Rapid Colorimetric Determination of Mercury by Tin(II)-Strong Phosphoric Acid Reduction Method

By Toshiyasu KIBA, Ikuko AKAZA and Osamu KINOSHITA

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Tin(II)-strong phosphoric acid, a new powerful decomposing and reducing agent first described by the present authors[1], has been widely employed in this country for the determination of sulfur in various materials; e. g. sulfates[2], sulfide ores[3], iron and steel[4], organic compounds[5], rayon staple fiber, acetylcellulose[6] and proteins[7]. The reagent has also been applied for rapid determination of selenium in various forms. The selenium is reduced by the reagent into gaseous hydrogen selenide, which is absorbed in an alkaline solution, and then the amount is determined colorimetrically[8].

A further attempt was made by the present authors to reduce mercury in various compounds to the metallic state by treating the samples with tin(II)-strong phosphoric acid. The mercury was driven out from the reaction medium by heating and its vapor was carried in a current of carbon dioxide into an absorbing solution containing sulfuric acid and potassium permanganate. The mercury retained in the solution as mercury(II) ions was determined colorimetrically by the usual dithizone method. This new method is very rapid and simple, and moreover, the error caused by the volatillization of mercury during the digestion of the samples by ordinary methods is totally eliminated for the analysis is carried out in a closed system in carbon dioxide.

Experimental

Apparatus.—The apparatus used in this study is shown in Fig. 1. It is composed of two parts, a reaction vessel (A) and an absorbing part (B). The reaction vessel (A) is a round-bottomed flask of hard glass having a glass cap fitted to its top

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[1] T. Kiba et al., This Bulletin, **28**, 641 (1955).

[2] T. Kiba, and I. Akaza ibid., **30** 53 (1957).

[3] T. Kiba, I. Akaza and N. Sugishita, ibid., **30**, 972 (1957).

[4] K. Kitagawa and Shibata, *Japan Analyst* (*Bunseki Kagaku*), **7**, 181 (1958).

[5] T. Kiba and I. Kishi (present surname, Akaza), This Bulletin, **30**, 482 (1957); S. Ohashi, ibid., **28**, 645 (1955).

[6] H. Terada and M. Yoshida, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **61**, 1301 (1958).

[7] S. Akabori and T. Fujiwara, *Bull. Chem. Biolog.*, **40**, 1983 (1958).

[8] T. Kiba, I. Akaza and H. Hachino, This Bulletin **32**, 641 (1959).

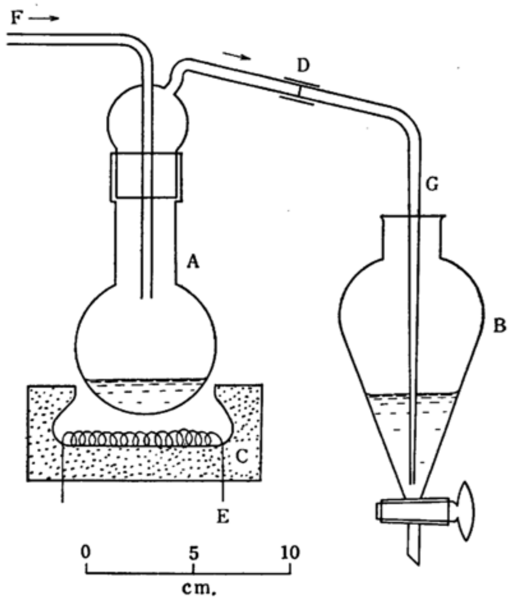

Fig. 1. Apparatus for reduction of mercury compounds and absorption of mercury vapor evolved.

A: Reaction vessel, a round bottomed flask.
B: A separatory funnel.
C: Electric heater.
D: Short piece of rubber tubing.
E: A.C. electric current regulated by a variable transformer.
F: Carbon dioxide gas introduced into A.
G: Gas-delivery tube.

and provided with an inlet and an outlet tube for the gas. The absorbing part (B) is a separatory funnel of about 100 ml. capacity. A gas delivery tube (C) is connected with a piece of rubber tubing (D) to the outlet arm of the reaction vessel (A) and inserted into the absorbing solution in the separatory funnel. A Kipp's apparatus is employed for the production of carbon dioxide, which is purified by three gas-washing bottles (not shown in Fig. 1) and introduced into the reaction vessel through the inlet arm. The solutions used for the purification of carbon dioxide are described later.

