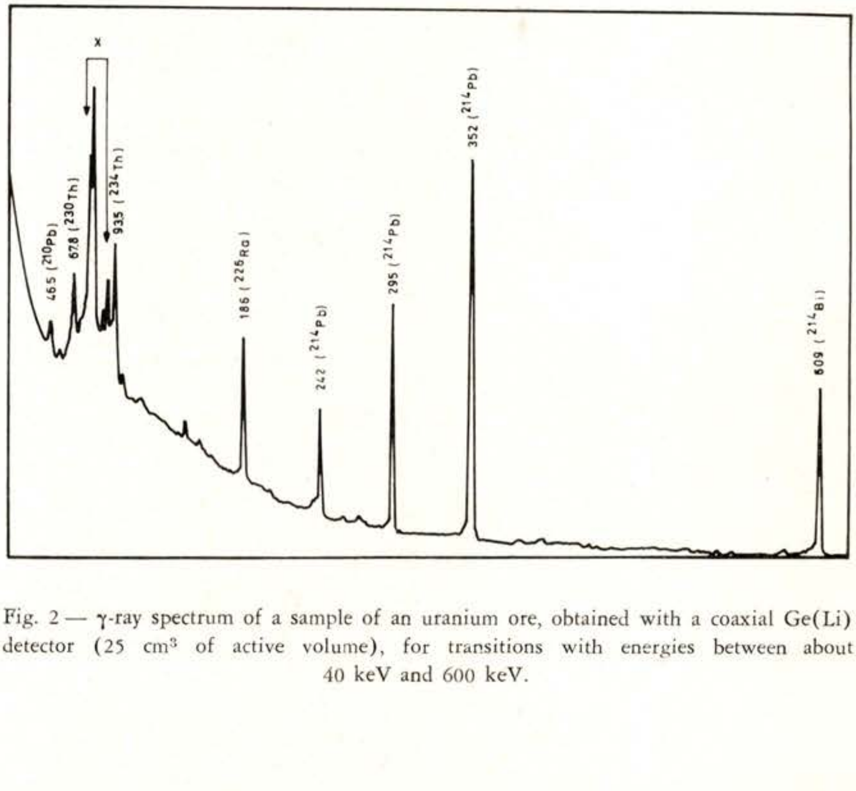

Fig. 2 — γ-ray spectrum of a sample of an uranium ore, obtained with a coaxial Ge(Li) detector (25 cm$^3$ of active volume), for transitions with energies between about 40 keV and 600 keV.

i) to judge the possibilities of γ-ray spectrometry to measure concentration of uranium below 0.1%;

ii) to apply a similar technique to mineral ores containing a mixture of uranium and thorium.

As far as point i) is concerned we have obtained the γ-ray spectrum of samples containing 0.02 %, 0.04 % and 0.1 % of uranium. The corresponding activities were calculated from the counting rate of the following peaks: 93.5 keV (group I), 186 keV (group III) and 352 keV and 609 keV (group IV). The linearity for the first two transitions is very good as can be seen in figure 3 but the points corresponding to the last sample and the last two transitions deviate clearly from

