☐ WGK 148

MONSANTO CHEMICAL COMPANY
W. G. KRUMMRICH PLANT LABORATORY

STANDARD ANALYTICAL METHOD

DATE ISSUED	PAGE	NUMBER
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WRITTEN BY	APPROVED BY
RFS	RFS

ATTACHMENTS: WGK Drawing 143

PRODUCT: General Method No. 4

TEST: Total Chlorine in Chloro-Organic Compounds

THIS FORM ☐ SUPERSEDES METHOD _____ ISSUED ON 8/12/54

THIS FORM ☒ REVISES INSTRUCTIONS

SCOPE

This method is used to determine total chlorine in organic compounds. The organic chloride is converted to sodium chloride by sodium peroxide fusion and determined by Volhard titration.

EQUIPMENT

a. Parr Peroxide Bomb assembly and accessories (Parr Instrument Co., Moline, Illinois)

1. Fusion cup, 22 ml. (Cat. No. 2AC)
2. Cup cover (Cat. No. A7AC5 or A7AC5N)
3. Body, for 22 ml. bomb (Cat. No. 6AC)
4. Screw cap, for 22 ml. body (Cat. No. 5AC2)
5. Rubber gasket (Cat. No. 27AC)
6. Wrench (Cat. No. 21AC)
7. Bench socket (Cat. No. A22AC2)
8. Peroxide dipper, 15 g. capacity (Cat. No. A34C4)
9. Ignition Housing (Cat. No. A90AC)

b. Safety shield - manufactured of transite (see attached drawing).

c. Ignition housing cover - a 6" x 6" heavy steel wire screen, such as B and S 10 ga. with 0.125 inch mesh opening.

d. Blast burner, operated on gas and air (Aloe Scientific Co., St. Louis, Cat. No. 20910) or equivalent.

e. Small metal dipper, to hold ca. 2 grams Na_2CO_3 (Anhy.).

f. Water bath.

g. Usual laboratory apparatus.

REAGENTS

a. Sodium Chloride, A.R. grade (Mallinckrodt Chemical Company), or equivalent.

DSW 551111

b. Silver nitrate, A.R. grade (Mallinckrodt Chemical Company), or equivalent.

c. Ammonium Thiocyanate, A.R. grade (Mallinckrodt Chemical Company), or equivalent.

d. Nitric acid, A.R. grade (Mallinckrodt Chemical Company), or equivalent.

e. Ferric Ammonium Sulfate, A.R. grade (Mallinckrodt Chemical Company), or equivalent.

f. Sodium Carbonate, A.R. grade, (Mallinckrodt Chemical Company), or equivalent.

g. Sucrose (table sugar is satisfactory).

h. Sodium Peroxide, Calorimetric Powder, Low Sulfur, A.R. grade (Mallinckrodt Chemical Company, Cat. No. 7865).

SOLUTIONS

a. 0.1 N $AgNO_3$ - Dissolve 17.0 grams $AgNO_3$ in water and dilute to 1-liter.

b. 0.1 N NH_4CNS - Dissolve 7.6 grams NH_4CNS in water and dilute to 1-liter.

c. Ferric Alum Indicator - Dissolve 100 grams $Fe(NH_4)(SO_4)_2 \cdot 12H_2O$ in 300 ml. distilled water. Add 50 ml. conc. HNO_3 and mix well.

STANDARDIZATION

Prepare Sodium Chloride, Primary Standard, by drying at 110°C. for 3 hours.

1. Weigh, on an analytical balance, to the nearest 0.0001 g., a 0.2200 - 0.2500 g. portion of the dried NaCl. Transfer to an 800-ml. beaker. Add ca. 200-ml. distilled water and 5 ml. conc. HNO_3. Add 40.00 ml. 0.1 N $AgNO_3$ and boil the mixture gently until the precipitate is coagulated. (About 15 min.) Cool to room temperature and back titrate the excess 0.1 N $AgNO_3$ with 0.1 N NH_4CNS using 2 ml. Ferric Alum indicator. Take the first permanent orange-pink color as the endpoint.

