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**THE DETERMINATION OF CHLORINE
IN POLYURETHANE PLASTIC**

by

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ABSTRACT

Chlorine may be determined in polyurethane by gravimetric or spectrophotometric techniques. The sample is burned in a special combustion tube with two oxygen inlets, the products of combustion are absorbed in a solution containing sodium hydroxide and hydrogen peroxide, and the chlorine is measured either gravimetrically as silver chloride or spectrophotometrically using mercuric thiocyanate and ferric perchlorate. Eighteen determinations of chlorine in known solutions of sodium chloroacetate or perchloric acid gave an average recovery of 98.3% with a standard deviation of 2.8%.

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INTRODUCTION

The problem initiating this work was the necessity of determining chlorine in polyurethane in the 100 to 300 p.p.m. range. This particular material had been analyzed by a number of laboratories with very discordant results. A study of the literature showed that there was no lack of methods for determining chlorine -- the difficulty lay in finding a means of freeing it from the organic material without loss, and then proving that the results were correct.

EXPERIMENTAL

An attempt was made to analyze this material by the "Parr Bomb" sodium peroxide fusion technique followed by a gravimetric determination. Results by this method were extremely variable, and it was abandoned. Probably the difficulty resulted from the presence of cyanide from the partial decomposition of the sample. Experience with the method in this application indicated that it would be of doubtful value in any case. The sample size was severely limited, and most fusions contained a residue of unburned carbon.

The decomposition of the sample was next attempted by fusion in a platinum crucible with a mixture of carbonate and nitrate salts. Results by this technique were disappointing. Unless a very small sample was taken there was always some smoking, with attendant doubts. The modest sample size produced quantities of chlorine suitable only for a spectrophotometric measurement, and the large amounts of nitrate introduced made that impossible. The determinations were therefore made gravimetrically as silver chloride. The values obtained had poor precision, even though weighed on a semimicro balance, and this fact, added to the uncertainties of the fusion, led to the rejection of the method. Later, when a more reliable method had been found, it was possible to go over these results again and see that, in spite of the poor precision, the average amounts of chlorine found were correct.

The next attack on the problem of decomposing the sample was a straightforward combustion in a stream of oxygen, absorbing the chlorine from the combustion products. Difficulty was encountered when the plastic began to char in the combustion boat. Heavy smoke was evolved, and tarry products condensed on the cooler parts of the tube. Heating the exit end of the combustion tube did not improve matters because no oxygen was getting past the smouldering plastic in the combustion boat.

The tube was modified by adding a 6-inch long side arm about the middle of its length and inserting a packing of platinum gauze near that point. See Figure 1. The gauze was heated to red heat, and it was

1. Oxygen control valves	5. Platinum gauze
2. Pyrex glass semi-ball joints, 12/5	6. Glass delivery tube
3. Quartz combustion tube, 57 mm. x 15 mm. I.D.	7. Meker burners
4. Platinum boat	

Figure 1. Combustion Assembly for the Determination of Chlorine in Polyurethane.

found that by regulating the rate of addition of oxygen through the inlets indicated, all the smoke and tar could be burned in this second hot zone.

The advantages of the combustion method are that the product is not contaminated with other materials, as it was in the other cases, and the sample size is effectively unlimited since the boat may be refilled as many times as desired. The actual combustion is a rather delicate operation and requires constant attention to regulate the rate of heating and the flow of oxygen.

Standard samples were of course not available for checking the procedure. Because the form in which the chlorine was present was not known, two compounds were chosen for standard substances, sodium chloroacetate and perchloric acid. It was thought that the latter would indicate if the oxidized forms of chlorine were being reduced to chloride. Standard solutions were made of each material, and the sizes of the aliquots taken were adjusted to give amounts similar to the chlorine found in the samples. Perchloric acid aliquots were absorbed in filter paper in order to have some combustible material present.

For the final measurement of chlorine gravimetrically, the directions of Hillebrand et al. (1) were followed. The spectrophotometric method chosen was that of Zall, Fisher, and Garner (2).

APPARATUS AND REAGENTS

Apparatus

Balance, semimicro.

Combustion boat, platinum, 4 inches x 1/2 inch.

Combustion tube, quartz, with two oxygen inlets and packing of platinum gauze. See Figure 1.

Crucible, filtering, Monroe, 20-ml.

Spectrophotometer, Beckman, Model DU, with 1-cm. cells.

Reagents

Ferric perchlorate, 0.25M solution in water.

