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The Spectrophotometric Determination of Perchlorate Ions by Solvent Extraction with Crystal Violet[*1]

Sumio UCHIKAWA

Faculty of Education, Kumamoto University, Kumamoto

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A micro quantity of perchlorate ions is extracted into chlorobenzene with crystal violet. The absorbance maximum of the extract in the organic layer is found to be at 595 mμ. The maximum and the constant extraction was obtained in the pH range of 2—7. In order to ascertain the optimum conditions for the determination of perchlorate ions, various factors have been studied: the effects of the concentration of the dyestuff, the pH of the solution, the standing time of the solution, the times of the extraction, and the presence of diverse ions. The recommended procedure for the calibration curve is as follows: Two milliliters of a crystal violet solution (1×10^{-3} M), 5 m*l* of a potassium phosphate buffer solution (1 M, pH 5.8), and various volumes (0—10 m*l*) of a standard perchlorate solution (2×10^{-5} mol/*l*) are mixed. The mixed solution is diluted to 25 m*l* with water. An aliquot (10 m*l*) of the solution is then poured into a separatory funnel and is shaken for 5 min with 10 m*l* of chlorobenzene. The absorbance of the organic layer is measured at 595 mμ against the reagent blank solution. Beer's law is obeyed in the perchlorate range of 10^{-7}—8×10^{-6} mol/*l* in the aqueous layer before the extraction. Considerable amounts of chloride, iodate, and sulfate ions do not interfere.

Methods for the quantitative determination of perchlorate have recently been reviewed.[1] Generally, the methods fall into three categories: (1) reduction to chloride by fusion, (2) reduction to chloride in a solution with titanium(III) or another reductant, and (3) precipitation as an insoluble salt, such as tetraphenylarsonium perchlorate. Most of the published methods are, however, either subject to numerous interferences or else it is difficult to make them work quantitatively. In 1960, Burns and Muraca[2] reported a method for the determination of perchlorate by reduction with titanium(III) using osmium tetroxide as a catalyst. In 1962, Johannesson[3] published an isotope dilution method. Alley and Dykes[4] determined the amount of perchlorate by titrating chloride ions with silver nitrate, which had been derived by reducing perchlorate ions with titanium hydride in 1 : 3 sulfuric acid. In these methods, however, the sensitivity is not very high.

On the other hand, the solvent extraction methods for the determination of perchlorate using cationic dyestuffs, such as methylene blue[5,6] and brilliant green,[7] or chelate cations, such as the 1, 10-phenanthlorine-iron(II) cation[8,9] and the 2, 2′-dipyridyl-iron(II) cation,[10] have recently been reported. Those authors had reported in a previous paper[11] that crystal violet, a kind of cationic dyestuff, was extractable with nitrate ions into chlorobenzene, and that the absorbance in the organic layer was proportional to the amounts of nitrate ions taken up. It has been found by the present author that crystal violet can also be extracted with perchlorate ions into chlorobenzene. The present work is a study as establish a method for the determination of a small amount of perchlorate by solvent extraction with crystal violet.

Experimental

Apparatus. The spectrophotometric measurements were made with a Hitachi Model 139 spectrophotometer with 10-mm cells. The shaking was done with an Iwaki Model KM shaker. The pH measurements were made with a Horiba M3 pH meter. The centrifuging was

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done with a Shimazu Model C centrifugal separator. The separation of the organic layer from the aqueous layer was carried out with a separatory funnel with a capacity of about 120 m*l*.

Materials. *Crystal Violet Solution.* A 1.0×10^{-3} M solution was prepared by dissolving guaranteed crystal violet in pure water.

Standard Perchlorate Solution. A stock solution containing 5.0×10^{-3} mol perchlorate ions per liter was prepared by dissolving guaranteed potassium perchlorate (dried at 110°C) in pure water. The working solution was then prepared by diluting the stock solution properly.

Buffer (Photassium Phosphate Solution). Guaranteed potassium dihydrogen phosphate (34.0 g) was dissolved in water, and the pH of the solution was made 5.8 by adding a dilute sodium hydroxide solution; then the total volume was made to 250 m*l* with water, making a 1 M solution.

Water. It was better, for good precision, to deionize the water by using an ion-exchange resin column.

Solvent. Chlorobenzene was purified by distillation. All the other reagents were of analytical grade and were used without further purification.