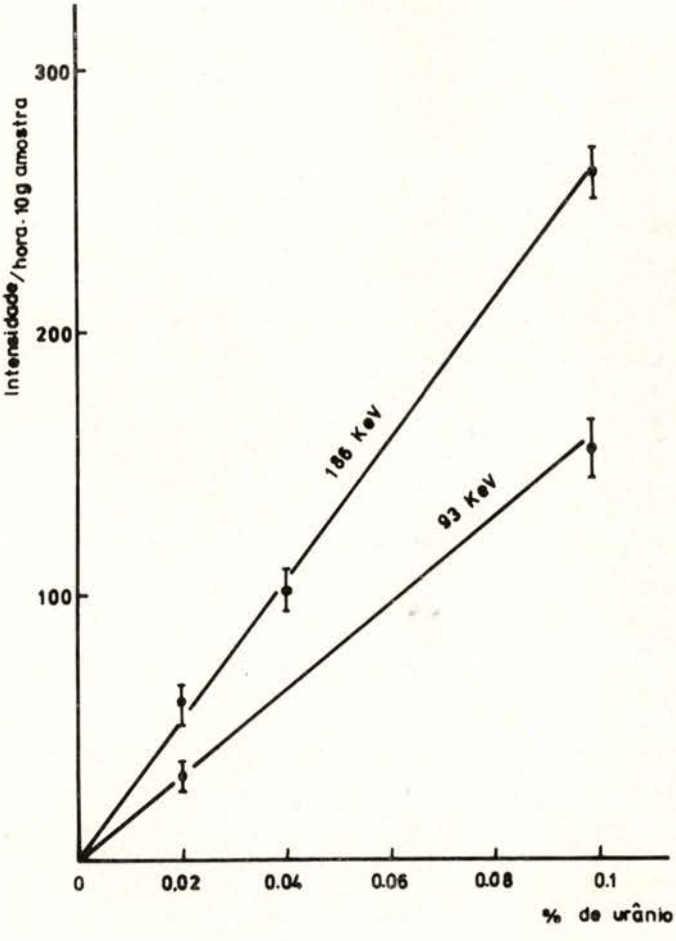

Fig. 3 — Activities of uranium ore standards measured from 93.5 keV and 186 keV transitions.

the straight line (fig. 4). This shows that in this sample the nuclei of group IV are not in radioactive equilibrium. In fact the ratios between the intensites calculated from fig. 4 and those actually measured gave a constant value equal to 1.6 .

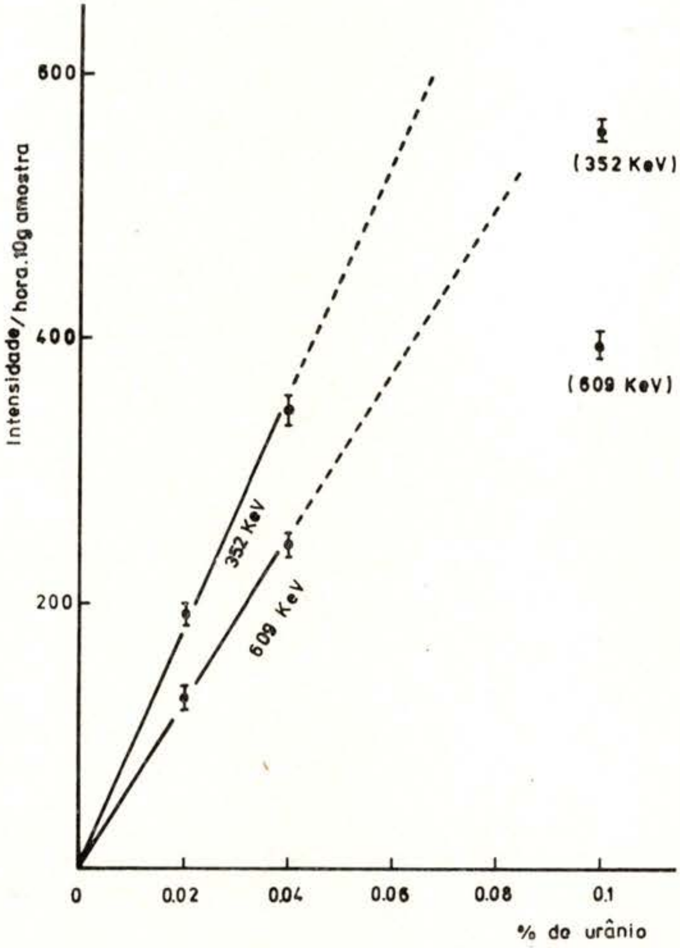

Fig. 4 — Activities of uranium ore standards measured from 352 keV and 609 keV transitions.

As far as point ii) is concerned we decided to study a specially unfavourable sample for this kind of measurements since it contained 0.04 % of uranium and 1 % of thorium. We show in figure 5 that although the measurements are practically impossible using the

93.5 keV or 242 keV transitions, they are still possible with the 186 keV, 352 keV and 609 keV transitions. These latter transitions are completely separated from the ones corresponding to the decay of thorium and its daughter nuclei.

