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ON THE EMPLOYMENT OF LIQUID EMULSION IN THE TITRATION OF URANIUM FROM RADIOACTIVE MINERALS

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With the increase of interest in the titration of uranium and other radio-elements, especially in minerals with low content in these elements, several methods of titration have been recently developed which make use of nuclear emulsion.

In existing methods for the titration of minerals in solution, ready-made slides are used. In the present work, we develop a method in which the solution to be titrated is mixed with liquid emulsion; the slide obtained is compared with another slide containing a standar solution, prepared under analogous conditions.

We shall limit ourselves here to the case of minerals which contain solely elements of the uranium family. The titration of minerals which contain both the thorium and uranium families, or the thorium family alone, will be the subject of a later study.

Method of Titration

Spread evenly on a glass slide the liquid emulsion mixed with a standard solution of uranium salt; on another identical slide, spread liquid emulsion mixed with the mineral solution. The

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two slides should be prepared jointly in order to make the comparison; equal masses of the emulsion, containing equal quantities of the solutions should be used. After drying, the slides are left in the refrigerator for several days exposure, before they are developed.

Before making the comparison between the two slides, histograms should be made of the number of alpha particles that do not make part of stars, against the range in the emulsion, both for the standard solution and for the solution to be titrated, This histogram determines by analysis, the percentage of radioactive elements present.

Fig. 1 represents the histogram obtained with the solution of uranyl acetate (Baker) used as standard. It is seen that there are two groups of α particles with practically the same number of tracks; the first group corresponds to U_{238} and the second group to U_{234}. This is what one should expect for a chemically pure salt. As 3.5 % of the particles from the second group are due to U_{235} [1] we see that the total number of α tracks is 2.035 times the number of α particles due to U_{238}. The histogram of the standard solution should be made once for all in order to verify its composition.

Fig. 2 gives the histogram of an uranium mineral (uraninite from Brejaubas) which does not contain the thorium family as evidenced by the fact that no thorium stars were observed. We see that there are three groups of α tracks. The first group corresponds to U_{238}. The second group, three times larger than the first, corresponds to U_{234}, Th_{230} and Ra_{226} [2]. The third group is due to Po_{210}. It is found that within the statistical errors the Polonium group contains the same number of particles as the U_{238} group. This is frequently the case with compact rocks when there is no sensible loss of Rn. In such cases (and we shall restrict ourselves to them), there is no need for making the histogram of the mineral. The total number of single tracks is then 5.1 times the U_{238} tracks. In this number we have included the tracks corresponding to U_{234}, Pa_{231} and Th_{227} which contribute to the second and third group with

3x0.035 the number of U_{238} tracks [1].

For the titration itself, one proceeds in the following manner:

First, count the number of alpha particle tracks per microscope field on the slide with the standard solution. The count is made in various fields and the arithmetic average N_p is obtained. $N_p/2.035$ is the mean number per field of alphas due to U_{238}.

Count also the number of alpha particle tracks which <u>are not part of a star</u>, on a microscope field of the slide with the mineral solution. N_m is the average rate in this case. $N_m/5.1$ is the mean number per field of alphas due to U_{238}.

The time of exposure being the same for the two slides,

$$r = \frac{2.035 N_m}{5.1 N_p} \qquad (1)$$

gives the relation between the number of uranium atoms counted in equal quantities of the radioactive mineral solution and the standard solution [3].

Knowing the number of uranium atoms per unit of volume for the standard solution, one can determine the number of the mineral solution, obtaining then the U_{238} content of the mineral.

Once this content is known, the corresponding quantity of radium can be calculated, using the equation for the secular equilibrium:

$$\lambda_a N_a = \lambda_b N_b \qquad (2)$$

λ_a and λ_b being the constant of disintigration of uranium and radium respectively, N_a the number of uranium atoms and N_b the number of radium atoms in the given mineral mass.

If there is sizable diffusion of Rn in the rock the average number of tracks per field due to U_{238} is obtained for the slide with mineral solution, in the following way: One multiplies the average number of single tracks per field, by T_1/T, where T_1 is the number of particles belonging to the U_{238} group in the histogram of the mineral and T is the total number of particles in the histogram.

Results of Observation:

In order to verify the method, we have made the following measurements:

1) Comparison between three solutions of uranyl acetate (Baker) of 1/500, 1/1,000 and 1/2,000 concentrations.

