Chemical Environmental Analysis

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  - Sampling
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Functions and tasks of an Environmental Laboratory

Environmental Analysis can be carried out

+ as mobile on-site analysis:	rapid tests with mobile analytical equipment

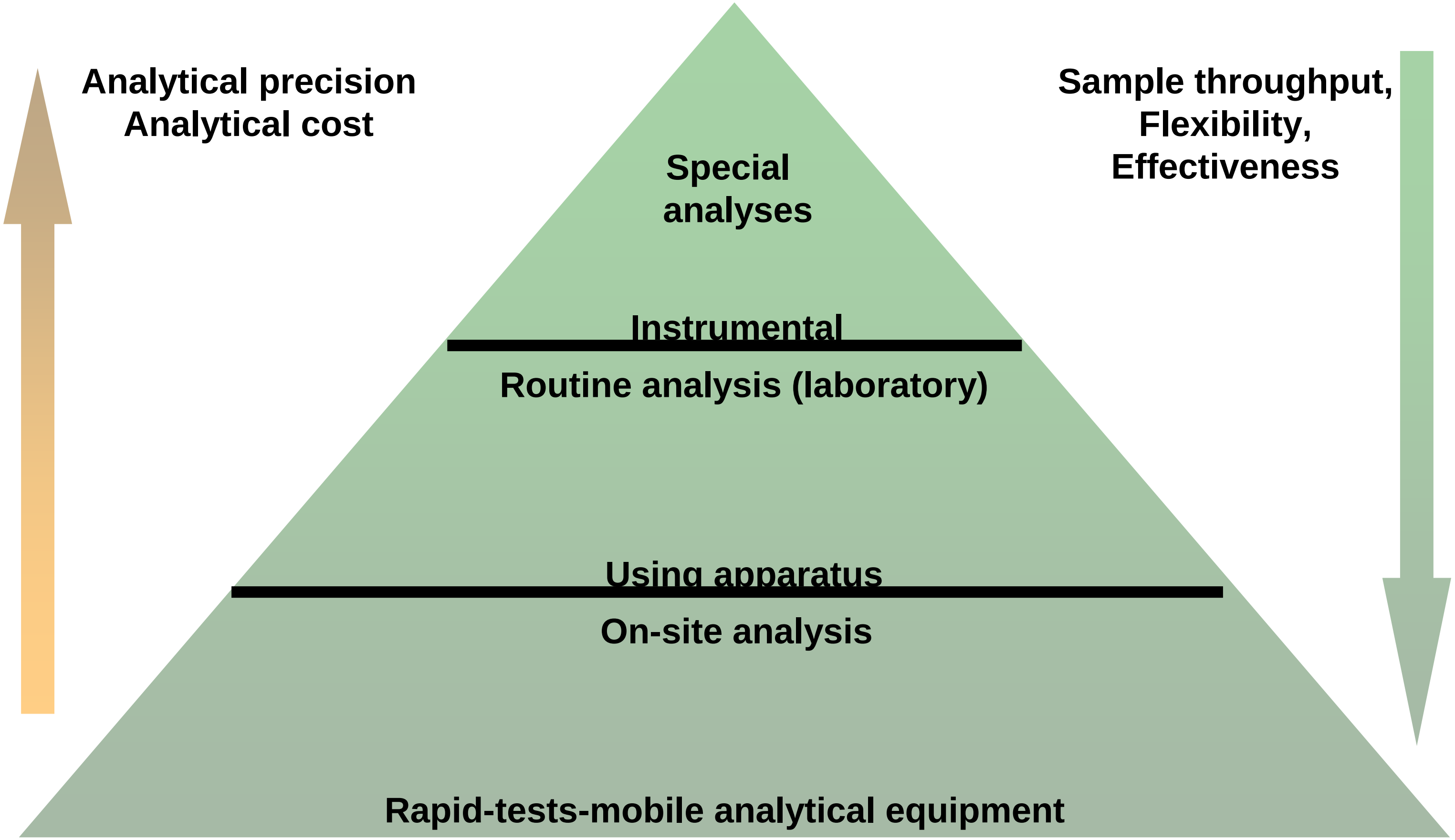
The utilization of tests which are quick and simple to perform, and measurements at the sampling site make it possible to make immediate decisions about protective actions which must be taken.

The preliminary investigation of environmental samples which are strategically taken leads to a reduction of number of samples that must be examined with expensive and laborious analytical procedures in an analytical laboratory (*G. Schwedt*, 1996).

+ in an environmental laboratory:	from routine analysis to special instrumental analyses based on ISO, DIN, EN, VDI and other standards.

Functions and tasks of an Environmental Laboratory

Environmental Analysis can be carried out as mobile on-site analysis and in an environmental laboratory.



Analytical precision
Analytical cost

Sample throughput,
Flexibility,
Effectiveness

Special analyses

Instrumental

Routine analysis (laboratory)

Using apparatus

On-site analysis

Rapid-tests-mobile analytical equipment

Functions and tasks of an Environmental Laboratory - Examinations

The overall task of an Environmental Laboratory is the examination of

+ gases: e.g. gases from combustion or fermentation processes, gaseous fuels, air analysis

+ liquids: e.g. water samples such as ground water, potable (drinking) water, sewage water, landfill leachate, extracts and eluates, liquid fuels

+ solids: e.g. soil, sediments, sludge, biomass, solid fuels, ashes, filter residues

Functions and tasks of an Environmental Laboratory - Objectives

Goals of Chemical Analysis

„Chemical Analysis is the science of the extraction and use-oriented interpretation of information about material systems with the help of scientific methods“

> Definition from the Analytical Chemistry Section of the Society of German Chemists, GDCh.

Today, analytical chemistry provides a service function which extends far beyond chemistry itself to almost all areas of the sciences, of medicine and of technology.

Results of chemical analyses lead to technological, medical and legal decisions – which also demonstrates the great responsibility placed on the analyst.

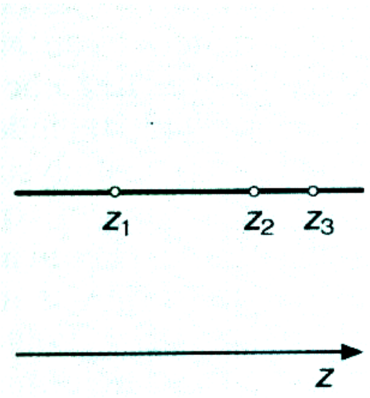
Functions and tasks of an Environmental Laboratory - Objectives

Goals of Chemical Analysis

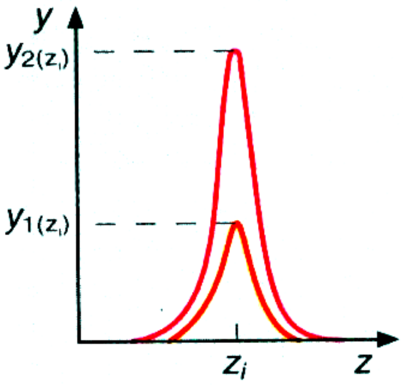
For chemical environmental analysis the most important analytical aspect is the content analysis of environmental chemicals:

- qualitative analysis determines the kind of material (e.g. a chemical element) along with information about the smallest detectable concentration.

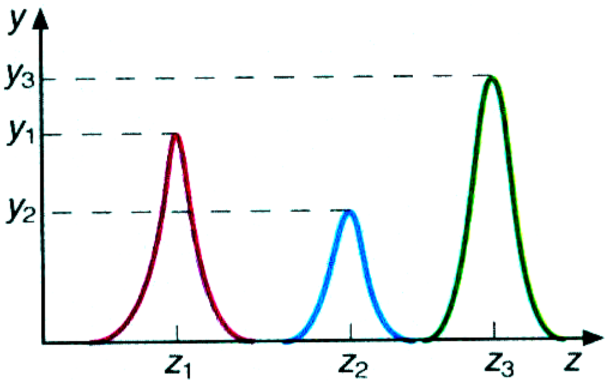
- quantitative analysis determines the concentration (or amount) in a material system (the matrix).