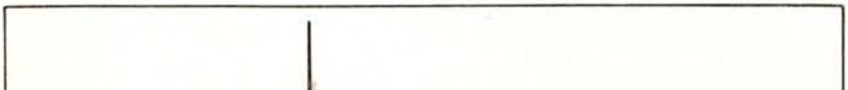

Fig. 5 — Spectrum of a ore sample with 0.04 % of uranium and 1 % of thorium, obtained with a coaxial Ge(Li) detector (25 cm$^3$ of active volume).

## 3 — X-RAY SPECTROMETRY

Figure 6 shows a spectrum of a monazite crystal obtained with a Ge (hyperpure) detector. One can notice the thorium X-rays produced by autofluorescence and also a small percentage of uranium. The concentration of uranium is obviously greater in the spectrum displayed in figure 7 which corresponds to thorianite. Actually the presence of uranium revealed by X-ray spectrometry is probably the best way to distinguish this mineral from another — thorite — which is very similar. Figure 8 shows another spectrum obtained with the same detector but now the concentration of uranium is even greater since it corresponds to a sample of pitchblende. It is also worth noting the existence in this spectrum of the X-rays characteristic of lead which is not present in the mineral ores containing thorium. To be more precise one must say that lead is always present in all radioactive minerals but in some cases, like the one we have mentioned above, its concentration is so small that it can not be detected by X-ray analysis.

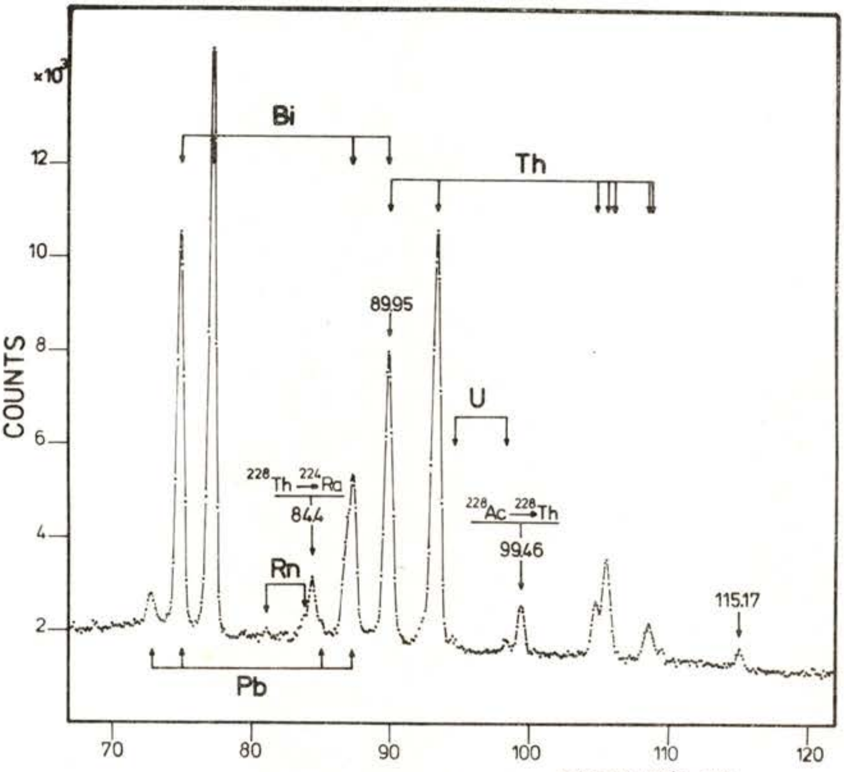

Fig. 6 — Spectrum of a ore sample of monazite obtained with a Ge (hyperpure) detector (presence of thorium and absence of uranium).

Another information that one can extract from this spectrum is the existence of tungsten which as far as we know is the first time that has been detected in association with uranium.

