

High Resolution Continuum Source AAS (HR CS AAS)

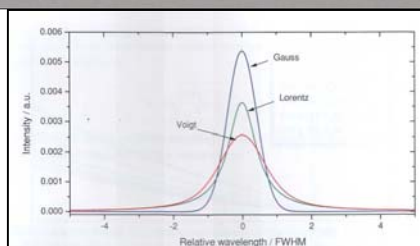
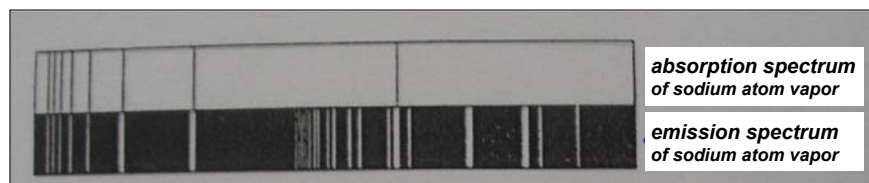
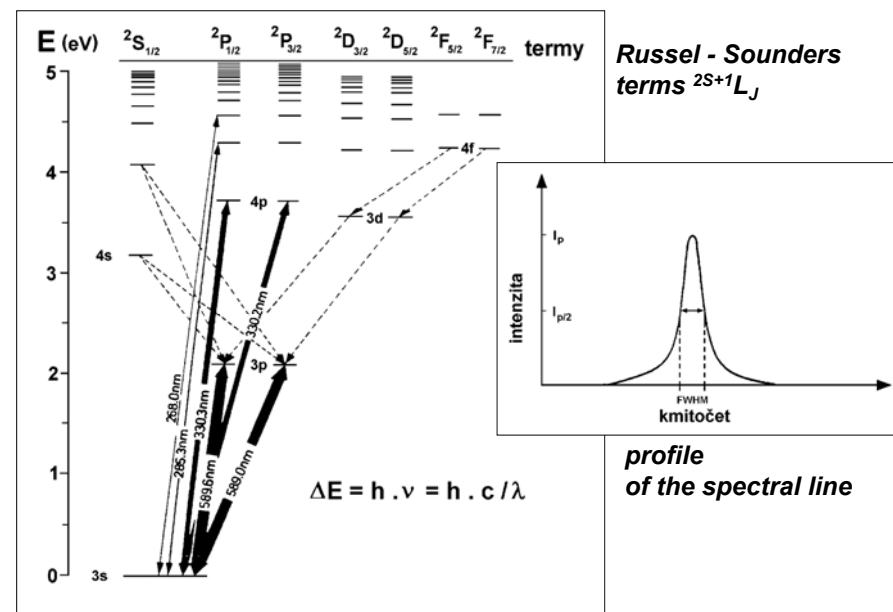


