

C. Gerhardt compendium

NITROGEN ANALYSIS

THE JEAN DUMAS METHOD

Evolution

The Dumas combustion method has become established since the 1980s as a substitute to acid digestion. The Dumas method is a fast and convenient alternative to the classic Kjeldahl method for almost all solid and liquid samples.

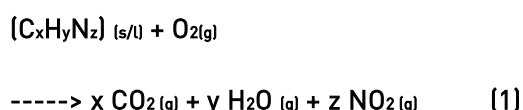
Jean Dumas (Fig. 1) published his combustion method in Paris back in 1848. This makes the method considerably older than Kjeldahl digestion. While researching the composition of natural oils, Dumas tried combusting his samples, initially to analyse the carbon and hydrogen contained therein.

Combustion therefore makes it possible to analyse multiple parameters, while Kjeldahl digestion is only suitable for nitrogen.

The initial aim back then, however, was to control the rigid reaction conditions using technical solutions, in other words

- Combusting the samples in a controlled manner at the maximum temperatures possible
- Using high-purity oxygen for combustion
- Selectively collecting the resultant combustion products
- Calculating the composition of the initial sample from the change in weight in condensation traps

If we assume that pure oxygen was used in the combustion, we can apply the following reaction equation to the combustion reaction for organic samples (equation 1):



Carbon and hydrogen in the solid or liquid sample (C_xH_yN_z) are fully converted into the corresponding products carbon dioxide CO₂ and water H₂O, nitrogen is initially oxidized to NO₂.



Fig. 1: Jean Dumas, 1848

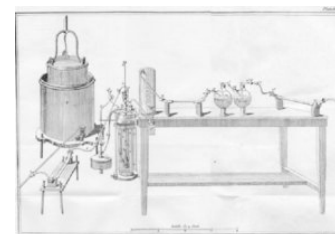


Fig. 2: Combustion equipment designed by Lavoisier 1789



Fig. 3: Dumas analysis system DUMATHERM from C. Gerhardt 2021

Early technical solutions

In 1789, Antoine Lavoisier designed the first decomposition instrument for performing a controlled high-temperature pyrolysis process (decomposition without the addition of oxygen) and subsequently analysing the resultant gases. He succeeded here in solving four crucial problems:

- Reaching a temperature high enough to ensure complete combustion
- Generating high-purity oxygen or sufficient heat without nitrogen contamination for combustion
- Selective collection of carbon dioxide and water without mutual interference
- Sufficiently precise scales to determine the differences in weight before and after combustion

Lavoisier generated the necessary energy/temperature with a gas discharge lamp (Fig. 2, at centre). He routed the resultant energy/heat into the apparatus with the sample and successfully broke it down. The resultant gases were collected in condensation traps (Fig. 2, on right). Differential weighing before and after combustion enabled quantitative conclusions to be made about the composition of the sample. [1]

However, he was still faced with the problem that high pressure is created when the combustion products are formed, and glass equipment of this type was not always able to withstand the pressure. Then, in 1789, Justus Liebig made a revolutionary discovery in his laboratory in Giessen, Germany: pure oxygen can also be generated *in situ* and used directly to combust organic samples. His apparatus was considerably simpler and less dangerous to handle than Lavoisiers'. Liebig used oxygen-rich metal salts, which release gaseous oxygen when energy is added by burning coal (Fig. 4, on left).

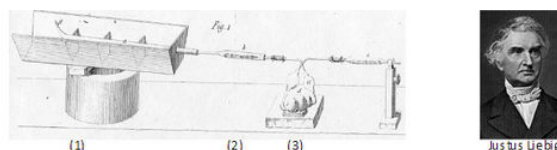


Fig. 4: Combustion equipment designed by Liebig with *in situ* generation of pure oxygen in the combustion pipe (1). The emergent gases can be analysed with cooling traps for water (2) and carbon dioxide (3).

Another revolutionary innovation was the condensation trap for carbon dioxide (item 3 in Fig. 4), which consisted of a glass vessel made up of 5 spheres, half-filled with potassium hydroxide solution. The carbon dioxide from the sample reacted here to form potassium carbonate (K_2CO_3) and could thereby be completely separated out of the flow of gas from the combustion products. Differential weighing of the cooling traps (2) and (3) before and after the analysis provided quantitative conclusions about the hydrogen and carbon content of the combusted sample. The American Chemical Society honoured the importance of this discovery by including Liebig's 5-sphere gas condenser in its logo, where it stands to this day (Fig. 5, on right).

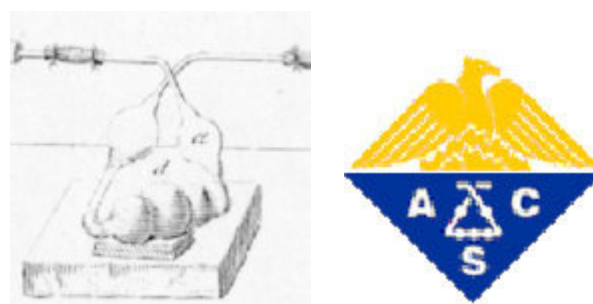


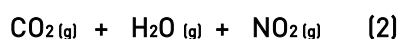
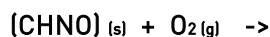
Fig. 5: 5-sphere condensation trap for carbon dioxide from Liebig and the logo of the American Chemical Society (on right) with eagle and gas condenser.

