

## MICRODETERMINATION OF CHLORINE IN CHLORO-ORGANIC COMPOUNDS

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The procedure consists in decomposing the compounds in a nickel capsule with sodium metal enclosed in a sealed glass tube at 350°C. The chloride formed is converted into hydrochloric acid through cation-exchange resin. The acid is titrated with a standard alkali. The method is applicable to solids as well as to liquids and avoids the uncertainties and difficulties associated with argentometric titrations and gravimetric finishes.

### Introduction

The determination of chlorine along with other halogens and sulphur in organic compounds has been subjected to exhaustive studies and numerous modifications. Organically bound chlorine is determined through its conversion into the chloride form. This conversion, better known as mineralisation, can be achieved by either oxidation or reduction methods.

The oxidation methods involve combustion with oxygen or alternatively decomposition with oxidising reagents.<sup>1,2</sup> The reduction methods<sup>2</sup> on the other hand consist of hydrogenation of the element or its fusion with reducing reagents, viz., sodium, potassium, magnesium and lithium. Further, sodium, sodium biphenyl and biphenyl sodium dimethoxymethane complex<sup>3</sup> in suitable solvents have been suggested for the reductive removal of chlorine.

After the chlorine has been rendered into the inorganic form its determination can be carried out by conventional methods. The mineralisation steps hitherto followed, however, require special decomposition and/or absorption apparatus. The Pregl catalytic combustion with oxygen, the Carius oxidation with hot nitric acid under pressure, and the Parr oxidation with sodium peroxide in a metal bomb are all encumbered with manipulative difficulties and restrictions. The oxygen flask method of Schoeniger<sup>4,5</sup> offers the maximum advantage, but for microwork in particular, the observance of scrupulous precautions against the introduction of chloride from the worker's fingers<sup>6</sup> or from outside is called for. Besides, the handling of volatile liquids is not as easy as that of solids in this technique.

The superiority of the sealed tube technique, in which an organic halogen compound is fused with sodium and the resultant sodium halide is

suitably determined, has been quite successfully demonstrated in the submicrodetermination of chlorine,<sup>7</sup> bromine and iodine.<sup>8</sup> This technique has now been extended to the determination of chlorine in organic compounds on the micro-scale. The method is eminently applicable to solids and liquids, particularly chlorinated petroleum fractions which are under investigation in these laboratories.

In the present studies, the sodium chloride resulting from the fusion of an organic compound with sodium was stoichiometrically converted through a cation exchange resin into hydrochloric acid. The acid on titration against centinormal alkali revealed the original chlorine content of the compound.

The use of the cationic exchange resin obviates difficulties which are encountered when chloride is determined by the usual argentometric titration or precipitation methods. Thus Musgrave et al. have determined chlorine along with other halogens on the semimicro-scale in fluorine-organic compounds through the application of cation exchange column.<sup>3,9,10</sup>

The present method is based on fusion with sodium and the application of a cation exchange resin on the micro-scale. Further, a nickel capsule is used within the sealed glass tube for affecting the fusion without exposing the glass to the corrosive action of the alkali metal.

The method is widely applicable and is free from many errors and difficulties. The oxygen flask method and the present method have been found to be comparable but the latter method has the advantage that the sample to be analysed cannot escape the sealed tube nor an outside contamination can ruin the determination. Results by this method are recorded in the table and they do not deviate more than  $\pm 0.1\%$  from the theoretical.



TABLE I.—DETERMINATION OF CHLORINE IN ORGANIC COMPOUNDS BY ION-EXCHANGE RESIN (NON-NITROGENOUS).

