



ED-XRF: a powerful tool for determination of elemental composition of organic compounds

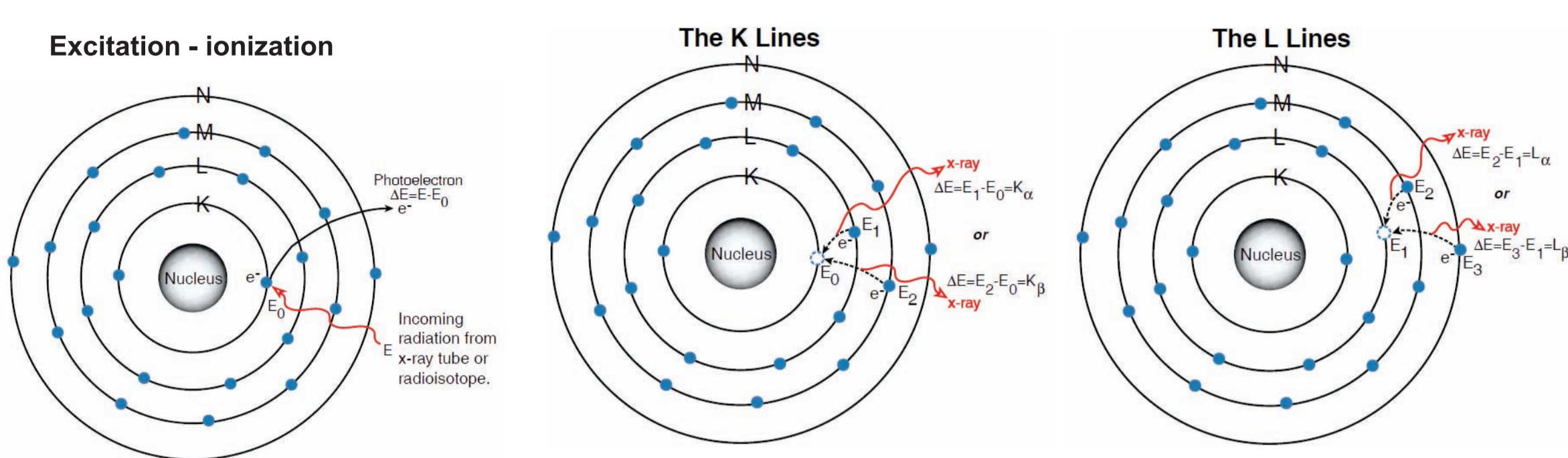
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Introduction: In the year 2008, a simultaneous ED-XRF spectrometer was purchased to the Institute of Organic Chemistry and Biochemistry with the aim to replace classical chemical procedures of P, S, Cl, Br and I determination in synthesized organic compounds and to extend the range of determined elements. The disadvantages of classical methods (based on mineralization and subsequent titrimetric determination) are elaborateness, time consumption and relatively big amounts of substances required for determination of any individual element (6 - 15 mg). Furthermore, the classical chemical methods do not allow determination of several elements in the presence of other interfering elements and to detect (and to determine) additional elements, which were not expected to be present in a sample.

