1 November 1963 RSIC-90

423962

EXTRACTION-PHOTOMETRIC DETERMINATION OF PERCHLORATES IN THE PRESENCE OF CHLORATES

By

V. A. Golosnitskaya and V. I. Petrashen

Translated From
Zhurnal Analiticheskoi Khimii,
17, No. 7, 878 - 881 (1962)

Redstone Scientific Information Center

U S ARMY MISSILE COMMAND
REDSTONE ARSENAL, ALABAMA

Destroy; do not return.

DDC Availability Notice: Qualified requestors may obtain copies of this report directly from DDC.

Publicly available from: Office of Technical Services, Department of Commerce, Washington 25, D. C.

1 November 1963 RSIC-90

EXTRACTION-PHOTOMETRIC DETERMINATION OF PERCHLORATES IN THE PRESENCE OF CHLORATES

By

V. A. Golosnitskaya and V. I. Petrashen

Translated From
Zhurnal Analiticheskoi Khimii,
17, No. 7, 878 - 881 (1962)

Translated from the Russian by
Ingeborg V. Baker

Translation Branch
Redstone Scientific Information Center
Directorate of Research and Development
U. S. Army Missile Command
Redstone Arsenal, Alabama

EXTRACTION-PHOTOMETRIC DETERMINATION OF PERCHLORATES IN THE PRESENCE OF CHLORATES

By

V. A. Golosnitskaya and V. I. Petrashen

During the quantitative determination of oxygen compounds of chlorine, particular difficulties are encountered in determination of perchlorates in the presence of chlorates. All known methods of determining perchlorates may be subdivided into three basic groups: Gravimetric methods. These are based on precipitation of perchlorates either by several organic reagents (methylene blue, tetraphenylarsonium chloride, nitron /1-3/), or by potassium acetate from an alcoholic solution in the form of $KClO_4$ /4/. Volumetric methods. In some variations of these methods ClO_4^- ions are reduced to Cl^- by salts of trivalent titanium or bivalent tin /5-8/, and the excess is then titrated back by various oxidizers. In other variations, ions ClO_4^- are also reduced to Cl^- by amalgam of zinc, trivalent titanium and others /8, 9/, or by fusion with various reducers /10-12/, after which the chlorides formed are determined by an argentometer. Photometric methods. These consist either of precipitation of ions ClO_4^- by an excess of colored reagents /13, 14, 16/, or by formation with various colored reagents of colorless perchlorate complexes (for example, with tetrapyridine of copper having an intense blue tint) /15/. In both instances the optical denisty of partically decolorized solutions of dyes, is measured.

For experimental verification of the various methods of determining

ClO_4^- we have selected, in our opinion, more perspective ways, namely:

1. Haight's /8/ volumetric method. When determining perchlorates only, this method gave satisfactory results; but with the combined presence of ClO_4^- and ClO_3^- ions, generation of gaseous chlorine occurred, leading to considerable losses of chlorides. Determination errors ran 10-12%. We have attempted to initially decompose chlorates by means of various reducers (SO_2, Fe^{2+}, hydrazine and others) but have not obtained satisfactory results.

2. A colorimetric method with methylene blue /16/. During the verification of this method, the determination showed that it suffered from two major deficiencies: (a) it was extremely sensitive, even to small fluctuations of temperature (a fluctation of 2-3° led to an error of 8-10%), and (b) it was too prolonged (4 hours were required for one determination).

3. A colorimetric method with copper tetrapyridine /15/. Upon verification of this method, the following deficiencies were disclosed: (a) unsuitability of this method in the presence of ClO_3^- ions; (b) the method was extremely prolonged (up to 40 hours are required for one determination).

Based on experimental verification of the indicated method, we have concluded that the known methods did not give sufficient speed and accuracy for determining perchlorates in the presence of chlorates. Thus, our investigations have been directed toward developing new methods. Extraction-photometric methods attracted our attention.

Proceeding from the theoretical conditions introduced and developed by Kuznetsov /17-19/, we worked out a method of determining perchlorates in the presence of chlorates based on the formation, determined by ions with chromatic reagents, of large dyed hydrophobic molecules, which are easily extracted by organic solvents.

