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THE DETERMINATION OF NITROGEN BY THE DUMAS METHOD
NR 050-274 Contract Nonr-248(21)

Alphon H. Corwin, Research Contract Director
Ann L. Claggett, Research Assistant
The Johns Hopkins University
Baltimore, Maryland
December 31, 1952

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THE DETERMINATION OF NITROGEN BY THE DUMAS METHOD

Report on Experimental Work under Contract No.: Nonr 248(21)

Alsoph H. Corwin, Research Contract Director
Ann L. Claggett, Research Assistant

The Johns Hopkins University, Baltimore, Maryland
December 31, 1952

Summary

The standard difficultly combustible materials which we have used in our work, uric acid and benzaldehyde dinitrophenylhydrazone, were sent out to three commercial microchemical laboratories as unknowns with the request that Dumas analyses be performed. The values obtained were low by one part in 33, or 3.2% absolute, for uric acid, and 3.8% absolute for benzaldehyde dinitrophenylhydrazone. These errors agree with our own experience for the method before modification.

Our report presents details of a number of modifications in apparatus which we have found to be advantageous. Chemically, we have shown that the sublimate reported previously has a copper/nitrogen ratio consistent with the assumption that it is the cuprous derivative of cyanogen. In the absence of halogen, we have shown that combustion with hydrogen accompanying the carbon dioxide prevents the formation of this sublimate chiefly through the formation of a copper cracking surface. A reworking of the effect of cuprous oxide shows that it does not reduce carbon dioxide, as originally thought, but that carbon monoxide can still give high results if an improperly designed furnace is used. We have also found V, Zr, and Ti are not satisfactory in the tube but that Si is partially satisfactory.

Our main problem during the last six months has been occasioned by the difficulties encountered in the combustion of compounds containing bromine. This apparently forms cyanogen bromide and is much more difficult to deal with than the cyanogen previously considered. We found that each increment in the amount of hydrogen used during the combustion improved the results and finally concluded that generation at the rate of 0.5 ampere is sufficient to achieve a satisfactory result. No trouble was encountered with chlorine, iodine, or sulfur.

We are thus able to report a satisfactory analytical method for nitrogen in the presence of C, H, O, Cl, Br, and I, which will be equally satisfactory for compounds which volatilize and for those which decompose with formation of tar or charcoal.

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I. Review of Previous Work under this Project

Our previous report gave an introduction to the literature on the Dumas method for the determination of nitrogen, with a summary of the difficulties which have been encountered, together with additional observations which have been made in our own laboratories. It was concluded that there were two different types of difficulty encountered with the method. One of these had to do with compounds containing C, H, O, and N which would decompose without melting to a mobile liquid. Such compounds give low results by the standard Dumas technique, either macro or micro. The second difficulty arose from the presence of additional elements, such as Cl, Br, I, or S. This latter difficulty was not investigated during the first part of this research and attention was concentrated on the substances which contained only C, H, O, and N.

The method used in our research was to select two compounds which gave unacceptably low values by the standard Dumas technique and to analyze them repeatedly under varying conditions to learn the source of the difficulty and how to overcome it. Analyses on these compounds were interspersed with others on a standard, easily combustible compound, to make sure that acceptable results on the difficultly combustible materials were not due to a compensating error on the high side with an easily combustible material. The samples chosen for this work were uric acid and the 2,4-dinitrophenylhydrazone of benzaldehyde, as difficultly combustible materials and 2,4-dimethyl-3,5-dicarbethoxypyrrole (called "standard pyrrole") for the easily combustible material.

It was learned that the low results obtained with the difficultly combustible materials were due to the retention of nitrogen in the tube filling and that part of the retained nitrogen appeared at the tip of the filling in the form of a sublimate containing copper and nitrogen. This sublimate moves down the tube at temperatures substantially in excess of 360°, the boiling point of mercury. The nitrogenous residue in the tube does not only take the form of a "charcoal" as has been thought by some previous investigators, but in addition is in the form of one or more copper-nitrogen compounds. In some instances, the presence of a Cu-N derivative may be demonstrated by roburning the copper oxide of the tube filling in oxygen and showing the formation of NO by means of the diphenylamine-sulfuric acid color reaction. In other cases, this reaction is negative but the compounds may be demonstrated by hydrolysis in the Kjeldahl apparatus, under which conditions ammonia is liberated. The latter behavior would be typical of a nitride of copper, as well as of a cyanogen derivative. It was believed that the sublimate was some sort of copper-cyanogen complex. This and other information presented in the report led us to the conclusion that the difficulty in the Dumas method arose from the formation of cyanogen during the combustion and our efforts were directed toward the destruction of this material.

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Three methods were tried in attempts to destroy cyanogen. The first involved the addition to the gas stream of water, which should hydrolyze the material. This turned out to be cumbersome. The second was the use of electrolytically generated oxygen. The third was the use of electrolytically generated hydrogen during the combustion, followed by oxygen to remove charcoal. This method was originally used as a convenient method for securing a high and steady concentration of water during the combustion. It appeared, however, that the hydrogen could serve another purpose as well. The formation of the copper derivative of cyanogen requires the presence of copper oxide and this material does not seem to form in the presence of copper as the cracking surface. Accordingly, hydrogen during the combustion would serve to renew the copper cracking surface which could be generated initially.

The method which we finally adopted used hydrogen for 10 minutes at 0.1 amp. before the combustion to prepare a copper cracking surface. During the combustion hydrogen was generated at the rate of 0.05 amp. After the preliminary combustion, followed by a short sweep with carbon dioxide to remove the hydrogen, the polarity was reversed and oxygen was generated for 10-15 minutes at 0.2 amp. to remove the charcoal.

Just before our report was presented, a study of the Dumas method appeared in "Analytical Chemistry", 24, 661 (1952) by W. C. Alford. This relied on the use of a large excess of oxygen during the combustion, essentially as is done during the combustion for C and H. The excess of oxygen is removed by copper and the final sweeping is then performed with CO₂ as in the Dumas procedure. From our studies, it appears that this procedure should also provide a satisfactory answer to the problem, since the formation of cyanogen does not present a source of difficulty in the C and H procedure but only in the Dumas method which utilizes combustion in CO₂, a material in which cyanogen is stable. Because of the necessity for subjecting our procedure to closer study, we have not had an opportunity to make an intercomparison of the two methods but we hope to do this privately in our laboratory during the next month or two.

Our earlier studies also included attempts to use tube fillings other than copper oxide and copper but these attempts were not fruitful. The report ended with a statement of future research, which included attempts to establish the nature of the sublimate more accurately and combustion of materials containing other hetero-elements.

