Liebig and Combustion Analysis

William B. Jensen

Department of Chemistry, University of Cincinnati
Cincinnati, OH 53706

The basic tenets of organic combustion analysis were introduced by Lavoisier in the 1780s (1). Essentially the organic material is oxidized to carbon dioxide and water. The former is absorbed using a solution of potassium hydroxide and the latter using anhydrous calcium dichloride. From the difference in the masses of the absorbents before and after combustion, one can determine the masses of carbon dioxide and water formed and, from a knowledge of the gravimetric composition of these two compounds, one can calculate the weight of carbon and hydrogen present in the original organic sample:

mass C = 0.273 (mass of CO_2 formed) [1]
mass H = 0.112 (mass of H_2O formed) [2]

The total mass of any oxygen and nitrogen present in the sample is assumed to be equal to the difference between the mass of the original sample and that of the carbon and hydrogen present:

mass (O & N) = mass sample - mass (C & H) [3]

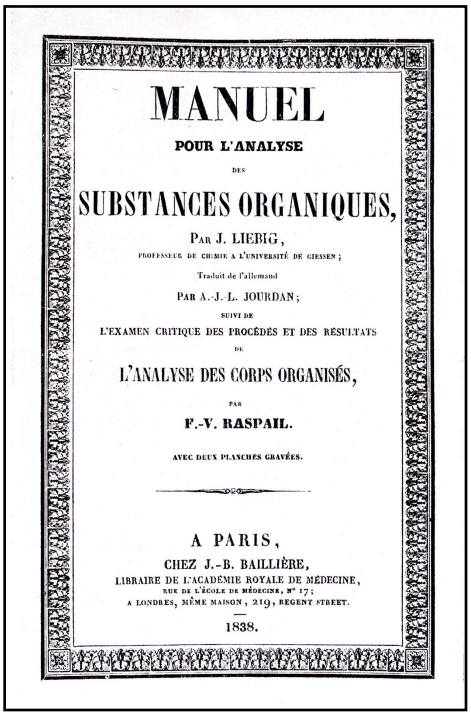
MANUEL
POUR L'ANALYSE
DES
SUBSTANCES ORGANIQUES,
PAR J. LIEBIG,
PROFESSEUR DE CHIMIE A L'UNIVERSITÉ DE GIESSEN;
Traduit de l'allemand
PAR A.-J.-L. JOURDAN;
SUIVI DE
L'EXAMEN CRITIQUE DES PROCÉDÉS ET DES RÉSULTATS
DE
L'ANALYSE DES CORPS ORGANISÉS,
PAR
F.-V. RASPAIL.
AVEC DEUX PLANCHES GRAVÉES.
A PARIS,
CHEZ J.-B. BAILLIÈRE,
LIBRAIRE DE L'ACADÉMIE ROYALE DE MÉDECINE,
RUE DE L'ÉCOLE DE MÉDECINE, N° 17;
A LONDRES, MÊME MAISON, 219, REGENT STREET.
1838.

Figure 1. Title page of the 1838 French translation of Liebig's *Anleitung zur Analyse der organischer Körper.*