Standard Procedure. Mix 2 m*l* of the crystal violet solution, 5 m*l* of the potassium phosphate solution, and an aliquot of the standard perchlorate solution (2×10^{-5} mol/*l*). Dilute the mixed solution to 25 m*l* with water. Take an aliquot (10 m*l*) into a separatory funnel. Shake the solution with 10 m*l* of chlorobenzene for 5 min. After the solution has then been left for 30 min, transfer the organic layer to a centrifuging tube and centrifuge for 5 min (2000 rpm). Then transfer the organic solution into a 10-mm cell and measure the absorbance at 595 mμ, using a reagent blank or chlorobenzene itself as a reference.

Results and Discussion

Absorption Spectra. Figure 1 shows the absorption spectra; curve 1 is a spectrum of the extract when perchlorate ions are absent, while curve 2 is that of the extract with perchlorate ions. It is thus found that when a small amount of perchlorate ions is present, the cation of crystal violet is quite extractable into the organic layer. The absorbance maximum is at 591 mμ in the aqueous phase (curve 3), but in the organic phase the maximum is slightly shifted to 595 mμ (curves 1 and 2). This slight red shift in the organic layer may be attributed to the association between cations and anions in chlorobenzene.

The Effect of the pH Value. In order to study the effect of pH on the extraction, a series of perchlorate solutions (4×10^{-6} mol/*l*) of various pH values were prepared by adding a dilute sulfuric acid solution or a dilute sodium hydroxide solution; the solutions were then treated according to the procedure described above. The results are shown in Fig. 2. It was found that there is a maximum and constant absorbance in the organic phase over the pH range from 2 to 7. In an alkaline solution, crystal violet precipitates.

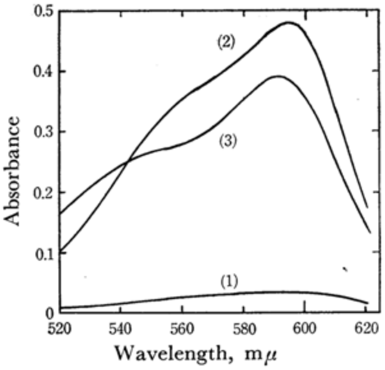

Fig. 1. Absorption spectra.

Curve 1 : Spectrum of organic phase extracted from the aqueous solution (10 m*l*) contained crystal violet (8×10^{-5} mol/*l*), KH_2PO_4 (0.2 mol/*l*), but ClO_4^- is absent, pH 6.
Curve 2 : Spectrum of organic phase extracted from the aqueous solution (10 m*l*) contained the same component as that of curve 1, and ClO_4^- (4×10^{-6} mol/*l*), pH 6.
Curve 3 : Spectrum of aqueous solution contained crystal violet (4×10^{-6} mol/*l*) and KH_2PO_4 (0.2 mol/*l*), pH 6.
Reference : Curves 1 and 2, chlorobenzene Curve 3, water

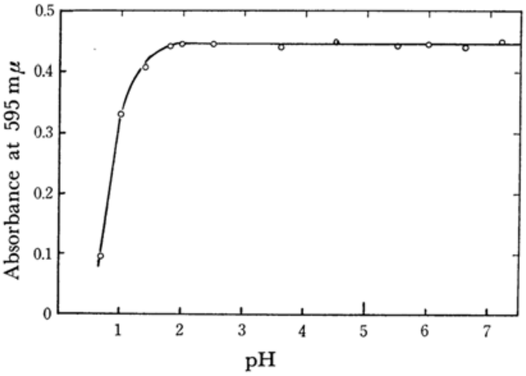

Fig. 2. Effect of pH.