II. Studies Performed During the Last Six Months.

A. Comparison with Other Laboratories.

One criticism which might be directed against the work summarized in the previous report is that the low results which we obtained with our standard compounds before modification of the method are not necessarily

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representative of the method. To examine this, we sent out samples of our two standard difficultly combustible compounds as unknowns to three commercial microchemical analytical laboratories with the request that Dumas analyses be performed. The results are as follows:

Uric acid. Calcd. 33.33%. Found: A, 31.84%. B, 32.58, 32.66%. C, 32.29, 32.02%.

BDNP. Calcd. 19.57%. Found: A, 19.19, 18.99%. B, 18.70, 18.65%. C, 18.62%.

The average value of the five commercial analyses for uric acid is 32.28%, which is low by one part in 33 or 3.2% absolute. The average value for five analyses for BDNP is 18.83%, which is 0.74% low or 3.8% absolute. This agrees with our experience that the absolute error in the analysis of BDNP is greater than that for uric acid. Our worst compound was mercuric cyanide in which the absolute error was 6.5%.

B. Changes in Apparatus.

Heaters. In our previous report it was noted that we were using Fisher combustion furnaces for our tube heaters. These have given trouble of several sorts but we have not been able to find a commercial tube heater which we felt was a completely satisfactory substitute. Several months ago our Fisher furnace burned out and after repairs it no longer gave satisfactory performance. The difficulty was due to too large a temperature differential between the center of the furnace and the ends, where critical parts of the tube filling are present. The result of this temperature differential was that only the metallic copper was maintained at the temperature indicated by the thermocouple. Since this is not involved in the decomposition of the sample or in the combustion of difficultly combustible gases, the temperature indicated by the thermocouple becomes meaningless with respect to the conditions of combustion. Our difficulties with this furnace led us to work on heater design to secure an arrangement which would be satisfactory.

One prime necessity in the Dumas method is that the tube heater should be capable of quick heating and quick cooling. Some commercial furnaces of the split type are so constructed that they cannot be moved back from the combustion tube without changing the position of the tube. This makes them entirely unacceptable for the Dumas combustion. Others not of the split type cool too slowly for use in the Dumas method.

Our first trial for a tube heater consisted of a single coil of heavy Nichrome wire wound for bare clearance of the combustion tube, with the individual turns in contact and with no outside insulation. This could be brought to temperature (750°) in four minutes from a start with a cold combustion tube. Its cooling time was slower but was satisfactory for the Dumas method, since the tube became cool before it was necessary to open it for the introduction of a new sample. By the omission of insulation, differences between the middle and the ends were minimized.

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The single coil tube heater proved to have two disadvantages. To secure complete heating of the space occupied by the sample and its combustion products, it was necessary to move the sample heater until it came into contact with the tube heater. This frequently broke down the oxide coating on the two heaters with a consequent short circuit. This finally resulted in burning out the sample heater, which was constructed of finer wire than the tube heater. The other disadvantage of the single coil tube heater was that the regeneration of portions of the combustion tube filling was made difficult. It was necessary to push the tube heater off the end of the tube and perform the regenerations with the sample heater. With a split furnace that can be pushed back this operation is simple. With a coil that must be slid off the combustion train, it is difficult.

Both of the difficulties of our first design were overcome in our second design, which we consider to be a satisfactory answer to the problems involved. This design was originated by our instrument maker, Mr. Joseph Walter. In this design, the tube heater is made up of three coils of heavy resistance wire (Jolliff Alloy K) and the sample heater is a fourth. These are individually mounted on small blocks of Morinite (Johns-Manville) to furnish rigidity. The heaters are wired in series and supplied with individual switches which can be used to cut out any single heater or combination of heaters while leaving the others on. They were then calibrated against an ammeter. Since all of the coils are constructed of wire of the same size, adjustment of the applied voltage to give a predetermined amperage will bring all of them to the same temperature. When one heater is cut out, readjustment of the amperage to the original value will bring the remaining furnaces to the original temperature. This constant current heating system has proved to be very satisfactory in our work. Bringing the sample heater into close contact with the tube heaters makes no difference, since the coils are connected in series and there is no greater potential difference between adjacent coils when they are in contact than there is when they are separated. Regeneration of portions of the tube filling can be accomplished readily with this arrangement by heating the desired section of the tube heater.

After further experience we have returned to the use of Nichrome in our heater elements.

Generator Relief Assembly. In our previous report we noted that good results could be obtained by the incorporation of an electrolytic generator into the CO₂ train of the gas generator. When this generator is in operation, one of the two gases formed is utilized, the other must be discarded. This was done manually in our first apparatus but an automatic method for accomplishing the gas relief was desired.

We have now designed a gas relief assembly for the generator which is shown in Figure 1. We first experimented with frits rendered non-wettable with various impregnations, including dri-film and other silicone coatings. These turned out to be unreliable, since continued contact with bicarbonate solution finally penetrated all the films that we were able to prepare and rendered the frits wettable.

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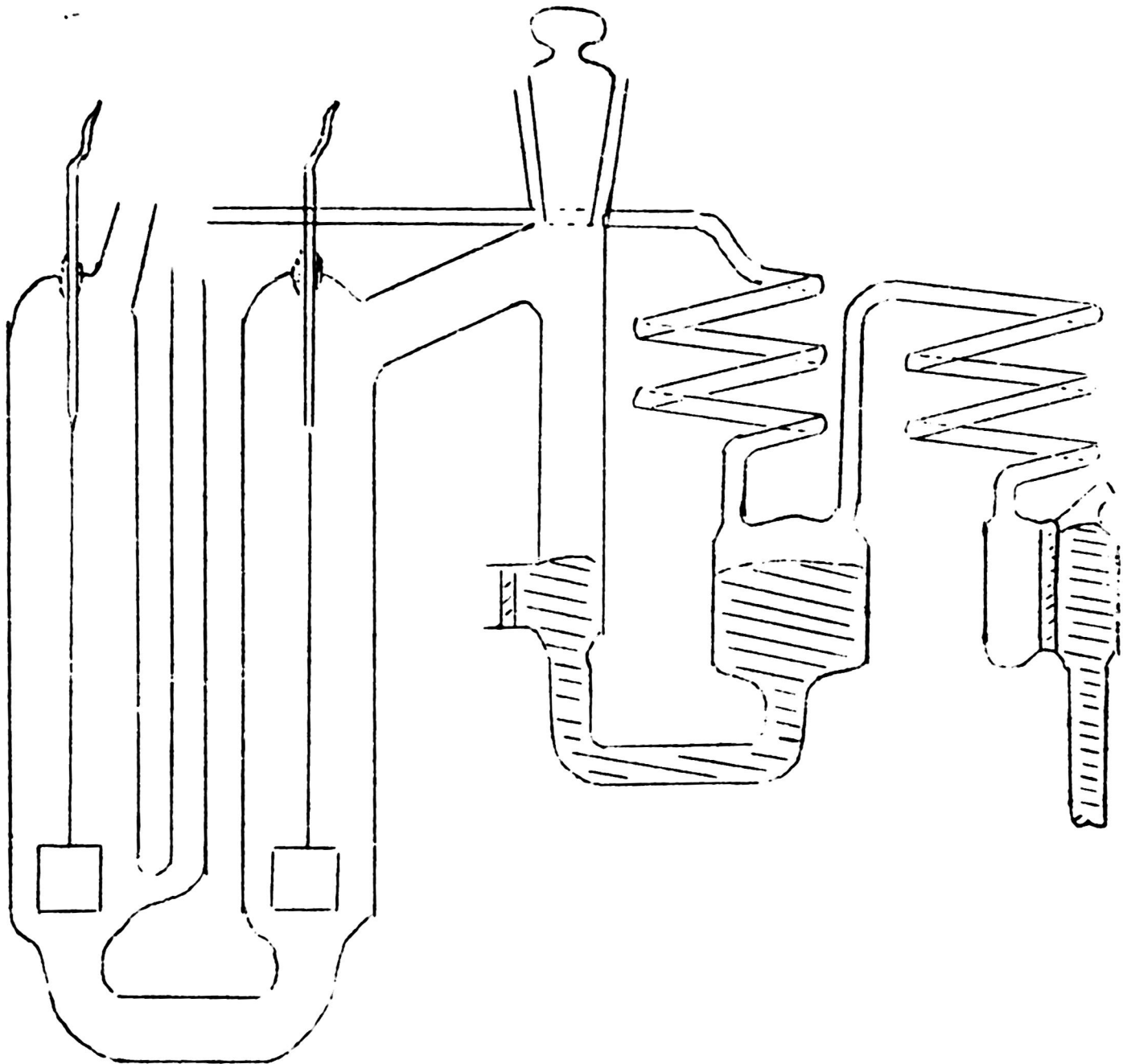