2. Similarly, titrate 40.00 ml. 0.1 N $AgNO_3$ vs. 0.1 N NH_4CNS omitting the sample and the boiling.

Calculations

$$\text{Ratio} = \frac{\text{ml. } AgNO_3 \text{ (Step 2)}}{\text{ml. } NH_4CNS \text{ (Step 2)}}$$

$$\approx NH_4CNS = \text{ml. } NH_4CNS \text{ (Step 1)} \times \text{Ratio}$$

$$\text{net ml. } AgNO_3 = \text{ml. } AgNO_3 \text{ (Step 1)} - \approx NH_4CNS$$

$$N\ AgNO_3 = \frac{\text{weight of NaCl}}{\text{net ml. } AgNO_3 \times 0.05845}$$

$$N\ NH_4CNS = \text{Ratio} \times N\ AgNO_3$$

SAFETY

Na_2O_2 is a highly reactive reagent. When mixed with water it reacts violently to form NaOH. If it comes in contact with paper or other combustibles, it may cause the combustible to ignite. Keep Na_2O_2 off your person and away from flammable materials. If accidental contact is made, immediately flush affected area with copious quantities of water.

During the fusion, dangerously high temperatures and pressures develop inside the bomb. Use only bombs which you have inspected and know are in good condition. Observe all precautions noted under DETERMINATION.

DETERMINATION

1. Carefully inspect the fusion cup to make sure there are no defects, such as, holes, cracks, etched interiors, bulged spots, etc. If defects are noted, discard the cup.

2. Remove the old gasket from the cup cover and wash both the cup and cover thoroughly with soap and water.

3. Rinse both pieces with distilled water and then acetone.

4. Heat in a 110°C. oven until thoroughly dry and cool in a desiccator.

5. Using the special dipper, add 2.0 grams Na_2CO_3 (anhydrous) to the fusion cup.

6. If instructed by the specific method, add the amount of sugar called for by that method.

7. Weigh, on an analytical balance, to the nearest 0.0001 gram, the bomb and its contents. Record the weight.

8. Add directly to the bomb, on the dry ingredients, the amount of sample as directed in the specific method.

CAUTION: Under no circumstances should the total organic content of the bomb exceed 1.0 grams. Amounts in excess of this are extremely dangerous. The sample itself should not contain more than trace amounts of water.

NOTE: Grind solid samples to pass through an U. S. Standard Sieve No. 60 prior to adding to the bomb.

9. Reweigh the bomb and contents on the same analytical balance to the nearest 0.0001 g. Record the weight.

NOTE: Some specific methods may call for the weighing of the sample by difference from a sealed weighing bottle. This is to prevent erroneous weights because volatile components of the sample are lost during open weighing.

10. Place a new rubber gasket in the bomb cover and add one scoop, 15 grams, of Na_2O_2 to the bomb. Brush any excess off the rim of the cup.

11. Put cover on the bomb and screw tightly into the body. Use the special Parr wrenches provided to tighten the body.

12. Mix the contents of the bomb thoroughly by shaking vigorously for 1 to 2 minutes. Invert the bomb frequently while shaking to insure good mixing. Pack the ingredients in the bottom of the bomb by tapping several times.

CAUTION: There is a possibility of the bomb igniting spontaneously during shaking. If it does, immediately drop it in the water bath and leave the area.

13. Place the bomb in the ignition housing directly centered over the hole. Place the wire screen cover over the housing.

14. Purge the shield with air by turning on the air to the burner full force. Allow to blow for 2 - 3 minutes to remove any gas which may have accumulated inside the shield.

15. Turn off the air; turn on the gas to the burner and light immediately.

CAUTION: If the burner does not light immediately, turn off the gas and purge the shield with air before again attempting to light the burner.

16. By adjusting the amount of air and gas admitted to the burner, regulate the flame until a fine needle of blue flame results which ends just below the bottom of the bomb.

17. Center the point of the flame directly under the bomb and heat the bomb to cherry redness. Allow to heat for exactly two minutes at cherry redness.

18. Turn off the burner, remove the bomb from the housing, invert, and strike sharply on the top 1 or 2 times.

19. Allow the bomb to cool in air for at least one minute, and immerse gradually in the water bath. DO NOT ALLOW THE WATER TO COVER THE BOMB.

20. When the bomb has reached room temperature, remove from the body and wash the outside of the bomb with distilled water.

21. Remove the bomb cover and place the bomb on its side in an 800 ml. beaker. Wash the cover into the beaker with a fine stream of water from a wash bottle. Be sure to wash off any of the fusion mass which might adhere to the cover.

