THE DETECTION OF OXY-HALOGEN ANIONS

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Analytical chemists have been slow in developing the chemistry of the anions. Most of the research in this field has come in response to pressure from the industries. One group of anions that has been notably neglected is the oxy-halogen group. These anions have been known for a long time, but, with the exception of chlorate and hypochlorite, little attention has been given to their systematic detection. Ordinary textbooks do not treat them at all, and advanced manuals refer to them in a very sketchy way.

I. The Detection of Perchlorates in the Presence of Chlorides and Chlorates.[1]—Perchloric acid has now become a very important analytical reagent, and a considerable interest in the properties of its salts has developed. The perchlorate ion forms no salts of sufficient insolubility for use in its separation. Neither does it show any specific property that may be used for its identification. Its detection depends upon its conversion into the chloride ion, which is detected as silver chloride in the usual way. Various reducing agents have been proposed for this purpose; for example, zinc, titanous salts, hyposulfites, etc. The tests have been repeated in the laboratories at the University of Illinois, and have been found unreliable and worthless.

Apparently the most satisfactory method for converting perchlorate into chloride is ignition in an alkaline medium. Ordinarily, this requires full red heat,—about 600°C. It occurred to us that this decomposition might be effected more easily by catalytic means. This procedure as developed is outlined in Table I. The solution is mixed with a drop or so of manganous nitrate, alkalyzed by potassium carbonate and evaporated to dryness in a casserole. Upon gentle ignition to 250°-300°, the residue darkens owing to the formation of manganese dioxide. At the same time the perchlorate is broken down into sodium chloride and free oxygen. After cooling, the residue is extracted with dilute ammonium hydroxide, and the test for chloride is made in the regular way. The test is very sensitive: 0.001 mg. in 0.1 cc. gives a distinct opalescence. Care must be taken that the manganous nitrate and potassium carbonate are chloride-free.

It remains to be shown whether or not the method has quantitative possibilities. The chloride determination was made both volumetrically and gravimetrically on the reduced perchlorate and it was found that the average ratio of moles of perchlorate to chloride was 1.0-0.98. This does point to the fact that this method presents a quantitative procedure. This scheme of ignition with manganous nitrate may have other advantages; for example, thiocyanates may be destroyed, and their interference with the test for chloride thereby obviated.

Since the above results for the reduction of the perchlorate were so favorable, the detection of the perchlorate in the presence of chlorates and halides was

TABLE I.—DETECTION OF Cl^-, ClO_3^-, AND ClO_4^- IN THE PRESENCE OF EACH OTHER

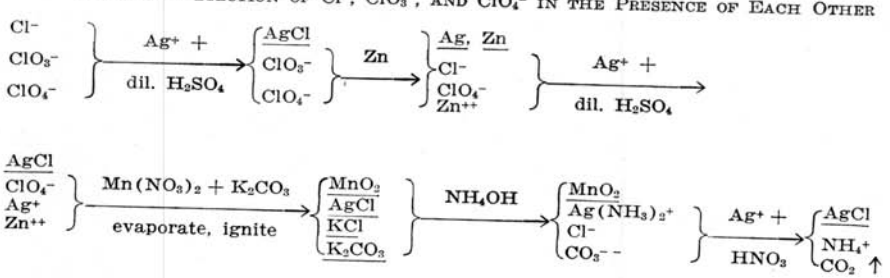

TABLE II.—ANALYSIS OF A SOLUTION CONTAINING IO_3^-, BrO_3^-, ClO_3^-, I^-, Br^- AND Cl^-

To 5 cc. of the solution add equal volumes of conc. $Ba(C_2H_3O_2)_2$ and alcohol. Cool in an ice bath, filter and wash precipitate with ice-cold 50% alcohol.

Precipitate: $Ba(IO_3)_2$, $Ba(BrO_3)_2$. Extract precipitate with hot water.		Filtrate:
Solution: $Ba(BrO_3)_2$. Test for BrO_3^- by (A) or (B). (A) Add Zn, HCl and CCl_4, and shake well. Amber color in CCl_4 indicates BrO_3^-. (B) Add H_3PO_4 and $Mn(NO_3)_2$. A violet color indicates BrO_3^-.	Residue: $Ba(IO_3)_2$. Dissolve in warm dilute HNO_3. Test for IO_3^- by (C) or (D). (C) Add Zn, HCl and CCl_4 and shake. Violet color in CCl_4 indicates IO_3^-. (D) Add H_3PO_4 and starch solution. Cover with a layer of $Na_2S_2O_3$. Blue ring indicates IO_3^-.[3]	$Ba(ClO_3)_2$, BaI_2, $BaBr_2$, $BaCl_2$. Proceed to Table III.

