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Colorimetric Determination of Chloride in Concentrated Hydrogen Peroxide

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▶ Aluminum containers, commonly employed for storage of concentrated hydrogen peroxide, exhibit accelerated corrosion in the presence of traces of dissolved chloride. To study this effect, development of a sensitive method was necessary for determining chloride in concentrated hydrogen peroxide. A colorimetric method, based on the reaction of mercuric thiocyanate with chloride ion to release thiocyanate, which forms a reddish orange complex with iron(III), is capable of determining chloride in 90% hydrogen peroxide, up to 4 mg. per liter with a sensitivity to 0.01 mg. per liter and an accuracy equal to or better than 0.1 mg. per liter. Variables are studied with respect to hydrogen peroxide decomposition, reagents, temperature, and interferences

DEVELOPMENT of a method for determination of trace quantities of chloride in concentrated hydrogen peroxide was undertaken in conjunction with studies of the corrosive effect (6, 7) of such chloride on aluminum containers. The government specification for hydrogen peroxide (MIL-H-16005C) permits a maximum chloride content of 1 mg. per liter (1 p.p.m. on a weight-volume basis).

The method described is a modification and extension of that proposed by Zall, Fisher, and Garner (8), and is intended for the determination of 0.01 to 4 mg. per liter of chloride in concentrated (90%) hydrogen peroxide.

REAGENTS AND STANDARD SOLUTIONS

Mercuric thiocyanate, saturated solution in deionized water (0.07% at 25° C.). Filter to remove excess.

Ferric Perchlorate. Dissolve 14.0 grams of pure iron wire in dilute nitric acid. Add 120 ml. of perchloric acid (70%) and heat to fumes of perchloric acid. Continue fuming for 30 minutes. Cool, add 100 ml. of hot deionized water, and boil for 5 to 10 minutes to remove chlorine. Cool and dilute to 1 liter with deionized water.

Composite Reagent. Prepare as needed by mixing 2.00 parts by volume of ferric perchlorate solution with 1.00 part by volume of mercuric thiocyanate solution. The reagent is stable for approximately 8 hours.

Standard Solutions. By suitable dilutions of a sodium chloride master solution (0.1 mg. of Cl⁻ per ml.) prepare standard solutions ranging from 0 to 40 γ of Cl⁻ per ml., in increments of 2 γ per ml. These will be employed in preparation of the calibration curve.

CALIBRATION

Pipet 5.00 ml. of each standard solution into 10-ml. volumetric flasks and add 1.0 ml. of 6N sodium hydroxide and 0.6 ml. of perchloric acid (70%). Add 3.00 ml. of the composite reagent and fill to the 10-ml. mark with deionized water. Mix, transfer to a test-tube colorimeter cell, and compare the yellow-orange color against water at approximately 460-mμ wave length (KS-47 filter is satisfactory). The color is stable for approximately 1 hour, with gradual increasing absorbance thereafter. Plot the colorimeter readings, or absorbances, against the corresponding micrograms of chloride present. Make a separate calibration for each new solution of mercuric thiocyanate reagent prepared. Conduct the calibration at approximately the ambient temperature expected during the actual analysis. A representative curve (Figure 1) indicates that Beer's law is not obeyed. The curve shows an approximate sensitivity of 0.5 γ in the lower portion of the curve—below 30 γ of chloride. The sensitivity decreases at higher chloride concentrations.

PROCEDURE

Transfer 50 ml. of the hydrogen peroxide sample into a covered 500-ml. tall-form borosilicate glass beaker. Carry along duplicate reagent blanks. Add 10 ml. of deionized water and 1.0 ml. of 6N sodium hydroxide. Place on a steam bath to initiate a vigorous reaction. Maintain the temperature of the solution between 75° and 90° C. until decomposition is almost complete, then evaporate to dryness on the steam bath. Dissolve salts and rinse inside of beaker with 1 to 2 ml. of deionized water. Add 0.6 ml. of perchloric acid (70%) and 3.00 ml. of the composite reagent. Transfer the solution to a 10-ml. volumetric flask, rinsing the beaker at least twice with deionized water. Dilute to the 10-ml. mark, mix, and compare against water with the photoelectric colorimeter, as described under calibration. Obtain the quantity of chloride from the calibration curve and deduct the average of the blanks.

Several samples may be run simultaneously, except for peroxide decomposition, which should preferably be conducted in pairs. Suitable safety precautions should be taken when handling concentrated hydrogen peroxide, especially during decomposition.