Experimental Section

Twelve organic reagents representing basic dyes, having large colored cations such as green malachite, crystal violet, methyl violet, butyl rhodamine, brilliant green, and others were selected for investigation.

Also investigated were 9 extractives representing organic solvents immiscible with water, such as benzene and its homologs (toluene and xylene), chloroform, dichlorethane, tetrachloride of carbon and others.

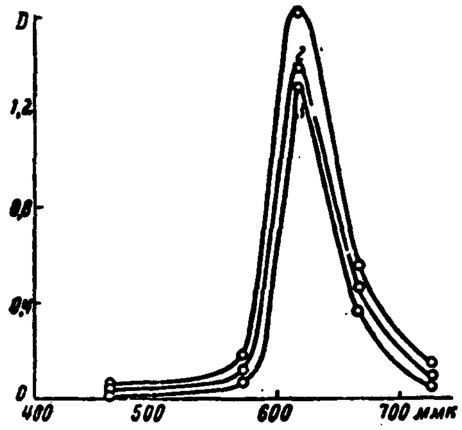

Figure 1. Light absorption curve of the extractives:
1 — Benzene; 2 — toluene; 3 — m-xylene.
Phase photometer FM.

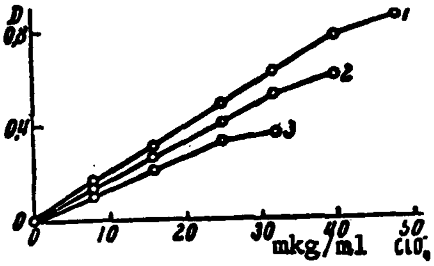

Figure 2. Dependence of optical density on the concentration of ClO_4^- ions:
1 — in benzene extract; 2 — in toluene extract;
3 — in m-xylene extract.

The work methods consisted of the following:

a. Studies were made on the reaction of the extractives with each dye for determining whether or not the dye extracts itself.

b. Reactions of each dye with ClO_4^- ions, and the relationship of the obtained compounds with the extractives were studied.

c. Reactions of each dye with ClO_3^- ions and the relationship of the obtained compounds with the extractives were studied.

Evaluation of the preliminary test results was done visually.

Two dyes were selected: (a) Brilliant green, which produced a colored compound with ClO_4^- ions extractable by benzene, toluene and metaxylene, but which did not produce an extractable compound with ClO_3^- ions; (b) Maladrite green, which produced a colored compound with ClO_4^- ions, was noticeably extractable by benzene and considerably less by toluene and m-xylene, but which did not produce an identical compound with ClO_3^- ions.

Since the maximum optical density was valid in the case of brilliant green, all further work was performed with this dye only, and benzene, toluene and m-xylene served as the extractives.

Benzene, toluene and m-xylene extracts have a maximum light absorption capability at a wave length of approximately 619 millimicrons (Fig. 1). A red light filter was used effectively.

During the selection of optimum conditions and clarification on the employment of extractives for determining ClO_4^- ions, the value of the optical density of the extractives served as the criterion.

The following was established:

The optical density of toluene and m-xylene extracts in a compound of perchlorate and dye remained constant for a period of 3 hours, and that of benzene, for over 6 hours.

When benzene was used as an extractive for the purpose of maintaining a constant value of optical density, it was necessary to use a 15 multiple molar excess of the dye; and for toluene and m-xylene, a 20 multiple excess of quantity in relation to ClO_4^- ions. By further increasing the quantity of dye, the value of the optical density remained constant.

The optical density of the extractives remained unchanged within the limits pH of the water phase from 7 to 4.5; and with a further increase of acidity, a decrease in the optical density was observed.

The extractives conformed to the law of Lambert-Beer, for benzene with 0-40 mkg/ml ClO_4, for toluene with 0-32 mkg/ml ClO_4, and for m-xylene with 0-21 mkg/ml ClO_4 (Fig. 2). With higher concentrations of ClO_4^- ions the proportionality was disrupted.

