Monsanto Chemical Company

Anniston Method No. 14-53-48

SUBJECT: Water Content of Liquid Aroclors

METHOD: Titration with Karl Fischer Reagent

Outline

The Aroclor is dissolved in a mixture of benzene and methanol which has been titrated with Fischer reagent to the characteristic end point. Fischer reagent is a solution of iodine, sulfur dioxide, and pyridine. Iodine is consumed as long as any water is present. The solution is again titrated to obtain the water content introduced by the Aroclor.

Solutions and Apparatus

Karl Fischer Reagent: Weigh into a flask 264 grams of pyridine, Barrett 2-A or Eastman 214-H, and add 61 grams of liquid or gaseous sulfur dioxide. Add the liquid sulfur dioxide directly from the inverted cylinder by attaching to the outlet valve a glass tube extending into the pyridine. Sulfur dioxide gas can be bubbled into the pyridine until proper amount is added. Store in a glass stoppered bottle.

Transfer 65.6 grams of the pyridine-SO^2 mixture and 134 ml of absolute methanol to a 1 liter Florence flask. Cool thoroughly in an ice water bath. Add 16.9 grams of iodine, stopper, cool again before shaking. Alternately cool and swirl until the iodine is in solution. Makes 200 ml of reagent. Store in glass stoppered bottle. Let stand 24 hours before using. When fresh, one ml of reagent is equivalent to about 0.0033 gms. of water.

Aroclor Solvent: Mix 2 parts dry benzol with 1 part anhydrous methanol. The dry benzol is prepared by shaking the commercial grade with anhydrous calcium chloride, decanting into a flask and distilling, rejecting the first 10% to come over. Keep in glass stoppered bottles with minimum exposure to air.

Micro Buret: 10 ml. x 0.05 ml. Koch automatic with glass stoppered reservoir. Eck and Krebs #2460. Equip reservoir with a moisture guard tube containing Drierite or a similar dehydrating agent.

Procedure

Heat a clean 500 ml. narrow mouth Erlenmeyer flask in an oven or on hot plate until thoroughly dry. Sweep out for 10 minutes or until cool with air which has been thoroughly dried by passing thru tubes containing 8 mesh Drierite. Disengage the flask from the aspirating train and immediately close with a paper cap held by a rubber band.

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Without delay, transfer 100 ml. of the benzene-methanol solvent to the flask thru a small hole punctured into the paper cap. Cover again with paper. Titrate at once with Karl Fischer reagent to distinct red-brown end point which does not fade after swirling several times. The Fischer reagent is dispensed from the microburet the tip of which projects into the flask thru the puncture in the paper cap. At the end point any water content of the solvent has been reacted. Superimpose a fresh paper cap immediately.

Obtain weight of the solvent and well-covered flask on a Torsion balance or equivalent. Quickly introduce with a dry pipette about 100 grams of the slightly warmed Aroclor to be tested. Cover at once and weigh again to obtain the weight of Aroclor to nearest gram. Shake until the Aroclor is dissolved.

If the mixture is cloudy, warm slightly. If cloudiness persists another mixture should be prepared.

Puncture a small hole in the paper cap for the insertion of the buret tip and titrate with Fischer reagent to the first definite brown color, agitating with a gentle swirling motion. The end point should persist through several swirls. The end point may slowly fade through slow access of atmospheric moisture in which case it is restored by a drop or two of reagent. If not so restored, the end point may have been a false one or the closure is faulty. A definite end point is impossible if humid air is not well excluded.

From the amount of reagent required and the weight of Aroclor used, calculate the water content in p.p.m.

Calibration of Fischer Reagent and Standard Water Solution

Standard water solution in methanol: Transfer exactly 0.40 ml. of water from a micro buret or a 1 ml. measuring pipet to a 100 ml. volumetric flask. Fill to the mark at once with anhydrous methanol and mix. One ml. of solution then contains 4000 micrograms of water in addition to any water which may be present in the methanol.

Transfer exactly 5 ml. of the above standard water solution (equivalent to 0.02 grams of water) to a 250 ml. Erlenmeyer flask which has been dried and swept with dry air. Close with paper cap and titrate with Fischer reagent in the same manner as the sample. The end point is sharp. A methanol blank, found by titrating 5 ml. of the methanol used in making up the standard water solution to a like end point, must always be subtracted from this titration.

Divide the amount of water taken by the net Fischer reagent required to obtain the titer of the Fischer reagent in terms of water.

Example: A 5 ml. aliquot of standard solution, equivalent to 20,000 micrograms of water, required 6.61 ml. of Fischer reagent while 5 ml.

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of the methanol required 0.55 of Fischer reagent.

$$20{,}000/(6.61 - 0.55) = 20{,}000/6.06$$
$$= 3300 \text{ micrograms water/ml.}$$

Recalibrations: Because the Fischer reagent deteriorates rapidly, its titer must be determined for each days use. If the same standard water solution is used in recalibration as in the initial calibration, the titer of the Fischer reagent must be calculated from its total water content (including that introduced by the methanol). The total water is the product of the initial gross titration and its titer. This in the example above the total water content of a 5 ml. aliquot is 6.61 X 3300 = 21813 micrograms. If on recalibration 7.37 ml. of Fischer reagent is 21813/7.37 = 2960 micrograms of water per ml.

Two or more calibrations should be made with agreement within 0.025 ml.

Calculation of H_2O sample

Standardization of Standard H_2O sol.

Titrate 5 ml. mixture H_2O sol.
Titrate 5 ml. of methanol
Tit of 5 ml. mixture = A
Tit of 5 ml. methanol = B

A - B = ml. reagent for H_2O added = 5/100 of .4
Divide 5/100 X .4 by A - B = factor grams of H_2O/ml.
Multiply factor X B giving gms. of H_2O in 5 ml. of methanol.
Add this wt. of H_2O to .02 already added giving H_2O in 5 ml. (Total)

$$\frac{\text{Factor}}{H_2O \text{ St'd Titration}} = T_1$$

T_1 X sample Titration = T_2

$$\frac{T_2 \text{ X } 1{,}000{,}000}{\text{wt. sample}} = \text{ppm } H_2O$$

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