LABORATORY AND PLANT

A Modification of the Dumas Method, and the Application of the Kjeldahl Method to the Determination of Nitrogen in Nitronaphthalenes^{1,2}

By Paul H. M.-P. Brinton, F. M. Schertz, W. G. Crockett and P. P. Merkel

SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA, ST. PAUL, MINN.

In carrying out nitration investigations in connection with nitronaphthalenes it is necessary to make frequent determinations of nitrogen. Unfortunately, the convenient method of Kjeldahl has been found to give low results when applied to nitronaphthalenes, and it has been necessary to have recourse to the method of Dumas, which requires constant attention, and unusual care in execution if the results are to be reliable.

The investigation here recorded had as its aim the determination of the relative values for nitrogen in typical nitronaphthalenes by a modified Dumas method; the Kjeldahl method, as modified by Jodlbauer, Gunning, and others;³ and the phosphorus iodide method,⁴ which is also a modification of the Kjeldahl process. Five samples of nitronaphthalenes, which we supposed to be typical of the more highly nitrated mixtures likely to be met in the nitration tests, were prepared with every precaution to secure uniformity in the individual lots, and were analyzed by the three procedures.

THE DUMAS METHOD

The Dumas method has long been recognized as a standard one for the determination of nitrogen in the vast majority of nitrogenous organic substances, and is conceded to be accurate if carried out with all the necessary precautions. There are so many sources of error, however, and the manipulations require such unusual attention to details that it is not suited to routine control work. In the present investigation every effort was made to eliminate sources of error, and a procedure was finally developed by which concordant results were obtained on certain pure standards. The procedure and apparatus are not held to be the simplest possible for the attainment of accurate results, but this combination does yield the accuracy desired, and for the present purpose it was not considered necessary to strive for greater simplicity.

APPARATUS

The apparatus, as developed mainly by F. M. Schertz, is shown in the accompanying cut, in which the various items are not drawn to scale, and from which all parts of the apparatus not necessary to the understanding of the process (such as furnace, supports, etc.) are omitted.

Generator—On the floor under the table a heavy 20-liter glass bottle serves as the carbon dioxide generating chamber. On a shelf 8 ft. above the generator are two 10-liter bottles, containing saturated sodium carbonate solution and 1:1 sulfuric acid, respectively. These bottles are connected with the generator bottle as shown in the cut. It is essential that the stopcocks, *a* and *b*, of these feed bottles be located at the low level shown, and not close to the feed bottles, since the latter arrangement would cause a back pressure of CO₂ in the feed tubes, sufficient to prevent the flow of liquid. A drop of about 8 ft. is required to establish the pressure necessary for the whole system. The stopper of the generator bottle carries three tubes: one the common outlet of the forked feed tubes, one the delivery tube to

the measuring bottles, and one the drain tube, which reaches to the bottom of the chamber and carries the stopcock, *c*.

The big generator bottle is completely filled with boiled and cooled water, the tubes leading from the feed bottles are filled with their respective solutions, and the stopper of the generator is firmly inserted and made entirely tight with sealing wax.

Measuring Bottles—Two bottles, R and S, of 2.5-liter capacity are each fitted with three-hole stoppers, through which pass three tubes connecting the two bottles. The first of these tubes is a long siphon reaching to the bottom of each bottle. The other two tubes end just below the stoppers, and each of these two tubes has a 3-way stopcock in the center. The stopcock *g* connects with the generator through tube *d*, and stopcock *f* connects with the furnace through tube *n*. Before inserting the stoppers into these bottles, one of them (say, S) is filled nearly full of cold, recently boiled water. The level of the water should be about an inch below the ends of the tubes which terminate just under the stoppers. The stoppers are inserted and fixed in place with sealing wax.

A U-tube is inserted between the measuring bottles and the furnace in the position shown, to prevent the excessive passage of water into the combustion tube.

Absorption System—Three Schiff nitrometers are connected as shown in the illustration. It will be seen that by manipulation of the two 3-way stopcocks, *u* and *y*, it is possible to connect any one of the nitrometers with any other, or with the outer air through the tube leading into the drain bottle E. Nitrometer II is encased in a water jacket with a thermometer, for more exact control of volume when reading. This nitrometer is accurately calibrated. The others need not be. The regular gas inlet arms of nitrometers II and III are closed, as they are not needed. No mercury is required in these two nitrometers, but in I such an amount of mercury is added that its surface shall come about half way between the inlet arm and the leveling bulb arm. All gases coming from the combustion tube enter the absorption system through nitrometer I. Bulb D is inserted between leveling bulb A (which functions as a permanent reservoir) and nitrometer I, to act as a trap for any air which might be mechanically carried down into the nitrometer on pouring caustic solution into A, as well as for any small amount of nitrogen that might find its way into the leveling arm. By adjusting the relative positions of A and D, the trapped air or nitrogen can be expelled through A or returned to the nitrometer as the case may demand.

