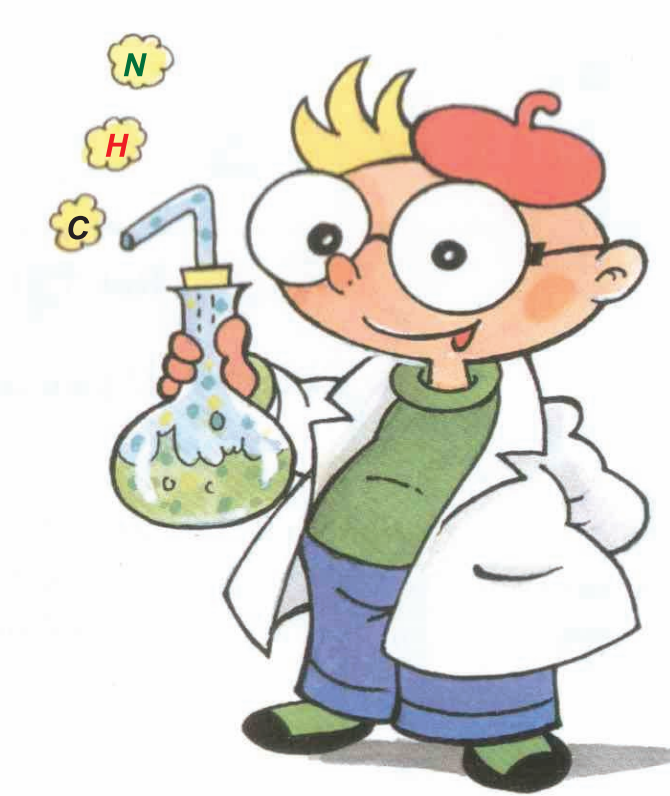
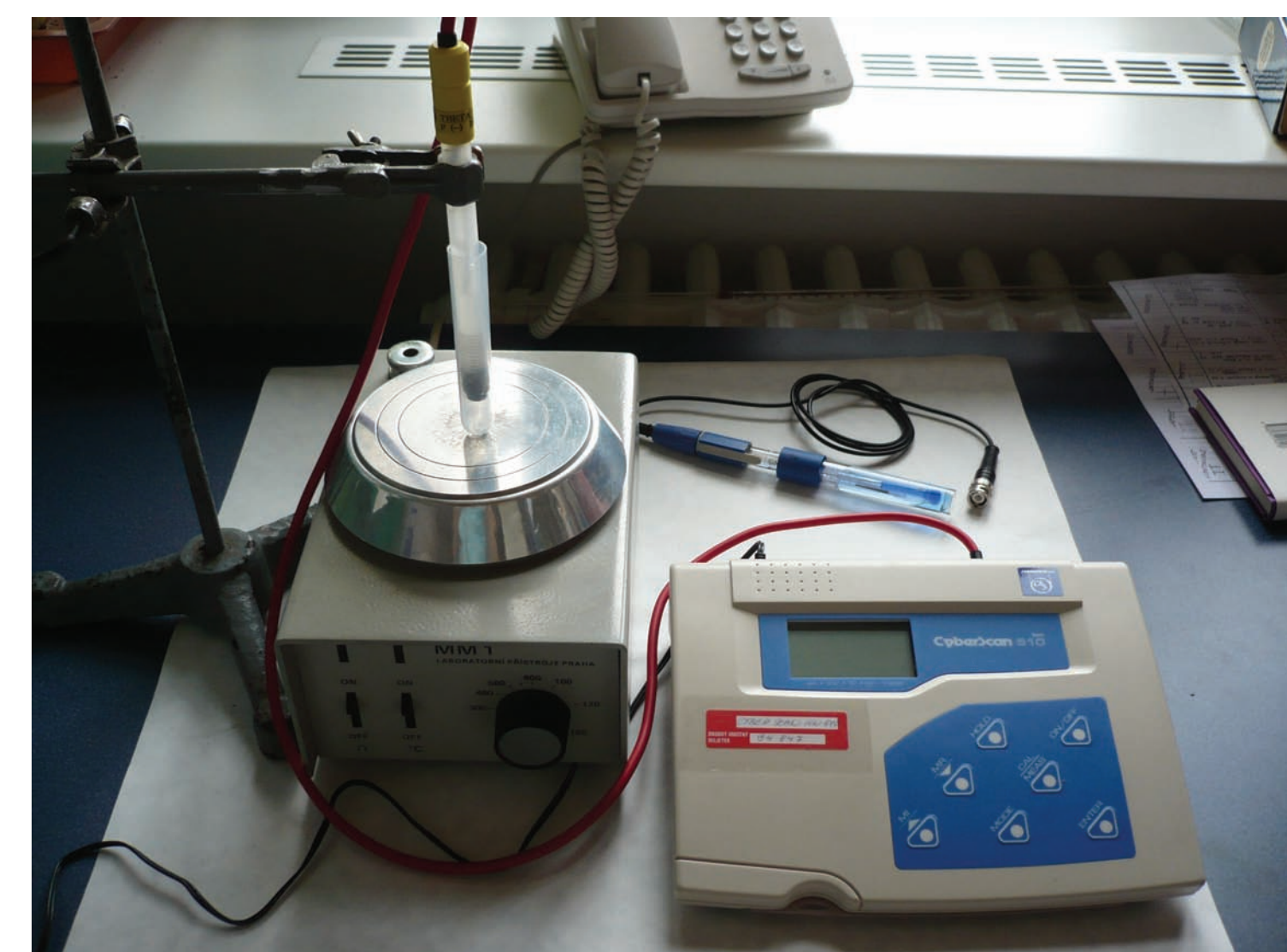


