SPECTROPHOTOMETRIC DETERMINATION OF ULTRAMICRO AMOUNTS OF ANIONS
BY CATALYTIC REACTIONS

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Kinetic methods based on the catalytic reaction have been reviewed for several anions. The methods are of extremely high sensitivity and selectivity, finding increasing application to trace analysis of materials of geochemical and environmental interest. The determination of iodine or nitrite is based on their catalytic effects on the color-fading of iron(III) thiocyanate complex in dilute nitric acid. The reaction allows the differential determination of iodide-iodine and iodate-iodine at trace level. Traces of bromide can be determined by its catalytic effect on the oxidation of iodine to iodate by permanganate in acid medium. The reaction ($2\text{NaN}_3 + \text{I}_2 \longrightarrow 2\text{NaI} + 3\text{N}_2$) is catalytically promoted in the presence of sulfur compounds. This catalytic reaction leads to the development of sensitive methods for the determination of thiosulfate, thiocyanate and sulfide. Improved catalytic methods for cyanide and fluoride are also quoted.

1 Introduction

Slow reactions under ordinary conditions can usually be made to proceed at a satisfactory rate in the presence of catalysts. In this respect catalytic methods for trace analysis differ from ordinary analytical methods such as titrimetric and photometric methods. In most of the catalytic reactions employed in analysis, quantitative measurements are made before the system reaches equilibrium. In order to determine the amount of the substance which acts as a catalyst, it is necessary to measure the rate of the indicator reaction or, in several cases, the length of its induction period. The rate of a chemical reaction can be measured from the amount of the reactant disappearing, or from the amount of the product being formed, in unit time. The reaction rate depends on the concentration of the catalyst which takes part in particular cycles.

Kinetic methods using catalytic reactions are of extremely high sensitivity and superior to the spectrophotometric method based on stoichiometric reactions. The sensitivity of the catalytic method or the minimum amount of catalyst that can be detected depends upon the relative rate of the catalyzed and uncatalyzed reactions and particularly upon the stability of this uncatalyzed reaction (reagent

blank). In some cases, catalytic methods are characterized by their high selectivity.

Oxidation-reduction reactions form the largest group of catalytic reactions. Even though most of the catalytic methods reported are concerned with the determination of transition metal ions, a few involve catalysis by anions of non-metals.

There is a general approach that may be employed to estimate the concentration of the catalyst without obtaining the entire rate curve. The reaction is allowed to proceed for a strictly determined time interval and after this time interval the concentration of one of the substances in the solution is determined by measuring the absorbance. This is called a fixed time procedure. In this procedure a plot of absorbance vs the catalyst concentration yields a calibration curve for the determination of the catalyst. In practice the duration of the reaction is strictly controlled by stopping the reaction at a given moment by extraction of the reactant or by other methods.

The rate of a chemical reaction is strongly dependent on the concentration of the reactants and temperature. Therefore, for exact determinations, it is essential to control the concentration of the reagents and the reaction temperature.

The application of catalytic analysis is a relatively young field. It is definitely most useful for the determination of ultramicro amounts of chemical species.

The present author and co-workers have been exploiting many spectrophotometric catalytic methods for anions in ppb levels using a fixed time procedure. The application of these methods to geochemical and environmental materials has also been developed by Japanese scientists. Various catalytic methods investigated by Utsumi et al. will be summarized in the following sections.

2 Determination of Iodide and Iodate

The author et al. found that the reddish orange color of iron(III) thiocyanate complex which was formed by the reaction of potassium thiocyanate with an excess of iron(III) salt in a dilute nitric acid solution, faded very slowly owing to the oxidation of thiocyanate, but rapidly in the presence of minute amounts of iodide or iodate. This catalytic action of iodine turned out to be greatly affected by the presence of a small amount of nitrite. The catalytic reaction was studied extensively and a new micro-determination method for iodide established^{1)~4)}. The catalytic method has been applied to the determination of ultramicro amounts of iodine existing in the forms of both iodide and iodate⁵⁾. In the presence of more than 1000 ppm chloride, iodate shows the same catalytic effect as iodide, and thus the total iodine can be determined in the presence of a large amount of chloride. Iodide in iodide-iodate mixture is first oxidized to iodine by the nitric acid solution of ammonium iron(III) sulfate, which is the reagent of this determination. The resulting iodine is removed by extraction with carbon tetrachloride. Iodate remaining in the aqueous layer quantitatively is then determined by the present method. The difference between the total iodine and the iodate-iodine gives the iodide-iodine.