PRECAUTIONS AGAINST CONTAMINATION

Decomposition and evaporation should be conducted in a hood with suction off to minimize motion of at-

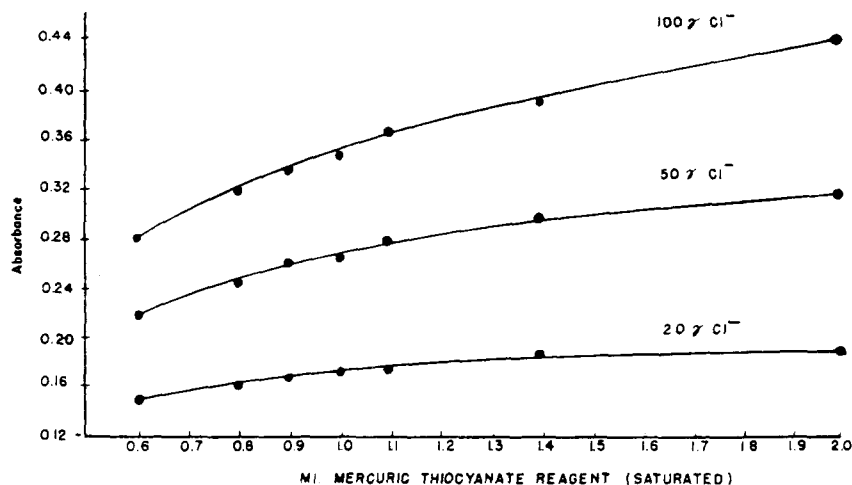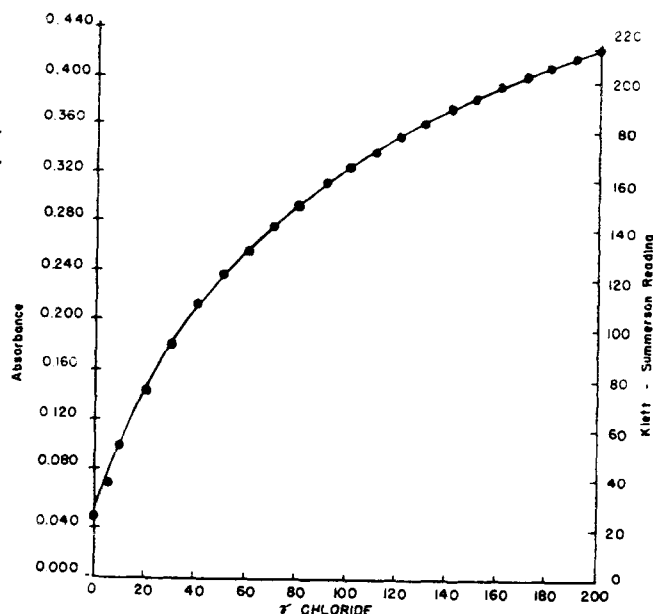**Figure 1. Calibration curve (K. S. No. 47 filter)**

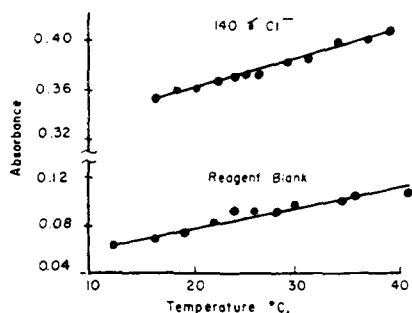**Figure 2. Effect of mercuric thiocyanate on absorbance**

Figure 3. Effect of temperature on absorbance

mospheric contaminants (principally volatile chlorides and sulfides). During evaporation, hood doors should be kept tightly closed. Dripping of condensed steam can be avoided by maintaining a stream of cold water in the hood and avoiding excessive steam. A special isolated room specifically designed for the determination of chloride would help minimize atmospheric contamination. Tobacco smoke will cause con-siderable contamination. Introduction of traces of skin perspiration during handling should be avoided.

RESULTS

The accuracy of the procedure was tested with hydrogen peroxide (90%), containing varying amounts of added sodium chloride. Table I presents a quantitative comparison of chloride added with chloride recovered, up to 3.00 mg. per liter. Accuracy is either equal to or better than 0.1 mg. per liter, with an average deviation of 0.03 mg. per liter.

DISCUSSION

Preliminary Treatment. The colori-metric determination of chloride in hydrogen peroxide by the mercuric thiocyanate method presented diffi-culties not previously encountered with similar methods for determining chloride in waters (8).

Under the test conditions the pres-ence of more than 25 γ of hydrogen peroxide caused low results, probably because it decomposes thiocyanate to sulfuric acid and hydrocyanic acid (5), as follows:

$$6H_2O_2 + Hg(CNS)_2 \rightarrow$$
$$H_2SO_4 + 2HCN + HgSO_4 + 4H_2O$$
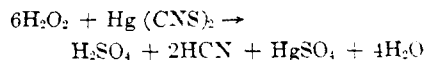
Virtually complete decomposition of the hydrogen peroxide sample is thus neces-sary.

It was necessary to conduct the perox-ide decomposition under alkaline con-ditions, to avoid loss of chloride by volatilization. One milliliter of 6N sodium hydroxide was found optimum as an additive, resulting in an average decomposition time of 30 minutes per sample. More than 1.3 ml. caused attack on the glass, producing a siliceous precipitate. Smaller amounts increased decomposition time and caused loss of chloride—for example, 0.1 ml. of 6N sodium hydroxide increased decomposi-tion time to 4 hours and resulted in complete loss of chloride, originally present as 1.3 mg. per liter.

