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Photochemical Analysis. I. Photonometric Titration of Thallic Ion by Uranyl Photoreduction Reaction

Yu YOKOYAMA and Shigero IKEDA

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka

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Photonometric titration of thallic ion is described, in which uranous ion, the titrant, is generated by photoreduction of uranyl ion in a sulfuric acid solution containing sodium lactate. Uranyl ion could be reduced with the light at wavelengths longer than 300 mμ, whereas thallic ion could not be reduced with the light in this wavelength range. Selective photoreduction of uranyl ion was accomplished by eliminating wavelengths below 300 mμ with a filter. In this photonometric titration, reaction solutions were irradiated without stirring at 29.5±0.5°C. The absorbance of uranous ion produced was measured at 655 mμ every fixed irradiation time, and the absorbance was plotted against the irradiation time. Induction period, which means the period during which the absorbance remains actually zero, was in a linear relation with thallic concentration. Thus the titration of thallic ion was satisfactorily carried out in the concentration range from 0.01 to 0.1 mM. The results proved the feasibility of titration in a completely sealed container and suggest a possibility of titration on a microvolume of reaction solution.

Photonometric titration was first proposed by Bricker and Schonberg.(1) In photonometric titration, titrant is photochemically generated in a solution containing a substance to be determined. However, no titration systems have been investigated except apferric-ferrous,(1) cobaltic-cobaltous,(2) and anthraquinone-reduced anthraquinone(3) systems. In the present paper, a photonometric titration by uranyl-uranous redox system is described. The photoreduction of uranyl to uranous ion has been utilized as preliminary treatment in volumetric titration of uranium by Rao *et al.*,(4,5) but in the present case this reaction is performed for generation of titrant.

The previous experiments on potentiometric titration(6,7) showed that, in spite of effective stirring of reaction solution, there existed a time lag (approximately less than one second) between addition of a titrant and indication of potential, as is the case with all conventional titrations. In the photochemical reaction, it is possible to generate a titrant homogeneously. In the present work,

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1) C. E. Bricker and S. S. Schonberg, *Anal. Chem.*, **30**, 922 (1958).

2) H. D. Drew and J. M. Fitzgerald, *ibid.*, **38**, 778 (1966).

3) T. Kuwana, *ibid.*, **35**, 1398 (1963).

4) G. G. Rao, V. P. Rao and M. V. R. Rao, *Anal. Chim. Acta*, **15**, 97 (1956).

5) G. G. Rao, V. P. Rao and N. C. Venkatamma, *Z. anal. Chem.*, **150**, 178 (1956).

6) Y. Yokoyama, N. Tsuji and S. Suzuki, *Bunseki Kagaku (Japan Analyst)*, **15**, 20 (1966).

7) N. Tsuji and Y. Yokoyama, *ibid.*, **17**, 939 (1968).

therefore, an attempt was made to perform the titration in a stoppered reaction vessel without stirring. A reaction vessel of 10 mm in light path length and 5 m*l* in volume, provided with a ground stopcock, was designed, and used throughout the present work.

In photochemical reactions, some substances react with a product of the photochemical reaction and some take part in the reaction as a quencher. In a series of our photochemical experiments, these actions of coexisting substances were found to be applicable to the determination of microamounts of substances. These results will be published in succession, and hereafter *the chemical analysis based on the photochemical reaction will be called "the photochemical analysis."*

The photochemical analysis has the following advantages over other analytical methods. (1) The titrant is generated in a reaction vessel, as the titration proceeds. Consequently, unstable substances can be utilized as titrant. (2) The determinable concentration range is of the same order as, or less than, that in the coulometric titration. (3) The titration can be performed in a completely sealed container and, therefore, there is a possibility of titration on a microvolume of reaction solution. On the other hand, the shortcomings are as follows. (1) The temperature of reaction solution must be kept constant, as is usual in experiments of reaction rate measurement. (2) Interference of coexisting substances could occur in two different ways, that is, the reaction with a photochemical reaction product and the quenching reaction.