Hydrogen peroxide, analytical reagent, 30%.

Mercuric thiocyanate, saturated alcoholic solution.

Nitric acid, analytical reagent, concentrated.

Oxygen, cylinder gas.

Perchloric acid, analytical reagent, 70%.

Silver nitrate, analytical reagent, 5% solution in water.

Sodium chloride standard solution, 100 mg. per liter in water. Dilute as necessary for working standard solutions.

Sodium hydroxide, 2% solution in water.

RECOMMENDED PROCEDURE

Place in the combustion boat a weighed sample of sufficient size to contain 2 to 3 mg. of chlorine. Heat the platinum gauze to redness with a Meker burner and adjust the oxygen flow to a gentle stream, with most of the oxygen being introduced in the middle tubulature. Mix 10 ml. of sodium hydroxide solution and 1 ml. of hydrogen peroxide in a 25-ml.

test tube, and place it under the bubbler tip at the end of the combustion tube. Insert the loaded combustion boat to a point midway in the first half of the combustion tube, and heat it slowly and carefully. Adjust the rate of heating and the flow of oxygen so that all the combustion products are consumed in the second hot zone. When the sample has completely burned, it may be necessary to move the flame about on the tube to drive out the last of the tar. Allow the boat and tube to cool and rinse both with water. These washings, combined with the solution from the receiver tube, are boiled in contact with a piece of platinum to remove hydrogen peroxide.

For a spectrophotometric determination, make the solution to some definite volume with water and transfer a suitable aliquot to a 25-ml. volumetric flask. Neutralize with perchloric acid and add 3 ml. in excess, followed by 3 ml. of saturated alcoholic mercuric thiocyanate and 2 ml. of ferric perchlorate solution. Dilute to volume and mix thoroughly. After 10 minutes measure the absorbance against a reagent blank at 460 m μ . Prepare a calibration curve by aliquoting 50, 100, and 200 γ of chlorine into 25-ml. flasks from the standard sodium chloride solution and carrying them through the procedure.

If a gravimetric determination is desired, transfer the entire sample solution to a 250-ml. beaker, neutralize and add 0.5 ml. of concentrated nitric acid and 5 ml. of 5% silver nitrate solution. Let the precipitate digest overnight and filter on a platinum filter crucible. Wash with 1% nitric acid, dry for 1 hour at 150° C., and weigh on a semimicro balance.

RELIABILITY

The results of the analysis of known samples prepared from sodium chloroacetate and perchloric acid are shown in Table I.

Table I

RESULTS OF CHLORINE DETERMINATIONS ON SODIUM CHLOROACETATE
AND PERCHLORIC ACID

<u>No. of determi- nations</u>	<u>Chlorine taken, mg. (acetate)</u>	<u>Chlorine taken, mg. (perchlorate)</u>	<u>Method</u>	<u>Chlorine found, %</u>	<u>Standard deviation, %</u>
6	4.71		Grav.	96.5	4.8
8	4.71		Color.	95.6	1.3
4		0.951	Color.	102.8	1.9

Table II shows the results obtained on two samples of polyurethane plastic foam by each of these methods. Results are also shown for the nitrate-carbonate fusions finished gravimetrically although this technique is not as reproducible as the others.

Table II

ANALYSIS OF POLYURETHANE PLASTIC SAMPLES

<u>Sample</u>	<u>Sample wt., grams</u>	<u>No. of analyses</u>	<u>Method</u>	<u>Chlorine found, %</u>	<u>Standard deviation, %</u>
A	5	6	Grav.	0.023	0.003
B	5	6	Grav.	0.030	0.002
A	5	5	Color.	0.026	0.003
B	5	6	Color.	0.029	0.001
A	2	4	Fusion	0.027	0.003
B	2	4	Fusion	0.030	0.003

SUMMARY

The determination of 200 to 300 p.p.m. of chlorine in polyurethane plastic may be accomplished by burning the sample in a special

combustion tube in a stream of oxygen. The chlorine in the combustion gases is absorbed in alkaline peroxide and may then be determined by any of numerous established procedures. The analysis of known materials indicates that the recovery of chlorine is approximately 98% complete.

REFERENCES

- (1) Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., "Applied Inorganic Analysis," 2nd ed., pp. 731-32, John Wiley & Sons, Inc., New York, 1953.
- (2) Zall, D. M., Fisher, D., and Garner, M. Q., Anal. Chem. 28, 1665-68 (1956).