

# Empirical Formula by Microanalysis

The development of modern chemistry during the last two centuries owes more to accurate methods of quantitative analysis than to any other group of experimental techniques.

In this experiment, students take part in a microanalysis of an organic compound for the elements carbon, hydrogen and nitrogen. It is interesting to note that although the equipment used in this modern analysis is sophisticated, the basic methods are little changed from those developed in the nineteenth century. Particular attention should be paid throughout to the fastidious regard for accuracy on the part of the analyst and to the many safeguards incorporated in the methods to insure that no sample, combustion product, distillate, etc. is ever inadvertently lost. Really accurate results are only achieved through the analyst's long experience and careful checking of the apparatus by repeated determinations of materials with accurately known compositions.

The analysis is carried out in two stages. First, carbon and hydrogen are determined simultaneously and then, by means of an entirely different technique and apparatus, the compound is analyzed for nitrogen.

## Carbon and Hydrogen Determination

In this part of the analysis, a sample of the substance is burned in a fast stream of pure oxygen and oxidized completely to carbon dioxide and water, which are absorbed in separate tubes in an absorption train.

A small sample is weighed into a platinum boat and transferred into the silica combustion tube. The oxygen is purified by passing it over heated platinized asbestos to oxidize any organic impurities. The oxidation products are removed before they reach the combustion tube by the same absorbents used in the later absorption train.

When the weighed material for analysis is heated carefully by means of the hand-held burner, it sublimes and is carried slowly toward the hot (900°C) portion of the silica tube. This process must not be hurried, since too high a concentration of sample vapor entering the hot tube could cause a minor explosion and probably incomplete combustion of the sample. The likelihood of explosion is further reduced by the glass wool plug in the tube. The gases emerging from the combustion tube pass while hot over a roll of silver gauze which serves to remove any halogen present as silver halide and, by acting as a good heat conductor, prevents condensation of water in the otherwise cool region of the ground joint. The gases now pass on to the first of the pre-weighed tubes in the absorption train. This contains anhydrous magnesium chlorate(VII) (magnesium perchlorate), which absorbs water. The black substance in the center tube is a specially prepared hydrated manganese(IV) oxide which catalytically removes oxides of nitrogen. This tube is not weighed at any time during the analysis.

The third tube, the weight of which is accurately known, contains brown granules of soda-asbestos for absorption of carbon dioxide. Some magnesium chlorate(VII) is also present to prevent any water loss from the soda-asbestos. The first and third tubes are reweighed at the end of the combustion and the increases in their weight respectively give the weights of water and carbon dioxide produced.

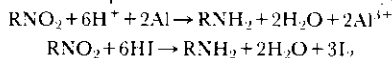
## Nitrogen Determination

The method used in this part of the analysis is one of the many modifications of the technique devised by Kjeldahl (pronounced Keldale) for analysis of brewing grain at the Carlsberg laboratories in 1883.

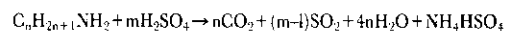
The Kjeldahl analysis for nitrogen gives best results when the element is present in an amino ( $-\text{NH}_2$ ) group. Since we do not always know the chemical nature of a material for analysis, the first operation on a weighed sample is

to heat it gently for 30 minutes with a mixture of reducing agents containing red phosphorus, hydriodic acid and even the aluminum cup in which the sample was weighed. Note that the long neck of the Kjeldahl flask acts as an air condenser at this stage.

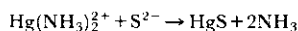
Examples of two reactions which may occur are shown below. A nitro compound is used for illustration only.



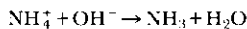
Concentrated sulfuric acid is now added and the mixture heated to boiling. The refluxing drives off all the iodine, and the nitrogen in the amino compound is slowly converted to ammonium ions. The conversion is speeded up by the addition of about 0.5g of a mixture containing mercury(II) sulfate as a catalyst and potassium sulfate to raise the boiling point of the sulfuric acid. At the end of this digestion, a colorless liquid remains together with some white solid. The nitrogen from the original compound is largely present at this stage as ammonium sulfate or ammonium hydrogen sulfate.



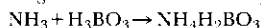
The entire contents of the flask are transferred into a Markham still and sodium hydroxide and sodium sulfide solutions added to form an upper layer. No mixing is encouraged at this stage to avoid premature loss of ammonia. A black precipitate forms at the interface of the two layers. This is mercury(II) sulfide, the formation of which releases any ammonia trapped as a mercury(II)-ammine complex, e.g.



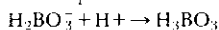
When steam is passed through, complete mixing takes place and ammonia is released:



The steam distillation continues for six minutes with the ammonia gas being absorbed in a boric acid solution.



After the condenser has been carefully rinsed with distilled water, the ammonium borate is finally titrated using exactly 0.1000M hydrochloric acid and a mixed indicator of methyl red and bromocresol green. The color change is from blue-green to a faint pink.



Care is taken during the steam distillation to prevent sodium hydroxide solution from splashing through the guard tube at the top of the inner tube of the still. Even so, a blank determination was carried out—that is, the same reagents were distilled for the same time but the sample was omitted. The titre for the blank distillation was 0.04 cm<sup>3</sup>.

## The Student's Part in the Experiment

*Carbon and hydrogen analyses:* Students should be prepared to read and write down the weights of each of the two absorption tubes, both initially and after the combustion. The weights of the platinum boat empty and with the sample are also required.

