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THE DETERMINATION OF CHLORINE AND IONIC CHLORIDE IN ORGANIC COMPOUNDS

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FOREWORD

This report was prepared by the University of Cincinnati under USAF Contract No. AF 33(657)-10944. The contract was initiated under Project No. 7360, "The Chemistry and Physics of Materials," Task No. 736005, Composition, Atomic and Molecular Analysis". The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command. Mr. F. F. Bentley was the project engineer.

This report covers the work carried out from June 1964 to August 1964.

The work was performed at the Analytical Branch, Physics Laboratory by Mr. T. M. Downer, Jr.

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ABSTRACT

A rapid method for the determination of chlorine is described. The method is applicable to the chloride ion formed following an oxygen flask combustion procedure or for soluble ionic hydrochlorides. The percentage of chloride is determined by titrating the chloride ion with silver nitrate using an adsorption indicator, 2',7'-dichlorofluorescein to detect the endpoint. Compounds containing carbon, hydrogen, nitrogen, chlorine and sulfur were successfully analyzed.

This report has been reviewed and is approved.

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INTRODUCTION

The determination of chlorine in organic compounds can be performed in many ways once the chlorine has been converted to some suitable ionic form. The method used in this laboratory is the Schoniger oxygen flask method where the chlorine is quantitatively converted to the chloride ion by combustion in an oxygen filled flask. The chloride ion formed is determined potentiometrically using silver nitrate as the titrant and a salt bridge-calomel electrode as the reference electrode and a silver electrode as the indicating electrode. Using a manually operated instrument, the potentiometric titration takes longer to perform than the method proposed in this report. The proposed method can be performed in five minutes or less once the chlorine has been converted to the chloride form. A simple titration with silver nitrate using an organic dye as the indicator is all that is required. In the procedure to be described, 2',7'-dichlorofluorescein is the organic dye that functions as an adsorption indicator in the titration of chloride ion with silver nitrate. The titrations are conducted in an acetone-water media where the solubility of the silver chloride is reduced relative to that in water alone. The theory and applications of adsorption indicators can be found in several textbooks (2, 3, 4). Dichlorofluorescein functions well as an indicator in slightly acid, neutral or basic media being more acid than fluorescein itself. Ingram (1) reports using the dye with a saturated solution of sodium acetate buffer. In this procedure, we proposed the use of an inorganic basic buffer such as magnesium carbonate (basic) or calcium carbonate.

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MATERIALS AND METHODS

Reagents

Silver Nitrate — Reagent grade — 0.01N solution

Potassium Chloride Stock Solution — 0.01M solution

Calcium Carbonate — Reagent grade - Low in chloride content

Magnesium Carbonate Basic — Reagent grade - Low in chloride content

Sodium Acetate — Reagent grade·crystal — Saturated solution

Acetone-water mixture 90:10 (v/v) Acetone c.p. and deionized water

2',7'-dichlorofluorescein indicator solution - 0.01 grams dissolved in 100 ml ethanol with 2.5 ml of 0.01N sodium hydroxide.

Apparatus

Micro-titration assembly composed of the following:

(1) 5 ml burette graduated in 0.01 ml intervals

(2) magnetic stirrer

(3) 100 ml beakers and teflon stirring bars

Schoniger combustion apparatus

500 ml Schoniger oxygen flasks

Selection of Sample Size

In the determination of the chlorine content of an organic compound containing chloride ions, the selection of the sample size is made so as to minimize in so far as possible, the various errors that are involved in the determination. In this procedure, in order to produce a sharp color change at the endpoint, there must be at least 0.60 - 0.80 mg of chloride ions present, otherwise an excess of silver nitrate must be added to see the sharp change. The major aim is to adjust the volume of the titrant consumed in the titration of the chloride ions so that it is relatively large compared with the errors associated with the endpoint determination and burette reading. If the volume of titrant consumed is 4.50 ml, then an error of 0.05 ml in the endpoint evaluation and burette reading leads to an error of approximately 1% in the per cent chloride present. An error of 0.050 ml is regarded as considerably greater than one should encounter in endpoint evaluation or burette reading. Consider the following equation:

$$(1)\quad \%\ \text{Chloride} = \frac{N_s V_s}{} \times \frac{35.457}{\text{wt. sample (grams)}} \times 100$$

Where N_s = Normality of the silver nitrate solution

V_s = Volume of silver nitrate consumed

35.457 = Atomic Weight of Chlorine

Substitute the following values in equation (1): $N_s = 0.01$, $V_s = 4.50$ ml and solve for sample weight

$$(2)\quad \text{Weight of Sample (grams)} = \frac{.160}{\%\ \text{Chloride}}$$

or

$$(3)\quad \text{Weight of Sample (milligrams)} = \frac{160}{\%\ \text{Chloride}}$$

Equation (3) provides a very simple and precise means for selection of the sample size provided some idea of the magnitude of the chloride content is available. In some cases, due to insufficiency of sample, it is not possible to select the size of the sample by the above considerations. In such cases, it is strongly advised to utilize as large a sample as can be obtained, short of the above criterion. In cases where it is not possible to have at least 1 mg of chloride ion present, one should add a known volume of standard chloride solution to the unknown and subtract the amount of titrant necessary to titrate this standard from the final volume of silver nitrate used in the titration.

Procedure

A. Organically bound chlorine or insoluble ionic chloride samples.

Weigh out the appropriate sample size yielding 1 - 1.6 milligrams chloride ion. Transfer to a standard size Schöniger ashless filter paper flag. Liquid samples are weighed in a sealed capillary and transferred to the flag, rolled and crushed just before combustion. The sample is combusted in a 500 ml oxygen filled Schöniger flask containing 5 ml deionized distilled water. Allow the contents of the flask to condense out, transfer to a 100 ml beaker with 90:10 acetone-water (v/v) to total volume of 40 ml. Proceed with Step C.