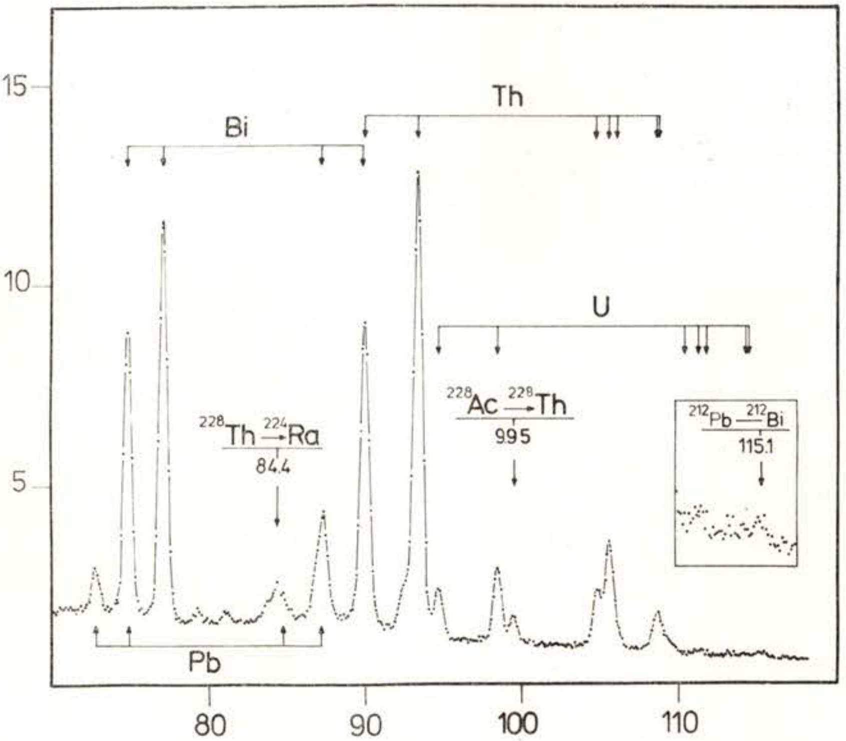

Fig. 7 — Spectrum of a sample of thorianite obtained with a Ge (hyperpure) detector (presence of thorium and uranium).

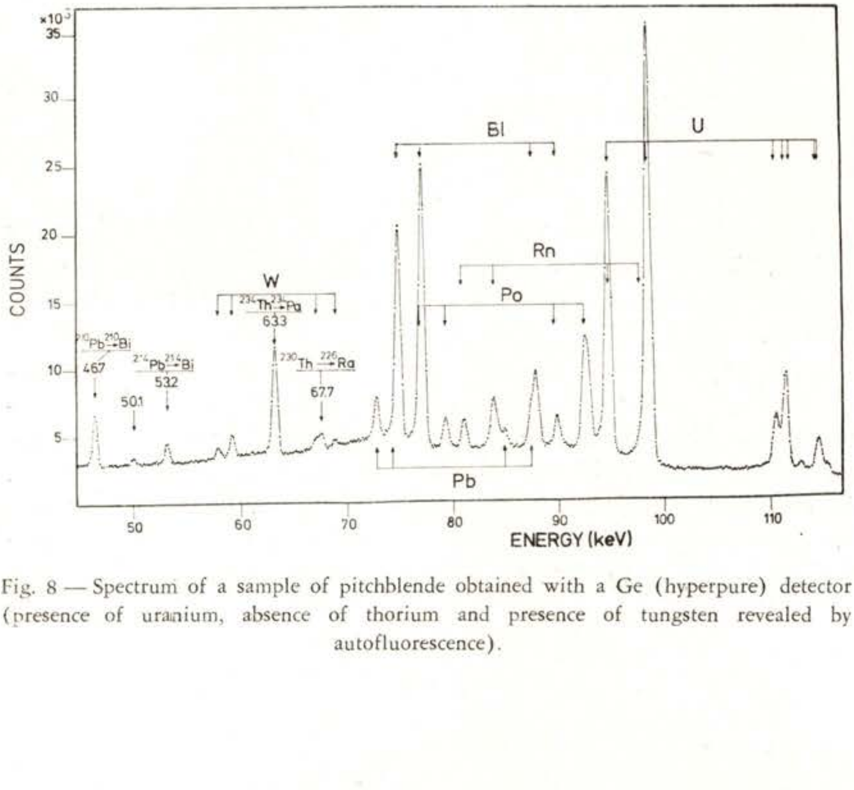

Fig. 8 — Spectrum of a sample of pitchblende obtained with a Ge (hyperpure) detector (presence of uranium, absence of thorium and presence of tungsten revealed by autofluorescence).

