JUN 10 1969

Spectrophotometric Determination of Perchlorate*

IS-658

James S. Fritz and Patricia A. Campbell

Institute for Atomic Research and Department of Chemistry

Iowa State University, Ames, Iowa

MASTER

ABSTRACT

Perchlorate is extracted from aqueous solution by n-butyronitrile as ferrous 1,10-phenanthroline perchlorate. The amount of perchlorate is calculated from spectrophotometric measurement of the absorbance of the extract. Moderate to large amounts of chloride, sulfate or nitrate cause little or no interference. Chlorate is slightly extracted but the interference can be corrected.

Methods for the quantitative determination of perchlorate have been reviewed recently (4). Generally the methods fall into three categories: 1) reduction to chloride by fusion 2) reduction to chloride in solution with titanium(III) or other reductant 3) precipitation as insoluble salts such as tetraphenylarsonium perchlorate. Most of the published methods are either subject to numerous interferences or else they are difficult to make work quantitatively. In 1960, Burns and Muraca (1) obtained good results for ammonium perchlorate by reduction with titanium(III) using osmium tetroxide as a catalyst. In 1962, Johannesson (2) published an isotope dilution method for perchlorate in which volatile anions were removed by evaporation.

* Contribution No. 1320. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:
A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.
As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

The present determination of perchlorate is based on solvent extraction. Ferrous 1,10-phenanthroline sulfate (ferroin) is not extracted from aqueous solution into organic liquids. However, if ferroin is added to an aqueous solution containing perchlorate, ferrous 1,10-phenanthroline perchlorate is extracted into n-butyronitrile and the amount of extraction is proportional to the amount of perchlorate present. Perchlorate is determined by measuring the absorbance of extracted ferrous 1,10-phenanthroline perchlorate spectrophotometrically.

REAGENTS AND SOLUTIONS

Ferroin. A 0.01M solution of ferroin, ferrous 1,10-phenanthroline sulfate, was prepared using ferrous sulfate and 1,10-phenanthroline.

Perchlorate. A standard solution of 0.100M sodium perchlorate was prepared. More dilute perchlorate solutions were prepared by diluting aliquots of this solution to a definite volume.

Foreign Anions. Solutions were prepared using reagent grade sodium, potassium or ammonium salts.

Buffer. The acetate buffer was approximately 0.1M in sodium acetate and 0.1M in acetic acid.

Solvents. n-Butyronitrile was obtained from Eastman Chemical Products and was used without purification. Reagent grade acetone was used.

PROCEDURE

Add a 2-ml. sample containing 0.0001 to 0.01 mmole of perchlorate to a glass-stoppered centrifuge tube. Add 3 ml. of acetate buffer and

check to see that the pH is 5.0 to 6.0. If necessary add a little sodium hydroxide or hydrochloric acid to adjust the pH. Pipet exactly 4.00 ml. of n-butyronitrile into the centrifuge tube and shake for at least 1 minute. Centrifuge briefly. Pipet exactly 2.00 ml. of the butyronitrile layer into a 25-ml. volumetric flask and dilute to volume with acetone. (Near the upper end of the perchlorate range it is better to use a 50-ml. volumetric flask.) Measure the absorbance of the extracted solution at 510 m μ . Read the amount of perchlorate from a Beer's law plot prepared by extracting and measuring the absorbance of known perchlorate standards using this same procedure.

DEVELOPMENT OF METHOD

Solvent. Most organic solvents do not extract ferroin perchlorate from aqueous solution. Margerum and Banks studied the extraction of iron as the ferrous-1,10-phenanthroline complex from solutions containing perchlorate (3). They found nitrobenzene to be the best solvent for this extraction. However nitrobenzene has a yellow color and is not an ideal solvent for extraction work. Recently n-butyronitrile and benzonitrile have become commercially available. Both of these solvents are water-white and either extracts ferroin perchlorate completely in a single extraction. n-Butyronitrile was chosen for the present work because the organic and aqueous layers settle out more rapidly after shaking.

pH. Extraction of perchlorate as ferroin perchlorate gives an absorbance that is essentially constant in the pH range of about 5 to 10. In more acidic or in more alkaline solutions, the absorbance is lower.

