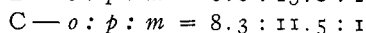
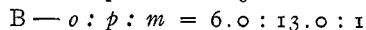
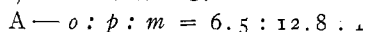


ratios may be calculated for the materials designated "A," "B" and "C."



As meta-cresol boils only 3° higher than *p*-cresol, it seems certain that in the original materials dealt with the amount of *p*-cresol must much exceed the amount of *m*-cresol. Weiss and Downs in the preparation of their graphs made up synthetic mixtures in which the ratio of para to meta was fixed at about 1 : 1 and they state that that is the approximate ratio in which they exist in their oils.

The question arises whether their method would give reliable results when applied to the tar acids dealt with by the author. In the present method such variation in the ratios of the cresols present would be eliminated, at any rate to a considerable extent, although the ratio of cresols worked with in the preparations of the synthetic mixtures was not varied as far as to include a ratio, $m : p = 1 : 1$, so that definite figures cannot be given.

It would be interesting to follow up this and the other points raised at greater length but the author has not now access to the necessary crude materials.

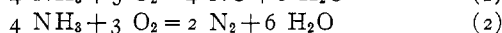
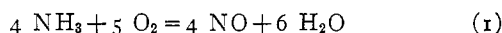
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ANALYTICAL CONTROL OF THE AMMONIA OXIDATION PROCESS¹

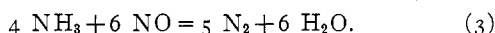
By GUY B. TAYLOR AND JOS. D. DAVIS

Received October 17, 1917

In the manufacture of nitric acid from ammonia, a mixture of air and ammonia gas is passed over a suitable catalytic material heated to temperatures above red heat. Two reactions occur:



It has been suggested that reaction (2) may come about by means of the intermediate reaction,²



In testing out a particular type of commercial oxidizer, the authors believe they have found evidence that under certain conditions this reaction does occur. The oxidizer in question was so constructed that the burned gases remained hot for some time. Further, there was irregular local cooling of the catalyst due to eddy currents in the burned gases. Consequently, there must have been considerable ammonia passing such points unburned. In fact, analysis of samples taken from points near the cold spots showed ammonia while in samples taken outside the catalyst chamber the ammonia content was very low. The authors believe that most of the NH_3 passing through the cold spots was subsequently "burned" by the hot NO . Results with this apparatus were uniformly about 10 per cent lower than those obtained with the same lot of catalytic material in a differently constructed oxidizer.

The nitric oxide is converted into nitric acid by passing the gases through suitable absorption towers,

much the same as in the arc process of direct fixation of atmospheric nitrogen.

The efficiency of an ammonia converter depends upon establishing conditions favorable to reaction (1) and suppressing as far as possible reaction (2). If the ultimate product desired is nitric acid, little or no free ammonia should be allowed to pass the converter unchanged.

In order to test the efficiency of conversion, analyses of the entering ammonia-air mixture and the exit nitrose gases must be made. The former offers no special difficulties but the nature of the acid gas creates a special problem. As soon as the gas sample cools, the nitric oxide begins to react with the excess oxygen present to form NO_2 , which partially dissolves in the condensed water, so that the gas taken into any sampling device consists of a mixture of nitrogen, oxygen, and nitrogen oxides of indeterminate molecular species.

The principle upon which the efficiency calculation is based is as follows: the ratio of the nitrogen combined as ammonia to total nitrogen in the intake gas is equal to the ratio of the nitrogen derived from the ammonia to total nitrogen in the exit gas.

Let a = nitrogen combined as NH_3 } in the air-ammonia sample
 b = free nitrogen }
 and c = nitrogen combined as nitrogen oxides } in the exit gas sample
 d = free nitrogen }
 f = nitrogen combined as ammonia escaping oxidation }

The nitrogen in each sample must of course be expressed in terms of the same unit. Then

$$\frac{a}{a+b} = \frac{c+f+x}{c+d+f} \quad (3)$$

where x is the free nitrogen derived from the reaction expressed by Equation (2). The efficiency is then expressed by the relation

$$\frac{c}{c+f+x} = \text{Yield} \quad (4)$$

or, substituting the value of x from (3),

$$\frac{c(a+b)}{a(c+d+f)} \times 100 = \text{Per cent Yield.} \quad (5)$$

EXPERIMENTAL METHODS

In the course of some experiments on ammonia oxidation, several methods of procedure were developed:

METHOD 1—The apparatus is sketched in Fig. I. Air was passed through the meter *A*, the water seal and pressure gauge *B*, and the bottles *C* containing ammonia liquor (7 to 8 per cent NH_3). The ammonia-air mixture passed over the catalyzer in *D* and the acid gases out through *E*.

The tubes *H H'*, capacity about 1200 cc., were filled with water. *K* contained 20 cc. $N/5 \text{ H}_2\text{SO}_4$ and *K''* 15 cc. $N/2 \text{ NaOH}$ plus 3 cc. of 3 per cent hydrogen peroxide.

The ammonia-air sample was drawn through *K* by allowing a measured volume of water to flow from *H*. Before drawing the acid sample the air in *K''* was displaced by pure oxygen passing in at *G* and out at *F*. The two samples were then drawn simultaneously so

¹ Published by permission of Director of U. S. Bureau of Mines.

² Reinders and Cats, *Chem. Weekblad*, 9 (1912), 47-58.

that about one liter of gas was taken into each sample in about one hour. The excess acid in *K* was titrated with $N/5$ alkali for the determination of the value of *a*. The gas in *K''* was displaced with oxygen into *H'*, noting the total volume of water drawn therefrom. The two tubes *H H'* were then detached and immersed in a large tank of water, a manometer attached and the temperature and pressure noted. The gas in *H'* was analyzed for nitrogen by absorbing the oxygen in alkaline pyrogallol. The composition of the air in *H* was taken as 79 per cent nitrogen. This furnished the data necessary for the calculation of the values *b* and *d*.

For determination of the value *c* the contents of *K''* were washed into a small Erlenmeyer flask and boiled for about 5 minutes, then thoroughly cooled and the excess alkali titrated with $N/5$ NaOH, methyl orange indicator and a companion flask. The nitrite present tended to destroy the indicator in acid solution, turning the color a permanent yellow, unaffected by either acids or alkalis. By taking care not to run over the end-point, noting the first change in shade from the color of the companion flask, this titration was accurate and satisfactory. The boiling and cooling was found to be absolutely necessary in order to recognize the end-point at all. Carpenter¹ condemned the alkali H_2O_2 reagent for absorbing nitrous gases on account of the difficulty

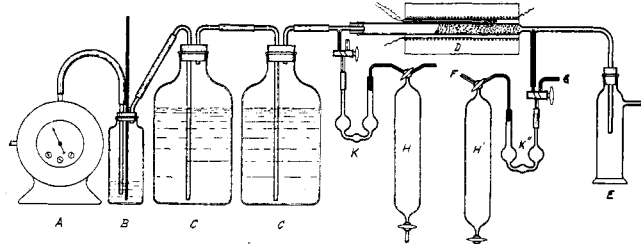


FIG. I—ANALYTICAL CONTROL OF AMMONIA OXIDATION

of the end-point and proposed the use of a solution of hydrogen peroxide alone, but we have not found it as efficient as the alkali, when the gas is bubbled through it.

When methyl red or sodium alizarine sulfonate is used as an indicator, the boiling is not necessary, both indicators working fairly well in the presence of nitrites. Sodium alizarine sulfonate is rather the better indicator to use, being more sensitive. Methyl red is destroyed to some extent by the nitrite but the end-point is sufficiently sharp even when $N/10$ solutions are used.

