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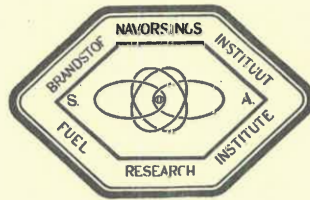
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VERSLAG No. ....

REPORT No. 27

VAN .....

OF 1951



U110/413

**BRANDSTOFNAVORSINGSINSTITUUT**  
**VAN SUID-AFRIKA.**

**FUEL RESEARCH INSTITUTE**  
**OF SOUTH AFRICA.**

**ONDERWERP:**  
**SUBJECT:** PREPARATION OF REAGENTS FOR USE IN GAS ANALYSIS

APPARATUS

**AFDELING:**  
**DIVISION:** CHEMISTRY

**NAAM VAN AMPTENAAR:**  
**NAME OF OFFICER:**

PREPARATION OF REAGENTS FOR USE IN GAS ANALYSIS APPARATUS.

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The absorption pipettes and combustion tubes are mounted on the apparatus in the following sequence, starting from the burette.

I. CARBON DIOXIDE ABSORBENT. 1, 2.

Potassium hydroxide solution, 40% by weight is used in a contact pipette. Due to the small amount of carbon dioxide present in normal air it is not necessary to protect the solution from contact with the atmosphere. The solution is filtered before using. 180 ml. of the solution can absorb approximately 6 litres carbon dioxide gas.

II. UNSATURATED HYDROCARBONS. (ILLUMINANTS)  
ABSORBENT. 3, 4.

Fuming sulphuric acid containing 20% to 25% free sulphur trioxide is used in a bubbler pipette. The reagent is protected from contact with the atmosphere by connecting the near compartment to a single pipette containing potassium hydroxide solution.

180 ml. of acid can absorb one litre of unsaturated hydrocarbon gas.

III. OXYGEN ABSORBENT. 5, 6.

Dissolve 100 gm. pyrogallol in 300 ml. of distilled water and store in a well stoppered bottle. Dissolve 3 kilogram potassium hydroxide in 2 litres of distilled water, filter and store in a rubber-stoppered bottle.

150 ml. of the potassium hydroxide solution is poured into a contact pipette and 30 ml. pyrogallol solution added.

The reagent is protected from contact with the atmosphere by slowly pouring liquid paraffin onto the reagent in the back compartment of the pipette.

Two pipettes filled with alkaline pyrogallol are used to determine oxygen. 180 ml. of the reagent can absorb approximately ten times its own volume of oxygen.

The solution must be freshly prepared to prevent carbon monoxide being evolved as the solution becomes saturated with oxygen.

#### IV. CARBON MONOXIDE ABSORBENT. 7, 8, 9.

Dissolve 96 gm. of sodium chloride in 450 ml. of distilled water. Add 13 gm. of cuprous chloride and stir until solution is complete. Add slowly and with constant stirring 500 ml. of concentrated hydrochloric acid. Transfer the solution to a 2 litre Erhlemeyer flask partially filled with copper wool or strip (which has been properly reduced), and close with a tight fitting stopper. The stopper is fitted with two glass tubes, one extending to the bottom of the flask, and the other just into the neck. The flask is flushed with nitrogen and allowed to stand until colourless (straw coloured).

In filling the pipettes (which are partially filled with copper wool) the solution is displaced by nitrogen to avoid oxidation. Two bubbler pipettes are used. The reagent is protected from contact with the atmosphere by liquid paraffin.

As soon as the solution in the first pipette shows the slightest change in colour it should be placed in the second position and a pipette containing fresh solution placed in the first.

The gas sample must be passed into the potassium hydroxide solution to remove acid vapours after carbon monoxide has been absorbed.

V. HYDROGEN COMBUSTION AGENT. (COPPER OXIDE WIRE).

10, 11.

C. p. copper oxide wire (-10 + 20 mesh) is used. The wire is heated in a furnace at 900°C for 3 to 4 hours.

The copper oxide is packed in a Pyrex U-tube. The tube can be heated electrically to at least 300°C. The combustion is best done at 270° ± 10°C.

The copper oxide must be regenerated by passing air over it at 300°C after each determination.

VI. HYDROCARBON COMBUSTION AGENT. (PRECIPITATED COPPER OXIDE).

305 gm. cupric nitrate trihydrate and 5 gm. ferric nitrate nonahydrate are dissolved in 3 litres of distilled water. A slight excess of 30% sodium hydroxide solution is added and the solution boiled for 20 minutes, allowed to cool and filtered. The excess alkali is then removed by washing with water and decantation. The precipitate is then filtered and the paste allowed to dry to a hard cake. It is then crushed to about 10 mesh size. The material is then completely reduced with hydrogen at 400°C, and thoroughly oxidised at the same temperature. This reduction and oxidation is done in a silica tube (½ inch diameter) heated in a furnace similar to that used for carbon and hydrogen determinations.

