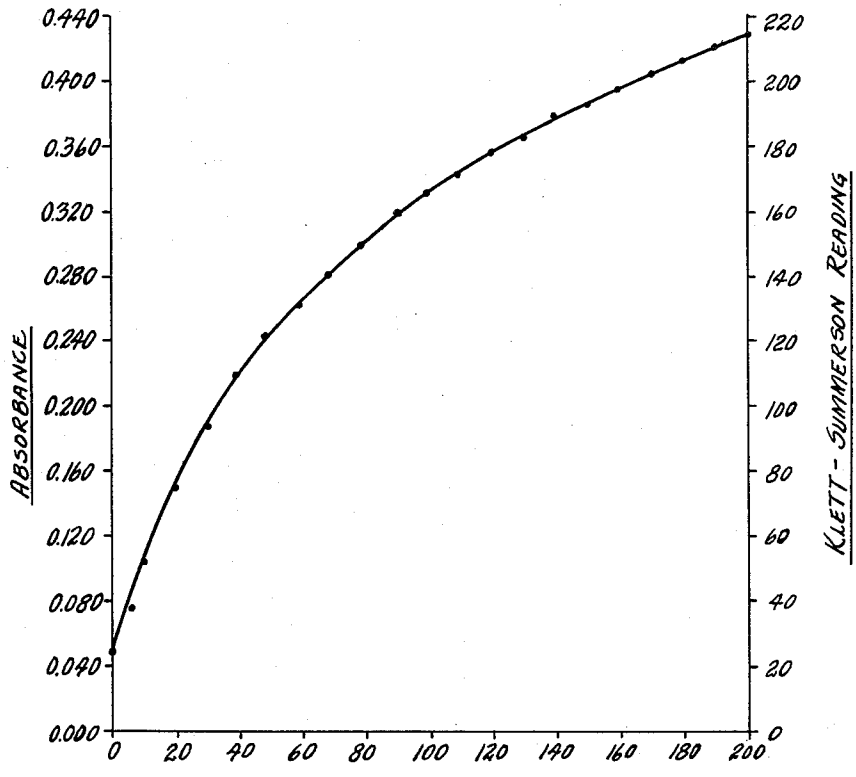
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COLORIMETRIC DETERMINATION OF CHLORIDES IN LIQUIDS

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CALIBRATION CURVE (K.S. #47 FILTER)

INVENTORS.
ISIDORE GELD
IRVING F. STERNMAN
BY Max A. Garner
ATTORNEY

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COLORIMETRIC DETERMINATION OF CHLORIDES IN LIQUIDS

Isidore Geld, Flushing, and Irving F. Sternman, Rosedale, N.Y., assignors to the United States of America as represented by the Secretary of the Navy

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The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This invention relates to the determination of trace amounts of chlorides in liquids, and particularly to such determination of chlorides in hydrogen peroxide.

The presence of traces of chlorides in hydrogen peroxide is known to cause corrosive pitting attacks on aluminum containers in which the peroxide is commonly stored. Previous procedures for the determination of chlorides in liquids, such as in hydrogen peroxide, in water, in boiler and feed waters, and in biological fluids, for example, have not been entirely satisfactory, due, among other reasons, to their inaccuracy when the chlorides are in trace amounts, to inaccuracy arising from unintentional contamination of the materials, and to the poor reproducibility of the tests. The classical volumetric and gravimetric methods of analysis require prohibitively large samples, the decomposition of which in the case of hydrogen peroxide would be lengthy, potentially hazardous, and subject to possible considerable contamination. Chlorides are present in the ambient atmosphere, on the skin and many surfaces, and are present as impurities in water and many reagents. Also ammonia and tobacco smoke in a laboratory atmosphere may by contamination of the materials during a determination give decidedly undependable and inaccurate results in some methods.

An object of this invention is to provide a relatively simple, practical, and accurate method for the determination of chlorides in concentrated hydrogen peroxides that will be accurate, even for trace amounts of the chlorides, such as from 0.01 to 4 mg. per liter in 90% hydrogen peroxide.