Since no appreciable ammonia escaped oxidation in tests where this method was used, the value of *f* is zero. The absorption of the acid in *K''* was practically complete. The water drawn from *H'* was never acid and that remaining in the tube was titrated after shaking when especial accuracy was required. This rarely increased the value of *c* more than one per cent.

METHOD II—This method was essentially the same as Method I, except that the nitrogen-oxygen mixture, after absorption of the acid, was drawn over hot copper to remove the oxygen, thus eliminating the analysis of the gas collected in *H'*. A small Meyer sulfur bulb was used as an absorber and a 4-liter aspirator bottle substituted for *H'*, Fig. I.

¹ "Note on Some Condition Affecting the Oxidation of Nitrous Acid to Nitric Acid," *J. Soc. Chem. Ind.*, 5 (1886), 287.

The above methods were especially useful in small scale experiments where sampling into evacuated bottles as described below would have seriously interfered with the constancy of the gas flow through the catalyzer tube.

METHOD III—For larger scale experiments samples taken into evacuated bottles have been found convenient. This is the only method permitting determination of the ammonia escaping oxidation, *f*. Bottles of known volume, 1 to 2.5 liters capacity, were provided with single capillary stopcocks and evacuated to less than 2 mm. pressure. Ground glass stoppers were more satisfactory but soft rubber stoppers served well enough when the samples were drawn immediately after evacuating.

Sufficient $N/5$ H_2SO_4 was admitted to the ammonia sample and a measured volume of water, after absorbing the ammonia, until the residual air was at atmospheric pressure.

Enough condensation occurred in the acid sample to permit sucking in a measured volume of water containing hydrogen peroxide to absorb the acid fumes. The volume of the bottle minus that of solution introduced gave the volume of the oxygen-nitrogen gas which, together with its analysis, furnished the necessary data for calculating the free nitrogen. The acid solution was titrated with $N/5$ NaOH for free acid and then distilled with caustic into $N/5$ H_2SO_4 for determination of ammonia *f*. Since this ammonia was present as nitrate, its equivalent was added to the free acid already found for the calculation of *c*. While this method requires rather more manipulative skill than the average works chemist possesses, the authors consider it the best available and have used it quite extensively for control work with very satisfactory results. Duplicate determinations on samples taken at the same instant should agree within 1 per cent, but in practice agreement so close will hardly be consistently obtained unless the gas flow is very uniform. It is desirable to check the analysis method and the standard solution used by the analysis of gas samples containing a known amount of nitric oxide. The NO required may be conveniently prepared by means of a nitrometer.

It is often desirable to know whether or not there has been a leak between the point where the NH_3 sample was taken and the point where the nitrous gases were sampled. To determine this it is only necessary to measure the amount of oxygen admitted to the sample of nitrous gases and use water to which a known amount of standard H_2O_2 has been added for absorption. All the combined nitrogen in the sample will now be present as nitric acid. After the excess oxygen gas has been determined the liquid is divided into two parts. In one part the acid is determined by titration with standard alkali and in the other part the excess H_2O_2 is determined by titration with permanganate. The oxygen used is now known and the amount required for the oxidation of the ammonia converted may be calculated, any excess being due to leakage. Obviously, the yield may be calculated from a knowledge of the relation of combined nitrogen to oxygen in both the NH_3 air sample and the sample of nitrous gas. A few such calculations

were made with results agreeing fairly well with those by the regular method of calculation.

The vacuum method offers a convenient means of following the reactions in an absorption system; for example, it is a simple matter to determine the efficiency of a given tower by sampling and analyzing the gas on both sides of it. Ordinarily the leakage will not be great enough to interfere.

OTHER METHODS—Analysis of the ammonia-air intake gas may be made by ordinary gas analysis methods by taking proper precautions. In common gas analysis practice it is customary to make all volume readings with the gas saturated with water vapor. When mercury is used as a confining liquid, the walls of the burette are always kept wet. This precaution is essential because of the very different vapor pressures of the solutions used as selective absorbents.