The concentrations of crystal violet, phosphate and perchlorate in the aqueous solutions before the extractions were 8×10^{-5} mol/*l*, 0.2 mol/*l* and 4×10^{-6} mol/*l* respectively.
Reference : Reagent blank

The Effect of the Crystal Violet Concentration. To a constant volume of the perchlorate solution (2×10^{-5} mol/*l*), various volumes of the crystal violet solution were added, after which the experiments were worked out as above. As is shown in Fig. 3, when chlorobenzene was used as a reference, the absorbance of the extracts increased with the amount of crystal violet added, independently of the presence of perchlorate (curves 1 and 2). However, when the mole ratio of crystal violet to perchlorate ions was kept at more than 10 : 1,

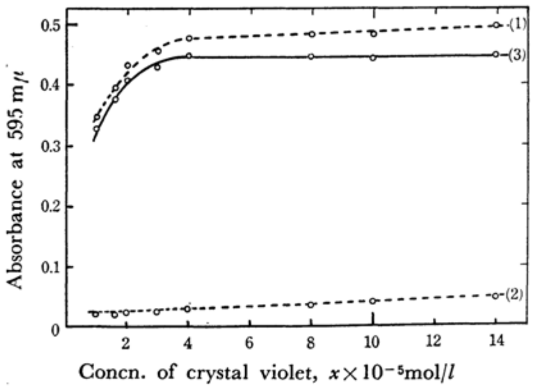

Fig. 3. Effect of concentration of crystal violet.

The concentration of phosphate in the aqueous solutions before the extractions was 0.2 mol/l.
pH of aqueous layer : 6
Curves 1 and 3: Perchlorate (4×10^{-6} mol/l) was present.
Curve 2: Perchlorate was absent.
Reference: Curves 1 and 2, chlorobenzene
Curve 3, reagent blank

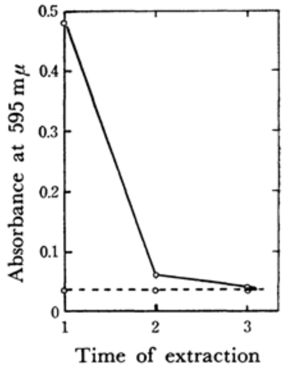

Fig. 4. Effect of times of extraction.

The concentrations of crystal violet, phosphate and perchlorate in the aqueous solution before the first extraction were 8×10^{-5}mol/l, 0.2 mol/l and 4×10^{-6} mol/l respectively.
pH of aqueous layer: 6
----: Only perchlorate was absent.
Reference: Chlorobenzene

a constant absorbance was obtained, using the reagent blank solution as a reference (curve 3).

The Effect of the Potassium Phosphate Concentration. When the concentration of phosphate is low in the aqueous phase, it is time-consuming to separate the two phases. A good separation was observed when the concentration of phosphate was above 0.1 mol/l, and 0.04—0.2 mol/l of phosphate had no influence on the absorbance of the extract. The salt was thus useful not only as a buffering agent but also as a salting-out agent.

The Effect of the Shaking Time. The shaking time in the extraction was varied from 1 to 15 min, while the other variables were kept the same. Only a 1-min shaking was enough to attain a good extraction.

The Stability of the Color. When chlorobenzene was used as a reference, the absorbance of the reagent blank and that of the extract of perchlorate increased slightly with the standing time. However, for the reagent blank, the absorpance of the extract of perchlorate did not change at all for 30 min.

The Effect of the Times of Extraction. The effect of times of extraction was examined by successive extractions with each 10-ml portion of chlorobenzene. As is shown in Fig. 4, one extraction is enough for the determination of perchlorate.

The Effect of the Temperature of the Solution on the Extraction. It was observed that the absorbance of the organic phase is affected by the temperature of the solution when chlorobenzene was used as a reference. When the extractions were done at 15°C and 28°C, the absorbances of the extracts of perchlorate (4×10^{-6} mol/l) were 0.481 and 0.492 respectively. On the other hand, those of the reagent blanks were 0.036 and 0.045 respectively. Therefore, when the reagent blank is used as a reference, the absorbance is almost independent of the temperature at 15—28°C.

The Choice of an Organic Solvent. Beside chlorobenzene, various other solvents were tested for the extraction. It was found that the perchlorate of crystal violet is extractable into neigher benzene, toluene, cyclohexane, carbon tetrachloride, nor tetrachloroethylene, while by such solvents as 1, 1, 2, 2-tetrachloroethane, 1, 2-dichloroethane, cyclohexanol, and cyclohexanone, which have a comparatively larger dielectric constant than chlorobenzene, crystal violet itself was remarkably extracted. Trichloroethylene was as useful as chlorobenzene, but the absorbance of the organic layer was reduced to half the value of chlorobenzene.