Some of the buffers employed to maintain a constant pH affected the quantitative results adversely and caused some scatter of experimental points. To avoid this many of the studies were carried out in approximately neutral solutions (with regard to acidity). Solutions buffered at pH 5 or pH 6 with sodium acetate-acetic acid gave consistent results and this is probably the better method.

Absorption Maximum and Molar Absorptivity. An absorption spectrum of a solution of ferroin perchlorate which had been equilibrated with water was found to be virtually identical with the spectrum of ferroin in water. The molar absorptivity in n-butyronitrile was measured by dissolving a known weight of solid ferroin perchlorate and measuring the absorbance at 510 mμ. The molar absorptivity was found to be 11,100, which is essentially the value obtained in water.

From the absorbance and molar absorptivity, the concentration of the ferrous-1,10-phenanthroline ion in the organic phase can be calculated. Knowing the amount of perchlorate in the aqueous phase and assuming quantitative extraction, the amount of perchlorate in the organic phase will be known. By this reasoning the ratio of perchlorate to ferroin was found to be 2.2. This is slightly larger than the theoretical value 2.0, corresponding to extraction of $\text{Fe}(1,10\text{-phenanthroline})_3(\text{ClO}_4)_2$.

Shaking Time. Although under some conditions perchlorate can be extracted with only a few seconds shaking, the presence of a buffer and of some foreign ions makes somewhat longer shaking necessary. For this reason at least 1 minute shaking is recommended for all samples.

Color Stability. The color intensity of extracted ferroin perchlorate remains constant for several hours, but fades slightly on standing overnight.

Beers Law Plot. Using sodium perchlorate standards and acetate buffer, extractions with n-butyronitrile and measurements of absorbance at 510 m μ resulted in a linear Beer's law plot over the range 0.0001M to 0.002M perchlorate (in the original aqueous solution). A molar absorptivity of 4420 for perchlorate was obtained using pH 6 and acetate buffer. Extraction from approximately neutral, unbuffered solutions gave a slightly higher molar absorptivity.

EFFECT OF FOREIGN ANIONS

The proposed analytical method for perchlorate will be of practical use only if other common anions cause no interference, at least when present in moderate concentrations. Extraction of 0.004 mmole of perchlorate in the presence of varying amounts of sulfate, shows that sulfate has almost no effect on the absorbance even when present in a molar quantity 500 times that of perchlorate (see Figure 1). Nitrate is slightly extracted either alone or when mixed with perchlorate (see Figure 2). 0.1 Mmoles of nitrate increases the absorbance of perchlorate about 0.1 absorbance unit. Nitrate in amounts less than about 0.005 mmole has a negligible effect on the extraction of perchlorate. The absorbance caused by larger quantities of nitrate can be corrected using the curve in Figure 2.

Large amounts of chloride decrease the absorbance somewhat for the extraction of perchlorate (see Figure 3). However, 0.1 mmole or less chloride has no effect on the perchlorate absorbance.

Chlorate is partially extracted under the same conditions used for the extraction of perchlorate (see Figure 4). At first it was thought that

Fig. 1. Extraction of 0.004 mmole of perchlorate in the presence of varying amounts of sulfate. Sample volume 4 ml.

Fig. 2. Extraction of nitrate. Sample volume 4 ml.

Fig. 3. Extraction of 0.004 mmole of perchlorate in the presence of varying amounts of chloride. Sample volume 4 ml.

Fig. 4. Extraction of chlorate. Sample volume 4 ml.

the chlorate salt might contain a small amount of perchlorate impurity and that the perchlorate was actually the extracted species. This was disproved by noting that a second and third extraction of aqueous sodium chlorate containing ferroin with fresh portions of n-butyronitrile gave essentially the same absorbance as obtained in the first extraction. Also a carefully purified sample of sodium chlorate gave essentially the same absorbance on extraction as the unpurified chemical reagent.

Since chlorate extracts much less than perchlorate, it is possible to determine perchlorate in samples containing moderate amounts of chlorate. A curve of the type shown in Figure 4 is used to correct for the absorbance due to the chlorate. Of course this requires a knowledge of the approximate amount of chlorate present.

