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Determination of Perchlorate Ion With Tetraphenylarsonium Chloride

JOHN E. GOING AND RONALD T. PFLAUM

Abstract. A detailed study of precipitation reaction of perchlorate ion with tetraphenylarsonium chloride is reported. Optimum conditions for quantitative precipitation of perchlorate ion were determined. A gravimetric and a spectrophotometric method for perchlorate ion are proposed. The spectrophotometric method is based upon dissolution of $(C_6H_5)_4AsClO_4$ in acetonitrile and subsequent measurement of absorbance at 264 mμ. Results on selected samples prove both methods to be accurate and reproducible.

INTRODUCTION

A variety of analytical methods for the determination of perchlorate ion have been described in the chemical literature. Gravimetric (8, 14), titrimetric (4, 6), spectrophotometric (2, 3, 7, 9, 10, 11, 13, 15, 16) and radiochemical (12) methods using a variety of reagents have been prepared. The popularity of an optical measurement is clearly evident.

Tetraphenylarsonium chloride has been used as a reagent for perchlorate ion by a number of workers (2, 5, 8, 13). It is striking that a clear, concise, gravimetric procedure of analysis, applicable to a variety of perchlorate samples, is lacking in the literature. Although the absorption characteristics of the tetraphenylarsonium cation have been used for the determination of perchlorate ion (5), a spectrophotometric method likewise has not been described.

This work was concerned with a study of the preciptation reactions of perchlorate ion with tetraphenylarsonium chloride. A gravimetric method and a spectrophotometric method for perchlorate ion are proposed. The results of analyses on selected samples are presented.

EXPERIMENTAL

Apparatus and Reagents. A Cary Model 14 recording spectrophotometer with 1.00 cm. matched silica cells was used for all absorbance measurements. All pH measurements were made with a Beckman Zeromatic pH meter equipped with standard glass-calomel electrodes.

Potassium perchlorate was prepared from reagent grade potassium carbonate and perchloric acid. The freshly prepared salt was recrystallized from water and dried at 300°C.

Pyridinium perchlorate was prepared by the dropwise addition of 72% perchloric acid to a solution of pyridine in glacial acetic acid. The white crystalline salt was filtered, washed with acetic acid, and vacuum dried. Quinolinium perchlorate and brucinium perchlorate were prepared by the same procedure with diethyl ether as the solvent instead of acetic acid.

Tetraphenylarsonium chloride was obtained from the G. Frederick Smith Chemical Co. and was used as received. Tetraethylammonium perchlorate was prepared from tetrathylammonium hydroxide and perchloric acid.

Acetonitrile was obtained from the Matheson, Coleman and Bell Division of the Matheson Co. The solvent was purified by refluxing over phosphorus pentoxide for 24 hours distilling through a one meter packed helices column.

All other chemicals were of reagent grade quality.

Study of the Precipitation Reaction. The addition of tetraphenylarsonium chloride to a solution of perchlorate ion results in the formation of an amorphous white precipitate. The effects of heat, pH and ionic strength on the completeness of precipitation were investigated. The physical characteristics of the precipitate in mixed solvent systems were also observed.

Solutions containing 17.25 mg. of perchlorate ion were prepared at various pH values from 1.95-11.30. Diverse ions and miscible organic solvents were added to separate solutions. The recovery of tetraphenylarsonium perchlorate was determined for a variety of solutions.

Absorptimetric Study of Tetraphenylarsonium Perchlorate. Ultraviolet absorption spectra of acetonitrile solutions of tetraphenylarsonium perchlorate were obtained. The conformance of the system to Beer's law was studied over the concentration range of 0.199 - 4.77 x 10^{-4} M perchlorate ion.

RESULTS AND DISCUSSION

Tetraphenylarsonium chloride acts as a precipitant for many univalent anions and for a few divalent anions. Noteworthy among the common anions which form precipitates with the reagent are dichromate, periodate, permanganate, perrhenate, persulfate, tetrafluoroborate, tetraphenylborate, and triiodide. In addition, many metal ion complexes can also be precipitated with the reagent. The presence of any of these ions would constitute a natural source of interference and would lead to high results in a determination of perchlorate ion.

Tetraphenylarsonium perchlorate precipitates out of aqueous solution as a finely divided amorphous solid. The addition of sodium chloride to the precipitation medium results in the formation of a more granular precipitate. The larger particles have little tendency to adhere to the walls of the reaction vessel.

