Hilditch and Paul (26) state that of all the sources which they studied, cottonseed gave the most potent antioxidant activity. We also have found that cottonseed meal is an excellent antioxidant in fats and oils, superior in fact to oat flour in this respect. This activity is independent of the gossypol content, for ether-extracted meats carry the effective principle. The antioxidant in cottonseed meal is soluble in water (28). Further work on its properties is now in progress.

It will be clear that the opportunities for research activities in this field, especially in the study of fundamental reactions, are still practically unlimited.

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Evolution Volumetric Method for Carbon Dioxide

By L. B. HITCHCOCK and R. E. DIVINE

A METHOD for determining combined carbon dioxide in soaps and other detergents was published by the authors of this paper in OIL AND SOAP, January, 1938, Vol. 15, No. 1.

The method was based on the fact that in a system free from gases other than aqueous vapor, carbon dioxide may be liberated from carbonates and distilled into a measured quantity of an alkaline absorbent. The excess of the latter may be accurately titrated.

Further experience with the method as originally described has shown that modification of both apparatus and details of procedure are necessary in order that the results may be consistently accurate.

When the method is applied to detergents containing soap, in order to make sure that no volatile fatty acids distil into the receiver with CO_2, a 3 bulb or 4 bulb Allihn condenser has been substituted for the calcium chloride tube which served as a spray trap in the original apparatus. The tubulure of the condenser has a side tube sealed into it to which the rubber tube leading to the receiver is attached. The separatory funnel through which reagents are introduced is attached to the condenser by a one-hole rubber stopper. The stem of the separatory funnel is prolonged by sealing on a narrow tube which extends down to the center of the lowest condenser bulb when the funnel is in place. This tube must be sufficiently narrow to insure adequate clearance between its exterior and the inner walls of the condenser so that vapors from the boiling evolution flask may condense and reflux without impeding the flow of CO_2 into the receiver.

The evolution flask remains the same as originally recommended, namely a one-liter, Pyrex, round bottom flask with long neck. The receiving flask carries only one connection through which is the passage for admitting CO_2. Two or three pieces of light copper wire are twisted together and disposed vertically in the evolution flask during a test with the aim of moderating or preventing bumping when the acidulated detergent solution is heated under vacuum. A good vacuum is important. When the assembled apparatus is exhausted for a test, the internal pressure should be only a few millimeters of mercury higher than that corresponding to the tension of aqueous vapor at the temperature of the liquid.

A good Bunsen aspirator (water pump) will give satisfactory results, although the Hyvac pump is more certain. A mercury column should be used to indicate the degree of exhaustion, closing off the connection during an actual test. Air leaks are inadmissable. The best way to avoid air leaks is to make sure that all connections are clean and well fitted and to wet rubber and glass surfaces with water before making up connections.

The most satisfactory source of heat we have found is a small argand gas burner with chimney and a regulating lever at the base. This type of burner supplies all the heat necessary for the determination and is adapted to exact control.

A blank test on the reagents used in the evolution flask shows a significant amount of CO_2. For this reason a deduction must be made from the quantity of CO_2 found in a test. It is essential that all reagents used be measured or weighed so that the correction may be valid. The most suitable way of preparing distilled water free from CO_2 is to boil it under vacuum. A large Pyrex round bottom flask is suitable and convenient for this purpose. It may be heated directly with a small bunsen flame. About 15 minutes boiling suffices to remove gases to such extent that bumping takes place.

A test of detergent for combined CO_2 is made as follows: A sample representing 0.200 CO_2 or less is weighed and transferred to the evolution flask and to it are added 400 ml. unboiled distilled water followed by 5 ml of absorbent solution. If the presence of bicarbonate is suspected, add 10 ml of absorbent solution. The mouth of the flask is then covered with a small beaker, or a plug of cotton is put into it to prevent circulation of air, and the flask is heated over steam until the sample is dissolved. It is then cooled under the tap until only moderately warm and 20 grams of crystallized magnesium chloride dissolved in 30 ml water are added and mixed in. The flask is now completely cooled and connected with the condenser.

25 ml of absorbent solution are measured into a 250 ml Erlenmeyer flask and the latter is connected with the condenser, as shown in the accompanying cut, and the assembled apparatus is evacuated.

25 ml 1:1 HCl are carefully added to the evolution flask, followed by 25 ml trichlorbenzol and some aqueous methyl orange indicator. Heat is then applied, and boiling begins promptly and will slow down gradually as CO_2 distils over. Heating should be continued for 30 minutes, then the source of heat removed and the evolution flask filled with boiled distilled water at about 50°C. With caution the water may be added until it reaches the upper bulb, but the operator should be ready to close off the rubber tube leading to the receiver in case any sudden ebullition takes place in the evolution flask. The rubber connection to the receiver is now closed with a pinch cock, disconnected from the condenser and the receiver is filled with air free from CO_2 by connecting it to a wash bottle containing strong alkali. It is then closed with a rubber stopper and set aside until wanted for titration.