In dealing with ammonia gas it is obviously necessary to have the walls of the burette dry and to absorb the ammonia in a reagent whose vapor tension is equal to the partial pressure of the water vapor in the sample. Now this result is accomplished if the gas is thoroughly dried and the absorption made in a reagent whose vapor tension is practically zero.

The apparatus employed consisted of a special bulb form of compensated burette with graduations extending from 140 to 165 cc., easily readable to ± 0.02 cc. Clean, dry mercury was used as a confining liquid and the ammonia was absorbed in concentrated sulfuric acid. The sample was introduced into the burette through a U-tube filled with pieces of solid potassium hydroxide, which thoroughly dried it.

This method proved very satisfactory in practice, and checked the vacuum bottle method. Its advantages are ease of manipulation and simplifying of the calculation, since no temperature or barometer observations are required and no titrations are made. The calculation follows:

$$a = \text{contraction in volume of the sample}$$

$$b = \text{volume after contraction} \times 0.79 \times 2.$$

An equally simple method suggested itself for analysis of the nitrous gases. It was thought that a sample of the nitrous gases drawn into a nitrometer containing mercury and sulfuric acid, and then shaken, would convert all the nitrogen oxides to NO and cause the excess oxygen to disappear. Analysis of the remaining mixture of nitrogen and nitric oxide would give the values for *c* and *d* in volumes as in the burette method for the NH₃-air mixture.

In experiments with this method it was found that a concentrated solution of chromic acid¹ rapidly absorbed NO and effected quantitative separation of this gas from artificially prepared mixtures of nitrogen and nitric oxide. When the method was applied to the nitrous gases the results were always low. A series of experiments was then made by introducing a measured volume of air into the decomposition bulb of a duPont nitrometer and adding a known quantity of nitric acid dissolved in concentrated sulfuric acid. After shaking several minutes the residual gas was measured, transferred to a gas analysis burette and the NO absorbed

by passing into a pipette containing the chromic acid reagent. Mercury was used as a confining liquid and the walls of the burette were kept wet. The results in every case showed that the residual gas measured corresponded to that calculated, assuming disappearance of the oxygen in the volume of air used and evolution of nitric oxide from the nitric acid introduced. However, analysis of this gas always showed a considerably less percentage of NO than that calculated as well as a small amount of oxygen as determined by absorption in alkaline pyrogallol. Evolution of the NO in the nitrometer bulb in the presence of nitrogen instead of air gave more nearly the correct percentage of NO in the residual gas. In view of these results the nitrometer method appeared unavailable.

A second method for eliminating titrations was devised. Fig II shows the essential details of the apparatus. The ammonia air sample is drawn into the gas burette (2) through the drying tube (1) containing pieces of solid potassium hydroxide. Burette (2) is provided with a right angle two-way stopcock at the top and a leveling tube below not shown in figure. It is filled with

