A STUDY OF THE QUANTITATIVE DETERMINATION
OF NITROGEN

THESIS

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MASTER OF SCIENCE

By

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CHAPTER I

DEVELOPMENT OF THE METHODS OF NITROGEN DETERMINATION

Although nitrogen is one of our most abundant elements, it is one of the most costly of the elements required for plant and animal life. Because nitrogen is so inert chemically, its fixation and assimilation by plants is a difficult process.

Nitrogen is determined thousands of times daily in our industrial and research laboratories. For the estimation of nitrogen in an organic substance, there are three general methods available.

The soda-lime method consists in heating the substance with soda-lime and determining the ammonia which is liberated. This method is limited in application to certain types of compounds and is now being done away with in favor of the Kjeldahl method.

In this method, an organic substance is heated with concentrated sulfuric acid; the nitrogen in combination is converted into ammonium sulfate. The ammonia is then displaced with a concentrated solution of sodium hydroxide and collected in a known volume of standard acid. The amount of ammonia can then be determined by titration.

The Dumas method provides for the measurement of nitrogen when the substance is ignited in a combustion tube in the presence of copper oxide. The application of this method is quite extensive.

The Kjeldahl method of determining nitrogen has recently entered the second half-century of its usefulness. In the year 1883, the method was made public for the first time in a lecture delivered to the Chemical
The determination of nitrogen occupies a place of special and important significance in the ultimate analysis of organic materials. While the quantitative estimation of carbon and hydrogen is usually of interest only in purely scientific studies...the determination of nitrogen is especially important in technical practice since it affords the only fairly accurate means now known of evaluating the protein content of various animal and vegetable products which are often best assayed through this content. Consequently, there is frequent and imperative necessity for nitrogen determinations in technical research laboratories, in agricultural experiment stations, in physiological institutes.¹

A close examination of the methods of determining nitrogen before Kjeldahl's method appeared will give us reason to appreciate his contribution more. The Will-Varrentrapp method, brought out in 1841, was welcomed, for its distinguishing feature was the conversion of the nitrogen into a compound whose determination was relatively simple and sure as compared with the uncertainties of the techniques at that time. It gave way, however, in favor of another method which not only is as reliable but simpler, quicker, less expensive, and more convenient.

The Dumas method is probably more accurate and reliable than other modern procedures, but formerly this was not so. Though it was introduced ten years before the Will-Varrentrapp method, it was not used extensively until twenty years later. "Some of the problems that had to be solved before the Dumas method could become worthy of a place in the chemist's armory were the discovery of: (1) tractable sources of carbon

dioxide; (2) methods of completely removing the air from the combustion tube; (3) sure means of de-oxidizing nitrogen oxides; (4) impeccable reducing agents for the copper spiral, since hydrogen was found to be absorbed and later released; (5) simple yet trustworthy azotometers.\textsuperscript{2}

The Dumas and Will-Varrentrapp methods at the present are tedious and not well suited to large-scale, routine analyses. Attempts made merely to oxidize the samples were not successful. Boiling with caustic solutions or fusion with alkalis gave the right results only with ammonium compounds. Although alkaline permanganate gives incomplete oxidation,\textsuperscript{3} it formed the basis of Wanklyn's method (1887) of determining the protein content of vegetable materials.\textsuperscript{4}

At this point Kjeldahl introduced a modification of Wanklyn's method by boiling the sample with dilute sulfuric acid and an excess of permanganate solution. The yield was made higher by this change but was as yet incomplete. By further experimentation he found that practically all the nitrogen in the materials in which he was interested could be changed to ammonium compounds by first digesting with concentrated sulfuric acid and then adding potassium permanganate crystals. By carefully checking each step he produced a method which was really practical when his paper was published.

This method proved to be relatively simple and applicable to routine analyses. "The improvements and modifications ran chiefly in the following channels: (1) the use of mercury and copper compounds, etc., as accelerators in digestion, a field opened up by Wilfarth in 1885; (2) the inclusion of potassium sulfate in the digestion mixture, an advance

\textsuperscript{2}Ibid., p. 458. \textsuperscript{3}Ibid., p. 459. \textsuperscript{4}Ibid., p. 460.
suggested by Gunning in 1889; (3) the development of multiple digestion and distillation equipment...; (5) extension of the method to materials requiring pre-treatment before digestion with the acid.\textsuperscript{5}

Jodlbauer, in 1886, modified the Kjeldahl method to be applicable to nitrates, alkaloids, and various other compounds by the addition of the easily nitrated phenol followed by reduction of the nitrophenol-sulfonic acid.

A comparison of the method now used with the original procedure shows variation in the use of the same flask for digestion and distillation, the omission of the permanganate and the use of catalysts, the use of paraffin to abate foaming, a safer method of adding the alkali preparatory to distillation and the back-titration of the standard acid with standard alkali in place of the iodimetric titration recommended by Kjeldahl.

There are many modifications of the Kjeldahl method now in practice. The chief purpose of this investigation is to find the good points of the variations and to combine or eliminate them into fewer procedures. It is probably impossible for a single Kjeldahl procedure to be applicable to all substances. The procedure for the determination of nitrates, for example, differs from the procedure in which nitrates are not to be determined; also, in different types of samples, dairy feed and coal, for example, the procedures are unlike.

It was not the purpose of this work to develop a new method; however, a few semi-successful thrusts were made. It was found that tellurium is a good catalyst in the digestion, though not the most efficient when used

\textsuperscript{5}Ibid.
singly. Subsequent to this investigation, it was found in literature that the mixture $\text{SeO}_2$ and $\text{TeO}_2$ in equal parts was a very effective catalyst.

A purpose which was accomplished, though largely subjective, was to acquaint the author with research, both in the library and in the laboratory.

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CHAPTER II

BRIEF ANALYSIS SCHEME OF THE KJELDAHL METHOD

It is necessary, to determine the nitrogen content of a substance by the Kjeldahl method, to have a standard solution of sodium hydroxide approximately 0.1 N and a standard sulfuric acid solution approximately 0.2 N. About 1.0 g. of the substance to be analyzed was weighed out to 0.1 mg., the weight of the sample depending upon the nitrogen content. A multiple of the gravimetric factor is recommended. This factor is obtained by multiplying the molecular weight of ammonia (17.032) by the normality of the sodium hydroxide and then by 0.1 (100/1000). The sample was wrapped in a piece of filter paper and dropped into a 500 ml. Kjeldahl digestion flask. A blank was first run to determine the nitrogen content, if any, of the materials used, substituting a nitrogen-free substance for the sample (pure sucrose was satisfactory).