For the counting, 100 X objective and 6X eyepieces were used; aproximately 1,000 tracks were counted. The result of the measurements is shown in the graph in Fig. 3. Taking the 1/500 solution as standard, the concentrations 0,00098± 0,00003 and 0,00048± 0,000015 respectively were obtained for the 0,001 and 0,005 solutions. (The errors indicated are probable errors).

2) Titration of a uranyl nitrate solution (Baker) taking as reference a solution of uranyl acetate.

The acetate solution used was 1/4,000 and that of nitrate, 1/1,000. The result obtained for the concentration of nitrate was 0,001± 0,00003. 45X objective, and 6X eyepieces were used, and about 1,000 tracks were counted. It was assumed that in the nitrate there were only U_{238}, U_{234} and U_{235}, as in the acetate (both being from the same laboratory).

3) Determination of radium content in the uraninite from Brejaubas (M. Gerais).

The solution used as standard was 1/4,000 uranyl acetate (Baker). The histogram of Fig. 3 was obtained for the mineral solution. It showed about 200 alpha particles which did not pertain to the elements U_{238}, U_{234}, Th_{230} and Ra_{226}. (The majority of them were due to Po).

In measurements made in two slides employing the same 1/2000 mineral solution, the results obtained were 275 and 263 mg of radium per ton, respectively (1,000 track counts made per slide).

These results are in accord with those of Costa Ribeiro [4], who obtained for this mineral a content of 253 mg of radium per ton, with individual values ranging between 232 and 273 mg.

In all the measurements, the time spent between the preparation of the slides and their development was approximately

three days.

Preparation of the Solutions:

Considering that the neutrality of the solutions of uranium salts used is important to guarantee the sensibility of the nuclear emulsion [5], all the radioactive solutions employed were neutralized, being previously treated with citric acid. This acid forms a complex with the uranium[6,7] and avoids its precipitation when the solution is neutralized by amonium hydroxide [8].

Preparing the Slides:

Take a sheet of glass of uniform thickness (preferably one prepared by Ilford especially for nuclear slides), and cut the slides into the dimensions desired. A surface of approximately 22.8 cm^2 was used in the presente work. Weigh the slides on an accurate scale: the reason for the weighing will be obvious from what follows:

Given masses of the solutions to be compared are mixed with known masses of the emulsion. The weighing of the emulsion and of the solution is recommended as being more precise than measuring the volume; for instance, the measurement of 0.5 cm^3 of solution with a precision pipette of 0.1 cm^3 is susceptible to an error of 2.5%. Nearly two grams of emulsion and about 0.5 cm^3 of solution were used per slide.

Place the mixtures in a bath at 51º C for 20 minutes, in order that the emulsion should melt. Stir it with a glass rod. Spread the liquid over the slides which are placed on a level plane, and leave them to dry. To facilitate drying, the plate containing the slides may be warmed a little by putting a lamp beneath it and by using a ventilator in order to circulate air over the emulsion.

To compare the thickness of emulsion in the several slides, weigh the plates again after drying. The relation between the mass of emulsion and the mass of the glass gives a number proportional to the thickness of the emulsion. This number allows one to reduce the results of the counting in the several plates to the same

thickness.

Developing and Fixing:

I - developer [9] Distilled water - 1,000 cm^3
Boric acid - 35 g
Sodium sulphite (anhydrous)-18 g
Potassium bromide - (10 % solution) 8 cm^3
Amidol - 4.5 g

Developing time : 20 minutes

Developing temperature: 28º C

II - Stop bath:

0.2 % acetic acid solution

Time: one hour

Temperature: 28º C initially, gradually lowered to 4º C

III - Fixing bath:

40 % sodium hyposulphite solution

Temperature: 10 to 15º C

After fixing the slides are washed in water at 10º C, which is renewed each half hour.

Counting:

A field is selected, with a diameter which is large in relation to the range of the particles. Count the tracks within the field, and to this number add half the number of those tracks not entirely contained within. This sum is the number of tracks per microscopic field, referred to in the titration method.

Conclusions:

The method of titration developed in the present work gave a 3 % precision in the conditions of our measurements.

The following advantages of the present method over other methods of titration with emulsion are apparent:

The fact that there is absorption of alpha particles only by the emulsion itself presents an advantage over those methods in which the solution is not placed directly in the emulsion [10].