Figure 1.

Hydrogen-oxygen generator with automatic gas relief assembly. Carbon dioxide enters the system at the right and is controlled by the height of mercury at the frit. It then passes to a mercury trap which equilibrates pressure on opposite sides of the generator. It is then conveyed to the generator where it is mixed with the desired gas and leaves through the exit tube at the left. Excess gas on the opposite side of the generator is relieved through the frit at the left side of the mercury trap. The trap and the generator are filled at the standard taper stopper which is held in place with a modified Kronig's cement.

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We finally decided upon a mercury-filled assembly. This is more complicated than the impregnated frit but it has the advantage of reliable operation. For operation at 0.3 amperes or below, a 10 mm. fine frit was satisfactory. For a larger generator with 3 ampere capacity, a 30 mm. fine frit was used. The operation of the device is intermittent. Pressure builds up in the outer chamber of the generator until the mercury has been pushed away from the frit. Gas then discharges through the frit until the mercury rolls over the edge and seals it off. Because of surface relationships, the pressure necessary to force the mercury away from the frit is appreciably greater than that which will allow it to flow back. This results in intermittent operation.

Nitrogen Measuring Device. The nitrogen measuring device described by Clarke and Winans (Anal. Ed. 14, 522 (1942)) has been modified by attaching it to the "nitrometer" by a small standard taper ground joint which is sealed on with beeswax and rosin cement. A Deckman 5 cc. beaker is used to catch the effluent mercury and the gain in weight of the beaker is noted instead of the loss in weight of the mercury container. This modification makes for greater speed in operation and the weighing of the mercury from one run can be postponed until the most convenient time while another sample is started.

We have also modified the "nitrometer" itself. Instead of two stopcocks, we use a single 120°, three-way, pressure stopcock at the top of the nitrometer. Before installing this, we occasionally lost a sample due to leakage of the stopcock. The use of a pressure stopcock obviates this difficulty. Our nitrometer is shown in Fig. 2.

Sulfuric Acid Valve. We have used the magnetic valve described by Pagel (Anal. Ed. 16, 344 (1944)) ever since it was suggested. Our first modification was to turn it upside down so that bubbles would not be caught in the seat. However, we have experienced some difficulty with the operation of the valve. This is due to the introduction of small amounts of grit during the filling process. If some material becomes lodged in the valve, a slow leak will result which will necessitate premature refilling of the generator. To get around this, it became our custom to repolish the valve each time the generator was filled. This added extra work and we finally decided to design a different type of valve.

The valve which we are now using is a mercury injection device shown in Fig. 3. It relies upon the fact that a static column of mercury will support a much higher static column of sulfuric acid. If the sulfuric acid is placed in an inner tube and the mercury in an outer concentric tube with an exit tube sealed to its top, the flow of the sulfuric acid may be started or stopped by changing the height of the mercury column. When it is lowered, acid will flow from the inner tube into the outer and through the exit tube to the generator. Control of the mercury height is secured by means of a surgical syringe. To guard against accidental breakage, this syringe is enclosed in a brass armor. It is driven by a screw impinging on a brass plate