Bohumil Dočekal

Institute of analytical chemistry of the CAS, v.v.i., Brno



Grotrian diagram of energy levels for Na atom with electronic transitions

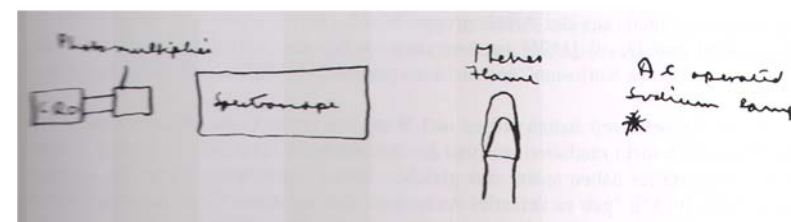


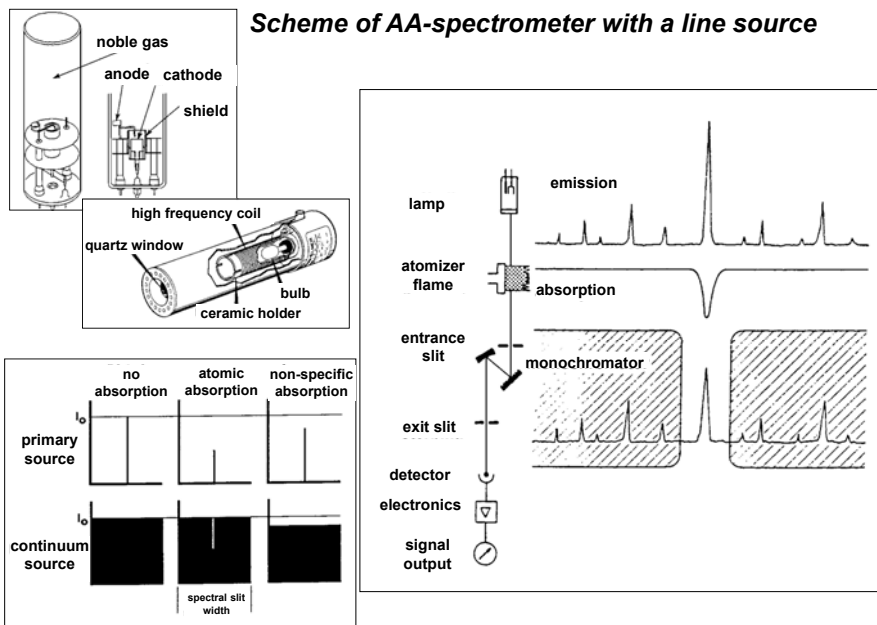
- *natural line width – Heisenberg principle*
(0.01-0.14 pm) $\Delta E \Delta t \sim 10^{-9} \cdot 10^{-8} \text{s}$
- *Doppler broadening – motion of individual emitters*
e.g. for Na at 2500°C, 1 bar is $\Delta \lambda = 4.5 \text{ pm}$
- *collision broadening (Lorenz) –*
 pressure broadening (on line wings) ~ 1 pm
 Starck effect for charged particles
- *overall line profile – Voigt profile*

Sir Alan Walsh – results from the years 1952-1962

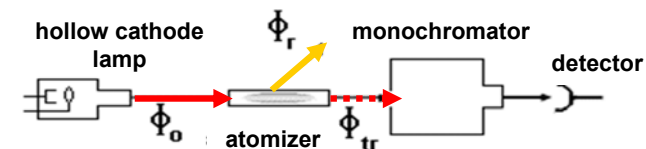


Notes from his notebook referred to April / May 1952





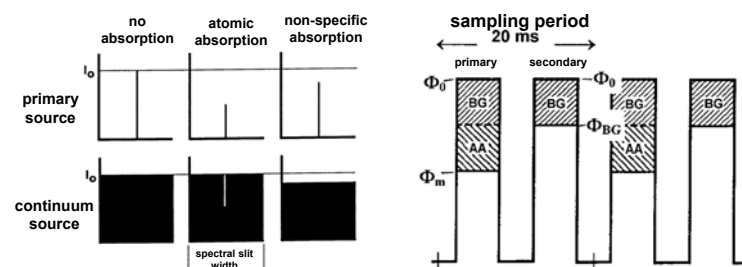
Non-specific absorption



attenuation due to light scattering $\sim r^6 / \lambda^4$

nonspecific absorption – molecular absorption, light scattering background attenuation

Continuum source (deuterium) background correction system



Simultaneous multielement atomic absorption continuum source spectrometer

O'Haver et al., H.Becker-Ross et al.

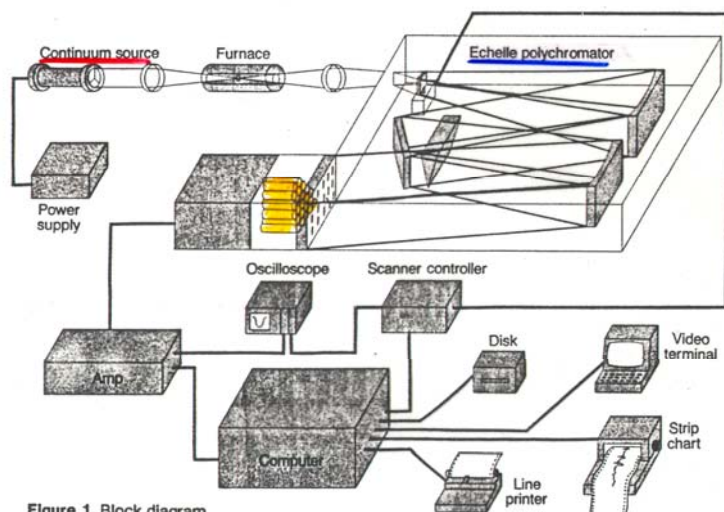
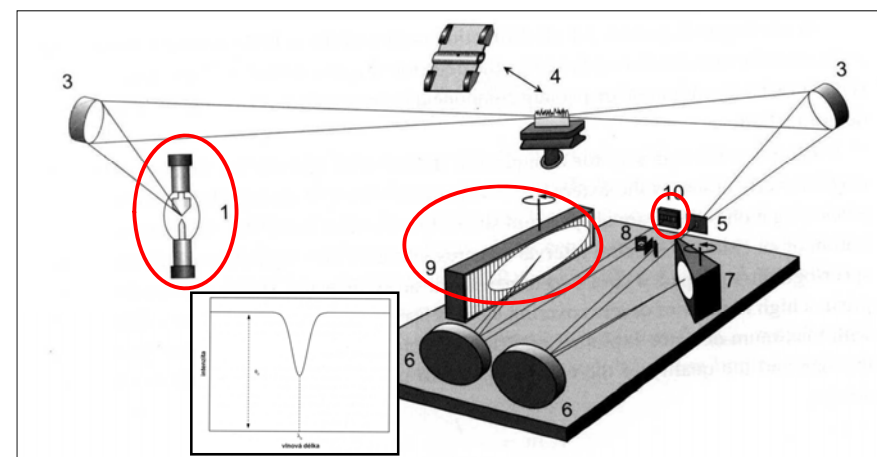