Experimental

Reagents. Uranyl standard solution (0.05 M) was prepared by dissolving G. R. uranyl acetate in water containing a small amount of sulfuric acid. The factor of this solution was determined to be 0.965 by gravimetry as uranyl oxinate. Thallic standard solution (0.025 M, $f=0.937$) and thallous standard solution (0.05 M, $f=0.993$) were prepared by dissolving thallic oxide of 99.9% purity and E. P. thallous sulfate in 1.2 N sulfuric acid solution, respectively. The factors of these solutions were determined iodometrically. Sodium lactate solution (0.2 M), and sulfuric acid solution (5 N) were also used in phtochemical reaction. In addition, sulfuric acid (1 N) solutions of the following salts were prepared: bismuth nitrate, mercuric sulfate, silver sulfate, zinc sulfate, and cadmium sulfate. The following reagents were prepared for iodometric titration of thallium: 0.01 M thallous chloride standard solution, 0.01 N sodium thiosulfate solution, 1% potassium iodide solution, 1% starch indicator solution, 20% phenol-glacial acetic acid solution, bromine mixture which was prepared by dissolving 50 g of sodium dihydrogenphosphate monohydrate and 50 g of ammonium chloride in 450 m*l* of saturated bromine water, and phosphate-chloride mixture containing 50 g of sodium dihydrogenphosphate monohydrate and 50 g of ammonium chloride in 450 m*l* water.

Apparatus. In order to follow the photoreduction of uranyl ion, a Shimadzu Ltd. Model QV-50 spectrophotometer was utilized with some modification. A side wall of the absorption cell compartment was replaced with a new side wall equipped with a window and a shutter. In front of the shutter a 120 W medium pressure mercury lamp, which was employed as the light source for photochemical reaction, was attached together with a lens system, and the optical axis was addjusted so as to intersect that of the monochromator at right angles. The cell holder was positioned at the intersection. A 10 mm × 10 mm quartz absorption cell with four transparent sides was used in place of a usual absorption cell, and also served as a photochemical reaction vessel. The cell was fitted with a ground stopcock. The mercury lamp and its power unit were components of a Hitachi Ltd. Model 203 fluorescence spectrophotometer. The light intensity from the lamp stabilized within 15 min from initial ignition. Absorption spectra were recorded with a Hitachi Ltd. Model EPS-2 automatic recording spectrophotometer.

Procedure. The reagent solutions were mixed in a 25 m*l* measuring flask, and diluted to 25 m*l*. Approximately 5 m*l* of the mixed solution was transferred into a reaction vessel, which was then set in the cell holder. For photochemical reaction, the reaction vessel was irradiated with the mercury lamp with the shutter open. After irradiation for a definite time, the absorption of uranous ion produced was measured at a wavelength of 655 mμ with the shutter closed. Irradiation was continued with the shutter open for further reaction.

Total thallium was determined according to the following procedure, which was a modification of the method proposed by Sill *et al.*[8] To a solution containing thallium was added 15 m*l* of 5 N sulfuric acid, 30 m*l* of water and 50 m*l* of the bromine mixture. The solution was boiled to oxidize completely thallous to thallic ion until the coloration of the solution became light yellow. After being cooled, 0.4 m*l* of the phenol solution was added to remove free bromine and then total thallium was titrated with 0.01 N sodium thiosulfate solution. Before titration of thallium, 0.01 N sodium thiosulfate solution was standardized against 0.01 M thallous chloride standard solution. Titration of thallic ion in the presence of thallous ion was carried out in the same way as for the determination of total thallium, except that bromine mixture was replaced with phosphate - chloride mixture and heating was omitted. The titration of thallic ion could be performed in the presence of uranyl ion without any interference of uranyl ion.

Results

Measurement of Absorption Spectra. Transmittance curves of uranyl, uranous and thallic ions were recorded in the wavelength range from 250 to 700 mμ. They are shown in Fig. 1. The curve of uranyl ion was that of a solution containing 10 mM uranyl ion, and 40 mM sodium lactate in 1 N sulfuric acid (hereafter called the uranyl mixed solution), and the curve of uranous ion was

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[8] C. W. Sill and H. E. Peterson, *Anal. Chem.*, **21**, 1268 (1949).

obtained with the uranyl mixed solution after exposure to the mercury lamp until the absorption characteristic of uranous ion was no further increased. Uranous ion has an absorption maximum at 655 mμ (molar absorptivity $\varepsilon=48.9$), and hence the ion was determined spectrophotometrically at this wavelength. For comparison a transmittance curve of a solution containing merely 10 mM uranyl ion in 1 N sulfuric acid was also recorded, and found to be identical with the curve for the uranyl mixed solution. The curve of thallic ion was recorded with a solution containing 10 mM thallic ion, and 40 mM sodium lactate in 1 N sulfuric acid (hereafter called the thallic mixed solution). A transmittance curve of thallous ion was also measured, which is not shown in Fig. 1, and was found merely to shift to a shorter wavelength by approximately 40 mμ compared with the curve of thallic ion.