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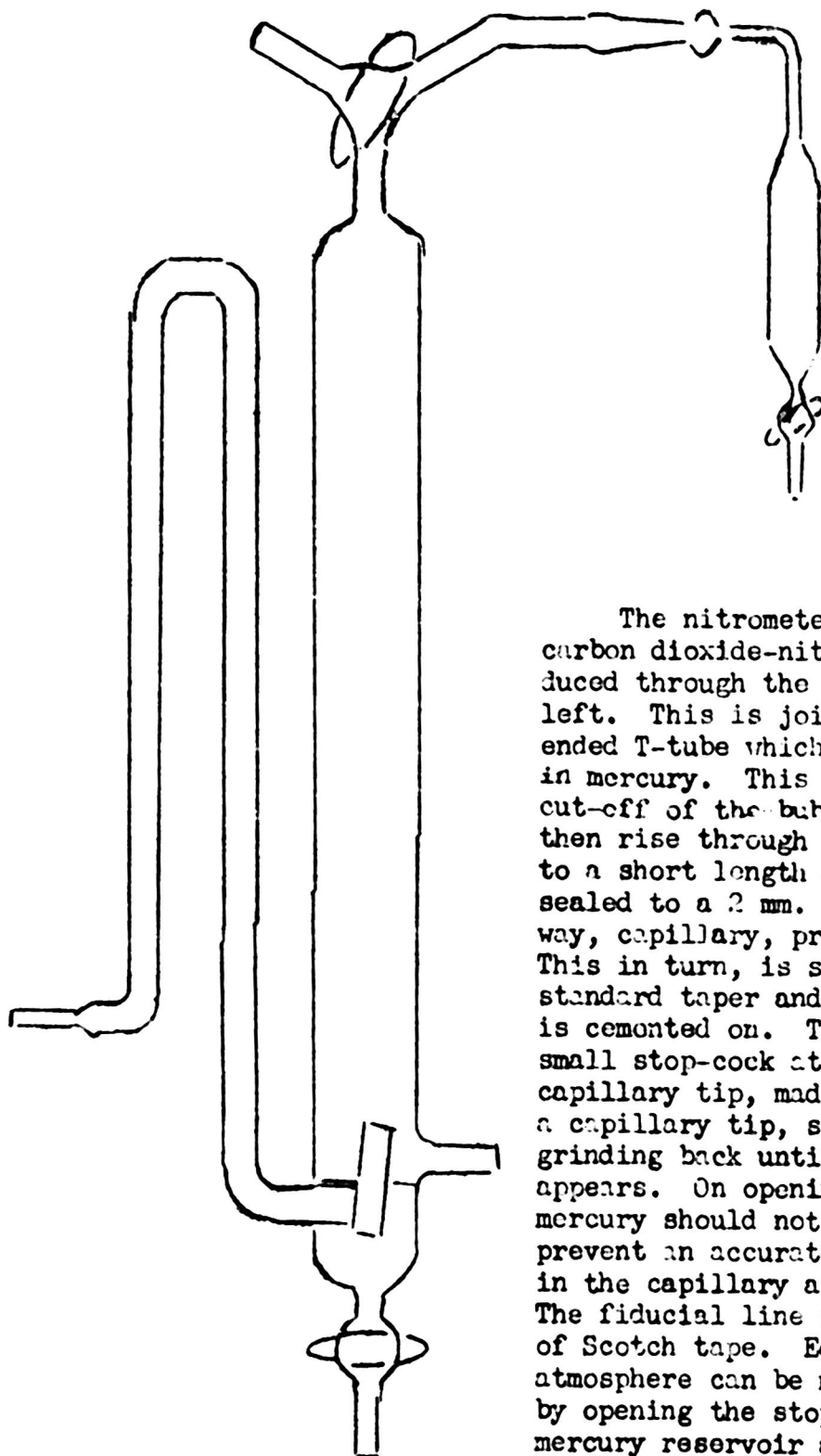


Figure 2.

The nitrometer assembly. The carbon dioxide-nitrogen mixture is introduced through the long capillary at the left. This is joined to a tilted, open ended T-tube which is partially immersed in mercury. This tube insures sharp cut-off of the bubbles. The bubbles then rise through a long column of KOH to a short length of 6 mm. o.d. tube sealed to a 2 mm. capillary on a three-way, capillary, pressure stop-cock. This in turn, is sealed to a small standard taper and the mercury reservoir is cemented on. This reservoir has a small stop-cock at the bottom and a fine capillary tip, made by drawing the end to a capillary tip, sealing it off and then grinding back until the desired tiny hole appears. On opening the stop-cock, the mercury should not run fast enough to prevent an accurate stop of the meniscus in the capillary at the fiducial line. The fiducial line is made with a piece of Scotch tape. Equilibration with the atmosphere can be made before measuring by opening the stop-cock to connect the mercury reservoir and the air. The mercury which comes out is caught in a 5 cc. Beckmann pH beaker and weighed.

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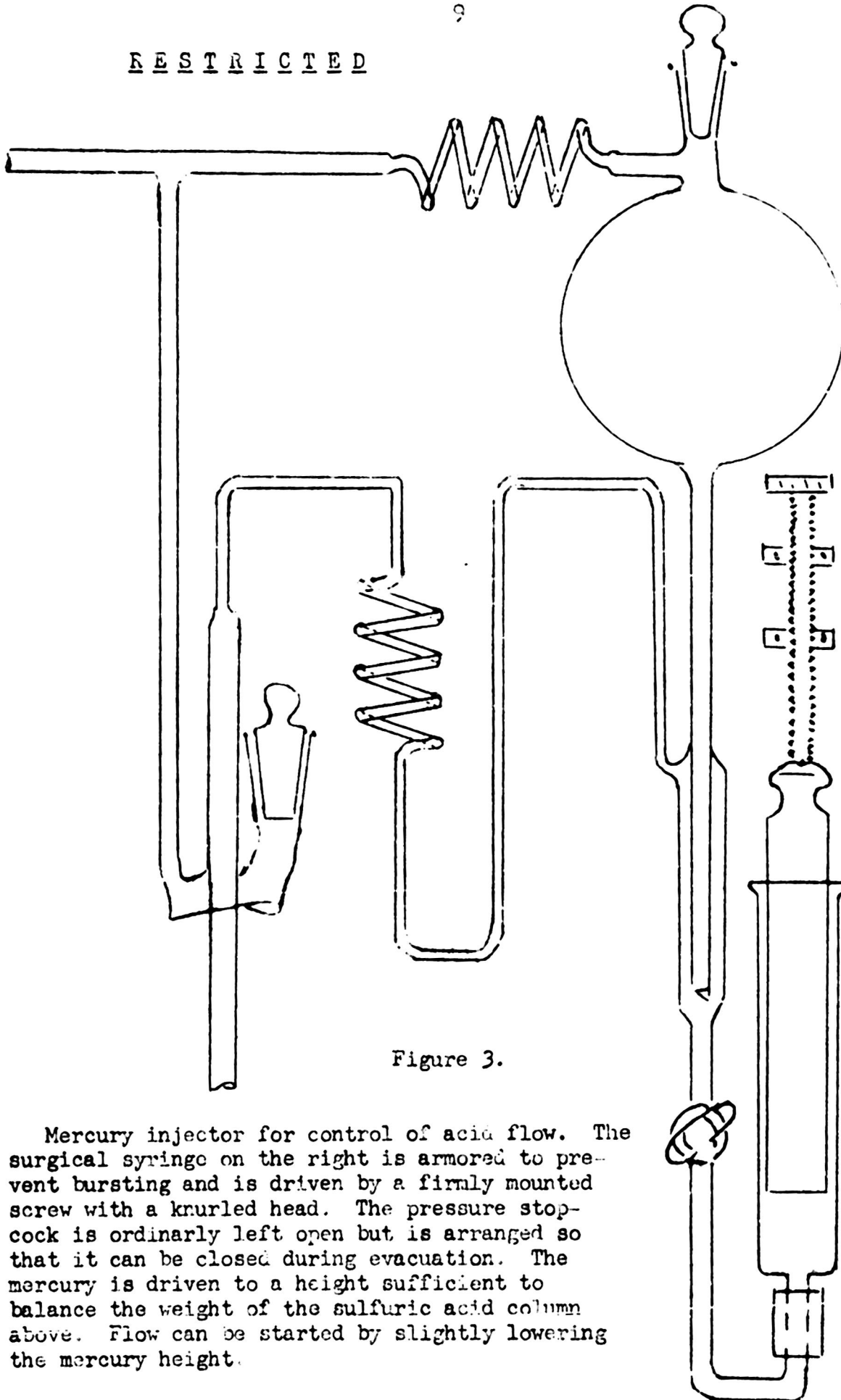


Figure 3.