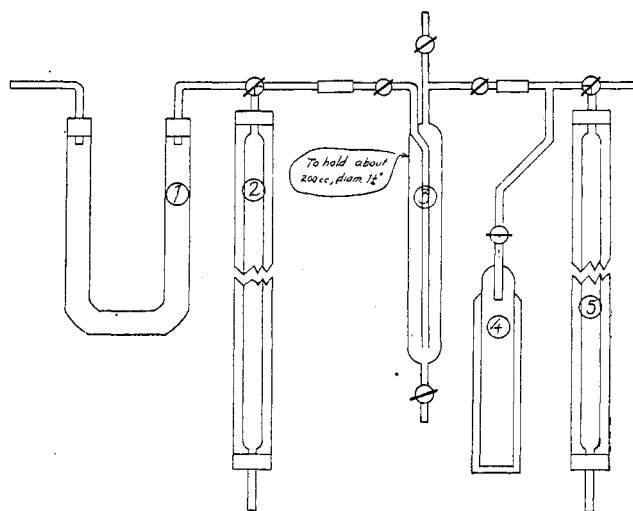


FIG. II—ANALYTICAL CONTROL OF AMMONIA OXIDATION

dry mercury. Bulb (3) is detached from the apparatus and completely filled with water containing hydrogen peroxide and indicator.¹ A small leveling bottle is attached by means of a flexible rubber tube at the bottom. About 10 cc. of pure oxygen, which need not be measured, are introduced into the bulb through one branch of the T tube. The nitrous gases are then drawn from the oxidizer into the bulb through the same tube by allowing 70 to 80 cc. of water to run out into the leveling bottle. This can be done without loss of acid since the indicator shows plainly the diffusion of any acid through the water while the sample is being taken. The bulb is then shaken until all the nitrogen oxides are absorbed. It is then restored to its position (Fig. II) and the residual gas transferred to the mercury-filled burette (5). The walls of this burette are kept wet. The gas is now passed into alkaline pyrogallol in the Williams pipette (4), the residual nitrogen brought back into the burette and measured. This volume is called *d*, and is discarded. The ammonia sample in (2) is

¹ Bohmer. *Z. anal. Chem.*, 21 (1882), 212.

¹ Methyl red or sodium alizarine sulfonate.

now bubbled slowly into the acid liquid in (3) until neutral, noting the volume required. The air from (3) is measured in burette (5) and this volume multiplied by 0.79 corresponds to the nitrogen volume b .

In calculating the yield by the general formula

$$\frac{c(a + b)}{a(c + d + f)}$$

neglecting f , since by the above procedure a and c are equal, we have

$$\frac{a + b}{a + d}$$

The volume of dry gas introduced from (2) into (3) corrected to moisture saturation, minus the volume of air measured, gives the volume of ammonia. This volume must be divided by two to obtain the corresponding volume of nitrogen, a , to be applied in the formula. When the yield is known to be in the neighborhood of 90 per cent approximate results may be obtained by simple division of the measured nitrogen volumes, *i. e.*, b/d .

While the method has not been thoroughly tested experimentally, it is presented here because the principle involved offers possibilities for development of a rapid method of works control.

DISCUSSION

It was realized at the beginning of this investigation that no method of determining the efficiency of an industrial process appeals to a manufacturer more than pounds put in to pounds taken out. In order to put our analytical results upon an unquestionable foundation, the method was checked by experiments in which the ammonia input was determined by weight and the total acid produced absorbed.

These experiments were carried out as follows: two tared flasks containing a known weight of carefully analyzed ammonia solution were connected in series so that air could be blown through them, the air-ammonia mixture passing over a catalyzer in a glass tube. The acid gases were absorbed in a series of wash bottles containing water and finally in the last ones 10 per cent NaOH solution. The ammonia was determined by weighing the flasks and re-analyzing; the acid, by titrating the HNO₃ absorbed in the water and analyzing the alkaline solutions for nitrate and nitrite. Although the absorption system was quite elaborate some acid passed through unabsorbed. This was estimated by frequent samples of the issuing gas. Method II was used for checking the above outlined procedure because the time in drawing the samples could be made to coincide more nearly with the length of the run. The results follow:

Time Min.	Condi- tions	Liters Air Room NH ₃ Taken	GRAMS RECOVERED				Grams HNO ₃ End Loss Train	PER CENT YIELD	
			Water Bottles	Alkali as Nitrate	Bottles as Nitrite	Total Grams HNO ₃		By Weights	By Analy- sis
144	200	10.82	24.40	1.40	4.90	0.90	31.60	79.0	82.5
180	270	13.44	33.00	1.40	6.80	1.05	42.25	85.1	87.0
172	187	8.74	22.70	0.60	3.15	0.60	27.05	83.8	85.5

There is no doubt in our minds that the analysis method gives the true efficiency of conversion. The complete absorption of the acid gases was exceedingly difficult and losses undoubtedly occurred through leaks at rubber connections. These facts account for the

slightly lower results of the total absorption method. Had we cared to elaborate the train, no doubt all the acid could have been absorbed and the agreement would have been better.