2.1 Procedure for the determination of iodide⁴⁾

The determination of iodide can be made by measuring the absorbance at 460 nm at a fixed time after the addition of 2.0 cm³ of ammonium iron(III) sulfate solu-

tion(prepared by dissolving 6 g of the reagent in 100 cm³ of 7.0 N HNO₃) to 10.0 cm³ of the sample solution kept at a given temperature, to which 1.0 cm³ of a mixed reagent(5 × 10⁻³ mol dm⁻³ in KSCN and 7 × 10⁻⁴ mol dm⁻³ in NaNO₂) has been added previously. By employing four different combinations of temperature and reaction time, iodide ions can be determined in four different concentration ranges:

25 °C, 12 min: 0.5 ~ 10 ppm, 30 °C, 20 min: 0.05 ~ 1 ppm
45 °C, 25 min: 0.005 ~ 0.1 ppm, 60 °C, 30 min: 0.0005 ~ 0.01 ppm.

The ppb levels of iodide in rain and river waters could be determined with the conditions of 60 °C, 30 min.

2.2 Some experimental results

2.2.1 The reaction rate Reaction rate curves shown in Fig. 1 were obtained by measuring the absorbance of the solution at different reaction time under the condition of procedure(2.1). As seen in Fig. 1, iodate showed a catalytic effect on the reaction rate different from iodide in the absence of chloride. The solution of 0.01 ppm iodide becomes almost colorless after 30 min. These results indicate that the sensitivity of the method increases with increasing reaction time.

2.2.2 The effect of various ions Metal ions such as silver, mercury(I and II), manganese(II) and iron(II) interfered. Oxidizing or reducing anions also interfered with the determination of iodide ion.

2.3 Applications

2.3.1 Determination of iodide and iodate in sea water It is known that iodine in sea water exists in the form of both iodide and iodate. Yonehara⁶⁾ has reported the colorimetric determination of minute amounts of iodide and iodate in sea water by the catalytic method. In the presence of 2000 ppm chloride, iodide and iodate show the same catalytic effect on the color-fading of the iron(III) thiocyanate. The total iodine content in sea water is usually determined by the catalytic method using a sample diluted about ten times. The iodide in the sample is first oxidized to free iodine by sodium nitrite solution and nitric acid solution of ammonium iron(III) sulfate. The resulting free iodine is removed and the iodate is determined by a similar procedure. According to this method, the iodate and total iodine contents in sea water can be determined rapidly and accurately. It requires only about 2 cm³ of sea water.

2.3.2 Determination of iodine in silicate rocks Yonehara et al.⁷⁾ have developed a photometric method for the determination of minute amounts of iodine in

Fig. 1 Reaction rate curves (Temperature; 60 °C)

—●— No I⁻, —○— 0.01 ppm I⁻,
—△— 0.01 ppm IO₃⁻(as I⁻).

silicate rocks. A rock is fused with potassium hydroxide, and the cake is treated with water and sulfuric acid. The iodine in the solution is reduced to iodide by sodium sulfite, and the iodide is then oxidized to free iodine by sodium nitrite. The free iodine thus obtained is extracted with carbon tetrachloride and then back-extracted with a sodium hydroxide solution. The iodine in this aqueous layer is determined photometrically by the method based on the catalytic effect of iodine on the color-fading of iron(III) thiocyanate. Iodine as low as $0.007 \mu\text{g}$ in a 1 g sample of silicate rocks can be determined in this way.

3 Determination of Nitrite

The author and co-workers⁸⁾ found that the catalytic reaction described above (2.1) was characterized by an induction period, the length of which depended on the nitrite ion concentration. Detailed investigation on the behavior of nitrite ions have shown that the kinetic effect can be applied to the determination of nitrite ions.