Another object is to provide a relatively simple, accurate, safe and practical colorimetric method of determining the presence and amounts of chlorides in various liquids, such as hydrogen peroxide, water, boiler and feed water and biological fluids, and which may be performed with a minimum chance of inaccuracy due to possible contamination by chlorides and other materials not originally in the specimens under determination.

Other objects and advantages will be apparent from the following disclosure of the invention, and the novel features will be particularly pointed out in connection with the appended claims.

The accompanying drawing illustrates a typical graph that may be employed in the practice of the method of this invention.

Considering first the application of this method to the determination of the amount of chlorides in hydrogen peroxide, a colorimeter employed in the practice of the method was of the photoelectric type provided with a 1 to 1.2 cm. cell and a 460 millimicron filter, identified as a Klett-Summerson colorimeter with a No. KS–47 filter (approximately 470 millimicrons) and a 1.2 cm. test tube cell.

Reagents and standard solutions employed in this method, and hereinafter referred to, are as follows:

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 40γ of Cl^- per ml., in increments of 2γ per ml. These will be employed in preparation of the calibration curve.

Sodium hydroxide, 6 N. Dissolve 240 grams of reagent-grade sodium hydroxide in deionized water and dilute to one liter.

A plurality of calibration solutions are prepared as follows:

Into each of a plurality of 10 ml. volumetric flasks, pipet 5.00 ml. of each standard solution and add to such flask 1.0 ml. of 6 N sodium hydroxide and 0.6 ml. of perchloric acid (70%). To each also add 3.00 ml. of the composite reagent and fill the flask to the 10 ml. mark with deionized water. Mix the contents in each flask separately. Transfer a portion of the solution in each flask to a test tube colorimeter cell and within one hour compare the yellow-orange color against water at approximately 460 mμ wave length (KS–47 filter is satisfactory). Then plot the colorimeter readings, or absorbencies, against the corresponding micrograms of chloride present. A separate calibration should be made for each new solution of mercuric thiocyanate reagent prepared. The calibration should be conducted at approximately the same ambient temperature expected during the actual analysis. The graph of the drawing, which is typical, indicates that the graph is a curve and hence Beer's law is not obeyed, and that the sensitivity decreases at higher chloride concentrations.

The following is one example of procedure in a test.

(1) Place 50 ml. of the concentrated hydrogen peroxide to be tested into a covered 500 ml. tall-form borosilicate glass beaker. Carry along duplicate reagent blanks.

(2) Add to this beaker 10 ml. of deionized water and 1.0 ml. of 6 N sodium hydroxide or other hydroxide of an alkali metal.

(3) Cover the beaker with a watch glass and insert a thermometer.

(4) Place beaker on a steam bath to initiate a vigorous reaction in the mixture in the beaker. This reaction destroys or decomposes the hydrogen peroxide into water and oxygen both of which can escape as steam and gas.

(5) Maintain the temperature of the solution in the beaker between 75° C. and 90° C. until decomposition of the peroxide has been completed. To do this, remove the beaker from the steam bath when the temperature of the solution in the beaker rises to about 75° C. to 80° C. and allow the decomposition of the peroxide in the beaker to continue until the temperature of the solution rises to 90° C.

(6) Then cool the beaker and its contents in an ice bath. If effervescence continues to increase in the ice bath, reaching to a height of two inches below the top of the beaker, swirl the solution in the beaker moderately until the reaction subsides; so that the solution will cool uniformly.

(7) When the reaction temperature of the solution in the beaker decreases to about 75° C. to 80° C., remove the beaker from the ice bath and allow decomposition of the peroxide in the beaker to continue under ambient

temperature conditions. If the reaction appears to be too slow, the beaker and its contents can be again heated on the steam bath to restore moderate effervescence.

(8) When decomposition of the peroxide in the beaker is almost complete, remove and rinse with deionized water into the solution in the beaker, the covering face of the cover glass and the thermometer, and then evaporate on the steam bath the contents of the beaker to dryness. With experience, the use of the thermometer can be eliminated and the decomposition of the peroxide regulated by judging the extent of the effervescence.

(9) Dissolve the salts or residues in the beaker which were so evaporated to dryness, with one to two ml. of deionized water added to the beaker and the contents swirled or agitated to get into the solution any chloride adhering to the sides of the beaker.