Figure 1. Block diagram of SIMAAC

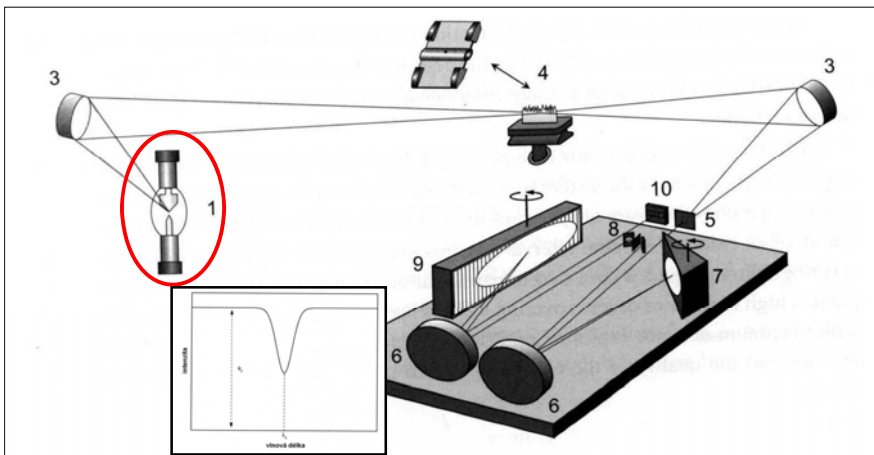
J.M.Harnly: *Anal.Chem.*, 58, 933A-943A (1986).

Continuum Source AAS



Scheme of a sequential HR-CS-AAS instrument, spectral range of 190-850 nm, double monochromator DEAMON with focal length of 300 mm. 300 W Xenon high pressure discharge lamp – 1, elliptical mirrors – 3, atomizer – 4, entrance slit – 5, parabolic mirror – 6, Littrow prism for spectral order selection – 7, mirror with 30 μ m wide diaphragm – 8, echelle grating with 75 grooves per millimeter – 9, CCD-detector with 512 individual pixels, 24 x 24 μ m in dimension, having spectral range of approx. 200 pm – 10

Continuum Source AAS



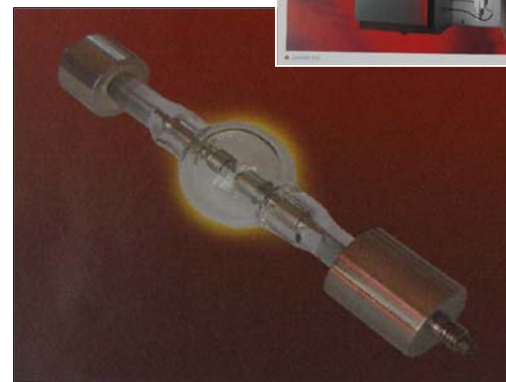
Scheme of a sequential HR-CS-AAS instrument, spectral range of 190-850 nm, double monochromator DEAMON with focal length of 300 mm.
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Continuum Source AAS