Since a large part of the world reserves of uranium, including the Portuguese, consists of minerals with low concentration we decided to apply this techique to one of them — saléeite (fig. 9).

As an example of a secondary mineral of uranium we show in figure 10 a spectrum of uranocircite. In it one cannot detect the presence of lead and on the other hand one can see the existence of barium. The presence of barium is extremely useful to identify this mineral since its classification by conventional methods is very difficult.

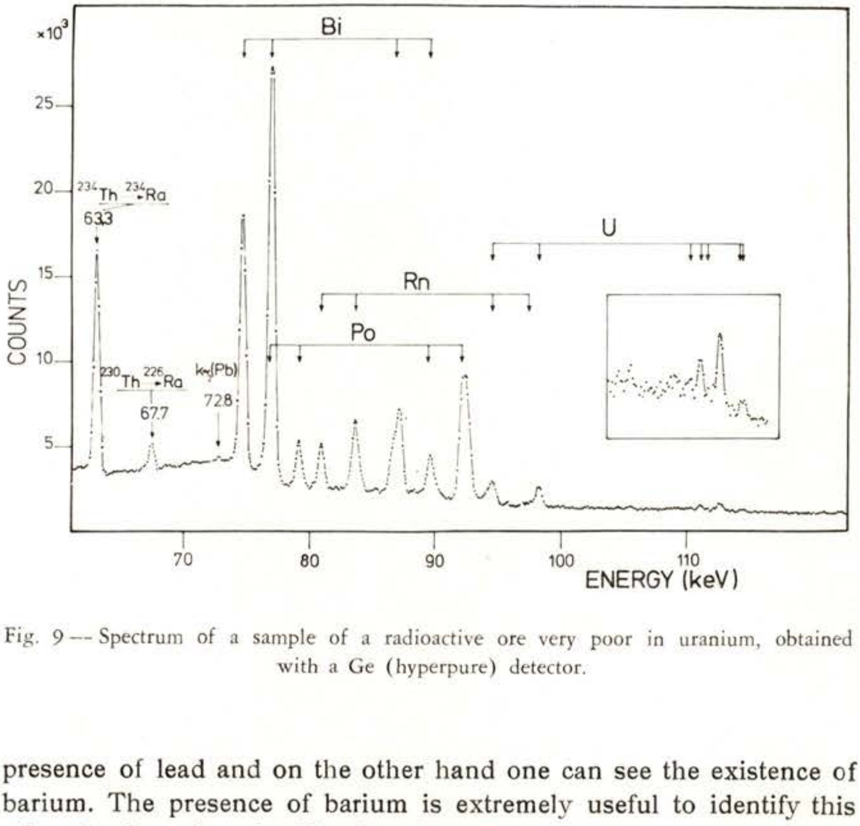

Fig. 9 — Spectrum of a sample of a radioactive ore very poor in uranium, obtained with a Ge (hyperpure) detector.

Finnally figure 11 shows another piece of the spectrum of monazite already displayed in figure 6. It is now possible to see the different rare earth elements present in this mineral. The good resolution of this spectrum enables us to measure their relative concentrations. As far as we can judge from the analysis of two monazite crystals from different mines (Madagascar and Norway) the relative concentrations of rare earth elements do not vary significantly.