(10) Add 0.6 ml. of perchloric acid (70%) and 3.00 ml. of the composite reagent to the solution in the beaker.

(11) Transfer this last solution from the beaker to a 10 ml. volumetric flask, rinsing the inside of the beaker at least twice with deionized water and putting this rinse water into the 10 ml. volumetric flask with the rest of the solution therein. Dilute this solution in the volumetric flask to the 10 ml. mark, mix the contents of this volumetric flask such as by shaking or swirling, for example, and compare its color against water with the photoelectric colorimeter, as described above in connection with calibration. The water is colorless, or at zero color absorbance, and one should then "zero" the colorimeter before examining the solution from the volumetric flask. This water used for this comparison need not be deionized water.

(12) Obtain the quantity of chloride by reference of the colorimeter reading for the solution from the volumetric flask to the calibration curve prepared, as explained above, note it as a tentative value. Obtain the average value of the blanks in terms of chloride and deduct it from the tentative value. The remainder is the true value of the chloride that was present in the peroxide tested. The blanks result normally in a small correction. Several samples may be run simultaneously, except for peroxide decomposition, and the latter can be done in not more than pairs at a time for safety sake. Suitable safety precautions should be taken when handling concentrated hydrogen peroxide, especially during its decomposition.

To avoid serious errors in the determination, special precautions must be taken in the practice of the method to avoid contamination.

Decomposition and evaporation should be conducted in a hood with suction off to minimize motion of atmospheric 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 considerable contamination, and hence smoking in the analysis area should be prohibited. Introduction of traces of skin perspiration during handling should be avoided. Rubber gloves should be worn to prevent introduction of sodium chloride from skin perspiration into the solutions.

Adequate precautions should be taken to keep sources of volatile chlorides and sulphides well removed from the work area. Determinations should be completed without unnecessary delays, preferably within a four hour period, to minimize effects of atmospheric contaminants.

After the graph has been prepared, and a reading made on the colorimeter as to the color absorbance for the test specimen, one locates the amount of such absorbance on the vertical ordinate of the graph, then by going horizontally at that level to the graph, one locates a point on the graph that when followed in a vertical line downwardly therefrom will indicate on the values of the horizontal ordinates the amount of chloride present to give that color absorbance. This then is a tentative determination of the amount of chloride or its concentration present in the specimen of hydrogen peroxide which was tested. It is best to obtain the average value of the blanks in terms of chloride and deduct it from the tentative value. The remainder is the true value of the chloride concentration in the hydrogen peroxide specimen tested. The use of such blanks is common in chemistry but for the record it may be said that a blank is a test run without the peroxide, which will indicate the amount of any chloride present in the components used for the test. This chloride in the test components is subtracted from that determined by the test of the peroxide, and the difference will indicate just the amount of chloride in the peroxide itself. The column MIL–H–16005 C of Table 1 relates to a military specification used by the U.S. Navy to set forth the requirements for the purchase of hydrogen peroxide and is included for comparison purposes.

The colorimetric determination of chloride in hydrogen peroxide by the mercuric thiocyanate method presented difficulties not previously encountered with similar methods for determining chloride in waters.

Under the test conditions the presence of more than 25γ of hydrogen peroxide caused low results, probably because it decomposes thiocyanate to sulfuric acid and hydrocyanic acid, 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 necessary.

It was necessary to conduct the peroxide decomposition under alkaline conditions, to avoid loss of chloride by volatilization. One milliliter of 6 N 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 6 N sodium hydroxide increased decomposition time to 4 hours and resulted in complete loss of chloride, originally present as 1.3 mg. per liter.

Although decomposition of the alkaline 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 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 eight 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, which is approximately 0.07% at 25° C. This concentration can vary, depending on the ambient temperature during preparation. 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:

$$2Cl^- + Hg(SCN)_2 \rightleftharpoons HgCl_2 + 2SCN^-$$

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.