Titrations are made drop-wise with N/4 HCl and phenolphthalein indicator. A blank test is run exactly the same as above, using the same quantities of reagents and 400 ml unboiled distilled water. The difference between the two titrations is equivalent to CO_2 in terms of N/4 HCl. 1 ml N/4 HCl is equivalent to 0.0055 CO_2.

A comparison of the direct titration of 25 ml absorbent solution with the titration of the blank test will show the quantity of CO_2 in the reagents + 400 ml unboiled water. The absorbent solution is prepared by mixing equal volumes of normal NaOH and normal barium chloride solutions and standing over night. The resultant clear solution will be very nearly half normal in alkaline strength. It is a very efficient absorbent for CO_2.

This method is capable of giving very precise results which are very slightly higher than theoretical when it is employed on chemically pure sodium carbonate. When tested in Committee work on special samples of synthetic detergents, the results were equal in accuracy to those obtained by the gravimetric train method.

Report of the Soap Analysis Committee—1940

M. L. SHEELY, Chairman

Tetra Sodium Pyrophosphate in Soap—In view of the extensive use of tetra sodium pyrophosphate in certain types of soap, the Committee undertook cooperative studies on its determination in soap products. The program included the following determinations on a sample of soap powder containing tetra sodium pyrophosphate as well as other builders including sodium silicate.

1. Determination of tera sodium pyrophosphate by zinc acetate gravimetric method.
2. Determination of tetra sodium pyrophosphate by conversion to orthophosphate by acid treatment and determination of total P_2O_5 by official A.O.C.S. method.
3. Moisture determination on the soap sample at time of analysis to permit calculation of results to a definite moisture basis.

Procedure No. 2 (above) was intended only as a check determination on Procedure No. 1, since the sample under study contained no added orthophosphate. Obviously this method could not be considered specific for tetra sodium pyrophosphate if both forms of phosphate were present.

Fourteen laboratories participated in these studies and the reported results are shown in Tables I and II. As a matter of record, the procedure followed by the Committee was as follows:—

Determination of Tetra Sodium Pyrophosphate ($Na_4P_2O_7$) in Soap Products

Reagents Required

1. Neutral Ethyl Alcohol (94% or higher). Denatured alcohol, formula No. 30, or 3-A may be used.
2. Acetic acid, glacial. C. P. grade.
3. Bromphenol Blue, 0.04% solution. Dissolve 0.4 grams Bromphenol Blue in distilled water and make up to 1 liter.
4. Zinc acetate, 3.7% solution. Dissolve 44 grams of $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ in water. Add glacial acetic acid to make the final solution to a pH of 3.3 (about 200 ml of glacial acetic acid), and make the volume to 1000 mls with distilled water. (pH may be determined by using Bromphenol Blue as an indicator with a series of color standards ranging from a pH of 3.0 to 4.0, or by the electrometric method.)
5. Acetic acid, dilute solution, pH 3.4. Make up this solution by adding a few drops of acetic acid to distilled water, to a pH of 3.4.

Procedure

Digest hot, a 5 gram (±0.01) sample with 200 ml of freshly boiled neutral alcohol. Filter through a filter paper or a Gooch crucible with suction, washing with hot alcohol until free from soap. Wash the alcohol insoluble portion remaining on the filter paper with hot water until washings are neutral to phenolphthalein. Combine filtrate and washings and transfer to a 250 ml volumetric, cool to room temperature and make up to mark with distilled water.

Transfer an aliquot containing an equivalent of approximately 0.1 gram of tetra sodium pyrophosphate to a 250 ml beaker, and adjust the pH using Bromphenol Blue as an inside indicator to between 3.3 and 3.5 by adding glacial acetic acid. pH adjustment can also be accomplished at this point by using a glass electrode. Adjust the final volume to approximately 75-100 ml with distilled water and add an excess of 3.7% solution of zinc acetate, dropwise, with constant stirring. Filter off the precipitated zinc pyrophosphate using an ashless filter paper or a tared Gooch crucible and wash the precipitate thoroughly with dilute acetic acid (pH 3.4).

Dry the zinc pyrophosphate carefully over a low flame and ignite to constant weight at a dull red heat and calculate to tetra sodium pyrophosphate.

Calculation:

$$\frac{\text{Wt. of } Zn_2P_2O_7 \times 0.8728 \times 100 = \%\ Na_4P_2O_7}{\text{Wt. of Sample}}$$

Conclusions

A meeting of the Committee was held on October 1, 1940 at the Stevens Hotel, Chicago. It was the opinion of the Committee, after due consideration of the data, that the results by the proposed zinc acetate, gravimetric