Although decomposition of the alka-

line hydrogen peroxide was vigorous, with rapid evolution of copious amounts of vapor, no significant mechanical loss of liquid occurred, as tests of the vapor with wet pH paper revealed no alkaline spray. However, some hydrogen peroxide vapor is evolved with the oxygen, and may cause low results if allowed to condense on glassware used for subsequent operations. Addition of 10 ml. of water to the hydrogen peroxide sample helped maintain a controllable decomposition rate.

Color Reaction. REAGENTS. Use of the perchlorate ion (8) in the composite reagent and for acidifying the hydrogen peroxide decomposition residue results in a considerably lower blank than with nitrate or sulfate anion. The composite reagent, which is stable for 8 hours, reduces the number of handling steps and possibilities of contamination. Another advantage is elimination of possible error from ammonia in the laboratory atmosphere during the colorimetric procedure. Ammonia, if in contact with the neutral mercuric thiocyanate, will precipitate mercuric hydroxide, causing high results. The composite reagent, which is acidic, will absorb the traces of ammonia without precipitation of mercury.

The proposed procedure specifies a saturated solution of mercuric thiocyanate (8), which is approximately 0.07% at 25° C. (3). This concentration can vary (1), depending on the ambient temperature during preparation. Figure 2 shows the effect of mercuric thiocyanate on the absorbance of 20, 50, and 100 γ of chloride. In place

of the composite reagent, 2.00 ml. of ferric perchlorate and varying amounts of mercuric thiocyanate solutions were used. It is evident that slight changes in the concentration of the mercuric thiocyanate may have a significant effect on the results, especially with higher concentrations of chloride, necessitating a new calibration curve for each new mercuric thiocyanate solution prepared. This phenomenon may be the result of the mass-action effect of mercuric thiocyanate in the reaction:

$$2Cl^- + Hg(SCN)_2 \rightleftharpoons HgCl_2 + 2SCN^- \quad (4)$$
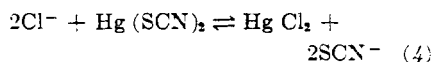
This equation may also explain the apparent lack of conformity to Beer's law, because increasing concentrations of chloride will also increase the concentration of mercuric chloride and partially shift the reaction to the left. Addition of concentrated mercuric chloride to the developed color will cause complete bleaching (2).

TEMPERATURE. Large variations of temperature have a significant effect on the absorbance (Figure 3). Chloride determinations should therefore be conducted at approximately the ambient temperature encountered in calibration.

INTERFERENCES. By the proposed method, the contaminants and additives generally present in commercial 90% hydrogen peroxide produce an error of less than 0.01 mg. of chloride per liter, in the concentrations shown in Table II. The maximum allowable limits specified in MIL-H-165005C, and an analysis of a sample of commercial 90% hydrogen

peroxide, are included for comparison. The data indicate that such contaminants and additives will not interfere, even in concentrations significantly higher than those normally encountered. Interferences from hydrogen peroxide, sulfides (4), tobacco smoke, and ammonia have been cited.

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Isatin Tests for Aromatic Hydrocarbons and Phenols

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▶ Methods for the detection and determination of polynuclear hydrocarbons and phenols in polluted air are badly needed. The reaction of certain isatin derivatives with phosphorus pentachloride apparently yields isatin chlorides which readily give cationic resonance dyes with phenols and polynuclear aromatic hydrocarbons. The reaction of 10 isatin derivatives with polynuclear aromatic hydrocarbons to give a hitherto unknown class of indigoid dyes absorbing at very long wave lengths has been developed into a new method for the spectral detection of the more basic aromatic hydrocarbons. As phenols and volatile hydrocarbons are not present in the neutral aromatic fraction of air particulates collected with a high volume air sampler, the isatin test procedure applied to these fractions is probably specific for the pericondensed aromatic hydrocarbons.

IN PREVIOUS work, aromatic aldehyde–phosphorus pentachloride reagents were used for the detection and determination of various types of aromatic compounds (11, 12). That study has produced two procedures of value in air particulate analysis—a sensitive method for the determination of aromatic compounds (13), and sensitive color and spectral tests for many types of aro-

matic compounds, such as benzo(a)pyrene, 2-acetylaminofluorene, and phenol (11-13).

In the hope of originating simple specific methods for the detection and/or determination of small families of hydrocarbons or even individual hydrocarbons, the task of developing and investigating new types of colorimetric methods was undertaken.

The approach considered necessary has been a study of the spectral characteristics of the dyes produced by the interaction of aromatic hydrocarbons or phenols with a new class of reagents. The variables which have been found to be important are the basicity of the hydrocarbons and the molecular struc-