The advantage over the drop method [11] is in that it is not necessary to count all the tracks in the regions where the solution is present on the plates.

The method of soaking ready-made plates in solution presents difficulties concerning the equilibrium of the concentrations between solution and nuclear emulsion [12] and the velocity of diffusion of different elements in the emulsion [13]- difficulties which do not appear in the present method.

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1 The isotopic composition of uranium is 99,28/0.0057/0.71 for $U_{238}/U_{234}/U_{235}$. U_{238} and U_{234} being in secular equilibrium do emit equal numbers of α particles per second (ν). U_{235} having a period equal to 1/5 and en ebundance of 0.72 that of U_{238} emits $0.035\,\nu$ particles per second.
In a uranium mineral, besides U_{234} and U_{238}, there is Th_{230}, Ra_{226} and Po_{210}. The first four elements are in general in equilibrium and the percentage of Po depends on the amount of radon retained in the rock. There are also the U_{235}, Pa_{231} and Th_{227} in equilibrium among themselves. These are the elements which produce single α tracks.

2 Ra_{226} produces by disintegration Rn, whose period is 3.8 days and gives rise to a star. The Ra_{226} stars can, however, be neglected as compared with the single tracks in view of the radon diffusion.

3 In formula (1) the fact that a small number of Ra atoms gives rise to 4 branch stars (about 1% in three days), was neglected. Also the 5-branch stars due to Th_{227} (Ra_{223} has a period of 11.4 days), were neglected. For greater times of exposure one should take these into account. The correct formula for r is then $r = 2.035N_m/5.14N_p$ where N_m is now the average number per field of single tracks plus 4-branch stars plus twice the 5 branch stars. The factor 5.14 contains a term 0.035 corresponding to Ra_{223}.

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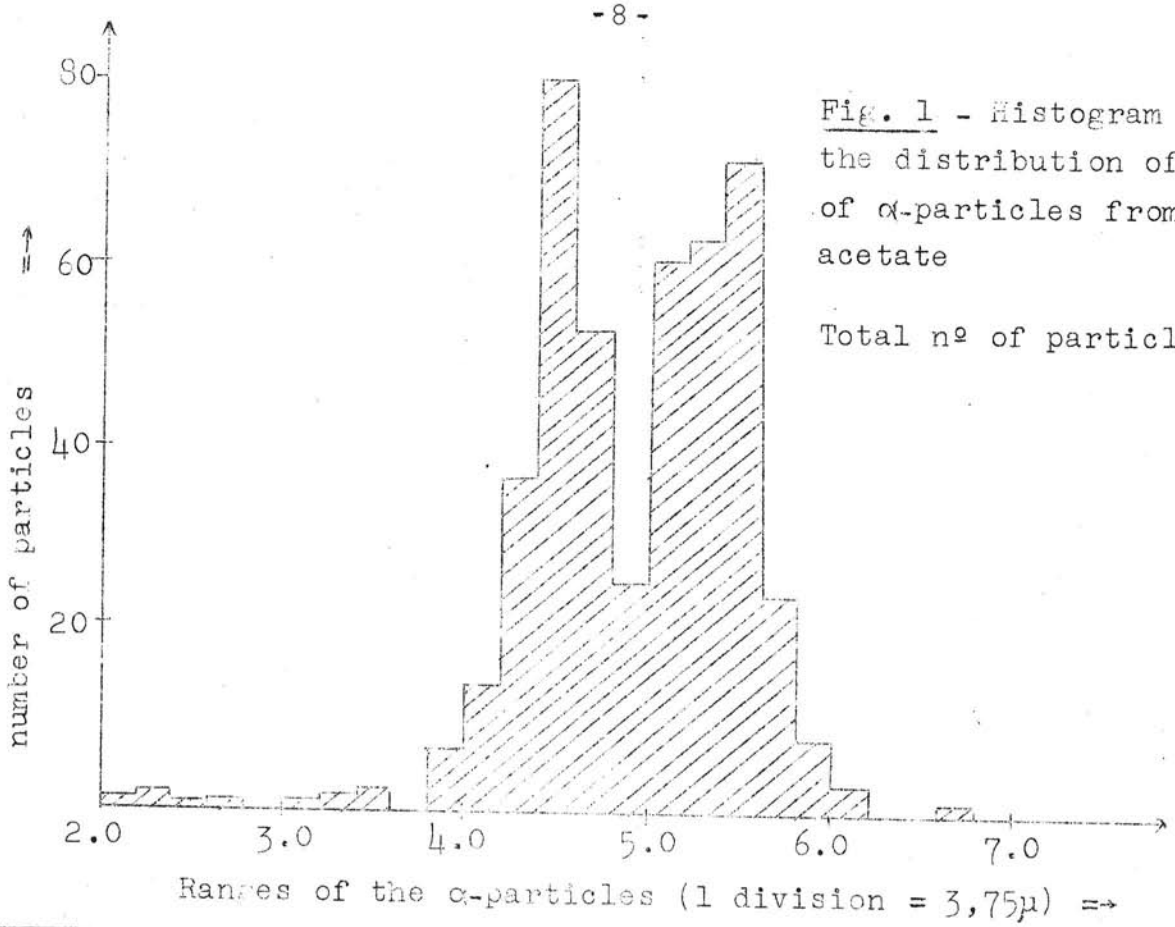

