

CHAPTER 2

DESCRIPTION OF THE ANALYTICAL METHOD TO DETERMINE
THE ELEMENTAL COMPOSITION OF OILS AND FATS

8. Take a tube of green glass *to* (Fig. 1)¹, that is closed at one end and has an internal diameter of 7 to 8 mm², an external diameter of 10 mm, a volume of 26 mL³ and is slightly bent at point *o*. Heat it with a flame for about half an hour to fully dry the inside. To this end, it should be gradually heated from *t* to *o*, whereby the open end *o* is held higher than the closed end *t*. Close the tube with a *cork* and determine its weight in a large Fortin balance⁴.

9. Weigh an aliquot of the material to be analyzed on a small, highly sensitive balance that is accurate to 1 mg when loaded with 20 g. If the material is a solid, it should be divided as finely as possible. Its weight must be at least 450 to 500 mg. Pour it into a porcelain crucible containing 45 to 50 g of cupric oxide⁵ that has just been heated until red. The two components are mixed by means of a well-dried glass pestle as quickly as possible. When the material is ready, place the crucible between two hot furnaces to reduce the likelihood of the oxide absorbing water vapor from the air. Use a funnel to introduce into the tube: 1. 1 g of copper oxide; 2. the mixture; 3. about ten grams of copper oxide. The latter must be ground in successive portions in the crucible to completely remove any of the mixture that might have stuck to the wall of this container; 4. 1 g of copper shavings that have already been roasted in air to oxidize their surface. This copper must be packed down by using a thick platinum wire.

10. Determine the weight of the filled tube with its *cork*. The weight of the copper oxide can then be calculated by subtracting the sum of the weights of the organic material, the copper and the tube. Given, 1. the density and the weight of the copper; 2. the density and the weight of the oxide; 3. the density and the weight of the organic material, the calculation of the volumes of each substance is straightforward. Calculating their sum total and subtracting this from the volume of the tube gives the volume of air introduced by these materials.

11. Now, fill a narrow, graduated flask having a ground glass stopper with mercury after an accurate determination of its volume up to its neck. The volume of the flask should be between 900 and 1000 mL. It is put upside down in a dish filled with mercury and secured by means of an ingenious contraption invented by Gahn and which we know about in France thanks to Berzelius. Next, the end *a* of a bent tube is brought

under the neck of the flask as indicated in Fig. 2⁶ After the curved part *bda* has been filled with mercury to ensure that no air enters the flask. In addition, a cork must be provided at *c* that fits exactly in the aperture *o* of tube *t* (Fig. 1) and into which it is introduced to a depth of at least 1 cm. The tall part of the tube (Fig. 2) must be at least 760 cm and its volume calculated from the line *ba* must be between 2.0 and 2.5 mL. This volume is determined by means of mercury, in the same way as the volume of the first tube.

12. Tube *to* (Fig. 1) is now positioned in a brick lined furnace that has a length of some 42 cm⁷, a width of 14 cm and a depth of 6 cm. The openings in the grate and in the walls must have been sealed with clay. Inside the furnace, the tube is tilted slightly, as shown in Fig. 3. Tube *cbda* is then fixed in position and the cork is luted with sealing wax⁸.

13. Then burning charcoal is placed in the furnace in such a way that only the copper and half of the copper oxide on top of the mixture are heated. The latter is protected from the heat by a tinplate⁹ shield *e*. When the oxide is sufficiently hot, the shield is moved further away from *o* and more charcoal is added to fill the gap. This way, the end *t* is heated only very gradually. Because heating must be slow, the shield may only be moved away further when hardly any more gas is given off. Once you have started to heat part of the tube, the temperature of this part must be raised until it is a dull red and kept at this level for the remainder of the operation. Contact between the charcoal and the tube must be avoided, since the latter may become too soft and burst. Finally, when the end *t* is being heated, the temperature of the tube must be maintained for ten to fifteen minutes after the evolution of gas has ceased.¹⁰

14. After the combustion of the organic material is finished, tube *to* is allowed to cool down. When it has reached ambient temperature, the height to which the mercury column in tube *cbda* has risen above the level in the dish¹¹ is determined before the tube is detached. In this way, the volume of gas contained in both tubes can be calculated.

15. Now check whether the water present in tube *cbda* is tasteless and whether it causes litmus paper to change to a permanent red. It will always turn slightly red because the water is saturated with carbon dioxide. Now heat the end* of tube *t* to ensure that there is no moisture present when it is weighed. After it has cooled down a little, the cork is inserted again and the tube is weighed. The difference between the original weight (10)¹² and the present weight is entirely due to: 1. the fact that the tube no longer contains any organic material, and 2. that the copper oxide has transferred part of its oxygen to the combustible part of this

* Only the very end must be heated to prevent the copper oxidizing as a result of the air present.

material, assuming that the outer surface of the tube was equally moist during both weighing operations.

