BOORUM & PEASE

MONSANTO CHEMICAL COMPANY

Anniston, Alabama
Plant Laboratory

STANDARD ANALYTICAL METHOD

Method No. 039

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Product	AROCLORS	5/23/61	1 OF 4
		WRITTEN BY	APPROVED BY
Test	THERMAL-CHEMICAL STABILITY TEST	W.W.K.	W.W.K.

This Method ☐ Supersedes ☒ Revises Instructions Issued On 4/27/61

BOORUM & PEASE "NOTEBOOK" (R)

SCOPE

This method describes the procedure for measuring Thermal-Chemical Stability of Aroclors. The sample is exposed to heat in a sealed ampoule followed by chemical exposure to alcoholic sodium hydroxide and the resulting chlorides determined potentiometrically.

EQUIPMENT

1. 32 mm Pyrex tubing - This tubing is used for making ampoules for test. The tube is sealed off at one end and drawn to ca. 8 mm diameter at the other end at a point approximately 120-130 mm from the sealed end. Ampoules are thoroughly washed with 10% HNO_3, distilled water, and AR grade Acetone and dried before use.
2. Blue M Oven, Model OV-580C.
3. 50-ml glass syringe. Clean thoroughly with AR grade Acetone and dry.
4. 13 ga. x 3-1/2" hypodermic needles. Clean same as syringe
5. Support for ampoules while in oven and while drying.
6. 200-ml tall form beakers (Berzelius type).
7. Magnetic stirrer.
8. Teflon covered magnetic stirring bar 1" long. This bar should be cylindrical and of one piece molded construction.
9. Microburet graduated in 0.01 ml subdivisions.
10. Silver billet electrode (Beckman Cat. No. 39261).
11. L & N glass electrode (Cat. No. 1199-30).
12. L & N pH assembly (Cat. No. 7664-A1).
13. Crystallizing dish 75 x 150 mm - to be used as water bath.

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14. Usual laboratory glassware.

REAGENTS

1. Methanol (chloride free) - 5 liters of methanol are refluxed with 0.5 g Analytical Reagent Grade $AgNO_3$ for 1/2 hour. The methanol is then distilled from the $AgNO_3$, discarding the first 100 ml. to flush the apparatus. 90% of the charge is distilled from the flask and the contents of the flask are discarded. The methanol should be checked to assure purity by titration. The chloride ion concentration should be less than 0.02 ml. of 0.0025N $AgNO_3$ per 100 ml. of methanol.

2. Sodium Hydroxide Reagent - Analytical Reagent Grade NaOH is used to prepare this reagent. A 0.1N solution is prepared by dissolving 4.0 grams of analytical reagent grade NaOH in 1 liter of chloride free methanol. (For Anniston, 8.0 g. of 50% plant NaOH may be used).

3. Sulfuric acid - Prepared by a 50:50 volumetric dilution of Analytical Reagent grade concentrated sulfuric acid with chloride free distilled water. The acid is always poured into the water with constant stirring to prevent any dangerous build-up of heat.

4. 0.0025N $AgNO_3$. Dissolve exactly 0.4247g. of AR grade $AgNO_3$ in 1 liter of chloride free distilled water containing 3.0 ml of concentrated HNO_3. This solution should be standardized against a pure chloride standard. A sodium chloride crystal such as used in infrared spectrophotometer cells is a good source of pure NaCl. Store $AgNO_3$ in a dark bottle.

5. Acetone (chloride free) - Prepared by distillation from $AgNO_3$ as described above, for methanol and should also be checked by potentiometric titration to assure optimum purity. Normally a chloride content of less than 0.02 ml of 0.0025N $AgNO_3$ per 100 ml. is derived by this method. (Note: If the solvent per se gives no greater titration volume than 0.02 ml, then the distillation need not be carried out).

SAFETY

Aroclors are irritating to the skin. The vapors of hot materials are irritating to the eyes and upper respiratory system. If accidental contact is made with the eyes, flush immediately with large quantities of water for at least 15 minutes and get immediate medical attention. This test is carried out at elevated temperatures. Be very careful of thermal burns. Also, on occasion, ampoules have broken when unstable material is in them. When removing the ampoules from the oven after testing, a face shield must be worn in case of violent breakage.