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

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 the following table:

TABLE 1

Effect of Impurities or Additives

Impurities or Additives	Concentration Producing less than 0.01% Error, mg./l.	Analysis of Commercial H_2O_2 (90%),[1] mg./l.	MIL-H-16005C Maximum Limits, mg./l.
Chloride		0.4	1
Nitrate	20	1.2	10
Phosphate	10	0.4	5
Sulfate	20	2.4	10
Tin	12	[2]	6
Aluminum	2	0.2	
Ammonium	5	0.9	

[1] Analysis supplied by manufacturer.
[2] None added.

The data indicate that such contaminants and additives will not interfere, even in concentrations significantly higher than those normally encountered.

When the specimen liquid, such as boiler or feed water, or biological fluids are to be tested, the procedure is similar except that decomposition operation of the test specimen is unnecessary but evaporation to dryness or a small volume is necessary. Such liquids may be acid or alkaline and the calibration and tests should be performed with liquids that are alkaline. Hence it is advisable to add a small amount of the alkali metal hydroxide to the test liquid, before adding the solutions that were described as added to the solution of the dried residue from the peroxide decomposition action. Otherwise the procedure is as described in connection with liquids containing hydrogen peroxide. The precautions and details of procedure are important for the testing of liquids that are free of hydrogen peroxide, in order to reduce the danger of contamination that would give inaccurate results.

It is understood that the following reaction takes place from left to right almost completely.

$$2Cl^- + Hg(SCN)_2 \rightleftharpoons HgCl_2 + 2SCN^-$$

The liberated SCN^- reacts with Fe^{3+} to give a reddish-orange color, as follows:

$$SCN^- + Fe^{3+} \rightleftharpoons FeSCN^{2+}$$

It will be understood that various changes in the details, steps and materials, which have been herein described in order to explain the nature of the invention, may be made by those skilled in the art within the principle and scope of the invention as expressed in the appended claims.

We claim:

1. A colorimetric method for the determination of trace amounts of chlorides in hydrogen peroxide which comprises heating in an approximately closed container a mixture of the hydrogen peroxide, diluted with deionized water, and a hydroxide of an alkali metal to initiate a vigorous reaction in the mixture that changes the peroxide into oxygen and water until the temperature of the mixture rises to between about 75° C. and 80° C., then discontinuing the heating and when the temperature of the mixture rises to about 90° C., cooling the mixture until the temperature decreases to between about 75° C. and 80° C., then, after cessation of effervescene indicates that decomposition of the hydrogen peroxide has been completed, evaporating the mixture to dryness, then dissolving such dried mixture in deionized water, then adding to the dissolved mixture a small amount of perchloric acid and of a mixture of about two parts by volume of ferric perchlorate solution with about one part by volume of mercuric thiocyanate solution, whereby when the color of the product so obtained is compared with the varying intensities of colors of solutions containing different and known amounts of a chloride in a mixture of perchloric acid, ferric perchlorate solution, hydroxide of an alkali metal, and mercuric thiocyanate in the proportions added to the hydrogen peroxide, one may observe the amount of chloride in said hydrogen peroxide tested.

2. The colorimetric method for the determination of small amounts of chlorides in hydrogen peroxide, which comprises providing in an approximately closed container a mixture of the hydrogen peroxide, diluted with deionized water, and a hydroxide of an alkali metal, initiating by heat a reaction of such mixture that decomposes the peroxide, maintaining the temperature of the reacting mixture between about 75° C. and about 90° C., until the decomposition of the peroxide has been completed, evaporating to dryness this mixture, dissolving this dried mixture in deionized water, and adding to such dissolved mixture a small amount of perchloric acid and of a mixture of solutions of ferric perchlorate and mercuric thiocyanate, whereby when the color of the product so obtained is compared with the colors of varying intensities of solutions containing different and known amounts of a chloride, plus perchloric acid, ferric perchlorate, a hydroxide of an alkali metal, and mercuric thiocyanate in the same relative proportions in which they were added to the hydrogen peroxide, one may ascertain the amount of chloride in the hydrogen peroxide tested.