3.1 Procedure

To 10.0 cm^3 of the sample, 1 cm^3 of the mixed reagent solution ($5 \times 10^{-3} \text{ mol dm}^{-3}$ in KSCN and $1 \times 10^{-3} \text{ mol dm}^{-3}$ in KI) is added and kept in a water bath at 25.0°C for 10 min. The reaction is initiated by adding 2 cm^3 of the iron(III) reagent solution (prepared by dissolving 6 g of ammonium iron(III) sulfate in 100 cm^3 of 7.0 N HNO_3). The absorbance is measured at 460 nm at a certain time after the addition of the iron(III) reagent solution. By taking absorbance measurements at the reaction time of 7, 13, 19 or 24 min, nitrite ions in the concentration range of $0.5 \sim 10$, $0.05 \sim 1$, $0.005 \sim 0.1$ or $0.0005 \sim 0.01 \text{ ppm}$ can be determined respectively.

3.2 Some experimental results

Fig. 2 Reaction rate curves (Temperature; 25°C)

NO_2^- : (1) 10 ppm, (2) 1 ppm, (3) 0.1 ppm, (4) 0.01 ppm, (5) distilled water.

3.2.1 The reaction rate The kinetic reactions were examined for each solution (10.0 cm³) containing 10, 1, 0.1 or 0.01 ppm nitrite ions and for distilled water. The curves shown in Fig. 2 were obtained by measuring the absorbance of these solutions at various reaction time. In the absence of nitrite ions (curve 5 in Fig. 2), the color-fading of the iron(III) thiocyanate complex began approximately 20 min after the initiation and the solution became almost colorless after 32 min. In the presence of nitrite ions, the color-fading was accelerated with increasing nitrite ion concentration. These results indicate that the length of the induction period is greatly affected by the concentration of nitrite ions, and that nitrite ions ranging in concentration from 0.0005 to 10 ppm can be determined by measuring the absorbance at different reaction time.

This kinetic reaction rate depended not only on the concentration of nitrite present, but also on the concentration of iodide and nitric acid, and especially on the temperature.

Commercially available nitric acid usually contains trace amounts of nitrite ions as impurity. If such nitric acid is used as a reagent, it is found impossible to determine nitrite ion concentration of less than 0.01 ppm in a sample. Nitrite ions in 100 cm³ iron(III) reagent solution was found, however almost completely decomposed by using 10 mg of urea and by heating for 10 min.

3.2.2 The effect of various ions Metal ions, such as silver, mercury(II) and iron(II) interfered with the determination of nitrite ion. Oxidizing or reducing anions, such as chromate, sulfide, sulfite, thiosulfate and cyanide in 0.1 to 1 ppm level also interfered.

4 Determination of Bromide

The oxidation reaction between iodide and potassium permanganate in an acid medium is shown in Eqs. (1) and (2).

The author and others found that the reaction (1) is very fast compared to the reaction (2), which is catalytically prompted by the presence of trace amounts of bromide ion. The catalytic effect of chloride is weaker than that of bromide. The catalytic reaction has been studied colorimetrically and a new method for the determination of bromide established⁹⁾.

4.1 Procedure

To 10.0 cm³ of the sample, add 1 cm³ of the potassium iodide solution (1 mg I⁻/cm³) and 0.7 cm³ of sulfuric acid solution (1:1), and then mix. Place the solution in a water bath at 15 °C (or at 25 °C) for about 15 min. Start the reaction by adding 0.7 cm³ of the potassium permanganate solution (0.04 mol dm⁻³). Mix thoroughly and let the solution stand in the water bath. Exactly 3.5 min (or 70 s) after the addition of the potassium permanganate solution, add 5 cm³ of carbon tetrachloride and immediately shake the mixture for 30 s in order to extract the remaining free iodine. After the phase separation, transfer the organic layer to a 50 cm³ separatory funnel. To the organic layer, add 5 cm³ of water, 1 cm³ of the ammonium iron(III) sulfate solution (6 g/100 cm³ of 6 N HNO₃), and 0.5 cm³ of mercur-

ric thiocyanate solution (0.3 g/100 cm³ of ethanol), and shake the separatory funnel for about one min. The aqueous layer is thus colored with iron(III) thiocyanate.

Measure the absorbance of the aqueous layer at 460 nm.