Mercury injector for control of acid flow. The surgical syringe on the right is armored to prevent bursting and is driven by a firmly mounted screw with a knurled head. The pressure stopcock is ordinarily left open but is arranged so that it can be closed during evacuation. The mercury is driven to a height sufficient to balance the weight of the sulfuric acid column above. Flow can be started by slightly lowering the mercury height.

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attached to its head. Connection to the apparatus is secured by means of butyl rubber pressure tubing tightly wired on over glands. A pressure stopcock is interposed between the syringe and the valve. This is shut off during the evacuation process. By this means, the height of the mercury column between the valve and the syringe can be shortened from the 76 cm. which would be required if it were to support full atmospheric head. The syringe must be well greased with a tacky stopcock grease to prevent the loss of mercury which presses against it.

In use, we do not attempt to generate gas continuously but instead we back the screw up three turns from its closed position, allow the mercury to equilibrate for a few seconds and then return the screw to its original position. A mark on the knurled head permits this position to be found. This operation of the screw injects enough sulfuric acid to just refill the generator with gas. With a little calibration, the amount of sulfuric acid required for the refilling can be gauged satisfactorily.

The most difficult part of the operation of the valve comes when the generator is to be recharged with sulfuric acid and bicarbonate. After the solutions have been replaced, it is necessary to evacuate the generator to remove the air. Before starting this, the plunger of the syringe should be freshly greased. The pressure stopcock in the mercury line is then carefully and slowly turned off. After the generator is evacuated, the generation of carbon dioxide can be started. This should be performed by two persons, one to operate the pressure stopcock, the other to operate the syringe. When operating the pressure stopcock, it is always necessary to turn it slowly. Its friction is considerably greater than that of an ordinary stopcock and it must be supported and turned carefully to avoid straining the glass connections and causing a rupture. It is equally important to avoid advancing the screw attached to the syringe while the stopcock is closed since this could create sufficient hydrostatic pressure to rupture the syringe.

Before opening the pressure stopcock, the screw impinging on the syringe head is backed up the number of turns desired to start the flow of acid. This usually requires about fifteen turns. The stopcock is then opened by one operator, the second operator draws the syringe barrel back and supports it while the first operator immediately closes the stopcock. In this manner, mercury can be pumped out of the system against an unfavorable head. If the greasing of the barrel has not been complete, however, air will be drawn into the system from the outside instead of mercury from the inside. This will negate the effect of the evacuation and require an extra evacuation after the air has been forced through the mercury column. If the syringe fits closely, the greasing is thorough and the operations are conducted expeditiously, this trouble will not appear. When the pressure inside the generator is within 20 cm. of atmospheric, the stopcock may be opened and the plunger adjusted freely.

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To guard against too rapid generation of carbon dioxide with consequent danger of explosion of the generator, the tube leading acid to the generator is made of 3 mm. od. glass and has a coil spring for the double purpose of slowing up the acid flow and providing a strain reliever for the closed glass system. The exit glass tubing is made of 8 mm. od. stock to provide easy exit for the gas after generation. Using this system, one has leeway if the acid is accidentally allowed to flow too freely. As an added precaution, the bicarbonate bottle has a burlap cover placed around it and is drawn up with a drawstring at the top. While the apparatus is evacuated, the operator always wears a face mask.

While the operation of the mercury injector has turned out to be thoroughly satisfactory, we are concerned over the hazards inherent in its design. If the glass holding the mercury should be broken, serious damage could result. The time at which this appears most likely to occur is at the time of the first generation of carbon dioxide following evacuation of the apparatus. Since the operators of the valve must have their hands under the strong sulfuric acid at this time, the chances of injury seem real.

Because of these hazards, we have designed still a third type of acid injector. This has not yet been built and tried but we anticipate building it as soon as one of our generators requires recharging, which should be in about two or three months.

The design which we propose is sketched in Fig. 4. Unlike previous designs, the delivery tube from the sulfuric acid container is constructed so that siphoning will not occur. A magnetic plunger is placed inside the glass pump tube. This plunger is constructed so that it fits closely enough to move the viscous sulfuric-phosphoric acid mixture upwards when it is lifted rapidly but will allow them to flow by it in place when it returns to its rest position. In this manner, sulfuric acid can be pumped into the generator at will but there is no reliance upon the fit of a valve to retain it while there is no pumping. This system also lends itself to purging by evacuation more readily than any of the ones which we have used. The exact dimensions and details of construction will have to await experimental determination.

C. The Sublimato.

In our previous report, we recorded the finding of a sublimato which qualitative analysis showed to contain copper and nitrogen. This material was not obtainable in a form which lent itself to weighing of the original sample nor were we able to subject it to procedures designed for purification. Only samples considerably less than 100g were available. Under these conditions, we decided that the best analytical procedure would be the determination of the copper/nitrogen ratio. The two elements had to be determined on aliquots of the same sample.

