Fritz Pregl received the Nobel Prize for chemistry in the year 1923 because he had improved earlier methods of quantitative organic microanalysis, thus making possible the study of substances which are available only in small quantities (3-5 mg). The same quantity of substance, which had formerly been sufficient for only one analysis, from that time on could be used for more than 500 analyses. Pregl devoted himself to research into nitrogen and sulphur compounds, organic compounds containing chlorine, bromine and iodine and a number of other organic compounds.

The importance of his work lay mainly in the fact that he made possible the study of mass, elementary composition, structure and the relations between elements in substances of which only a few mg were available. Thanks to his improvements, other scientists were able to work with greater precision. Biochemists were able to study the structure and function of enzymes, hormones, vitamins and other organic compounds which exist in the human body only in tiny quantities.

Pregl’s working method still remains in use, although his name is not preserved.

Fritz Pregl was born in 1896 in Ljubljana. His mother was Austrian and father Slovene who was a treasurer at the Kranjska hranilnica. When he was 6 his father died and he remained alone with his mother. After elementary school he attended the classical grammar school in Ljubljana. Throughout his grammar school years he distinguished himself primarily in science subjects with the exception of mathematics. He had poor results also in humanities and social sciences and in Slovene language. After grammar school he moved to Graz to the nearest university to study medicine. Despite his relatively average school results he became a brilliant student.

After graduating in medicine (1899) he completed his doctoral thesis entitled The Causes of high value of the coefficient in normal human urine. Although he was being offered several distinguished positions at different universities in Austria, he requested study leave for post doctoral education. He visited the most important laboratories in Europe. During that period he worked and studied with Wilhelm Ostwald and Emil Fischer. When he returned to Graz he was engaged at the Institute of Medicinal Biochemistry as chief forensic expert. After 1913 he became director and professor at the same institute.

Pregl and his colleagues succeeded in reducing the quantity of test substance and shortening the working time. At that time Pregl required approximately 10 mg of substance for analysis. Ten to a hundred times less than usual. For example, to study male sexual hormones in order to obtain 15 mg of pure hormones, had previously required no less than 15 000 litres of urine (Pregl, 2006).

The foundations of elementary organic analysis were laid by Liebig and Dumas. For determination of carbon and hydrogen, the substance was combusted and the escaped gases were
trapped in specific solutions. But due to the Pregl’s method, Liebig’s method was drastically reduced in size. The carbon dioxide as a product of carbon combustion was trapped in a small tube containing soda lime and water as hydrogen was trapped in a similar tube containing phosphorus pentoxide (Pregl, 1923).

New tendencies in learning and teaching

There has been a tendency over the last few years to modernise science teaching by moving from fact-based, ‘inert’ knowledge to meaningful, ‘contextualised’, knowledge. The specialists in science teaching with the help of researchers in a number of different fields, from developmental psychology to the history of science have addressed the key factors in the successful study and teaching of science. Teaching should be active, which means not only ‘hands-on’ but also ‘minds-on’; this dual context can be achieved with a problem-based approach that triggers reflection, motivating and directing our attention. Teaching should not strengthen or even trigger the creation of misconceptions and alternative concepts, which is why the naïve concepts or ‘pre-concepts’ that pupils already have need to be addressed. The connection between, and transition from, naïve concepts or even misconceptions to formal scientific concepts can be assisted with examples from the history of science: such examples (Wong et al., 2008) have a positive effect on the understanding of contents as well as on the understanding of scientific processes and the nature of science (process-based knowledge). Alongside this type of learning, pupils come to an understanding of their own thought processes (metacognitive knowledge). Pupils should be stimulated by those elements from science that relate to their everyday lives. According to the theories of some constructivist researchers emphasising the role of culture in learning science, meaningful knowledge should constitute a clear but diverse structure of knowledge (Driver et al., 1994). This firm structure can only be built through the process of connection and integration, which means the recognition of the same concepts and principles across different teaching subjects at least within school science, hence the diversity. All these requirements, recommendations and guidelines - which can also be found under the name of ‘inquiry-based learning (IBL)’ - are often very difficult for teachers to implement in practice; this paper presents one of the ways in which they might be implemented at least in part. Why study the role of Fritz Pregl in the history of science? Why is he something special? Can we understand his work? Is it possible to remake or to demonstrate the Liebig – Pregl experiment in quantitative determination of hydrogen and carbon in organic compounds?” Sometimes very trivial questions open more new questions and trigger more creative thinking than the typical examples which

Figure 1. outlines the relationship of these ‘trips’ to the central question and demonstrates that they are linked through posing sub-questions.
usually appear in textbooks. These kinds of questions are highly motivational because they create a sense of doubt or dissonance. Such an approach to studying history cases has been taken by a number of workers Andreoli et al. 2002; Bartholow, 2006; Hanson & Hoyt, 2002.

