CLTM-48
ISSUED: 4-27-61
REVISED:

THERMAL CHEMICAL STABILITY TEST FOR INCOMING SHIPMENTS OF 1499 PYRANOL

I. SCOPE

This test method describes a procedure for measuring the Thermal Stability of Pyranol (1499), by exposing it to heat (240°C) in a sealed glass ampoule, (limited volume of air). The resulting chlorides are determined potentiometrically and their magnitude is a measure of the Thermal Stability of the Pyranol. The Thermal degradation figure obtained is an empirical representation of the increase in both free chlorides and those with unstable chemical bond to the biphenyl radical.

II. APPARATUS AND EQUIPMENT

A. 32 x 200 mm Pyrex test tube.
B. Glassworkers torch, glasses and various equipment.
C. Oven operational to 250°C or over, and controllable to ± 2°C
D. Balance accurate to 0.01 gram. Torsion Balance Style 129 adequate.
E. 50 ml. glass syringe, 7" 14 gauge stainless steel needle and stopcock.
F. Support for ampoules while in oven.
G. Beaker 200 ml. tall form (Berzelius).
H. Magnetic stirrer and stirring bars (1" Teflon covered).
I. Microburette graduated in 0.01 ml. divisions.
J. Silver electrode (billet type). Beckman #1261 adequate.
K. Glass electrode. Beckman #4919-V4 shielded.
L. pH Meter suitable for use with glass electrode. Model GS Beckman preffered because instrument has expanded scale for greatest sensitivity to incremental EMF changes. Somewhat less sensitive meter, such as, Beckman "Zeromatic" or Leeds Northrup line operated pH meter may be used.
M. Water bath - Use an individual glass water bath 150 mm in diameter 75 mm high and containing 600 ml of water heated to 40°C ± 1°C.
N. Pipette 25 ml.
O. Burette or pipette, graduated to deliver 0.5 ml.
P. Wash bottles for pure Acetone, Methanol, and water.

Reagents

A. Methanol (chloride free) may be deionized through an ion exchange column or may be distilled from $AgNO_3$ crystals. Chloride ion concentration should be less than 0.01 ml of 0.005 N $AgNO_3$ per 100 ml. of Methanol.
B. Sodium Hydroxide, 0.1 N prepared by disolving 4.0 grams of analytical reagent grade NaOH pellets in one liter of chloride free Methanol.
C. Sulfuric Acid, 50-50 by volume - Dilute analytical reagent grade concentrated Sulfuric Acid with chloride free (distilled or deionized) water.

CAUTION: Always pour acid into the water with constant stirring to prevent any dangerous build-up of heat.

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D. Standard Silver Nitrate solution. 0.005N. Prepare by diluting ampoule of concentrated aqueous silver nitrate. Standardize against a pure chloride standard. (0.1N Silver Nitrate ampoules may be purchased from Anachemia, Montreal, Canada.)

E. Acetone, chloride free. Chloride ion concentration should be 0.01 ml of 0.005 N silver nitrate or less.
Acetone may be distilled from silver nitrate crystals if necessary.

III. REFERENCES

Spec. E4C48-S1 - Unstable Chlorine Compounds in Askarels.

IV. PROCEDURE

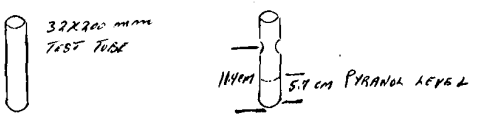
A. Ampoule preparation

1. The 32 x 200 mm test tubes are thoroughly cleaned by (a) rinsing with acetone, (b) washing with detergent or soap and water, and (c) well rinsed with deionized and distilled water. Thoroughness is paramount here because a contaminated test tube can void the whole test.

2. Oven dry the ampoule for at least three (3) hours at about 100°C .

3. Remove the ampoule from the oven after drying and allow to cool to about room temperature (25 - 30°C).

4. Neck down the ampoules by standard glass blowing procedures at a point approximately 11.4 Cm from the bottom of the test tube. Since the Pyranol (50 gms) occupies about 5.7 Cm. of the tubes length, this will provide an equivalent volume of air over the sample. See figure below.



5. The cleaned and necked ampoules are covered with aluminum foil to prevent contamination and stored until used.

B. Test Procedure

1. Weigh into a clean tared ampoule 50 grams (± 0.1 gm) of Pyranol using a 50 ml. syringe equipped with a stopcock and an 8" 14 gauge needle.

2. Care must be taken not to wet the neck of the ampoule with Pyranol. During the sealing operation temperatures get high enough to decompose the Pyranol.