3. The colorimetric method for the determination of small amounts of chlorides in hydrogen peroxide, which comprises providing in an approximately closed container a mixture of the hydrogen peroxide, diluted with deionized water, and a hydroxide of an alkali metal, decomposing the hydrogen peroxide in this mixture at a temperature between about 75° C. and about 90° C., evaporating to dryness this mixture with decomposed hydrogen peroxide, dissolving this dried mixture in deionized water, and adding to such dissolved mixture a small amount of perchloric acid and a mixture of solutions of ferric perchlorate and mercuric thiocyanate, whereby when the color of the product so obtained is compared with the colors of varying intensities of solutions containing different and known amounts of a chloride, plus perchloric acid, ferric perchlorate, a hydroxide of an alkali metal, and mercuric thiocyanate in the same relative proportions in which they were added to the hydrogen peroxide, one may ascertain the amount of chloride in the hydrogen peroxide tested.

4. The colorimetric method for the determination of trace amounts of chlorides in hydrogen peroxide, which comprises providing in an approximately closed container, a mixture of a specimen of said hydrogen peroxide, diluted with deionized water, and a hydroxide of an alkali metal, placing this mixture in said container in a hood with suction off, there completely decomposing the said peroxide component in said mixture, and then following complete decomposition of the peroxide component, evaporating the mixture to dryness, dissolving the dried mixture in deionized water, and adding to such

solution of said dried mixture and said water, a small amount of a preformed mixture of solutions of ferric perchlorate and mercuric thiocyanate to obtain a colored solution, whereby a comparison of such color with the colors of comparison solutions formed, at the same ambient temperature as said colored solution, of deionized water, a part of the same preformed mixture of solutions of ferric perchlorate and mercuric thiocyanate, in the same concentrations as used in the said colored solutions, and different and known amounts of a chloride, will enable one to determine the amount of chloride in said peroxide.

5. The method according to claim 4, wherein said decomposition of said peroxide is performed at a temperature below about 90° C.

6. The method according to claim 4, wherein said decomposition of said diluted peroxide specimen is performed in a temperature range between about 75° C. and about 90° C.

7. The colorimetric method for the determination of trace amounts of chlorides in hydrogen peroxides, which comprises providing in an approximately closed container, a mixture of a specimen of said hydrogen peroxide, diluted with deionized water, and a hydroxide of an alkali metal, placing this mixture in said container in a hood with suction off, there completely decomposing the said peroxide component in said mixture at a temperature between about 75° C. and about 90° C., and then following complete decomposition of the peroxide component, evaporating the mixture to dryness, dissolving the dried mixture in deionized water, adding to such solution of said dried mixture and said water, a small amount of a preformed mixture of solutions of ferric perchlorate and mercuric thiocyanate to obtain a colored solution, and also preparing a plurality of comparison solutions, at about the same ambient temperature as said colored solution, containing deionized water, a part of the same preformed mixture of solutions of ferric perchlorate and mercuric thiocyanate, in the same concentrations as used in making said colored solution, and different, known amounts of a chloride, whereby a comparison of the color of said colored solution with the color of said comparison solutions will enable one to determine the amount of chloride in said peroxide specimen.

8. The colorimetric method for the determination of trace amounts of chlorides in hydrogen peroxides, which comprises providing in an approximately closed container, a mixture of a specimen of said hydrogen peroxide, diluted with deionized water, and a hydroxide of an alkali metal, placing this mixture in said container in a hood with suction off, there completely decomposing the said peroxide component in said mixture at a temperature between about 75° C. and about 90° C., and then following complete decomposition of the peroxide component, evaporating the mixture to dryness, dissolving the dried mixture in deionized water, adding to such solution of said dried mixture and said water, a small amount of a preformed mixture of solutions of ferric perchlorate and mercuric thiocyanate to obtain a colored solution, also preparing a plurality of comparison solutions, at about the same ambient temperature as said colored solution, containing deionized water, a part of the same preformed mixture of solutions of ferric perchlorate and mercuric thiocyanate, in the same concentrations as used in making said colored solution, and different, known amounts of a chloride, and plotting a graph representing the color absorbance, such as can be determined by a colorimeter, of the comparison solutions for the known contents of chlorides therein, whereby the color absorbance of said colored solution, as determined by a colorimeter, when applied to said graph, will enable one to determine the amount of chloride in said peroxide specimen.

9. The method according to claim 8, wherein a small amount of perchloric acid is also added to said solution of the dried mixture in deionized water, and also to said comparison solutions.

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