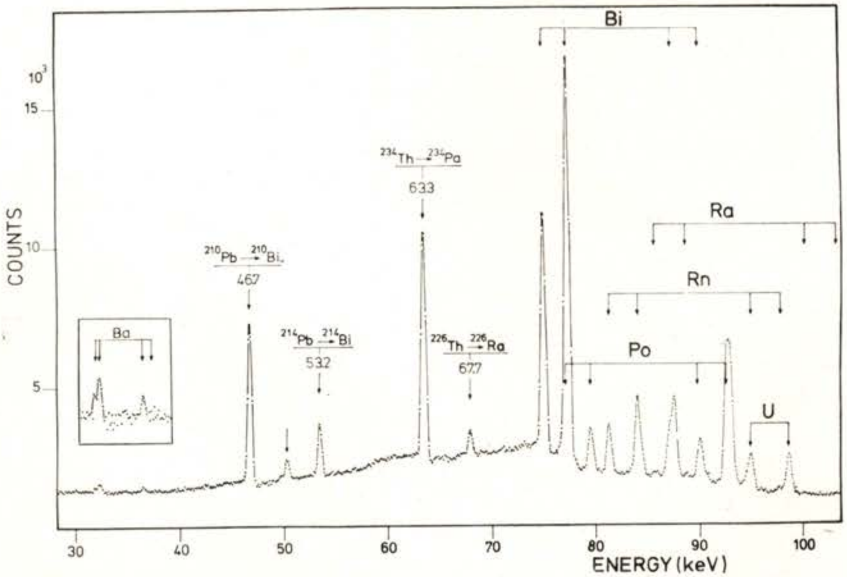

Fig. 10 — Spectrum of a sample of uranocircite obtained with a Ge (hyperpure) detector (absence of lead and presence of barium revealed by autofluorescence).

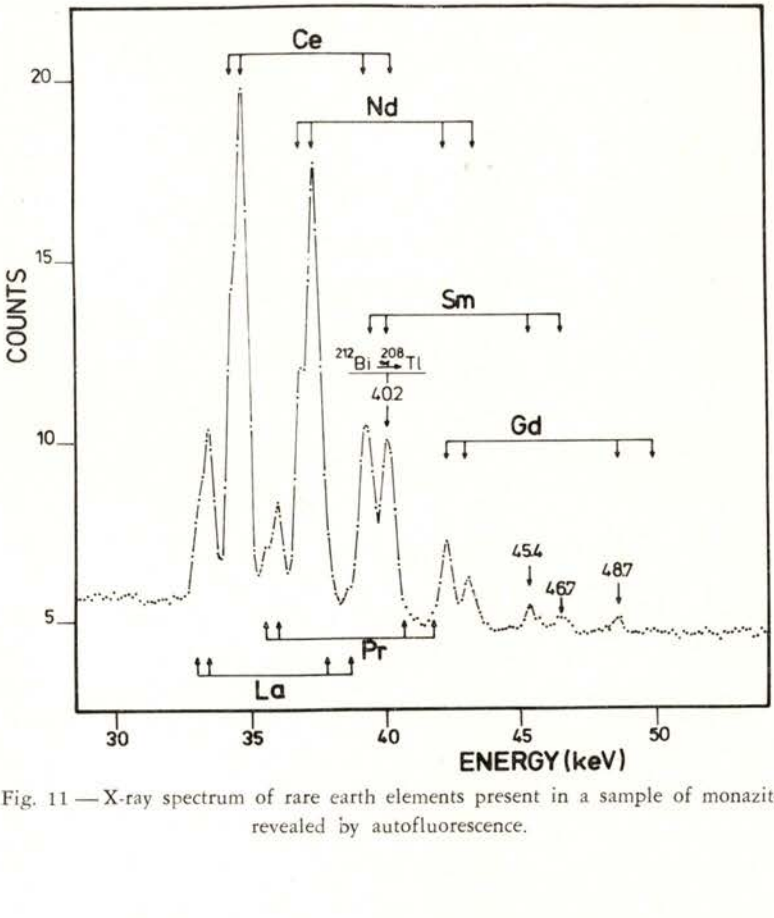

Fig. 11 — X-ray spectrum of rare earth elements present in a sample of monazite revealed by autofluorescence.

## 4 — CONCLUSION

In this paper we have shown how to use Ge(Li) and Ge (hyperpure) spectrometers in the qualitative and semi-quantitative analysis of radioactive minerals. This method reveals with high accuracy even the presence of non radioactive elements due to a process of X-ray emission by autofluorescence. Further work and specially more precise quantitative measurements are presently in progress and will be published elsewhere.

We woul like to thank the « Departamento de Física da Universidade de Coimbra » and specially Miss Maria Alice Alves for lending us the standard radioactive samples used in this work. Thanks are also due do Mrs. Maria da Graça Canelhas from « Museu e Laboratório Mineralógico e Geológico da Universidade de Lisboa », Mr. Lencastre from « Junta de Energia Nuclear » and the private collector Mr. Costa e Silva for lending us the samples that were analysed.

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