About 25 ml. of concentrated sulfuric acid were added to the Kjeldahl flask. About 10 g. of potassium sulfate and a pinch of powdered metallic selenium were mixed with the sulfuric acid and sample and the flask heated under a hood, at first gently (until spattering and frothing had ceased) and then more vigorously until the contents were a pale yellow color. This was allowed to cool and was then diluted with approximately 100 ml. of water and allowed to cool again. A few pieces of zinc to prevent bumping, a piece of paraffin to abate frothing, and a few drops of methyl red were then added. 55 ml. of concentrated sodium hydroxide solution (40 g. of sodium hydroxide to 50 ml. of water) were carefully
poured down the neck of the flask and, without shaking, the flask was connected with the distillation apparatus. Mixing was done cautiously and distillation begun. The distillate was collected in standard sulfuric acid, the amount equivalent to 50.00 ml. of the standard sodium hydroxide solution. The excess acid was then titrated with the standard sodium hydroxide solution and the percentage of ammonia calculated.

A sample calculation follows:

Normality of NaOH ............... 0.1000 N
Normality of H₂SO₄ ............... 0.1988 N
Weight of sample (6 times factor weight) .... 1.0219 g.
Volume of sulfuric acid in receiving flask (equivalent to 50.00 ml. of standard NaOH) .... 25.15 ml.
Volume of sodium hydroxide (titration) .... 27.97 ml.

Percentage nitrogen = \frac{50.00 - 27.97}{6} = 3.67%
CHAPTER III

A DETAILED STUDY OF THE KJELDAHL METHOD

Standard solutions of sodium hydroxide and sulfuric acid were made and the appropriate amount of sample weighed out as described on page 6.

The sulfuric acid which is added to digest the mixture, hydrolyzes the NH$_2$-group\(^1\) to give ammonia, and also acts as an oxidizing agent, converting the organic matter into carbon dioxide, water, or other easily volatile products. For example,

\[
\begin{align*}
\text{CO(NH}_2\text{)}_2 + \text{H}_2\text{O} + 2\text{H}_2\text{SO}_4 & \rightarrow \text{CO}_2 + 2\text{NH}_4\text{HSO}_4, \\
\text{C}_6\text{H}_5\text{O}_5 + n\text{H}_2\text{SO}_4 & \rightarrow 6\text{C} + 5\text{H}_2\text{O} + n\text{H}_2\text{SO}_4, \\
\text{C} + 2\text{H}_2\text{SO}_4 & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 2\text{SO}_2.
\end{align*}
\]

In the digestion of the sample it is advisable to heat with a small flame until much of the frothing has ceased and then gradually to increase the amount of heat as the digestion proceeds. To compare the times for digestion in this study, it was necessary to use a shielded flame and to allow it to remain unchanged throughout the digestion to insure the same conditions of heat for each sample. For this reason, the absolute time for digestion is not of value but the comparative time is meaningful. The following table gives the comparative time of digestion for several widely used digestion mixtures. A sample of 1.0 g. of dairy feed was used and the completion of digestion was determined by the presence of a

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\(^1\)J. C. Olsen, Quantitative Chemical Analysis (5th ed., revised; 1918), p. 294.
pale yellow color in the mixtures.

**TABLE 1**

**KJELDAHL DIGESTION MIXTURES**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Digestion Mixture</th>
<th>$T_{S2}/T_{S1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1$</td>
<td>25 ml. of concentrated H$_2$SO$_4$ and 10 g. of K$_2$SO$_4$.</td>
<td>1.00</td>
</tr>
<tr>
<td>$S_2$</td>
<td>25 ml. of a solution of 200 g. of P$_2$O$_5$ in 1 liter of concentrated H$_2$SO$_4$.</td>
<td>0.63</td>
</tr>
<tr>
<td>$S_3$</td>
<td>25 ml. of a solution of equal amounts of fuming H$_2$SO$_4$ and concentrated H$_2$SO$_4$. (20-50% SO$_3$)</td>
<td>0.89</td>
</tr>
<tr>
<td>$S_4$</td>
<td>25 ml. of a solution of 4 parts of concentrated H$_2$SO$_4$, 1 part of fuming H$_2$SO$_4$, and 100 g. of P$_2$O$_5$ per liter of mixture.</td>
<td>0.84</td>
</tr>
<tr>
<td>$S_5$</td>
<td>Sample was mixed with 2 g. of P$_2$O$_5$, then heated with 5 ml. of a mixture of 4 volumes of concentrated H$_2$SO$_4$ and 1 volume of fuming H$_2$SO$_4$ until brisk evolution of gas slackened and then continued heating after a further quantity of 15 ml. of the acid mixture had been added.</td>
<td>0.87</td>
</tr>
</tbody>
</table>

About 10 to 15 g. of potassium sulfate was added according to Gunning's modification. The potassium sulfate forms potassium bisulfate with the acid, and this serves to raise the boiling point of the sulfuric acid. According to the approximation that an increase in temperature of 10° C. doubles the speed of a chemical reaction, this addition of potassium sulfate should make the digestion complete in about half the time that would otherwise be necessary. In this work it was found that 10 g. of potassium sulfate in 25 ml. of concentrated sulfuric acid boils at about 13° C. higher than the acid alone, and the time necessary for digestion is about three eighths as long. This is in accord with the
approximation. Sodium sulfate or sodium pyrophosphate may be substituted for the potassium sulfate.\(^2\)

It has been reported that,\(^3\) with the return condensers constructed of lead, amounts of potassium sulfate and sulfuric acid in the presence of mercury determine the completeness of the hydrolysis. For instance, in the presence of 0.7 g. of mercuric oxide, when 25 ml. of commercial "96 per cent C. P." sulfuric acid and 10 g. of potassium sulfate were used, incomplete decomposition was obtained, but, when 15 ml. of sulfuric acid were used with amounts of potassium sulfate varying from 10 to 50 g., excellent results were obtained. When more potassium sulfate was employed, the results were somewhat lower. Sodium sulfate seemed to give varying results.