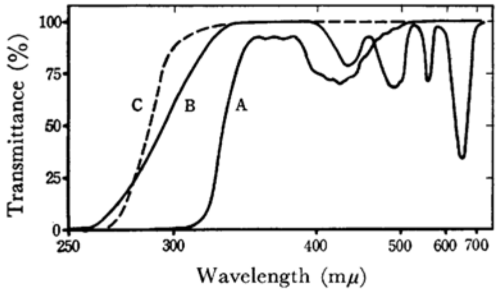

Fig. 1. Absorption spectra of uranyl, uranous, and thallic ions.

A: 10 mM uranyl ion (with 40 mM Na lactate and 1 M H_2SO_4)
B: 10 mM uranous ion (obtained by exposing the solution A to mercury lamp)
C: 10 mM thallic ion (with 40 mM Na lactate and 1 N H_2SO_4)

Irradiation without Filter. The uranyl mixed solution was transferred into the reaction vessel, and irradiated with the mercury lamp without any filter. The absorbance of uranous ion was measured every fixed irradiation time, and the amount of uranous ion produced was calculated by using the molar absorptivity of uranous ion. The thallic mixed solution was also irradiated under the same conditions. Thallous ion thus produced was determined by iodometric titration every fixed irradiation time. Results are presented in Fig. 2. Uranyl ion was reduced to a considerable extent within the irradiation time, as would be expected, and also the reduction of thallic ion took place, even if only slightly.

Irradiation with Filter. The uranyl and the thallic mixed solutions were irradiated through a soft glass filter for eliminating the light of wavelength shorter than 300 mμ. Other conditions were the same as mentioned above. The relation between the amount of ion reduced and the irradiation time is shown in Fig. 2. The reaction of thallic ion could not be observed, and at the same time the efficiency of uranyl photoreduction was slightly lowered.

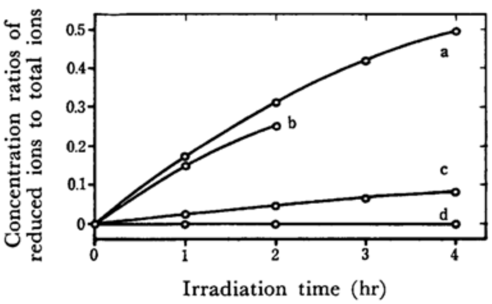

Fig. 2. Photochemical reaction of uranyl and thallic ions.

a and b : 10 mM uranyl ion (same solution as A in Fig. 2)
c and d : 10 mM thallic ion (same solution as C in Fig. 3)
a and c : without filter, b and d: with filter

Stoichiometry of Reaction between Thallic and Uranous Ions. The uranyl mixed solution was exposed to the light of the mercury lamp to produce uranous ion. Exposure was continued until uranyl ion was completely reduced. To each 10 m*l* of the solution (containing 10 mM uranous ion) was added an aliquot of the 25 mM thallic standard solution and then water to make up to 13 m*l*. After mixing, the absorbance of of the mixture was measured. The results showed that one mole of thallic ion reacted with one mole of uranyl ion. Therefore, it is considered that the overall reaction proceeds according to the following equation.

$$U^{4+} + Tl^{3+} + 2H_2O = UO_2^{2+} + Tl^+ + 4H^+$$

Photonometric Titration Curve and Calibration Curve. Uranyl ion was photochemically reduced in the presence of thallic ion. Test solutions contained various amounts of thallic ion together with 10 mM uranyl ion, 40 mM lactate and 1 N sulfuric acid. The solutions were irradiated through the filter in the cell compartment kept at 29.5±0.5°C under the same conditions as before, and the absorbance of uranous ion produced was measured at 655 mμ every fixed irradiation time. An example of a photonometric titration curve is shown in Fig. 3. It is seen that the curve consists of two parts, that is, the first part where the absorbance remains actually zero, and the second part where the absorbance steadily increases. In order to follow the change in concentration of thallic ion during irradiation, thallic ion in the test solution was iodometrically determined. While thallic ion existed before the point where the titration curve begins to rise, the ion was not detected after the

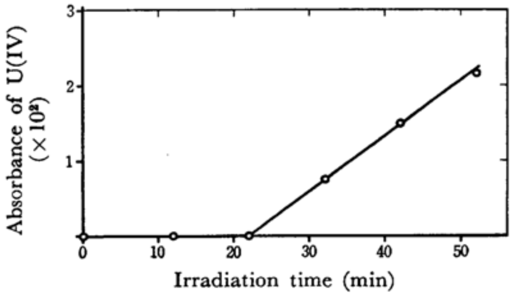

Fig. 3. Photonometric titration curve of thallic ion.