Photoelectric colorimeter.—A "Hirama photoelectric colorimeter" with 1 cm. cells was used with a filter of 517 mμ.

Reagents.—*Strong phosphoric acid.*—Four hundred grams of commercial ortho phosphoric acid of extra pure grade ($d=1.7$) is placed in a 300 ml. conical beaker, and dehydrated by heating on a 500 W. hot plate until a thermometer dipped in the liquid indicates 300°C. If the heating takes too long the liquid will become turbid and viscous and useless for the purposed in view. During the heating, the water vapor and the mist of phosphoric acid coming off should be rapidly removed from the neighborhood of the liquid surface, through a glass tube, one end of which is held near the surface of the liquid, the other end being connected to a suction pump. This saves much time in the dehydration.

Tin(II)-strong phosphoric acid.—Fifty grams of tin(II) chloride dihydrate of extra pure grade is placed in a 300 ml. conical beaker and on it is poured 250 g. of the strong phosphoric acid prepared as described above. The content is heated to 300°C within 30 min. in the manner of the preparation of the strong phosphoric acid. After cooling the tin(II)-strong phosphoric acid thus obtained, a very viscous and possibly slightly turbid liquid is produced, which may be stored in a closed vessel.

Carbon dioxide.—Carbon dioxide produced in the Kipp's apparatus is purified by passing through three gas-washing bottles containing, respectively, water, 2% vanadium(II) sulfate solution in 6 N sulfuric acid, 1% potassium permanganate solution in 10% sodium carbonate. This is introduced into the reaction vessel through a glass tube.

Standard mercuric chloride solution.—A 1.3539 g. portion of mercuric chloride of pure chemical grade dried in a vacuum desiccator is weighed accurately and dissolved in one liter of distilled water. This solution is used as a stock solution. One milliliter of the solution is diluted to 100 ml. with water before use. One milliliter of this diluted solution contains 10 μg. of mercury. According to Sandell[9] the mercuric ion is usually absorbed on the glass wall of the vessel, especially when the solution is extremely diluted. However, the effect is not noticeable when the diluted solution is employed soon after the preparation.

Dithizone chloroform solution.—A 0.001% (w/v) and a 0.005% (w/v) solution are prepared according to Sandell[9], and the former is used for 0 to 20 μg. of mercury and the latter for 0 to 50 μg. of the metal.

Hydroxylamine hydrochloride solution.—Twenty grams of hydroxylamine hydrochloride is dissolved in 65 ml. of water, and neutralized with aqueous ammonia using thymol blue as indicator. The solution is transferred into a separatory funnel and 10 ml. of 4% sodium diethyldithiocarbamate solution is added to it and mixed well. After a few minutes, 10 ml. of chloroform is poured into the vessel and the content is shaken vigorously to transfer the metal chelates into the organic layer. After the two layers are disengaged, the chloroform layer is rejected. To the aqueous layer, hydrochloric acid is added drop by drop till the red color of the indicator appears. This solution may be employed for the experiment.

Potassium permanganate solution.—A suitable amount of solid potassium permanganate of extra pure grade is dissolved in water and filtered through a glass-sintered crucible to make 0.1, 0.5 and 1 N solution.

Sulfuric acid.—Concentrated sulfuric acid of pure grade is diluted with water to a concentration of 10%.

Acetic acid solution.—6 N.

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[9] E. B. Sandell, "Colorimetric Determination of Traces of Metals", 2nd Ed., Interscience Publishers, Inc., New York (1950), pp. 441-452.

Ferric chloride solution.—Ferric chloride hexahydrate is dissolved in water to make a solution containing 10 mg. of iron(III) ion per ml.

Cadmium chloride solution.—Crystalline cadmium chloride is dissolved in water to make a solution containing 3.5 mg. of cadmium ion per ml.

Mercuric oxide.—Mercuric oxide of extra pure grade is used as a powder, and the mercury content was estimated by the ordinary potassium thiocyanate titration method as 97.30% pure.

Alumina. — As a diluent of solid samples, powdered alumina of utmost purity for chromatography is used.