analytikjenaAG

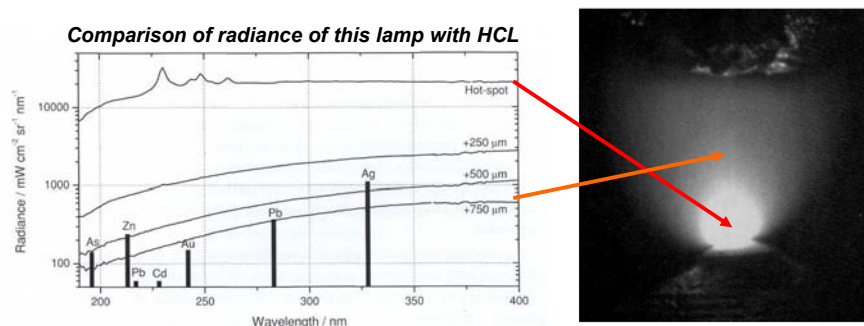
contrAA 300
(ANALYTIK Jena, Germany)



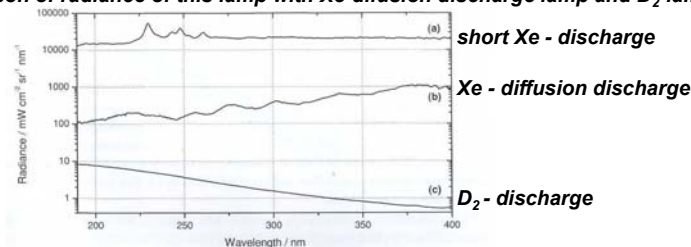
High pressure Xe-discharge lamp with a short arc (GLE, Berlin, Germany) and detail (right) of the discharge operated in hot spot mode.

High pressure Xe-discharge lamp with a short arc operated in hot spot mode.

Comparison of radiance of this lamp with HCL



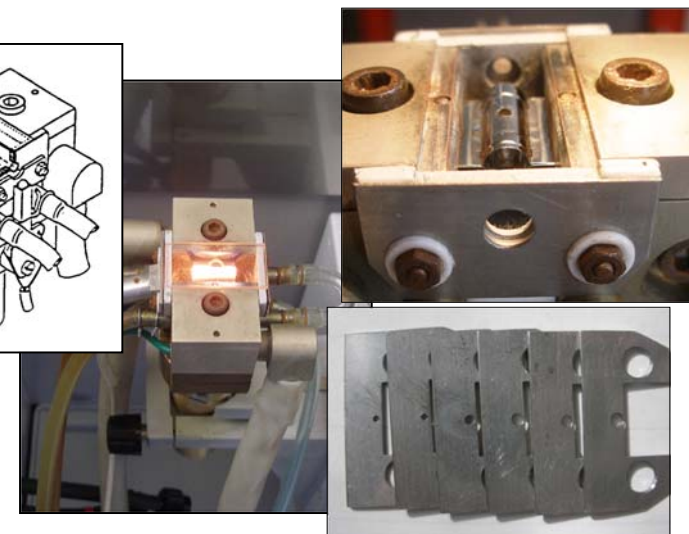
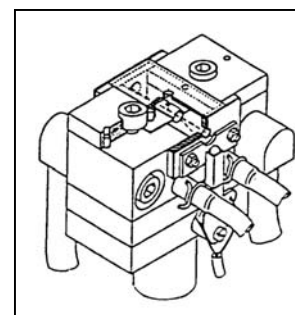
Comparison of radiance of this lamp with Xe-difusion discharge lamp and D₂-lamp



B. Welz, H. Becker-Ross, S. Florek, U. Heitmann: High-Resolution Continuum Source Atomic Absorption Spectrometry, Wiley-Verlag Chemie, Weinheim 2005 (ISBN 3-527-30736-2)

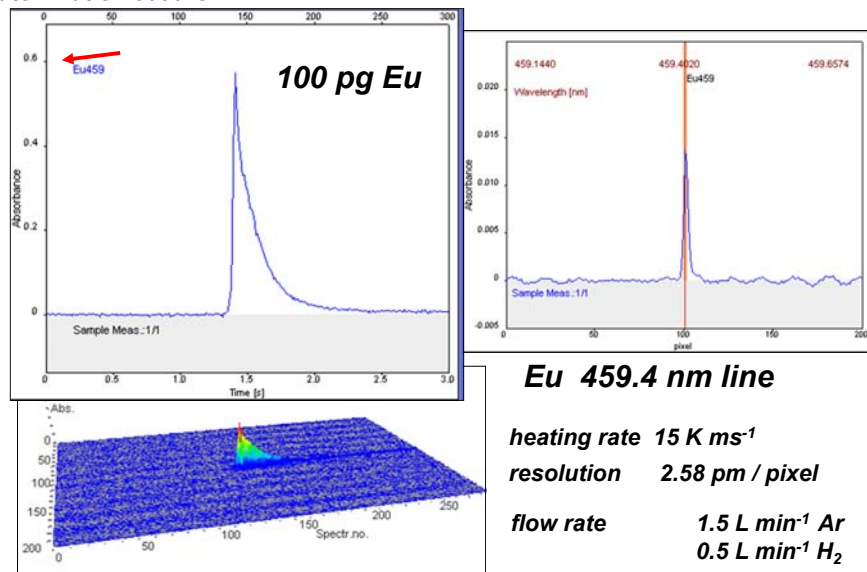
Electrothermal HR CS AAS – tungsten tube atomizer WETA 82