1. Qualitative



2. Quantitative

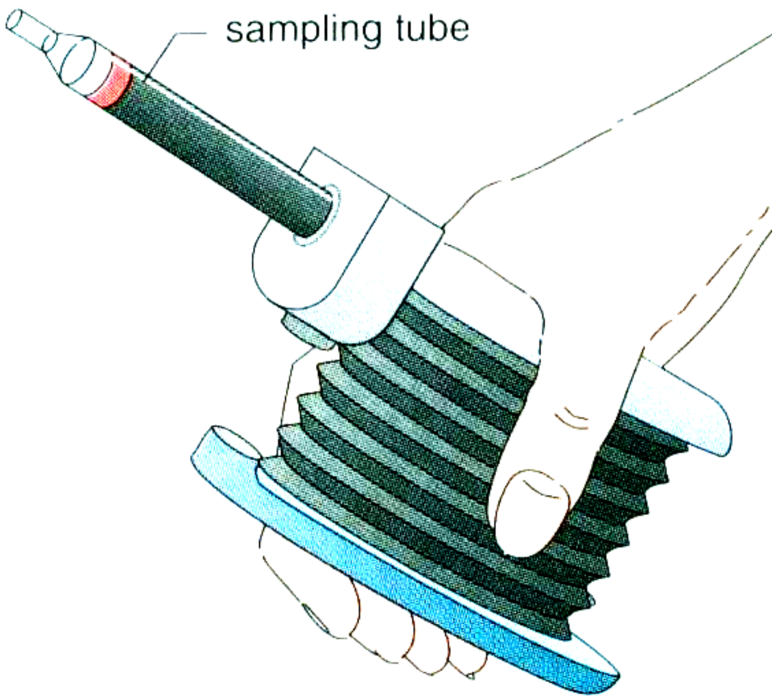


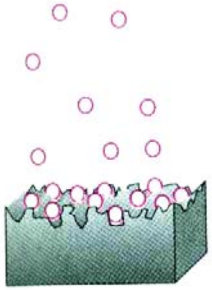
3. Qualitative and quantitative

Gas Analysis - Sampling

Representative sampling of gases is often difficult because gas can contain aerosols and dust particles.

One simple sampling method is the usage of a sampling tube filled with activated charcoal or silica gel for the adsorption of organic solvent vapors in conjunction with a pump.





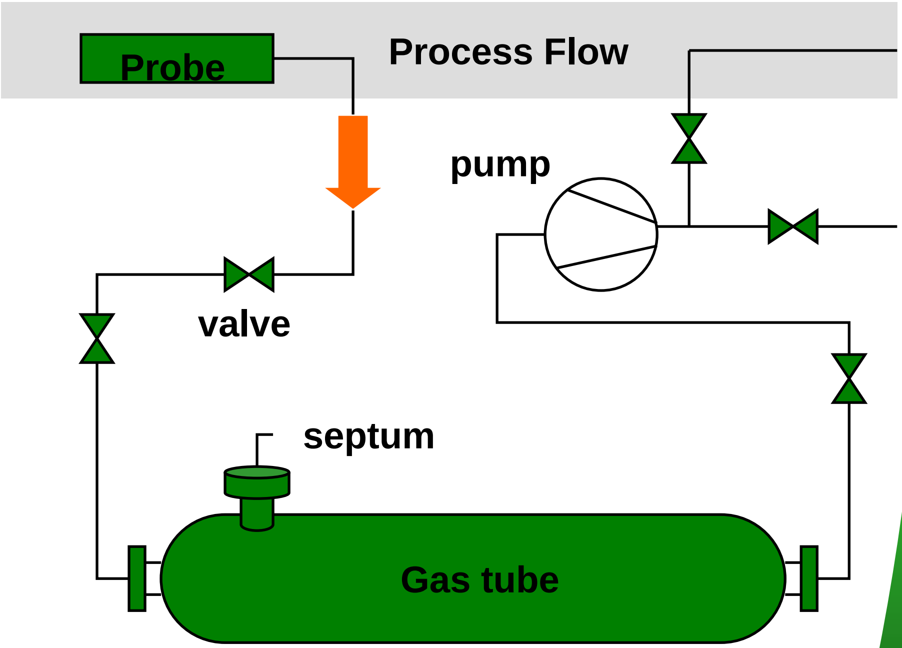
1. Adsorption e.g. activated charcoal

Gas Analysis - Sampling

Representative sampling of gases is often difficult because gas can contain aerosols and dust particles.

One simple sampling method is the usage of a sampling tube filled with activated charcoal for the adsorption of organic solvent vapours in conjunction with a pump.

The direct sampling of gaseous materials is also possible using glass vessel or special plastic containers. The sample is drawn in through the glass tubing using a pump.



Gas Analysis - Sampling

Sampling gases

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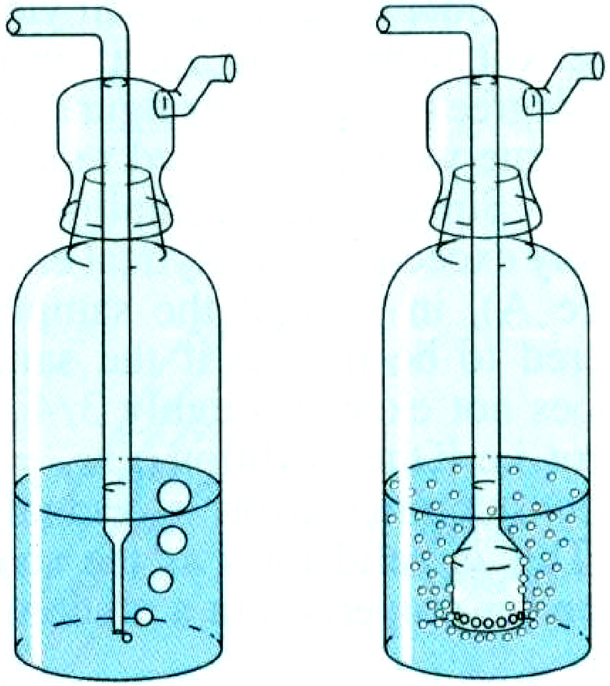


Impinger
10–20 L/min

Glass frit
2–20 L/min

Liquid absorpion systems make selective sampling possible owing to the ability to select the solution used.

Gas Analysis - Chromatography

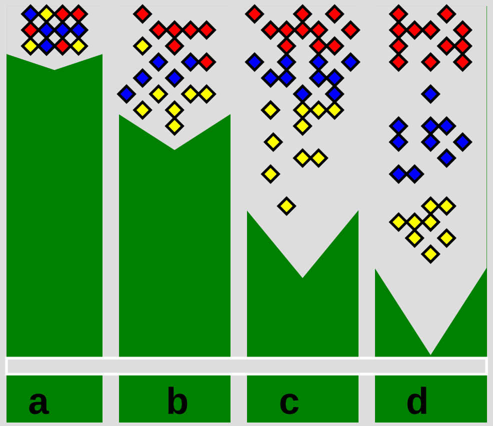
Depending on the analyte which has to be examined, the following analytical methods can be applied:

Analyte: organic solvent vapor

The activated charcoal or silica gel of the sampling tube has to be extracted with an appropriate solvent (CS_2, CH_2Cl_2, CH_3OH).

The extract can be analysed with gas chromatography (GC)

The term chromatography is applied to those physical methods in which there is a substance transformation via partioning between a resting (stationary) phase and a moving (mobile) phase.



1.Chromatographic process

Gas Analysis - Gas Chromatography

Depending on the analyte which has to be examined, the following analytical methods can be applied:

Analyte: organic solvent vapor
The activated charcoal or silica gel of the sampling tube has to be extracted with an appropriate solvent.
The extract can be analysed with gas chromatography (GC):

The sample (extract) is applied to a column with a syringe. The different components are transported through the thermostated column with the aid of a carrier gas (e.g. Helium), and the chromatographic process takes place at a pre-defined temperature there. After leaving the column, one after another the separated substances in the gas phase pass a detector which displays each individual component using a recorder or an integrator.

