were isolated as barium salts in Ref². were converted to sodium salts before use by trituration with a slight excess of sodium sulfate (molar ratio 1:1.25).

1. Åkerfeldt, S. *Acta Chem. Scand.* **14** (1960) 1019.
2. Åkerfeldt, S. *Acta Chem. Scand.* **16** (1962) *In press.*
3. Åkerfeldt, S. *Acta Chem. Scand.* **17** (1963) *In press.*
4. Feuer, G. and Wollemann, M. *Acta Physiol. Acad. Sci. Hung.* **10** (1956) 1.
5. Grunert, R. R. and Phillips, P. H. *Arch. Biochem. Biophys.* **30** (1951) 217.

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Identification of An Impurity in Chlorine Gas from Mercury Cells

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When brine is electrolyzed in technical cells with mercury cathodes and graphite anodes chlorine gas is obtained which is saturated with water vapor at 60–70°C, and which also contains carbon dioxide, air, hydrogen, and traces of other impurities. The moist gas is first cooled, either directly with water or indirectly, then dried with sulfuric acid, and finally condensed after compression and cooling.

In the gas ducts leading to the drying equipment and in the drying equipment itself various kinds of impurities are deposited, thus interfering with the operation. Part of the impurities generally accompanies the chlorine to the condensation department, and then becomes dissolved or dispersed in the liquid phase, causing trouble in the customers' bleaching equipment, etc.

For these reasons it would be valuable to identify the compounds in order to, *e.g.*, find suitable methods for an easy removal of the deposits, but also to elucidate the mechanism of formation.

Earlier investigations. In some technical reports, solid impurities in chlorine gas are mentioned. Billiter¹ states, *e.g.*, that salt particles might be entrained in the gas stream at high loads. In some plants in USA glass fiber filters are employed in the chlorine pipes from the cells.

Wranglén² investigated corrosion products from hard rubber (ebonite) linings on cell covers and frames. In the deposits examined the chlorine content reached about 65 %. Age determination according to the ¹⁴C method showed that up to 70 % of the impurities might originate from graphite, whereas only 30 % of the carbon was "fresh".

Penfield and Cushing³ describe a fractionating column for removal of chlorinated organic compounds, the concentration of which is said to reach 0.2 % in liquid chlorine. The impurities had a "taffy-like" consistency and such a high vapor pressure that they sublimated at room temperature. About 1/3 was identified as chloroform and 1/6 as insoluble in chloroform, consisting mainly of hexachloroethane and hexachlorobenzene. By fractionating the chlorine in a column the impurity content decreased to less than 0.01 %.

Finally in a US patent⁴ a method is described for purifying moist chlorine gas by injection of liquid chlorine. The hydrate thereby formed is said to bind such impurities as carbon tetrachloride, chloroform and hexachloroethane.

Chemical analysis of a sample. In connection with cleaning the drying towers in the Domsjö chlorine plant, which must be done at about 6 months' intervals, a sample of the deposits was taken. It had a fine crystalline structure, a pale yellow color, and a typical intense odor.

The crystals were only slightly soluble in ethanol and chloroform, but almost completely soluble in benzene. They sublimated upon slight heating. The melting point range of the sample was 220–260°C (the wide range indicates that the sample was impure).

The compound was purified by sublimation and chemically analyzed. The following result was obtained: C 27.8; H 0.5; O 10.5; Cl 59.6. (Sum 98.4 %). The corresponding molecular composition is represented by the formula $C_7H_{1.5}O_2Cl_4$. The high oxygen content is remarkable, since oxygen containing impurities have apparently not been reported in the literature earlier.

Fig. 1. Infrared absorption spectrum of the substance deposited in chlorine drying towers.

Infrared absorption spectrum of the compound. As a supplement to the chemical analysis the infrared absorption spectrum of the compound was recorded, cf. Fig. 1. For the analysis a pellet was prepared from 1 mg of the substance and 300 mg KBr. The minima at the wave numbers 700–750 and 1670–1680 cm^{-1} indicate that the substance is a chlorinated aromatic compound containing carbonyl groups.

An examination of oxygen containing chlorine compounds⁵ with melting points above 220°C showed that the substance might be 2,3,5,6-tetrachlorobenzoquinone-1,4, i.e., $\text{C}_6\text{Cl}_4\text{O}_2$ (chloranil). The infrared absorption spectrum shown in Fig. 1 also agrees well with a published spectrum for chloranil⁶.

Discussion of the results. Melting point determination and chemical analysis indicate that the collected sample consists mainly of chloranil. The infrared absorption spectrum confirms this assumption.

The fact that the compound contains oxygen may indicate that it is formed at the electrolysis by oxidation of the anode graphite. If this is the case, it would be impossible, with the present cell construction, to avoid the formation of such compounds.

Since the deposition seems to be connected with local changes in gas velocity and temperature, it is difficult to estimate the

total amount of chloranil formed, but the quantity deposited in the drying towers would be equivalent to 1–10 ppm in the cell gas. To this must be added impurities which are not deposited in this part of the equipment.

Chloranil is very resistant to oxidation and is insoluble in many common solvents. However, the substance can be reduced with, e.g., sulfite, to tetrachlorohydroquinone, which is easily soluble in alcohol, ether etc.

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1. Billiter, J. *Die technische Elektrolyse der Nichtmetalle*, Springer, Wien 1954, p. 306.
2. Wranglén, G. *Svensk Kem. Tidskr.* **68** (1956) 396.
3. Penfield, W. and Cushing, R. E. *Ind. Eng. Chem.* **31** (1939) 377.
4. Redcay, A. K. Gulf Oil Corp, *US pat. No.* 2,785,055 (1957).
5. Huntress, E. H. *Organic Chlorine Compounds*, J. Wiley & Sons, New York 1948, p. 497.
6. Kainer, H. and Otting, W. *Chem. Ber.* **88** (1955) 1921.

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