

# Determination of chlorine in organic compounds containing mercury

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A simple method for determination of chlorine utilizing masking of the interfering mercury with ethylenediaminetetraacetic acid (EDTA) is described. The sample of organic material is ignited in an oxygen atmosphere. The products of ignition are absorbed in a solution of EDTA in hydrogen peroxide. Chlorine is determined argentometrically.

Описан простой метод определения хлора с использованием маскировки интерферирующей ртути этилендиаминететрауксусной кислотой (ЭДТА). Образец органического материала сжигают в атмосфере кислорода, продукты сжигания абсорбируют раствором ЭДТА с перекисью водорода. Хлор определяют аргентометрически как хлориды.

The standard procedure for the determination of chlorine in organic compounds of mercury consists in decomposition of the material, separation of mercury and determination of chlorine as chloride. Decomposition of the sample could be achieved by wet mineralization [1, 2], ignition in a stream of oxygen [3—7] or nitrogen [8], ignition in a flask with oxygen [9], etc. [10, 11]. Chlorine and mercury could be separated by distillation [1], electrolytic separation of mercury [2] or reduction with zinc [9, 12]. Chlorine may be separated also on dry way by absorption in sodium carbonate [3, 4], silver wool [5] or in the decomposition product of permanganate [6—8]. Chlorine is determined mostly mercurimetrically [3, 4, 6—8] or argentometrically [9, 10]. We wish to report a direct determination of chlorine in the ignited sample after masking the interfering mercury with ethylenediaminetetraacetic acid.

## Experimental

### Chemicals

Solution of ethylenediaminetetraacetic acid (disodium salt,  $\text{Na}_2\text{EDTA}$ ),  $0.05 \text{ mol l}^{-1}$ .  
Hydrogen peroxide 30%, A.R. grade.

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Solution of silver nitrate,  $0.02 \text{ mol l}^{-1}$ . Standardization was made in the usual way against NaCl.

2-Propanol, A.R. grade.

Oxygen for medical use.

Samples with different contents of chlorine and mercury were prepared by mixing of glucosaminium chloride or 4-chlorobenzoic acid and mercuric oxide. Additional analytical samples were mercuric chloroanilate, 4-chloromercuribenzoic acid, phenylmercurichloride, and 4-methylphenylmercurichloride. Purity was checked by means of elemental analysis.

### Apparatus

Samples were ignited in filter paper Schleicher & Schüll 589 in ground conical 500 ml flasks provided with a platinum coil sealed in the stopper. Quartz wool used for admixing to the sample was purified with boiling dilute nitric acid and distilled water, and dried at  $160^\circ\text{C}$ . Chlorine in ionic form was potentiometrically titrated in the dark using Radiometer PHM 28, silver and saturated calomel electrodes. Prior to each titration the silver electrode was cleaned with powdered calcium carbonate.

### Methods

The sample (10 to 40 mg) wrapped in a filter paper together with a small amount of quartz wool avoiding to fall the non-ignited residue into the absorption solution was put into the platinum coil. The neck of the ignition flask filled with oxygen,  $\text{Na}_2\text{EDTA}$  solution (5 ml), and 3 drops of hydrogen peroxide, was made wet with water. The sample was ignited and immediately put into the flask. After about 5 min the flask was agitated for 60 min in a shaking machine and the content quantitatively brought into a 250 ml beaker by a stream of distilled water so that the total volume did not exceed 50 ml. After addition of 2-propanol (25 ml) the solution was titrated in the dark with silver nitrate using potentiometric indication of the end point. Near the end point the titrant was added in 0.1 ml portions and 1 min before each addition of titrant was waited for the electrode potential to attain equilibrium.