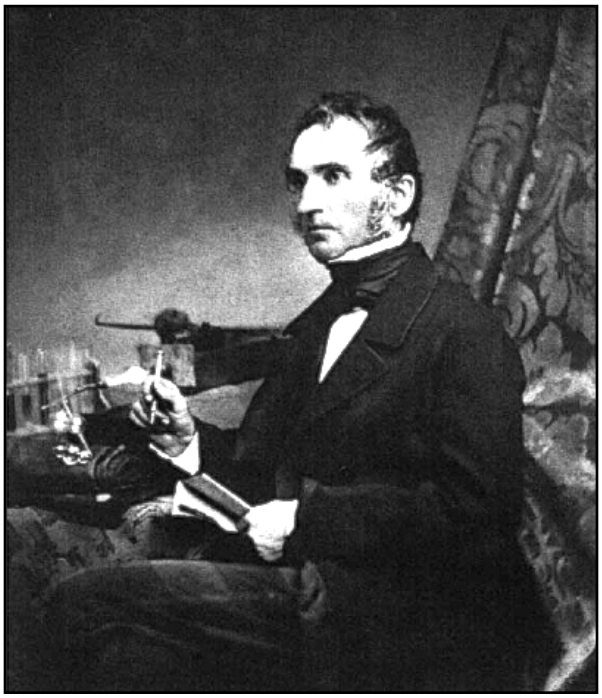

Figure 2. Justus von Liebig (1803-1873) posing with his apparatus for combustion analysis.

Though simple in principle, the translation of these assumptions into a reliable routine laboratory procedure required many refinements (Gay-Lussac & Thenard 1810, Berzelius 1813, Döbereiner 1816, Prout 1820, 1827) until it reached its standard form with the publication in 1837 of the monograph, *Anleitung zur Analyse der organischer Körper* (figure 1), by the German chemist, Justus Liebig (figure 2), based on improvements he had made in the technique earlier in the decade. Additional methods for the separate determination of organic nitrogen (Dumas 1831, Kjeldahl

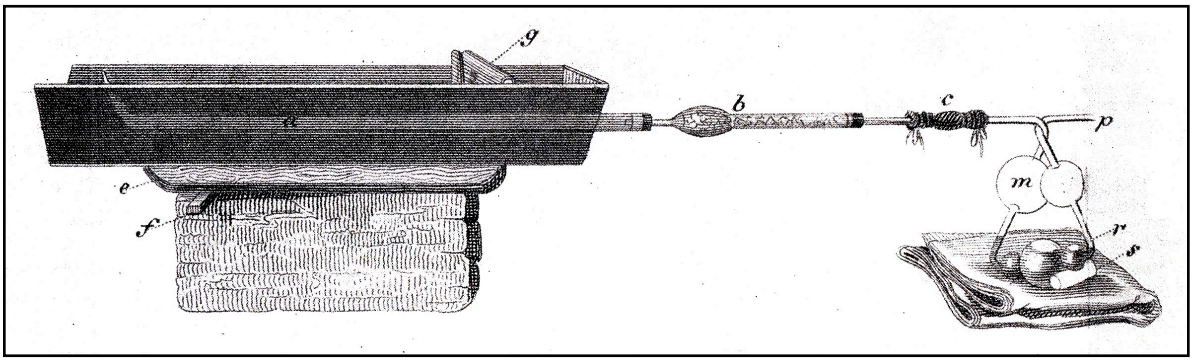

Figure 3. A period woodcut of Liebig's original apparatus for combustion analysis. *Left to right:* The metal charcoal furnace (*g*) resting on a brick and slab of ceramic tile (*e*), the calcium dichloride drying tube for the absorption of water (*b*), the rubber tube connector (*c*), and the potash or *Kali* bulb (*m*) for the absorption of carbon dioxide.

1883), and for the determination of sulfur (Carius 1860) and the halogens (Piria 1857, Carius 1860) soon followed.

In Liebig's original apparatus (Figure 3), the organic sample was mixed with copper oxide which, on heating, provided the dioxygen gas required for the oxidation of the sample:

$$\text{heat} + 2CuO(s) \rightarrow 2Cu(s) + O_2(g) \qquad [4]$$

This mixture was placed in a small porcelain tray or "combustion boat" and inserted into a heat resistant glass "combustion tube" sealed at one end, along with additional copper oxide. This, in turn, was placed in a metal trough or furnace where it was surrounded with burning charcoal. The open end of this tube was connected via a cork with a calcium dichloride drying tube to absorb the evolved water vapor and this, via a section of rubber tubing, with a characteristically shaped potash or so-called *Kali* bulb (figure 4) containing a concentrated solution of potassium hydroxide for the absorption of the evolved carbon dioxide. Interestingly an projection of this Liebig absorption bulb was incorporated into the logo (figure 5) of the American Chemical Society upon its founding in 1876, reflecting the large number of the society's founding members who were familiar with its use and importance.