The difference in the behavior of the two sulfates is probably due to differences in the tendencies of the acid sulfates to retain water.\(^4\) Consequently, the hydrolysis of the refractory compounds with sodium sulfate is not recommended, although with very closely controlled conditions excellent results can be obtained.

A study of the variation of velocity of digestion in Kjeldahl determinations caused by the action of various elements shows that some, particularly those of the third and fourth groups of the periodic system, retard attack considerably.\(^5\) This retarding action is overcome if

\(^2\)Ibid., p. 287.

\(^3\)Journal of the Association of Official Agricultural Chemists, I (1920), 72.

\(^4\)Ibid.

accelerator metals are present simultaneously.

The most efficient catalyst to use is powdered metallic selenium. Although the digestion with a drop of metallic mercury is somewhat faster, it tenaciously retains ammonia as

\[ \text{H}_2\text{N-Hg-OSO}_2\text{O-Hg-NH}_2 \]
even in the presence of a hot alkali, and it is therefore necessary to add a large excess of sodium sulfide. This converts the mercury quantitatively into mercuric sulfide, which combines with sodium sulfide to form soluble \( \text{Hg(SNa)}_2 \) and the ammonia is liberated.\(^6\)

In the Kjeldahl method for maximum protein, the minimum amount of precipitating agent for 1 g. of mercury has been reported to be approximately 1.2 g. of pure \( \text{Na}_2\text{S-3H}_2\text{O} \) or about 2.8 g. of pure \( \text{Na}_2\text{S}_2\text{O}_5\cdot5\text{H}_2\text{O} \), when the precipitant is added with the alkali and approximately 2 g. when the precipitant is added before the alkali.\(^7\) The use of mercury precipitation agents in excess of the minimum requirement is advisable. With \( \text{Na}_2\text{S}_2\text{O}_5\cdot5\text{H}_2\text{O} \), a generous excess is recommended, while with commercial sodium sulfide a slight excess appears to be most satisfactory. In the regular Kjeldahl method the color of the precipitate during distillation is a fairly reliable index to the proper use of the precipitating agents used in these tests. Black precipitates indicate adequate precipitation except with sodium thiosulfate, where a brown-black precipitate indicates the use of a sufficient amount.

Table 2 gives the relative time required for digestion using various catalysts. There is little choice between mercury and selenium, keeping


in mind that mercury must be precipitated. A pinch of selenium (about 40 mg.) proved to be sufficient catalyst since ten times that amount hastened the digestion very slightly. A sample containing 320 mg. of selenium digested in 27 minutes; when 38 mg. of selenium were used, the time for digestion was 30 minutes; and when 16 mg. of selenium were used, complete digestion was accomplished in 43 minutes. In these experiments and the ones from which the data of Table 2 were compiled, 1.0 g. of dairy feed was used in each case and complete digestion was determined by the change to a pale yellow color. This evaluation is not scientifically exact, but an approximation of the maximum error would be about ten per cent. In samples 1 to 7, the error in the per cent of nitrogen was never greater than 0.8 parts per 1000. Complete determinations were not made with samples 8 and 9.

### TABLE 2

**CATALYSTS FOR KJELDAHL DIGESTIONS**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Catalyst</th>
<th>$\frac{TS_2}{TS_1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_1$</td>
<td>No catalyst used</td>
<td>1.00</td>
</tr>
<tr>
<td>$S_2$</td>
<td>SeOCl$_2$</td>
<td>0.75</td>
</tr>
<tr>
<td>$S_3$</td>
<td>Te</td>
<td>0.50</td>
</tr>
<tr>
<td>$S_4$</td>
<td>Mixture of 1 part of CuSO$_4$ and 2 parts of FeSO$_4$</td>
<td>0.41</td>
</tr>
<tr>
<td>$S_5$</td>
<td>CuSO$_4$</td>
<td>0.45</td>
</tr>
<tr>
<td>$S_6$</td>
<td>CuO</td>
<td>0.40</td>
</tr>
<tr>
<td>$S_7$</td>
<td>Se</td>
<td>0.30</td>
</tr>
<tr>
<td>$S_8$</td>
<td>HgO</td>
<td>0.25</td>
</tr>
<tr>
<td>$S_9$</td>
<td>Hg</td>
<td>0.21</td>
</tr>
</tbody>
</table>
Subsequent to this experimental work, it was found in literature that results have been reported using tellurium oxide as a catalyst.

At 302° M. [J. Milbauer] followed (colorimetrically) the change of sucrose in concd. H$_2$SO$_4$ in the presence of the catalysts HgSO$_4$, Ag$_2$SO$_4$, CuO, SeO$_2$ and TeO$_2$ and in a current of air, O, ozone, N, CO$_2$, Cl, SO$_2$, H, and HCl. The catalysts and gases used separately hastened the chemical changes occurring in sucrose. The mixture SeO$_2$·TeO$_2$ in equal parts was the most effective catalyst; Cl the most effective gas. Together the combination SeO$_2$·TeO$_2$ and Cl reduced the reaction time from 1650 min. to 24 min.\(^8\)

In kjeldahlization of sucrose by concd. H$_2$SO$_4$ at its b. p., catalytic activity increases in the order: no catalyst, Ni, As, Ag, Pd, Sb, Pt, V, Au, Te, Cu, Hg, Se; at 302° the order is: Ni, no catalyst, As, Ag, Pd, Au, Sb, Pt, Hg, Cu, Te, V, Se. If time necessary for oxidation of 100 mg. of sucrose in 100 cc. H$_2$SO$_4$ is taken as 1, the times required in the presence of 140 mg. SeO$_2$, 374 mg. HgO, 100.4 mg. CuO and 161 mg. Te are, resp., 1/26, 1/6, 1/7 and 1/7 at 302° and 1/49, 1/43, 1/38 and 1/4 at the b. p. of H$_2$SO$_4$. Of mixed catalysts the most effective at 302° are SeO$_2$ + HgSO$_4$ (1 : 1) and SeO$_2$ + CuSO$_4$ (3 : 1); for both of these the time is 1/49. Mixts. of SeO$_2$ + HgSO$_4$ + CuO at 302° are less effective than the individual couples.\(^9\)

This data can probably be inferred roughly to apply to samples of dairy feed, but no results to this effect were available.