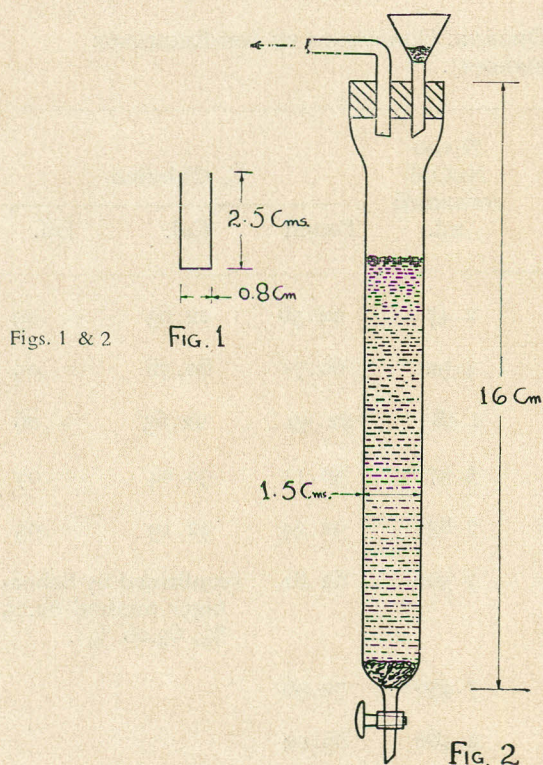
No.	Substance	Weight mg.	N/100 NaOH consumed ml.	% Chlorine		
				Found	Cal.	Dif.
1.	<i>p</i> -Chlorobenzoic acid .. ..	3.88	2.47	22.56	22.65	- .09
2.	Sodium chloride .. ..	2.871	4.92	60.71	60.76	- .05
3.	<i>o</i> -Chlorobenzoic acid .. ..	3.89	2.48	22.59	22.65	+ .06
4.	D. D. T. .. ..	3.797	5.37	50.11	50.04	+ .07
5.	Carbon tetrachloride .. ..	3.008	7.83	92.24	92.19	+ .05
6.	Compound X (Crystalline solid from chlorinated gasoline.)	4.232	7.500	62.81	(confirmed by Schoeniger method 62.75 %, 63.06 %).	
7.	Chlorinated gasoline (B) SDR .. ..	3.721	7.450	70.96		
8.	Chlorinated gasoline .. ..	2.507	4.460	63.02		
9.	Chlorinated gasoline (100-150) .. ..	2.350	4.022	60.63		
10.	Chlorinated gasoline (SDR) .. ..	2.165	4.204	68.79		
11.	Chlorinated gasoline Sp. gr. 1.52 .. ..	4.113	7.770	66.93		
12.	Pet (B) Sp. gr. 1.415 1.52 .. ..	4.426	7.859	62.90		

### Reagents and Apparatus

1. Sodium metal.—The sodium metal was purified by Burger's procedure<sup>11</sup> which may be described as follows: The metal is treated with petroleum ether (100-120°C.) by decantation to wash off the liquid paraffin or naphtha in which it is originally stored. It is then heated in a flask containing petroleum ether (100°-120°C.) and 2% amyl alcohol (a filter paper in the stopper allows ventilation). The metal melts and the outer carbonate layer peels off. The clear molten sodium settles down at the bottom of the flask. The peeled-off carbonate layers float on the surface which are removed by decantation. A fresh amount of petroleum ether and amyl alcohol is added, and sodium is again brought to molten stage. The flask is shaken so that the metal is broken into small globules. The metal is cooled and then drawn in the form of a wire.

2. Sodium hydroxide solution N/100.
3. Methyl red - methylene blue indicator.
4. Amberlite IR-120 (H.) (60 mesh) cation exchange resin.
5. Nickel Capsules.—Nickel capsules were made of pure nickel metal of the size indicated in Fig. 1
6. Fusion tubes.—Pyrex glass test tube of 11 mm. diameter and 7.0 cms long.
7. Glass column.—A column of dimension shown in Fig. 2 was used with arrangement for the filtration of the fused mass.
8. Transfer pipette.
9. Heating block.—A cross sectional view is shown in Fig. 3. The Dural block has cavities for





