Fluorometric Microdetermination of Uranium. I. Fluorescent Material for the Determination

By Masaki NAKANISHI

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Introduction

Hexavalent compounds of uranium, the uranyl salts, have peculiar fluorescent property. Their fluorescence is observed by irradiating either the crystal or the solution with the ultraviolet light. This phenomenon is utilized to detect or determine a small amount of uranium in analytical chemistry, and has found its use in the microdetermination of the element.(1) On the other hand, however, another type of fluorometric method is possible, in which uranium is brought into an activator of some solid solution (so-called fluorescent material), and this method will be treated in this paper.

The activating action of uranium on fluorescent materials in solid solution state was widely studied by E.L. Nichols and M.K. Slattery.(2)(3)(4) They found that sodium fluoride

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(1) C.W. Sill and H.E. Peterson, *Anal. Chem.*, **19**, 646 (1947).

(2) E.L. Nichols and M.K. Slattery, *J. Opt. Soc. Am.*, **12**, 449 (1926).

(3) M.K. Slattery, *J. Opt. Soc. Am.*, **19**, 175 (1929).

(4) M.K. Slattery, *Proc. Nat. Acad. Sci.*, **14**, 777 (1928).

and lithium fluoride, activated by the addition of a small amount of uranium, show bright luminescence of yellow and green hue respectively in the ultraviolet light, the brightness of which exceeds that of solid uranyl salts under the same excitation.

For the detection of a minute quantity of uranium, J. Papish and L.E. Hoag,(5) and then F. Hernegger(6) recommended the fluorescence method, in which the fluorescent material, formed with sodium fluoride as a ground material and uranium as an activator, is used.

Afterwards F. Hernegger and B. Karlik(7) developed this method into the microdetermination of uranium.

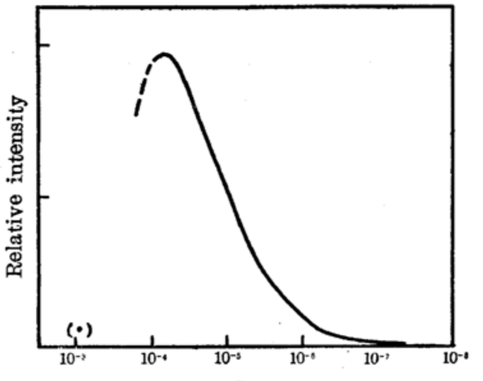
In connection with the geochemical researches on radioactive elements, which have been pursued more than ten years in this laboratory, the writer examined the details of this fluorescence method and confirmed it to be available, especially for geochemical purposes, for which the determination of less than one millionth gram of uranium was required.

Even in comparison with the radioactivity measurement method,(8) which has been hitherto most sensitive for radioactive elements, this fluorescence method is more delicate, so far as uranium is concerned, on account of the feeble radioactivity of uranium.

Fluorescent material of sodium fluoride activated by uranium shows a vivid yellow fluorescence, when irradiated with rays of the ultraviolet region. The intensity of the fluorescence varies remarkably according to the uranium content of the fluorescent material, and by the present treatment no more than 10^{-9} gram of uranium is necessary to produce the noticeable fluorescence.

Fluorescent Material of Sodium Fluoride Containing Uranium

Relation between Uranium Content and Fluorescence Intensity.—Some different quantities of uranium were mixed in aqueous solution with about 20 mg. of sodium fluoride. After drying, fluorescent beads were prepared by fusing the residue on a platinum loop, the procedure of which will be detailed in the following papers. Fluorescence of each bead caused by the excitation of ultraviolet rays was investigated regarding its luminescence intensity by the photographic spectrophotometry. Fig. 1 shows the results: the ordinate (intensity) is drawn to an arbitary scale, the abscissa shows the amount of uranium contained in about 20 mg. of sodium fluoride. As is seen in Fig. 1, the maximum intensity is reached at about 5×10^{-5}g. of uranium in a bead. In the photographic experiment concerned, the time of exposure was too short to catch an image corresponding to 10^{-8} g. of uranium. By visual observation, however, fluorescence due to 10^{-8} g. of uranium is still bright, and as uranium content decreases from 10^{-8} g., the fluorescence becomes rapidly fainter and finally almost vanishes at about 10^{-9} g. Pure sodium fluoride presents no fluorescent phenomenon.



Amount of uranium in 20 mg. NaF bead

Fig. 1.—Fluorescence intensity.

In case a bead contains 10^{-4} g. of uranium or more, it is supersaturated with regard to uranium, and the excessive uranium compound interferes with the proper formation of fluorescent material, the intensity of which depends much upon the experimental conditions. Therefore the fluorescence intensity of 10^{-3} g. of uranium indicated in Fig. 1 is no more than an example.

If we consider the narrow region of uranium content, the fluorescence intensity is reasonably regarded to be linear to the uranium content between about 10^{-5} and 10^{-9} g. On this base lies the microdetermination method of uranium, and its favorable range of application extends from 10^{-5} to 10^{-8} g. of uranium.

Fluorescence Band Spectrum.—Like many other fluorescent and phosphorescent substances, this fluorescent material has some emission bands. To obtain the quantitative spectral energy distribution of the luminescence, the photographic spectrophotometry(9) was applied here again.

As an intensity scale, the tungsten filament lamp was used. Its brightness was reduced to some different extents, and the corresponding spectra were photographed on a plate, together with the spectrum of the fluorescence in question. The time of exposure was the same for

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(5) J. Papish and L.E. Hoag, *Proc. Nat. Acad. Sci.*, **13**, 726, (1927).

(6) F. Hernegger, *Anz. Akad. Wiss. Wien*, **70**, 15, (1933).

(7) F. Hernegger and B. Karlik, *Sitz. Akad. Wiss. Wien, Abt. IIa*, **144**, 217, (1935).

(8) Wm. D. Urry, *Am. J. Sci.*, **239**, 191, (1941).

(9) H.B. Dorgelo, *Phys. Z.*, **26**, 756, (1925).

each spectrum. The work was made at room temperature, and an ordinary panchromatic plate was employed. The bead of sodium fluoride contained 10^{-4} g. of uranium, nearly the optimum proportion to form the fluorescent material. A filtered mercury vapour lamp of high pressure was employed to excite the bead, where the effective ultraviolet light extended from 2480 to 3660 Å. Then followed the determianation of blackness of the photographic image corresponding to these spectra with the microphotometer, and next the calculation of spectral energy distribution relative to the standard lamp, and at last correction for inequality of the standard lamp through the spectral region. Spectral energy distribution of the fluorescence thus obtained is graphically shown in Fig. 2. The fluorescence bands cover the region from 5300 to 6150 Å of wave length. It is obviously seen in Fig. 2 that the fluorescence includes four distinct partial bands, in which two are remarkably strong. Relative intensity of these four band maxima are tabulated.(10)

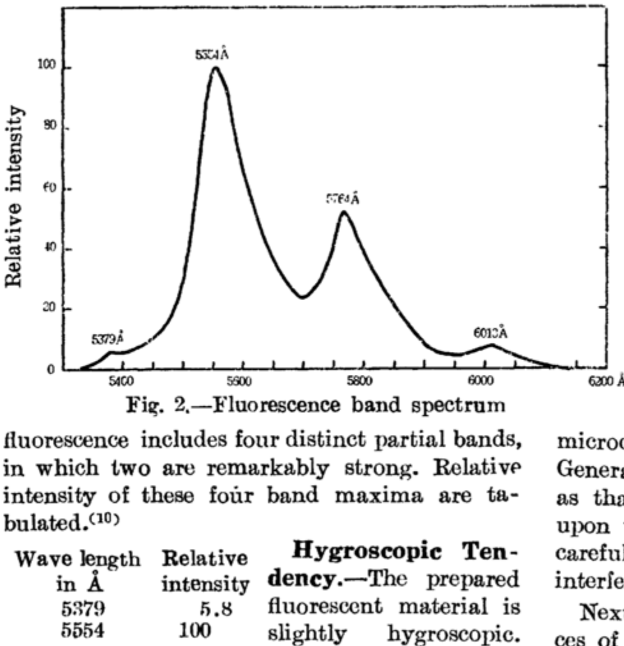

Fig. 2.—Fluorescence band spectrum

Wave length in Å	Relative intensity
5379	5.8
5554	100
5764	51.8
6013	7.6

Hygroscopic Tendency.—The prepared fluorescent material is slightly hygroscopic. The disc-like bead of this material on a platinum loop is often dewed with water from atmospheric moisture in wet weather. The fluorescence intensity of the bedewed bead becomes less intense especially for the smaller uranium content. Even after drying and refusion, it does not reveal its proper intensity. In most cases this treatment makes the fluorescence more intense, because it means prolonging the time of fusion, or in other words increased loss of ground material, sodium fluoride, by evaporation. Therefore the fluorescent beads of both sample and standard must be prepared immediately before the comparison in the same way. And if it is required to reserve the beads, they should be kept in a desiccator.

Interfering Substances.—We can enumerate many examples of the fluorescent material which is remarkably affected by a small amount of impurities; but the fluorescent material applied to the uranium determination is fortunately less affected by other impurities.

The interferences by other impurities will be generally examined on the analytical-chemical side.

Niobium and zinc are reckoned to be the only elements, except uranium, which act as activator for sodium fluoride. They produce luminescence of clearer green and orange hue respectively and less intense. But it is usually unnecessary to pay particular attention to niobium, because it is only a very minor contamination of ordinary samples, but special mineralogical or metallurgical ones, and furthermore is easily separated from uranium by the chemical procedures. Almost the same applies to zinc. Although we can not neglect the influence of zinc, inasmuch as it is a relatively abundant element, it is eliminated by any proper chemical treatment.

Impurities which form luminescent substances with uranium are to be removed too. These impurities include fluorides of other alkali metals and calcium, strontium chloride, borax, microcosmic salt, sodium phosphate, etc.(3) Generally their fluorescence is not so bright as that of sodium fluoride. It depends also upon the purification of sodium fluoride and careful manipulation to prevent this kind of interference.

Next in order is reference to the interferences of heavy metals. For example, iron is most likely to contaminate and severely reduces the intensity of fluorescence by the probable absorption of ultraviolet light. Manganese colors the bead green, but has almost no influence on the flourescence. Thorium, if more than 10^{-5} g. of the element is mixed in the bead of about 20 mg. weight containing 10^{-8} g. of uranium, gives a somewhat orange color to the bead, but reduces only a little the fluorescence intensity. Generally speaking, heavy metals can hardly disturb the test, if they are removed by any means to an imponderable trace comparable with the present amount of uranium.

Some earths, e.g. silica, titania, form complex fluorides with sodium fluoride which do not take the place of sodium fluoride in the

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(10) As for the wave length of band maxima, Nicho's and Slattery (ibid.) reported at 534, 557, 577, 606, 634 mμ, and Hernegger and Karlik (ibid.) at 555, 577, 602, 626 mμ. For the fine structure at the liquid air temperature, see (3).

luminescence test, but their influence can be prevented, too, by treating with more sodium fluoride.

Then insoluble matters, *e.g.* alumina, often cover the effective surface of the bead, if they remain much in the bead after fusion, which diminish or extinguish the luminescence to a greater extent. These difficulties are avoided in practical cases by ordinary chemical treatments, the details of which will be mentioned in the succeeding papers. After all, it is concluded that every kind of contamination is undesirable, but it interferes little if its quantity is as small as that of the uranium.

Summary

As the most sensitive method for the determination of uranium, the fluorescence method is recommended. Fluorescent material of sodium fluoride containing a small amount of uranium (10^{-4} to 10^{-9} g. per 20 mg. of sodium fluoride) was investigated in this paper from several sides.

Relation between fluorescence intensity and uranium content is described, and the fluorescence band spectrum was studied by spectrophotometry, regarding its spectral energy distribution.

Various interfering factors to this method were examined too, especially as to its analytical application.

In conclusion, the writer wishes to express his hearty thanks to Prof. K. Kimura, to whom he is much indebted for the continual stimulation and the kind guidances.

Chemical Institute, Faculty of Science,
the University of Tokyo, Tokyo