DETAILS OF OPERATION—Removal of Air—The big generator bottle being completely filled with water and the stopper sealed in as before described, all connections are made as shown in the cut. Stopcock *c* is opened and a little acid is admitted through cock *b*, a little water running out through cock *c* to make room for the acid. Cock *b* is closed, and a little sodium carbonate solution is then admitted through *a*. Any air in *d* and in the top of the generator bottle is blown out through *d* by the carbon dioxide generated, and then the 3-way cock, *g*, is closed, whereupon water is forced out through the open cock, *c*, until the generator contains only pure carbon dioxide. Cock *c* is now closed, and *b* is opened, allowing about a liter of the acid to run into the generator. The carbonate solution

¹ Received March 31, 1921.

² Published by permission of the Chief of Chemical Warfare Service, U. S. Army.

³ Marshall, "Explosives," II, 731.

⁴ Cope and Taylor, Bureau of Mines, Technical Paper 160.

is now let in until no more will flow because of the pressure of the carbon dioxide in the generator.

Stopcock *g* is now adjusted so that carbon dioxide flows from the generator into the bottle *S*, which forces the water from that bottle through the siphon into bottle *R*, while the air from *R* is forced out through *n* by properly adjusting stopcock *f*. When all the water from *S* has passed into *R*, cocks *g* and *f* are adjusted so that carbon dioxide from the generator flows into *R*, forcing the water back through the siphon into *S*, while the carbon dioxide from *S* is forced into the combustion tube through *n*. By repeating these operations a few times, and admitting sodium carbonate solution to the generator as needed, the generator, measuring bottles, connecting tubes, and combustion tube will be freed from original air and will contain only carbon dioxide of the grade furnished by the generator, which, however, contains a very slight amount of air—hence the necessity of the measuring bottles.

APPARATUS FOR THE DETERMINATION OF NITROGEN IN NITRONAPHTHALENE BY DUMAS METHOD

It is, of course, not necessary to go through this whole operation before every analysis, for if the train be kept closed, air is not admitted to any part of the generating system, and only the combustion tube and nitrometers must be cleared before each run. The sealed stoppers of the generator and measuring bottles need never be removed, as the spent liquor is run out of the generator by the long siphon tube.

The Combustion Tube—The hard Pyrex glass combustion tube is wrapped with asbestos paper and over this is wound iron wire. This prevents bulging, and prolongs the life of the tube greatly. The copper oxide is prepared by long ignition in nickel crucibles, and preserved in stoppered bottles, with the usual precautions.

In the middle of the tube is placed a plug of ignited asbestos, about 1 in. long, and the half of the tube toward the nitrometer side is filled with coarse copper oxide and the reduced copper spiral in the conventional way. On the other side of the asbestos plug a short layer (an inch or two) of medium grade copper oxide is placed, and after this the intimate mixture of sample and fine copper oxide. It has been found desirable to dilute the sample quite freely with copper oxide, so that the layer containing the sample is from 5 to 7 in. long. Behind this comes an oxidized copper spiral.

The Combustion—In starting the run, the charged tube is heated by lighting the burners under it from the end nearest the nitrometers to within about 3 in. of the asbestos plug, at the same time passing a brisk current of carbon dioxide through the tube. A damp towel is laid over the part of the tube containing the sample to guard against prematurely liberating nitrogen. About one measuring bottle of carbon dioxide is passed through the tube to clear the system of air. This gas passes into nitrometer I, in which the level of