### Results and discussion

Existing methods of chlorine determination in organic compounds of mercury require necessarily the separation of chlorine and mercury. Especially mercurimetric or argentometric determinations of chlorides are interfered by mercury and charged with errors. We therefore tried to find a method without separating mercury from chlorine. Masking of mercury by ethylenediaminetetraacetic acid was found to be most convenient. This reagent gives with  $\text{Hg(II)}$  more stable compounds than chlorides. Stability constant of mercuric chelatonate  $\log K_{\text{HgEDTA}} = 22.1$ , whereas  $\log K_{\text{HgCl}_2} = 12.8$  [13]. Of the methods tested, the

simplest one proved to be ignition of the sample in a flask with oxygen and absorbing the products in a solution of  $\text{Na}_2\text{EDTA}$  and hydrogen peroxide at pH 5 to 5.5. Ignition products of organomercuric compounds in oxygen are  $\text{Hg(I)}$ ,  $\text{Hg(II)}$ , and elemental mercury [14]. During absorption in the solution of EDTA with peroxide  $\text{Hg(I)}$  and  $\text{Hg(II)}$  change into mercuric chelatonate and chlorine gives chloride. Elemental mercury is almost insoluble in the absorption solution and remains in the flask as tiny drops. Although it is known that  $\text{Hg(I)}$  with EDTA is disproportionated and gives mercuric chelatonate and elemental mercury [15], it may be assumed that peroxide shifts the reaction equilibrium towards the mercuric compound and elemental mercury arises predominantly already during the ignition of the sample.

Mercuric chelatonate is stable in a relatively wide range of pH values [15]. The absorption solution may be prepared preferentially of  $\text{Na}_2\text{EDTA}$ , this being simultaneously a buffer which adjusts the pH to the optimum value of 5 to 5.5. The determination of chloride was carried out by argentometric titration with silver nitrate using potentiometric indication of the end point. As will be shown later, neither mercuric chelatonate nor elemental mercury interfere with the chloride determination. Titration cannot be carried out in direct light because of reduction on the silver electrode resulting in a permanent drop of its potential. Titration is favourably influenced by addition of 2-propanol which lowers the solubility of  $\text{AgCl}$  and keeps down the adsorption phenomena.

The determination of chlorine in materials containing varying quantities of Cl and Hg was simulated by mixtures of mercuric oxide and 4-chlorobenzoic acid or glucosaminium chloride. Results are given in Table 1. In all cases the content of

Table 1  
Determination of chlorine in samples with mercuric oxide added

Sample	Given		Found mg Cl
	mg $\text{HgO}$	mg Cl	
1	0	4.10 <sup>a</sup>	4.12
2	3.5	2.55 <sup>a</sup>	2.52
3	9.3	3.54 <sup>a</sup>	3.50
4	21.0	2.54 <sup>a</sup>	2.56
5	30.0	3.34 <sup>a</sup>	3.42
6	0	4.47 <sup>b</sup>	4.47
7	10.0	4.84 <sup>b</sup>	4.83
8	21.0	3.25 <sup>b</sup>	3.38
9	30.0	4.26 <sup>b</sup>	4.23
10	34.0	2.08 <sup>b</sup>	2.11

Chlorine added as: a) glucosaminium chloride, b) 4-chlorobenzoic acid.

chlorine given and found correlates and the dispersion variance of results is in the range of usual experimental errors. *t*-Test for paired data ( $n = 10$ , probability = 95%) gave  $t = 0.595$ , tabulated critical value being  $t = 2.262$  [16].

The determination of chlorine in organic compounds containing mercury was tested with several materials. Results are given in Table 2. Confidence of the

Table 2  
Determination of chlorine in samples containing Cl and Hg

Sample	Calculated % Cl	Found % Cl	Confidence interval $\pm$ %
Mercuric chloroanilate	17.40	17.44	0.23
4-Chloromercuribenzoic acid	9.92	9.73	0.17
Phenylmercurichloride	11.32	11.41	0.25
4-Methylphenylmercurichloride	10.83	10.75	0.21

proposed method was evaluated statistically by calculation of confidence intervals [17] for five determinations (probability 95%) and satisfies usual requirements for elemental analysis. However, this method cannot be used for masking mercury in the determination of iodide which forms more stable compounds with Hg(II) than with EDTA; cf. [13, 15].

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