# Quantitative Determination of Non-Aminoid Nitrogen in Aliphatic and Aromatic Compounds

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It became apparent during the course of investigation of the titanium trichloride-ferric chloride titrimetric method of analysis of nitro-aliphatic compounds (1), that the method was unsuitable for a rapid, accurate, and easily performed analysis.

By combining the essential feature of the titrimetric method, namely the reduction of the nitro group with titanium trichloride, with the Kjeldahl digestion of the amine hydrochloride, it was found possible to recover quantitatively the nitrogen of the nitro group in the form of ammonia. A test of the method with compounds of the aromatic and aliphatic series with groups such as nitro, azo, diazo, and other non-aminoid groups present gave excellent and rapid results.

**Apparatus:** A simplified and inexpensive Kjeldahl distillation-aeration apparatus designed some years ago by Dr. R. C. Corley, Purdue University, containing the accumulated improvements of graduate students in the department, (See Fig. 1) was used.

**Reagents:** All reagents are of analytical grade.
>Sodium hydroxide—50% solution.
>Boric acid—2% solution.
>Standard sulfuric acid—.0100 N solution.
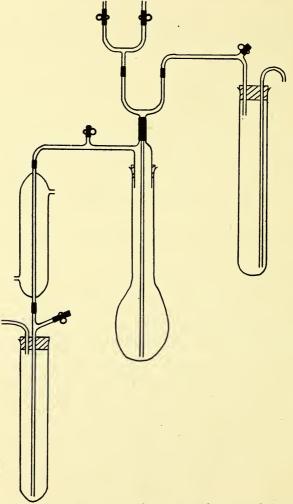>Concentrated sulfuric acid for digestion solution.
>Cupric sulfate (anhydrous), Mercuric Oxide, and Potassium Sulfate.
>Methyl-red and brom-cresol-green—0.1% alcoholic solution mixed in
>· the ratio of 1:5 (Ma & Zuazaga).
>Titanium trichloride—20% solution in concentrated hydrochloric acid.

**Method:** Reduction and digestion of sample: The compound is weighed by difference in a small ampule made from a two inch test tube. The ampule is placed into a 100 ml. Kjeldahl flask which contains approximately one ml. of a 20% titanium trichloride (in conc. HCl) solution and two ml. of 95% ethanol. If the compound is volatile, the Kjeldahl flask is stoppered and allowed to stand at room temperature for 5 to 10 minutes with occasional shaking. This step is not necessary for the non-volatile compounds. After standing, the stopper is removed and the sample slowly warmed to the boiling point and held there for two minutes. At this point, approximately 50 mg. each of HgO, $CuSO_4$, and $K_2SO_4$, plus 5 ml. of concentrated $H_2SO_4$ are added and the sample is digested on a sand bath until completely decomposed. Bumping is minimized by the addition of several small glass beads to the flask.

**Distillation and Aeration:** The digested sample is allowed to cool. The ampule is broken with a glass rod to prevent entrapment of ammonia

and the rod and flask are rinsed with distilled $H_2O$. The Kjeldahl flask is then connected to the aeration apparatus and a rapid stream of air is drawn through for a minute to remove any $SO_2$ or $SO_3$ fumes that may be present in the flask. After the condenser is rinsed with distilled water, the boric acid tube containing 35 to 40 ml. of 2% boric acid is attached to the apparatus. The aeration is begun and the 50% NaOH



is allowed to enter the flask. When the contents become a brownish color, the addition of 50% NaOH is discontinued. The flask is then heated with a micro burner for 3 minutes. At the end of this time the ammonia is completely distilled from the flask and the boric acid tube is removed and suitably rinsed. The boric acid solution is then titrated with standard acid using the mixed indicator.

**Discussion of Method:** After the sulfuric acid is standardized by the usual $Na_2CO_3$ method, it is restandardized with $(NH_4)_2SO_4$ of known purity using the Kjeldahl procedure. This will automatically take care of the minute amount of $NH_3$ that may be present in any of the reagents used.

Essentially the boric acid method of Ma and Zuazaga is followed (5).

The method proved extremely valuable in the case of the compounds listed in Table II, most of which are unstable when heated and decompose between 30-40°C. Thus, the Dumas combustion method gave high results for nitrogen and carbon and hydrogen combustion gave low results for both carbon and hydrogen. These results were obtained because the compounds decomposed so rapidly in the combustion tube that complete oxidation of the breakdown products did not take place. Also the dextrose reduction method (2) could not be used for the compounds since the compounds could not be heated until after they were reduced.

### Table I.

| | Nitrogen,% | | |
| | Calcd. | Found | |
|---|---|---|---|
| $CH_3CH_2NO_2$ | 18.66 | 18.62 | 18.65 |
| $CH_3CH_2CH_2NO_2$ | 15.72 | 15.67 | 15.70 |
| $(CH_3)_2C(NO_2)CH_2NH \cdot CH(CH_3)_2$ | 17.49 | 17.42 | 17.42 |
| $CH_3CH_2CH(NO_2)CH(CH_3)CO_2(CH_2)_2CH_3$ | 6.93 | 6.99 | 6.95 |
| Oxime* | 20.26 | 20.28 | 20.27 |
| $CH_3CH(NO_2)CH_2CH_2C\equiv N$ | 21.87 | 21.67 | 21.70 |
| $C_5H_6NO_2$ | 11.38 | 11.30 | 11.33 |
| Picrate derivative of an amine* | 8.80 | 8.76 | 8.78 |

* New compounds.

### Table II.*

| Amine diazotized | Nitroamine coupled** | Nitrogen,% | |
| | | Calcd. | Found |
|---|---|---|---|
| Aniline | M | 20.15 | 20.1 |
| $\beta$-Naphthylamine | B | 14.58 | 14.6 |
| $p$-Aminobenzoic acid | M | 17.40 | 17.3 |
| $p$-Chloroaniline | B | 15.18 | 15.3 |
| $p$-Chloroaniline | M | 17.90 | 17.6 |
| $o$-Nitroaniline | M | 21.65 | 21.6 |
| $m$-Nitroaniline | M | 21.65 | 21.4 |
| $p$-Aminoazobenzene | M | 22.0 | 22.4 |

 * Compounds prepared and analyzed by Gerhard Van Biema, Purdue University, 1943.
** M = 1-N-morpholino-2-nitropropane.
   B = 1-di-$n$-butylamino-2-nitrobutane.

The method is much superior to the titrametric determination as given by various investigators (1,3,4).

**Conclusion.** This is a rapid and accurate method for the determination of nitrogen in volatile aliphatic, unstable aromatic compounds, as well as stable aromatic non-aminoid compounds. Titanium trichloride proved to be an excellent reducing agent. Determinations are made on semi-micro scale using an efficient time saving aeration-distillation apparatus for the distillation of ammonia formed from the decomposed compound.

## References

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