In the following teaching sequence, we have devised a number of ‘trips’ or routes one can take in order to find an adequate answer to the question: “How to remake the Liebig –Pregl experiment in quantitative determination of hydrogen and carbon in organic compounds?” (Figure 1).

This question can form the basis for a series of activities that link the different fields, contents and goals required by the science curriculum at the lower level of secondary school. This seemingly straightforward question opens up a series of secondary questions that are sufficiently motivational in nature but, at the same time, not so complex that pupils would be unable to find the answer on their own, in a group or with a little gentle prompting from the teacher.

A trip to the history of chemistry

Figure 2. Liebig’s condenser (cgi.ebay.com)

The art of analysis developed slowly through history. The noun “test” and verb “to test” came from early assayers, who used small cup-like pots named Cupule or Testus. In the 18th century, the awareness of purity was raised. The concept of purity was a sign for constant properties. At this time chemistry became the art of separation. Following Pregl’s work we detected Liebig. Because the method is still called the Pregl-Liebig method, the first spontaneous question was: who was Liebig? - and it wasn’t very difficult to discover. Every chemist knows at least one piece of the chemical equipment, which is called Liebig’s condenser (Figure 2).

But also Liebig was not the first inventor of the so called Pregel-Liebig analysis (Brock, 1992). In the year 1830, he had just optimised the apparatus already used by his precursors. He used the coal fire instead of dusty charcoal. Water was absorbed in a bulb with CaCl$_2$ which could be weighted directly. Carbon dioxide was similarly weighted directly by absorption in a solution of potassium hydroxide. Oxygen was determined by difference.

Liebig’s apparatus was cheap and could be operated by a single student (Figure 3).

Figure 3. Liebig’s apparatus (Liebiganal, 2010)

Going from Liebig back in history we discovered whose method and apparatus he had improved. This was William Prout’s apparatus. In the year 1827, he replaced the potassium perchlorate (KClO$_4$) as a source of oxygen with CuO and measured the differences in gas volume.
His apparatus was expensive and it was impossible to measure the amount of gasses as precisely as it could be measured by absorption and by weighting (Figure 4).

And Prout improved the apparatus of Gay Lussac. In 1815, he adopted combustion and used potassium perchlorate ($\text{KClO}_4$), a very dangerous and explosive reagent for oxidizing agent. Gay Lussac used the ideas of Berzelius but, instead of heating and burning substances with the lamp, Gay Lussac adopted combustion with an oxidizing agent. Berzelius transformed the cumbersome French apparatus (Figure 5) into a simpler horizontal arrangement. Carbon dioxide and water were trapped by absorption and condensation, and then weighted directly.
We found out that for over 150 years, from the time of Lavoisier until the second world war, combustion analysis was the primary tool. Much of our knowledge was developed using this tool. The principal improvements involved increasing convenience and reducing the sample size. Before the combustion technique organic substances were analysed by distillation. Products such as gas oil or phlegma and residue were weighted; this was rather proximate analysis.

Going from Liebig forward towards Pregl, the same apparatus was improved by Dumas and Hoffman. Hoffman (1860) replaced coal heating with the bunsen burner. If we connect all the chemists involved in development of this analytical method in a time line we get this figure (Grdenič, 2007).

Lavoisier → Berzelius → Guy Lussac → Prout → Liebig → Dumas → Hoffman → Pregl

A trip to the school laboratory

In order to rebuild something similar to Pregl’s apparatus we had to answer to the following questions.

- What kind of equipment do we have?
- What kind of reagents do we have?
- Which are the crucial parts of the apparatus?

In every school there is some unused equipment stored in a secret shelf covered by dust. Comparing our aim with the school reality, the nearest choice was Dumas’ equipment

Figure 6.

