Fluorometric Microdetermination of Uranium. IV. Measurement of the Fluorescence Intensity and Determination of the Uranium Content in Natural Substances

By Masaki NAKANISHI

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Mesurement of the Fluorescence Intensity

In the way successively described in the foregoing papers, uranium is extracted from the sample in question and mixed with sodium fluoride to prepare the fluorescent material. The prepared fluorescent bead produces a vivid yellow luminescence under the excitation of ultraviolet ray.

This report will recount the particulars in measuring the fluorescence intensity. As shown in the first report of this series, the fluorescence intensity varies with the uranium content of each fluorescent bead, and the larger the content is, the more intense becomes the fluorescence within the range of uranium 10^{-4} to 10^{-9} g.

The bead from an unknown sample is compared on its luminescence intensity with those of known content of uranium, and the uranium content of the former is determined by interpolation.

The high tention mercury lamp was used as the sourse of ultraviolet light, in combination with the glass filter prepared for this purpose.

The measurement is performed, as a rule, with the aid of the photographic spectral photometry, but the visual observation is also often applied expediently.

By the Photographic Spectral Photometry.—As is often available in the measurement of a faint gleam, the photographic spectral photometry is the effective means for measuring the fluorescence intensity.

On the same photographic plate, fluorescence band spectra of both known and unknown beads are photographed in parallel, and the blackness of these bands is compared at the corresponding wave length. In order to avoid the effect of ultraviolet light, which is reflected on the surface of the bead, on the photographic plate, it is necessary to disperse the fluorescence into a spectrum, making use of a spectrograph.

Procedures.—The fluorescent bead is supported at a fixed position on the optical axis closely before the widely opened slit of the spectrograph, and is irradiated from a fixed slant direction with the ultraviolet light condensed with a quarz lens of short focus.

As the direction and the position of the discal bead settled in its place affect considerably the density of the photographic plate, they must strictly be fixed.

In order to determine the uranium contents of the unknown beads, the observation of the fluorescence spectra of at least two different known beads are necessary. Spectra of the known and the unknown are taken successively on the same plate, where the time of exposure must be constant for every spectrum, in accordance with the rule of the photographic photometry. The exposure is usually about 10 minutes for the bead containing 10^{-6} g. of uranium, provided that an ordinary panchromatic plate is used. But the time of exposure should be decided by the trial run, for it is subjected to the nature of the plate, as well as the optical system, the intensity of fluorescence and the breadth of the slit.

After the photographing, the plate is developed and the photographic density of each spectrum is estimated at 555 mμ with the microphotometer.

The obtained values of photographic density for known beads are referred to their contents of uranium, and the relation between content and density is established in a convenient way, say, graphically. The particulars of the photographic spectral photometry are omitted here.(1)

By the Visual Observation.—In estimating the intensity of the fluorescence, the photographic photometry has the superiority above other methods, especially for such a faint luminescence as in the present case. But the procedures are somewhat tedious, and if they are faultily followed in any point unexpected results are likely to be obtained. In these respects the following method facilitates the course and provides the satisfactory results.

In this method the intensity comparison of the unknown beads with the known is made with the naked eye, instead of the spectrograph. It is of course possible to make the comparison in the simple way, in which the intensity of the unknown bead is observed in the ultra-

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(1) H.B. Dorgelo, *Physik. Z.*, 26, 756 (1925); R. Frerichs, "Handbuch der Physik", Berlin, 1928, Vol. 19, Chapter 23.

violet light and compared with those of several known beads containing different quantities of uranium. But more accurate results are expected by the following device based on the same principle.

Procedures.—The colorimeter of the Duboscq type is used for this purpose for the sake of convenience. Any turbid solution of an arbitrary concentration is applied to the absorbing layer in the vertical cylinders. Just under each cylinder the fluorescent bead is placed severally. In the one position under one cylinder an arbitrary bead for comparison is settled and kept fixed during the process, and in the other position known and unknown beads are placed one after another. These two beads are compared by the balancing method in the ultraviolet light.

As the fluorescence is in general fairly faint, the microscopic part of the colorimeter is removed to eliminate the absorption and to make the loss of light due to magnification minimum. The fluorescent beads are arranged in such a way that those two images are observed side by side in the scope.

The uranium content in the bead in question is determined as follows.

According to the absorption law of light, the intensity I of the fluorescence in question after passing through the layer d of the turbid solution is given by

$$I = I_0 e^{-kd'},$$

where I_0 and k represent the initial intensity and the absorption constant respectively.

On the other hand, we obtain a similar equation for an arbitrary bead for comparison,

$$I' = I_0' e^{-kd'},$$

where each figure has the corresponding meaning.

When the apparent intensities of both images come equal,

$$I = I'$$

or $$I_0 e^{-kd} = I_0' e^{-kd'}$$

therfore $$I_0 = I_0' e^{-k(d'-d)}.$$

To obtain the values of the two unknown constants, I_0' and k, more than two beads containing different amounts of uranium are compared on their luminescence intensity with the arbitrary bead for the comparison in the manner as given above. Then the uranium content of an unknown bead is obtained from these values of constants in the same procedure.

The above calculation is valid only within the range in which the fluorescence intensity is linearly proportional to the content of uranium of the bead.

This visual observation method has the advantages, in spite of its simplicity, over the photographic photometry in several points. The latter method is not free from imperfections for the purpose of this kind in the following points.

(a) The fluorescence is too faint to make an image on the photographic plate in case the content of uranium is small. In consequence, the time of exposure must necessarily be prolonged. Meanwhile the bead may be wet by the atmospheric moisture especially in the damp weather, and consequently the fluorescence intensity is likely made feeble.