In a recently published article Fox¹ has raised the question of possible oxidation of ammonia to ammonium nitrite by hydrogen peroxide. This point was carefully tested in a number of experiments and no evidence secured of any such oxidation in significant quantity under the conditions obtaining in the above outlined procedures. The following experiment seems to be conclusive.

A sample of the nitrose gases was drawn into a 2-liter evacuated bottle from an experimental converter running at low velocity so that no unchanged ammonia passed the catalyzer. A solution containing 40 cc. *N*/5 NaOH, 15 cc. 3 per cent hydrogen peroxide and 3.5 cc. *N*/5 NH₄OH was introduced into the bottle immediately, followed by 100 cc. distilled water. The NaOH was in excess of that needed to neutralize the acid present. After vigorous shaking the bottle was allowed to stand several minutes. Then an excess of *N*/1 H₂SO₄ was added to fix the ammonia. The contents of the bottle were transferred to a Kjeldahl distillation apparatus, made alkaline with NaOH, and the ammonia distilled into *N*/5 acid. Exactly that amount of ammonia taken was recovered. No ammonia was oxidized.

We have further evidence pointing to the *fact* that under the conditions of analysis the use of H₂O₂ in alkaline solution does not affect the accuracy of the results by oxidation of NH₃ to nitrite.

Two chemists using the vacuum method described above made a number of analyses of parallel samples, one using alkali with H₂O₂ and the other using water with H₂O₂ for absorbing the nitrous gases. The results agreed very well, showing that there could not have been appreciable oxidation of NH₃ by H₂O₂ in alkaline solutions.

Moreover, Hoppe-Seyler² found no evidence of oxidation of ammonia in solutions of ammonia, or ammonium carbonate, or when a fixed alkali was present, by dilute hydrogen peroxide on 24 hrs. standing. It was necessary to concentrate such solutions by evaporation to small volume before nitrite could be detected by colorimetric methods. The statements of Schönbein, Weith, and Weber³ are not to be taken to mean that ammonia is oxidized by hydrogen peroxide "abundantly" under all conditions.

Fox's,⁴ analytical method is based on the assumption that NO in the presence of an excess of oxygen reacts immediately to NO₂ (or N₂O₄). It has been shown by a number of investigations⁵ that the reaction $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$ occurs in measurable time and that a mixture of NO₂ and NO behaves toward alkali as N₂O₃, being rapidly absorbed as nitrite. In Fox's method all the acid would be absorbed but it is

¹ THIS JOURNAL, 9 (1917), 737-43.

² Ber., 16 (1883), 1917-24.

³ Ibid., 7 (1874), 1745.

⁴ Loc. cit.

⁵ Holwech, Z. angew. Chem., 21 (1908), 2131; Le Blanc, Z. Elek., 12 (1906), 541; Foerster and Koch, Z. angew. Chem., 21 (1908), 2161 and 2209; Foerster and Blich, Ibid., 23 (1910), 2017.

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.

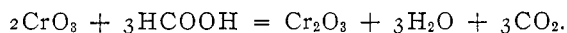
BUREAU OF MINES
WASHINGTON, D. C.

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

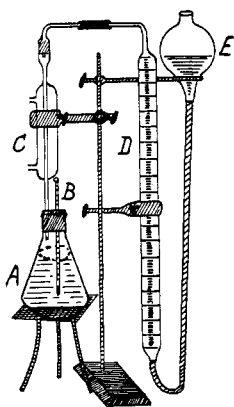
By F. TSIROPINAS

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.	Cc. of CO ₂		Difference Gram
		Generated Actual	Found Corrected	
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