Figure 6. Dumas’ equipment

1. CuO and KClO₃
2. CuO
3. Sample mixed with CuO
4. CuO
5. CaCl₂ and H₂SO₄: These substances absorb H₂O
6. Liebig’s 5-bulb apparatus: the concentrated solution of caustic potash (KOH) absorbs CO₂
7. Potassium succinate and dry potash, K₂O: Traps H₂O and CO₂ that escape from 6.

The increase in weight of 5 measures the amount of H₂O formed in the combustion, and the increase in weight of 6+7 measures the amount of CO₂.

We used these ideas and simplified them as much as possible. The final result was this sketch Figure 7.
Figure 7. Design of simplified apparatus

8. Sample mixed with CuO.
9. CaCl$_2$ and H$_2$SO$_4$ absorb H$_2$O
10. The concentrated solution of caustic potash (KOH) absorbs CO$_2$

For this kind of apparatus we got also all the necessary chemicals and the balance within the precision of 0.1 g.

**A touch of theory**

The elements of carbon and hydrogen are estimated by their combustion in an atmosphere of pure oxygen to form carbon dioxide and water.

\[
\begin{align*}
C \text{ (sample)} + O_2(g) & \rightarrow CO_2(g) \\
4H \text{ (sample)} + O_2(g) & \rightarrow 2H_2O
\end{align*}
\]

Carbon dioxide is trapped in the solution of potassium hydroxide, the result is solid potassium carbonate.

\[
CO_2(g) + 2\text{KOH(aq)} \rightarrow K_2\text{CO}_3(s) + \text{H}_2\text{O(l)}
\]

Water is trapped in dry calcium chloride.

\[
2\text{H}_2\text{O(g)} + \text{CaCl}_2(s) \rightarrow \text{CaCl}_2\cdot2\text{H}_2\text{O}_8(s)
\]
Our hypothesis was: because of using the same basic chemical reactions, the result of analysis must be approximately the same. All the differences between the obtained results and theoretical results are due to simplification of the apparatus and to imprecise balance (Figure 8).

**A trip to chemical calculations**

If we take glucose as a sample then we have:

Sample: glucose – C$_6$H$_{12}$O$_6$

- mol weight of glucose: 180 g/mol
- carbon: 72 g/mol - 40.0%
- hydrogen: 12 g/mol - 6.7%

If the weight of the sample is 0.4 g then we have to recover 0.16 g C in the amount of 0.53 g CO$_2$, and 0.027 g H in the amount of 0.24 g of water.

**Experimental work**

Before conducting the experiment we had to draw the apparatus, learn how to prepare CaCl$_2$ sicum (which is the meaning of sicum), learn how to prepare the saturated solution of KOH, and prepare all these chemicals, taking into account also the safety measures.

**Figure 8. Our apparatus filled with chemicals before the procedure**
After the experiment was done, we measured the weight of the CaCl$_2$ and the weight of KOH solution and the results were: 0.2 g H$_2$O and 0.4 g CO$_2$. By comparing this with the theoretical results (0.24 g of water and 0.53 g CO$_2$) our method was not very promising. Therefore we had to make some changes and improve the method.

Because we detected too small amount of CO$_2$, we concluded that the combustion of the sample was not complete. Therefore we improved the apparatus by sucking the air through it. But in this way there is a of detecting also the carbon dioxide from the air, therefore we also put a trap for carbon dioxide before the combustion zone.

The idea of the new apparatus is on Figure 9.

The final version was slightly different Figure 10.
With this apparatus we got the results of 0.3 g of water and 0.4 g of CO₂. We were close to theoretical value with water (between 0.3 and 0.2 g) but results for carbon dioxide were again too low. How to continue, how to improve our method to get better value also for carbon dioxide?

Conclusion

We therefore discovered that our hypothesis has held. We can return to our research side-trip and emphasise that research itself often leads us into unknown and unexpected territory and that we find out things that we did not actually expect. Here is also the time to reflect on whether our experiments were adequate. What we have learned from this trip to Fritz Pregl’s method is that it is not only great ideas and new theories that lead towards scientific discoveries, but that equipment and techniques are important too. In this way our research may continue by adding piece to pieces of equipment to reach the final form of Pregl’s apparatus (Figure 11). But also this is not a guarantee to obtain the same results as Pregl did. A lot of hidden skills and experience are needed, and these could not be learned in a limited time. More important than the answer to our research question is the knowledge acquired in this way. This knowledge is more stable, more durable and could be transferred to others fields of knowledge or to school subjects.

References