elimination of radiation of the hot atomizer (stray light) in AAS measurement

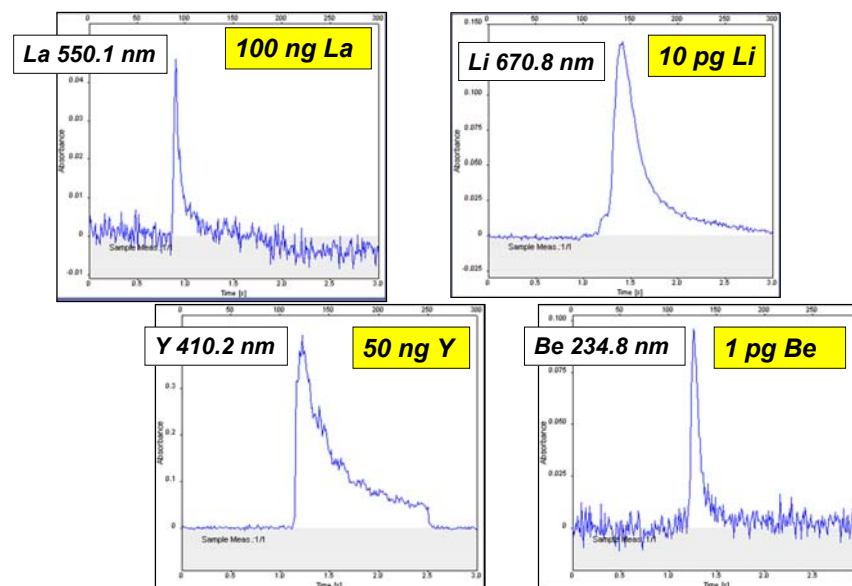


Electrothermal HR CS AAS – tungsten tube atomizer WETA 82

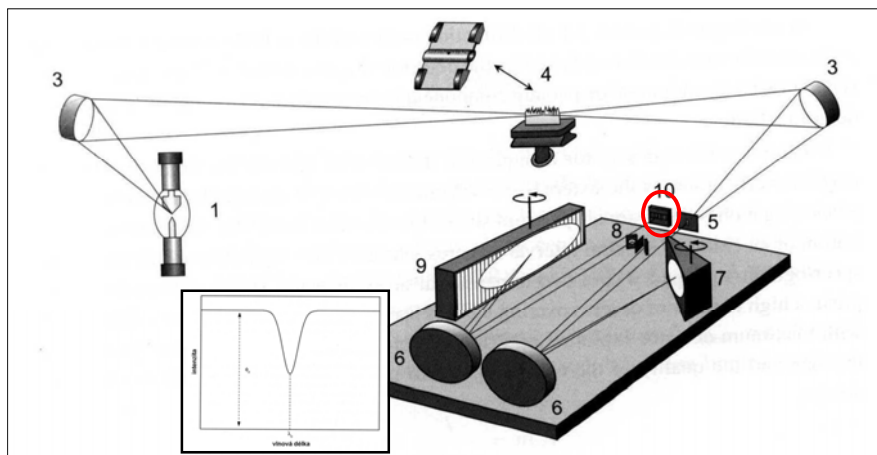
atomization 3000°C



High pressure Xe-discharge lamp – Universal source for determination of any element

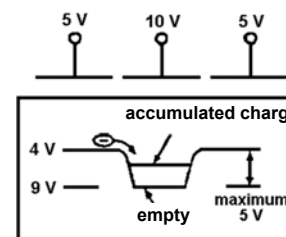


Continuum Source AAS

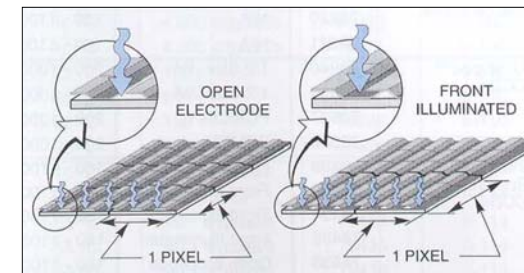


Scheme of a sequential HR-CS-AAS instrument, spectral range of 190-850 nm, double monochromator DEAMON with focal length of 300 mm.