# Analytical Laboratory - A Brief History, Present Services Provided, Presumed Developments

Stanislava Matějková, Lucie Holasová, Štefan Štanga and Magdalena Hošková

Room No. 181  
Phone: 220 183 118  
e-mail: stanislava.matejkova@centrum.cz



## History of Organic Elemental Analysis in IOCB

The Analytical Laboratory, formerly named Central Analytical Laboratory, is a part of the IOCB from its foundation in early fifties of the 20-th century. At the beginning the laboratory was a key source of information about either newly synthesized compounds or the isolated ones from natural materials.

The laboratory performed many types of classical chemical analyses including elemental analysis (C, H, N, S, P and halogens), determination of  $^{14}\text{C}$  and  $^2\text{H}$ , volumetric determination of double and triple bonds, chemical determination of some functional groups, iodine number and saponification number.

The laboratory was superintended by Jiří Horáček, later by Václav Pechanec.

The first automatic analyzer Perkin Elmer 240 A was purchased in 1969, a new model 2450 C in 1983 and the current PE instrument in 1999.

An instrument for optical rotation measurement was purchased in 2001.

A CyberScan Ion 510 Meter with fluoride ion-selective was purchased electrode was in 2006.

## Key Current Services - Elemental Analysis & Optical Rotation

The standard analytical services provided to the scientific staff of the IOCB include elemental analysis and optical rotation measurement of organic compounds and some other analytical determinations using volumetric analysis or ion selective electrode.

**Elemental analysis of organic compounds (EA)** - The laboratory provides analytical capabilities for measuring content of hydrogen, carbon, nitrogen, fluorine, chlorine, bromine, iodine, phosphorus and sulphur in organic compounds. An automated CHN analyzer (PE 2400 Series II CHNS/O Analyzer) is used in C, H and N mode.

The determination of other mentioned elements is based on volumetric methods, fluorine is determined by use of ion selective electrode.

**Measurement of optical rotation / specific rotation (OR)** - The ordinary optical rotation of plane polarized light can be measured in the UV/Vis range at six different wavelengths (365 nm, 405 nm, 436 nm, 546 nm, 589 nm and 633 nm) using the polarimeter Autopol IV. The sample cells for 0.5, 1.5 and 2.8 mL are available.



The PE 2400 Series II CHNS/O Analyzer (Perkin Elmer, USA) serves for simultaneous determination of C, H, and N in organic compounds. In the CHN operating mode the instrument employs a classical combustion principle to convert the sample elements to simple gases ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{N}_2$ ). The PE 2400 analyzer performs automatically combustion and reduction, homogenization of product gases, separation and detection.

A microbalance MX5 (Mettler Toledo) is used for precise weighing of samples.

The accuracy of CHN determination is better than  $\pm 0.30\%$  abs.

The instrument was installed in 1999.

The AUTOPOL IV (Rudolph Research Analytical, USA) is a microprocessor based automatic polarimeter for measurement of optical rotation ( $\pm 89^\circ$  Arc), specific rotation ( $\pm 999,99^\circ$  Arc) and concentration (0 – 99,9 %). The Autopol IV comprises Glan Thomson calcite quartz prism polarizer. The highest resolution is  $0.001^\circ$  Arc for optical rotation,  $0.001^\circ$  below  $90^\circ$  Arc and  $0.01^\circ$  between 100 to  $999.99^\circ$  Arc for specific rotation and 0.001 % for concentration. However, usually the resulting values of specific rotation are given with one decimal place. The polarimeter accepts sample cells up to 200 mm.

The instrument was installed in 2001.

## Perspectives & Developments

The aim of the further development of the analytical laboratory is to decrease demands on required amounts of samples for analyses and to increase both the precision and accuracy of analytical results using more reliable and robust instrumental methods. To fulfill the aim we would like to upgrade laboratory and instrumental equipment of the analytical laboratory.

Firstly, we plan to buy an X-ray fluorescence spectrometer primary dedicated for determination of "light" elements (from sodium). The instrument allows simultaneous identification and quantification of a lot of elements. X-ray fluorescence is an accepted technique for analyzing the elemental composition of samples in the concentration range between  $10^{-4}\%$ ...100%. The calculation of the sample composition is based on the intensity of the main elemental lines. The tested SPECTRO iQ spectrometer is equipped with an air cooled 50 W end window X-ray tube. The primary tube spectrum is monochromatized and polarized by a doubly bent HOPG crystal. Solids, pressed pellets, liquids or loose powder can be used in different methods. The excellent analytical performance of the SPECTRO iQ was demonstrated in various application reports.