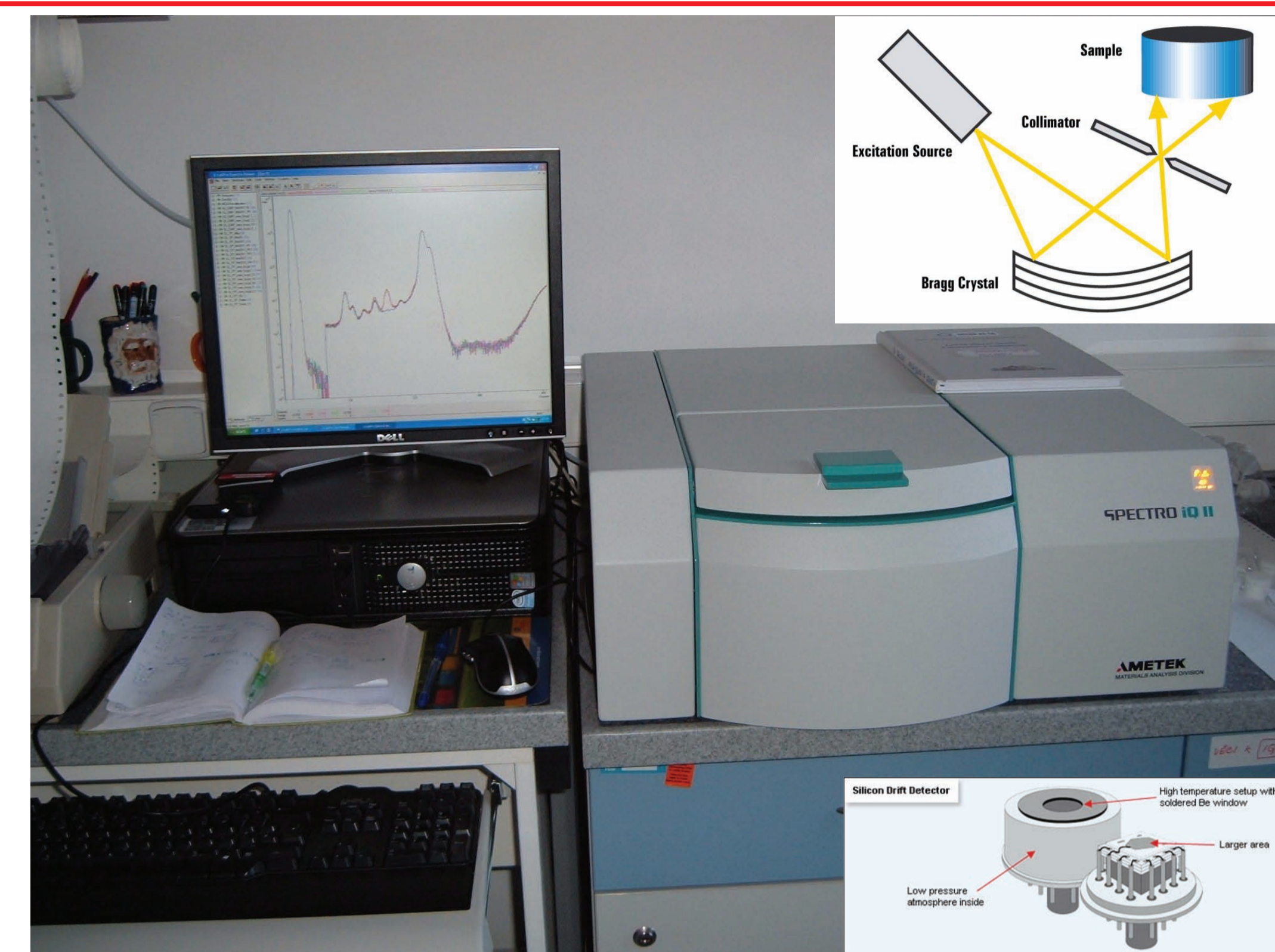
Principle of the method:



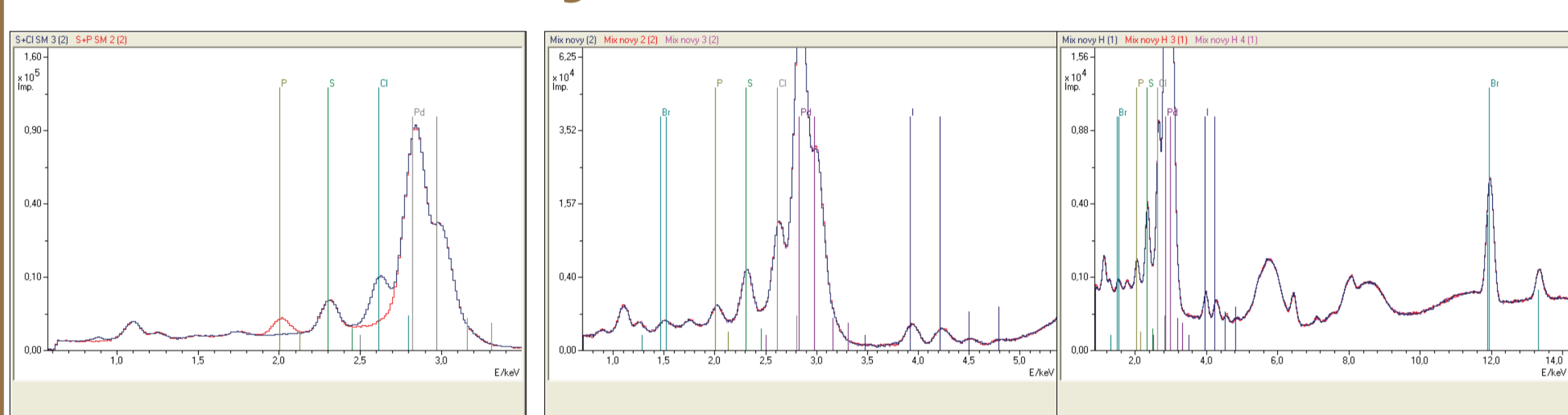
A liquid, solid or powder sample is excited in a sample compartment of the analyzer with X-rays emitted from an X-ray tube. The innermost electrons of various atoms are ejected from the inner shells creating vacancies in the process called the photoelectric effect. The vacancies present an instable condition for the atomic system. Electrons from outer shells occupy the vacancies; the corresponding energy differences cause an emission of characteristic secondary (fluorescence) X-rays. The frequencies of emitted radiation are characteristic for individual elements. The intensity of a particular line corresponds to the content of an element in the sample. All element specific X-ray fluorescence signals are detected simultaneously in a fixed mounted semiconductor detector and evaluated. Hence, an X-ray fluorescence spectrum is obtained, which characterizes the elemental composition of the sample.

