WGK 146

MONSANTO CHEMICAL COMPANY
W. G. KRUMMRICH PLANT LABORATORY

STANDARD ANALYTICAL METHOD

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2/11/65	1 OF 6	12,722
WRITTEN BY: JJL	APPROVED BY: DCA	
ATTACHMENTS: WGK Method No. 12,741, Drawing Nos. 229 & 305		

PRODUCT: Aroclors

TEST: Thermal-Chemical Stability Test

THIS FORM ☐ SUPERSEDES METHOD _____ ISSUED ON 3/16/62
☒ REVISES INSTRUCTIONS

SCOPE

This method describes the procedure for determining the combined chemically and thermally unstable chlorides in chlorinated biphenyls. Sealed ampoules of the sample are exposed to heat under controlled conditions. The samples are then hydrolyzed by alcoholic NaOH. The resulting chlorides are finally titrated potentiometrically with standard silver nitrate solution.

EQUIPMENT

a. 32 mm. pyrex tubing - Kimball Glass Co., Toledo, Ohio, Cat. No. 46470, or equivalent.

This is used to make the ampoules. The tube is sealed on one end and drawn to a radius of 7-10 mm. at a point 150-200 mm. from the sealed end. Glass walls near the ampoule tip should be as thin as possible. (Refer to Drawing No. 229) These ampoules are washed with cleaning solution, then with a 10% nitric acid solution, followed by alternate rinses of distilled water and acetone. The final rinse should be an acetone rinse. The ampoules are dried in an oven at 240°C. for 4 hours immediately prior to using.

b. Oven - Blue M Electric Co., Blue Island, Illinois, Model No. OU580C - with a 1" hole drilled in the left side 10 inches back from the front and 12-1/2 inches up from the base. A stopper and thermometer are placed in this opening.

c. Thermometer, -5 to 360°C. range, - Fisher Scientific Co., St. Louis, Mo., Cat. No. 15-005, standardized at 240°C.

d. Micro buret, 1 ml. with 0.01 ml. divisions - Fisher Cat. No. 20-110, or equivalent.

e. pH meter - Leeds and Northrup Cat. No. 7664, or equivalent.

f. Silver billet electrode - Beckman Part No. 39261, or equivalent.

g. Glass electrode - Fisher Cat. No. 11-505-75, or equivalent.

h. Berzelius beaker, 200 ml. tall form, Fisher Cat. No. 2-546, or equivalent.

i. Funnel, pyrex long stem, modified. Refer to Drawing No. 305.

j. Usual laboratory apparatus.

REAGENTS

a. 0.1 N methanolic sodium hydroxide.

1. Sodium hydroxide - Fisher Scientific Cat. No. S-315.

2. Methanol - Union Carbide Co., St. Louis, Mo.

Dissolve 4.0 g. of sodium hydroxide in 500 ml. methanol in a 1 liter volumetric flask (The methanol should have a blank titration of not more than 0.05 ml. of 0.0025 N $AgNO_3$ per 100 ml. of methanol). Dilute to volume with methanol.

b. Sulfuric acid, AR grade, Mallinckrodt Cat. No. 2876, or equivalent.

Diluted 1:1 with distilled water.

NOTE: Pour the acid into the water.

c. Silver nitrate, AR, Mallinckrodt Chemical Co., St. Louis, Mo., Cat. No. 2169, or equivalent. 0.1 N solution, standardized.

Dissolve 17.00 g. $AgNO_3$ in distilled water and dilute to 1 liter. Standardize against Primary Standard NaCl using a silver wire/mercurous sulfate electrode system.

d. Silver nitrate solution 0.0025 N.

Dilute 25.0 ml. standardized 0.1 N $AgNO_3$ to one liter with distilled water. Store in a dark glass container.

N = 0.025 x N of $AgNO_3$ used.

e. Acetone, Mallinckrodt Cat. No. 2440, or equivalent.

A blank determination of 100 ml. acetone must not exceed 0.10 ml. 0.0025 N $AgNO_3$.

SAFETY

Aroclors are irritating to the skin. The vapors of the 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 and get immediate medical attention. Methanol and acetone are highly flammable and normal precautions must be used when handling these reagents. Never use them around flames or spark-producing equipment.

This test is carried out at elevated temperatures. Be careful of thermal burns. A face shield should be worn when removing the ampoules from the oven for protection from possible breakage of the ampoule.

DETERMINATION

NOTE: All equipment used in this test must be chloride free. See Discussion.

1. Place a freshly cleaned, dry ampoule in a suitable holder on a beam balance.
2. Weigh to the nearest 0.1 g. and record the weight.
3. Place the modified funnel (see attached Drawing No. 305) in the ampoule. The tip of the funnel should extend into the main body area of the ampoule. The funnel should be supported in an iron ring on a ring stand.
4. Pour about 75 ml. of sample into a clean, dry 200 ml. beaker.
5. Carefully pour 50 $\pm$ 2 g. of sample through the funnel into the ampoule.
6. Allow the funnel to drain. Tapping the top of the funnel slightly may aid in removing the last drop from the funnel tip.
7. Carefully remove the funnel by gliding the bulbous end near the tip up the side of the neck of the ampoule. As the bulbous section nears the top of the ampoule, position the funnel tip in the center of the ampoule neck and complete the funnel removal in a smooth manner.

NOTE: If any sample drips from the funnel onto the neck of the ampoule, or if the funnel tip touches the neck of the ampoule while the funnel is being removed, discard the ampoule and start over.