16. To arrive at the elemental composition of the organic material¹³ the following must be determined: 1. the amount of gas that remained in the tubes after the experiment; 2. the proportion of carbon dioxide, oxygen, and nitrogen present in the products as well as the proportion of carbon and hydrogen that might have escaped the oxidative action of the copper oxide.

17. Empty tube *to* and fill it with mercury up to where the cork of tube *cbda* was inserted and determine the volume of this amount of mercury. Repeat the determination for the part of tube *cbda* that was filled with gas after the tubes had cooled to ambient temperature (14). Given the volume of the original copper, the volume occupied by the gas after the experiment is calculated by determining the volume occupied by the mixture of the copper oxide and its reduction product¹⁴, adding these two volumes and subtracting their sum from the combined volume of the two empty tubes. This volume is then normalized to 0°C, 0% humidity and a pressure of 760 mmHg.

Determination
of the amount
of gas still
present in the
tubes after the
experiment

18. It is very difficult to measure the exact volume of the gas that has been collected in the flask by lowering it into the dish until the mercury level inside the flask is the same as the level in the dish and then reading on the graduation the volume occupied by the gas. Accordingly, the following method is used: carbon dioxide that is saturated with water is introduced into a narrow bell jar that is graduated in mL, in an amount that is assumed to be necessary to fill the flask completely when added to the gas already present, the amount of which has been estimated from the graduation of the flask. Then this acid gas is transferred into the flask, filling it up to where the neck starts. Subsequently, the carbon dioxide is absorbed by potash¹⁵ and the *residual gas* is transferred to a narrow, graduated tube. This last operation is carried out in a tank of water. Subtracting the volume of this residual gas from the volume of the flask gives the amount of carbon dioxide that was contained in the flask. Subtracting the amount that was added gives the amount resulting from the analysis. As for the *residual gas*, 1. the oxygen content is determined by means of phosphorus; 2. hydrogen and carbon, if present, are determined after the oxygen has been absorbed by detonation with a known mixture of hydrogen and excess oxygen; 3. finally the nitrogen is determined by allowing phosphorus to absorb the oxygen still present after the detonation.

Determination
of the
composition of
the gas in the
flask

19. Since we know the composition of the gas in the flask and the total volume of the gas left in the tubes when the experiment had finished, it is easy to determine the composition of the latter¹⁶ and with

these data, the elemental composition of the organic material can be calculated.

A. DETERMINATION OF THE CARBON CONTENT

20. By normalizing the volume of the carbon dioxide to a pressure of 760 mmHg, a temperature of 0°C and 0% humidity, its oxygen and carbon contents can be calculated, to which the carbon must be added that may be present in the *residual gas* that is insoluble in potassium hydroxide (18). In the analysis yielding the largest amount of inflammable gas (the cholesterol analysis), the volume of the carbon dioxide resulting from the combustion of the *residual gas* was less than 4 mL.

B. DETERMINATION OF THE HYDROGEN AND OXYGEN CONTENTS

21. A. Subtracting the oxygen contained in the carbon dioxide (A) from the oxygen that the copper has provided to burn the organic material, gives the oxygen that the copper has provided to oxidize part of the hydrogen present in the organic material; the proportionality rule, allows us to calculate how much hydrogen was oxidized*.

B. There was some oxygen from the atmosphere present in the tubes. This oxygen had to compete with that of the copper oxide when burning the organic material; this has to be taken into account. Nothing is simpler since both the amount of oxygen present in the tubes at the start of the experiment and the amount after the combustion are known. It is evident that the difference between these two amounts represents the amount of hydrogen that was burned; this can be determined in the same way as in A above.

C. To the sum of these two amounts of hydrogen, the amount that may be present in the *residual gas* (18) must also be added. This amount never exceeded 8 mL in my analyses.

D. Finally, the sum of the amount of carbon and the three amounts of hydrogen is calculated and subtracting this from the sample weight gives the amount of water that has been formed from a fourth amount of hydrogen and all the oxygen contained in the sample.