DETERMINATION

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This test must be run in duplicate

1. Remove a clean, dry ampoule from the drying oven.

2. Place it in a suitable holder and weigh on a beam balance to the nearest 0.1 g.

3. Add ca. 40 ml of Aroclor to a clean dry 50-ml syringe.

4. Without touching the side of the ampoule neck, carefully slip the needle inside the ampoule.

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5. Add 50 ± 1.0g. of Aroclor and re-weigh accurately. Record the weight.

6. Carefully withdraw the needle so as to not wet the ampoule neck.
Note: If any Aroclor gets on neck, discard ampoule and start over.

7. Using an oxygen-gas flame, seal off the neck of the ampoule. Extreme care must be taken not to expose the Aroclor to over heating. Also, care must be taken so that the glass is never heated to white heat during the sealing because this yields light so intense that the radiation might be detrimental to the Aroclor.

8. Place the two ampoules in the support and put in the oven regulated to 240 ± 2°C.

9. Leave in the oven for 2 hours ± 2 minutes. Note: Do not open oven during this period.

10. When the ampoule is removed, allow it to cool to room temperature. For 1254, cool only to 50 or 60°C.

11. The ampoule is opened by scratching with a file and striking the neck sharply with a spatula blade.

12. Pour the contents into a 200-ml beaker.

13. Rinse the ampoule with 10 ml of chloride free Acetone. (If 1254 is transferred at 50 to 60°C., cool this solution to R.T. before proceeding).

14. By pipet, add 25.0 ml of methanolic-NaOH.

15. Add 25 ml of chloride free Acetone.

16. Using a pair of clean tongs add a stirring bar to the beaker. (DO NOT TOUCH BAR WITH HANDS).

17. Cover the beaker with a watch glass.

18. Place beaker in the water bath containing ca. 1-1/4" of water at 40°C. ± 1°C.

19. Stir the sample as fast as possible without pronounced splashing for 5 ± 0.5 minutes.

20. Remove beaker from water bath and add 0.5 ml of 1-1 H_2SO_4. DSW 331763

21. By graduate add 65 ml of chloride free Acetone.

22. The sample is titrated potentiometrically with 0.0025 N $AgNO_3$ to the biggest break using a silver-glass electrode system.

Note: Normal samples require extremely small amounts of $AgNO_3$. For this reason the titration is run using 0.01 ml additions and allowing sufficient time for equilibrium to be established before recording the emf change. If a change of 1 mv or less is observed per 0.01 ml increment for 3 or 4 additions, then increase the additions to about 0.05 ml until a larger change is observed. Then proceed with 0.01 ml additions.

23. Run a reagent blank as follows:

a. 25 ml alcoholic NaOH
b. 35 ml Acetone
c. Stir 5 minutes @ 40 ± 1°C.
d. 0.5 ml 1-1 H_2SO_4
e. 65 ml Acetone
f. Titrate as in Step 22.

CALCULATIONS

$$\text{Gross ppm Cl} = \frac{(\text{ml } AgNO_3 \text{ Step 22} - \text{ml blk Step 23}) \times 0.0025 \times 35460}{\text{sple. wt.}}$$

Thermal-Chemical Chlorides = gross ppm Cl - Free ppm Cl*

Item C = Thermal-Chemical Chlorides - Hydrolysis Stability Chlorides **

Report both Thermal-Chemical Chlorides and Item C to the nearest 0.01 ppm. If duplicates, do not check within 0.10 ppm, re-run.

* Free chlorides are determined in Method 014

** Hydrolysis Stability Chlorides are determined in Method 010

DISCUSSION

Temperatures and times are very critical in this test. The temperature at which this test is run (240°C.) is very near the point where decomposition takes an almost vertical swing up. Therefore, the oven used in this test must be very precise and accurate.

This Thermal-Chemical test gives a combined thermal and chemical stability. "Item C", the difference between T-C and HST Cl^- can be interpreted as an expression of thermal stability.

REFERENCE

1. General Electric Report CLTM No. 48, Thermal Chemical Stability Test for Incoming Shipments of 1499 Pyranol, by J. F. Tracy, dated 4/27/61.

2. P. G. Benignus' memo to W. W. Klemme on 4/6/61.

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