

## 5. Detection Methods

### 5.3 Elemental analysers

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Abstracted from Wikipedia "Elementaranalysatoren", last access 15.05.2018

**Elemental analysers** are instruments which can determine elements, mostly in solid samples, without further digestion. For the elements carbon (C), hydrogen (H), nitrogen (N), oxygen (O) and sulfur (S) this is mostly realised by combustion analysis. For such a C, H, N and S analysis, fine milled or mortared samples (maximum 10 mg) are placed in Sn-foil-capsules (or Ag-foil-capsules) in the analyser. The samples are burnt in pure oxygen at 1800 °C. The combustion gases are transported with a carrier gas (mostly helium) over 600 to 900 °C hot copper or tungsten contacts. The nitrogen oxides (NO<sub>x</sub>) are reduced to molecular nitrogen (N<sub>2</sub>). Subsequently, the combustion gases (CO<sub>2</sub>, H<sub>2</sub>O, SO<sub>2</sub>, N<sub>2</sub>) are separated in specific separation columns (adsorption and desorption columns) or gas chromatographically and one after the other transferred to a thermal conductivity detector (TCD) and quantified. Because tungsten can interfere with sulfur, it is only used as reducing agent for CHN-analytcs. If S has to be analysed as well, Cu is used.

In this method, the order of the elements is technically fixed exactly (detected as so-called peaks); so the elements can be unambiguously identified (qualitative analysis) and the quantitative analysis is realised by the peak areas (integral over time) for the elements C, H, N and S. With the known weigh-in, the mass-percentage (in % or ppm) is calculated for each element automatically by the instrument. Another detection method works with gas-specific detectors (mostly IR detectors) for CO<sub>2</sub>, H<sub>2</sub>O and SO<sub>2</sub>, instead of complete gas separation. Nitrogen (N<sub>2</sub>) is here detected by a TCD as well.

In contrast to the CHNS-determination, for detection of oxygen CO is formed quantitatively from oxygen under inert or reductive conditions (only pure helium or forming gas as carrier gas) at high degrees of 1200 to 1400 °C at a fine distributed carbon contact. This CO is subsequently separated from formed nitrogen (N<sub>2</sub>) by a specific separation column or GC-column and measured by a TCD. Alternatively, CO detection is possible by a CO-specific IR detector.

In the laboratories of the working group Soil Science (AUF, University of Rostock) the elemental analyser vario EL cube of the firm Elementar is available for the analysis of C, N and S in solid samples such as soil, plants, chars and similar environmental samples. The limit of detection for these elements is < 40 ppm. The combustion is realised at 1200 °C, but for special requirements 1400 °C are possible. Samples are milled and mortared and weighed in in Sn-foil-capsules: soil 25-30 mg, plants 8-12 mg, bone char and suchlike < 10 mg. An auto sampler (80 places) processed the placed samples to the combustion and subsequent analysis. Theoretically, analysis of liquid samples is possible. However, a special equipment is necessary for it.

CNS-Analysers such as the vario El cube (<https://www.elementar.de/de/inhalte-produktseiten/vario-el-cube.html>) or the UNICUBE of the firm Elementar can be upgraded for the analysis of O und chlorine (Cl) (<https://www.elementar.de/de/produkte/organische-elementaranalyse/unicube.html>). Oxygen is reacted at 1150 °C and could be detected by a TCD or IR-detector For Cl determination the sample is burnt as well and the formed Cl is detected in an electro-chemical measuring cell. Phosphorus cannot be detected by this instrument. For specific low S determination an IR detector is additionally available, whose detection limit is < 2 ppm.

For the **detection of P** different analysers are available. Detection of P is possible by a **wavelength dispersive X-Ray fluorescence** detector (WDXRF).

For example the firm Rigaku has the analyser Primini Biofuel (<http://www.directindustry.de/prod/rigaku/product-31512-886449.html>), which can detect P, Cl and S in biodiesel and suchlike.

Abstracted from Wikipedia "Röntgenfluoreszenzanalyse" (X-Ray fluorescence analysis), last access 15.05.2018

In this method the sample is excited by X-ray and the formed fluorescence is measured. Generally, it can be differentiated between energy dispersive X-Ray fluorescence detection (EDXRF) and wavelength dispersive X-Ray fluorescence detection (WDXRF). An EDXRF detector is measuring the energy of the emitted fluorescence quants. For WDXRF detection, the emitted fluorescence is aligned parallelly by a collimator, deflected by an analyser crystal and detected by a detector. The crystal splits up the polychromatic secondary radiation by deflection to the different wave lengths. Qualitative determination of element is done by diffraction angle of X-ray and quantitative determination by measurement of intensity of the

X-ray. The different detectors affect resolution, measurement time, necessary power of X-ray source, necessary costs and the error rate of the system.

The resolution of the WDXRF systems depend on the crystal and the design of the optics. Resolutions of 20 eV to 5 eV are possible. The EDXRF systems have resolutions of 600 eV to 120 eV. Therefore, the WDXRF system is much more precise and very close peaks can be separated. However, the high-precision crystals and optics are expensive and error-prone and the WDXRF systems have a longer measurement time than the EDXRF systems. Additionally, the WDXRF system is less energy efficient than the EDXRF system, because the direct excitation in the EDXRF system causes only few energy loss whereas in the WDXRF system a 100 times higher power is necessary to produce the same yield of X-ray quants. Therefore, the EDXRF systems is much more cost-effective than the WDXRF system but has a much lower resolution. That means that the decision for the one or the other system depends on the planned application and scientific question.

X-Ray fluorescence analysis cannot be used for elements lighter than boron. Usable analysis values are possible from the element fluorine and good values from sodium, because X-ray of lighter elements is easily absorbed without entering the detector. The quantitative upper limit depends on the reference sample. As far as we know, such instruments are currently not available at the University of Rostock or the Leibniz Institutes.

**For citation:** Zimmer D, Baumann K, Berthold M, Schumann R (*insert year of download*): Handbook on the Selection of Methods for Digestion and Determination of Total Phosphorus in Environmental Samples. Version 1.0. DOI: 10.12754/misc-2020-0001

*Handbook on the selection of methods for digestion and determination of total P in environmental samples*