Instrumentation:

The SPECTRO iQ II (SPECTRO Analytical Instruments, Germany) spectrometer was developed specifically for demanding process control applications. It is intended for providing multi-elemental analyses of liquid, solid and powder samples primarily for process control, where rapid analysis and reliable analytical results are especially important. The SPECTRO iQ II instrument uses a polarized primary radiation for increased sensitivity and a significant noise reduction (that is especially important for determination of the light elements). The samples are excited by a forced air cooled low power Pd end window X-ray tube combined with a doubly curved HOPG crystal for monochromatization and polarisation of the primary tube spectrum. A VITUS-Silicon Drift Detector (SDD) with Peltier cooling is used to collect the fluorescence radiation from the sample. The resolution of the SDD is better than 160 eV for Mn K α . All radiation paths are flushed with helium. All measurement parameters are controlled by the system PC. The analysis is non-destructive, thus the sample after analysis (eventually after a solvent evaporation) can be used further. One position sample chamber and appropriate sample cups allow very precise sample positioning which increases the stability and reproducibility of the measurements.



Qualitative analysis:

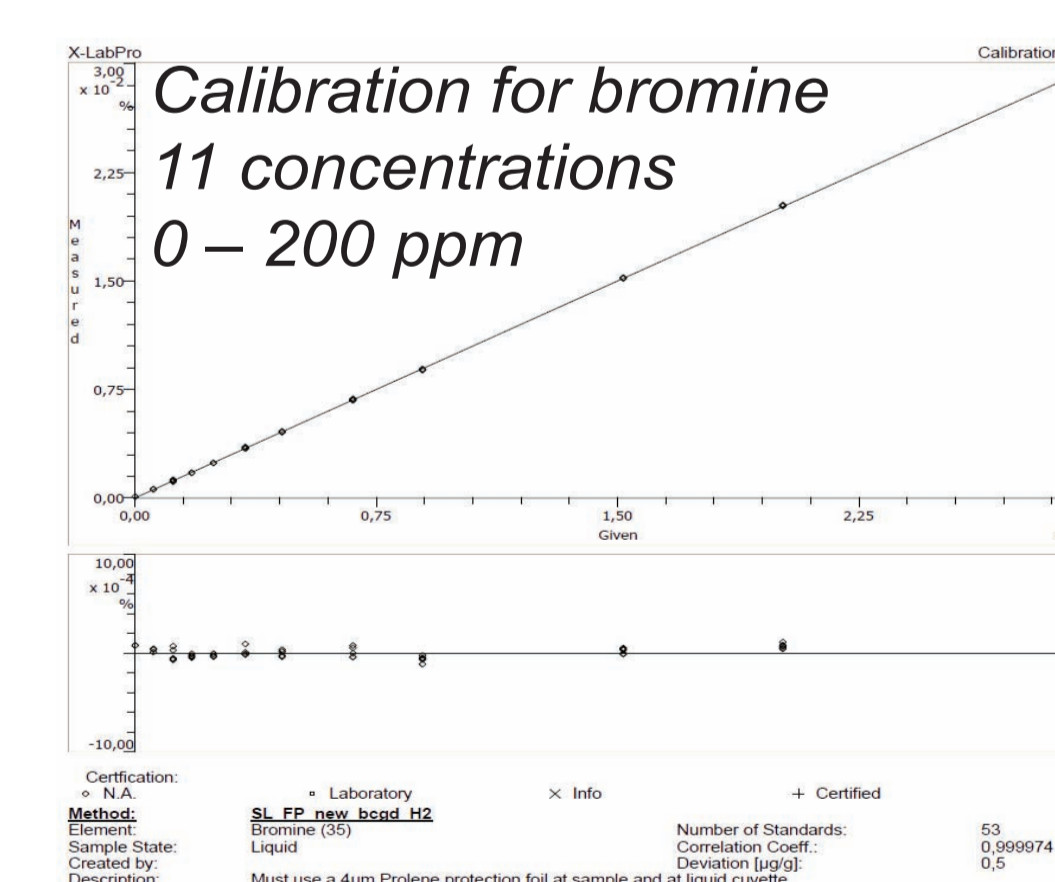
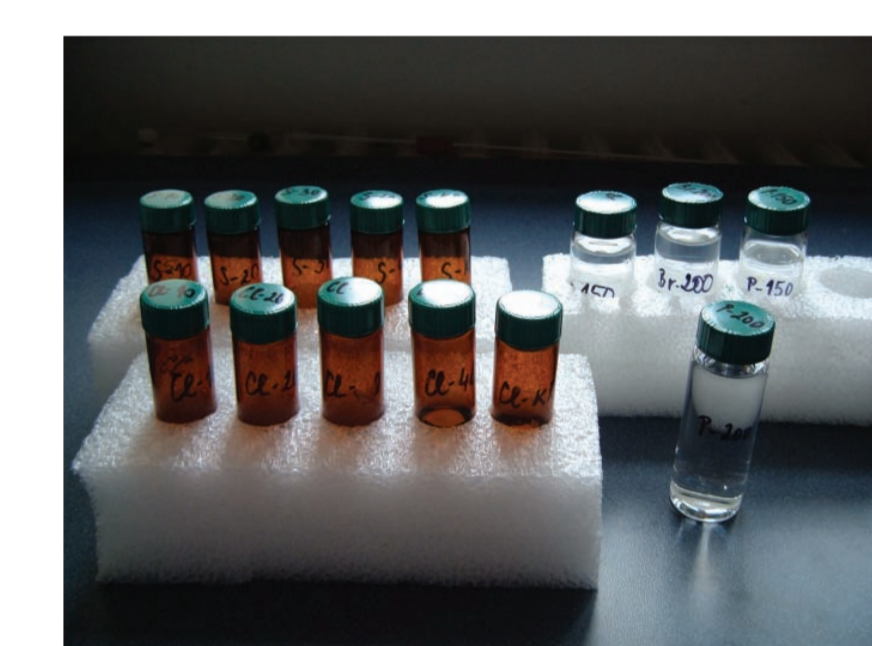
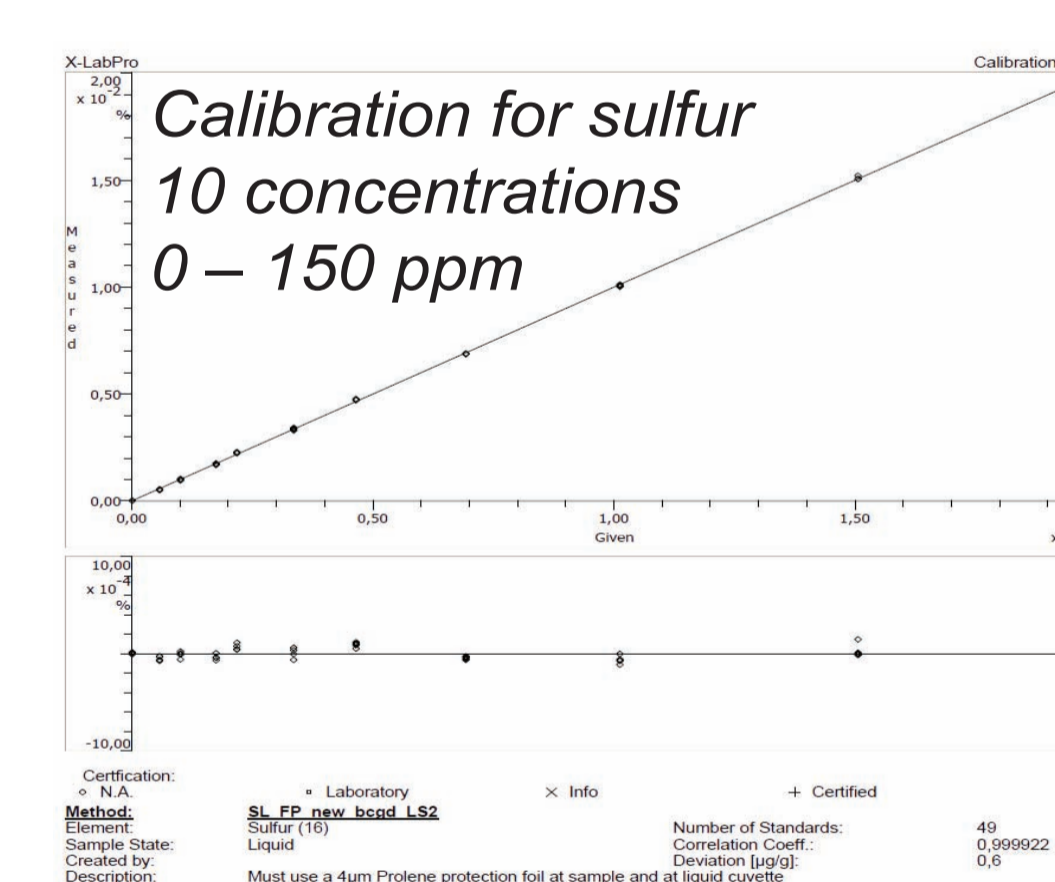