Copper sulfate has been used quite extensively as a catalyst, especially in agricultural methods. Selenium or selenium oxychloride has a slight advantage over copper sulfate; precipitated elemental selenium is more suitable and economical than selenium oxychloride. The copper sulfate gives up oxygen more readily to the organic matter than the sulfuric acid does; but the sulfuric acid then re-oxidizes the copper so that at the end of the operation the copper is still present as copper sulfate. That is to say, the copper salt acts catalytically as an oxygen

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\(^8\)Milbauer, op. cit.

carrier.\textsuperscript{10}

For digesting 10 g. of coal, comparative experiments were performed\textsuperscript{11} by using in one case a mixture of 11 parts of mercuric oxide and 89 of potassium sulfate as a catalyst and in another case a mixture of 98 parts of potassium sulfate and 2 of selenium powder. The disappearance of char in the latter case occurred in 33 minutes whereas 87 minutes were necessary for the other. To complete the reduction of the nitrogen required about 90 minutes more in both cases. The time of digestion is, therefore, shortened appreciably when selenium is used in place of mercury for the Kjeldahl determination of nitrogen in coal and coke.

A series of determinations was made\textsuperscript{12} on a high-protein flour and on a sample of ground bran with the catalyst (0.1 g. copper, 0.7 g. mercuric oxide, or 0.1 g. selenium). The digestion of the samples with selenium and with mercuric oxide was almost complete in 30 minutes and was complete in 45 minutes, while the digestion with copper was complete in 1 hour. It appears that there is greater danger of losing nitrogen by extremely long digestion with selenium than with other catalysts.

H. C. Messman reports\textsuperscript{13} that by using 20 ml. of sulfuric acid and 8 g. of a mixture consisting of 90 parts sodium sulfate, 7 parts mercuric sulfate, 1.5 parts copper sulfate and 1.5 parts powdered metallic selenium

\textsuperscript{10}Smith, \textit{op. cit.}, p. 117.


\textsuperscript{13}"Metallic Selenium as a Catalyst in Kjeldahl Digestions," \textit{Cereal Chemistry}, IX (1932), 357.
for each gram of sample, digestion is complete in 15 to 20 minutes.

Results show that with the exception of wheat bran and wheat shorts, the percentages of nitrogen obtained after digestion for 30 minutes with mercuric oxide and selenium agree better than those obtained after digestion for 30 minutes with either selenium or mercuric oxide alone. R. A. Osborn and A. Krasnitz verify the fact that a combination of selenium and mercuric oxide is better than either used singly.

The digested mixture was allowed to cool and then diluted with approximately 100 ml. of distilled water. When this had cooled, 55 ml. of concentrated sodium hydroxide (40 g. of sodium hydroxide to 50 ml. of water) were carefully poured down the neck of the distillation flask, forming a separate layer below the sulfuric acid.

This required careful technique as some ammonia will be formed when the two solutions contact each other. One way to avoid this is to connect the flask after dilution with the distillation apparatus and add the alkali through a side arm which is connected just above the stopper where the flask is attached. This gives a more nearly complete recovery of the nitrogen and it is not necessary to cool the digested mixture thoroughly after it has been diluted.

A few pieces of granulated zinc (to reduce bumping) and a piece of

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paraffin (to reduce frothing) were added to this mixture without shaking. The zinc dissolves slowly in the alkaline solution with the evolution of hydrogen.\textsuperscript{17} Fragments of pumice stone or of platinum are also often used to prevent bumping. A few drops of methyl red were added to the acid before the sodium hydroxide was poured in. This made it possible to determine whether sufficient alkali had been added to neutralize the acid after the solutions were mixed. The distillation flask was then tightly connected with the condenser and the mixing of the solutions begun. This was accomplished by slowly rotating the flask so that a steady stream of gas was liberated until the mixture showed alkaline. The flame was then applied and distillation continued.

The ends of the condensers were submerged in the standard sulfuric acid (approximately 0.2 N) which contained a few drops of methyl red. The amount of acid used is the amount equivalent to 50.00 ml. of the standard sodium hydroxide solution. This amount may be varied for large amounts of nitrogen.

Distillation was continued until about 150 ml. had distilled over. The excess acid was then titrated and the per cent of nitrogen calculated. The difference between the volume of sodium hydroxide required for this titration and the amount equivalent to the standard sulfuric acid used, divided by the number of factor weights taken, gives the per cent of nitrogen.

The mechanical positive error\textsuperscript{18} caused by spattering of the alkaline solution which is being distilled over can be avoided if the excess alkali

\textsuperscript{17}Smith, \textit{op. cit.}, p. 117.

added before distillation is kept within reasonable limits. The bumping caused by sodium sulfate can be avoided by evaporating off most of the sulfuric acid before neutralization.

The amount of alkali obtained from glass during the distillation is so small that condensers need not be constructed of block tin as is often recommended. Rubber stoppers and rubber connections\textsuperscript{19} must be avoided because amines and azoles are used as accelerators in vulcanizing rubber, and the rubber continues to give off alkaline-reacting substances even after long use.

By making the vapors from the distillation pass through a fairly narrow tube which in its upward course is given a snake-like bending,\textsuperscript{20} then after two right-angle bends, takes the form of a pipette, the necessity of using a water cooled condenser is avoided.

By the original Kjeldahl method the conversion of nitrates to ammonia was very uncertain. To overcome this difficulty, phenol or salicylic acid is dissolved in the sulfuric acid. In the Gunning-Jodlbauer modification the digestion is carried out with sulfuric acid which contains 40 g. of phenol or salicylic acid per liter. The nitrate is converted to nitro-phenol and then reduced to amido-phenol which is completely hydrolyzed by caustic soda with liberation of ammonia. The reduction is greatly accelerated by the addition of zinc or sodium thiosulfate. These reactions take place according to the following equations:

$$C_6H_5\cdot OH + HNO_3 \rightarrow C_6H_4\cdot OH\cdot NO_2 + H_2O;$$

$$C_6H_4\cdot OH\cdot NO_2 + 3H_2 \rightarrow C_6H_4\cdot OH\cdot NH_2 + 2H_2O;$$

\textsuperscript{19}Ibid.

\[ \text{C}_6\text{H}_4\cdot \text{OH} \cdot \text{NH}_2 + \text{NaOH} \rightarrow \text{C}_6\text{H}_4\cdot \text{OH} \cdot \text{ONa} + \text{NH}_3. \]

The reactions in reality are more complicated than represented, as several sulfuric acid molecules combine with one benzene ring. This simply shows the transformation of the nitrate radical into ammonia. If salicylic acid is used, one gram is dissolved in the concentrated sulfuric acid. The mixture is allowed to stand 30 minutes, and then 2 g. of zinc dust are added to reduce the nitrosalicylic acid to aminosalicylic acid. If sodium thiosulfate is used to reduce the nitrosalicylic acid, the addition of the alkali sulfate is omitted (the solution contains sodium bisulfate from the thiosulfate).