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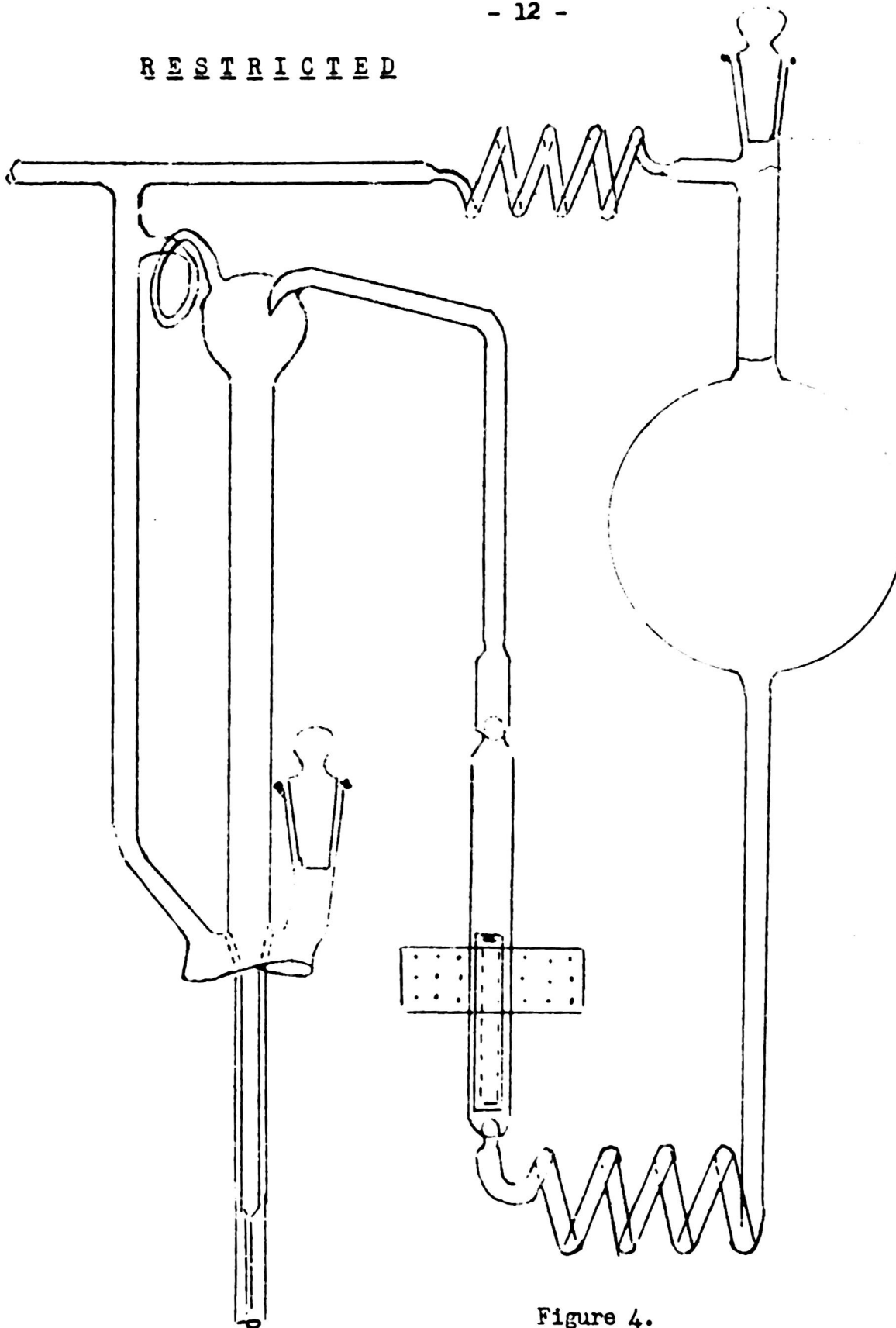


Figure 4.

Magnetic pump for injection of acid. (This has now been found to be the most satisfactory means for introducing acid.) The delivery tube of the pump is high enough to prevent siphoning of acid when the reservoir is full. The check valves are spheres of Teflon. Turning on the current in the electromagnet raises the permanent magnet, which is sealed in Pyrex, and pumps the liquid part way up. The electromagnet may be raised further by hand or the pump may be operated several times in succession and the acid will be pumped over.

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To determine the copper content spectrophotometrically, the sublimate had to be dissolved in glacial acetic acid, which is not an ideal solvent for the ammonia determination which also had to be made. This is true because of the difficulty of freeing acetic acid from traces of ammonia. The copper content was determined by allowing the sample to form a complex with an excess of etioporphyrin II. The amount of free porphyrin and of copper complex could then be determined, because of the difference in their absorption bands, and from this the amount of copper present could be calculated. The determination was performed by Mr. Winslow Caughey of this department. In a typical sample, 40.0γ of copper was found.

To render the acetic acid aliquot basic for the purposes of ammonia determination, about 8 cc. of 50% sodium hydroxide was required for 5 cc. of the acetic acid solution. To secure a solvent low in ammonia, commercial C.P. acetic acid was fractionated and the fraction giving the smallest reading on nesslerization was used. The 50% sodium hydroxide solution was warmed in a water bath with aeration to free it from residual ammonia. By taking these precautions, the blank was diminished materially but not eliminated completely. To correct for the remaining blank, the transmission point on the spectrophotometer was set using a reagent blank instead of distilled water. Readings were taken on a Beckman spectrophotometer. A calibration curve was prepared using a standard solution of ammonium sulfate containing 2γ of ammonia per cc. Analysis of the sample of sublimate referred to above gave an ammonia content of 9.6γ, corresponding to N of 7.9γ.

In the analyses preceding, the value for copper should be good to within 1-2% but the value for ammonia is estimated to be reliable only to $\pm 15\%$. The Cu/N ratio found is 5.07 \pm about 15%. The value calculated for $\text{Cu}(\text{CN})_2$ is 2.27, that for $\text{Cu}_2(\text{CN})_2$, 4.55. Accordingly, we may conclude that, within our experimental error, the analysis is not inconsistent with the conclusion that the material is the cuprous complex of cyanogen, while both analysis and properties are inconsistent with the assumption that the material is cupric cyanide.

D. Significance of Combustion in the Presence of Hydrogen.

In our previous report, we left open the question of the significance of the generation of hydrogen during the combustion. If all the hydrogen were burned before the combustion started, it would serve to present a fresh copper cracking surface to the decomposition products of the sample. Since cuprous cyanogen can be formed from cupric oxide and cyanogen but not from metallic copper and cyanogen, a copper cracking surface should be more effective in preventing the formation of this compound. On the other hand, any oxygen in the compound itself could conceivably be used in forming cupric oxide from the copper so that hydrogen might be necessary to keep a copper cracking surface always available.

If, on the other hand, the critical item in the combustion has nothing to do with the copper cracking surface but only with the presence

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of water formed by the continuous combustion of hydrogen, then a combustion performed in the presence of a good supply of reduced copper for a cracking surface but without added hydrogen during the combustion should produce low results.

In an attempt to resolve this question, several combustions were performed on BDNP (benzaldehyde dinitrophenylhydrazone). Since this contains nitro groups, it should partially exhaust the copper cracking surface when no hydrogen is available to replenish it and should, therefore, provide a good test of the alternatives. Three combustions performed with a copper cracking surface but without added hydrogen during the combustion gave values of 19.48%, 19.55% and 19.40%, an average of 19.48% N, as against 19.57%, theoretical. This result is not as low as would be expected if water were necessary during the combustion to destroy cyanogen. It should be recalled that performing the combustion without hydrogen at either time, that is neither before nor during the combustion, gives very substantially low results, around 18.5%. Thus it appears that the presence of hydrogen during the combustion is not essential as long as a copper cracking surface is present. This surface may be generated previous to the combustion or during it in this case. Hence, we may conclude that the copper cracking surface is more important than the simultaneous formation of water in the combustion.

As will appear in the discussion which follows, bromine also gives trouble during the Dumas combustion. This trouble is also overcome with the use of hydrogen. In this case, however, orienting experiments indicate that the difficulty is greater than in the case of the nitro compound. A single combustion with a copper cracking surface but with no hydrogen during the combustion gave a value of 3.87 instead of 4.61 theoretical. A combustion with no copper initially at the cracking surface but with hydrogen generated during the combustion gave a value of 4.34 instead of 4.61. Even the use of hydrogen at the rate ordinarily used for the uric acid and BDNP combustions gave low results. A discussion of the solution to this problem is presented later. It lies in the use of excess hydrogen both before and during the combustion. Our theory is that in this case cyanogen bromide is formed which destroys the copper surface more effectively than either the nitro group or cyanogen, with the result that excess hydrogen is required to keep a copper surface constantly clean. Taken by itself, this experiment might seem to indicate that the presence of nascent water is the critical factor. Taken in conjunction with the work on the BDNP, this interpretation does not seem tenable. It would have been desirable to confirm this with more experiments but more pressing problems required our attention.