The SPECTRO iQ II spectrometer allows a qualitative detection of elements from Na to U (except Pd) in different types of sample forms (e.g. liquids, solutions, massive solid or powder samples (except gases)). We have got the cups for analyses of liquid samples (solutions, emulsions and suspensions) and furthermore for powder samples and pressed tablets. The limits of detection are different depending on individual elements; commonly they are in range from one to tens ppm. Actually, in the cases of non-soluble samples the XRF technique enables to perform fast qualitative elemental analysis of suspensions or powders for decision about the subsequent analytical procedure.

Quantitative analysis:

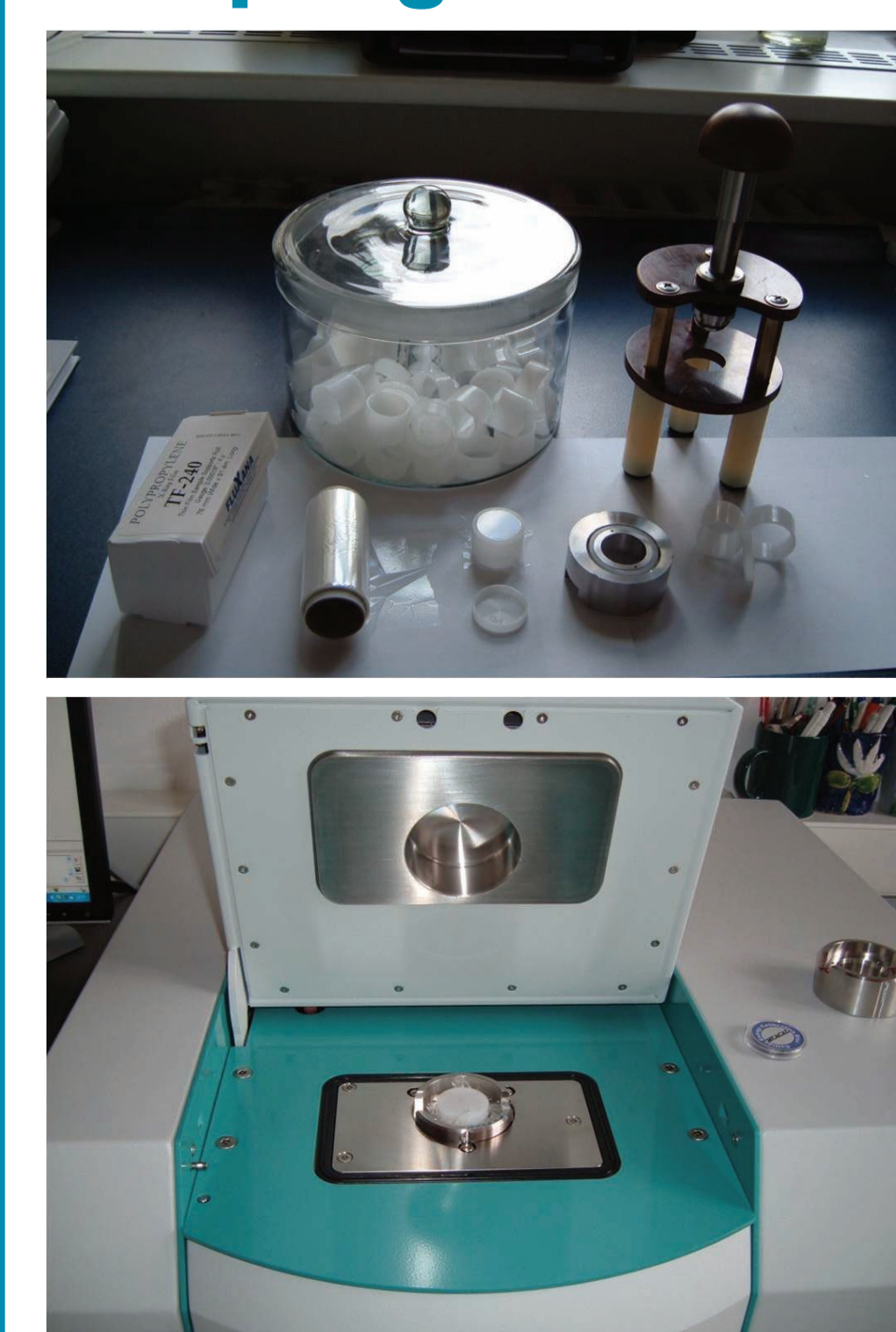
Currently, we can perform quantitative analyses of the elements, which we have been doing with titration methods, i.e. P, S, Cl, Br and I. New methods for the determination of Al, Si, K, Cr, Co, Ni, Cu, Zn, Ag, Cd, Pt, Au, Pb and Hg are established (in methanol as solvent, Al in toluen/oil matrix and Pt, Ni, Cd and Au also in water). Nowadays the quantitative analyses are limited to sample solutions in methanol (water), because the calibration models for methanolic solutions are developed. The „light“ solvent as a homogenous, isotropic matrix ensure the reliability of quantitative data. Thus at least a minimal solubility of analyzed sample in methanol (water) is required to prepare a defined sample solution. For simultaneous analyses of the all elements required we need 1 - 5 mg of a sample. Of course, this value depends on the content of determined elements in a particular sample. The sample preparation procedures developed allow to analyse without significant problems even very volatile substances, hygroscopic samples and/or viscous liquids. Considering the results of many performed tests, both precision and accuracy of results obtained via X-ray fluorescence method is comparable to the current methods' performance characteristics. The calibration range is usually 0 – 200 ppm. The estimated accuracy of determination of any individual element is ca ± 0.3 %.