4.2 Some experimental results

4.2.1 The calibration curve The calibration curves shown in Fig. 3 were obtained by the procedure described above using 10 cm³ of standard bromide, chloride and bromide in the presence of 10 ppm chloride. Chloride gives a curve similar to bromide when the concentrations of chloride are more than a hundred times as much as bromide. As natural waters always contain small amounts of chloride, the determination of bromide in the presence of chloride was also investigated⁹⁾. The bromide contents in natural waters such as rain water and river water were determined successfully by the calibration curves.

The same calibration curve as that for bromide is also obtained for bromate solutions with concentrations given as bromine.

4.2.2 The effect of various ions Sulfide, thiosulfate, thiocyanate and cyanide ions interfered with the determination of bromide. Silver and mercury(II) ions interfered strongly.

4.3 Applications

The determination of bromine in silicate rocks Takahashi et al.¹⁰⁾ have reported the photometric determination of micro amounts of bromine in silicate rocks by means of its catalytic effect. They have first investigated in detail the iodine-potassium permanganate reaction in the presence of bromide as a catalyst⁹⁾ and have established optimum conditions for the determination of bromine. They found that the log absorbance vs the concentration of the catalyst yields a linear relationship at a constant reaction time.

The determination of bromine in silicate rocks consists of decomposing the silicate rock sample by fusion

Fig. 3 Calibration curves

—○— Br⁻, —□— Cl⁻,
—△— Br⁻ in the presence of 10 ppm Cl⁻

Reaction temp.; 15 °C, Reaction time; 3.5 min

with potassium hydroxide, leaching the melt with water, oxidizing bromide to bromine with potassium permanganate¹¹⁾, extracting by benzene, back extracting by sodium hydroxide solution, and finally determining the bromine by the improved catalytic method. In this way, 0.25 ~ 0.5 g rock samples with more than 0.04 ppm bromine can be analyzed accurately.

4.4 Another catalytic method

By a further investigation of the oxidation of iodine to iodate with various oxidizing agents, the author et al.¹²⁾ found that, when ammonium cerium(IV) sulfate is used as the oxidizing agent, this oxidation reaction is catalytically promoted by trace amounts of bromide in the presence of a large amount of potassium dichromate in nitric acid solution. This reaction proceeds fairly slowly at room temperature, so that favorable conditions for the procedure can be realized. A new method for the determination of a minute amount of bromide using this reaction has been studied.

5 Determination of Thiosulfate, Thiocyanate and Sulfide

Iodine does not react with sodium azide, but the following reaction is catalytically promoted by the presence of micro amounts of sulfur compounds such as thiosulfate, thiocyanate and sulfide.

This catalytic reaction has been applied to the photometric determinations of ultramicro amounts of thiosulfate¹³⁾, thiocyanate¹⁴⁾ and sulfide¹⁵⁾.

The catalytic reaction proceeds at a very fast rate compared to the ordinary catalytic reaction, so that the reaction may terminate within a short period of time. However, the extent of the catalytic reaction depends on the concentration of catalyst. The reaction is also slightly affected by temperature.

5.1 Procedure and results

5.1.1 The determination of thiosulfate One cm^3 of an aqueous solution ($1/6 \times 10^{-3} \text{ mol dm}^{-3}$ in KIO_3 and 1 mol dm^{-3} in KI) is placed in a glass tube with a glass stopper, and 1 cm^3 of 1 mol dm^{-3} acetic acid is added in order to liberate iodine ($\text{IO}_3^- + 5\text{I}^- + 6\text{H}^+ \longrightarrow 3\text{I}_2 + 3\text{H}_2\text{O}$). The iodine reacts with the large excess of iodide to form triiodide ion which has a maximum absorbance at 350 nm ($\text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^-$). Then 3 cm^3 of sodium azide solution (20 g/100 cm^3) are added. To the solution which is kept at 25°C , 5 cm^3 of the sample solution is added and mixed. At 3 min after the mixing, the absorbance of the remaining triiodide ion is measured at 350 nm.

The calibration curve was in a good linear relationship for the concentration range from 0.01 to 0.15 ppm of thiosulfate ions.

Copper, iron(III), sulfite and cyanide ions interfered.