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21 Olsen, op. cit., p. 284.


23 Smith, op. cit., p. 118.
CHAPTER IV

NITROGEN CONTENT BY NESSLERIZATION

Many forms of apparatus for colorimetric analysis, some of them very costly, have been devised, but for ordinary laboratory work simple apparatus suffices. The outfit should consist of Nessler tubes made of colorless glass of uniform bore and with flat polished bottoms.\(^1\) Tubes graduated to 50 ml. or 100 ml. are of convenient size provided the height of the column containing the solution is about 20 cm. The tubes should be kept in a Nessler rack—a test tube rack painted a dull black with an opal glass reflector mounted at the bottom. The base should be suitably bored so that light can be reflected up the tubes.

Ammonia Nitrogen

Nesslerization is used most often in water and sewage analysis. Free ammonia is recovered quantitatively only when the distillation mixture is maintained at a pH of about 7.4; all water requires the addition of a phosphate buffer solution to maintain a constant pH of the water during the distillation process.\(^2\)

The distillation method for the determination of ammonia nitrogen used in this work is the one recommended in The Standard Methods of


Water Analysis, eighth edition. In this study, the accuracy and efficiency of the method were of major importance, and hence a known solution was used in lieu of a fresh water sample. Therefore, just the Nesslerization was studied, and the distillation was omitted.

Reagents.--(1) Ammonia-free water.

(2) Nessler reagent.³ 50 g. of potassium iodide were dissolved in a minimal volume (about 35 ml.) of cold ammonia-free water. A saturated solution of mercuric chloride was added until a slight precipitate persisted. 400 ml. of 9 N potassium or sodium hydroxide, clarified by sedimentation, were added. This solution was diluted to 1 liter, allowed to clarify, and decanted. This reagent should give the characteristic yellow color with ammonia within 5 minutes after addition, and should not produce a precipitate with small amounts of ammonia within two hours.

(3) Standard ammonium chloride solution. 3.818 g. of ammonium chloride were dissolved in ammonia-free water and diluted to 1 liter; from this stock solution the standard solution was prepared by diluting 10 ml. to 1 liter with ammonia-free water: 1 ml. contains 0.01 mg. of nitrogen, equivalent to 0.01288 mg. of NH₄⁺.

Procedure.--A series of 16 Nessler tubes containing the following volumes of standard ammonium chloride solution, diluted to 50 ml. with ammonia-free water were prepared: namely, 0.0, 0.1, 0.3, 0.5, 0.7, 1.0, 1.4, 1.7, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, and 6.0 ml. The standards contain 0.01 mg. of nitrogen for each milliliter of the standard solution.

The standards thus prepared and the portions of the sample to be studied were Nesslerized by adding 1 ml. of Nessler reagent to each tube.

³ Ibid., p. 41.
It was not necessary to stir the contents of the tubes after Nesslerizing. The temperature of both standards and prepared samples was practically the same. The tubes were allowed to stand at least 10 minutes after addition of the reagent; the color produced in the portions of the solution to be determined was then compared with that in the standards by looking through them at a white or mirrored surface so placed in front of a window that the light was reflected upward.

Through a series of 10 determinations using this method, the results were quite consistent, as shown in Table 3. The test appeared to be most sensitive in the range of 2 to 6 parts of nitrogen per 5,000,000.

**Table 3**

<table>
<thead>
<tr>
<th>No.</th>
<th>Parts of Nitrogen as Ammonium per 5,000,000 (Correct)</th>
<th>Parts of Nitrogen as Ammonium per 5,000,000 (Experimental)</th>
<th>Difference per 5,000,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.55</td>
<td>0.3</td>
<td>-0.05</td>
</tr>
<tr>
<td>2</td>
<td>0.70</td>
<td>1.0</td>
<td>+0.30</td>
</tr>
<tr>
<td>3</td>
<td>1.05</td>
<td>0.8</td>
<td>-0.25</td>
</tr>
<tr>
<td>4</td>
<td>1.75</td>
<td>1.4</td>
<td>-0.35</td>
</tr>
<tr>
<td>5</td>
<td>2.80</td>
<td>1.9</td>
<td>-0.90</td>
</tr>
<tr>
<td>6</td>
<td>0.25</td>
<td>1.1</td>
<td>+0.85</td>
</tr>
<tr>
<td>7</td>
<td>0.50</td>
<td>0.5</td>
<td>0.00</td>
</tr>
<tr>
<td>8</td>
<td>0.75</td>
<td>0.7</td>
<td>-0.05</td>
</tr>
<tr>
<td>9</td>
<td>1.25</td>
<td>1.1</td>
<td>-0.15</td>
</tr>
<tr>
<td>10</td>
<td>2.00</td>
<td>1.5</td>
<td>-0.50</td>
</tr>
</tbody>
</table>

Average (absolute) difference ±0.34
Albuminoid Nitrogen

Albuminoid nitrogen is the nitrogen equivalent of ammonia formed or liberated from nitrogenous matter by the action of alkaline permanganate in water after expulsion of ammonia nitrogen by distillation.\(^4\) It bears a variable ratio to organic nitrogen in highly polluted waters, and in waters of apparently slight pollution the values obtained by this method are related to color and colloidal matter.

Nitrite Nitrogen

The method used in this work for the determination of nitrite nitrogen is the official method as given by the Association of Official Agricultural Chemists.\(^5\)

Reagents.--(1) Sulfanilic acid solution. 1 g. of sulfanilic acid was dissolved in hot water, cooled, and diluted to 100 ml.