Tetraphenylarsonium perchlorate is readily soluble in acetone and acetonitrile. Precipitation or recrystallization from an acetone-water mixture results in the formation of well defined crystals. Easily filterable crystals can be obtained by precipitation from mixed solvent systems.

Optimum conditions for the quantitative precipitation and recovery of perchlorate ion were determined in this study. Precipitation from a warm solution and a subsequent digestion period were found to be requisite for quantitative precipitation. Excess precipitant (25%) insures complete precipitation. Solubility loss upon washing with minimum volumes of cold water was found to be insignificant. An ion product of 3.98 x 10^{-9} at 25°C for $(C_6H_5)_4AsClO_4$ has been reported (5). Heating of the salt at 110°C for 1 hour was found to be sufficient for the removal of absorbed water. A minimum decomposition temperature of 150°C has been reported (5).

The effect of pH on the precipitation of perchlorate ion was investigated as a potentially critical variable. The results of this study are presented in Table 1. It can be seen that pH is not a significant factor in solutions less basic than pH 10.3.

Table 1. Effect of pH on Precipitation
(17.25 Mg $C10_4^-$ Present)

pH	Mg. $C10_4^-$ Found.
1.95	17.25
2.10	17.29
2.45	17.27
10.30	17.29
11.30	17.35

In solutions of higher pH, insoluble tetraphenylarsonium hydroxide is coprecipitated with the perchlorate salt.

Absorption curves of acetonitrile solutions of $(C_6H_5)_4AsClO_4$ are shown in Figure 1. The absorption of the tetraphenylarsonium cation is characterized by absorption maxima at 258, 264, and 271 mμ with molar absorptivities of 2580, 3420, and 2840, respectively. These values are similar to those reported for aqueous solutions of $(C_6H_5)_4AsClO_4$ (5). A shoulder on the absorption curve at 220 mμ ($\varepsilon = 35{,}200$) is also evident. This absorption band has been used for the indirect determination of tetrafluoroborate ion (1).

The conformance of acetonitrile solutions of $(C_6H_5)_4AsClO_4$ to Beer's law is shown in Figure 2. Plots of the three absorption maxima are presented to show the linear dependence upon concentration over the concentration range of 0.199 - 4.775 x 10 M^{-4}(2-47 p.p.m. ClO_4^-)

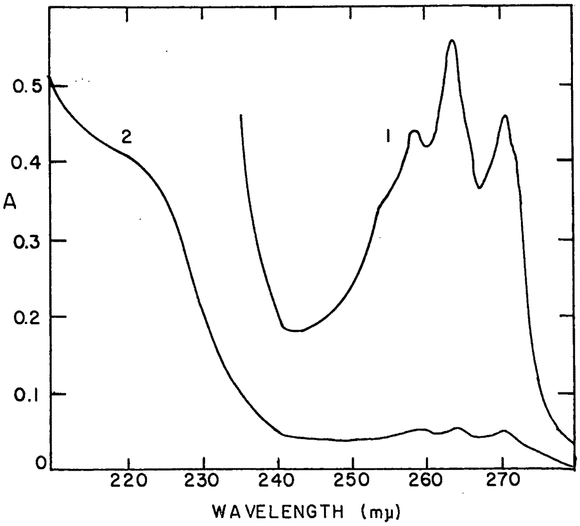

Figure 1. Absorption Spectra of Tetraphenylarsonium Perchlorate in Acentonitrile
1. 1.592 x $10^{-4}M$
2. 9.948 x $10^{-6}M$

