extremely doubtful that the NO could go completely to NO₂ in his apparatus, in which case results calculated by the formula given would be too low.

ACKNOWLEDGMENTS

The authors have had valuable assistance, in the work on which this paper is based, from Lieut. G. A. Perley, Mr. J. H. Capps, and Mr. L. R. Lenhart; Mr. A. S. Coolidge performed many of the experiments in trying out the nitrometer method.

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A VOLUMETRIC METHOD FOR THE DETERMINATION OF FORMIC ACID OR FORMATES IN THE PRESENCE OF HYDROXIDES, CARBONATES, OXALATES AND ACETATES

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Received August 16, 1917

This method is based upon the well-known fact that formic acid is quantitatively oxidized to carbon dioxide by chromic acid in boiling solution, and that therefore every 44 parts by weight of carbon dioxide correspond to 46 parts of formic acid according to the equation,

APPARATUS—The accompanying sketch shows the arrangement of the apparatus used: *A* is an Erlenmeyer flask of resistant glass with a capacity of about 500 cc.; *B* is a thermometer for the control of the temperature of the contents of the flask; *C* is a 15-in.

Liebig reflux condenser, for the condensation of the vapors produced during the boiling of the liquid and is connected by means of a glass tube and heavy rubber tubing to *D*, the gas collector. The latter consists of a glass tube, about 1.5 in. in diameter, having a capacity of approximately 600 cc. and is graduated in cc.'s; connected to this gas collector by means of a rubber tube is the reservoir *E*, by means of which the air in the collector may be discharged and the water level

obtained, when the CO₂ gas has been collected in the graduated tube. To prevent the absorption of gas by the water used for leveling purposes, a 1-in. layer of paraffin oil is floated upon the surface.

REAGENT—50 g. of C. P. sodium bichromate are dissolved in 500 cc. of distilled water, 80 cc. of C. P. concentrated sulfuric acid added and the liquid boiled for 5 minutes to expel all dissolved gases; then it is allowed to cool to room temperature.

PROCEDURE (1)—In the absence of other substances which give CO₂ when boiled with chromic acid, the procedure is as follows: A solution is prepared, so that 50 cc. of the same will contain from 0.5 to 1.0 g. of formic acid; 50 cc. of this solution are emptied by means of a pipette into the clean Erlenmeyer flask and if alkaline, 2 to 3 drops of methyl orange are added, and the solution made acid with dilute sulfuric acid (1 : 1); 400 cc. of the chromate solution are now

added and the flask attached to the condenser; the stopper at the top of the condenser is removed and the reservoir raised until the graduated tube is filled to the zero mark. The stopper is now firmly replaced and a reading is made upon the graduated tube for correction of the air displaced by the stopper. The reservoir is then lowered and observation is made to assure that the apparatus is air-tight. If no leakage is observed, the reservoir is again raised to a level slightly below that of the liquid in the collector, the cooling water turned on, and the contents of the flask are heated to boiling. As the gas collects, the reservoir is lowered from time to time so that atmospheric pressure is maintained. The boiling is continued until the volume of the gas is practically constant, which requires from 15 to 20 minutes. The flame is now removed and the flask placed in a water bath and cooled until the temperature is reduced to that at which the operation was started; the reservoir is brought to the same level as the liquid in the collector and the volume of the gas noted. A correction is made for the air displaced by the stopper at the beginning of the operation and atmospheric pressure and room temperature are recorded. The volume of the gas must now be reduced to normal barometric pressure and a temperature of 0° C. according to the following well-known formula,

$$V_1 = \frac{V(C - h)}{760(1 + at)}$$

where V_1 = reduced volume, V = volume actually found, C = barometric pressure, h = tension of water vapor at temperature t , a = 0.00366, and t = room temperature.

Taking the results of Guye, the weight of 1 cc. of CO₂ gas at 760 mm. and at 0° C. is 0.0019768 g. Therefore, the number of cc. multiplied by 0.0019768 gives the weight of carbonic acid gas generated. This result calculated to 100 g. of material and multiplied by 46/44, or 1.04545, will give the percentage of formic acid.

Trial experiments with known quantities of C. P. sodium formate (recrystallized from alcohol) gave the following results:

(0.5 Gram Sodium Formate Used in Each Case)

Temp. ° C.	Pressure Mm.	GENERATED Actual	CC. OF CO ₂ Corrected	HCOONa Found	Difference Gram
25° C.	747	187	163.1	0.4988	—0.0012
21° C.	743	185	163.7	0.5001	+0.0001
26° C.	743	188	162.2	0.4955	—0.0045
27° C.	743	190	163.0	0.4979	—0.0021

PROCEDURE (2)—In the presence of carbonates, bicarbonates, oxalates and acetates, the following procedure is to be followed: take sufficient material that the formic acid content will range between 2.5 and 5.0 g. Dissolve in 50 cc. of water, boil a few minutes, make alkaline with NaOH if bicarbonates are present and add a 10 per cent solution of calcium chloride in sufficient quantity to precipitate all of the carbonates and oxalates. Allow the precipitate to settle, filter into a 250 cc. graduated flask, wash thoroughly with boiling water, cool to room temperature and fill to the mark. Take 50 cc. of the filtrate and proceed as directed under Procedure (1). Trial experiments with known quantities of C. P. sodium formate mixed with

different quantities of sodium carbonate, oxalate and acetate (which is not oxidized by the chromate solution) gave the following results:

(0.5 Gram Sodium Formate Used in Each Case)

Temp. ° C.	Pressure Mm.	GENERATED Actual	Cc. of CO ₂ Corrected	HCOONa Found	Difference Gram
22° C.	739	186	162.9	0.4976	—0.0024
25° C.	739	188	162.2	0.4955	—0.0045
18° C.	737	184	163.9	0.5005	+0.0005
18° C.	737	183	163.0	0.4979	—0.0021
28° C.	748	190	163.2	0.4985	—0.0015
27° C.	748	189	163.3	0.4989	—0.0011
16° C.	746	180	163.8	0.5004	+0.0004
20° C.	746	183	163.4	0.4974	—0.0026
Average.....					0.4982

SUMMARY

I—From the above results it can be seen that this method is an accurate and reliable one for the technical determination of formic acid or formates in the presence of carbonates, oxalates and acetates.

II—An added advantage is that the time required for an analysis does not exceed one hour and, furthermore, it requires but little attention; and preparations for subsequent determinations can be made during the intervening time.

NOTE—Thorpe in his "Dictionary of Applied Chemistry" calls attention to a method devised by Rupp and published in the *Archiv. der Pharmazie*, **243**, 69 for the determination of formates. Rupp uses sodium hypobromite as the oxidizing agent and not potassium bichromate, as stated by Thorpe.

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A STUDY OF THE ESTIMATION OF FAT IN CONDENSED MILK AND MILK POWDERS¹

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It was found by Röse² that, if whole milk was treated with ammonia and alcohol, the casein was dissolved to such an extent that the fat could be removed quantitatively by a mixture of equal volumes of ethyl and petroleum ethers. Subsequently, E. Gottlieb³ failed to corroborate the results of Röse, but found that if he extracted, after the treatment with ammonia and alcohol, first with ethyl ether and then with petroleum ether, he was able to obtain more accurate results than he could by the procedure outlined by Röse. Harding and Parkin⁴ claim that results from the application of the Röse-Gottlieb procedure to evaporated milk or milk powders show that the fat is not completely extracted. For the fat determination in evaporated milk they proposed to dissolve the protein in acetic acid and the fat in a mixture of alcohol and carbon tetrachloride before extracting the fat with petroleum ether. During shaking and centrifuging, rubber stoppers were used in contact with the solvents. The action of the solvents on the rubber stoppers would seem to be the cause of the higher results obtained by Harding and Parkin when the fat was extracted by the procedure

they outline rather than when it was extracted by the Röse-Gottlieb method. O. Laxa's¹ work on separator slime indicates that a small amount of fat adheres tenaciously to the protein. It would probably adhere none the less tenaciously in evaporated milk or milk powder. The presence of free fatty acids would not be expected in any appreciable quantity in condensed milk, but milk powder, on account of its tendency to develop rancidity, might have appreciable quantities, as shown by Eccher.² Hence, the Röse-Gottlieb method, which extracts only neutral fats, might fail to show the original fat content of the powder. Hunziker³ used dilute acetic acid to dissolve casein in condensed milk before extracting the fat with ether. It has been shown⁴ that acetic acid does not react chemically with butter fat.

In the work recorded here, the errors in the Röse-

MODIFIED RÖHRIG TUBE (Besterfeld)

Height of tube, over all (not including stopper), 37 cm., about.
Narrow part (below spigot), 19 mm. outside diameter.
Capacity of narrow part, to middle line of spigot, 28 cc.
Upper part (above spigot), 27 mm. outside diameter.
Tube must have a tight-fitting glass stopper.
No vent hole in neck. No graduations.

Gottlieb⁵ method have been studied and the method compared directly with a modified method in which a small amount of acetic acid as an aid in separating the fat from the casein, mixtures of petroleum ether, ethyl ether and ethyl alcohol (which are recoverable for repeated use) and a modified Röhrig tube, have been used.

The two mixtures, which must be kept separate, are used as solvents. The proportions for Mixture 1 are 400 cc. of petroleum ether, 200 cc. of ethyl ether and 20 cc. of 95 per cent ethyl alcohol. For Mixture 2 the

¹ Published by permission of the Secretary of Agriculture. Presented at the 54th Meeting of the American Chemical Society in Kansas City, Mo., April 10 to 14, 1917.

² *Z. angew. Chem.*, **1888**, 100.

³ *Landw. Ver.-Sta.*, **40** (1892), 1.

⁴ *This Journal*, **5** (1913), 131.

⁵ *Milchwirtschaft. Zentr.*, **42** (1913), 691.

² *Arch. Chem. Mikros.*, **6** (1913), 302.

³ Purdue Univ. Agri. Expt. Station, *Bulletin* **134** (1909).

⁴ Bahlman, *This Journal*, **7** (1915), 680.

⁵ U. S. Dept. of Agriculture, Bureau of Chemistry, *Circular* **66** (1911).