Figs. 1 &amp; 2

FIG. 1

FIG. 2

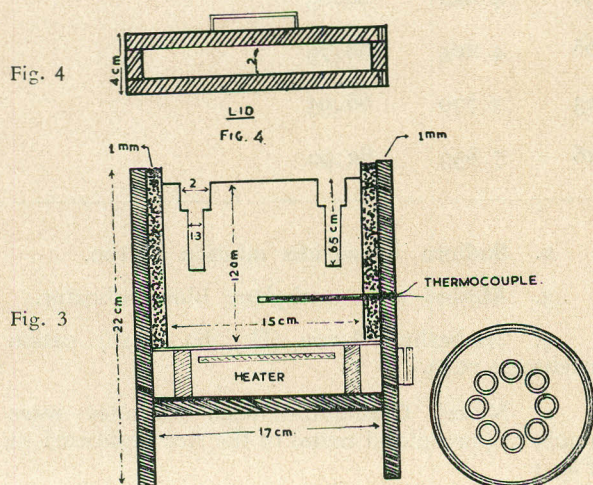


Fig. 4

FIG. 4

Fig. 3

eight fusion tubes. The cavities are made wider at the top so that it is easier to take out the tubes using a pair of forceps. The block is heated from below by 230 volts 800 watts circular element which is held in position by a disc of asbestos board. The Dural block and outer asbestos sheet are filled with asbestos wool which insures good insulation. The top of the block is covered with a lid, the cross section of which is shown in Fig. 4. The air gap between the upper and the

lower sides of the lid serves as an insulation. The thermocouple for measuring temperature is introduced through a hole on one side of the block and reaches the centre of the Dural block. The heating block is connected to the main supply through a Simmerstat control.

### Procedure

**Solid Substances.**—Two to 5 mg. of substance was weighed in a boat or weighing stick and transferred to the nickel capsule. A piece of sodium wire 3 cm. in length and 0.1 mm. dia. was cut and pressed between the folds of a filter paper. The piece was then immersed in ethanol for a few seconds and again pressed in the folds of a filter before its addition to the capsule. The nickel capsule was placed in the glass fusion tube which was then sealed at a point 2 cm. from the top. The sealed tubes were placed in the heating block and maintained at 350°C. After half an hour the tubes were taken out and placed in an asbestos tube stand.

When they had cooled down to room temperature, a scratch was made on each of them with a glass knife some 2.0 cm. from the point of sealing. They were opened by pressing a red-hot end of a glass rod to the moistened scratch. The uncombined sodium metal pieces were dislodged from their place by a slightly moist tip of the transference pipette. The metal was slowly allowed to react with small amount of water. When the whole of the sodium had reacted, 0.4 ml. of water were added and the tube was allowed to stand for 2 minutes when the whole fused mass went into solution.

In the meantime a small amount of filter pulp was placed in the filtering funnel fitted over the column and a small pad was formed which was washed 5-6 times with the distilled water.

The solution from the fusion tube was sucked in and out in the transference pipette in order to mix and dissolve the contents. The solution was finally transferred to the filter pad and in this way wash was given about six times. After each washing the filtered solution was allowed to pass through a 10 cm. long column of IR-120 H. into a 150 ml. flask. When the transference of the solution from the fusion tube had been effected completely, the filter pad was further washed with 25 ml. of water in portions of 3 ml. The amount of water required for washing the column free of the fusion solution was established by passing an equivalent quantity of sodium chloride through the column. The effluent from the column was then boiled for one minute and then titrated



against a standard solution of hydroxide using the mixed indicator.

*Blank.*—A blank determination was made in exactly the same manner without the organic compound.

*Liquid Substances.*—The liquid samples were drawn into previously weighed glass capillaries and the capillary was sealed and weighed again. Care was taken to avoid pyrolysis of the compound during sealing. The capillary tube was then sealed in the fusion tube and a piece of glass rod about 2 cm. long was also enclosed. When the fusion tube is shaken the glass rod pieces help in breaking the capillary containing the liquid. The rest of the procedure is the same as for solid samples.

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