22. By following the procedure as described above, the elemental composition of an organic material can be determined. However, there may be some doubt about the accuracy of the hydrogen value since the water formed was not collected, and I have carried out a preliminary experiment to determine directly the amount of water formed by the

* Please note that we are analyzing substances that contain more hydrogen than needed to convert the oxygen present in these substances into water.

combustion of the organic material. This enabled me to calculate the composition of the latter, since, the amount of oxygen provided by the copper oxide for the combustion was also known.

23. The water is collected in an apparatus¹⁷ comprising: 1. a tube *a** containing some 500 mg organic material and 55 to 60 g copper oxide; 2. a tube *b* containing about 40 g calcium chloride. A tube *c* is fitted at their ends so that it connects to tube *a* and a tube *a'* is connected to a tube *d* the open end of which is immersed in a mercury bath. Tubes *c* and *c'* are luted with sealing wax. The end of *c'* that is inserted into tube *b* is plugged with some fine cambric¹⁸ to prevent the calcium chloride from falling out of the tube while it is being filled¹⁹. Tube *a* is fastened to tube *c* by means of a rubber tube, the ends of which are attached tightly to the glass tubes with silk thread. Before the experiment, weigh: 1. tube *a'*; 2. tube *b* after it has been closed with two little *corks* that must be carefully retained. After the experiment, tube *d* is detached, the open end of tube *c'* is closed with its *cork*, then tube *a* is cut at *a'* after all the water that might have condensed between *a* and *a'* has been evaporated. The tube is then placed on the pan of a balance together with the portion *a'a''* of tube *a* and the second *cork*. When the balance is in equilibrium, all objects are removed from their scale pan and the portion *a'a''* is detached from the calcium chloride tube. Let it dry and put it again on the scale pan with the rubber tube and the silk thread which attached tube *a* to tube *b*. Then add the weights that are required to bring the balance in equilibrium again. If the original weight of the calcium chloride tube with its corks is subtracted from these weights, the difference corresponds to the weight of the water formed. Finally, by weighing tube *a* and the portion *a'a''*, the amount of oxygen that the copper oxide provided for the combustion of the organic material can be determined.

24. This experiment has many advantages: 1. It gives the volume of the carbon dioxide that will result from a known amount of organic material. With this knowledge, we can calculate what weight of this material will yield the maximum amount of carbon dioxide on combustion without exceeding the capacity of the flask. 2. It serves as independent proof of the analysis determining the elemental composition of the organic material on the basis of the amount of carbon dioxide collected. If the hydrogen content obtained by this method differs too much from the content as calculated, the combustion experiment must be repeated, this time making every possible effort to completely dry the interior of the tube and to introduce the mixture rapidly since these precautions have a significant effect on the accuracy of the analysis.

* This tube is similar to the tube Berzelius uses for the analysis of organic materials.

25. To find out the possible magnitude of the error that might result from the absorption by the copper oxide, being a porous material, of water vapor and air from the atmosphere while it is being mixed with the organic material, I carried out two experiments. In both of them I heated a tube filled with copper oxide under the same conditions as during an analysis. The tube was connected to a flask into which I had introduced a volume of pure carbon dioxide. In the first experiment in which I had deliberately not taken all possible precautions against errors, the tube contained 100 g pure oxide, almost double the amount that I always used in my analyses. 12 mg were lost. On analysis, the gas in the flask contained the original volume of carbon dioxide with an amount of air corresponding to what had been lost from the tubes except for an excess of 3 mL nitrogen. In the second experiment, where I meticulously avoided all sources of errors, the tube contained 60 g of copper oxide, which is the maximum amount I ever used. The loss was barely 6 mg and this time there was only a slight excess of nitrogen. In my opinion, these experiments counter any objections which may be made to the method I have used regarding the excess hydrogen this method tends to produce during the elemental analysis of organic materials.

26. The results of the analyses have been calculated using the specific weights of the gases involved as determined by Berzelius and Dulong²⁰.

weight of 1 L.....	{	dry carbon dioxide at 0°C	
		at a pressure of 760 mmHg.....	1.98033 g
		hydrogen.....	0.08937
		oxygen.....	1.43 228

27. Temperatures have been estimated in degrees centigrade (°C).

¹ The figures are on page 343.

² Chevreul indicates these distances as 0^m 007 and 0^m 008. The unit for volume he usually writes in full as "cubic centimetres" but in the next book, he also uses dl (deciliter). A bit later he indicates weights as 0%45 etc. Where appropriate these have been changed to mm, mL or mg.

³ Chevreul does not indicate the length of the glass tube, which on the basis of the internal diameter and the volume should be almost 60 cm. This could be because the volume is critical and the diameter not that predictable. Better to cut the right length after its volume has been measured.