Various samples containing mercury.—Commercial products, especially water-soluble insecticides and fungicides, are used as the samples of analysis, their mercury content having been determined by other methods.

Procedure. — Take an accurately measured sample containing mercury of 0 to 50 μg.—pipet a solution; weigh a solid—and put it into the reaction vessel (A in Fig. 1). The volume of the vessel should be varied according to the amount of the sample to be analyzed. Pour 5 to 10 ml. of the tin(II)-strong phosphoric acid over the sample. Put into the separatory funnel (B in Fig. 1) 5 ml. of 0.1 N potassium permanganate solution and 5 ml. of 10% sulfuric acid and mix well. Connect all the apparatus as shown in Fig. 1. Pass carbon dioxide very rapidly through the apparatus for two or three minutes to expel the air from the apparatus. The end of the gas-delivery tube (G) should reach the bottom of the separatory funnel. Reduce the flow of gas to a rate of one bubble per second, and heat the bottom of the reaction vessel by passing an electric current through the nichrome wire (E) placed in the diatomaceous block (C). Regulate the voltage of the current by a variable transformer. It is unnecessary to keep the temperature constant but it should be high enough to ensure that the content of the reaction vessel exhibits a white turbidity near the end of the reaction. After about fifteen minutes stop the heating, but continue the passing of the gas about five minutes longer.

Remove the separatory funnel, and pour into it about 15 ml. of 1 N sulfuric acid. To the colored solution add 1 ml. of 20% hydroxylamine hydrochloride solution to reduce the permanganate and, moreover, 2 ml. of 6 N acetic acid to stabilize the dithizonate which will be formed hereafter. Add 5 ml. of chloroform to the aqueous solution in the funnel and shake it vigorously for a while to saturate the aqueous phase with chloroform. After the layers are disengaged by standing the vessel for several minutes, reject the lower chloroform layer from the stem of the funnel. Then, add exactly 10 ml. of 0.05% dithizone-chloroform reagent using a pipet. Shake the vessel vigorously with an electric shaking machine for about two minutes. Allow the vessel to stand for several minutes and then drain the organic layer into an Erlenmyer flask containing unhydrous sodium sulfate as a dehydrant. Set it aside for a while till the water contained in the organic phase is absorbed and the layer becomes clear. Transfer the colored organic phase in a 1 cm. cell and read the absorbancy of the layer in a photoelectric colorimeter with a filter of 517 mμ. A blank test should be conducted with the dithizone-chloroform solution undergoing the same procedure without mercury.

Results and Discussion

Recovery of Mercury by This Method.— Employing an aliquot of the standard mercuric chloride solution, the determination of mercury in the amount between 5 and 50 μg. was made by carrying out all the procedure described above. Another aliquot of the standard solution was directly treated with dithizone-chloroform reagent and the absorbancy of the organic layer was read as described in the latter part of the procedure, which is similar to the ordinary method for the determination of mercury in solutions. The absorbancies measured on the same amount of mercury by the two methods are tabulated together in Table I, which shows good coincidence within the error unavoidable in colorimetry. The calibration curves obtained by the two methods can be represented by the following equations. In case ordinary colorimetry of the dithizone-chloroform phase was used:

TABLE I. COMPARISON OF THE ABSORBANCIES OF MERCURIC DITHIZONATE FOR THE SAME AMOUNT OF MERCURY

Amount of Hg μg./100 ml. $CHCl_3$	Absorbancy measured	
	Ordinary direct colorimetry	Via this reduction & evolution method
5	0.0928	0.0930
10	0.1722	0.1716
15	0.2580	0.2464
20	0.3172	0.3301
25	0.4205	0.4200
30	0.4878	0.4813
35	0.5695	0.5690
40	0.6475	0.6420
45	0.7190	0.7210
50	0.7975	0.7960

$$y = 0.0168 + 0.01569\,x$$

and if colorimetry following this reduction and evolution method was used:

$$y = 0.0156 + 0.01569\,x$$

where y is the absorbancy measured and x the amount of mercury taken in micrograms. The numerical values in the equations were calculated by the method of the least squares from the experimental data of more than two determinations of the same amount of the metal. In conclusion, it may be pointed out that only a negligible amount of mercury is lost in this reduction and evolution method, and a calibration curve prepared by the ordinary method with a standard solution of mercuric salt can be employed in this method as well.

