DIRECTIONS FOR TEST NO. 14-13-34

SUBJECT: Total Chlorine In Aroclors

METHOD: Peroxide Fusion # $AgNO_3$ titration

REFERENCE: Breamish, Determination of Organic Halogens, I. & E. C., Anal. Ed. 6, 5, 352 (1934).

Chlorine in Aroclors may be determined by fusion of the sample with sodium peroxide in a Burgess-Parr fusion cup, extracting the fusion with water, acidifying the water extract with nitric acid, and precipitating the chlorine by addition of an excess of silver nitrate. After filtration, the excess of silver nitrate is determined by titration against potassium thiocyanate, using ferric ammonium sulfate as indicator.

Apparatus

The fusion cup used is the Burgess-Parr Sulfur Bomb No. 3 for flame ignition. A lead gasket is used. For ignition, the bomb is suspended through a 1-3/16" round hole in a 1/8" transite plate. This allows the fusion cup to extend through the plate for about 5/8inch. Ignition is effected by strongly heating the bottom of the fusion cup with the full flame of a Meker burner for two minutes.

Charge for Fusion

The fusion mixture is made up of about 15 grams (one metal scoop) of sodium peroxide and 0.0 to 0.3 grams of finely powdered cane sugar, the amount of cane sugar depending upon the weight of carbon contained in the sample. The reagents should be free from chlorine, or a blank run and corrected accordingly. The fusion mixture is well mixed by placing the ingredients in a small bottle with rubber stopper and shaking vigorously.

SOLID AROCLORS: The non crystalline type are weighed in the form of small pellets. These are prepared by heating the Aroclor until such a consistency is reached as will permit dropping it from a glass stirring rod onto a tinned surface (a can top), each drop forming a pellet. When cool these pellets can be removed from the surface by inserting a spatula under them. .4 grams are used. The pellets are brushed into the bottom of the fusion cup and the fusion mixture placed on top of them. After tightening the li the charge is ready for fusion.

DSW 330753

DIRECTIONS FOR TEST NO. 14-13-34

SUBJECT: Total Chlorine in Aroclors

METHOD: Peroxide Fusion : $AgNO_3$ titration

REFERENCE: Breamish, Determination of Organic Halogens, I. & E. C., Anal. Ed. 6, 5, 352 (1934).

The crystalline type are weighed in the powdered form. .4 grams being used. They are charged in the same manner as the non-crystalline type.

LIQUID AROCLORS: .20 to .30 grams are weighed by dropping from a stirring rod onto a piece of thin hemispherically shaped glass, which has been just previously tared, and which remains on the balance. It is necessary to heat the more viscous aroclors to "dropping" consistency. The piece of glass then easily slides off the balance pan into the fusion cup.

The following quantities of sample, sugar, and $AgNO_3$ are used for the respective chlorine contents:-

Cl Content	Weight of Sample	Amount Sugar	$AgNO_3$
0.% - 30%	.18 - .20 Grams	0.0	50 cc
30% - 45%	.28 - .30 Grams	.15 g. (1/2 scoop)	50 cc
45% - 58%	.28 - .30 Grams	.30 g.(1 scoop)	50 cc
58% - 66%	.40 - .41 grams	.30 g. "	75 cc
66% - 70%	.40 - .41 Grams	.30 g. "	100 cc

Procedure

Place the fusion cup, which contains the prepared sample and fusion mixture, in the transite ignition plate and apply the full flame of the Meker burner to the bottom of the fusion cup for 2 minutes.

(CAUTION: Do not stand too near the fusion during ignitic

Then remove the flame and cool under the tap. When cool remove screw cap. Thoroughly rinse the cup cover with water, collecting the rinsings in a clean 400 cc beaker.

Then place the fusion cup on its side in the beaker and cover with a watch glass. 50 - 75 cc will be in the beaker from rinsing the cap, and this is sufficient to decompose the charge. Remove the cup and rinse well. When decomposition is complete, rinse off cover-glass and add pure

STLCOPCB4077398

DIRECTIONS FOR TEST NO. 14-13-34

SUBJECT: Total Chlorine In Aroclors

METHOD: Peroxide Fusion ; $AgNO_3$ titration.

HNO_3, with stirring, until acid is present in excess to the extent of about 10 cc. (About 50 cc of acid are required.)

Add exactly 50, 75 or 100 cc of standard silver nitrate solution from a pipette (depending upon chlorine present) and stir to effect coagulation of the silver nitrate precipitate Filter with suction through an asbestos pad on a 1-1/2" perforated porcelain plate and wash beaker and filter 4 time with small portions of cold water. Allow the filter to drai completely between washings. Transfer the filtrate back int the 400 cc beaker and rinse the flask twice, adding the rinsings to the beaker.

Add 5 cc of ferric iron indicator to the solution and titrat with standard KCNS solution until a distinct pink tint is just obtained.

Calculation of Chlorine Content

Subtract thevolume of KCNS required from the volume of KCNS required to titrate the amount of standard $AgNO_3$ solution used. This will give the volume of KCNS equivalent to the chlorine in the sample. Multiply the volume so obtained by the chlorine value of each cc of KCNS and divide by the weight of sample taken.