300 W Xenon high pressure discharge lamp – 1, elliptical mirrors – 3, atomizer – 4, entrance slit – 5, parabolic mirror – 6, Littrow prism for spectral order selection – 7, mirror with 30 μm wide diaphragm – 8, echelle grating with 75 grooves per millimeter – 9, CCD-detector with 512 individual pixels, 24 x 24 μm in dimension, having spectral range of approx. 200 nm – 10

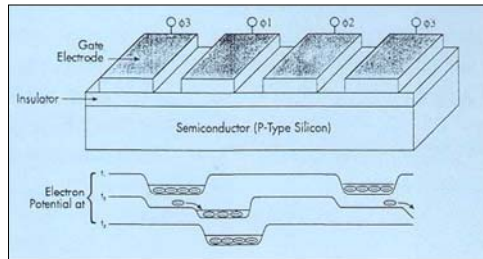


Scheme of the CCD detector



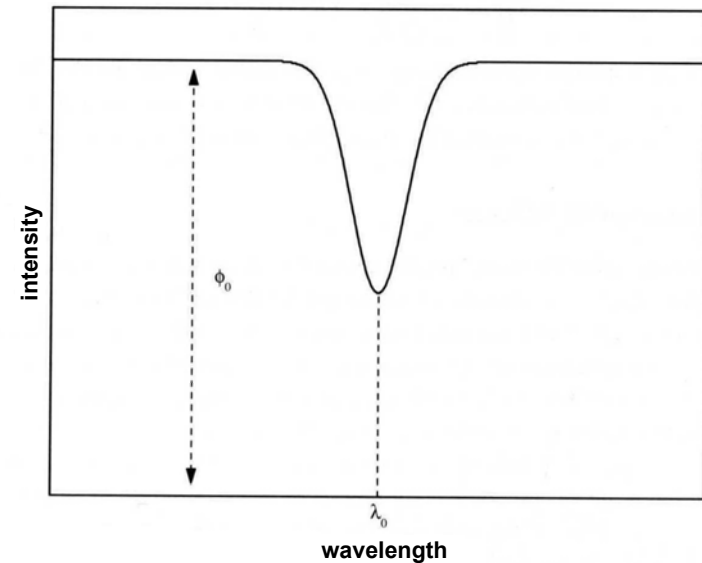
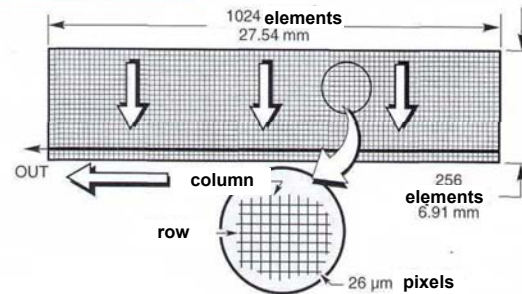
back-thinned CCD - higher spectral sensitivity in UV range, low noise, wide dynamic range