Furthermore, elemental composition of various complex samples is examined either in liquid or solid phase, e.g. for the waste management of the Institute, for monitoring of reaction kinetics, complexation of heavy metals or exchange of functional groups in ion-exchange chromatography. In fact, we can develop methods for determination of any element (from Na to U except Pd) but we need an appropriate standard (or standards) with a known (certified) content of the element to be determined. In future, it is possible to develop various quantitative methods in several other non-volatile solvents with proper elemental compositions (water, ethanol...) with respect to your requirements.



Sampled element	Averaged concentration measured, ppm	Calculated content of the element in the substance %	True content of the element in the substance %	Difference of calculated value and true one
P	65,56	12,07	11,81	+0,26
S	106,78	17,51	17,51	0,00
Cl	143,54	22,56	22,85	-0,09
Br	170,73	37,30	37,33	-0,03
I	254,88	51,34	51,17	+0,17

Sampling:



For a sample preparation 1 – 5 mg of solid substance is weighed using of a disposable weighing boat and transferred to a glass vial; ca. 5 ml of MeOH is added (precisely weighed). In the cases of liquid, viscous or volatile materials, the sample is weighed in a small glass crucible. Afterwards the crucible with the sample is placed into the glass vial containing a pre-weighed amount of MeOH (ca. 3.9 g). After dissolution 3 g of the prepared solution is weighed in the measuring cell with 4- μ m polypropylene supporting foil. Thereafter the cell is placed in the holder fitted with the second 4- μ m polypropylene foil as a safety window to protect the inner space of the instrument against leakage of the cell or its rupture.

Two types of measurement conditions are used: (i) a method for „light“ elements (Na - Ti) - tube settings: voltage 25 kV, current 1 mA; (ii) a method for „heavy“ elements - tube settings: 48 kV, 0.52 mA. The measuring time for a single spectrum is 180 s (under He flush 80 l/h) in both cases. Five consecutive spectra are recorded usually, each of the spectra is evaluated quantitatively using a corresponding calibration method and then the results are averaged.

To confirm the accuracy of analyses the set of standards is analysed periodically.