For example: If 50 cc of silver nitrate solution is equivalent to 61.4 cc of KCNS solution and the value of 1 cc of KCNS solution is .003770 gram Cl; then if it is found that 0.3 gram of sample shows a KCNS titration of 10.4 cc the percent of chlorine is:

$$\frac{(61.4 - 10.4) \times .003770 \times 100}{.3} = 64.09\% \text{ Cl}$$

In case the fusion mixture or other reagents contain chlori the amount must be determined and deducted from the chlorin found.

STLCOPCB4077399

DIRECTIONS FOR TEST NO. 14-13-34

SUBJECT: Total Chlorine In Aroclors

METHOD: Peroxide Fusion : $AgNO_3$ titration.

Page No. 4

373.6

Solutions Required

Standard $AgNO_3$ solution: About 0.10 N; dissolve 19.6 grams of silver nitrate in each liter of water. Protect the solution from light. Fifty cc of this solution will precipitate by theory 0.175 gram of chlorine.

Standard KCNS solution: About 0.08 N; dissolve 8 grams of KCNS in 1 liter of water. 1 cc = about .003 gram chlori

Ferric Iron Indicator: Use a saturated solution of ferric ammonium alum.

Pure Nitric Acid, 70%: Stock acid suffices provided it is colorless. It can be boiled in a beaker until colorless if necessary.

Standardization of Solutions

Weigh 0.3 and 0.15 gram portions of pure dry NaCl into separate 600 cc beakers. Add 250 cc of distilled water to each and 10 cc of pure 50% nitric acid. When solution is complete, add 50 cc of standard $AgNO_3$ solution from pipette Stir well and filter through an asbestos mat on a perforate porcelain plate, using suction. Wash filter and transfer the filtrate back to the beaker in the same manner as when working with a sample. Titrate the filtrates with standard KCNS solution, using ferric iron indicator.

The value of 50 cc of $AgNO_3$ solution in terms of KCNS solution is found by subtracting the cc of KCNS solution in titrating the 0.3 gram of NaCl from twice the number of cc. of KCNS solution used in titrating the 0.15 gram of NaCl.

This value is checked by titrating 50 cc of $AgNO_3$ solution added to 400 cc of water and 10 cc of pure 50% HNO_3 with KCNS solution. This titration should agree very closely (± 0.1 cc.) with the value found from the titrations of NaCl. The titration must be made slowly to avoid drainage error.

DSW 330756

STLCOPCB4077400

DIRECTIONS FOR TEST NO. 14-13-34

SUBJECT: Total Chlorine In Aroclors

METHOD: Peroxide Fusion $AgNO_3$ titration

Page No. 5

Since pure NaCl contains 60.66% Cl by theory, the value of the KCNS in terms of chlorine may be found by dividing the weight of chlorine in the NaCl taken by the cc of KCNS equivalent to the silver nitrate required.

Example:

Two 0.3 gram portions of NaCl show KCNS titrations of 13.11 and 13.13 cc.

Two 0.15 gram portions of NaCl show KCNS titrations of 37.28 and 37.24 cc.

The KCNS equivalent to 50 cc of $AgNO_3$ is then (37.28 + 37.24) - 13.12 or 61.4 cc.

By titration of 50 cc of $AgNO_3$ against KCNS solution, it is found that 61.36 cc are required. This agrees within .04 cc of the value obtained from the NaCl titrations.

The chlorine value of the KCNS is then, .6066 x .3 divided by 61.4 - 13.12 or .003770 grams Cl per cc of KCNS.

The chlorine value may also be calculated from the titration of 0.15 gram of NaCl. 0.6066 x .15 divided by 61.4 - 37.26 gives .003770 grams Cl per cc of KCNS.

Notes

1 - The fusion materials have explosive properties if wrongly handled; consequently care must be taken to use safe proportions, to secure a good mixture free of large lumps, and to properly seat the cover of the fusion cup. The fusion mixture must be kept away from water or moist air, either of which may ignite the charge. The fusion mixture should not be ground to reduce lumps.

2 - The method as described is not applicable to volatile organic compounds unless precautions are taken to avoid loss of sample during weighing.

3 - On account of the high chlorine content of many of the Aroclors and the small amount of sample taken, great accuracy is required in weighing, transfer, and mixing of the sample. The pupette and burette for measuring the standard solutions must be very clean to avoid drainage errors.

DSW 330757

STLCOPCB4077401

DIRECTIONS FOR TEST NO. 14/13/34

SUBJECT: Total Chlorine In Aroclors

METHOD: Peroxide Fusion : $AgNO_3$ titration

4 - Fusions which show black carbon deposites on the cover and side of the fusion cup may or may not give the full chlorine content. If a carbon deposit is found, a second fusion should be made using a smaller sample or reducing the amount of sugar in the charge or both.

5 - Mixing the fusion charge by shaking after the screw cap has been drawn down may lead to incomplete fusions. The mixing of the sample with the fusion mixture should be done in such a way that the sample is fully covered with the mixture.

6 - The temperature at which the standard solutions are standardized should be noted. In case room temperatures vary from this temperature, appropriate volume corrections should be made.

7 - The fusion mixture materials should be essentially free of chlorine. The chlorine content may be determined by making a blank fusion, that is, without addition of sample, and titrating in the usual way. Five cc of $AgNO_3$ may be added instead of 50 cc. The KCNS titration is then compared with titrations of 5 cc portions of $AgNO_3$ solution in like volumes of solution and nitric acid.

Copied/hp
10/15/34

DSW 330758

STLCOPCB4077402