Fig. 1 - Histogram showing the distribution of ranges of α-particles from uranyl acetate

Total nº of particles: 434

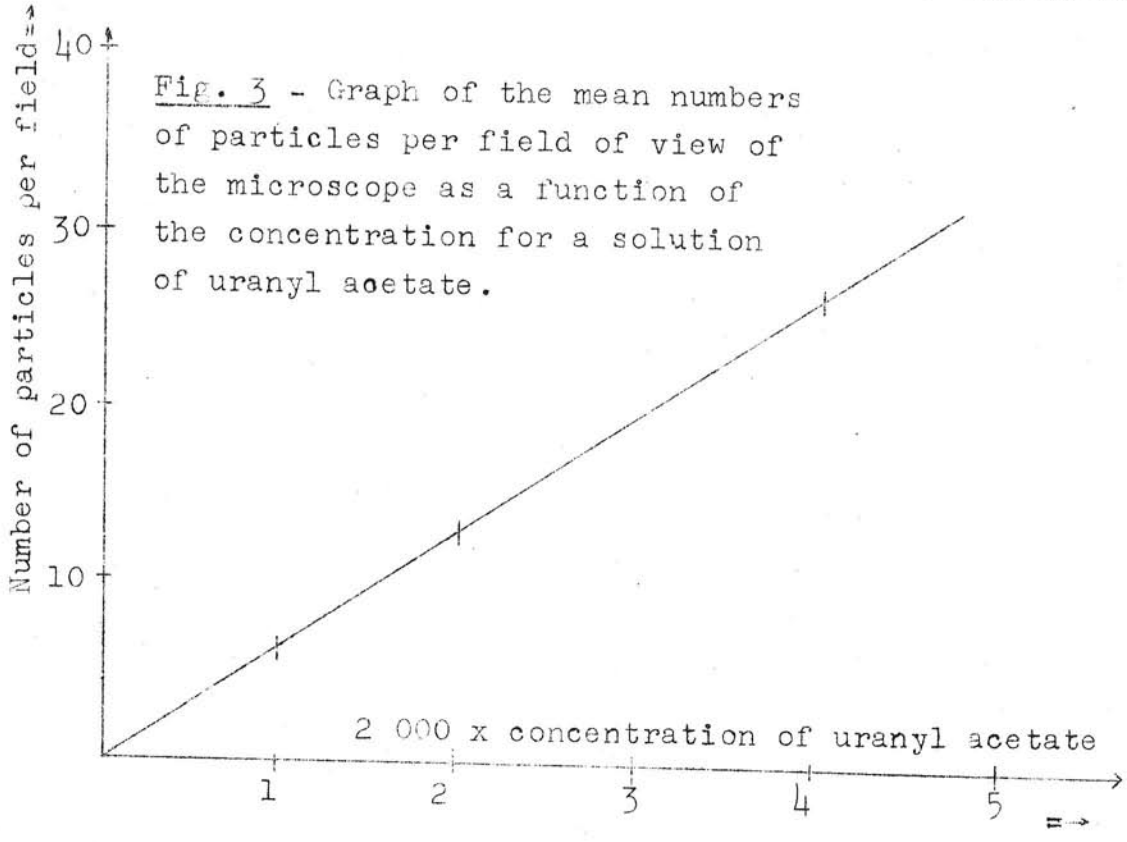

Fig. 3 - Graph of the mean numbers of particles per field of view of the microscope as a function of the concentration for a solution of uranyl acetate.