Dependence of the optical density of the solution on the concentration of ClO_4^- was studied under the following optimum conditions: (a) relationship of the organic and the water phase 1:1; (b) a 20 multiple excess of the dye (in moles); (c) a medium of the water phase pH in an interval of 6.8 to 7.0; (d) the length of the drain 1 mm; (e) optical density measured with a red light filter.

The dependence of the optical density on the concentration of ClO_4^- ions in the presence of ClO_3^- ions is shown in Figures 3, 4 and 5.

As shown by these figures, for benzene the concentration ratio $[ClO_3^-]:[ClO_4^-]$ did not exceed 1 : 1, and the optical density remained

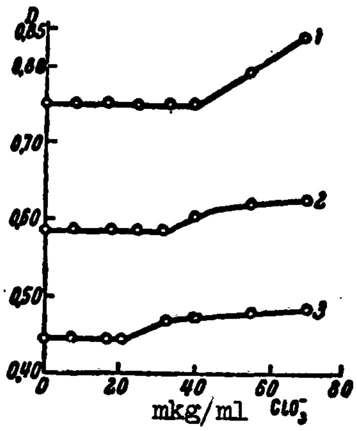

Figure 3. Dependence of the optical density on the concentration of ClO_4^- ions in the presence of ClO_3 in a benzene extract.
Perchlorate concentration:
1 — 40 mkg/ml; 2 — 32 mkg/ml; 3 — 21 mkg/ml

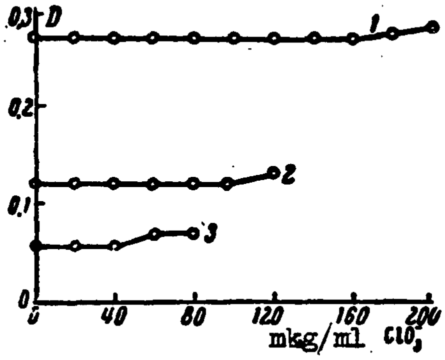

Figure 4. Dependence of the optical density on the concentration of ClO_4^- ions in the presence of ClO_3 ions, in a toluene extract.
Perchlorate concentration:
1 — 16 mkg/ml; 2 — 5.3 mkg/ml; 3 — 2.6 mkg/ml

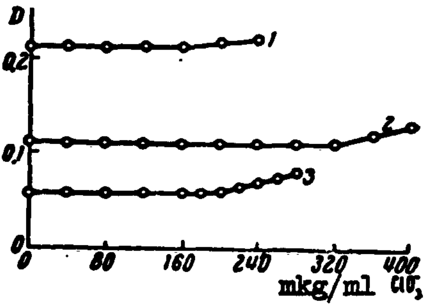

Figure 5. Dependence of the optical density on the concentration of ClO_4^- ions in the presence of ClO_3^- ions in an m-xylene extract.
Perchlorate concentration:
1 — 16 mkg/ml; 2 — 5.3 mkg/ml; 3 — 2.6 mkg/ml

constant; for toluene this ratio was 10:1.

For m-xylene the acceptable ratio of $[ClO_3^-]$: $[ClO_4^-]$ concentration varied, depending on the concentration of perchlorates. By decreasing the concentration of perchlorates from 16 to 1.8 mkg/ml, the ratio increased from 12:1 to 100:1.

Strong oxidizers (including hypochlorites) decolorized the dye and interfered in determining perchlorates. Thus, hypochlorites had to be preliminarily decomposed. Chlorides in the absence of chlorites, even in a 10,000 multiple proportion of their quantity, did not interfere in determining perchlorates when benzene was used; in a 100 multiple proportion when toluene was used, and in a 10 multiple proportion when m-xylene was used.

Chlorides in the presence of a permissible quantity of chlorates did not influence the value of the optical density of the benzene extract up to a 150 multiple, of toluene up to an 18 multiple, and of m-xylene up to a 10 multiple proportion of each of their quantities (in moles).

Cations Li^+, K^+, NH_4^+, Mg^{2+}, Ba^{2+} did not interfere with the determination. The maximum permissible content of anions is shown in the table below.