Modern combustion equipment

Sample feeding and combustion

While the acid digestion according to the Kjeldahl method destroys the organic sample in a rather rough-and-ready way, combustion provides a somewhat more elegant and time-saving option. The sample is oxidised in a controlled manner and the resulting gaseous products are subjected to further analysis. The objective is the complete conversion of the sample into the carbon dioxide,

water and nitrogen dioxide primary products (equation 2) without the carbon monoxide (CO) and nitrogen monoxide (NO) secondary products being produced from incomplete combustion.



As air has a nitrogen content in excess of 70%, it must first be ensured that the interfering atmospheric nitrogen is completely separated from the sample before the analysis. To do this, a powerful sampler is needed to reliably seal the sample from the ambient air, and the sample must be sufficiently purged before combustion.

Modern combustion apparatuses use helium technology to expel atmospheric nitrogen and to achieve the greatest possible precision in the analysis at the same time. In addition, the sample has to be packaged to ensure that no ambient air falsifies the analysis values.

The solid or liquid sample is packed in tin foil, then combusted in the combustion reactor in a flow of pure oxygen, and the resultant ash is then collected in the crucible.

The gaseous combustion products react completely in the presence of catalysts to the required oxides.

Next, the nitrogen oxides are reduced to elemental nitrogen while the two other secondary products, water and carbon dioxide, are separated out in special traps. In the remaining gas flow consisting of helium and nitrogen, the nitrogen can be measured using a thermal conductivity detector.

Modern computer controllers enable direct evaluation of the analysis data and almost maintenance-free use of the equipment.

Combustion reaction

During combustion, it must be ensured that there is a sufficient supply of oxygen, but for economic and environmental reasons, it is important to ensure that there is not an excess of oxygen.

In modern equipment, the optimum supply of oxygen is calculated according to the composition of the sample using a sample-specific combustion factor (equation 3):

Sample weight [mg] * combustion factor a

= oxygen quantity [ml] (3)

Additional combustion aids, such as the tin foil used to pack the sample, and the combustion catalysts, support high-temperature combustion and shift the reaction equilibrium towards the desired products carbon dioxide (CO₂) and water (H₂O). The secondary product carbon monoxide (CO) is not desired and is prevented in this way, which avoids excesses of oxygen.

Another effect of high-temperature catalysts is to reduce the activation energy. This accelerates the reaction dramatically, so that it takes less than three minutes.

Reduction using copper chips

The second chemical reaction in nitrogen determination is the reduction of nitrogen oxide (NO₂) to elemental nitrogen (equation 4). A metallic surface of copper has proven more effective here than tungsten.



Whereas tungsten expands in volume as it oxidises into tungsten oxide and therefore poses a risk of fracturing the glass in the hot reduction reactor, copper does not exhibit this characteristic and is, in addition, far more powerful. Once nitrogen oxide has been converted into nitrogen, all that remains is to remove the combustion products carbon dioxide and water from the flow of gas before the nitrogen can be detected.

Water removal

The water must be completely removed from the flow of gas in order to rule out interactions when detecting the analyte nitrogen.

The water can be removed from the analysis gases nitrogen (N₂) and helium (He) by an



intelligent diaphragm system, for example, in the Dumas-analytical system from C. Gerhardt (Fig. 4).

Carbon dioxide removal

Particularly effective traps need to be used to remove the carbon dioxide because carbon dioxide is detected in addition to nitrogen and would therefore falsify the results of the analysis.

Detection and evaluation

Thermal conductivity detectors are used to detect the nitrogen. Helium is a highly suitable carrier gas here because it has a strongly reduced thermal conductivity compared to the nitrogen that is being measured. Table 1 shows the thermal conductivity of the usual gases in the elemental analysis. The greater the difference in the thermal conductivity, the better the detection capability and precision of the machine. Helium as carrier gas and nitrogen as analyte are the ideal combination here. A reference gas flow in the detector (as was still necessary in classic detectors based on a Wheatstone bridge) becomes unnecessary with these.

Gas name	$\lambda_{300\text{ K}}$ [W/m*K]
Helium He	156.7
Carbon dioxide CO ₂	16.8
Nitrogen N ₂	26.0
Carbon monoxide CO	16.8

Tab. 1: Thermal conductivities λ of the gases used in elemental analysis at 300 K.

Conclusion

The nitrogen/protein analysis according to Dumas is a serious alternative to the acid digestion method according to Kjeldahl, if the sample material fulfils all the necessary prerequisites (sufficiently homogenous, easy handling etc.) of successful analysis with a combustion device. The combustion method is increasingly establishing itself as second reference method in addition to the Kjeldahl method, not least because modern combustion equipment is fully the equal of the Kjeldahl method when it comes to precision and universal applicability.

C. Gerhardt GmbH & Co. KG

Cäsariusstraße 97
53639 Königswinter
GERMANY

+49 2223 2999 - 0
info@gerhardt.de
www.gerhardt.de