CAUTION: If the fusion is incomplete, as indicated by the presence of unfused Na_2O_2, DO NOT attempt to dissolve the fusion mass. On rare occasions such imcomplete fusions have been known to flash. Place such a bomb in a sink and quench with copious amounts of water and start the analysis over.

22. Cover the beaker with a watch glass and add enough water around the edge of the watch glass to just cover the bomb.

23. If the reaction starts immediately, allow it to subside before proceeding. If it does not, heat gently until the reaction starts, and then remove until the vigorous reaction subsides.

24. Heat the solution to boiling and boil for 5 to 15 minutes to completely dissolve the fusion mass.

25. Remove from the heat, wash down the watch glass and the sides of the beaker with a fine stream of water from a wash bottle. Catch the washings in the beaker.

26. Remove the fusion cup from the beaker with a pair of clean, stainless steel tongs and wash both cup and tongs into the beaker thoroughly with water from the wash bottle.

27. With constant stirring, add conc. HNO_3 to the beaker to neutralize the excess caustic. Neutralize to litmus.

CAUTION: Add the HNO_3 in small increments. As neutralization is approached, the solution foams considerably. If the acid is added too fast, the solution may bubble over and the sample lost.

28. Add 5 ml. HNO_3 in excess and heat the solution to boiling.

29. Add 40.00 ml. 0.1 N $AgNO_3$ to the solution, unless otherwise directed, slowly and with constant stirring. Record the titer.

30. Boil the solution until the AgCl is coagulated and the supernatant liquid is clear (ca. 15 minutes).

31. Cool the solution to room temperature in a water bath.

32. Add 2 ml. ferric alum indicator and back titrate the excess $AgNO_3$ with 0.1 N NH_4CNS. The endpoint is reached in one drop of NH_4CNS causes a permanent orange-pink color to be imparted to the supernatant liquid.

NOTE: As the endpoint is approached, stir gently to avoid stirring up the precipitated AgCl. This will tend to obscure the endpoint.

33. Record the titer of 0.1 N NH_4CNS.

34. Make a blank determination on the reagents in exactly the same manner as the sample determination except omitting the sample. Use only 10.00 ml. 0.1 N $AgNO_3$ (Step 29).

CALCULATIONS

$$\text{milliequivalents (blank)} = [(\text{ml. } AgNO_3 \text{ (blank)} \times N) - (\text{ml. } NH_4CNS \text{ (blank)} \times N)]$$

$$\% \text{ Cl} = \frac{\{[(\text{ml. } AgNO_3 \text{ (sample)} \times N) - (\text{ml. } NH_4CNS \text{ (sample)} \times N)] - (\text{blank})\} \times 0.035457 \times 100}{\text{sample weight}}$$

Record the results to the nearest 0.1%.

DISCUSSION

The precision of this method is dependent on a number of variables. Among them are: amount of chlorine, volatility of the sample, ease of combustion of the sample, etc. Therefore, each specific method will contain the precision for that application.

Our experience has shown that we cannot determine macro amounts of chlorine accurately using 94% Ni bombs. We, therefore, use 36% Ni bombs exclusively for chlorine determinations. For chlorine in amounts less than 2%, we use the Parr Oxygen Bomb Technique.

The Parr Manual recommends that 0.5 g. organics be the maximum charge for the 22 ml. bomb. We have routinely used samples containing 1.0 g. organics in our laboratory without excessive bomb failure. However, we carefully inspect each bomb before fusion and discard any which show even the slightest evidence of excessive wear.

0.14 grams chlorine in a sample is maximum amount to be fused to provide sufficient back titration of 0.1 N $AgNO_3$ with 0.1 N NH_4CNS. If safety permits, the sample size should be chosen to contain between 0.10 and 0.14 g. chlorine.

The Parr Manual also directs that the reactants in the fusion cup should be mixed with a glass rod. Our experience has shown that this can be more dangerous, and produce no more reproducible results, than mixing by shaking. If spontaneous ignition takes place in the sealed bomb while shaking, it can be quickly detected by the heat. Disposal of the bomb in the water bath will quench any reaction should the bomb rupture.

Although the Parr Manual states that heating of the bomb should be stopped when it reaches redness, our experience has shown that poor fusions frequently result. When the fusions are held at redness for two minutes, we obtain consistently satisfactory results. We also obtain reasonable service lifetime from the bombs by limiting this period to exactly 2 minutes.