TABLE III.—ANALYSIS OF FILTRATE CONTAINING ClO_3^-, I^-, Br^- AND Cl^-

Evaporate alcohol, add water, $AgNO_3$ and a few drops of dilute HNO_3. Wash precipitate with very dilute HNO_3.

Precipitate: AgI, AgBr, AgCl.	Filtrate: ClO_3^-, Ba^{++}.
Transfer to beaker, add Zn and dilute H_2SO_4.	Remove Ba^{++} with Na_2SO_4. Filter and reduce ClO_3^- to Cl^- with Zn + dilute H_2SO_4. Test for Cl^- by $AgNO_3$ in regular way.
Filter and test filtrate for I^-, Br^-, and Cl^- in usual way.	

TABLE IV.—ELIMINATION OF CERTAIN HALATE AND HALIDE COMBINATIONS

Reagent	Product	Inferences	
		Present	Absent
Dil. H_2SO_4	None		ClO_3^-, or any halate-halide mixture
	Cl_2	ClO_3^-, or a Cl^--halate mixture	I^- (or Br^-)-halate mixture
	Br_2	Br^--halate, or Cl^--BrO_3^--1 mixture	I^--halate mixture
	I_2	I^--halate mixture	
$HC_2H_3O_2$	None		
	Br_2	Br^--halate, or Cl^--BrO_3^- mixture	Br^--halate mixtures
	I_2	I^--halate, or halide-IO_3^- mixture	I^--halate mixtures

not difficult, as shown in Table I. The choride is first removed as silver chloride. Then the chlorate is reduced with zinc and sulfuric acid to the chloride and precipitated and removed as silver chloride.

II. The Separation and Detection of the Members of the Halate-Halide Mixture.[2]—Another problem in the field of the oxy-halogen anions is the detection of chlorate, bromate and iodate in the presence of each other and in the presence of halide ions. We will hereafter refer to chlorate, bromate and iodate as the halate ions.

This problem involves one very positive limitation, namely: A mixture of halates and halides must not be acidified. Upon acidification, the system undergoes oxidation-reduction, with the destruction of the original components and the formation of free halogens. This limitation applies both to the composition of the unknown and the analytical procedure.

As a preliminary approach to the problem, a study was made of the solubilities of the metallic salts of these anions in water, alcohol and acetone. It was hoped that this study might reveal a way for separating the halide group from the halates. For example, it was hoped that some cation of the silver group might precipitate the halides, leaving the halates in solution. The search was unsuccessful. Every cation that precipitated Cl^-, Br^-, and I^- with anything like analytical completeness also gave insolu-

ble salts with certain of the halates, particularly iodate and bromate. The most promising separation was found in the precipitation of IO_3^-, and BrO_3^- as their Ba^{++} salts, using cold 50 per cent alcohol as the solvent. The halide ions could then be separated from chlorate as their silver salts and the halide mixture analyzed in the regular way. The procedure as finally worked out is shown in tables II and III.

Preliminary Procedures for the Detection of Halates and Halides in a Mixture

Several schemes, preliminary in nature, have been devised to indicate the presence or absence of the various halates and halides before beginning the general procedure. If the absence of one or more of these ions is shown, certain steps may be omitted, thereby saving time.

As indicated in Table IV, the principal reagents used are dilute sulfuric and acetic acids. The reaction products are Cl_2, Br_2 and I_2, which may be recognized by their reactions with carbon tetrachloride.

The limit of identification of the iodate and bromate ions by this procedure is as follows: iodate ion 0.2 mg. per cc, bromate 0.5 mg. per cc. The sensitiveness of these tests is not high, and the procedure is admitted not to be quantitative. On the other hand, the work seems valuable in an exploratory way, opening up an approach to what may some day be an important problem.

Bibliography

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