During the reduction and subsequent oxidation considerable shrinkage of the particles takes place. The material is screened to -10 + 20 mesh size, and packed in the combustion tube. The combustion tube consists of a silica U-tube (bent in a oxy-acetylene flame), 3.5 mm. in diameter and about 36 cm. long. The dead space in the tube is filled with silica rods. The catalyst is used at 700°C and is heated by means of an electric furnace.

The catalyst is regenerated by passing air over it at 600°C. This should be done after each determination!

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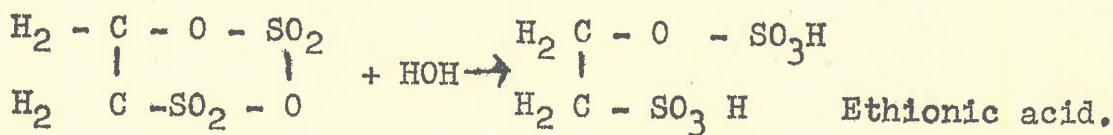
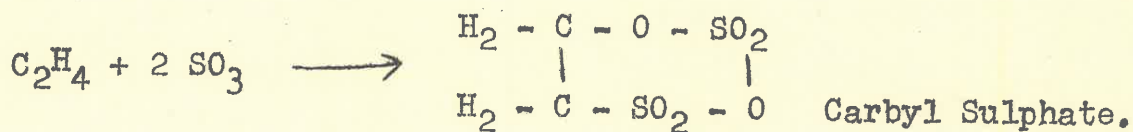
NOTES ON THE REACTIONS INVOLVED AND SOME PROPERTIES OF THE REAGENTS AND GASSES:

dium hydroxide cannot be used for the absorption of carbon dioxide on account of the difficult solubility of sodium bicarbonate which tends to clog the capillary tubes. It also has a greater chemical action on glass.

Carbon dioxide is dissolved to a considerable extent by water. A nearly saturated saline solution, slightly acidified with hydrochloric acid has a markedly lower gas-solubility coefficient than water, and should therefore be used as displacement liquid. Saturated saline solutions should not be used because a slight lowering of temperature will cause some of the salt to crystallize out and consequently clog the capillary tubes and the plugs of the stop-cocks of the sampling tubes.

When the supply of gas is not limited the displacement liquid should first be saturated by bubbling gas through the liquid.

When fuming sulphuric acid reacts with ethylene, ethionic acid and carbonyl sulphate is formed, the latter being the anhydride of ethionic acid. 14, 15.

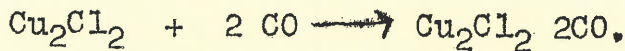


Pyrogallol, a trihydroxybenzene is a strong reducing agent in alkaline solutions. It is oxidized to products that have not yet been identified.

When pyrogallol solution becomes saturated with oxygen there is a danger of carbon monoxide being evolved if the solution is not fresh and strongly alkaline.

Cuprous chloride is insoluble in water but dissolves readily in concentrated sodium chloride solution. Cuprous chloride solution also absorbs saturated hydrocarbons but the solution is minimised by the presence of the sodium chloride.

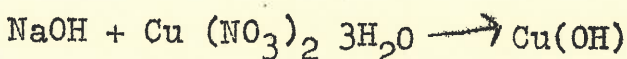
Carbon monoxide reacts with cuprous chloride as follows: 16)



The compound is unstable and is only formed when carbon monoxide exerts a pressure above the absorbent. The use of two pipettes is therefore indicated. It is, however, evident that the determination will never be quantitative. The acid solution has the advantage over the ammoniacal one that the presence of ammoniacal fumes in the manifold is avoided and that the acid solution reduces itself provided it is kept in contact with metallic copper.

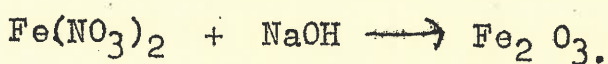
Acid cuprous chloride solution when saturated with carbon monoxide can be regenerated by heating at 60°C to 70°C in a flask fitted with a reflux condenser. Any cupric chloride formed can be reduced by adding a few drops of concentrated stannous chloride solution. Stannous chloride can also be used instead of metallic copper when preparing fresh solutions. 17.

When cupric nitrate is treated with alkali the reaction that takes place can be represented as follows:



Upon heating the precipitated copper, hydroxide breaks up to form copper oxide. 18.

Ferric nitrate and alkali reacts as follows:



This oxide of iron probably acts as a catalyst in reaction between copper oxide and hydrocarbon gas. 19.

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