Quantitative elemental analysis: nitrogen and sulfur

This chapter has dealt with the structure of benzene and with some of its reactions. It is well to remind ourselves again that all this discussion has meaning only because it is based upon solid facts. As we saw earlier (Sec. 2.26), we can discuss the structure and reactions of a compound only when we know its molecular formula and the molecular formulas of its products.

To know a molecular formula we must know what elements are present in the compound, and in what proportions. In Sec. 2.27 we saw how various elements can be detected in an organic compound, and in Sec. 2.28 how the percentage of carbon, hydrogen, and halogen can be measured.

Quantitative analysis for nitrogen is carried out either (a) by the *Dumas method* or (b) by the *Kjeldahl method*. The Kjeldahl method is somewhat more convenient, particularly if many analyses must be carried out; however, it cannot be used for all kinds of nitrogen compounds.

In the Dumas method, the organic compound is passed through a tube containing, first, hot copper oxide and, next, hot copper metal gauze. The copper oxide oxidizes the compound (as in the carbon–hydrogen combustion, Sec. 2.28), converting combined nitrogen into molecular nitrogen. The copper gauze reduces any nitrogen oxides that may be formed, also to molecular nitrogen. The nitrogen gas is collected and its volume is measured. For example, an 8.32-mg sample of *aniline* yields 1.11 mL of nitrogen at 21 °C and 743 mm pressure (corrected for the vapor pressure of water). We calculate the volume at standard temperature and pressure,

$$\text{vol. } N_2 \text{ at S.T.P.} = 1.11 \times \frac{273}{273 + 21} \times \frac{743}{760} = 1.01 \text{ mL}$$

and, finally, the percentage of nitrogen in the sample

$$\%N = \frac{1.26}{8.32} \times 100 = 15.2\%$$

In the Kjeldahl method, the organic compound is digested with concentrated sulfuric acid, which converts combined nitrogen into ammonium sulfate. The solution is then made alkaline. The ammonia thus liberated is distilled, and its amount is determined by titration with standard acid. For example, the ammonia formed from a 3.51-mg sample of aniline neutralizes 3.69 mL of 0.0103 M acid. For every milliequivalent of acid there is a milliequivalent of ammonia, and a

$$\begin{aligned}\text{milligram-atoms N} = \text{milliequivalents } NH_3 &= \text{milliequivalents acid}\\ &= 3.69 \times 0.0103 = 0.0380\end{aligned}$$

milligram-atom of nitrogen. From this, the weight and, finally, the percentage of nitrogen in the compound can be calculated.

$$\text{wt. N} = \text{milligram-atoms N} \times 14.01 = 0.0380 \times 14.01 = 0.53 \text{ mg}$$

$$\%N = \frac{0.53}{3.51} \times 100 = 15.1\%$$

Part of content taken from Morrison and Boyd Organic Chemistry, 6th edition, 1992.

Problem 14.11 A Dumas nitrogen analysis of a 5.72-mg sample of 1,4-diaminobenzene gave 1.31 mL of nitrogen at 20 °C and 746 mm. The gas was collected over saturated aqueous KOH solution (the vapor pressure of water, 6 mm). Calculate the percentage of nitrogen in the compound.

Problem 14.12 A Kjeldahl nitrogen analysis of a 3.88-mg sample of *ethanolamine* required 5.73 mL of 0.0110 M hydrochloric acid for titration of the ammonia produced. Calculate the percentage of nitrogen in the compound.

Problem 14.13 A Carius sulfur analysis of a 4.81-mg sample of *p-toluenesulfonic acid* gave 6.48 mg of $BaSO_4$. Calculate the percentage of sulfur in the compound.

Problem 14.14 How does each of the above answers compare with the theoretical value calculated from the formula of the compound? (Each compound is listed in the index.)

Answers		
	14.11	26%N
	14.12	22.8%N
	14.13	18.5%S