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## ESTIMATION OF SMALL QUANTITIES OF URANIUM IN THORIUM

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### ABSTRACT

Estimation of the intensity of the uranyl fluorescence furnishes a method for the determination of quantities of uranium as low as one-half microgram of uranium in one-half milliliter of glassy phosphoric acid. The test has been used to detect directly three parts of uranium in one million parts of thorium.

The characteristic fluorescence spectrum of uranyl ion furnishes a means for the unambiguous detection of small amounts of uranium. Although the fine details of the structure of the uranyl fluorescence spectrum depend on the environment of the ion, the main features are sufficiently constant to leave no question as to the identification of uranium by means of the spectrum. Whenever uranyl ion is excited to fluorescence, the spectrum exhibits the following features: a set of five or six narrow bands, with a constant frequency interval of about 800 wave numbers, beginning at about 4900 A° and extending toward the red. The second band at about 5100 A° is the most intense, the succeeding bands decreasing steadily in intensity. Because of its low intensity, the farthestmost red band is not always observed.

Because of the long half life (c.  $0.5 \times 10^{-3}$  sec.) of the excited state of uranyl ion, and because of the great chemical reactivity as an oxidizing agent of the ion in this state, the fluorescence is easily quenched,

*Chemistry - Uranium & Transuranic Elements*

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and to ensure maximum sensitivity of the test, care must be taken to prevent dissipation of the energy of the excited uranyl ion by paths other than the emission of radiation.

### EXPERIMENTAL

Light for the excitation of the fluorescence was furnished by a General Electric ANS high pressure mercury arc in a quartz jacket. Radiation from this source was gathered by a "spherical" condensing mirror improvised from a 5 inch watch glass aluminized on its concave surface, and passed through a copper sulfate filter and a Corning Glass #936 filter. This combination is opaque to most of the light of wave length greater than  $4200 \text{ \AA}$  and fairly transparent at shorter wave lengths. The samples under examination were contained in small glass-stoppered pyrex test tubes (1 or 2 cc volumetric flasks), and cooled in a dry ice-acetone bath in a transparent pyrex dewar. The samples were elevated just above the level of the acetone bath, excited through the transparent walls of the dewar, and the fluorescence examined with a pocket spectroscope.

### DETECTION OF URANIUM IN THE ABSENCE OF THORIUM

A set of samples was prepared as follows: 85%  $\text{H}_3\text{PO}_4$ , sp. gr. 1.7 was heated in a beaker until sufficient water was evaporated to give the remaining material sp. gr. 1.9. To one 10 cc portion of the phosphoric acid was added 1  $\mu$  U (as uranyl nitrate) in .2 cc of water; to a second was added 10  $\mu$  U in .2 cc of water; to a third 100  $\mu$  in .2 cc water and to a fourth 500  $\mu$  in .2 cc water. After one drop of concentrated nitric acid was added to each of the samples, all were heated on a hot plate for five minutes. Two cc samples were transferred to the glass-stoppered test tubes and examined for fluorescence in the manner described.

The sample containing 50  $\mu$  U per cc yielded a bright fluorescence, easily seen in a normally lighted room; 10  $\mu$  per cc gave a fluorescence less bright but still easily visible in the lighted room; 1  $\mu$  per cc fluorescence



was definitely visible in a darkened room, and the uranyl spectrum was unmistakable in the spectroscope. It was not possible to detect with certainty the fluorescence from the solution containing 0.1  $\mu$  U per cc. Since at most 0.5 cc of solution was illuminated in each case, the method will detect 0.5 microgram of uranium in the absence of large quantities of other metals. With quartz dewars and tubes and quartz lenses it may be possible to extend the sensitivity further.

DETECTION OF URANIUM IN THE PRESENCE OF THORIUM

Into each of three 30 cc beakers was weighed 1.5 gm of especially purified  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  (obtained from Berkeley). To one sample no U was added, to another 5  $\mu$  of U (as uranyl nitrate), and to the third 15  $\mu$  of U was added. To each was added 2 cc of 85%  $\text{H}_3\text{PO}_4$  and all were heated for 12 hours on a hot plate. At the end of this time an additional 1 cc of the 85% phosphoric acid was added to each and the heating continued for six hours. The samples were examined as has been described above. (The volume of each sample was slightly over 2 cc.) The samples to which 5  $\mu$  and 15  $\mu$  of U had been added (7 and 20 parts of uranium to one million parts of thorium respectively) yielded the test for uranium, with the brightnesses of the fluorescence somewhat less than in samples of uranium in phosphoric acid alone of corresponding concentrations. The test on the sample to which no uranium had been added was negative. Since it should have been possible to detect one third the intensity of uranyl fluorescence of the sample containing 7 ppm U, the original material contained less than 2 or 3 ppm U.

The test was extended as follows. A water solution of  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ , containing 10 gm Th, was extracted with ether according to the direction of Fontana (CC-384). The ether layer, containing according to Fontana 75% of the uranium and 4% of the thorium in the original sample, was evaporated to dryness. The residue was dissolved in water and precipitated with ammonium hydroxide, in order to free the material from organic impurities. The precipitated and washed hydroxides were then treated with phosphoric acid in the usual way. Evidently

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the precipitation was ineffective since the material yielded a bright greenish blue continuous fluorescence and a long lived yellowish phosphorescence -- behavior characteristic of many organic materials in glassy media at low temperatures. However, after the phosphoric acid solution was treated with 0.5 cc 30% hydrogen peroxide and heated for several hours to remove the excess peroxide, the continuous fluorescence was absent and a faint uranyl fluorescence, corresponding to about 1  $\mu$  U per cc was observed. Since the volume of solution was about 2 cc, the extract contained about 2  $\mu$  U. According to the data of Fontana, about 75% of the uranium should have been in the extract. The concentration of U in the original material is by this test about 0.3 ppm.

Fontana's data on the ether extraction were confirmed as follows. To 10 gm Th as  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  were added 10  $\mu$  U as uranyl nitrate. The solution was warmed and allowed to stand for several hours to ensure oxidation to the uranyl state of all the uranium. Three successive ether extractions with redistilled ether were made. Each extract was evaporated and treated with phosphoric acid and hydrogen peroxide in the manner described above. (The hydroxide precipitation was dispensed with). A sample of the finally purified material was also tested. The results were:

First extract	7-10 $\mu$ U
Second extract	2-4 $\mu$ U
Third extract	null (< 2 $\mu$ U)
Purified Th	null (< 3 ppm)

These results are in essential agreement with Fontana's. Furthermore, from them one may deduce that the final material contained less than 0.04 ppm U.

The test performed on the commercial  $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$  (Eimer and Amend) available in the laboratory indicates a U content of 8-10 ppm.