

## A Rapid Method for the Estimation of Chlorine in High Polymers

Many of the conventional fusion methods for the estimation of chlorine in polymers, e.g., Parr bomb ignition,<sup>1</sup> combustion in oxygen,<sup>2</sup> and lime fusion,<sup>3</sup> require drastic and sometimes lengthy reaction conditions for the conversion of the organic chlorine into ionic chloride. The Schoniger combustion technique<sup>4</sup> provides a rapid and convenient method for this conversion. This combustion procedure followed by an acid-base titration has been applied to the estimation of chlorine in polyvinyl chloride, polyvinylidene chloride, and Neoprene. The method consists of the catalytic oxidation of the chloride containing material over a hydrogen peroxide solution. The resulting hydrochloric acid is determined quantitatively by titration with sodium hydroxide. The total time required is about 35 minutes for liquid samples, and only 20 minutes for solids.

### Procedure

A commercial adaptation of the Schoniger flask (obtained from Arthur Thomas Co.) was used; this was a 500-ml. iodine flask with a platinum grid sample holder attached to a glass rod fused to the stopper.

### Calculation.

$$\text{Wt.-% Cl} = \frac{\text{titre} \times N_{\text{NaOH}} \times 35.5}{1000 \times \text{wt. of sample}} \times 100$$

### Results

Theoretical values were calculated from the polymer specifications, the Neoprene values represent analysis results kindly supplied by the E. I. du Pont de Nemours & Co.

### Discussion of Results

The chloride-acetate copolymers were found to contain 97 to 98% of their theoretical chlorine content. The Neoprene values were 98.5% of those reported by the manufacturer. The polyvinylidene chloride samples were found to contain 94 to 96.5% of their calculated values. These samples ranged from 17 to 73% in total chlorine content. The results average 2% low for the first two chlorine containing polymers but they are about 4% low for vinylidene chloride. The deviation from theoretical may be real and significant for some purposes. For most cases, the simplicity and economy of this procedure would justify its use.

TABLE I

Polymer	Found	% Cl, mean	Theoretical	% of theoretical Cl found
Polyvinyl chloride-acetate emulsion	16.9	16.7	16.8	97.0
Polyvinyl chloride-acetate powder	33.2	33.1	33.15	98.0
Neoprene AD	37.5	37.3	37.4	98.5
Neoprene WHV	37.3	37.3	37.3	98.5
Polyvinylidene chloride-acrylate emulsion	29.6	29.7	29.65	94
Polyvinylidene chloride pearls	70.5	70.7	70.6	96.5

### Preparation of Sample

(a) *Solids*. A sample of approximately 0.1 g. was weighed (to 0.1 mg.) into an ashless filter paper sample carrier, folded, and placed between the platinum grid.

(b) *Solutions or Latices*. A piece of filter paper approximately the same size as the grid was attached between the grid and then the whole stopper assembly weighed. The grid was dipped into the solution or latex and reweighed quickly. About 0.1 g. solid material was found to be a convenient pick-up. The stopper assembly was heated 10 minutes at 60°C. and 5 minutes at 130°C. to dry the sample, and a filter paper fuse was attached to the grid.

*Combustion*. Oxygen was bubbled into a 35% solution of hydrogen peroxide (30 ml.) in the combustion flask for 3 minutes. The paper fuse was ignited and the stopper held in the flask. When combustion was complete, the flask was shaken to absorb the hydrogen chloride and then allowed to stand for 10 minutes. The solution was then titrated against 0.1N sodium hydroxide using methyl orange as indicator. In cases where much carbonaceous matter was formed the solution was first filtered before titration.

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### References

1. T. Koide, T. Kubota, and Y. Umezawa, *J. Soc. Rubber Ind. Japan*, **24**, 295 (1951).
2. W. M. Phillips, *Plastics*, **12**, 587 (1948).
3. M. H. Swann and G. E. Esposito, *Anal. Chem.*, **26**, 1054 (1954). H. J. Schenk and H. Puell, *Kunststoffe*, **41**, 192 (1951).
4. W. Schoniger, *Mikrochimica Acta*, **1**, 123 (1955); **1-6**, 869 (1956).

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