5.1.2 The determination of thiocyanate One cm^3 of a mixed reagent solution ($1/6 \times 10^{-3} \text{ mol dm}^{-3}$ in KIO_3 and $1 \times 10^{-2} \text{ mol dm}^{-3}$ in KI) and 0.5 cm^3 of 1 mol dm^{-3} acetic acid are placed in a glass tube. After standing this solution for 5 min at 25°C , 3 cm^3 of sodium azide solution (20 g/100 cm^3) and 5 cm^3 of the sample solution are added. Three min after the mixing, 0.5 cm^3 of 1 mol dm^{-3} potassium iodide solution is added. Then, the absorbance of the solution is measured at

350 nm.

According to this method, the concentration ranging from 0.005 to 0.08 ppm of thiocyanate ion in 5 cm³ of the sample can be determined accurately.

When the concentration of potassium iodide in the mixed reagent solution is higher than 0.15 mol dm⁻³ the catalytic reaction does not proceed. On the other hand, the triiodide ion is quantitatively formed by the presence of more than 0.05 mol dm⁻³ iodide in the final solution. Therefore, two step adjustment of iodide concentration was essential for the determination of thiocyanate(See procedure).

5.1.3 The determination of sulfide The sample solution(10 cm³) is placed in a 15 cm³ glass centrifuge tube containing a precipitate of basic zinc carbonate formed by mixing 0.5 cm³ of zinc nitrate solution {3 g Zn(NO₃)₂·6H₂O/100 cm³} with 0.5 cm³ of sodium carbonate solution(1.5 g Na₂CO₃/100 cm³) and 0.5 cm³ of formaldehyde solution(37 %). After shaking, the precipitate containing zinc sulfide is separated by centrifugation. Then 5 cm³ of water is added to the precipitate, and the content is shaken vigorously. Three cm³ of the sodium azide solution(20 g/100 cm³) and 2 cm³ of the triiodide solution, which is prepared by mixing a mixed reagent solution($\frac{1}{6} \times 10^{-3}$ mol dm⁻³ in KIO₃ and 1 mol dm⁻³ in KI) with an equal volume of 1 mol dm⁻³ acetic acid, are added into the centrifuge tube. The absorbance is measured at 350 nm at 5 min after the addition of triiodide solution. According to this method, sulfide ion in the concentration range from 2 to 25 ppb can be determined. An interference of sulfite ion is removed by the addition of formaldehyde solution.

6 Determination of Cyanide

Guilbault et al.¹⁶⁾ have reported a sensitive, specific method for cyanide using catalytic reaction. p-Nitrobenzaldehyde reacts with cyanide to give intermediate cyanohydrin. The cyanohydrin produced reacts with o-dinitrobenzene to give a highly colored blue compound. Because cyanide is regenerated, a catalytic reaction occurs with increased sensitivity.

The author et al.¹⁷⁾ have investigated in detail the catalytic reaction and have established the method for the determination of ultramicro amounts of cyanide.

6.1 Procedure and results

In a 20 cm³ test tube are placed 2 cm³ of 0.2 mol dm⁻³ p-nitrobenzaldehyde in methyl cellosolve, 2 cm³ of 0.15 mol dm⁻³ o-dinitrobenzene in methyl cellosolve and 2 cm³ of 0.1 mol dm⁻³ sodium hydroxide solution containing cyanide ion. The mixture is allowed to stand for 20 min at 25 °C or for 60 min at 35 °C. The absorbance of the colored solution is measured at 555 nm with 1 cm cell against water. One to 100 ng of cyanide in 2 cm³ of the sample solution was determined by this way. As low as 0.01 ppm of cyanide in the waste water was also determined accurately.

Hypochlorite, sulfide, acetone, formaldehyde and metal ions such as Co(II), Hg(II) and Cu(II) which form complexes with cyanide interfered with the determination of cyanide.

7 Dtermination of Fluoride

The red complex between Xylenol Orange(XO) and zirconium ions has a maximum absorbance at about 550 nm. The author et al.¹⁸⁾ found that the binary(Zr-XO) com-

plex reacts with cetyltrimethylammonium chloride (CTC) to form a ternary complex which has a maximum absorbance at 605 nm and a high molar absorptivity. West et al.¹⁹⁾ have reported a spectrophotometric method for the determination of fluoride which is based on the catalytic effect of fluoride on the slow reaction between XO and slightly hydrolyzed zirconium solution. A more sensitive method¹⁸⁾ has been developed for the determination of ultramicro amounts of fluoride based on the above catalytic reaction in the presence of CTC.