Our general conclusion from this work is that, for a combustion to proceed smoothly in the presence of excess carbon dioxide as carrying gas, it is necessary to present a constantly renewed metallic copper cracking surface at the head of the combustion tube.

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E. Carbon Monoxide

Work performed in this laboratory before the start of this study led us to believe that carbon dioxide would react with cuprous oxide to produce carbon dioxide and that this reaction would progress down the tube. This conclusion was originally based upon the following experiment: The tube was filled for the length of the combustion furnace with commercial cuprous oxide. This was heated and a slow stream of carbon dioxide was passed over it for a time sufficient to have produced micro bubbles, if the material had been cupric oxide. The nitrometer was then filled and the gas formed was collected. The tube acted as a gas operator, rapidly filling the large bulb of the nitrometer. Two tests were performed upon the gas to establish its nature. It was first shown to be combustible, demonstrating that it was not nitrogen. It was then shown to reduce palladium chloride, indicating that it was probably carbon monoxide. This reasoning was based upon the assumption that the cuprous oxide was reasonably pure. It should be noted, however, that the tests performed did not exclude the possibility that the gas formed was hydrogen, evolved due to the presence of some impurity in the cuprous oxide.

We have now modified this experiment by producing cuprous oxide in the combustion tube by the reduction of cupric oxide with hydrogen. When the reduction is carried only partially to completion, a mixture of copper and cupric oxide is formed. Upon heating this for some time, interaction takes place with the formation of cuprous oxide. Material prepared in this manner appears to be indefinitely stable to carbon dioxide, even at 750°, and we were not able to detect the formation of carbon monoxide. Since this is more nearly analogous to the material which would be formed during a combustion, we are not now inclined to believe that cuprous oxide is capable of reaction with carbon dioxide to form carbon monoxide.

In spite of the fact that carbon monoxide does not give the complications which we earlier believed, it can still be the cause of high results in the Dumas analysis. This difficulty can arise when the ends of the combustion tube are not sufficiently hot. Incomplete combustion can take place at the sample heater, due to partial volatilization of the sample. The carbon monoxide can then pass over copper in the hottest part of the tube and arrive at the copper oxide, where combustion should take place, but where it will not due to insufficient heating. We observed this condition with a Fisher furnace heated so that the thermocouple was held at 750°. The gradient was so great that standard pyrrole gave very high and variable results and NBS dextrose gave 52 mm. of gas in a 2.7 mm. i.d. tube. Difficulties of this sort were entirely obviated when the uninsulated tube heater was used.

It should also be pointed out that work prior to this contract showed that a temperature of 750° was necessary to complete the combustion of methane by cupric oxide. This would not take place if the cupric oxide were held in a furnace with a large gradient. As an example, the oxime of pinacolone showed high results at 650° and excellent results at 750°.

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We conclude that it is necessary to use a furnace constructed so that the internal temperature gradient will be as small as possible.

F. Work with Metals.

Very few metals may be used in the Dumas tube. Most of them react with carbon dioxide to give carbon monoxide at these temperatures. Platinum and copper are notable exceptions and can be used in the combustion tube. Previous work has shown that iron, cobalt, nickel, nichrome all generate carbon monoxide. In addition, silver is unsatisfactory, probably because of tenacious gas adsorption.

We have now obtained a few more metals and tested them. Vanadium, 20 mesh, zirconium lumps or titanium lumps, crushed in a mortar, when used in the tube gave large quantities of a gas presumed to be carbon monoxide because of its combustibility.

Silicon, on the other hand, looked promising. Although a small amount of combustible gas was evolved when the whole tube was filled with silicon, this should be accommodated by a guard layer of cupric oxide to burn the carbon monoxide. Thus the presence of a small amount of silicon of the proper size would probably not be objectionable, providing that it proved to be useful for some purpose, such as reacting with halogens.

G. Determinations in the Presence of Chlorine.

Our survey of the literature leads us to the conclusion that no difficulties are to be expected due to the presence of chlorine. In this laboratory, we have occasionally had trouble with compounds containing chlorine but we have also a number of examples of compounds which contain chlorine which give good values by the standard Dumas procedure. One might conclude from such experiences that chlorine could give trouble on occasion. We now know that the proper conclusion is that chlorine itself is not responsible for the difficulty but rather the nature of the decomposition of some samples containing it is such as to give low results. This conclusion became the logical one when we realized that the source of our difficulties was not in the presence of hetero elements and that compounds containing only C, H, O, and N could also give difficulty. With this knowledge, the samples which give accurate values become the significant ones with respect to the behavior of a hetero element. Accordingly, we have not made any systematic studies on compounds containing chlorine but have spent our available time on the problem of compounds containing bromine, which presented a difficult problem to solve.

H. Determination in the Presence of Bromine.

We do not believe that the interference of bromine in the Dumas method has been clearly described in the literature. In various researches in this

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laboratory difficulties have been encountered in the combustion of substances containing both nitrogen and bromine. One group of materials which gave such difficulties was a series of betaine hydrobromides. These substances were found to have the expected analysis for bromine but the values for nitrogen by the Dumas procedure were low. Until we were aware of this source of error, difficulty was experienced in the interpretation of the results of research preparations. At the time, we looked upon the Dumas procedure as reliable and were experimenting with a new procedure for bromine. When our Dumas analyses gave values which could be interpreted reasonably and our bromine values did not fit this interpretation, we were at first inclined to question the bromine values and to accept the structures based on the nitrogen determinations. Further experience showed that the bromine analyses were the ones which were reliable, that the Dumas determinations were low and that the chemistry of the compounds did not agree with the assumptions based on the nitrogen values.

The hydrobromide of glycine betaine gave 5.65%, 5.96%, and 6.62% instead of 7.05%, the theoretical percentage of nitrogen. Bromine values on this compound were excellent. Consideration of our later results with uric acid and other compounds with C, H, O, and N only led us to the conclusion that this material would not be a suitable reference substance for the study of bromine-containing compounds because of the fact that it does not possess a reversible melting point. On the basis of our general criteria, it might be expected to give low nitrogen values even if the bromine were not present. Accordingly, it would not be possible to draw from this analysis, nor from those on other betaines, the conclusion that bromine is itself responsible for interference with the combustion.