signal reading from CCD - detector



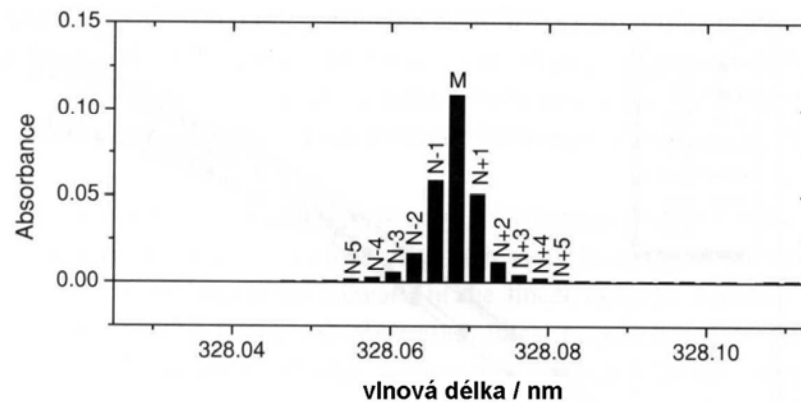
charge transfer

read-out
binning



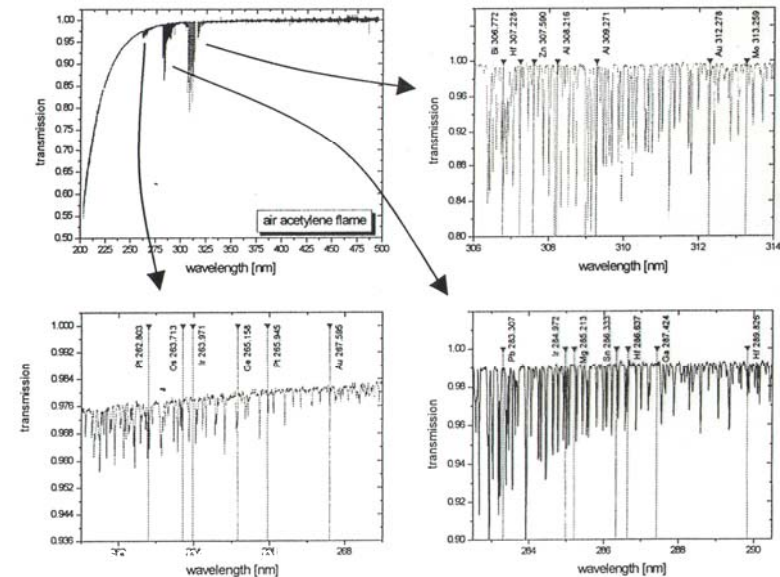
Scheme of continuous spectrum with one absorption line of the analyte.
 ϕ_0 represents original, non-attenuated radiation in measurement of atomic absorption.

Continuum Source AAS

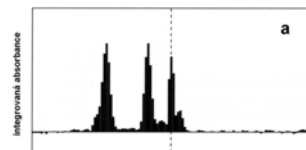


absorption profile of Ag 328,068 nm line monitored by CCD – pixels.
M - central pixel in maximum line profile, N – side pixels oriented symmetrically

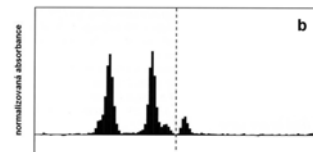
Overview spectra of the flame absorption



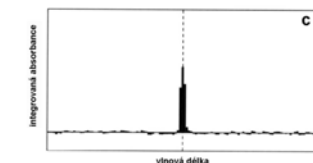
Correction of non-specific absorption in Continuum Source AAS



a – spectrum close to the analytical line (dashed line)

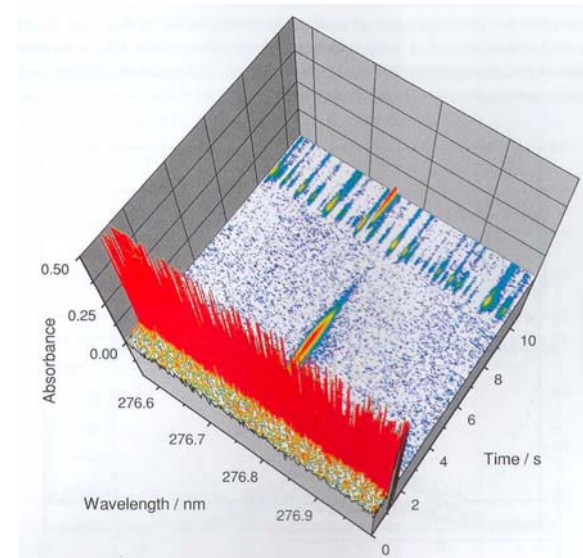


b – reference spectrum of the fine molecular structure used in compensation of background



c – absorption profile corrected for background

Time resolved spectrum in Continuum Source AAS

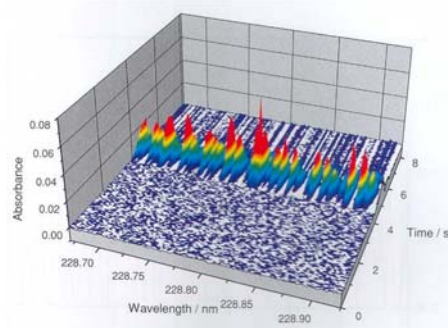


spectrum of coal close to Tl I 276.787 nm line, pyrolysis 600°C, atomization 1700°C