Determination of Minute Amounts of Mercuric Oxide.—A definite amount of mercuric oxide was mixed with a large amount of alumina and the mixture was analyzed by the tin(II)-strong phosphoric acid method. Minute amounts of mercury could be determined by this method as shown in Table II.

TABLE II. DETERMINATION OF MERCURY IN MIXTURE OF MERCURIC OXIDE AND ALUMINA

Sample taken mg.	Hg content μg.	Hg found μg.
15.90	30.7	30.2
13.32	25.7	25.5
14.59	28.2	28.3
14.65	28.3	28.4
14.73	28.4	28.7

Determination of Minute Amounts of Mercury in Solution.—Because of their volatility, mercury compounds can not be dried or their solutions evaporated without affecting the analytical result. So the co-precipitation method was employed to concentrate the mercuric ion using ferric hydroxide or cadmium sulfide as gathering agent. A suitable volume of a solution containing 20 μg. of mercury as chloride, and a suitable volume of ferric chloride solution containing 10 mg. of iron(III) ion per ml. were placed together in the reaction vessel. Sodium hydroxide solution was added dropwise to complete the ferric hydroxide precipitate, and the mixture was set aside from two hours to overnight till the precipitate settled. The supernatant solution was sucked out by means of a suction pump through a filter stick, a short glass tube containing an asbestos plug near one end, the precipitate being allowed to remain in the reaction vessel. The precipitate caught on the asbestos plug was transferred from the filter stick into the reaction vessel by pushing out the plug with a slender glass rod inserted through the other end of the glass tube. The analysis of mercury caught in the ferric hydroxide precipitate was carried out according to the procedure in which the asbestos plug was completely decomposed by heating with tin(II)-strong phosphoric acid as shown by the clear solution obtained.

Cadmium sulfide can also be employed as the co-precipitant. In this case a suitable volume of a solution containing a minute amount of mercury and of cadmium chloride containing 3.5 mg. of cadmium per ml. were put together in the reaction vessel. The pH of the solution was adjusted to about 1 by adding hydrochloric acid, and then hydrogen sulfide was introduced into the solution to precipitate cadmium sulfide. After the solution was left for several hours to let the precipitate settle, it was filtered by means of the filter stick as described above, and the asbestos plug was transferred to the reaction vessel containing the precipitate. The analysis was then carried out according to the procedure.

Both the ferric hydroxide and the cadmium sulfide co-precipitation method give good recovery of mercury in the solution as shown in Table III. In these cases some problems remain about the reaction of tin(II)-strong phosphoric acid with ferric ions and the metallic sulfides. The ferric ion is reduced to the ferrous by the reagent intended for the reduction of the mercuric ion, and excessive consumption of the reagent occurs if a larger amount of iron(III) ion is present. But when only about ten milligrams of iron(III) is used for the co-precipitation, the amount of the tin(II) ion in the reagent used is far in excess of the need of the iron(III) ion, and the reduction of mercury is not hindered.

TABLE III. RECOVERY OF 20 μg. OF MERCURY BY COPECIPITATION METHOD

Ferric oxide was used as a collector:

Amount of Fe^{3+} mg.	Hg found μg.	Recovery %
10	19.9	99.5
20	19.2	96.0
30	19.7	98.5
30	19.7	98.5

Cadmium sulfide was used as a collector:

Amount of Cd^{2+} mg.	Hg found μg.	Recovery %
3.5	19.3	96.5
〃	19.5	97.5
〃	19.3	96.5
5	19.2	96.0
〃	18.6	93.0

When cadmium sulfide is treated with the tin(II)-strong phosphoric acid, gaseous hydrogen sulfide is evolved at the same time, and the gas is carried with the carbon dioxide into the absorbing solution of potassium permanganate and sulfuric acid. The gas consumes the permanganate and the absorbing power of the solution for mercury vapor is markedly lowered. In this case a large amount of permanganate should be persent in the absorbing solution to oxidize the sulfide in the sample and keep adequate absorbing power for mercury vapor. This applies also to the analysis of mercury in sulfates. The question is what concentration of potassium permanganate should be kept in the absorbing solution for various amounts of sulfur in the sample. Fig. 2 shows the results of experiments to estimate the concentration of permanganate for good recovery of mercury in the presence of various amounts of sulfur as sulfate. When 1 N potassium permanganate solution is used as 1:1 mixture with 10% sulfuric acid, less than 2.0 mg. of sulfur can be allowed to be present in the sample without any hindrance to the determination of 20 μg. of mercury.