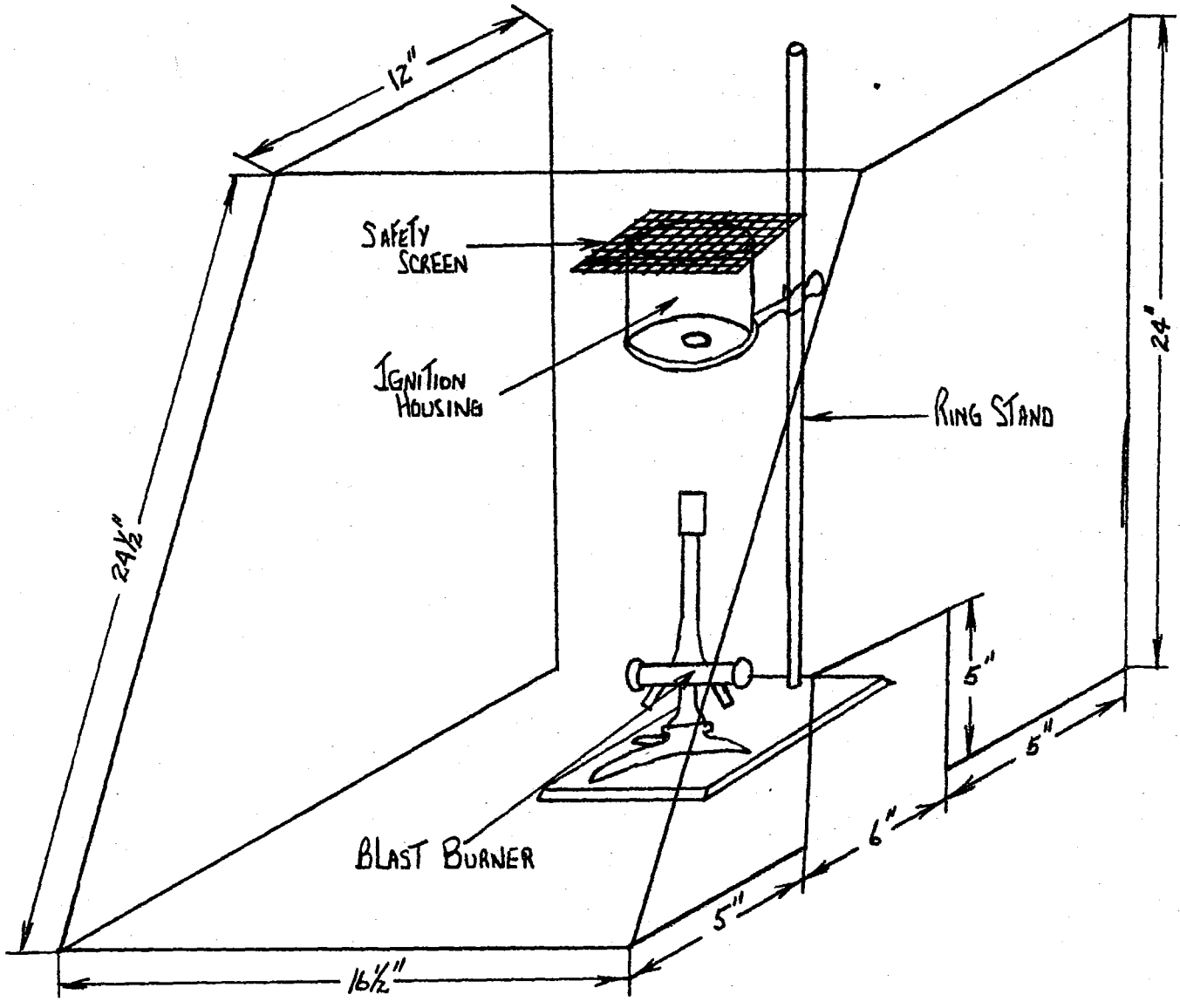
REFERENCES

a. Parr Instrument Company, "Peroxide Bomb Apparatus and Methods" Manual No. 121 (1954)

b. R. W. Sudhoff, "Determination of Chlorine in Organic Compounds Parr Bomb Method" (3/13/33), unpublished report, WGK Chief Chemists File.

c. S. M. Kulifay's memo to Vendette, 1/13/54, WGK Chief Chemists File.

IGNITION ASSEMBLY



SAFETY SHIELD

½" TRANSITE BOARD TOP BOTTOM AND BACK OPEN

DRAWING NO. 143

DSW 551118

STLCOPCB4089535