(2) Alpha-naphthylamine hydrochloride solution. 0.5 g. of the salt was boiled with 100 ml. of water and kept at constant volume for 10 minutes.

(3) Standard nitrite solution. Sodium nitrite, the amount equivalent to 1.1 g. of silver nitrite, was dissolved in nitrite-free water, diluted to one liter and then 10 ml. of this solution diluted to one liter, using in each case nitrite-free water. 1 ml. of the last solution is equivalent to 0.0001 mg. of nitrogen as nitrite.

Determination.—100 ml. of the sample were placed in a 100 ml. Nessler tube and treated with 1 or 2 drops of hydrochloric acid. 1 ml.

\(^4\)American Public Health Assn., op. cit., p. 45.

of the sulfanilic acid and 1 ml. of the alpha-naphthylamine hydrochloride solution were added and thoroughly mixed. This was set aside for 50 minutes with other Nessler tubes containing known quantities of the standard nitrite solution made up to 100 ml. with nitrite-free water and treated with hydrochloric acid, sulfanilic acid, and alpha-naphthylamine hydrochloride solution in the same manner as the sample. The quantity of nitrite was determined by comparing the depth of the pink color in the known and unknown solutions. Table 4 presents data recorded as nitrogen in the form of nitrite.

**TABLE 4**

**NITRITE NITROGEN BY NESSLERIZATION**

<table>
<thead>
<tr>
<th>No.</th>
<th>Parts of Nitrogen as Nitrite per 1,000,000,000 (Correct)</th>
<th>Parts of Nitrogen as Nitrite per 1,000,000,000 (Experimental)</th>
<th>Difference per 1,000,000,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.75</td>
<td>0.3</td>
<td>-0.45</td>
</tr>
<tr>
<td>2</td>
<td>1.50</td>
<td>0.6</td>
<td>-0.90</td>
</tr>
<tr>
<td>3</td>
<td>2.25</td>
<td>2.2</td>
<td>-0.05</td>
</tr>
<tr>
<td>4</td>
<td>3.00</td>
<td>2.5</td>
<td>-0.50</td>
</tr>
<tr>
<td>5</td>
<td>3.75</td>
<td>3.5</td>
<td>-0.25</td>
</tr>
<tr>
<td>6</td>
<td>0.63</td>
<td>0.5</td>
<td>-0.35</td>
</tr>
<tr>
<td>7</td>
<td>0.95</td>
<td>1.2</td>
<td>+0.25</td>
</tr>
<tr>
<td>8</td>
<td>1.55</td>
<td>1.9</td>
<td>+0.32</td>
</tr>
<tr>
<td>9</td>
<td>2.84</td>
<td>3.2</td>
<td>+0.38</td>
</tr>
<tr>
<td>10</td>
<td>3.78</td>
<td>3.6</td>
<td>-0.18</td>
</tr>
</tbody>
</table>

Average (absolute) difference ±0.36
This corresponds almost identically with the method given in the *Standard Methods of Water Analysis*. In this, the standard is diluted until 1 ml. is equivalent to 0.0005 mg. of nitrogen (0.001642 mg. of nitrite).

This was by far the most sensitive of the colorimetric tests, showing the presence of 1 part of nitrogen as nitrite in 1,000,000,000 parts of solution. A series of 10 determinations showed the results as given in Table 4.

**Nitrate Nitrogen**

The official method for determining nitrogen in the form of nitrate was used as given by the Association of Official Agricultural Chemists. Again this corresponds closely with the method recommended by the American Public Health Association in *Standard Methods of Water Analysis*.

**Reagents.**—(1) Phenoldisulfonic acid solution. 25 g. of pure white phenol were dissolved in 150 ml. of sulfuric acid, 75 ml. of fuming sulfuric acid (13-15% S0_3_) added, and heated at 100 degrees for 2 hours.

(2) Standard nitrate solution. 0.607 g. of pure sodium nitrate was dissolved in 1 liter of nitrate-free water. 50 ml. of this solution were evaporated to dryness in a porcelain dish, cooled, treated with 2 ml. of the phenoldisulfonic acid solution, stirred with a glass rod to insure intimate contact, and diluted to 500 ml. 1 ml. is equivalent to 0.01 mg. of nitrogen as nitrate. (This solution is permanent.) Standards for comparison were prepared by adding ammonium hydroxide to measured volumes of the standard solution in 100 ml. Nessler tubes.

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6 American Public Health Assn., *op. cit.*, p. 46.
Determination.—The official method gives a detailed procedure for the extraction of chlorine in the water sample, but since a known was used in these determinations which contained no chlorine, the procedure was omitted. A quantity of the sample which contained 0.05 mg. or less of nitrogen as nitrate was evaporated to dryness in a porcelain dish on a steam bath; when cool, 2 ml. of phenoldisulfonic acid were added as directed under (2). This was diluted with water and ammonium hydroxide slowly added until the maximum color was developed. This was transferred directly to a colorimetric cylinder as filtration was unnecessary and compared with the standards in the usual manner. The data have been recorded as nitrogen in the form of nitrate.

### TABLE 5

<table>
<thead>
<tr>
<th>No.</th>
<th>Parts of Nitrogen as Nitrate per 10,000,000 (Correct)</th>
<th>Parts of Nitrogen as Nitrate per 10,000,000 (Experimental)</th>
<th>Difference per 10,000,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.65</td>
<td>2.0</td>
<td>+0.35</td>
</tr>
<tr>
<td>2</td>
<td>2.20</td>
<td>2.5</td>
<td>+0.50</td>
</tr>
<tr>
<td>3</td>
<td>3.30</td>
<td>3.5</td>
<td>+0.20</td>
</tr>
<tr>
<td>4</td>
<td>4.40</td>
<td>4.0</td>
<td>-0.40</td>
</tr>
<tr>
<td>5</td>
<td>5.50</td>
<td>5.0</td>
<td>-0.50</td>
</tr>
</tbody>
</table>

Average (absolute) difference ±0.36

This test was found to detect 1 part of nitrogen in 10,000,000 parts of solution. The change of the intensity of the light green color in the
standards was greater where the nitrogen content was less than 2 parts per 10,000,000. A series of five determinations showed the results, as presented in Table 5.
CHAPTER V

CUMBUSTION ANALYSIS OF NITROGEN

The Dumas method, as was stated in Chapter I, provides for the measurement of nitrogen when the substance is ignited in a combustion tube in the presence of copper oxide.