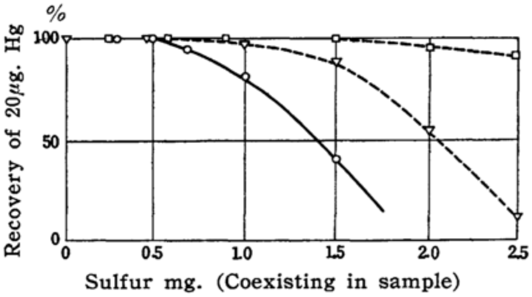

Fig. 2. Dependence of potassium permanganate concentration in the absorbing solution on the recovery of mercury.
Composition of the absorbing solution:
○: 5 ml. 0.1 N $KMnO_4$+5 ml. 10% H_2SO_4
▽: 5 ml. 0.5 N $KMnO_4$+5 ml. 10% H_2SO_4
□: 5 ml. 1 N $KMnO_4$+5 ml. 10% H_2SO_4

Effect of Chloride for the Analysis.—The colorimetry of mercury dithizonate is usually dependent on the concentration of the chloride ion in the aqueous solution. In this evolution method, when a sample contains a large amount of chloride, the chloride is given off as hydrogen chloride and absorbed in the absorbing solution. Many papers have been published on the dependence of the accuracy of the dithizone method on the chloride ion concentration, and a suitable pH range for the extraction of mercuric dithizonate by chloroform was reported[10]. However, when the amount of chlorides in the sample is not known, it is very difficult to make the absorbing solution in suitable composition for the colorimetric determination of mercury. In such cases the co-precipitation method is to be preferred.

Determination of Mercury in Organic Fungicides and Medicines.—Various methods have already been employed for the determination of mercury in organic compounds, but when the compounds are present mixed with large amounts of other substances or in the form of a solution of extremely low concentration, it is very hard to get an accurate result. Moreover, the decomposition of the compound is usually carried out by strong oxidizing acid with a reflux condenser, through which some of the mercury inevitably escapes during the treatment. If the tin(II)-strong phosphoric acid method is applied for the purpose, the powerful decomposing and reducing power of the reagent acts on the sample instantly, and the mercury vapor is evolved, leaving other interfering metals in the phosphoric acid medium. The procedure of the analysis is the same as in the case of inorganic substances.

Mercurochrome. — Crystals of mercurochrome were weighed and dissolved in water to give a solution containing 10 μg. of mercury per ml. Two or three milliliters of the solution was taken in the reaction vessel, and the analysis was carried out according to the procedure. The purity of the sample was estimated by iodometric titration using a large amount of the sample.

Ethylmercuric Phosphate.—A substance in tablet form having the trade name "Luberon" (Hokko Chemical Co.) which contains ethylmercuric phosphate among other substances, was employed for the analysis. A 0.4597 g. portion of the sample was dissolved in 1 l. of water, and 2 ml. of the solution was put in a run.

***p*-Toluolsulfonaniline Phenyl Mercury, Ethylmercuric Phosphate and Ethylmercuric Urea.**—A mixture of these compounds, some binding material, some surface active agent and coloring matter, is marketed with the trade name "Fumiron" (Hokko Chemical Co.). A 0.4952 g. portion of the sample was dissolved in 1 l. of water and 2 ml. of the solution was taken for analysis.

Methoxyethylmercuric Chloride. — A tablet having the trade name "Usplon" (Japan Special Fungicide Co.) which contains

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[10] T. Kato, N. Takei and A. Okagami, *Japan Analyst (Bunseki Kagaku)*, 5, 689 (1956).