the hydroxide solution is held just a little above the side arms by suitably lowering *A* and *D*. Stopcocks *w*, *u*, and *y* are adjusted so that the gas passes out through drain bottle *E*. After the passage of this bottle of carbon dioxide, the nitrometers and connecting tubes are completely filled with sodium hydroxide by manipulating the stopcocks and leveling bulbs. Exactly one bottle of carbon dioxide is now run as a blank. This gas, after passing through the furnace, enters nitrometer I at the bottom, and passes over into nitrometer II through the open stopcocks *w*, *u*, and *z*. (*u* is so set that nitrometers I and II are connected, but III is cut out.) At the start *A* and *D* are at about the relative levels shown in the cut. It is evident that there will be a gradual flow of sodium hydroxide solution from *A* to *C*, passing up through nitrometer I and down through Nitrometer II. There is thus a current of solution going along with the gas, and this greatly facilitates absorption. When the supply of sodium hydroxide in *A* becomes small, and that in *C* large, liquid from *C* is poured into a beaker and transferred to *A*. Any air will collect in the upper part of nitrometer II, and when the one bottleful of carbon dioxide has been passed through the system, stopcock *h*, between the measuring bottle and the furnace, is closed. Any small bubbles of gas in the upper part of nitrometer I, in the connecting tube between *w* and *z*, and in the upper part of nitrometer II, are collected in nitrometer II, and the cocks *w* and *z* are closed. The small volume of gas is read off in the conventional way, bringing the level of the liquid in *C* to coincide with the liquid surface in the nitrometer. This volume gives the blank for one bottleful of carbon dioxide, and in our experience it has been usually of the order of 1 cc. or less. If the generator has stood for some time the blank runs a little higher than when the generator is in more constant use. The little volume of air is expelled through *z*, *u*, *y*, and out through drain bottle *E*.

The combustion of the sample is now begun by opening stopcock *h* and allowing a very slow current of carbon dioxide to pass through the tube, *w*, *u*, and *z* being adjusted to permit the circulation just as they were in running the blank. Two or three burners are lighted at the extreme end nearest the generator, and at the same time two more burners are ignited under the coarse copper oxide, thus making the heated area extend from the reduced copper spiral to the asbestos plug in the center of the tube. The damp cloth is removed from over the center, and the sample is burned by very gradually heating from both sides. It must be strongly emphasized that the evolution of nitrogen must be gradual. During the combustion half a bottle (about 1.25 liters) of carbon dioxide are used, and a bottle and a half (3.75 liters) are used to sweep out all nitrogen. When most of the nitrogen has passed into the nitrometers, the rate of flow of the carbon dioxide is increased to a brisk stream.

For greater accuracy, large samples (about 1.5 g.) have been used, and this has necessitated the use of the third nitrometer. When nitrometer II becomes nearly full of nitrogen, the current of gas is deflected into nitrometer III by manipulating the 3-way cocks, *u* and *y*, and opening cock *v*. The current of gas is now up through nitrometer I, turning at *u*, passing through, and down into nitrometer III, where it collects. The flow of absorbent liquid is now down from *A*, up through nitrometer I, down through nitrometer II, and into leveling bulb *B*, from which it is transferred back to *A* when necessary, by means of a beaker.

After standing half an hour in the water-jacketed nitrometer II, the volume of nitrogen is carefully read, and then passed out through *z*, *u*, and *y*, into the drain bottle *E*. The nitrogen from nitrometer III is now transferred to the water-jacketed nitrometer, and its volume is read in the same way.

A complete run requires an hour and a half. When the run is finished the heat is turned off, the pinchcock at the inlet of nitrometer I is closed, and the furnace is allowed to cool under a slight pressure of carbon dioxide. The generator is then closed by turning cocks *g* and *f* between the measuring bottles to neutral positions.

Results—A large number of preliminary analyses were run both on the nitronaphthalenes and on specially purified nitro compounds; and the results of these runs were used in developing details of the method. After the method was developed three consecutive runs on each of the five samples were made, and the percentages of nitrogen found, without omission of any figures, are given in Table I.

SAMPLE.....	1	2	3	4	5
	14.31	14.65	14.89	16.10	16.91
	14.39	14.47	14.97	16.15	16.89
	14.28	14.71	14.93	16.19	16.74
AVERAGE.....	14.33	14.61	14.93	16.15	16.85

Just before, just after, and interspersed with these determinations, samples of specially purified picric acid and dinitrobenzene were run as checks on the accuracy of the operations. The following results were obtained.