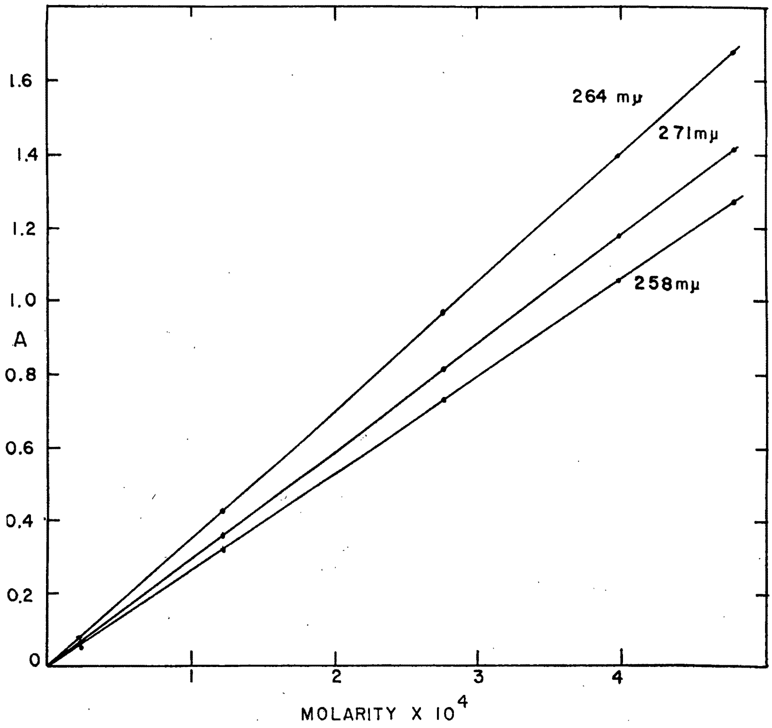

Figure 2. Beer's Law Plots of Tetraphenylarsonium Perchlorate in Acetonitrile

Gravimetric Procedure for the Determination of Perchlorate Ion.

Dissolve the perchlorate sample in approximately 50 ml. of distilled water. Add approximately 100 mg. of sodium chloride and heat the solution to 60°C.

Add tetraphenylarsonium chloride dropwise with stirring. A 25% excess of the precipitant is sufficient to ensure complete precipitation. Digest the reaction mixture for 1 hour.

Filter the solution into a previously weighed medium porosity sintered glass crucible. Wash the precipitate several times with 5 ml. portions of cold distilled water.

Heat the precipitate and crucible at 110°C to constant weight.

Analytical results of determinations of perchlorate ion in samples of potassium perchlorate are presented in Table 2.

Table 2. Gravimetric Determination of Perchlorate Ion

Sample	Mg. ClO_4^-, Present	Mg. ClO_4^- Found	Std. Deviation
1.	2.15	2.12	0.02
2.	4.31	4.32	0.02
3.	8.62	8.62	0.02
4.	17.25	17.29	0.04
5.	21.55	21.55	0.10
6.	43.11	43.16	0.09

Standard deviations were calculated on the basis of from four to six determinations. In the optimum region of 4-40 mg. Perchlorate, the average relative error was 0.12%.

The results of analyses on a series of organic perchlorate salts are presented in Table 3. The results show a marked improvement over the analyses of Bodenheimer and Weiler (3). These workers analyzed similar organic perchlorates by an indirect spectrophotometric method based upon the absorption of the tetrapyridine copper (II) cation.

Table 3. Gravimetric Analysis of Organic Perchlorates

	% ClO_4^-		M. W.	
Organic Salt	Calc.	Found	Calc.	Found
Pyridinium Perchlorate	55.4	55.3	180	180
		55.2		180
Quinolinium Perchlorate	43.3	43.3	230	230
		43.2		230
		43.2		230
Tetraethylammonium Perchlorate	43.3	42.9	230	231
		42.9		231
		43.0		232
Brucinium Perchlorate	20.1	20.1	495	493
		20.2		494
		20.2		494

Spectrophotometric Procedure for the Determination of Perchlorate Ion.

Precipitate tetraphenylarsonium perchlorate as outlined above. After digestion, filter the solution into a medium porosity sintered glass crucible. Wash the precipitate several times with 5 ml. portions of cold distilled water and discard the filtrates.

Rinse the crucible and precipitate with a few portions of acetonitrile. Transfer the washings to an appropriate volumetric flask and dilute to volume with acetonitrile.

Measure the absorbance of the solution at 264 mμ.

Calculate the amount of perchlorate ion from a previously prepared calibration curve.

Results on the analyses of selected samples are presented in Table 4. A comparison with gravimetric results on identical samples shows that the spectrophotometric method does not suffer from any appreciable los in accuracy.

Table 4. Spectrophotometric Determination of Perchlorate Ion

Sample	Mg. ClO_4^- Present	Mg. ClO_4^- Found
1.	1.29	1.28
2.	2.15	2.15
3.	4.31	4.30
4.	8.62	8.66
5.	12.93	13.0
6.	17.25	17.7

The choice of the gravimetric method versus the spectrophotometric method is largely one of personal preference. Both methods are convenient, accurate, and precise. Routine analyses on similar samples can be carried more conveniently spectrophotometrically.

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