TABLE IV. DETERMINATION OF MERCURY IN VARIOUS FUNGICIDES AND MEDICINES

Sample		Taken	Diluted to	An aliquot for analysis,	Mercury	
Trade name	Compound contained	g.	l.	ml.	Found μg.	%
Luberon (Hg content denoted : 2.5%)	Ethylmercuric phosphate	0.4597	1	2	23.9	
					23.9	
					24.5	
					23.5	
					av. 23.95	2.50
Fumiron (Hg content denoted : 2.5%)	*p*-Toluolsulfonaniline phenyl mercury Ethylmercuric phosphate Ethylmercuric urea	0.4952	1	2	24.0	
					25.5	
					25.4	
					av. 24.97	2.52
Usplon (Hg content : 2.5%)	Methylethylmercuric chloride	0.4683	1	2	22.8	
					23.0	
					23.0	
					av. 23.93	2.55
Mell (Tablet) (Hg content : 4.08%)	Dinaphthylmethane disulfonic acid phenyl mercury	0.3005	1	2	25.5	
					25.0	
					25.9	
					av. 25.47	4.24
Mell (Powder) (Hg content : 0.15%)	〃	0.01993	—	—	27.5	0.137
		0.01923	—	—	26.4	
		0.01555	—	—	21.4	
Thimerosal (Hg content : 48.3∼49.7%)	Ethylmercuric sodium thiosalcylate	1.15081	2.5	2	22.8	
					22.8	
					22.8	
					av. 22.8	49.5
Mercurochrome	Dibromohydroxy mercurifluorescein disodium salt	0.37411	10	2	20.9	
					20.1	
					20.9	
					20.6	
					20.3	
					av. 20.56	25.88

2.5% of mercury was used as a sample. A 0.4683 g. portion of the sample was dissolved in 1 l. of water and 1 ml. of the solution was taken for analysis.

Dinaphtholmethane Disulfonic Acid Phenylmercuric Salt.—This compound is contained in "Mell" (Takeda Pharmaceutical Co.) which is solid in two forms. One is a tablet containing the compound in high concentration, and the other is a powder of lower concentration. A 0.3005 g. portion of the tablet was weighed and dissolved in 1 l. of water, 2 ml. of which was used for analysis. The powder was weighed and placed directly in the reaction vessel.

Ethylmercury Thiosalicylate. — A sample dried in a vacuum desiccator containing sulfuric acid was weighed (1.1508 g.) and dissolved in water to a concentration of 1 : 25000. Two milliliters of the solution was pipetted into the reaction vessel and the analysis was carried out.

The data obtained by the above analyses are tabulated together in Table IV. This shows good reproducibility, and a run of the analysis for each sample can be carried out within thirty minutes without any difficulty. Various methods have been proposed by other authors[11-14] for each sample, but some of them are not versatile enough for different substances and the others are very tedious. By the tin(II)-strong phosphoric acid method, analysis can be carried out with inorganic and organic compounds in various forms without any pre-treatments or precaution.

Summary

A simple and rapid method for the determination of a minute amount of

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[11] J. Kanazawa and R. Sato, ibid., **8**, 440 (1959).

[12] D. Polley and V. L. Miller, *Anal. Chem.*, **24**, 1622 (1952).

[13] V. L. Miller and and D. Polley, ibid., **26**, 1333 (1954); **27**, 1162 (1955).

[14] H. Friedeberg, ibid., **27**, 305 (1955).

mercury in organic and inorganic compounds was established. This method uses the powerful decomposing and reducing power of tin(II)-strong phosphoric acid. In this method the sample is heated with the reagent in a round bottomed flask in a current of carbon dioxide. The mercury vapor evolved is carried with the carbon dioxide into an absorbing vessel which is a separatory funnel containing 10 ml. of 0.1 N potassium permanganate solution and 10 ml. of 10% sulfuric acid. The mercury vapor is oxidized again to the mercuric state and the ion is determined colorimetrically by the usual dithizone-chloroform method. After extracting the mercuric dithizonate with chloroform, the absorbancy of the organic layer is measured by a photoelectric colorimeter with a 517 mμ filter. Some organic compounds containing mercury and some inorganic mercuric compounds as mercuric chloride and mercuric oxide were analyzed by this method in extremely low concentrations, and satisfactory results were obtained. This method may be applied to various kinds of samples without special pre-treatments.

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Department of Chemistry
Faculty of Science
Kanazawa University
Kanazawa