	PICRIC ACID	DINITROBENZENE
	18.39	16.78
	18.46	16.61
	18.49	16.69
AVERAGE	18.45 Per cent Nitrogen	16.70 Per cent Nitrogen
THEORY	18.35 Per cent Nitrogen	16.64 Per cent Nitrogen

THE KJELDAHL-GUNNING-JODLBAUER METHOD

OUTLINE OF METHOD—A sample of about 0.5 g. is weighed into a 500-cc. Kjeldahl flask. (Convenient for this purpose is a spoon made from a rather heavy glass rod 15 in. long, by heating and molding one end to a spoon shape. The sample is dipped carefully from a weighed bottle, and transferred to the bottom of the flask, the spoon bowl being brushed off with a short bristled camel's brush, which has been cut off at its head and tied with fine copper wire to the short arm of a right-angled glass rod, the two arms of which measure 18 in. and 0.25 in., respectively. The bottle is again weighed, and the weight of the sample is obtained by difference. The brush must be a good one, with no loose hairs that might stay in the flask and raise the nitrogen content.) Thirty cc. of strong sulfuric acid, containing 2 g. of salicylic acid, are poured rapidly over the sample, and the flask is rotated and set on the steam bath. Most nitronaphthalenes will completely dissolve, and this should be attained if possible. Some samples, very high in nitrogen, will not give a clear solution, and a muddy residue remains even after many hours on the steam bath. With such a sample it has been found sufficient to heat for 2 hrs. with occasional agitation, and to proceed in spite of the muddy residue. After cooling, 2 g. of zinc dust are added in small portions, to avoid local heating. The flask is shaken occasionally for an hour or two, and allowed to stand over night. Next morning it is heated in a water bath for an hour at 70°, and then over a small flame until all visible action is over. After cooling somewhat, 1 g. of mercury or mercuric oxide is added, and the contents of the flask are gently boiled for 1 or 1.5 hrs. After cooling, 7.5 g. of potassium sulfate are added, and the boiling is continued for 1 or 1.5 hrs. The flask is cooled and 250 cc. of water are added to dissolve the cake, after which 25 cc. of 8 per cent sodium sulfide solution and 1 g. of granulated zinc are added. Ninety cc. of sodium hydroxide solution (750 g. to 1 liter of water), or enough to make the solution strongly alkaline, are poured into the flask, the latter is immediately connected with the condenser, and the ammonia is distilled off into standard acid, and titrated in the usual way.

In Table II are shown the percentages of nitrogen found in the five samples by this method.

SAMPLE.....	1	2	3	4	5
	13.74	13.93	14.20	14.93	15.55
	13.85	13.99	14.10	15.16	15.61
	13.67	13.84	14.17	14.91	15.41
		14.01	14.07		15.35
AVERAGE.....	13.74	13.94	14.14	15.00	15.48

THE PHOSPHORUS IODIDE METHOD

This method was carried out according to the details quoted by Cope and Taylor, and specific directions need not be given here. In Table III the percentages of nitrogen found by this method are shown.

SAMPLE.....	1	2	3	4	5
	13.94	13.61	14.05	15.22	16.27
	13.54	13.46	13.88	15.05	16.24
	13.49	13.85	14.24	15.13	16.12
	13.67	13.74	13.99	15.12	16.10
	13.92	13.64	13.83	15.03	16.02
	13.91	13.82	13.95		
	13.73		13.83		
	13.81				
AVERAGE.....	13.75	13.69	13.97	15.11	16.15

COMPARISON OF RESULTS BY THE THREE METHODS

The phosphorus iodide method was not found satisfactory in its present form, and the high cost of reagents did not encourage us to pursue work on the process. The addition of water to the phosphorus iodide occasionally causes annoying, although not dangerous, explosions. On some samples the results by this method are higher, and on some samples lower, than those by the other modifications of the Kjeldahl method.

An interesting relationship between the results obtained by the Dumas and the Kjeldahl-Gunning-Jodlbauer methods was found. In Table IV is shown a comparison of the average values found by these two methods, the last line of the table giving the ratios obtained by dividing the percentage nitrogen found by the Dumas method by that found by the modified Kjeldahl method.

SAMPLE.....	1	2	3	4	5
Per cent N by Dumas method	14.33	14.61	14.93	16.15	16.85
Per cent N by modified Kjeldahl method	13.74	13.94	14.14	15.00	15.48
RATIO.....	1.043	1.048	1.056	1.077	1.089

In the accompanying graph these ratios are plotted as abscissas against the percentages of nitrogen found by the modified Kjeldahl method as ordinates. It will be seen that the ratio is a linear function of the nitrogen content; and the determined points fall sufficiently close to the straight line to allow the true nitrogen content of a nitronaphthalene to be calculated with a surprising degree of accuracy from a determination by the Kjeldahl-Gunning-Jodlbauer method.

As an example, let us assume that 14.55 per cent nitrogen were found by the modified Kjeldahl method. The conversion factor corresponding to this percentage is found from the graph to be 1.064. Then 14.55 multiplied by 1.064 gives 15.48 per cent as the true nitrogen content of the sample of nitronaphthalene.