As a reference substance for the determination in the presence of bromine, we finally chose 2,4-dicarbethoxy-3-methyl-5-bromopyrrole. This material possesses a reversible melting point, is stable and can easily be prepared in a state of analytical purity. Its purity can be checked by analysis for C, H, and Br. We shall refer to this sample as "standard bromopyrrole".

Our first Dumas determination on standard bromopyrrole, performed several years ago, gave 3.97% instead of 4.61% calculated. A deposit was noted in the end of the combustion tube. This deposit resembled the sublimate later obtained with uric acid and with mercuric cyanide. It was decided to attempt to complete the combustion by heating the end of the tube. This procedure gave 5.06% instead of 4.61%. Evidently, the rubber connector had been overheated.

The deposit from the second of these analyses was driven by heat into the tip of the combustion tube and dissolved out with 1:10 nitric acid. It tested positive for halogen and for cuprous ion but negative for cupric ion.

At that time, a sample of *p*-bromophenacyl benzoate of known purity was analyzed by the Dumas method and gave gas equivalent to 0.5% N. To

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test our present procedure using hydrogen followed by oxygen, *p*-bromophenacyl bromide was burned. This substance contains 57% bromine. Combustion gave gases corresponding to 0.17% and 0.20% N. Thus a marked improvement had been secured by this modification of the combustion but the result was not entirely acceptable. Seven determinations were then performed on standard bromopyrrole, following the procedure found satisfactory for uric acid and for BDNP. Values obtained were: 4.02%, 4.36%, 3.83%, 4.10%, 4.29%, 4.07%, and 4.17%. The average was 4.13% instead of 4.61%. This represents an unacceptably low series of determinations, with the highest value still unacceptably low. We were forced to conclude that further experimentation would be required to find a modification of the method which would work in the presence of bromine.

One combustion was performed using no hydrogen but using oxygen generated at the rate of 0.2 amp. during the entire combustion. The result was 3.71% instead of 4.61% theoretical. We decided that the solution to the problem lay in the direction of more hydrogen rather than more oxygen.

It has already been pointed out that the use of hydrogen before but not during the combustion gave low results. In this experiment, hydrogen was generated at the rate of 0.25 amp. for 15 minutes. The result was 3.87% instead of 4.61%.

The converse experiment, using hydrogen during the combustion but not before was also tried. In this, hydrogen was generated at 0.25 amp. for 20 minutes during the combustion. The result was 4.34% instead of 4.61%. This represents a significant improvement. In another variation, the excess hydrogen was generated at a smaller rate for a longer time, 0.2 amp. for 30 minutes. This gave 4.20% instead of 4.61%. In still another variation, hydrogen was generated at 0.1 amp. for 10 minutes before the combustion and at 0.3 amp. for 20 minutes during the combustion. The result was 4.25% instead of 4.61%. The average of these three combustions using a higher rate of hydrogen generation was 4.26%. This result is probably significantly higher than that using our standard procedure. It should be understood that in each case, oxygen was used to remove the charcoal after the end of the hydrogen generation.

Following the clue given above, hydrogen was generated in one experiment at 0.25 amp. for 15 minutes before the combustion and at the same rate for 20 minutes during the combustion. This experiment gave a value of 4.52% instead of 4.61%. Another run was then made with a preliminary rate of 0.25 amp. for 15 minutes followed by 0.3 amp. for 20 minutes during the combustion. This gave 4.54% instead of 4.61%. It thus appeared that each increment in the hydrogen used gave a better result. Unfortunately, we were not able to increase the rate indefinitely because of the limitations of our generator design. The last experiment cited brought the electrolyte nearly to the boiling point and represented about the maximum obtainable with the small generator in use at that time.

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In order to circumvent the limitation placed upon us by the small generator, a larger generator was built and sealed into the carbon dioxide delivery tube. This is made of 30 mm. o.d. tubing. To permit working at smaller mercury heights in the relief assembly, the electrode on the gas exit side was placed 90 mm. below that on the relief assembly side. Carbon dioxide was introduced near the bottom of the gas exit side, as in the previous model. With this generator a current of 3 amperes could be maintained for a few minutes.

The rate of hydrogen generation was stepped up in the new apparatus to 0.5 amp. and the analysis of the bromo pyrrole went up to 4.59% and 4.58% instead of 4.61%. These values are considered acceptable.

It was noted that in all combustions involving this bromopyrrole, including those which gave acceptable values, staining of the combustion tube took place. The same phenomenon is observed when cupric bromide is heated in the tube and the staining can be ascribed to the volatilization of cupric bromide. If the filling is removed and the stain heated in a stream of hydrogen, the color becomes that of metallic copper, providing further confirmation of its nature. The stain itself is probably cupric oxide formed by the decomposition of the cupric bromide. The disadvantage of having it is that it tends to weaken the combustion tube, probably by the formation of copper silicate. This is a minor disadvantage, if accurate analyses can be obtained by the method.

Unfortunately, we have not had sufficient time to run repeated analyses using this new technique and thus to build up a statistical proof that the method proposed is reliable. We hope to be able to do this in the next few months in the laboratory, thus making the material available for publication.

I. Determination in the Presence of Iodine.

In the case of iodine, the possibility exists of burning the iodine to iodine pentoxide and thus avoiding the difficulties found in the combustions of compounds containing bromine. To find whether or not difficulties would be encountered with an iodine containing compound, two combustions were performed with 2-iodo-3,5-dicarboethoxy-4-methylpyrrole, a compound which melts reversibly and which can easily be obtained in a state of analytical purity. The results obtained were 4.00% and 3.99%. The theoretical value is 3.99%. Accordingly, we may conclude that iodine does not cause difficulty when the combustion is carried out by our new procedure.

J. Determination in the Presence of Sulfur.

In 1884, Victor Meyer reported work with an unidentified, unknown, volatile oil containing C, H, and S, which tested by the Dumas method for

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14% nitrogen. Later work revealed that there was no nitrogen in the compound. Meyer proved that the gas evolved was carbon monoxide and postulated that sulfur dioxide reacts with carbon dioxide to produce carbon monoxide. He said that the use of lead chromate in the tube prevented this difficulty. This observation has been repeated without further confirmation in the analytical literature.

In the Hopkins laboratories, difficulties have been encountered with some sulfur-containing compounds, although good results have been obtained with others. The latter result would not be expected if Meyer's conclusions hold under modern conditions of combustion.

Following the line of reasoning employed under the heading of chlorine compounds, we now attach more importance to the good results than to the bad ones. The fact that good results can be obtained indicates that sulfur as a hetero element does not necessarily interfere with the Dumas combustion. When a compound is encountered with which poor results are obtained, this should be ascribed to difficulties in the combustion due to other causes than the presence of the sulfur.

To test the method of combustion now employed, we burned two samples of purified dithizone. The results obtained were, 21.90% and 21.87%. The theoretical value is 21.86%. We conclude that the presence of sulfur does not interfere with our modified Dumas technique.

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