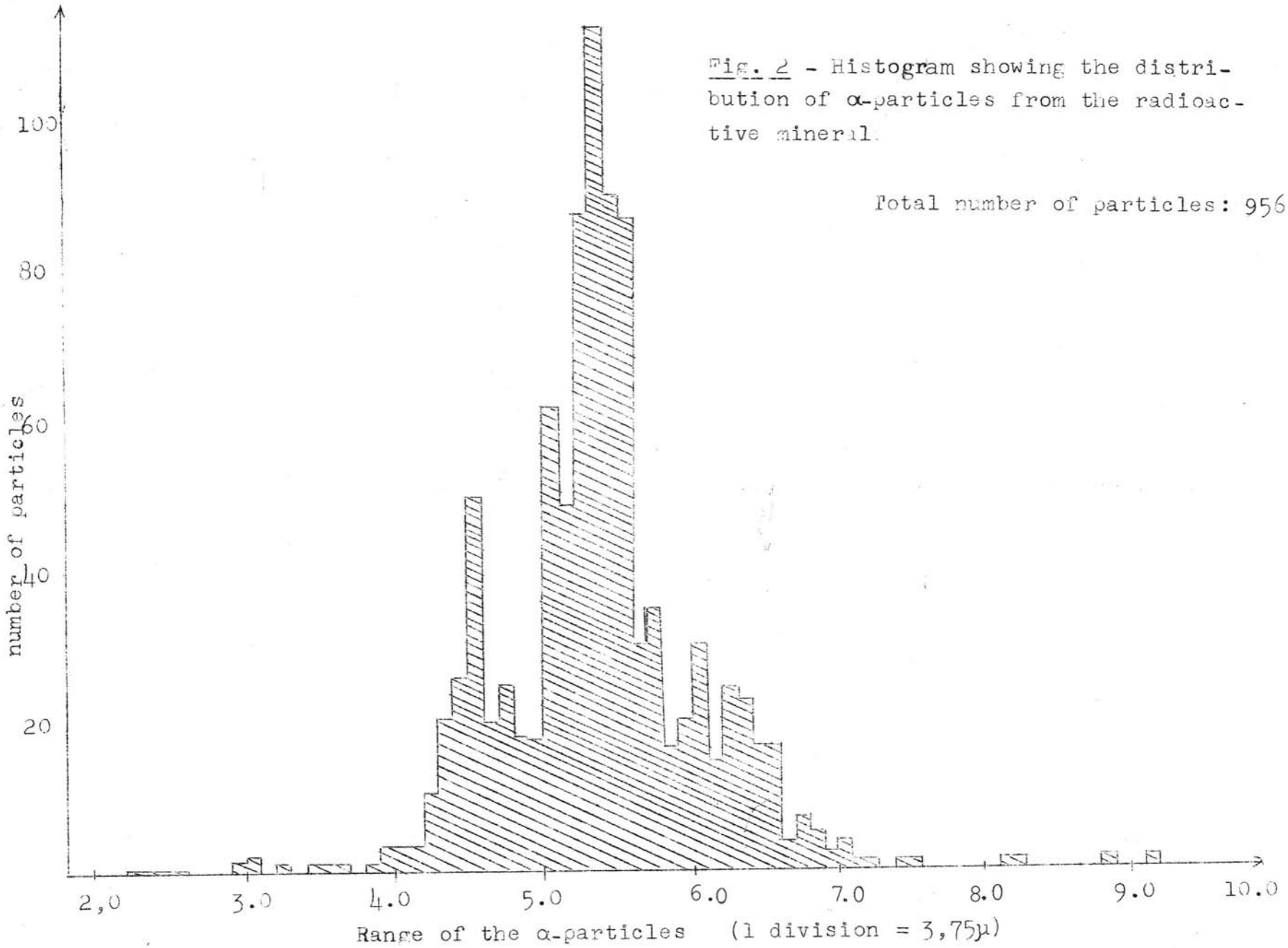

Fig. 2 - Histogram showing the distribution of α-particles from the radioactive mineral.

Total number of particles: 956