⁴ This kind of balance was also used by Lavoisier. It has an accuracy of 1/20 000.

⁵ In French, this copper oxide is called "deutoxyde de cuivre". According to a book published in 1823 (*Éléments de chimie appliqués à la médecine et aux arts*), this oxide is black and its salts are blue. It must therefore be copper (II) oxide. In 1811, Gay-Lussac and Thenard introduced potassium chlorate as an oxidizing agent in elemental analysis of organic compounds but in 1815, Gay-Lussac switched to the less hazardous cupric

oxide. The book also mentions that according to Berzelius, it contains 25 parts of oxygen per 100 parts of copper but then confuses the issue by stating that this corresponds to 2 oxygen atoms per copper atom. It does, but only for those who assumed the atomic weight of oxygen to be 8.

⁶ The figures referred to are shown on page 343, just before the Index.

⁷ Given the calculation of the length of tube *to* above, the bath seems to be rather short.

⁸ Ensuring an airtight seal at this joint is vital. If some gas were to escape during the experiment or air to be sucked in as it cools down, this would lead to a false reading of the volume of carbon dioxide formed during the experiment and finally to an underestimate of the carbon content of the sample.

⁹ Nowadays, "fer-blanc" only means tinplate but it may have had a different meaning at the time of writing.

¹⁰ Just a word of explanation of what has happened. Heating the tube has caused the air inside the tube to expand and the oxidation of the sample by the copper oxide has led to the formation of water and carbon dioxide. Gases moved out of the tube, through the vertical tube and into the flask while displacing some mercury but some gases stayed behind in the tube and some water condensed. The problem to be solved now is how to arrive at the data required to calculate the molecular formula of the sample.

¹¹ When the tube cools down, the gas inside the tube contracts and will cause the mercury in the vertical tube to rise.

¹² This number pertains to the sub-section describing when to determine the original weight.

¹³ This elemental composition is calculated from three measurements:

1. the weight of the sample;
2. the weight loss of the tube's contents;
3. the amount of carbon dioxide evolved during the combustion of the sample.

The latter amount (3) allows the carbon content of the sample to be calculated. The weight loss (2) is the sum of the sample weight (1) and the loss of oxygen (4) used to oxidize the sample, so subtracting the sample weight (1) from the weight loss (2) results in the amount of oxygen (4) that went into sample oxidation. Some of this oxygen ended up as carbon dioxide and this amount (5) can be calculated from the amount (3) evolved. Subtracting this amount of oxygen (5) from the total usage (4), gives the amount of oxygen (6) that ended up as water.

Accordingly, the hydrogen equivalent of this last amount (6) can be calculated but this is not the total hydrogen content of the sample. Some hydrogen combined with the oxygen present in the sample to form water (7). Therefore, the carbon content of the sample and the hydrogen equivalent of the amount of oxygen (6) must be added together and this sum must be subtracted from the sample weight (1). The difference (7) is the water formed from oxygen present in the sample, thus allowing the oxygen content of the sample to be calculated. The hydrogen equivalent of this water (7) must be added to the hydrogen equivalent of the amount of oxygen (6) originating from the copper oxide to arrive at the hydrogen content of the sample.

Of course there are some complications in that the combustion may not be perfect and that air present in the tube may also participate in the combustion of the sample. These are dealt with in the original text, which as a result can be somewhat confusing.

¹⁴ How this volume is determined has not been described in detail. Presumably, the residue in tube *to* was inserted in a pycnometer and weighed. However, this raises the question of why the copper shavings were kept separate.

¹⁵ The potash mentioned is probably potassium carbonate, which will absorb carbon dioxide under formation of potassium hydrogen carbonate but it could also be caustic potash. The latter is probably the most likely.

¹⁶ The assumption that the composition of the gas in the flask and the gas in the tubes is the same may not be correct.

¹⁷ Although the text does not mention this, this is the apparatus shown in Fig.4. on page 343. The whole description of the apparatus is rather confused.

¹⁸ Cambric or batiste is a lightweight, closely woven cotton or linen fabric.

¹⁹ We would use glass wool nowadays.

²⁰ This is a remarkable achievement since using current values for the relative molecular masses of the gases concerned leads to 1.9630 g for carbon dioxide, 0.0899 g for hydrogen and 1.4376 g for oxygen.

The values in the table also allow the relative atomic masses of carbon and hydrogen to be determined. Assuming the relative atomic mass of oxygen to be 16.0000 and using today's molecular formulae leads to a value of 12.2445 for carbon and 0.9984 for hydrogen. These are in fact the values the author has used throughout the work.