0.1 mM thallic ion (in the solution containing 10 mM uranyl ion, 40 mM Na lactate, and 1 N H_2SO_4). Measurement was made at 29.5± 0.5°C.

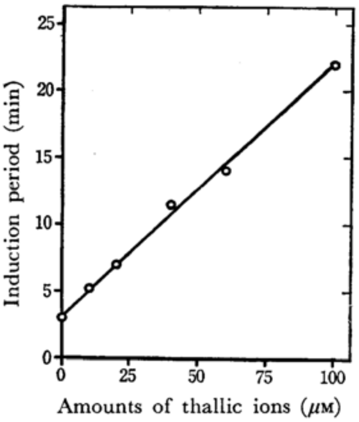

Fig. 4. Calibration curve of thallic ion.

Induction periods were obtained from a set of photonometric titration curves as shown in Fig. 3.

point. The induction period was dependent on the amount of coexisting thallic ion. Photonometric titration curves were constructed for thallic ion in a concentration range of 0 to 0.1 mM, and the induction periods were obtained from each of the curves. The measurement of the induction period was repeated three times for each thallic concentration, and the values observed were averaged. Figure 4 shows a plot of the induction periods against the concentration of thallic ion. Nearly linear relationship was obtained in the concentration range, but the plot did not pass through the origin. The effect of other metal ions on the photonometric titration of thallic ion was tested. Bi(III), Zn(II), and Cd(II) ions in concentration of 0.4 mM had no influence on the determination of thallic ion. But Hg(II) and Ag(I) were reduced under the same conditions as for the photonometric titration of thallic ion.

Discussion

Absorption Spectra. The uranyl spectrum obtained was similar in profile to those reported by Bell *et al.*,⁹⁾ Betts *et al.*¹⁰⁾ and others. Betts *et al.* showed that an absorption maximum of noncomplexed uranyl ion at approximately 415 mμ shifted to the vicinity of 420 mμ on complex formation with sulfate ion. Since the uranyl spectrum in Fig. 1 has the absorption maximum at 420 mμ regardless of the presence of lactate, it is reasonable to think that uranyl ions formed a sulfate complex. Bell *et al.* have recently reported that uranyl ion in two excited state energy levels (at 21270 and 20502 cm^{-1}) can be responsible for the photochemistry of uranyl ion. In the present investigation, therefore, the photochemical reaction of uranyl ion was carried out by use of the light in the wavelength range longer than 300 mμ (approximately 33000 cm^{-1}).

Thallic and thallous ions show no light absorption above approximately 320 mμ, and, therefore, in the longer wavelength range do not interfere with light absorption of uranyl ion. An intense absorption band exists below approximately 300 mμ. In consideration of the fact that thallic ions underwent the photochemical reduction by irradiation with unfiltered mercury lamp, the intense absorption band below approximately 300 mμ is supposed to be involved in the photochemical reaction of thallic ion.

Photoreduction of Uranyl and Thallic Ions. The initial concentration of uranyl ion affects not only the reaction rate of the uranyl photoreduction, but also the homogeneity of the photoreduction in the reaction solution. The number of photons absorbed by uranyl ion in the reaction vessel is diminished as the incident light from the mercury lamp proceeds from the front of the vessel to the back. Consequently there should be some difference in the amount of uranous ion produced along the path length of the incident light. An excessive increase in the uranyl concentration would enlarge the difference to such an extent that the homogeneity of the reaction solution can not be maintained by the diffusion process of the solutes. In consideration of the two factors, the reaction rate and the homogeneity of the photoreduction, the uranyl concentration of 10 mM was chosen in the present work, since in this concentration the reaction rate is moderate and a difference was not seen in the absorbance before and after vigorous mixing of irradiated reaction solutions.