7.1 Procedure

A 10 cm³ of the sample solution containing less than 100 ppb of fluoride, 1 cm³ of 2×10^{-4} mol dm⁻³ XO and 1 cm³ of 0.1 % CTC (in 3 N HCl) solutions are placed in a test tube. One cm³ of 2×10^{-4} mol dm⁻³ slightly hydrolyzed zirconium solution (in 0.02 N HCl) is added. The solution is allowed to stand for 40 min at 25 °C, and the absorbance is measured at 605 nm against water.

As low as 10 ~ 100 ppb fluoride can be determined in this manner.

7.2 Some experimental results

7.2.1 Hydrolyzed zirconium solution A 1×10^{-2} mol dm⁻³ zirconium oxychloride stock solution (in 0.02 N HCl) was allowed to age for 4 hours at 40 °C, being stored at about 5 °C. The working solution of 2×10^{-4} mol dm⁻³ was prepared by diluting the stock solution with 0.02 N hydrochloric acid. This solution may be used for up to 7 days.

7.2.2 The reaction rate Reaction rate curves shown in Fig. 4 were obtained by measuring the absorbance of the solution at various time under the condition of procedure (7.1).

7.2.3 The effect of various ions Sulfate, phosphate, aluminum and iron(III) showed interferences in this method.

Fig. 4 Reaction rate curves

○ blank, ■ 20 ppb F⁻, △ 50 ppb F⁻,
● 80 ppb F⁻, □ 100 ppb F⁻.

References

- 1) I. Iwasaki, S. Utsumi, T. Ozawa: Bull. Chem. Soc. Jpn., 26, 108 (1953).
- 2) S. Utsumi: Nippon Kagaku Zasshi, 74, 298 (1953).
- 3) I. Iwasaki, S. Utsumi, T. Ozawa: Nippon Kagaku Zasshi, 78, 474 (1957).
- 4) S. Utsumi, M. Shiota, N. Yonehara, I. Iwasaki: Nippon Kagaku Zasshi, 83, 32 (1964).
- 5) I. Iwasaki, S. Utsumi, N. Yonehara: Nippon Kagaku Zasshi, 85, 36 (1964).
- 6) N. Yonehara: Bull. Chem. Soc. Jpn., 37, 1101 (1964).
- 7) N. Yonehara, M. Yoshida, I. Iwasaki: Bull. Chem. Soc. Jpn., 43, 3796 (1970).

- 8) S.Utsumi, T.Okutani, A.Sakuragawa, A.Kenmotsu: Bull.Chem.Soc.Jpn., 51, 3496 (1978).
- 9) M.Shiota, S.Utsumi, I.Iwasaki: Nippon Kagaku Zasshi, 80, 753(1959).
- 10) K.Takahashi, M.Yoshida, T.Ozawa, I.Iwasaki: Bull.Chem.Soc.Jpn., 43, 3159(1970).
- 11) I.Iwasaki, S.Utsumi, A.Tomonari, I.Morita: Nippon Kagaku Zasshi, 80, 744(1959).
- 12) N.Yonehara, S.Utsumi, I.Iwasaki: Bull.Chem.Soc.Jpn., 38, 1887(1965).
- 13) S.Utsumi, T.Okutani: Nippon Kagaku Kaishi, 1973, 75.
- 14) S.Utsumi, T.Okutani, T.Yamada: Bunseki Kagaku, 24, 799(1975).
- 15) A.Sakuragawa, T.Harada, T.Okutani, S.Utsumi: Bunseki Kagaku, 29, 264(1980).
- 16) G.G.Guilbault, D.N.Kramer: Anal.Chem., 38, 834(1966).
- 17) T.Okutani, H.Kotani, S.Utsumi: Bunseki Kagaku, 26, 116(1977).
- 18) Unpublished research. T.Okutani, M.Tsukada, A.Sakuragawa, S.Utsumi: Partly presented at the 29th Annual Meeting of the Japan Society for Analytical Chemistry, Fukuoka, October, (1980).
- 19) M.L.Cabello-Tomas, T.S.West: Talanta, 16, 781(1969).

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