3. When weighing has been completed, wrap the lower portion of the ampoule with a wet paper towel prior to sealing. This will help protect the Pyranol from excessive heat during sealing.

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4. Close the neck of the ampoule with the torch by rapidly heating the necked area and drawing to a narrow point. (a) Do not extend the sealing period over a minute and a half. The intense light at sealing can decompose the Pyranol. Do not allow the flame to enter the open mouth of the test tube, as the intense heat can decompose the Pyranol. (b) Ampoule drawing may be facilitated by attaching a glass rod to the lip of the test tube.

5. The hermetically sealed ampoule is placed in an oven operating at 240°C ± 2°C, for two hours.

6. After two hours in the 240°C oven the ampoule is removed and allowed to cool to room temperature. The operator must wear a protective face shield and asbestos gloves when removing ampoules from the oven.

   Unstable materials in the ampoule can build up pressures sufficient to cause the ampoule to explode.

7. When the ampoule reaches room temperature the drawn neck is scored with a file and struck sharply to open. Safety glasses must be worn and care taken to minimize flying glass during this operation. Do not handle the neck of the ampoule as this may contaminate the sample.

8. Empty the contents of the ampoule into a tall form (Berzelius) 200 ml beaker.

9. Rinse the ampoule with 10 ml. of chloride free Acetone and pour this into the beaker with the Pyranol. Pour out the contents rapidly so as not to dribble the sample or Acetone over the outside of the ampoule.

10. Add 25 ml. of Methanolic NaOH using a 25 ml. pipette and an automatic pipettor. Do not use the mouth to fill the pipette.

11. Add an additional 25 ml. of chloride free Acetone using a graduate.

12. A clean teflon covered stirring bar is added to the beaker using forceps or other non-contaminating transfer device. Do not handle the stirring bar, as perspiration and other contaminants on the hand can alter results. Cover the beaker with a watch glass

13. Place the beaker in a 40°C bath ± 1°C. A 7 x 15 cm. crystalizing dish with 4 cm. of water in it is adequate to immerse that portion of the beaker occupied by the Pyranol sample.

14. The bath and sample are placed on a magnetic stirrer and stirred as fast as possible for five (5) minutes without causing pronounced splashing.

15. After the five (5) minutes of stirring remove the beaker from the bath, and 0.5 ml. of dilute (50-50 by volume), Sulfuric Acid is added to it by pipette or burette.

16. Add an additional 65 ml. of chloride free Acetone with a clean graduate.

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17. Titrate the sample potentiometrically using a silver-glass electrode pair as described in General Electric Test Method E4C48-S1, "Unstable Chlorine Compounds in Askarels".

18. Determine the reagent blank by performing the titration steps outlined above with the exception of the Pyranol addition, i.e., add 25 ml. of Methanolic NaOH and 35 ml. of chloride free Acetone to a 200 ml. Berzelius beaker, stir for five (5) minutes at 40°C ± 1°C in a water bath. Add 0.5 ml. of (50-50) dilute Sulfuric Acid and 65 ml. of additional chloride free Acetone. Titrate with 0.005N Silver Nitrate to obtain the systems and reagent blank in milliliters.

19. The Pyranol blank shall consist of the initial free chlorides on the initial Pyranol as received material as outlined in General Electric Test Method E4C41C.

20. The value obtained after the reagent and free Cl^- blanks have been subtracted shall be recorded as the gross thermal-chemical chlorides in parts per million.

21. To obtain the thermal expression of the increase in chlorides, brought about by the 240°C stress, the chemical portion of the "dechlorination" value (G.E. Test Method E4C48-S1) shall be subtracted from the gross value obtained in Step #20.

22. The thermal expression shall be recorded on a flow sheet (chart) so that trends can be determined.

23. The control limits will be the two sigma (σ) deviation from the ($\bar{x}$). New (σ) sigma limits will be calculated every fifty-two (52) samples.

24. Individual values falling outside the control limits (2σ) will require a second determination being made.

25. If the second value does not fall within the two sigma (2σ) control limits the material will not be released without the supervisor's approval.

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Calculations

$$\text{Gross Thermal Chemical } Cl^- \text{ ppm} = \frac{(\text{net volume of } AgNO_3 \times N \times 35.46 \times 10^3)}{\text{Sample net in grams}}$$

$$\text{Minus} \quad \left(\frac{\text{Free } Cl^- \text{ (GE E4C41C) + Reagent blank } Cl^-}{}\right)$$

Net Thermal Cl^- ppm = Gross Thermal Chemical Cl^- - Chemical (dechlorination) Cl^- in p

Report

The report shall include Lot #, Tank Car #, Date Received, Gross Thermal Chemical Cl^-, and Thermal Cl^-.

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