The work by Rao *et al.*⁴⁾ of the photoreduction of uranyl ion in the sodium lactate-sulfuric acid system showed that the reduction rate of uranyl ion was constant over sulfuric acid concentration from 0.10 to 2.0 N and that the reduction rate

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9) J. T. Bell and R. E. Biggers, *J. Mol. Spectry.*, **25**, 312 (1968).

10) R. H. Betts and R. K. Michels, *J. Chem. Soc.*, **1949**, 286.

reached a maximum value at a lactate-to-uranyl ratio as high as 4 to 1. Therefore, subsequent experiments were performed with 40 mM of sodium lactate and 1 N of sulfuric acid.

The fact that thallic ion undergoes photoreduction under certain conditions has already been reported by Benrath,[11] who observed that thallic ion was photochemically reduced in the presence of oxalic acid, tartaric acid, or alcohol. Figure 2 shows that the photoreduction took place in the presence of sodium lactate, also. However, the reaction could not be observed on irradiation through the soft glass filter.

Photonometric Titration Curve. In the photonometric titration, the absorption at 655 mμ could not be observed until the absorbance began to increase steadily, and thallic ion did not exist after the rising point of the titration curve. Thus this point could be considered to be the end point. The mechanism of the photoreduction of uranyl ion has not been made clear, and there is some possibility that thallic ion reacts with an intermediate of the photochemical reaction. Accordingly it seems that uranous ion is formed as a final product of the photochemical reaction in the absence of other reducible substances, and that, when thallic ion coexists, it is reduced preferentially before reduction of uranyl ion owing to the more positive oxidation potential of thallic ion.

The fact that the reaction solution containing no thallic ion showed a blank induction period suggests that a part of uranous ion is oxidized by something other than thallic ion. Hitherto it has been reported that uranous ion is oxidized by the air or oxygen dissolved in the solution, and the mechanism of this reaction has been studied by Halpern and Smith.[12] As a check, the uranyl mixed solution was irradiated with the mercury lamp after removal of the air with a rotary vacuum pump. The photonometric titration curve of this solution revealed that the absorbance at 655 mμ began to increase from the start of irradiation. In addition experiments done at temperatures down to 15°C indicated that there was a parallel relationship between the blank induction period and the solubility of oxygen. Thus it is certain that oxygen dissolved in solutions consumes uranous ion. However, because the temperature of reaction solutions is kept at 29.5 ± 0.5°C, the effect of dissolved air would be unchanged for each reaction solution, and thus the plot for each thallic concentration should be shifted equally by a constant value, that is, a blank induction period.

Application. Table 1 shows the results of determination of thallic ion by use of the calibration curve presented in Fig. 4. Although the measurement for 0.15 mM thallic ion was also tried and the result showed that the plot for this concentration still lay in the extension of the calibration curve, it seems that the measurement of a too long induction period is incovenient for practical use. On the other hand, for thallic ion less than 0.01 mM the reproducibility would become relatively worse.

TABLE 1. RESULTS OF DETERMINATION OF THALLIC ION

Concentration of thallic ion, μM		
Present	Found	Average
10	13, 8, 6	9
20	19, 22, 17	20
40	41, 43, 46	43
100	107, 96, 102	102

Hence it is found that photonometric titration can satisfactorily be applied to microdetermination of thallic ion in the concentration range from 0.01 to 0.1 mM. Further improvement of accuracy would be effected by increase in the optical path length of reaction vessel for absorption measurement.

The rise of temperature increases the reaction rate of the uranyl photoreduction, and, hence, affects the induction period. Therefore, the calibration curve shown in Fig. 4 can not be applied to the data obtained at other temperatures. Hg(II) and Ag(I) interfered with the determination of thallic ion owing to their reactivity against the photoreduction product, but there was no interference from such ions as Zn(II), Cd(II), and Bi(III).

For the first time in photonometric titration, and probably in all kinds of titration, the titration procedure could be carried out without stirring the reaction solution. This fact indicates that titration can be performed in a far smaller volume of reaction solution, when allowed to make use of microspectrophotometric technique, and that it is possible to carry out titration in a cell isolated completely from outside, because both the generation of titrant and the measurement of concentration of a reaction product can be made without breaking the isolation of the reaction system.

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[11] A. Benrath, *Z. Wiss. Phot., Photophysik Photochem.*, **14**, 217 (1915).

[12] J. Halpern and J. G. Smith, *Can. J. Chem.*, **34**, 1419 (1956).