Solvent	$[ClO_4^-]:[Cr_2O_7^{2-}]$	$[ClO_4^-]:[CrO_4^{2-}]$	$[ClO_4^-]:[NO_3^-]$	$[ClO_4^-]:[NO_2^-]$	$[ClO_4^-]:[F^-]$
Benzene	1:1	1:4	1:4	1:6	1:600
Toluene	1:5	1:20	1:12	1:60	1:1000
m-Xylene	1:2	1:60	1:3	1:100	1:2500

The positive side of using benzene is the possibility of determining perchlorates in a much broader diapason of concentrations (up to 40 mkg/ml); however, the permissible ratio $[ClO_3^-]$: $[ClO_4^-]$ must not exceed 1:1, in this case. Toluene and m-xylene, however, increase this ratio of concentration to 10:1 and 100:1 respectively; but the extracts conform to the Lambert-Beer law in a narrower interval of perchlorate concentrations (to 32 mkg/ml for toluene and 21 mkg/ml for m-xylene).

Summarizing the above, we consider it practicable to recommend the developed method for determining perchlorates using all three extractives, depending on the content of ClO_3^- and ClO_4^- ions in the analyzed objects.

The determination error comprises 0.06/ - 0.1 mkg/ml.

15 - 20 minutes are required to make one determination of perchlorates (with the presence of a calibration graph).

Findings

A new, rapid extraction-photometric method of determining perchlorates in the presence of chlorates, by using a brilliant green, and the extractives benzene, toluene and m-xylene, has been developed.

The influence of ions ClO_3^-, ClO^-, Cl^-, Li^+, K^+, NH_4^+, Mg^{2+}, Ba^{2+}, $Cr_2O_7^{2-}$, CrO_4^{2-}, NO_3^-, NO_2^-, F^- was studied.

The method permits the possibility of determining perchlorates in the presence of chlorates up to a 100 multiple proportion of their quantity, depending on the type of extractive used. Determination error comprises 0.06 - 0.15 mkg/ml.

Literature

/1/ Maurina, F. A., Deahl, N. I., J. Amer. Pharm. Assoc. 32, 301 (1943).

/2/ Smith, G. M., Willard, H., Ind. Engng. Chem. Anal. Ed II, 186 (1939).

/3/ Fedorova, O. S., ZhRFKhO (Zhurnal Russkogo Fiziko-Khimicheskogo Obschestva) 59, 206 (1927).

/4/ Arndt, F., Nachtwey, Ber. Deutsch. Chem.Ges. 59, 446 (1926).

/5/ Vilyamovich, E. T., Zavodskaya Laboratoriya 9, 1330 (1940).

/6/ Eagles D., Chem. and Ind. N 33, 1002 (1954).

/7/ Rothmund, V., Z. Anorgan. Chem. 62, 108 (1909).

/8/ Haight, G. P., Analyt. Chem. 25, 642 (1953).

/9/ Zagorcki, L., Krawcryk W., Chem. Analit. 3, 505 (1958).

/10/ Crump, N. L., Johnson N. C., Analyt. Chem. 27, 1007 (1955).

/11/ Kurz, E., Kober, G., Berl, M., Analyt. Chem. 30, 1983 (1958).

/12/ Biber, V., Barskaya, F., Zhurnal Prikladnoi Khimii 10, 740 (1937).

/13/ Fedorova, O. S., ZhRFKhO 59, 509 (1927).

/14/ Monnier, A., Chem. Zbl. 1, 816 (1917); Ann. Chim. Analyt. Annl. 20, 237 (1916); 22, 1 (1917).

/15/ Bodencheimer, W., Welcher, H., Analyt. Chem. 27, 1293 (1955).

/16/ Nabar, G. M., Ramachandran, L. R., Analyt. Chem. 31, 269 (1959).

/17/ Kuznetsov, V. I., Uspekhi Khimii 23, 654 (1954).

/18/ Kuznetsov, V. I., Zhurnal Analiticheskoi Khimii 6, 139 (1951).

/19/ Kuznetsov, V. I., Methods of Analysis of Metal and Alloys, Sbornik, Materialy Nauchno-Tekhnicheskogo Sovyeshchaniya, VIAM 2, ONTI, Moscow (1961).

Submitted to Editor
3 October 1961