Gas Analysis - GC Scheme

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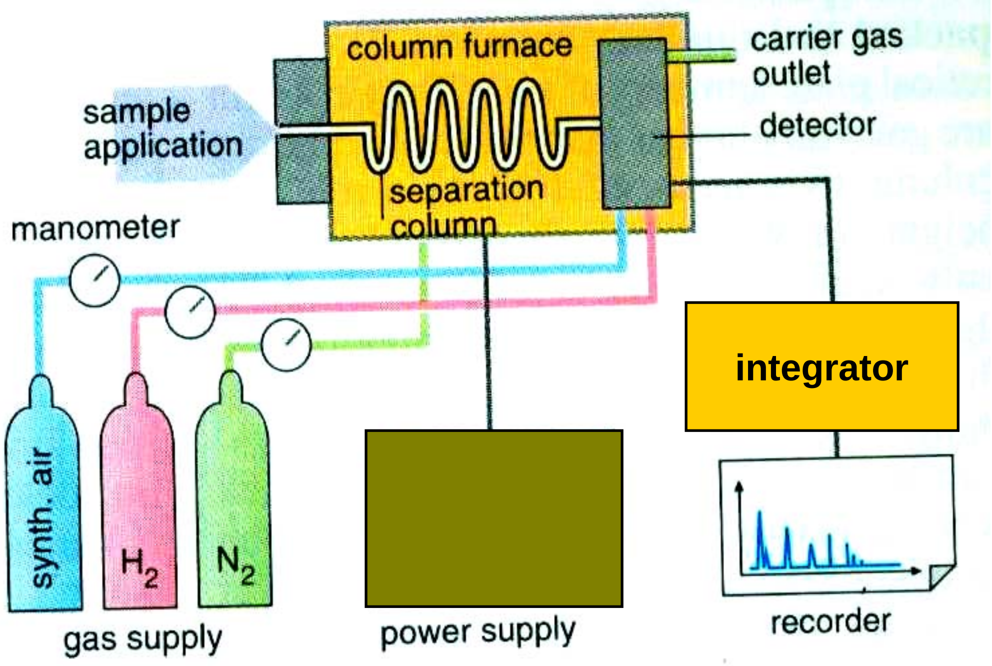
Depending on the substances
to be analysed,
different detectors are in use:

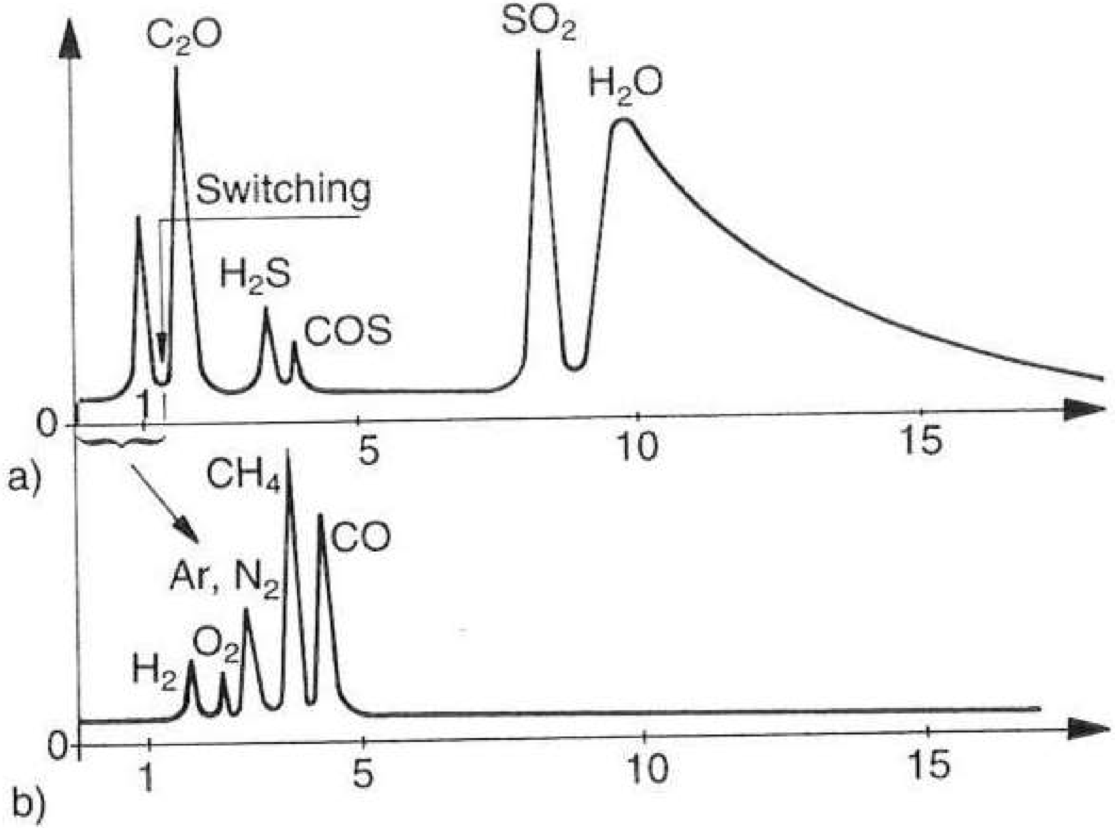
-FID (flame ionisation detector)
-ECD (electron-capture detector)
-PID (thermoionic detector)
-HCD (heat conductivity detector)

-GC-MS coupling



Gas Analysis - Example Combustion Gases

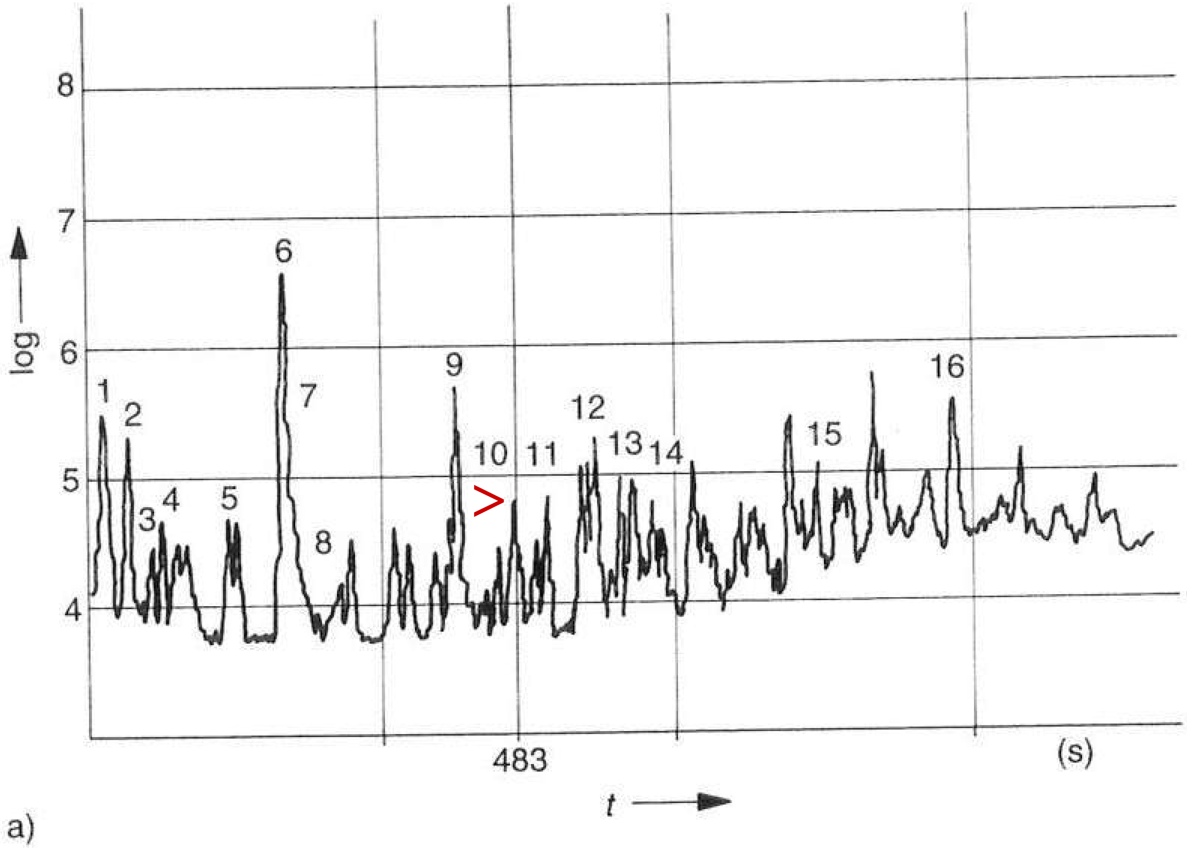
Analysis of combustion gases at high temperatures



Gas Analysis - GC (Ground-Level Sample)

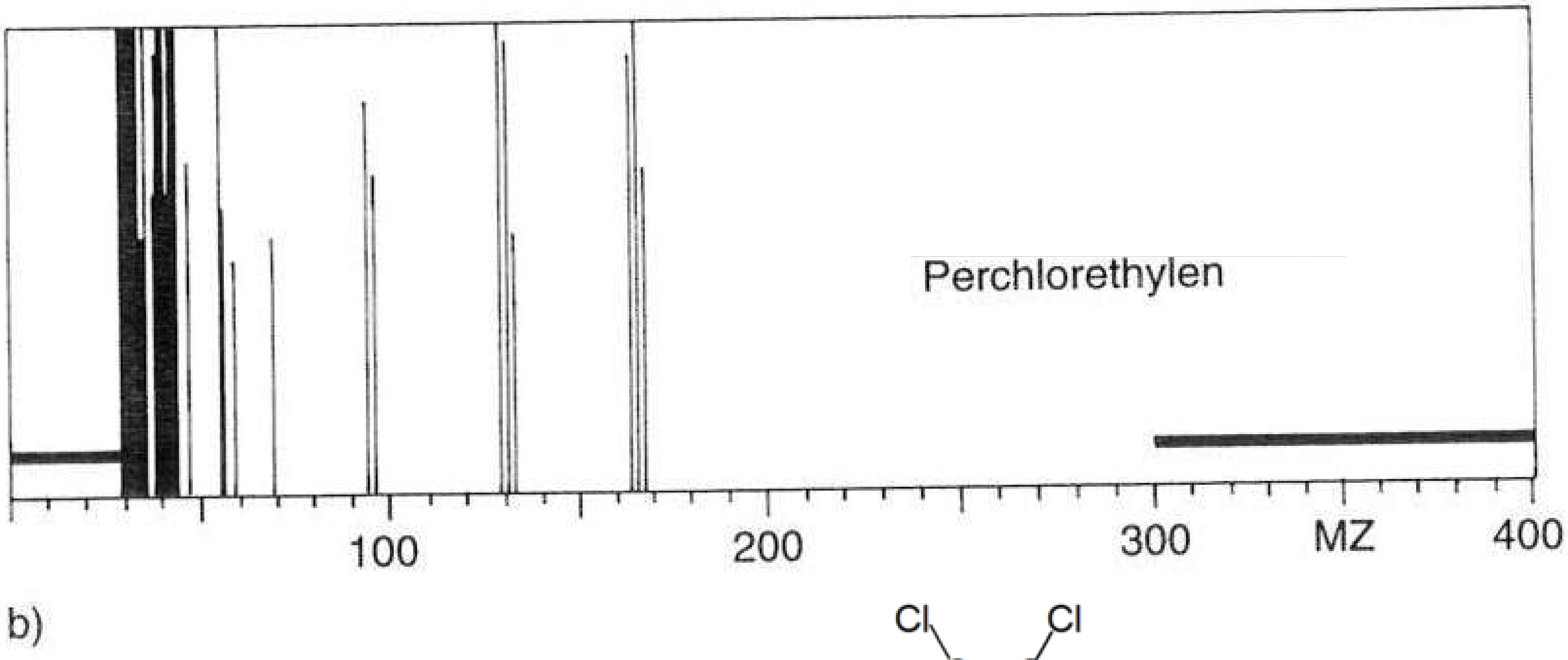
GC-MS-analysis of
A ground-level sample

Chromatogram

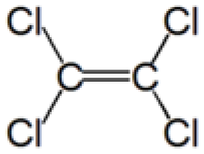


Gas Analysis - MS (Ground-Level Sample)

GC-MS-analysis of
a ground-level sample



Mass spectrum of perchloroethylene



Gas Analysis - IC

Depending on the analyte which has to be examined, the following analytical methods can be applied:

Analyte: acid generating gases like HCl, HF, SO_2 etc.

The solution from the liquid absorption system can be analysed with ion chromatography.

In ion chromatography, first described in 1975, an ion-exchange separation column is coupled with a suppressor column and a conductivity detector for on-line detection.

Ion chromatography is a fast multi-cation and multi-anion method. It can be used for either atomic or molecular ions, e.g.

Chloride, fluoride, sulphate, formiate, acetate, oxalate etc.

Gas Analysis - IC

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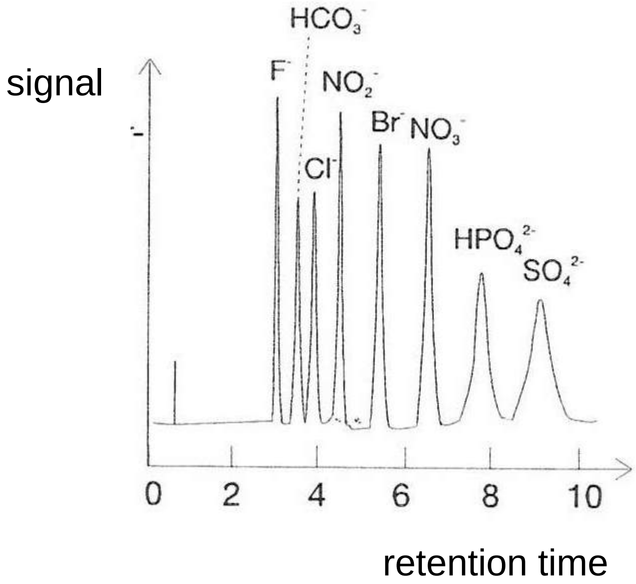


Water Analysis - Sampling

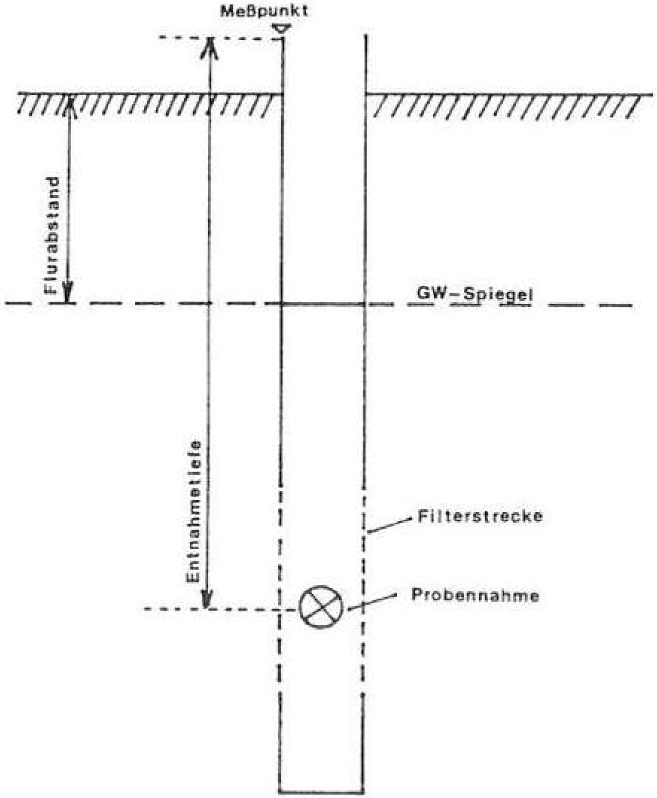
- random samples taken manually or automatically from pipes, bodies of water and effluents provide a picture of the water quality at the time of the sampling.

- mixed samples, which are usually taken using an automatic sampler, can be obtained based on time or volume

- samples of ground water should be taken from different dephts

- filtration is necessary in the presence of sand, suspended solids, or sediments

- minimum time of pumping is necessary (checked constant conductivity)

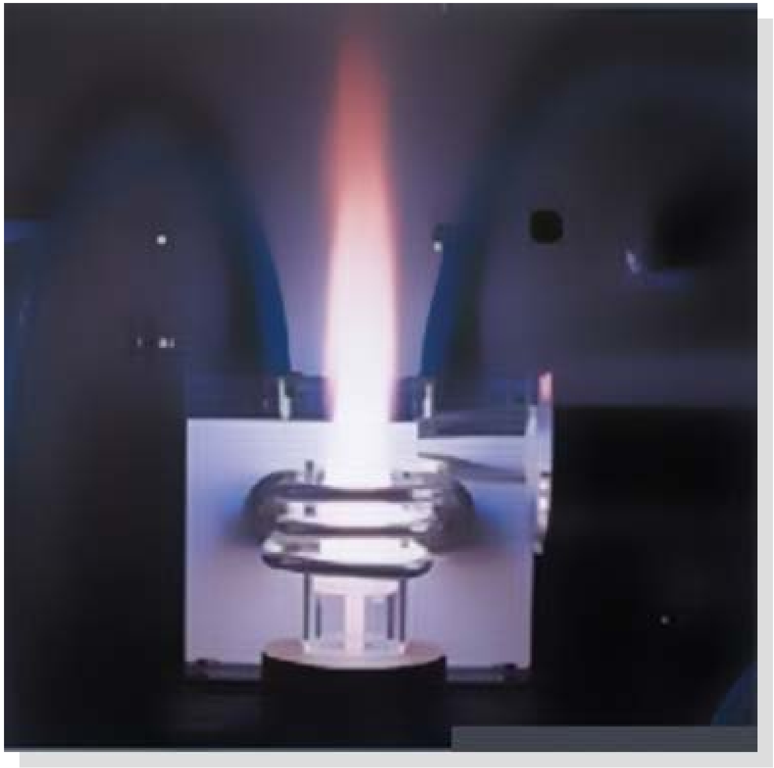


Water Analysis - ICP-OES

Analytical methods – Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

Water Analysis - ICP-OES

Analytical methods – Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), also referred to as (ICP-AES, A = atomic)



- very fast multi-element method

- different program routines for both qualitative screening or quantitative determinations

- suitable for the examination of
  - + drinking water
  - + sewage water
  - + landfill leachates

- advantages: almost no matrix effects, robust technique, great operating range

- disadvantages: well trained and experienced user required, high operating costs (Argon)

Water Analysis - ICP-OES

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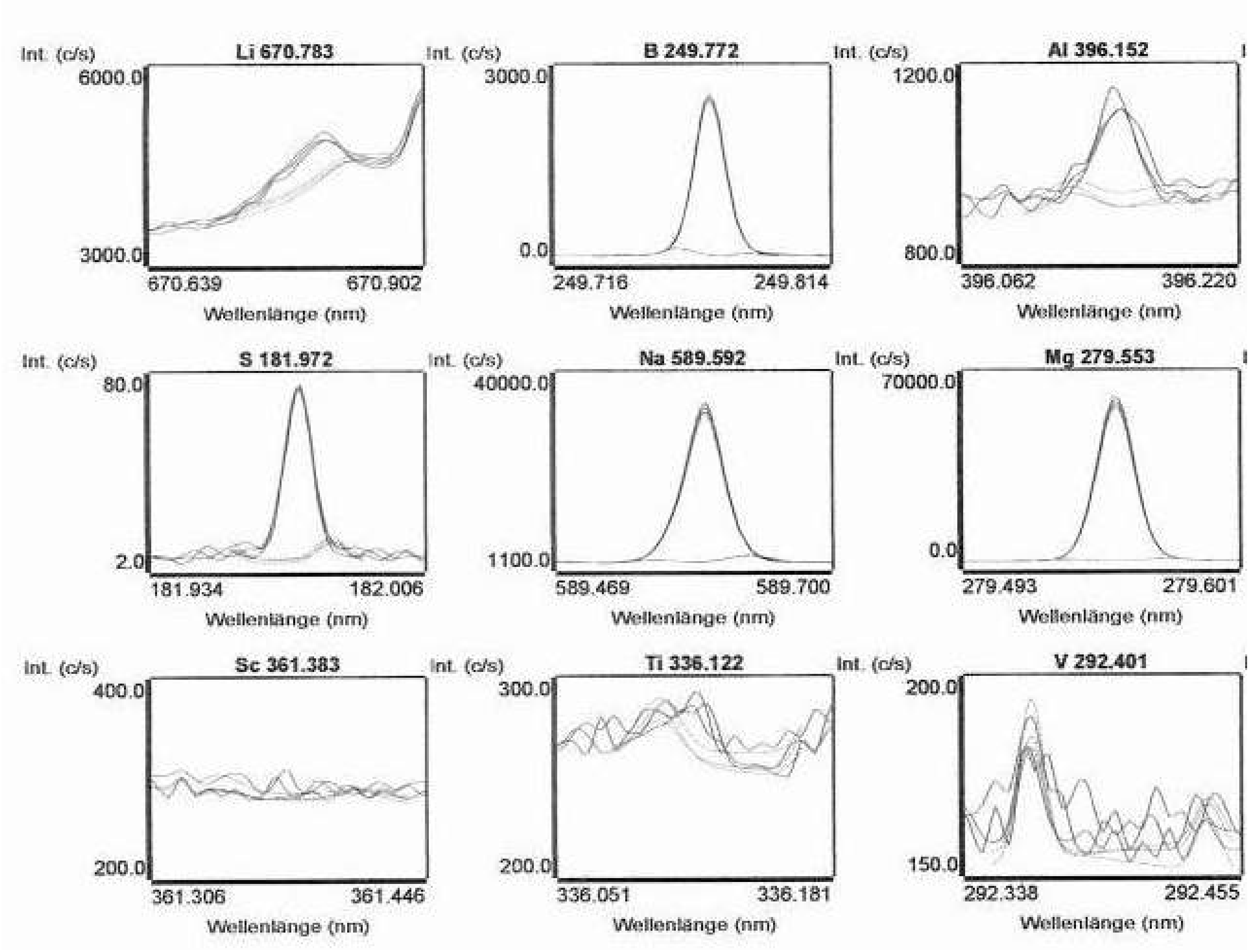

Water Analysis - ICP-OES

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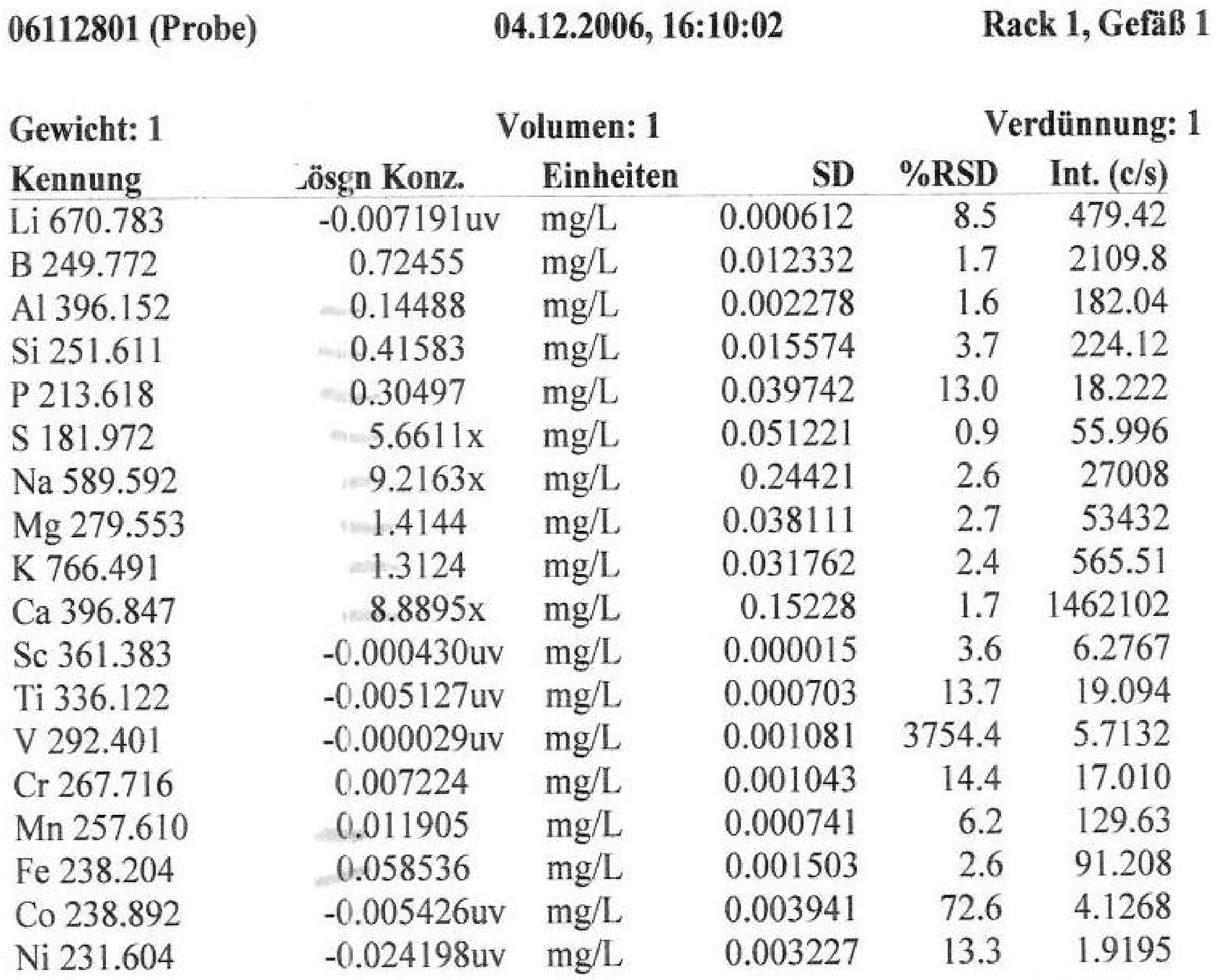


06112801 (Probe) **04.12.2006, 16:10:02** **Rack 1, Gefäß 1**

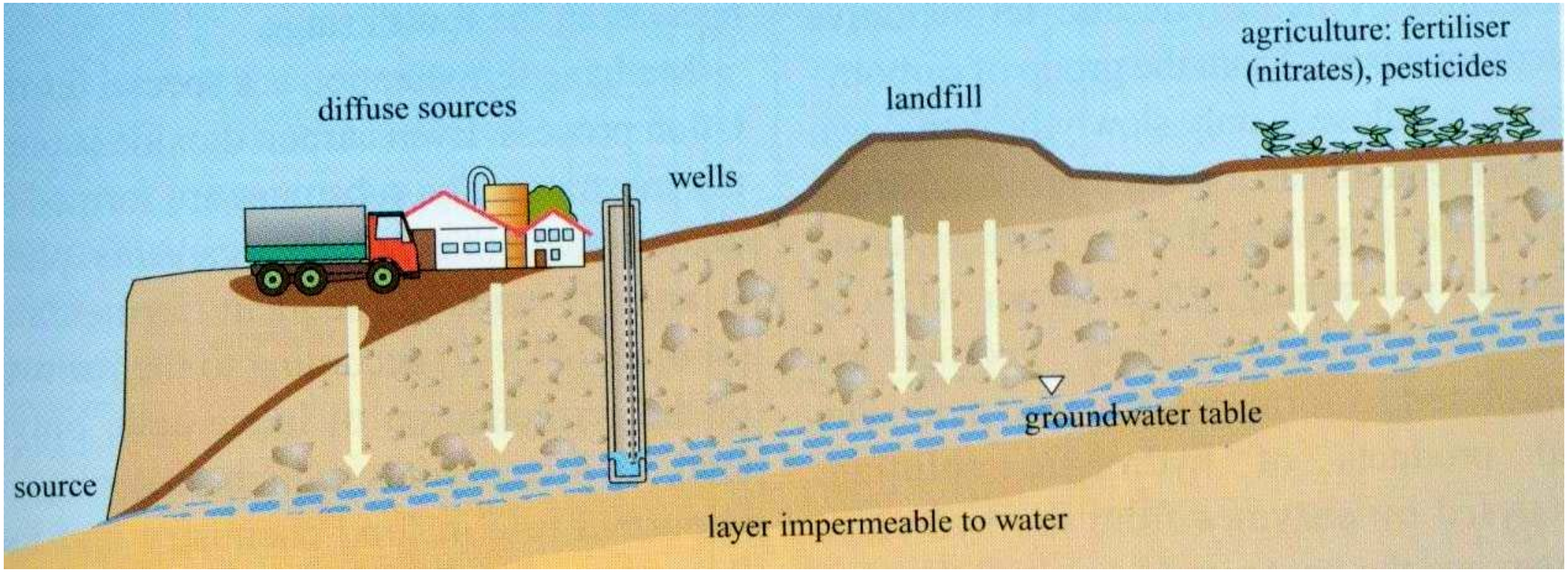
Gewicht: 1 **Volumen: 1** **Verdünnung: 1**

Kennung	Lösgn Konz.	Einheiten	SD	%RSD	Int. (c/s)
Li 670.783	-0.007191uv	mg/L	0.000612	8.5	479.42
B 249.772	0.72455	mg/L	0.012332	1.7	2109.8
Al 396.152	0.14488	mg/L	0.002278	1.6	182.04
Si 251.611	0.41583	mg/L	0.015574	3.7	224.12
P 213.618	0.30497	mg/L	0.039742	13.0	18.222
S 181.972	5.6611x	mg/L	0.051221	0.9	55.996
Na 589.592	9.2163x	mg/L	0.24421	2.6	27008
Mg 279.553	1.4144	mg/L	0.038111	2.7	53432
K 766.491	1.3124	mg/L	0.031762	2.4	565.51
Ca 396.847	8.8895x	mg/L	0.15228	1.7	1462102
Sc 361.383	-0.000430uv	mg/L	0.000015	3.6	6.2767
Ti 336.122	-0.005127uv	mg/L	0.000703	13.7	19.094
V 292.401	-0.000029uv	mg/L	0.001081	3754.4	5.7132
Cr 267.716	0.007224	mg/L	0.001043	14.4	17.010
Mn 257.610	0.011905	mg/L	0.000741	6.2	129.63
Fe 238.204	0.058536	mg/L	0.001503	2.6	91.208
Co 238.892	-0.005426uv	mg/L	0.003941	72.6	4.1268
Ni 231.604	-0.024198uv	mg/L	0.003227	13.3	1.9195

Water Analysis - Example Landfill

Water studies near landfills

Landfill leachate is described as water originating from precipitation or from refuse that flows through a landfill and takes up soluble substances from the refuse in the process. The major components of landfill leachate are water-soluble nitrates, sulphates, chlorides, heavy metals and high amounts of organic substances. If the landfill leachate is not purified in a treatment plant, it is usually fed back to the landfill, resulting in the concentration of contaminants.



Water Analysis - Monitoring

Monitoring landfills with respect to the outflow of pollutants is often done using water samples from bearing wells.

- substances can enter landfill leachates that are either water-soluble or slightly soluble but that can be transported with water via organic substances in a role as a solubiliser.

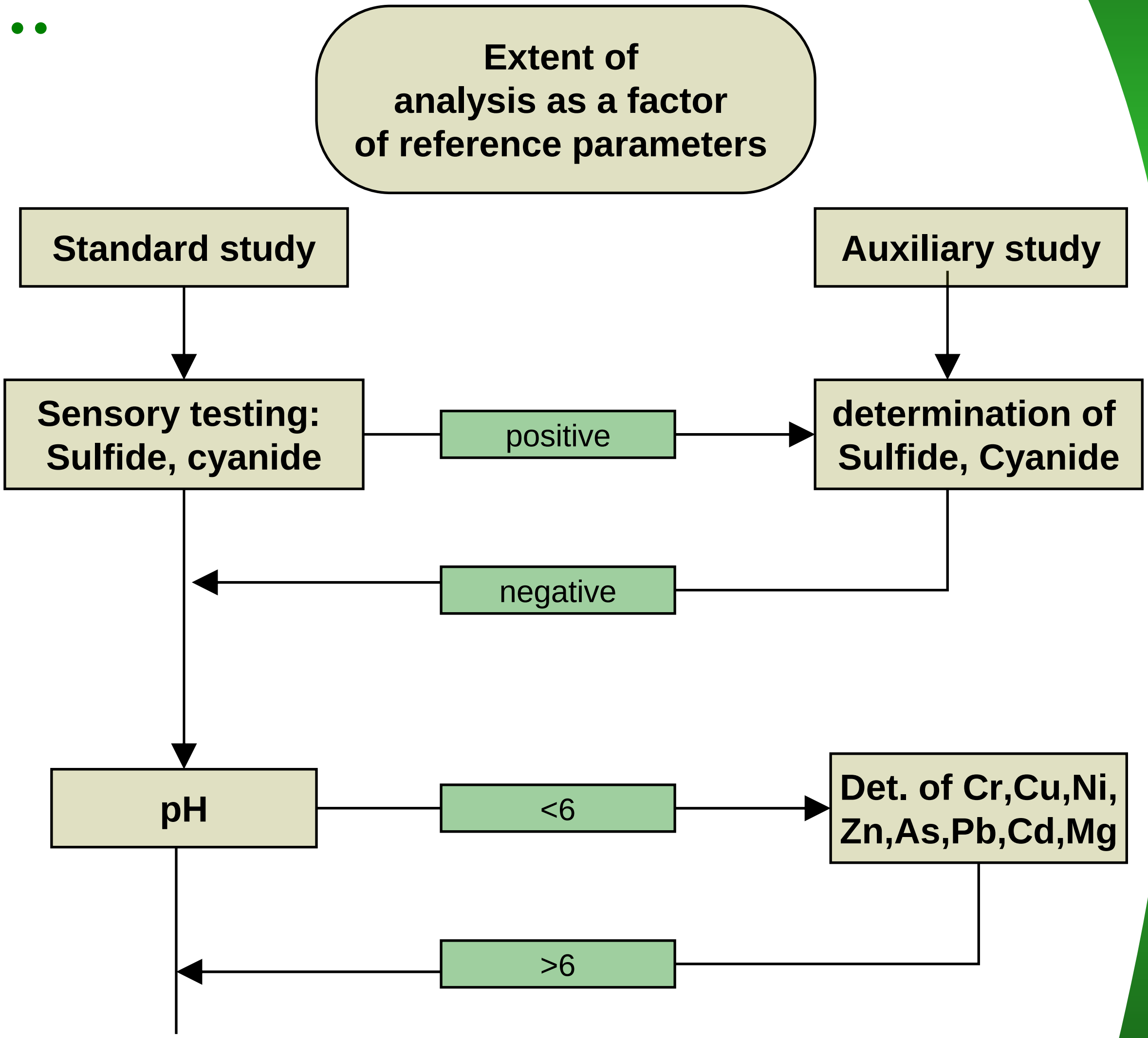
- instead of using a list of parameters with threshold values and guide values more and more state offices for ecology and responsible water control offices are switching over to establishing reference parameters and using them in the form of an analytical strategy as a standard study or an auxiliary study.

- only after a positive sensory smell test for hydrogen sulphide or hydrogen cyanide quantitative analysis (photometrically or with the aid of ion chromatography) must also be performed.

- the requirement for an analysis of heavy metals is linked to the pH value.

Water Analysis - Scheme

Only in acidic percolating waters it is to be expected that a mobilisation out of the landfill might have occured.



Extent of analysis as a factor of reference parameters

Standard study

Auxiliary study

Sensory testing: Sulfide, cyanide

positive

determination of Sulfide, Cyanide

negative

pH

<6

Det. of Cr,Cu,Ni, Zn,As,Pb,Cd,Mg

>6

continued

Water Analysis - Sum Parameter

- if a landfill has started to leak, usually there is extremely high impact with chlorides, sulphates and ammonium compounds in special solid waste leachates and with organic substances especially in domestic landfills.

- the high levels of organic substances become noticeable when determining cumulative parameters such as the chemical oxygen demand (COD; via oxidation with dichromate) or the amount of dissolved organic carbon (DOC).

  → if the COD is high, the suspicion raises that oily or tar-like substances are present in the percolating water

  → after extraction the hydrocarbon level has to be determined using IR spectrometry as a check.

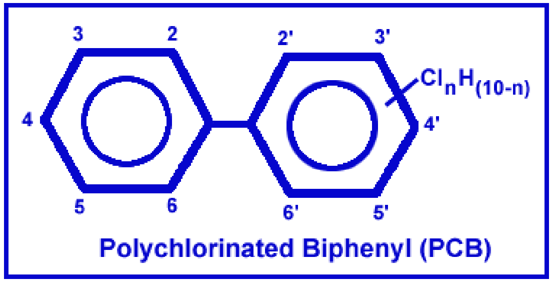
Water Analysis - Sum Parameter

- if there are high chloride levels, one must test for the presence of organic halogen compounds (as cumulative parameter AOX)

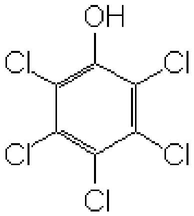
→ if the suspicions are confirmed, a gas chromatographic analysis is performed to determine the individual substances (e.g. GC-MS).

Halogenated hydrocarbons (HHC) are some of the most persistent and readily accumulating pollutants.

Groundwater contaminants that come from landfills will increase with time due to transformations that occur there. Percolating oils, which separate from the percolating waters, can contain high concentrations of polychlorinated biphenyls (PCBs), chlorobenzenes, persistent pesticides and dioxins.

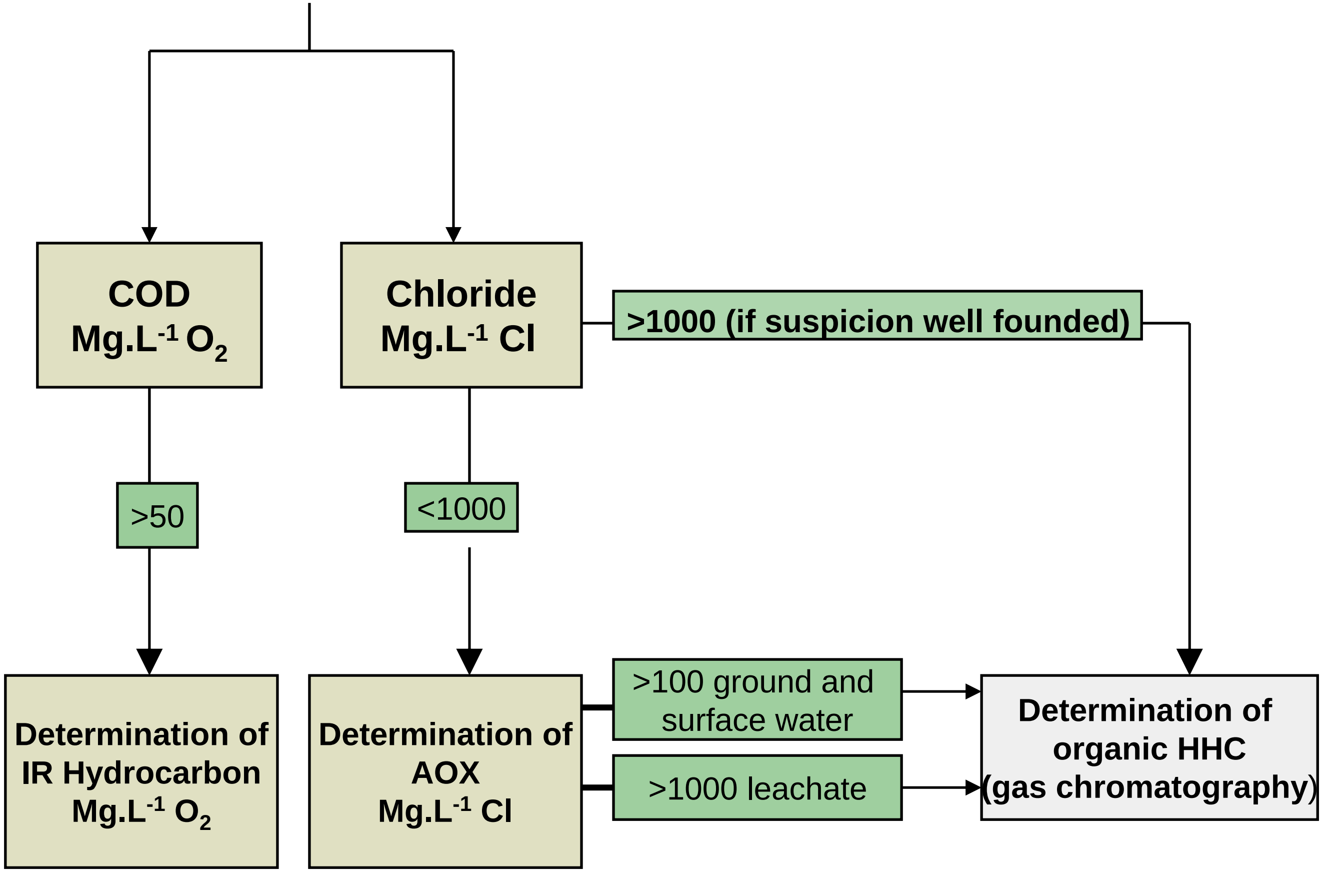


Polychlorinated Biphenyl (PCB)



PCP

Water Analysis - Scheme cont.



COD
Mg.L^{-1} O$_2$

Chloride
Mg.L^{-1} Cl

>1000 (if suspicion well founded)

>50

<1000

Determination of
IR Hydrocarbon
Mg.L^{-1} O$_2$

Determination of
AOX
Mg.L^{-1} Cl

>100 ground and
surface water

>1000 leachate

Determination of
organic HHC
(gas chromatography)

Analysis of solid samples - Sampling

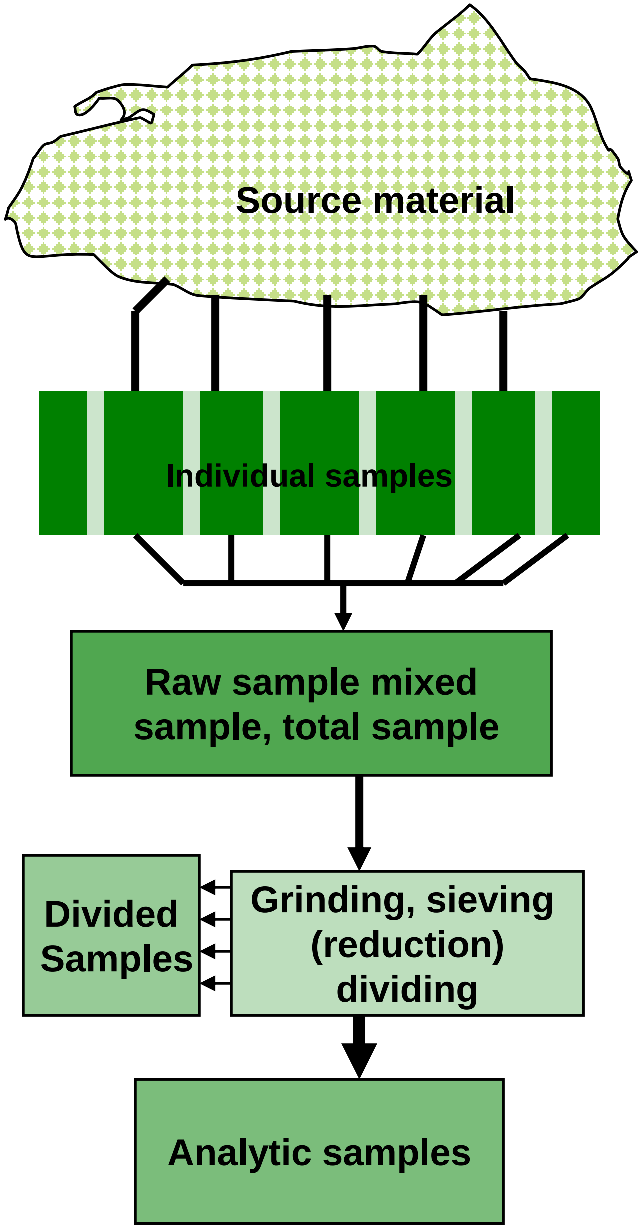
- a defined number *n* of individual samples are taken from a population such as a pile of refuse (the raw mixed or total sample).

- the actual analytical sample is obtained from the divided sample by repeated

  + grinding
  + sieving and
  + dividing

  (this is also referred to as sample reduction)

- the sampling error noticeably exceeds the analytical error as a rule



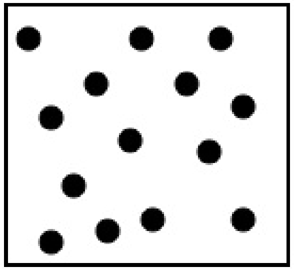
Analysis of solid samples - Sampling from Soils

- simple equipment such as shovels or siphon cylinders can be used

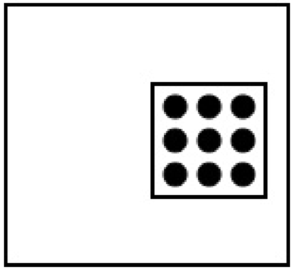
- since the soil sample is supposed to be representative of the total area to be analyzed, a variety of techniques can be suggested:

  → if there are spatial inhomogeneities, the normal method is used.

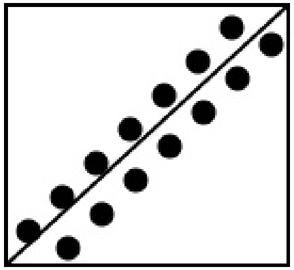
  → with homogenous soils, the sampling surface can be reduced in the form of parcels, diagonals or cross strips.



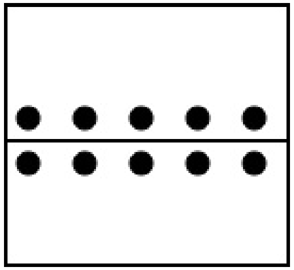
normal method



parcel



diagonal



cross-strip

Analysis of solid samples - Decomposition

A decomposition of a substance or a mixture of substances does not refer to the dissolution, but rather the conversion of slightly soluble substances into acid-or water-soluble (ionogenic) compounds.

Therefore, a decomposition is associated with a chemical change in the starting material or the matrix as a whole.

Based on the phase status of the decomposing agent, there is a division into

+ melt decompositions
+ wet decompositions (with liquid decomposing agents, e.g. acids)
+ decomposition by combustion

Analysis of solid samples - Microwave Decomposition

A very versatile method for the decomposition of solid material is the use of a microwave oven for a wet decomposition.

- instead of thermal initiation, microwave initiation is used.

- just several minutes instead of up to 3 hours are needed

- the sample is directly heated, but the vessel itself is only indirectly warmed up.

- PTFE pressure vessels for pressures up to 7 bar and temperatures up to 200 °C are used.

Analysis of solid samples - Analytics

The resulting solutions can be analyzed with standard techniques such as

+ ICP-OES
+ AAS
+ IC (ion chromatography) – after dilution or neutralization
+ gas chromatography
+ photometry
+ ...

Conclusion

- There is a variety of analytical methods for analysis of gases and liquids.
- For analysis of the solid phase, the analyte has to be transferred to gas or liquid-phase.
- Standard methods are usable.
- Regarding precision and expenses, first quick and simple methods.
- Since the error resulting from sampling exceeds the analytical error, a special focus has to be on the sampling and preparation.

Thank you very much for your attention!