Calibration Curve. On the basis of the above results, the procedure was worked out. The absorbance of each extract from aliquots (10 ml) of aqueous solutions (25 ml) containing various volumes (1—10 ml) of the standard perchlorate solution (2×10^{-5} mol/l) was measured at 595 mμ against the reagent blank. As is shown in Fig. 5, Beer's law is followed in the 1×10^{-7}—8×10^{-6} mol/l range of perchlorate ions in the aqueous layer before the extraction. The sensitivity of this method is 10 times greater than that of the 1, 10-phenanthroline iron(II) method.

Reproducibility. The standard deviation in absorbance was obtained from 10 reproducible measurements, using chlorobenzene as a reference. The standard deviation in the standard procedure at 15°C was 0.006 for both the extracts of perchlorate (4×10^{-6} mol/l) and those of the reagent

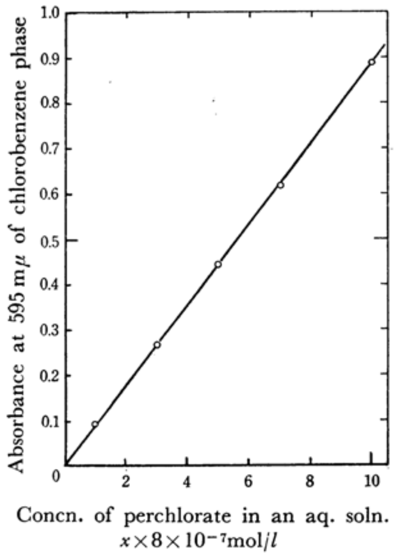

Fig. 5. Calibration curve.

The concentrations of crystal violet and phosphate in the aqueous solutions were 8×10^{-5} mol/l and 0.2 mol/l respectively.
pH of aqueous layer: 6
Reference: Reagent blank

blank. All the standard deviation values obtained under the following conditions the pH of the solution, 3; the concentration of crystal violet, 4×10^{-4} mol/l; the standing time of the solution before extraction, 18 hours; the temperature of the solution on extraction, 28°C—fell in the 0.006—0.009 range, whether perchlorate ions were present or not. According to the F-test, no significant difference in the 5% level was found between each of the above values and the value obtained by the standard procedure.

The Effect of Diverse Ions. Table 1 shows the absorbances of a series of extracts which have been treated according to the standard procedure. Measurement was done at 595 mμ, using chlorobenzene as the reference. Each solution contained 4×10^{-6} mol/l of perchlorate plus various amounts of diverse ions. The presence of a considerable amount of sulfate, iodate (about 1000 times that of perchlorate), and chloride (about 100 times that of perchlorate) did not interfere with the determination of perchlorate. The presence of chlorate, periodate and nitrate in the same amounts as perchlorate, however, gave a positive error. Iodide and thiocyanate interfered when present in any amount.

TABLE 1. EFFECTS OF DIVERSE IONS

Ion	Added as	Concn. mol/l	Absorbance at 595 mμ
None	—	—	0.481
ClO_3^-	$KClO_3$	4×10^{-6}	0.528
BrO_3^-	$KBrO_3$	4×10^{-5}	0.491
BrO_3^-	$KBrO_3$	2×10^{-4}	0.523
IO_3^-	KIO_3	4×10^{-3}	0.486
IO_3^-	KIO_3	2×10^{-2}	0.520
IO_4^-	KIO_4	4×10^{-6}	0.653
Cl^-	KCl	4×10^{-4}	0.484
Cl^-	KCl	2×10^{-3}	0.492
Br^-	KBr	4×10^{-5}	0.488
I^-	KI	8×10^{-7}	0.502
NO_3^-	$NaNO_3$	4×10^{-6}	0.500
SCN^-	KSCN	4×10^{-7}	0.516
SO_4^{2-}	Na_2SO_4	8×10^{-2}	0.482

Concn. of ClO_4^- in each case: 4×10^{-6} mol/l
Other variables were the same as those of the procedure.
Temp.: 15°C
Ref.: Chlorobenzene

Summary

A method for the spectrophotometric determination of perchlorate by solvent extraction has been proposed. A small amount of perchlorate ions is extracted into chlorobenzene with crystal violet; the absorbance of the organic layer is then proportional to the amount of perchlorate taken in. The extraction can be done in the pH range of 2—7. Considerable amounts of sulfate, iodate and chloride do not interfere, and the sensitivity of the method is higher than with other methods.

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