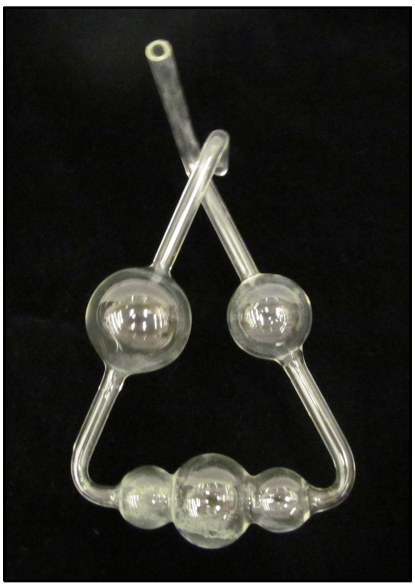

Figure 4. Closeup of a typical Liebig *Kali* bulb (Jensen-Thomas Apparatus Collection).

Figure 5. The logo of the American Chemical Society (ACS) showing the projected outline of a Liebig *Kali* bulb centered in the lower half.

Liebig's original apparatus was gradually modified over time. By the last quarter of the 19th century, trains of gas burners had replaced the charcoal furnace, and by the early 20th century these had, in turn, been replaced by electric tube furnaces. During this same period, the use of copper oxide as an oxygen source was gradually replaced by a direct flow of dioxygen gas stored in either a gasometer or in a tank of compressed gas.

The mass of analytical data on the composition of organic substances generated by these techniques formed the empirical basis for the various theories of

Figure 6. Dr. Melvyn Usselman
(1946-2015)

organic structure and isomerism developed throughout the 19th century. Indeed combustion analysis is still with us, though it is now largely automated and is performed on a micro rather than a macro basis.

In 2005 Dr. Melvyn Usselman of the University of Western Ontario (figure 6) built an exact replica of Liebig's original apparatus and had a group of undergraduate chemistry students use it to repeat some of Liebig's original analyses. The agreement between the original and modern results was excellent. This was done to refute the claims of several ill-informed philosophers and historians of science that Liebig's results were mere instrumental artifacts lacking in physical objectivity. When the present author visited the University of Western Ontario in 2006, Dr. Usselman made him a present of his reproduction and it currently resides in the Oesper Collections in the History of Chemistry, where it serves as the centerpiece of our display on combustion analysis (figure 7).

References and Notes

1. For the detailed history of combustion analysis see M. Dennstedt, *Die Entwickelung der organischen Elementanalyse*, Enke: Stuttgardt, 1899 and A. Rocke, "Organic Analysis in Comparative Perspective: Liebig, Dumas, and Berzelius," in F. L. Holmes, T. H. Levere, Eds., *Instruments and Experimentation in the History of Chemistry*, MIT Press: Cambridge, MA, 2000, pp. 273-310; For a brief but adequate overview, see A. Ihde, *The Development of Modern Chemistry*, Harper & Row: New York, NY, 1964, pp. 173-179.

2. J. Liebig, *Antleitung zur Analyse organischer Körper,* Vieweg: Braunschweig, 1837.

3. M. C. Usselman, A. Rocke, C. Reinhart, K. Foulser, "Restaging Liebig: A Study in the Replication of Experiments," *Ann. Sci,* **2005**, *62*, 1-55.

Figure 7. A reproduction of Liebig's original apparatus for combustion analysis based on Dr. Usselman's gift. *Background (left to right):* charcoal furnace and combustion tube, calcium dichloride tube, *Kali* bulb. *Foreground (left to right):* bellows and small funnel for filling the *Kali* bulb, extra charcoal and tongs, bottle of copper oxide and a porcelain combustion boat (Jensen-Thomas Apparatus Collection). Compare with figure 3.