B. Ionic chloride samples which are soluble in 90:10 (v/v) acetone-water.

Weigh out appropriate sample size and transfer to a 100 ml beaker. Liquid samples are weighed in a sealed glass capillary and crushed with a glass rod in a 100 ml beaker. Add 4 ml deionized water and 36 ml of acetone. Should the sample become cloudy from high solvent content, add a few ml of deionized water until solution becomes clear again. Proceed with Step C.

C. To the solution containing the chloride ions add:

1. Enough inorganic buffer (magnesium carbonate or calcium carbonate) to provide an intense white background when the solution is stirred rapidly.

2. 5 drops of indicator solution 0.1% 2',7'-dichlorofluorescein

Titrate to a pink endpoint immediately with 0.01 N silver nitrate with rapid stirring. Near the endpoint the formation of the pink color precipitate which remains for a few seconds is an indication to add the titrant more slowly. Fractions of a drop may be added by tipping the burette to the side of the beaker and rinsing with a few drops of 90:10 (v/v) acetone-water. With additions of a fraction of a drop, the endpoint is quite sharp. Calculate the per cent chlorine content from Equation (4) where N_s, V_s and 35.457 are the same as in Equation (1).

$$(4)\quad \%\ \mathrm{Cl} = \frac{N_s \quad V_s \quad \times \quad 35.457}{\text{Sample wt. (milligrams)}} \times 100$$

DISCUSSION

In the determination of chloride ion using the adsorption indicator method as reported by Ingram (1), the use of sodium acetate as a buffer works quite well for certain compounds as shown in Table 1 and Table 2. However, sometimes the endpoints were not so sharp or could not be distinguished at all in case of the Lysine-HCl and L-Arginine-HCl unless the samples were previously combusted. With the inorganic buffers, the endpoints were quite sharp and reproducible. In all cases, as shown in Table 1, a blank value of 0.030 ml had to be subtracted from the volume of silver nitrate used when 1 ml of standard KCl was used (0.592 mg Cl^-) to give the theoretical chloride ion content. The only explanation is that these solutions had to be over-titrated to produce the sharp color change. A blank of 0.030 ml had to be subtracted from all of the magnesium carbonate titrations to account for the chloride ion found in the inorganic buffer. These blank values were arrived at by titrating the KCl standard with silver nitrate using a potentiometric titration procedure with a silver indicating electrode and a salt-bridge reference electrode. Results shown in Table 3 had no blank values. The first two compounds were combusted in an oxygen flask while the last three compounds were run as ionic chlorides. D-L Sarocosine-HCl gave high results. These results check with results obtained potentiometrically.

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TABLE 1

TITRATION OF STANDARD KCl USING VARIOUS BUFFER SYSTEMS

Theory % Cl = 47.55	Sodium Acetate		Magnesium Carbonate		Calcium Carbonate	
Ml KCl Solution	Ml $AgNO_3$	% Cl	Ml $AgNO_3$	% Cl	Ml $AgNO_3$	% Cl
1 ml	1.720[a]	47.81	1.710[a]	47.52	1.710[a]	47.52
	1.710[a]	47.52	1.715[a]	47.67	1.720[a]	47.81
2 ml	3.370	47.67	3.390[a]	47.52	3.370	47.67
			3.410[a]	47.81		
3 ml	5.030	47.43	5.060[a]	47.43	5.050	47.62
			5.100[a]	47.81		
4 ml	6.720	47.52	6.820[a]	48.02	6.720	47.52
			6.810[a]	47.95		
5 ml	8.370	47.36	8.420[a]	47.47	8.420	47.64
	Average %	47.55	Average %	47.69	Average %	47.63

[a] A blank value of 0.030 ml was subtracted from these runs. The explanation can be made that on samples of 1 ml of standard KCl an excess of silver nitrage (1 drop) must be present to produce a sharp color change. All samples buffered with magnesium carbonate were high by 0.030 ml of titrant. This can be explained by the fact that the magnesium carbonate contained a small amount of chloride ion.

TABLE 2

% Chloride Found Using Sodium Acetate as Buffer

Compound	Theory % Cl	Found % Cl	Deviation
p-nitrobenzenesulfonylchloride	16.00	15.96	+0.04
		15.89	-0.11
		16.06	+0.06
		16.00	0.00
		16.10	+0.10
2',7-dichlorofluorescein	17.69	17.63	-0.06
		17.70	+0.01
		17.63	-0.06
Lysine-HCl*	19.41	19.63	+0.22
		19.59	-0.18
		19.48	+0.07
L-Arginine-HCl*	16.83	16.89	+0.06
		16.70	-0.13

* These compounds did not produce a good color change when run as an ionic chloride. These results are after combustion in a Schöniger flask.

TABLE 3

% Chloride Found Using Calcium Carbonate as Buffer

Compound	Theory % Cl	Found % Cl	Deviation	
p-nitrobenzenesulfonylchloride	16.00	15.93	-0.07	
		15.75	-0.25	
2',7'-dichlorofluorescein	17.69	17.66	-0.03	
		17.96	+0.27	
L-Arginine-HCl	16.83	16.71	-0.12	
		16.77	-0.06	
		16.70	-0.13	
		16.72	-0.12	
DL-Sarcosine-HCl	28.24	28.66	+0.42	+0.06
Potentiometric value	28.60			
		28.67	+0.43	+0.07
		28.70	+0.46	+0.10
		28.94	+0.70	+0.34
		28.81	+0.57	+0.21
L-Lysine-HCl	19.41	19.41	0.00	
		19.35	-0.06	
		19.49	+0.08	
		19.44	+0.03	
		19.53	+0.12	

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