*Nitrogen analysis:* The weights of the aluminum cup with and without the sample are needed, together with the final burette reading in the ammonium borate titration. The initial burette reading was 0.00 cm<sup>3</sup>.

Using these readings, students can work out the percentages of carbon, hydrogen and nitrogen in the original material. The difference between the sum of these figures and 100% gives its percentage of oxygen. Students should use the figures to obtain an empirical formula for the compound.

Note: Students who watch the next program in the series (*Molar Mass by Elevation of the Boiling Point*) will obtain a molar mass for the same compound which will enable them to decide on a molecular formula.

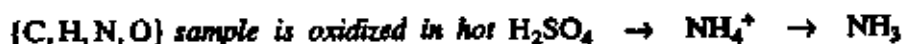
### To Obtain an Empirical Formula by Microanalysis

The film illustrates how an Empirical Formula is determined in a commercial analysis laboratory. Since the unknown compound contains *carbon, hydrogen, nitrogen* and *oxygen*, two independent experiments must be performed. In the first, the amounts of *carbon* and *hydrogen* in a sample are determined simultaneously by burning it in excess pure oxygen and collecting the reaction product  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in separate absorption tubes. The second experiment is the classic Kjeldahl method of analysing for nitrogen. It begins by using a series of reactions to convert the *nitrogen* in a known weight of sample to ammonia gas,  $\text{NH}_3$ . The latter is then treated with *boric acid* to give  $\text{H}_2\text{BO}_3^-$ , which is in turn titrated with 0.100 M  $\text{HCl}$ ; the number of moles of  $\text{HCl}$  used defines the amount of N in the original sample.

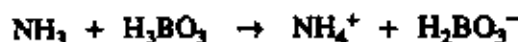
Use this sheet to record the experimental data as the film progresses, and then complete the requisite calculations and determine the empirical formula of our unknown.

Experiment One:	Final weight of $\text{H}_2\text{O}$ absorption tube	=	12.86151
	Initial weight of $\text{H}_2\text{O}$ absorption tube	=	12.85392
	Difference = weight of $\text{H}_2\text{O}$ absorbed	=	<u>0.00759</u>
	Final weight of $\text{CO}_2$ absorption tube	=	13.11563
	Initial weight of $\text{CO}_2$ absorption tube	=	13.09651
	Difference = weight of $\text{CO}_2$ absorbed	=	<u>0.01912</u>
	Weight of platinum boat + sample	=	0.42973
	Weight of platinum boat alone	=	0.41721
	Difference = weight of sample	=	<u>0.01252</u>
Experiment Two:	Weight of aluminum cup + sample	=	0.03013
	Weight of aluminum cup alone	=	0.01673
	Difference = weight of sample	=	<u>0.01340</u>

The Kjeldahl method for determining the amount of nitrogen in a sample (invented by Johan Kjeldahl in 1883 in the Carlsberg Laboratories in Copenhagen) is one of the most widely used of all chemical analyses. It consists of the following steps:



The  $\text{NH}_3$  is carried by steam distillation into a flask containing boric acid  $\text{H}_3\text{BO}_3$ , where  $\text{H}_2\text{BO}_3^-$  is formed according to the reaction



The resulting  $\text{H}_2\text{BO}_3^-$  is then titrated with standard  $\text{HCl}$ ,



Thus, the number of moles of N in the original sample is equal to the number of moles of  $\text{H}^+$  consumed in this titration step.

Calculations: Use the molecular masses:  $M_{\text{CO}_2} = 44.0098$  and  $M_{\text{H}_2\text{O}} = 18.01528$

- (a) No. moles of carbon  $n_{\text{CO}_2} = \frac{0.01912}{44.0098} = 4.341 \times 10^{-4}$   
 Mass of carbon = 0.00521 g
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- (b) No. moles of hydrogen =  $2n_{\text{H}_2\text{O}} = 2 \times \frac{0.0757}{18.02} = 8.424 \times 10^{-4}$   
 Mass of hydrogen = 0.00084 g
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- (c) Percent carbon in first sample  $\frac{0.00521}{0.01252} = 41.6\%$   
 Percent hydrogen in first sample = 6.7%
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- (d) Volume of 0.100 M HCl consumed in titration = 2.36 mL  
 No. moles of  $\text{H}^+$  consumed in titration  
 = no. moles  $\text{NH}_3$  released =  $n_N = 2.36 \times 10^{-3} \text{ L} \times 0.1 \frac{\text{mol}}{\text{L}} = 2.36 \times 10^{-4} \text{ mol}$   
 Mass of nitrogen in second sample  $\times 14.01 = 3.31 \times 10^{-3} \text{ g}$   
 Percent of nitrogen in second sample  $\frac{3.31}{13.40} = 24.7\%$
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- (e) Percent oxygen (by subtraction) = 27.0%

It is then convenient to determine the empirical formula of our unknown using the following Table.

Element	C	H	N	O
Percent by weight	41.6%	6.7%	24.7%	27.0%
Mass per 100 g sample	41.6 g	6.7 g	24.7 g	27.0 g
Atomic weight (M)	12.011	1.00794	14.0067	15.9994
Number of moles in 100 g sample = $m/M$	3.46	6.65	1.76	1.69
Divide by smallest number	2.05	3.94	1.05	1.00

The resulting final empirical formula is:

