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Academic Environmental Protection Studies on surface water quality in significant cross-border nature reservations Djerdap / Iron Gate national park and Carska Bara special nature reserve, with population awareness raising workshops

= RORS-462 =

FUNDAMENTALS OF ATOMIC AND MOLECULAR ABSORPTION SPECTROMETRY.

Instrumentation and Techniques of Atomic Absorption & UV VIS Spectrometry.

AEPS
common history, common future

Trainers

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Francisc Popescu */ University Politehnica Timisoara*

www.aeps.upt.ro

25 - 26 November 2020

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Fundamentals
Instrumentation and Techniques of Atomic Absorbtion Spectroscopy

Application on Analytik Jena ZEEnit 700P

Where AAS is used?

Atomic absorption spectrometry (AAS) is an analytical technique that measures the concentrations of elements. Atomic absorption is so sensitive that it can measure down to parts per billion of a gram ($\mu g/cm^3$) in a sample. The technique makes use of the wavelengths of light specifically absorbed by an element. They correspond to the energies needed to promote electrons from one energy level to another, higher, energy level.

Atomic absorption spectrometry has many uses in different areas of industry/chemistry:

- **Clinical analysis.** Analyzing metals in biological fluids such as blood and urine.
- **Environmental analysis.** Monitoring our environment – eg finding out the levels of various elements in rivers, seawater, drinking water, air, petrol and drinks such as wine, beer and fruit drinks.
- **Pharmaceuticals.** By using AAS the amount of catalysts used in the process can be determined in final product.
- **Industry.** Many raw materials are examined and AAS is widely used to check that the major elements are present and that toxic impurities are lower than specified – eg the lead level in concrete.
- **Mining.** By using AAS the amount of metals such as gold in rocks can be determined to see whether it is worth mining the rocks to extract the gold.

How AAS works?

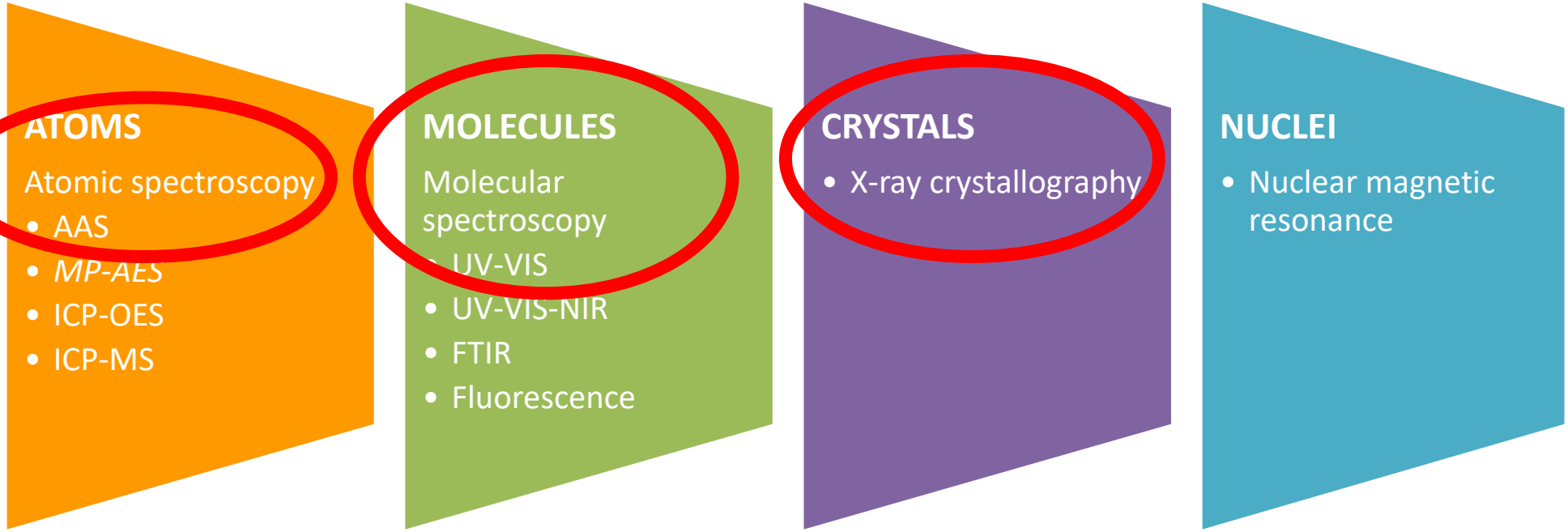
Atoms of different elements absorb characteristic wavelengths of light. Analyzing a sample to see if it contains a particular element means using light from that element. For example with lead, a lamp containing lead **emits** light from excited lead atoms that produce the right mix of wavelengths to be **absorbed** by any lead atoms from the sample. In AAS, the sample is atomized – ie converted into ground state free atoms in the vapor state – and a beam of electromagnetic radiation emitted from excited lead atoms is passed through the vaporized sample. Some of the radiation is absorbed by the lead atoms in the sample.

The greater the number of atoms there is in the vapor, the more radiation is absorbed. The amount of light absorbed is proportional to the number of lead atoms.

A calibration curve is constructed by running several samples of known lead concentration under the same conditions as the unknown. The amount the standard absorbs is compared with the calibration curve and this enables the calculation of the lead concentration in the unknown sample.

Theory behind AAS

Spectroscopy is a broad field with many subdisciplines, which can be classified by the type of material being analyzed.



Atomic spectroscopy includes a number of analytical techniques used to determine the elemental composition of a sample by examining its electromagnetic spectrum or its mass spectrum.

Atomic Spectroscopy	
Identification based on	
Electromagnetic spectrum	**Mass spectrum**
Atomic Absorption • Flame AAS • Graphite Furnace AAS • Vapor (Hydride) Generation AAS	
Atomic Emission • MP-AES • ICP-OES • X-ray Fluorescence (XRF)	• ICP-MS
Atomic Interference • X-ray Diffraction (XRD)	

AAS is based on the breakdown of a sample into atoms, followed by the measurement of the atom's absorption or emission of light.

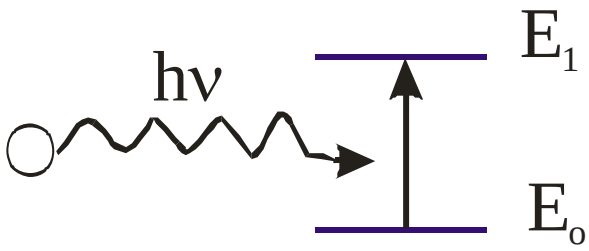
- ✓ deals with absorbance fluorescence or emission (luminescence) of atoms or elemental ions rather then molecules

  - atomization: process of converting sample to gaseous atoms or elementary ions

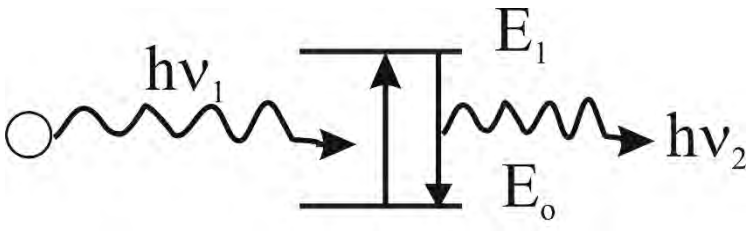
- ✓ Provides information on elemental composition of sample or compound

  - UV/Vis, IR, Raman gives molecular functional group nformation, but no elemental information.

- ✓ Basic process the same as in UV/Vis, fluorescence etc. for molecules



Absorbance



Fluorescence

Differences for Molecular Spectroscopy

- ✓ no vibration levels - that gives much sharper absorbance, fluorescence, emission bands
- ✓ position of bands are well-defined and characteristic of a given element
- ✓ qualitative analysis is easy in atomic spectroscopy (not easy in molecular spectroscopy)

Examples:

carbon

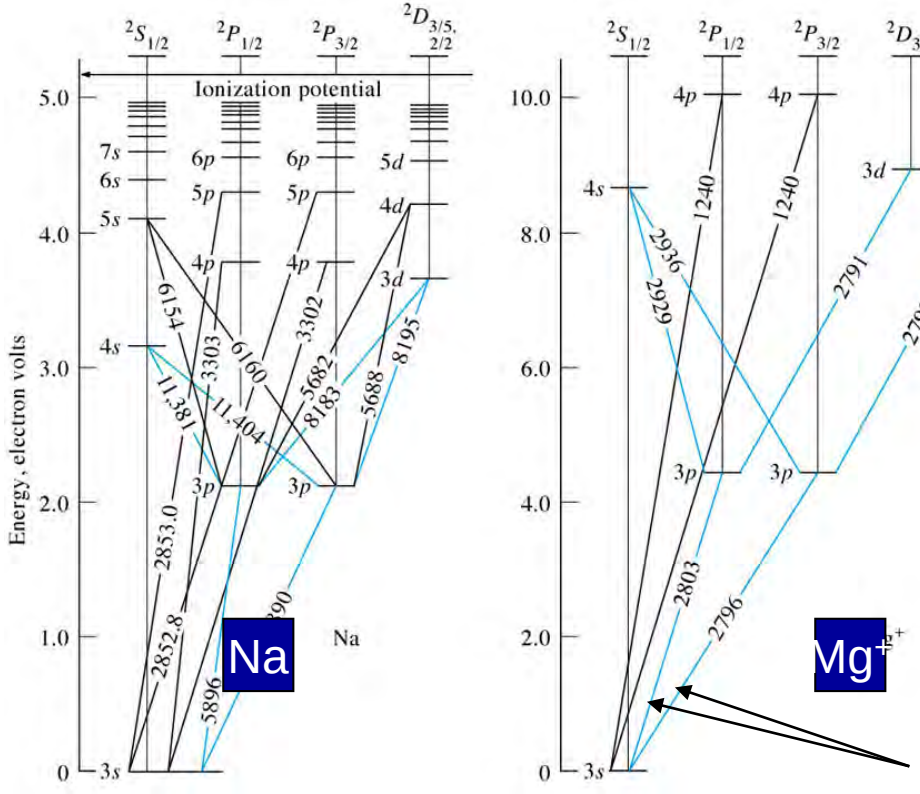
oxygen

nitrogen

Energy Level Diagrams

Energy level diagram for the outer electrons of an element describes atomic spectroscopy process.

- ✓ every element has a unique set of atomic orbitals
- ✓ p, d, f split by spin-orbit coupling
- ✓ Spin (s) and orbital (l) motion create magnetic fields that perturb each other (couple)
  - parallel → higher energy; antiparallel → lower energy



- **Similar pattern between atoms but different spacing**
- **Spectrum of ion different to atom**
- **Separations measured in electronvolts (eV)**
  - **1eV = 1.602x10^{-19} J**
  - **= 96.484 kJ ·mol^{-1}**
- **As number of electrons increases, number of levels increases**
  - **emission spectra more complex**
    - **Li 30 lines**
    - **Cs 645 lines**
    - **Cr 2277 lines**

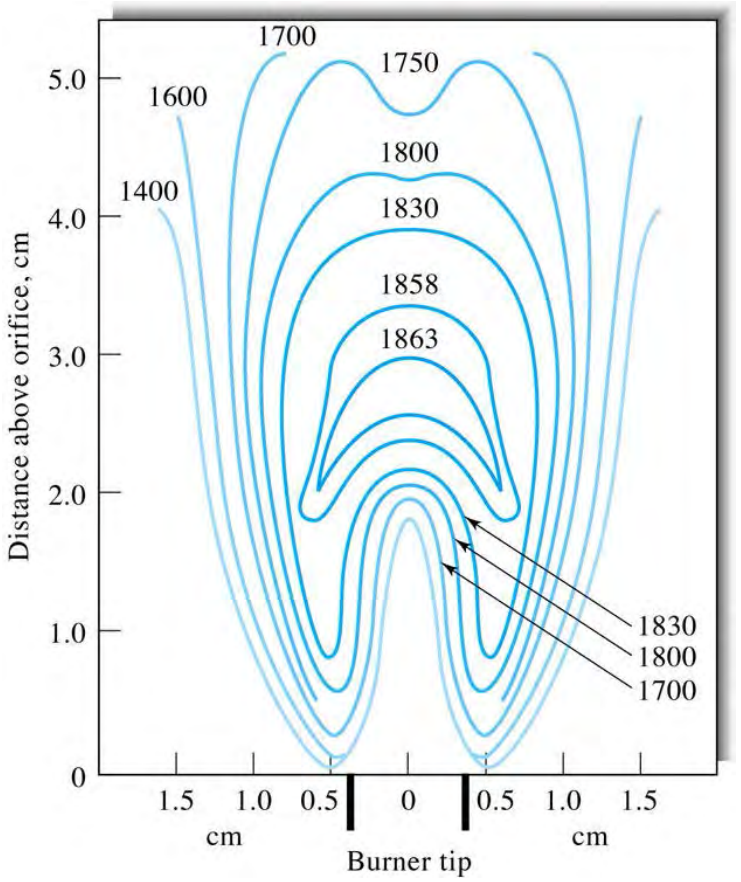
Note slight differences in energy due to magnetic fields caused by spin

In AAS the flame profile is higly important! Different mixes and flow rates give different temperature profile in flame:

- gives different degrees of excitation of compounds in path of light source

Flame Temperatures:

Fuel	Oxidant	Temperature
Gas	Air	~1800 °C
H_2	O_2	~2600 °C
Acetylene	O_2	~3000 °C

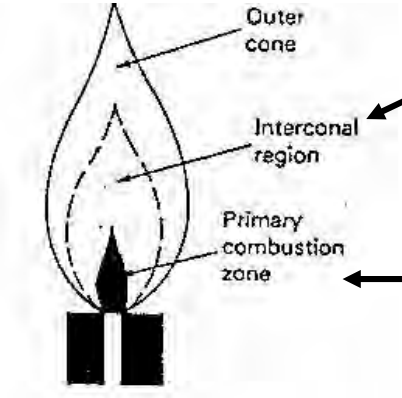


Types of Flame/Flame Structure – *selection of correct flame region is important for optimal performance*

a) primary combustion zone – blue inner cone (blue due to emission from C_2, CH & other radicals)
- not in thermal equilibrium and not used

b) interconal region
- region of highest temperature (rich in free atoms)
- often used in spectroscopy
- can be narrower in some flames (hydrocarbon) tall in others (acetylene)

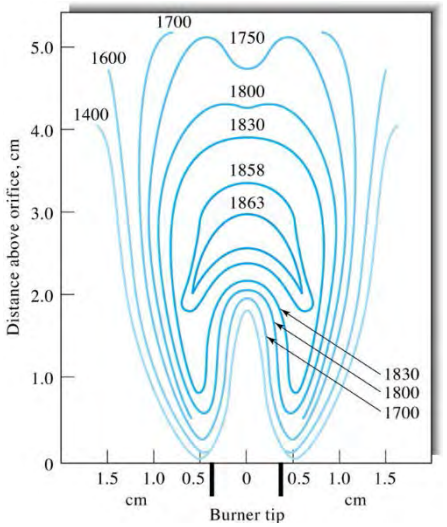
c) outer cone
- cooler region
- rich in O_2 (due to surrounding air)
- gives metal oxide formation



Primary region for spectroscopy

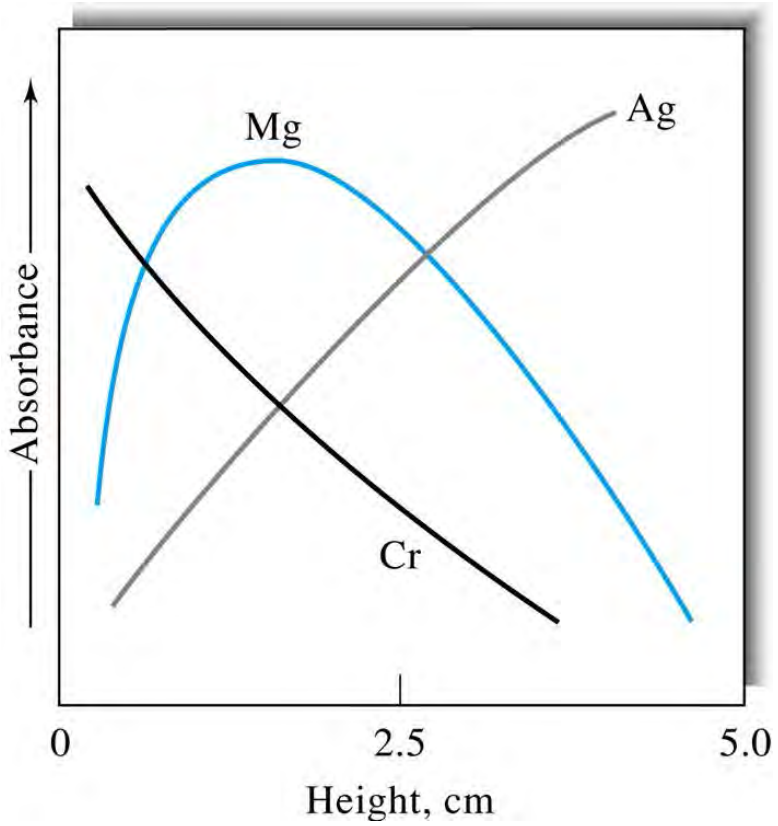
Not in thermal equilibrium and not used for spectroscopy

Temperature varies across flame – need to focus on correct part of flame



Flame profile: depends on type of fuel and oxidant and mixture ration

Most sensitive part of flame for AAS varies with analyte

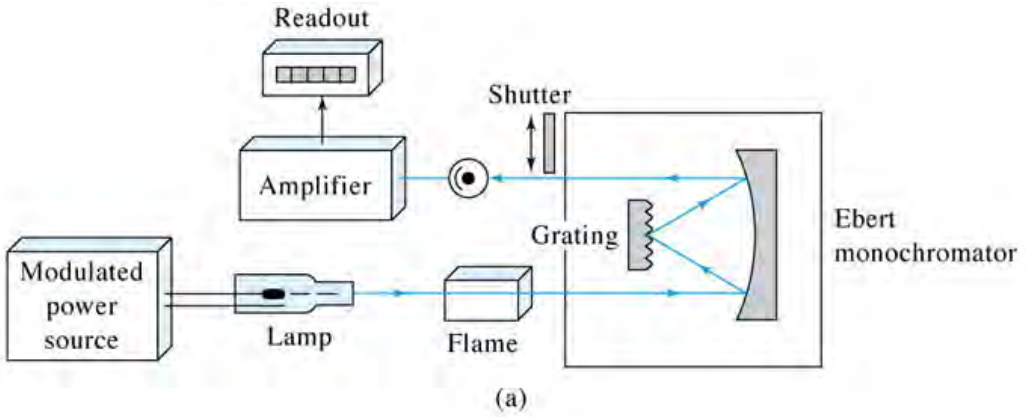


Consequences:

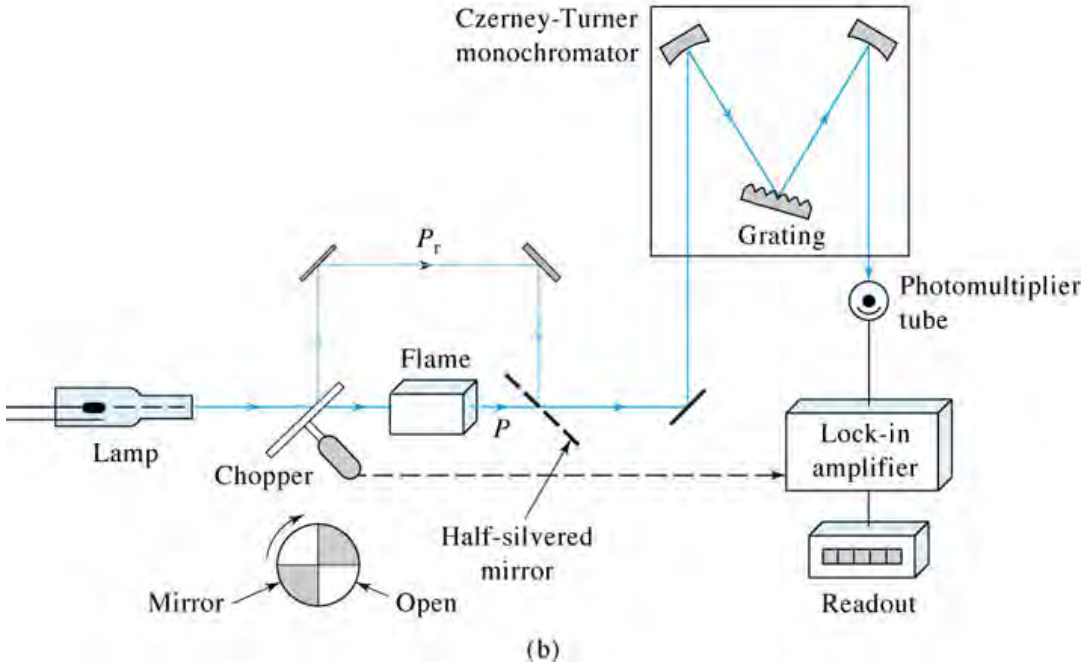
- Sensitivity varies with element
- must maximize burner position
- makes multi-element detection difficult

Basic instrument design (Flame atomizer)

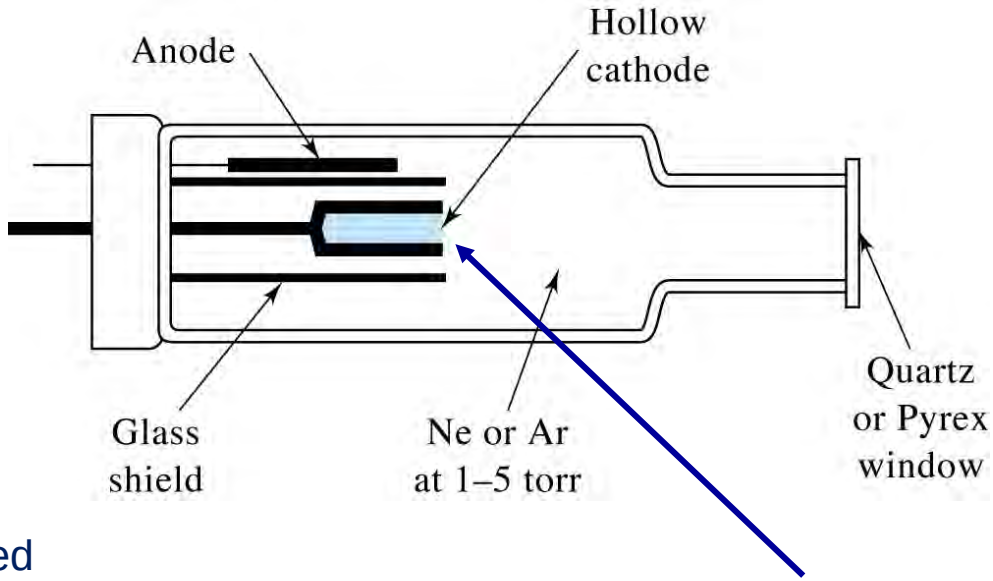
Single beam



Double beam



hollow cathode lamp (HCL)



Process: *use element to detect element*

1. ionizes inert gas to high potential (300V)

$$Ar \rightarrow Ar^{+} + e^{-}$$

2. Ar^{+} go to "-" cathode & hit surfaces
3. As Ar^{+} ions hit cathode, some of deposited element is excited and dislodged into gas phase (sputtering)
4. excited element relaxes to ground state and emits characteristic radiation

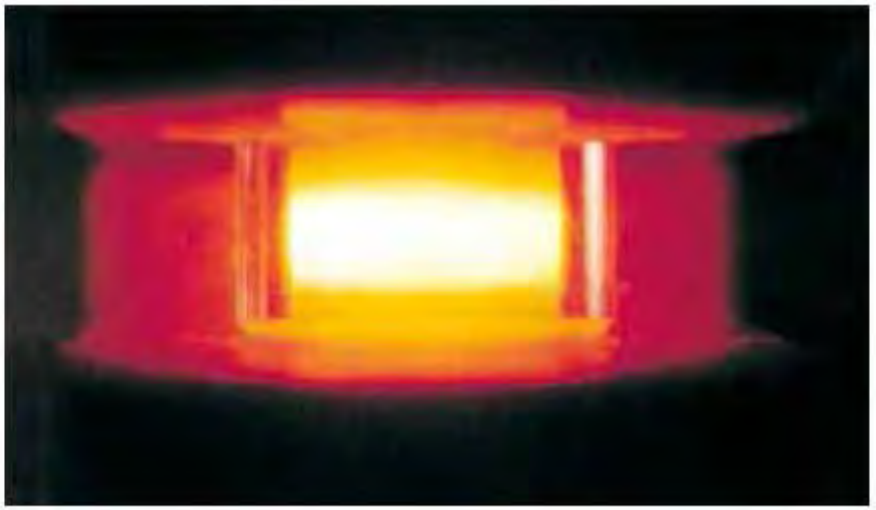
- advantage: sharp lines specific for element of interest
- disadvantage: can be expensive, need to use different lamp for each element tested.

The atomizer

The following atomization techniques are nowadays used in AAS:

- ✓ Flame technique
- ✓ Graphite furnace technique
- ✓ Hydride and Cold Vapor techniques
- ✓ HydrEA technique (combination of Hydride and Graphite furnace technique)

Flame

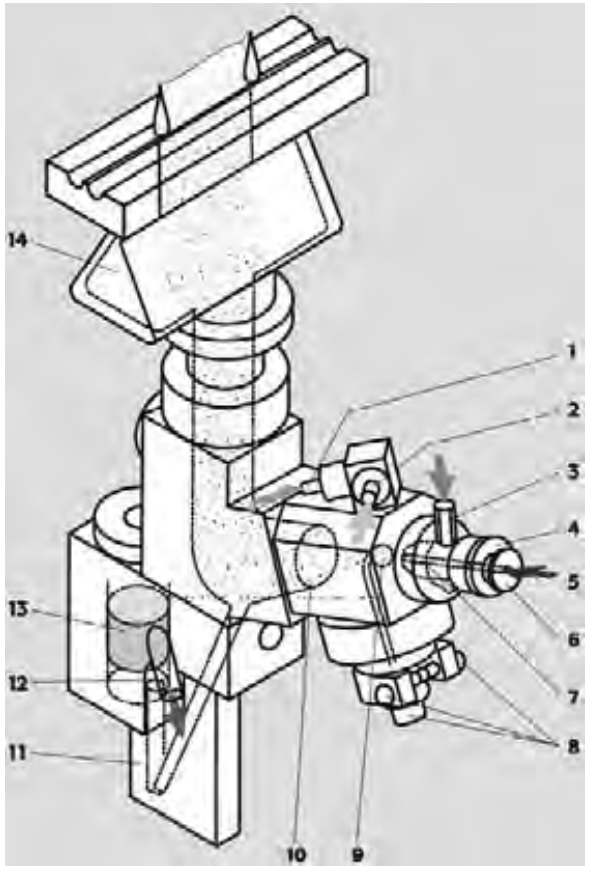


Graphite furnace

Hydride technique

Atomization in a flame

The sample is transferred into liquid form, e.g. by dissolution. The nebulizer aspirates the solution and transfers it into a fine aerosol. This is directed onto an impact bead for post-nebulization in order to create an even finer aerosol. Large droplets are separated in the mixing chamber, and the aerosol is mixed with the fuel gas and additional oxidant. The aerosol-fuel gas –oxidant mixture is ignited above the burner head.

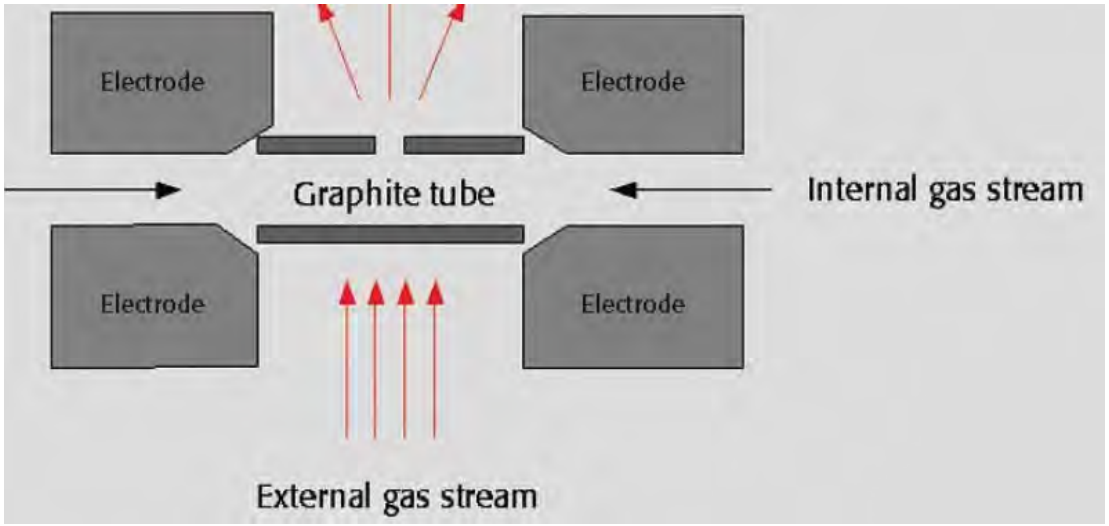


1 Additional oxidant supply
2 Fuel supply
3 Oxidant supply
4 Adjustment screw
5 Supply of solution for measurement
6 Lock nut
7 Nebulizer
8 Impact bead adjustment
9 Impact bead (silica; teflon coated)
10 Mixing chamber
11 Siphon trap
12 Siphon drain
13 Float
14 Burner head (50mm, 100mm)

Flame atomization if fast, economic and generates reproducible measurement results in the mg/L and % range.

Atomization in a graphite furnace

With this technique the sample to be investigated may be liquid or solid, and is introduced directly into a graphite tube. A controlled voltage is applied at the ends of the graphite tube, which is heated rapidly to high temperatures (up to 2600°C) due to its resistance. Using time-controlled stepwise heating of the graphite tube the sample solution is first dried, and then the matrix can be destroyed or removed, until finally the element of interest is atomized.



Graphite tube atomization results in LOD that are up to a factor of 1000 better than those obtained with flame atomization

Atomic Absorption Spectroscopy

Elemental Coverage in AAS

H					Flame Only												He
Li	Be				Flame & Furnace							B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	SB	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
				Th	Pa	U	Np	Pu	AM	Cm	Bk	Cf	Es	Fm	Mo	No	Lr

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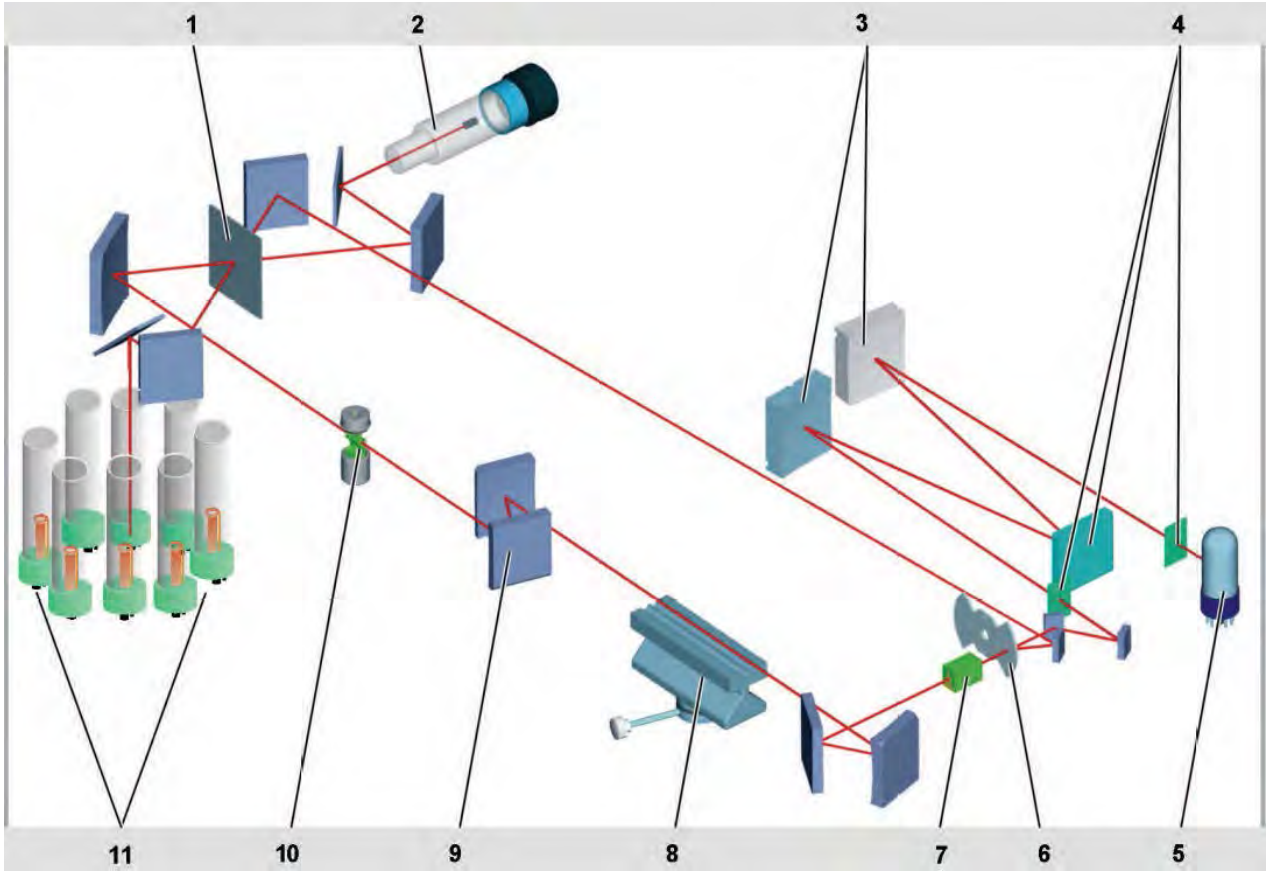
ANALYTIK JENA
ZEEnit 700P

AAS techniques with the ZEEnit 700 P

The ZEEnit 700 P as a compact device with 2 separate sample chambers includes, in combination with appropriate autosamplers and accessories, all important atomization techniques:

- ✓ Graphite tube technique for liquid samples.
- ✓ Graphite tube technique for solid samples.
- ✓ Flame technique stationary and as injection technique.
- ✓ Hydride and mercury cold vapor technique.
- ✓ HydrEA technique as coupling between hydride and graphite tube techniques.

Optical schematic of the ZEEnit 700 P



1 Beam splitter mirror
2 Deuterium hollow cathode lamp (D2HCL)
3 Monochromator mirror
4 Entrance slit, grid, exit slit
5 Photomultiplier
6 Sector mirror
7 Crystal polarizer
8 Burner in the flame sample chamber
9 Mirrors between the sample chambers
10 Electrodes with graphite tube in the furnace sample chamber
11 Lamp turret with 8 hollow cathode lamps

The sample beam or united sample/reference beam is projected onto the entrance slit of a grid monochromator, that is fitted with the fixed bandwidth of 0.2 nm / 0.5 nm / 0.8 nm / 1.2 nm.

Measurement principle of ZEEnit 700P

Graphite tube technique with Zeeman background correction

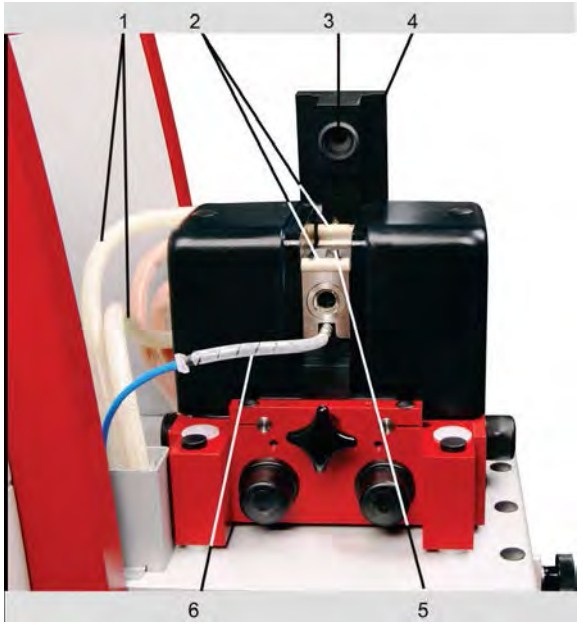
A unipolar, horizontal alternating magnetic field with a frequency of 200 Hz is applied to the graphite tube furnace. In the alternating field, the absorption levels of the analyte atoms of the current analysis line are split up into the horizontally polarized σ components σ+, σ– and the vertically polarized π components. The downstream crystal polarizer allows all radiation components with vertical alignment to pass without de-flection, the radiation components with horizontal alignment are sufficiently deflected that they do not impinge on the entrance slit. In both measurement phases "Magnetic field on" and "Magnetic field off", only the parts vertical to the magnetic field, i.e., only the vertically polarized parts of the HCL radiation, are considered.

All other techniques with deuterium background correction

The continuum radiation of a D2HCL is used for compensation of the background ab-sorption. The radiation of the line radiator (primary HCL) with its extremely narrow base line (resonance line) is element-specific and weakened non-specifically by scat-tering. In doing this, the total radiation is recorded. The radiation of the D2HCL is mainly weakened by the broad band, element-nonspecific absorption, the minimum element-specific part can be neglected. The formation of the difference between the two signals gives the element-specific absorption.

Zeeman graphite tube furnace

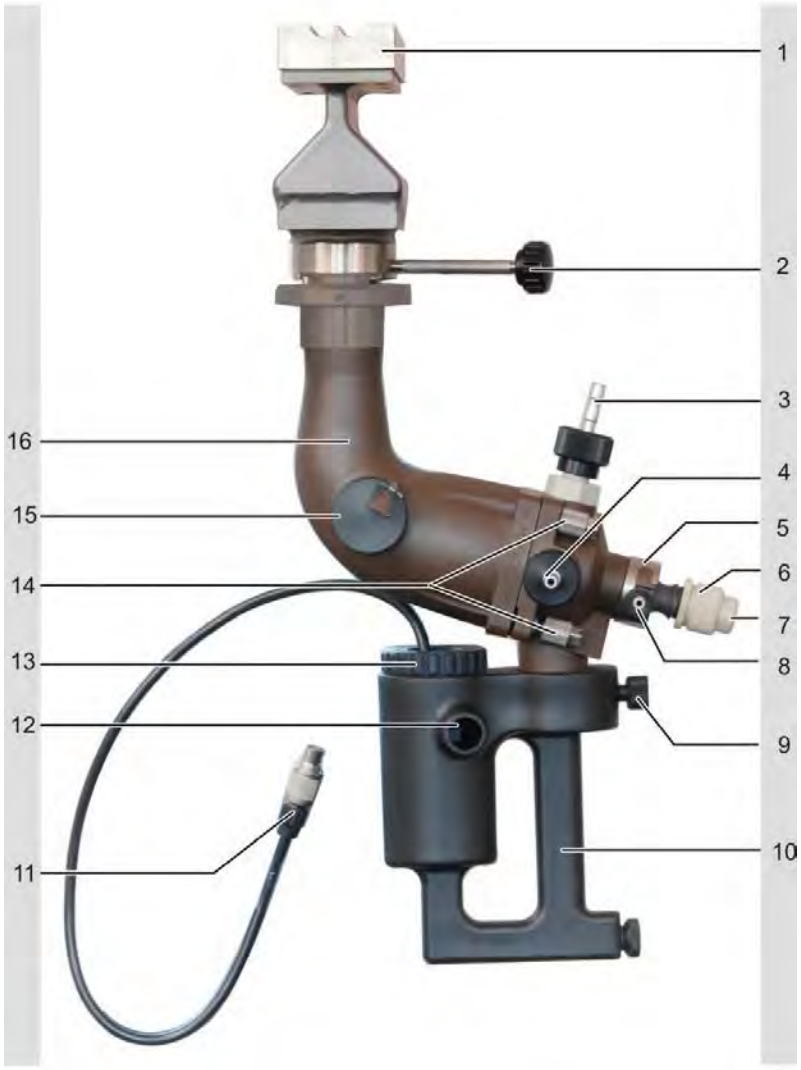
1 Inert gas supply purge gas (inner gas stream)
2 Cooling water supply
3 Pipetter opening
4 Cooling water supply
5 Inert gas supply protective gas (outer gas flow)
6 Stop for AS-GF
7 Locking screw
8 Furnace locking screw



Graphite tube furnace, open

1 Cooling water tubes
2 Furnace window
3 Upper electrode
4 Upper metal block, in the open position
5 Graphite tube furnace jacket
6 Protective gas supply

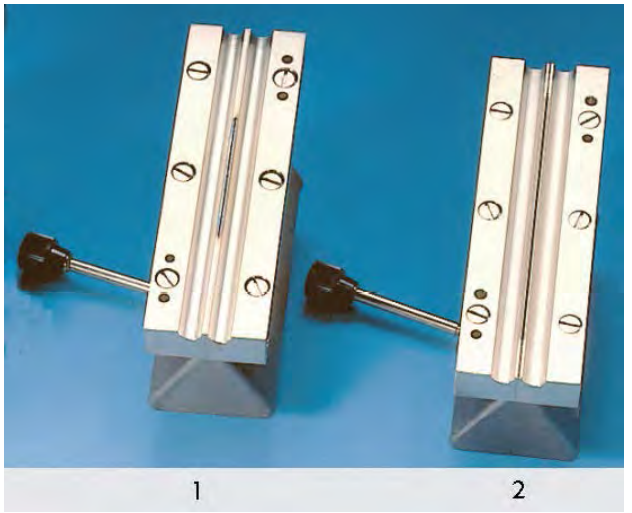
Nebulizer mixing chamber burner system for flame



1 Burner
2 Fixing screw for burner
3 Combustion gas supply
4 Additional oxidant supply
5 Locking ring for nebulizer
6 Nebulizer
7 Sample liquid supply
8 Oxidant supply
9 Fixing screw for siphon
10 Siphon
11 Connection of siphon sensor
12 Siphon outlet
13 Siphon sensor
14 Screw joints of mixing chamber parts
15 Safety plug
16 Mixing chamber tube

Burner types

1 50 mm one-slit burner
(standard burner)
2 100 mm one-slit burner



Lamp turrets and lamps

The ZEEnit 700 P has an 8-lamp turret with a write/read unit for coded lamps at the active position.

1 Antenna
2 Holder for lamps
3 Lamp with transponder

ASpect LS

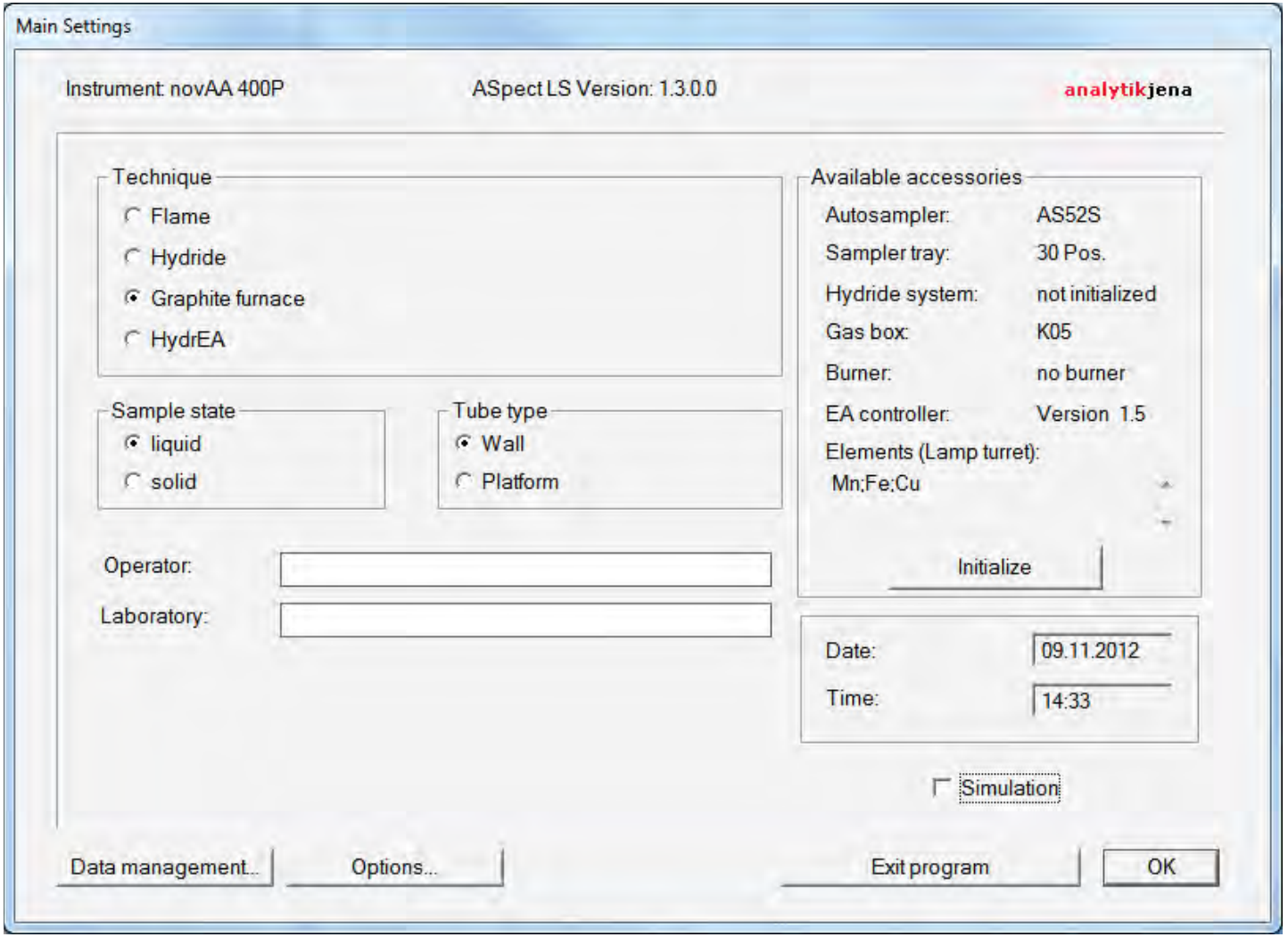
Software for Atomic Absorption Spectrometers

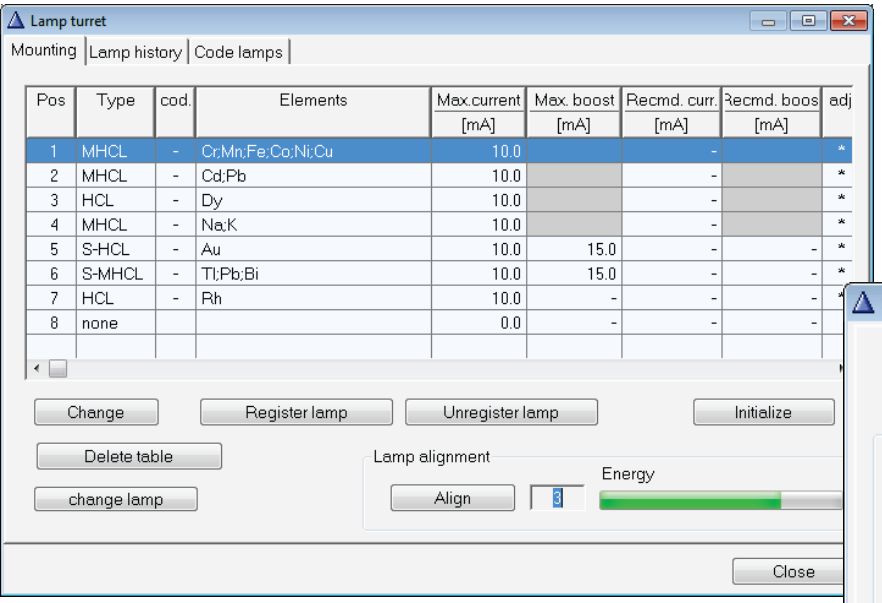
ASpect LS is the control and analysis software for the Analytik Jena AG atomic ab-sorption spectrometers.
The following accessories from Analytik Jena are supported by this software:

- ✓ AAS Autosamplers AS 51s/AS 52s and AS-F/AS-FD for flame and technique
- ✓ SSA 600 solid autosampler with or without liquid dosing
- ✓ Micropipetter unit MPE 60/MPE 60/2 and AS-GF for graphite tube technique
- ✓ Hydride systems HS60 / HS60A, HS55 / HS55A and hydride injector HS50 (hydride/Hg cold vapor technique)
- ✓ Hydride systems HS60 modular and HS55 modular
- ✓ SFS 6 Injection Switch (flame technique)

The method parameters for the measurement procedures can be optimized to the specific demands of the sample to be analyzed. The obtained data can be recalculat-ed, exported to various file formats and printed out.

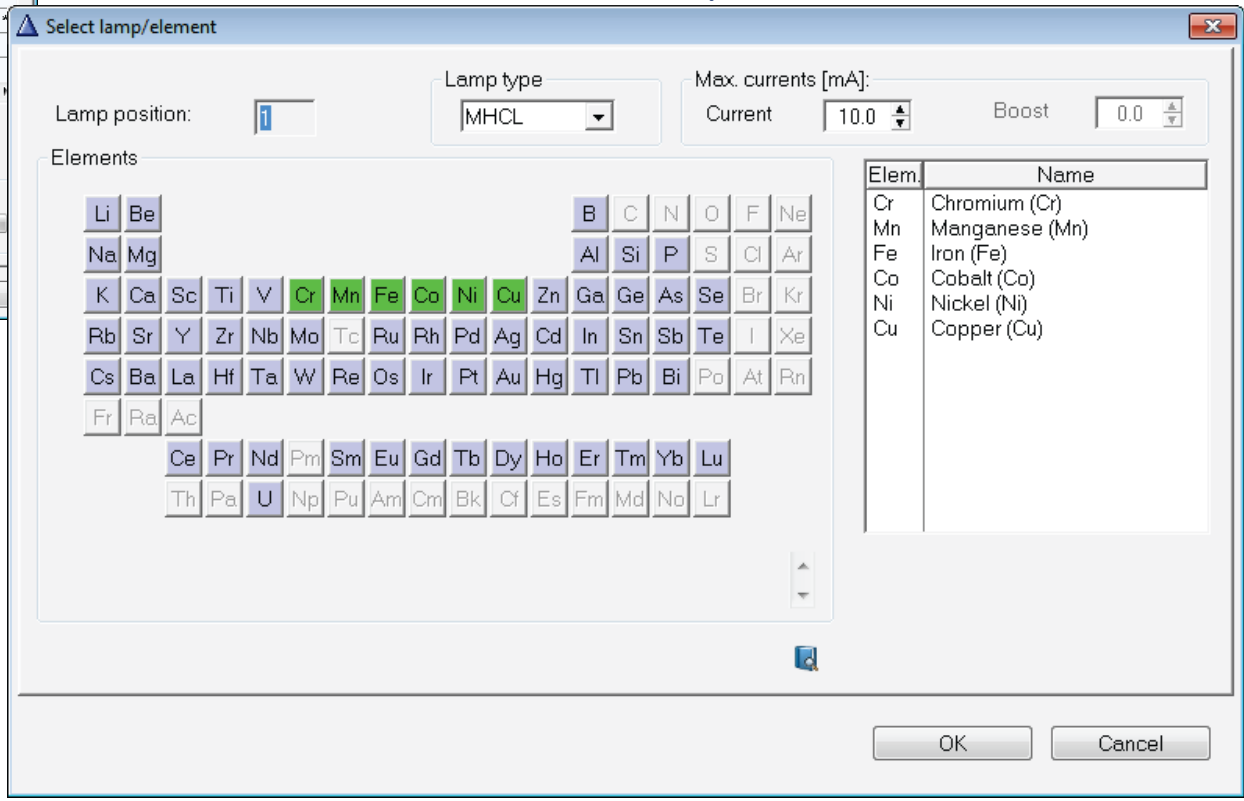
MAIN SETTINGS window

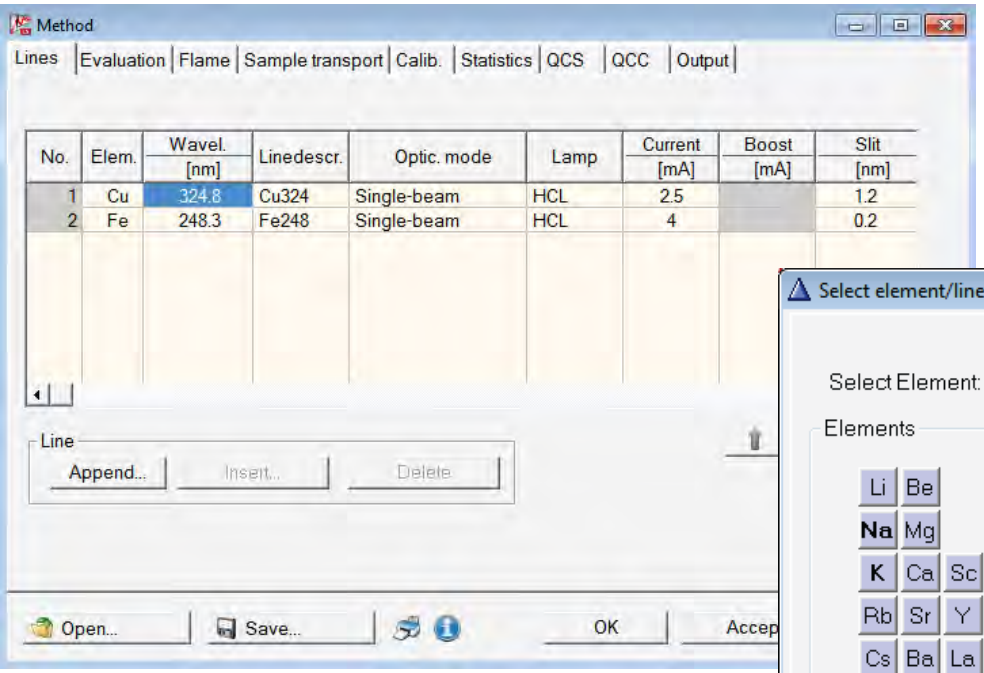




LAMP TURRET window

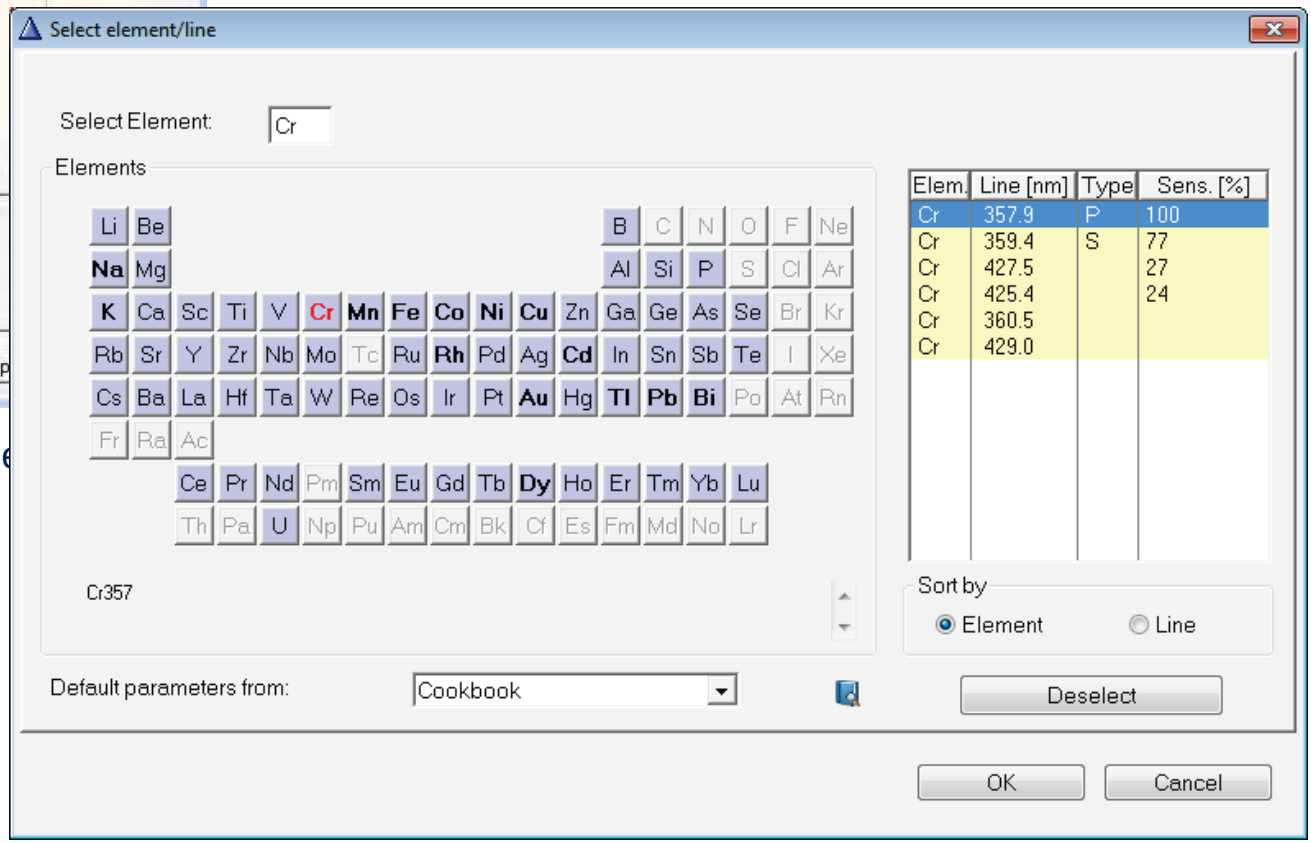
SELECT LAMP/ELEMENT window



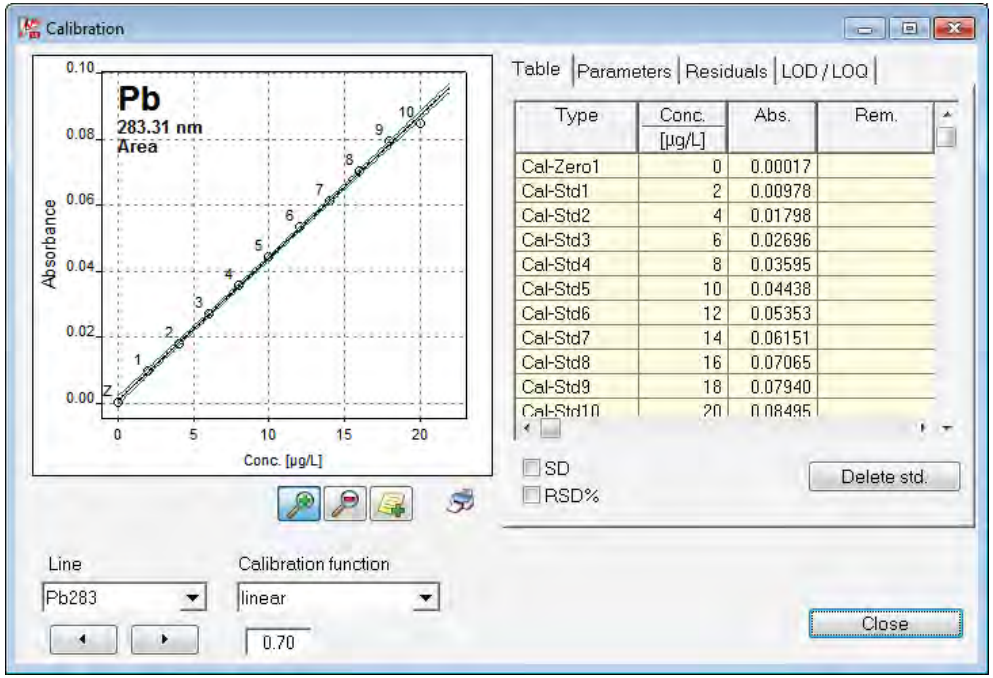


Window METHOD / LINES with selected eleme

SELECT ELEMENT/LINE window



CALIBRATION window



APPLICATION:

Pb Flame (Absorption) ZEEnit 700P

Performance: Pb

Charact. concentration	[mg/L/1%Abs]	:	0.3
Check concentration ("0.1 Abs.")	[mg/L]	:	7.0

Typical value (±30%) for 100mm-burner and C2H2/air flame

Spectrometer

Main line	[nm]	: 283.3	
Alternat. line	[nm]	: 217.0	-0.5x
Slit width	[nm]	: 1.2	
HCL current	[mA]	: 2.0	

Atomizer: Flame

Flame		:	C2H2/Air
C/O-Stoichiometric		:	0.13
Fuel flow	[NL/h]	:	65
Usable burner height	[mm]	:	5 - 10
Alternative flame		:	---

Notes

Diluent for stock solution	:	HNO3/1%
Ionisation buffer	:	KCl/0.1% or CsCl/0.1%
Interferences	:	Cu 216.5 nm / Fe 216.7 nm / Ni 216.6 nm Sb 217.6 nm / Pt 216.5 nm
Further alternative lines	:	261.4 nm - 17x / 368.3 nm - 30x
Background correction	:	---
Super-HCL	:	recommended (6/8 mA)
Contaminations	:	---

Element is toxic - careful handling!

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APPLICATION REPORT Example

ZEEnit 700P Page 1/8

Operator: FRANCISC *Laboratory:* FAC. MECANICA

Method Parameters Technique: Flame

Name: Plumb test *Version:* 1
Created: 9/1/202010:17 *Operator:* FRANCISC
Comment:
Lamp codes:
Pb: 191722

Lines

Line	*Elem.*	*Wavel. [nm]*	*Optic. mode*	*Lamp*	*Current [mA]*	*Boost [mA]*	*Slit [nm]*	*Meas time. [s]*	*PMT [V]*
Pb283	Pb	283.3	Single-beai	HCL	2	-	1.2	3.0	300

Evaluation/Background correction

Line	*Background corr.*	*Int.mode*	*AZDK*	*Smooth*	*D2 cur. [mA]*	*HC/BC rat.*
Pb283	no background	Mean	off	strong	-	-

Flame Parameters

Type: C2H2/air *Ox. control:* off
Burner type: 50 mm *Burner angle:* 0 deg *Nebulizer rate:* 0 mL/min

Line	*C2H2/air [L/h]*	*Burner height [mm]*
Pb283	55	6

Sample Transport

Autosampler: No *Delay time:* 5 s
Injection switch: No
Wash: after sample *Wash time:* 10 s

Calibration

Method: std. cal. *Std. prep.:* manual

Calibration Curve Parameters

Line	*Calib.func..*	*Intercept*	*Weighting*	*Check*	*Unit*
Pb283	linear	calculate	none	none	mg/L

Calibration table

No.	*Type*	*Pos*	*Rec*	*Pb [mg/L]*
1	Cal-Zero1	0	-	0
2	Cal-Std1	0	-	5
3	Cal-Std2	0	-	10
4	Cal-Std3	0	-	15
5	Cal-Std4	0	-	20

ASpect LS 1.5.5.0 Analytik Jena

ZEEnit 700P 11/24/202012:50 Page 5/8

Operator: FRANCISC *Laboratory:* PAC. MECANICA

Results

Results file: C:\Users\Public\Documents\Analytik Jena\ASpectLS\FL\RESULTS\Plumb test-20-09-01 1052.tps

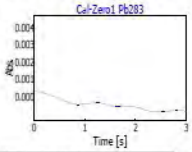
Instrument: ZEEnit 700P #150Z7P2108 *Technique:* Flame

Operator: FRANCISC (9/01/2020 10:52)

Comment:

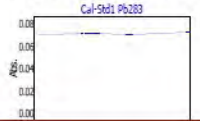
Line	Mean	SD	RSD[%]	CI	Unit	Rem.
Autozero	Plumb test(1)				Date:	9/1/202010:52
Pb283						
Cal-Zero1	Plumb test(1)				Date:	9/1/202010:53
Pb283						
Conc.1	0				mg/L	
Abs.	0.00014	0.00024	169.6			

Single values (Abs.): #1: -0.00011 #2: 0.00016 #3: 0.00038 (SEV: 257V)



Cal-Std1	Plumb test(1)				Date:	9/1/202010:54
Pb283						
Conc.1	5				mg/L	
Abs.	0.07699	0.00059	0.8			

Single values (Abs.): #1: 0.07682 #2: 0.07765 #3: 0.07651 (SEV: 257V)



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Operator: FRANCISC *Laboratory:* PAC. MECANICA

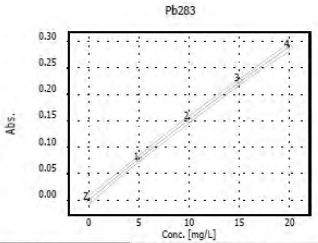
Line	Mean	SD	RSD[%]	CI	Unit	Rem.
Compute calib.	Pb283				Date:	9/1/202010:59

Pb283

R^2(adj.): 0.999287611 Slope: 0.01616 Abs./mg/L Char.conc.: 0.26981 mg/L/1%A

Method SD: 0.14966 mg/L

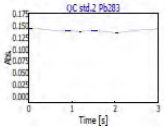
y=(a+bx)/(1+cx a=-.0005130 b=0.0161566 c=0.0056276



QC std.2	Plumb test(2)				Date:	9/1/202011:01
Pb283						
Conc.1	10.02	0.1564	1.6		mg/L	
Abs.	0.15283	0.00227	1.5			

Single values (Abs.): #1: 0.15046 #2: 0.15498 #3: 0.15304 (SEV: 257V)

QC:Nominal val.=10.00 mg/L Recovery=100.2 % OK



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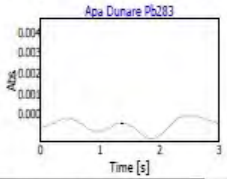
Operator: FRANCISC *Laboratory:* FAC. MECANICA

Line	*Mean*	*SD*	*RSD[%]*	*CI*	*Unit*	*Rem.*
Apa Dunare	Plumb test(2)				*Date:*	9/1/202011:05
Pre-DF: 1	*Wt.[g]:*		*Vol.[mL]:* 100	*AS-DF:* 1.0	*Blank corr.:*	off
Pb283						
Conc.1	0.0113	0.0142	125.6		mg/L	<LOD
Conc.2	0.0113	0.0142	125.6	0.7412	mg/L	<LOD
Abs.	-0.00033	0.00023	69.2			<LOD

Single values (Abs.): #1: -0.00020 #2: -0.00060 #3: -0.00020 (SEV: 257V)



Line	*Mean*	*SD*	*RSD[%]*	*CI*	*Unit*	*Rem.*
Apa potabila	Plumb test(2)				*Date:*	9/1/202011:07
Pre-DF: 1	*Wt.[g]:*		*Vol.[mL]:* 100	*AS-DF:* 1.0	*Blank corr.:*	off
Pb283						
Conc.1	0.0026	0.0030	114.9		mg/L	<LOD
Conc.2	0.0026	0.0030	114.9	0.7420	mg/L	<LOD
Abs.	-0.00047	0.00005	10.3			<LOD

Single values (Abs.): #1: -0.00049 #2: -0.00051 #3: -0.00042 (SEV: 257V)