8. Weigh the ampoule and sample to the nearest 0.1 g. on the beam balance and record the weight.

9. Seal the ampoule by using an oxygen-gas flame and pulling off a section 2" from the ampoule tip with a clean tweezers. Be careful not to expose the sample to overheating. Do not heat the glass to white heat. Radiation is detrimental to the sample. Do not allow combustion gases to enter the ampoule.

IMPORTANT: A very small torch flame must be used and the sealing accomplished very rapidly.

10. Place the ampoules in the support and put in the oven which has been previously heated and regulated at 240 $\pm$ 2°C. Do not open oven after the samples are introduced until the required time has elapsed.

11. After the ampoules have been in the oven for 2 hours $\pm$ 2 min., remove them and allow them to cool to room temperature. Wear a face shield when removing the ampoules.

NOTE: Allow the Aroclor 1254 to cool to 50-60°C.

12. Cover the ampoule with a rag and break off the neck by striking it sharply with a spatula blade.

13. Pour the contents into a chloride free 200 ml. beaker.

14. Rinse the ampoule into the beaker with 10 ml. of acetone.

15. Add 25 ml. of acetone to the beaker.

NOTE: When analyzing 1254 Aroclor, rinse ampoule with second 25 ml. portion and combine it with the 10 ml. wash. Do not add additional 25 ml. acetone to the beaker. Total acetone volume should be 35 ml.

16. Pipet 25 ml. of methanolic NaOH into the beaker.

17. Introduce a clean stirring bar by using a chloride free tongs. Do Not touch it with the hands.

18. Cover the beaker with clean aluminum foil and immerse in a water bath at 40 $\pm$ 1°C.

19. Place the water bath on the stirrer and stir the solution for 5 min., as fast as possible without splashing.

20. Remove the beaker from the bath and add 0.5 ml. 1:1 H_2SO_4.

21. Add 65 ml. acetone with a chloride free graduated cylinder.

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22. Titrate the sample potentiometrically with 0.0025 N $AgNO_3$ in 0.01 ml. additions from the micro buret. The endpoint is the point of maximum change in potential for the 0.01 ml. addition when using the line operated L and N pH meter and silver-glass electrodes.

23. Run a reagent blank using 100 ml. acetone, 25 ml. methanolic NaOH, and 0.5 ml. 1:1 H_2SO_4. Titrate as in Step 22.

CALCULATION

Gross chlorides, ppm =

$$\frac{(\text{ml. } AgNO_3 \text{ Step 22} - \text{ml. } AgNO_3 \text{ Step 23}) \times 0.0025 \times 35460}{\text{Sample Weight}}$$

Thermal-chemical chlorides = gross chlorides - free chlorides*

*Free chlorides are determined by Method No. 12,741.

Report all results to the nearest 0.01 ppm.

If duplicates do not check within 0.1 ppm, repeat the analysis.

DISCUSSION

1. All equipment used in this test should be successively washed with cleaning solution, distilled water, 10% nitric acid solution, then rinsed with distilled water and acetone in that order. A portion of the distilled water wash should be tested with $AgNO_3$ solution in a dark room to determine, by Tyndall beam, if it is chloride free. If a beam forms in the water wash within 1 minute after the $AgNO_3$ is added, the washing procedure must be repeated. It should be continued until the equipment is chloride free as indicated by this test.

2. Times and temperatures are critical in this test, and it is necessary to take all precautions to follow this procedure rigorously.

3. Ampoule dimensions, wall thickness and sealing technique must be carefully controlled in order to get reproducible results.

4. All ampoules must be thoroughly cleaned and thoroughly dried before being used in this analysis.

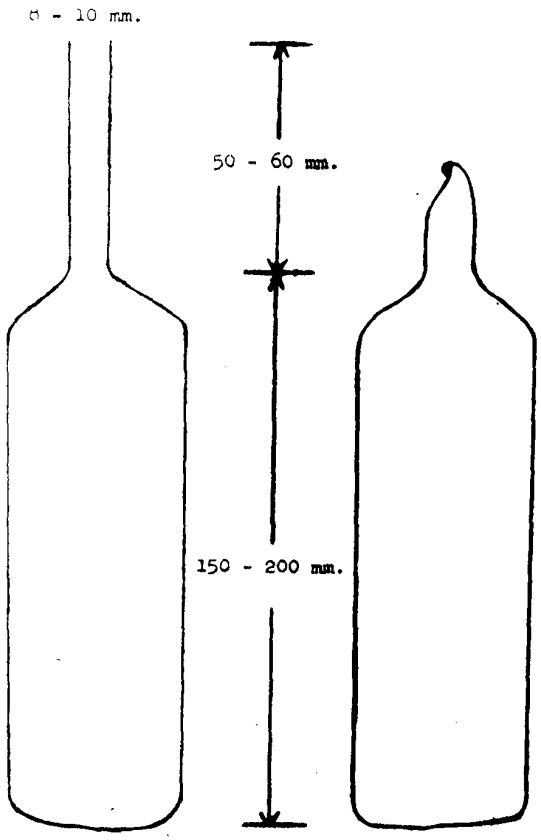
REFERENCE

1. W. W. Klemme's memo to P. G. Benignus, "Thermal-Chemical Stability Test", May 23, 1961.

2. Laboratory Notebook: 198, 3-5.

3. Anniston Method No. 039.

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DETAILS OF AMPOULES

Drawing No. 239

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