A weighed quantity of substance is ignited with copper oxide in an atmosphere of carbon dioxide. The carbon is thus oxidized to carbon dioxide and the hydrogen to water; the nitrogen is liberated as such and is determined volumetrically after collection over potassium hydroxide solution. Any oxides of nitrogen produced are reduced to nitrogen by means of a glowing copper spiral.

Preparing the Apparatus

Air-free Kipp for carbon dioxide.¹—Small pieces of marble were covered in a porcelain basin with dilute hydrochloric acid (1 vol. of HCl, d. 1.18, and 1 vol. of water). After the first vigorous reaction had subsided, the scum which had collected on the surface was poured off and the chips washed with water. The middle globe of the Kipp was more than half-filled with the chips, the opening from the lower globe being packed with chips of glass. The gas, when it was being delivered from the apparatus, was taken from the highest point in the middle globe through a glass tube shaped like a hook with the point upward. Dilute

hydrochloric acid was poured into the apparatus until the lowest globe and half of the uppermost globe were filled. As a rule a newly charged Kipp supplies sufficiently pure carbon dioxide only after standing two or three days.

Connections.—The Kipp was attached to the combustion tube by means of a Z-shaped glass tube. A short glass tube filled with asbestos wool to trap acid fog was used to connect this piece to the Kipp.

Filling the Combustion Tube

The combustion tube (about 90 cm. in length) was cleaned with bi-chromate-sulfuric acid mixture, washed with distilled water, and dried with gentle warming, drawing a current of air through by means of a water-jet pump. Coarse wire-form copper oxide and more finely broken copper oxide prepared from the coarse quality by powdering (not grinding) in a mortar so that, after dust had been removed with a sieve, the pieces were 1-2 mm. long, were kept in stock. The copper oxide was ignited in a nickel basin before use. Used copper oxide was ready for immediate reuse after it had been sieved and heated to redness in air.

A pad of asbestos about 4 cm. in length was gently packed into one end of the tube. Next to this a reduced copper spiral about 12 cm. long was inserted. To reduce the spiral, it was heated to redness in a flame and dropped into a test tube containing about 1 ml. of methanol. The flames were allowed to burn up through the spiral. The reduced copper spiral was followed by a long column of coarse copper oxide which extended to within 30-35 cm. of the other end of the tube. The sample was put in at this place.

A small weighing tube was half filled with the fine copper oxide and
weighed. A sample of the substance to be analyzed was then added and the tube weighed again. The nitrogen must not more than fill the nitrometer (100 ml. in these experiments); hence the per cent of nitrogen determined the weight of the sample. The sample was mixed with the copper oxide in the weighing tube and then poured into the combustion tube. More of the fine copper oxide was then added to the weighing tube and shaken. In this way all of the sample was "washed" into the combustion tube. This is then followed by the coarse copper oxide which extended to within 8 cm. of the end, and then an asbestos pad similar to the first was inserted. The end of the combustion tube containing the reduced copper spiral was attached to the nitrometer.

The base of the nitrometer, which was connected to the combustion tube by means of a stop-cock, was filled with mercury to a height just above the inlet. 50 per cent potassium hydroxide solution was used in the nitrometer, but any known concentrated solution of potassium hydroxide can be used; the essential point is to know the vapor pressure of the solution.

The Combustion

The combustion tube was heated on either side of the sample strongly but not nearer than about 15 cm. to the sample. Carbon dioxide was passed through the tube for a few minutes and then the tube was connected with the nitrometer, its stop-cock being open and the potassium hydroxide solution being transferred as completely as possible to the levelling bulb lowered for the purpose. After a few minutes, when the connecting tube and stop-cock had been washed out with the gas, the stop-cock was closed, the nitrometer filled, the levelling bulb lowered again, the stop-cock
cautiously opened so that one to two bubbles per second passed through, and the size of the bubbles which remained was observed. If these were not yet small enough, the washing out with carbon dioxide was repeated. As soon as sufficiently small bubbles were produced, the Kipp was closed and the stop-cock on the connecting tube fully opened.

Before the sample was heated, the stop-cock on the connecting tube was closed, the levelling bulb held just above the level of the stop-cock at the top of the nitrometer, and all the gas which had collected as well as accompanying impurities was driven into the upper part (above the stop-cock) of the nitrometer. The stop-cock at the top of the nitrometer was closed, the levelling bulb lowered again, the stop-cock on the connecting tube opened full, and the heating of the sample begun. Great care was taken that the bubbles entered the nitrometer at a rate never exceeding two bubbles in three seconds. Consequently, when the evolution of gas was vigorous, and particularly when the sample had been reached, the heat was applied more slowly until the rate of appearance of bubbles had considerably diminished. After all of the sample had vaporized, carbon dioxide was passed through the tube at the rate of two bubbles every three seconds. When all the nitrogen had been swept through, the Kipp was cut off and the nitrometer disconnected. The stop-cock at the base of the nitrometer was closed and the levelling bulb raised until the level of the potassium hydroxide was the same in the levelling bulb as in the nitrometer. It was allowed to stand at a distance from the combustion furnace for 15 minutes before the reading was taken. The temperature and barometric pressure, of course, were taken. From the volume collected, the per cent of nitrogen in the original sample was calculated.
A sample calculation follows:

Weight of sample ........................................... 0.2058 g.
Volume of nitrogen .......................................... 19.00 ml.
Temperature ................................................... 21° C.
Atmospheric pressure ...................................... 742 mm.
Vapor pressure of potassium hydroxide (30 mols of
potassium hydroxide per 100 mols of water) at
21° C. ................................................................ 14.8 mm.
Effective pressure on nitrogen .............................. 727 mm.
Weight of 1 ml. of nitrogen at 727 mm. pressure
and 21° C. .......................................................... 1.112 mg.
Per cent nitrogen = \( \frac{19.00 \times 1.112 \times 100}{205.8} \) ............................. 10.27%
Per cent nitrogen (calculated) ............................... 10.37%
Per cent error .................................................... 0.91%

Especial trouble was encountered in early experiments in getting the
nitrogen to be liberated not faster than two bubbles in three seconds.