(b) The procedures following after the photographing, e.g., the development of the plate and the measurement of the photographic density, are not easy.

(c) Each operation is subjected to the influences of many factors, and this presumably makes the possibility of the experimental error much.

The visual observation method overcomes these difficulties for all the simplicity in comparison with the photographic photometry. The writer therefore takes the former from his experiences for a suitable method in routine works, and he has got the satisfactory results by the method.

Determination of the Uranium Content in Natural Substances

On the uranium contents of various natural substances which are not regarded as radioactive, almost no direct determination has been carried out so far in this country. Since these nonradioactive substances usually contain such an amount of uranium as is most suitably determined by the fluorometric method, this procedure must furnish the useful means to manifest the geochemical circumstances of radioactive elements.

In dealing with rocks in which uranium is expected to be in the state of equilibrium with radium, the amount of the former is easily estimated indirectly from that of the latter.

The microdetermination of uranium is necessary, especially for the samples in which radioactive elements of the uranium series do not yet reach their equilibrium condition. In these circumstances the fluorometric method is an effective measure.

Included among these are samples from the hydrosphere as well as the biosphere. Furthermore some minerals of which ages are less than a million years from their formation, weathered minerals or rocks, etc. must be treated in the direct microdetermination method to determine uranium, because uranium is not expected to be in equilibrium with the disintegration products. The following sections will deal with some examples of natural substances treated with the fluorometric method of analysis.

The Uranium Contents of Rocks

Experiment.—The particulars of the treatment are omitted here, for the full description of the analytical procedures appeared in the previous papers.

About 1 g. of the sample suffices for the analysis. In case the sample is first fused with sodium carbonate and leached with hot water as recommended from the writer's experiences, the procedure must be repeated at least three times to make the complete extraction of uranium.

The leached solution containing a considerable amount of sodium carbonate is made acid with hydrochloric acid and evaporated to dryness. From this residue remove silica in the usual way, and to the resulting solution add a little ferric chloride (corresponding to about 20 mg. Fe_2O_3) and ammonium chloride. Boil the solution, make it ammoniacal, continue the boiling for a few minutes, and then filter the precipitate. The filtrate is treated two times more in the same way repeating the precipitation. The first precipitate generally contains some aluminum hydroxide.

Three precipitates are brought together. The combined mass must necessarily be reprecipitated, for it includes much impurities, especially sodium chloride derived from the mother liquor.

The obtained precipitate of iron hydroxide contains the total amount of uranium in the original sample. The after treatments run in the same way as already described.

The interferences of impurities are satisfactorily avoided even in such a normal course of procedures, so far as the common igneous rocks are concerned.

The results obtained on some examples of the rock are listed in Table 1.

Table 1

No.	Sample	Location	Uranium content, 10^{-6} g.U/g.
(1)	Sinter deposit (ferruginous)	Masutomi (Yamanashi Prefecture)	0.05
(2)	Sinter deposit (calcareous)	〃	0.004
(3)	Greywacke	〃	2.15 2.06
(4)	Shale (average sample)	Europe	0.67

The first sample (1) shows the uranium content of the sinter deposit at one of the chalybeate mineral springs in Masutomi district (Yamanashi Prefecture), which is widely known as one of the strongest radioactive spring regions in Japan.

The spring A 8 (as named by earlier investigators),⁽²⁾ from which the ferruginous sinter grew, is very radioactive owing to its large contents of radium and radon, but the uranium content of the spring water itself (0.3×10^{-6}g.U/g.) is not so large as expected. A part of the dissolved uranium in the spring water must be coprecipitated with iron near the orifice, but the larger part of the element is likely to remain in the solution, because the spring water contains some noticeable amount of carbonate.

The sample (2) is an example of calcareous sinter deposits formed from mineral waters of old times. It consists mainly of calcium carbonate. This sample was obtained in October, 1936, by Dr. Toshio Nakai, who found in it the extraordinarily large content of radium amounting to 1.75×10^{-10} g.Ra/g.⁽³⁾ The writer is much obliged to him for affording facilities to make use of the sample.

As the result of analysis a very small amount of uranium was found as given in Table 1. If uranium be present to the equilibrium amount to radium, the content would reach 5.15×10^{-4} g.U/g. On the contrary, however the observed value of uranium is 10^5 times smaller than the expected. This fact shows that uranium and radium are brought into the sinter deposits independently to each other by different mechanisms. Further, it would be natural that uranium does not behave in the same manner as calcium, when considered that uranium forms a soluble complex salt with carbonate. The uranium found in the calcareous sinter deposit will presumably have originated from the permeating mineral water.

The analysis of the sample (3) was attempted to know the uranium content of the ground, from which the strong radioactive springs arise. The sample was taken at the spot between B and C areas⁽²⁾ of Masutomi district.

The sample (4) is an average sample of various European shales, which the writer received by courtesy of Professor Eiichi Minami. The value obtained corresponds to that of mean basic igneous rocks.

Summary

Details of the methods of measuring the relative intensity of the fluorescence were described, in which the photographic spectral photometry and the visual observation method were related.

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(2) S. Oana and K. Kuroda, this Bulletin, **17**, 400 (1942).

(3) T. Nakai, this Bulletin, **15**, 420 (1940).

Several examples of uranium contents in rocks and sinter deposits determined by this method are treated from the geochemical interest.

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Chemial Institute, Faculty of Science,
the University of Tokyo, Tokyo
Laboratory of Chemistry, Faculty of Science,
Ochanomizu University, Tokyo