The effect of other foreign anions were studied in less detail. In Table I the qualitative effect of various anions is given. In each case an approximately neutral solution containing ferrous-1,10-phenanthroline sulfate and the anion in question was extracted with n-butyronitrile.

Table I. Effect of Miscellaneous Anions

<u>Anion</u>	<u>Degree of extraction</u>
Acetate	negative
Arsenate	negative
Borate	negative
Bromide	some extraction
Carbonate	negative
Chromate	negative

Cyanide	organic layer turns purple
Ferricyanide	negative
Fluoride	negative
Iodate	negative
Nitrite	extracts
Oxalate	negative
Periodate	strong extraction
Persulfate	reaction with ferroin, slight extraction
Phosphate	slight extraction
Sulfide	black precipitate forms which extracts
Sulfite	slight extraction
Tartrate	slight extraction
Thiocyanate	fine precipitate in aqueous layer; very strong extraction

RESULTS

The analysis of sodium perchlorate-sodium chlorate mixtures is reported in Table II. Corrections for the extraction of chlorate were obtained from Figure 4 and applied. No buffer was used in these determinations. The analysis of samples containing 0.01 mmole or less of chlorate gave good results. A sample containing 0.1 mmole of chlorate was in error because of the large correction.

Results for the determination of perchlorate in other samples of varying composition are given in Table III. A sodium acetate-acetic acid buffer was used and the pH was adjusted to 6.0 before extraction.

Good results were obtained for samples containing varying amounts of foreign anions and for samples that were originally acidic or basic.

Table II. Determination of Perchlorate in Chlorate-
Perchlorate Mixtures

ClO_3^- taken μ moles	ClO_4^- taken μ moles	Absorbance	Correction	Corrected absorbance	ClO_4^- found μ moles	Diff. μ moles
0.0	4.0	0.408	none	0.408	4.0	0.0
1.0	10.0	1.020	-0.002	1.018	10.0	0.0
50.0	10.0	1.050	-0.100	0.950	9.5	-0.5
10.0	8.0	0.820	-0.025	0.795	7.9	-0.1
10.0	8.0	0.818	-0.025	0.793	7.9	-0.1
100.0	3.0	0.439	-0.170	0.269	2.7	-0.3

Table III. Determination of Perchlorate in Samples. Conditions:

Sample Volume 2 ml.; 1 ml. of Ferroin, 3 ml. of

Acetate Buffer and 4 ml. of n-Butyronitile

Added to Sample

ClO_4^- taken μ moles	Other ion taken μ moles	Corrected absorbance	ClO_4^- found μ moles	Diff. μ moles
5.0(HClO_4)	none	0.452	5.0	0.0
5.0(HClO_4)	500(H_2SO_4)	0.450	5.0	0.0
5.0(HClO_4)	100(HCl)	0.453	5.0	0.0
3.0(HClO_4)	500(H_2SO_4)	0.272	2.85	-0.15
3.0(HClO_4)	100(NaOH)	0.276	2.9	-0.1
7.0(HClO_4)	500(H_2SO_4)	0.616	6.9	-0.1
7.0(HClO_4)	100(NaOH)	0.625	7.0	0.0

LITERATURE CITED

- (1) Burns, E. A., Muraca, R. F., ANAL. CHEM. 32, 1316 (1960).
- (2) Johannesson, J. K., Ibid. 34, 1111 (1962).
- (3) Margerum, D. W., Banks, C. V., Ibid. 26, 200 (1954).
- (4) Nabar, G. M., Ramachandran, C. R., Ibid. 31, 263 (1959).

FIGURE CAPTIONS

Figure 1. Extraction of 0.004 mmole of perchlorate in the presence of varying amounts of sulfate. Sample volume 4 ml.

Figure 2. Extraction of nitrate. Sample volume 4 ml.

Figure 3. Extraction of 0.004 mmole of perchlorate in the presence of varying amounts of chloride. Sample volume 4 ml.

Figure 4. Extraction of chlorate. Sample volume 4 ml.

END