The energy-dispersive X-ray fluorescence spectrometer could replace the classical titrimetric determinations of S, P, Cl, Br and I, which require quite high amounts of samples (8 – 15 mg per one determination of a single element). Furthermore, we expect that various elements (e.g. metals in organic samples - not determined yet) can be determined in future. The method is sufficiently sensitive and non-destructive. We suppose, that the required amount of a sample for determination of a set of elements decrease below 5 mg. Considering the minimal requirements on sample preparation for X-ray fluorescence analysis and the non-destructivity of the technique, the major part of the sample will be given back to the client.

Various sets of samples prepared in our laboratory were tested preliminary in collaboration with Ing. Kolečkář (Spectro CS) on X-ray fluorescence spectrometers in Germany and in glassworks Kavalier in Sázava. Both the sample preparation procedure and sample storage conditions have been developed. Satisfactory results have been obtained even at low concentration range. Hence, a successful implementation of the X-ray fluorescence spectrometry is expected for simultaneous determination of a set of elements in organic samples.

## Sample Requirements for Elemental Analysis

A sample should be submitted as the **dry (homogeneous) solid** or the **neat (non-volatile) liquid**. The minimum sample amount for elemental analysis depends on which elements are to be analyzed (1 - 15 mg). Please, use labelled glass vials for the samples; preferred are labels containing only capital letters and numbers, which are the only characters accepted by the instruments. The expected elemental composition (molecular formula) should be filled in the submission form.

In case the expected elemental composition differs more than 0.3% from results obtained (CHN automatic analysis), the measurement is repeated.

## Sample requirements for Optical Rotation

A sample should be submitted as the **dry solid** or the **neat liquid**. The minimum sample amount is 2 mg; the more sample you submit the higher accuracy of the measurement is obtained. On the other hand, compounds with high optical rotation can be analysed at amounts of ca. 0.5 mg. In this case please indicate precisely weight of the sample or do not hesitate to contact the laboratory staff.

The sample will be dissolved in the solvent specified in the submission form. Please, pay attention to the solvent selection as only well dissolved samples give accurate results and eventual crystallization can damage rather expensive sample cell. If you want to get back your dissolved sample please provide as with an empty labelled bottle of appropriate size and indicate this fact in the submission form. Furthermore, you should specify the **type of cell A (1.5 ml), B (0.5 ml) and C (2.8 ml)**.

The cell A is ordinarily used.

The required wavelengths values can be indicated in the submission form, the usual value is 589 nm.

## Other Services

A microbalance MX5 (Mettler Toledo) are available to weigh precisely very small amounts of samples (from 0.1 mg with precision of micrograms). Some additional chemical analyses are available upon request.

## The Elemental Analysis in Brief

The determination of C, H and N in solid/liquid samples is performed using an automatic PE 2400 Series II CHNS/O Analyzer. The sample weighed in a tin capsule is loaded in the instruments. When the tin is dropped into the high-heat oxygen environment of the combustion tube (heated at  $925^\circ\text{C}$ ), it creates a vigorous exothermic reaction. The sample temperature can reach  $1700^\circ\text{C}$ , which aids in the combustion process. The sample is first oxidized in a pure oxygen environment. Final products produced in the combustion zone include  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{N}_2$ . Elements, such as halogens and sulphur, are removed by scrubbing reagents in the combustion zone. The whole procedure excludes determination of ash. The resulting gases are homogenized and controlled to exact conditions of pressure, temperature and volume.  $\text{N}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are moved by helium into the column, separated by a frontal chromatography and detected by thermal conductivity detector. The whole procedure is controlled by a microprocessor taking into account data from analysis of blanks, internal and external standards. The analysis is finished in approx. 6 min.

**Determination of P** is performed after Kjeldahl digestion of the samples with a mixture  $\text{HClO}_4 + \text{HNO}_3$ . After necessary adjustments of the sample,  $\text{PO}_4^{3-}$  is titrated using a standard solution of  $\text{La}(\text{NO}_3)_3$ ; the indicator is eriochromblack T.

**For analysis of F** the sample is combusted by Schöniger method (i.e. in Erlenmeyer flask in oxygen atmosphere). Formed  $\text{F}^-$  is determined using ion selective electrode.

**For analysis of Cl or Br** the sample is combusted by Schöniger method. Formed  $\text{Cl}^-$  or  $\text{Br}^-$  are titrated by a solution of  $\text{Hg}(\text{NO}_3)_2$  for sodium nitroprusside as an indicator. It is impossible to determine Cl and Br, when they are both present in the sample.

**For analysis of I** the sample is combusted by Schöniger method. Iodine is determined by Leipter method described by following steps: (1) absorption of iodine in NaOH solution, (2) oxidation of various iodine forms to iodate by bromine, (3) reduction of the excessive bromine by formic acid, (4) reduction of iodate by iodide forming elemental iodine, (5) titration of iodine by a standard solution of thiosulphate.

**For analysis of S** the compound is combusted by Schöniger method and formed  $\text{SO}_4^{2-}$  ions are titrated in the presence of 2-propanol by a standard solution of  $\text{Ba}(\text{ClO}_4)_2$  with thoin as an indicator.