Eleven determinations were made before a satisfactory result was obtained.
The too rapid vaporization of the sample was the chief source of error.

The following table shows some results which were, for the most part,
unsatisfactory:

<table>
<thead>
<tr>
<th>No.</th>
<th>Substance</th>
<th>Wt. of Sample in gms.</th>
<th>Vol. of Nitrogen* (ml.)</th>
<th>%N₂ (Exp.)</th>
<th>% N₂ (Correct)</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Urea</td>
<td>0.0824</td>
<td>32.23</td>
<td>43.57</td>
<td>46.64</td>
<td>-6.58</td>
</tr>
<tr>
<td>2</td>
<td>Urea</td>
<td>0.0648</td>
<td>25.20</td>
<td>45.50</td>
<td>46.64</td>
<td>-6.75</td>
</tr>
<tr>
<td>3</td>
<td>Acetenilide</td>
<td>0.2058</td>
<td>19.00</td>
<td>10.27</td>
<td>10.37</td>
<td>-0.91</td>
</tr>
</tbody>
</table>

*Temperature = 21° C.; pressure = 742 mm.
If a closed combustion tube\textsuperscript{2} is used, the Kipp generator is not required as a source of carbon dioxide. A layer of magnesite or of manganese carbonate 15 cm. long\textsuperscript{3} is put in the closed end, followed by a 10 cm. layer of coarse copper oxide and then the sample.

Alternatively, an open combustion tube\textsuperscript{4} may be used with a test tube containing sodium bicarbonate attached by means of a water trap to the combustion tube. This is heated to sweep out the combustion tube before and after the sample is vaporized.

In microanalysis, F. Pregl recommends the following method for preparing marble chips to obtain pure carbon dioxide:

The marble is broken up to the size of hazel nuts, etched with dilute hydrochloric acid, washed, covered with water, and boiled for ten minutes. After cooling, it is placed in a large desiccator and covered with calcium chloride solution, which has been syphoned off from the exhausted Kipp generator and neutralized with marble. The desiccator is now evacuated, by means of a water pump, to remove the air from the pores of the marble. If, after half to one hour, no more bubbles escape from the marble, the vacuum is slowly abolished, when the pores fill with calcium chloride solution. In order to remove the last traces of air, it is again evacuated for thirty minutes after which the marble is ready for filling the generator.\textsuperscript{5}

The fundamentals of this analysis have been taken from Gattermann and Wieland, \textit{Laboratory Methods of Organic Chemistry},\textsuperscript{6} which, in turn, was worked out on the basis of Pregl's micro-procedure by Dr. F. Hölscer. Supplements were taken from Pregl's \textit{Quantitative Organic Microanalysis}\textsuperscript{7} and \textit{Quantitative Analysis} by Treadwell and Hall.\textsuperscript{8}

\textsuperscript{2}Treadwell and Hall, \textit{Quantitative Analysis} (1930), p. 371.
\textsuperscript{3}Ibid.
\textsuperscript{4}Ibid.
CHAPTER VI

SUMMARY

Experimental work with Kjeldahl analysis with special emphasis on the digestion mixture and catalyst showed that several combinations of sulfuric acid and phosphorus pentoxide are satisfactory. A digestion mixture of 25 ml. of a solution of 200 g. of P₂O₅ in one liter of concentrated sulfuric acid per gram of sample of dairy feed is the most efficient. The time of digestion using this mixture is about two thirds as long as with concentrated sulfuric acid alone.

The catalyst used in Kjeldahl digestions varies much in different adopted methods. Metallic selenium and metallic mercury both proved very efficient; there is little difference, keeping in mind that the mercury must be precipitated before distillation. The catalyst used in some cases is dependent upon the type of sample to be analyzed. Selenium oxychloride and copper sulfate are other widely used catalysts. Tellurium proved to be a good catalyst though not the best when used singly.

Colorimetric analysis of nitrogen is used extensively in water and sewage analysis. In these experiments, nitrogen was determined in the form of ammonia, nitrate, and nitrite by Nesslerization. A mixture of potassium iodide, mercuric chloride, and sodium hydroxide was used to detect the presence of nitrogen in the form of ammonia. The presence of one part of nitrogen as ammonia in 5,000,000 parts of solution produces a golden-yellow color which is detectable. The error in a series of ten
experiments in the analysis of ammonia nitrogen using this method was never greater than 1 part per 5,000,000.

Alpha-naphthylamine hydrochloride solution was used to analyze nitrite nitrogen by Nesslerization. The pink color formed detects accurately the presence of one part of nitrogen as nitrite per 1,000,000,000 parts of solution. Through a series of ten determinations, the error was never greater than 1 part per 1,000,000,000.

In these experiments the official method determining nitrogen in the form of nitrate was used as given by the Association of Official Agricultural Chemists. The phenoldisulfonic acid solution prescribed produces a detectable green color when one part of nitrogen as nitrate is present in 10,000,000 parts of solution. The error was never greater than one half part per 10,000,000 in five analyses.

Nesslerization analysis of nitrogen is easily carried out and has varying degrees of accuracy, all of which appear satisfactory for a water analysis.

The combustion analysis of nitrogen (Dumas method) is the most cumbersome of the methods used in this work; however, it has some advantages. Total nitrogen is determined in this way and the variations are fewer. The method of filling the combustion tube is the major point of question. Several analyses by the Dumas method were unsuccessful, probably because the vapors were allowed to pass through the combustion tube too rapidly. When the nitrogen analysis was carried out precisely as directed, however, an error of less than one per cent was obtained. A carbon and hydrogen analysis with a similar set up (Liebig's method) was made with satisfactory results.
BIBLIOGRAPHY

Books and Magazine Articles


Fresenius, C. R., Quantitative Chemical Analysis, New York, John Wiley and Sons, 1911.


Oesper, R. E., "Kjeldahl and the Determination of Nitrogen," Journal of
Chemical Education, XI (1934), 457-60.


Treadwell and Hall, Quantitative Analysis, New York, John Wiley and Sons, Inc., 1930.


Abstracts

Source: Chemical Abstracts, ed. E. J. Crane, Vols. XXVI (1932), XXVII (1933), and XXXI (1937), Columbus, O., The American Chemical Society, Annually.