SUMMARY

A modification of the Dumas method for determination of the nitrogen in organic substances has been worked out for use with compounds of high nitrogen content, and with sodium hydroxide in place of potassium hydroxide as the absorbing agent.

The various modifications of the Kjeldahl method having been found to give low results when applied to the determination of nitrogen in mixed nitronaphthalenes, a study of the exact degrees of variation between the true nitrogen

content, as shown by the Dumas method, and the apparent nitrogen content shown by the Kjeldahl-Gunning-Jodlbauer method has been made.

The degree of variation has been found to increase as a linear function of the nitrogen content, and a series of conversion factors has been plotted, which allows the convenient Kjeldahl-Gunning-Jodlbauer method to be used in the technical control of the nitration of naphthalene. The true percentage of nitrogen is found by multiplying the percentage found by the modified Kjeldahl method by the corresponding conversion factor.

Uniform High Temperature throughout a Large Volume¹

By E. F. Northrup

AJAX ELECTROTHERMIC CORPORATION, TRENTON, NEW JERSEY

The writer wishes to call attention to the possibilities now made commercially available of heating a space of considerable volume to temperatures exceeding 2000° C., the temperature being absolutely uniform throughout the space.

A heated chamber of this character can be used to the very best advantage for determining the properties of commercial refractories, or for the firing at high temperatures of ceramic materials, such as the spark plugs used in gasoline engines.

The result sought is obtained by the device shown in the figure. A crucible is turned up out of an electrode made of

near room temperature at all times. High frequency voltage (10,000 to 20,000 cycles) is applied at the terminals of the coil, which carries from 60 to 100 amperes of high frequency current. This current is readily supplied by a high frequency converter operated at 20 k. w.

In this case the lampblack, which is a semielectrical insulator, serves as a heat insulator. The heat insulation of lampblack at temperatures around 2000° C. is probably better than that of any other known material.

Under the above conditions the interior of the crucible attains within less than an hour a temperature of 2000° C., and can even be pushed up to 2500° C., and this temperature is, as nearly as optical means can determine, exactly the same throughout the interior of the crucible. There is no other device, so far as the writer is aware, which will heat a space of one-fifth cubic foot, or so, uniformly to this high temperature and in so short a time.

This arrangement is one of the simplest and most effective applications of high frequency current to heating. Problems connected with the heat treatment of refractories, or the graphitization of small pieces of carbon are studied with great ease and at uniform temperatures higher than have heretofore been made available by any other type of electric furnace. The temperature is furthermore under the most perfect control, and can be varied in the simplest manner in infinitesimal steps.

If it is desired to study the crushing strength of refractories when brought to very high temperatures, it is easy to produce the pressure on the refractory piece set in the bottom of the crucible by means of a graphite rod passed through a hole in the cover of the crucible.

If the problem requires the heating of a larger chamber than that shown in the figure, say, a chamber of the capacity of 1 cu. ft., the same results can be obtained by energizing the inductor coil with high frequency current obtained from a converter of greater power, converters rated at 60 k. w. now being commercially available.

Acheson graphite, the wall of the crucible being about 0.375 in., the interior diameter being 6 in., and the depth 12 in. The crucible is fitted with a graphite cover also about 0.375 in. thick. Screwed into the cover at its center is a tube of graphite which extends a foot or more above the cover. The hole through this tube serves as a sight hole for optically determining the temperature. This crucible is located in a cylinder made of micanite. It is packed about with lampblack, the lampblack being beneath the bottom and piled over the top of the cover of the crucible. On the outside of the micanite cylinder is a water-cooled coil of about fifty turns of flattened copper tubing. Water obtained from the supply mains flows through this coil and maintains the coil

¹ Received April 28, 1921.

During the month of June 1921, eighteen companies were organized in the field of chemicals, drugs, and dyes, with an aggregate capitalization of \$3,325,000, which is the smallest reported for any month in 1920 and 1921. The authorized capitalization for the six months ending June 1921 was \$65,625,000, as compared with \$109,731,500 for the first six months of 1920. The second quarter of 1921 falls considerably below the record for the first quarter, the comparative figures being \$25,115,000 and \$40,510,000. The following table shows the development of drug and chemical concerns since August 1914:

Five months 1914	\$ 16,838,000
Year 1915	65,565,000
1916	99,244,000
1917	146,160,000
1918	73,403,000
1919	112,173,000
1920	487,143,900
Six months 1921	65,625,000