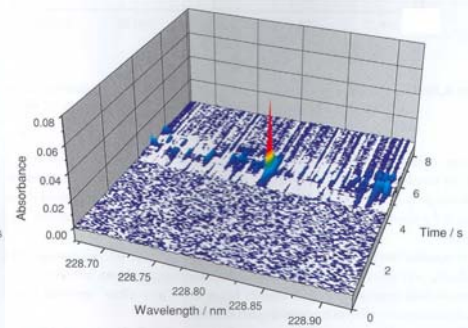
Time resolved spectrum

of human urine sample close to Cd 228,802 nm analytical line

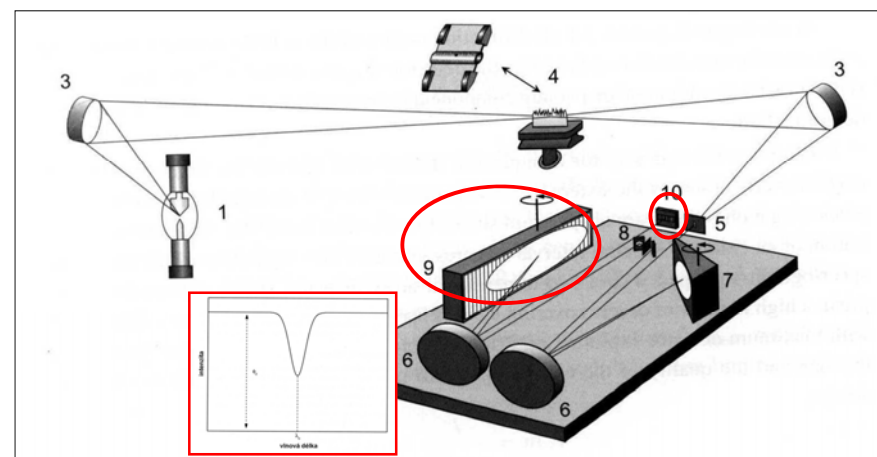
no correction



with background correction



Continuum Source AAS

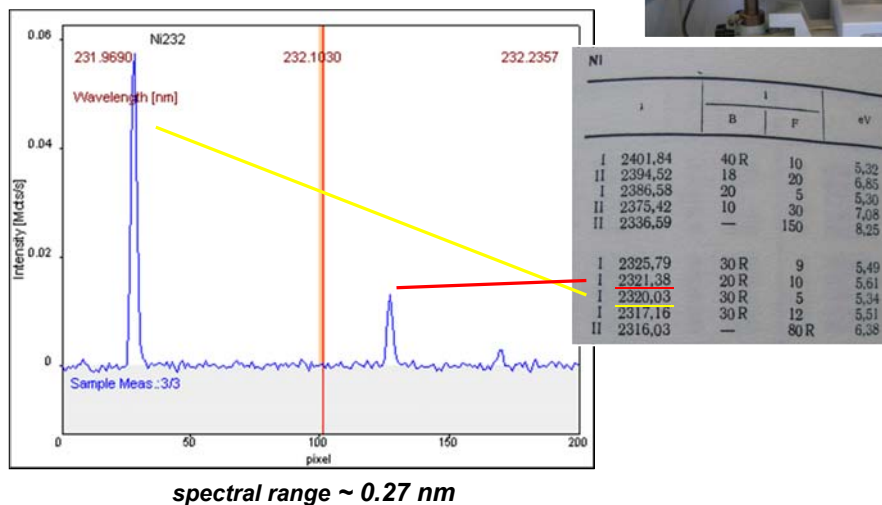


Scheme of a sequential HR-CS-AAS instrument, spectral range of 190-850 nm, double monochromator DEAMON with focal length of 300 mm.

300 W Xenon high pressure discharge lamp – 1, elliptic mirrors – 3, atomizer – 4, entrance slit – 5, parabolic mirror – 6, Littrow prism for spectral order selection – 7, mirror with 30 μ m wide diaphragm – 8, echelle grating with 75 grooves per millimeter – 9, CCD-detector with 512 individual pixels, 24 x 24 μ m in dimension, having spectral range of approx. 200 pm – 10

High spectral resolution

spectrum of Ni - Hollow Cathode Lamp at 232.0 nm
(Intensitron, 25 mA), resolution 1.34 pm / pixel

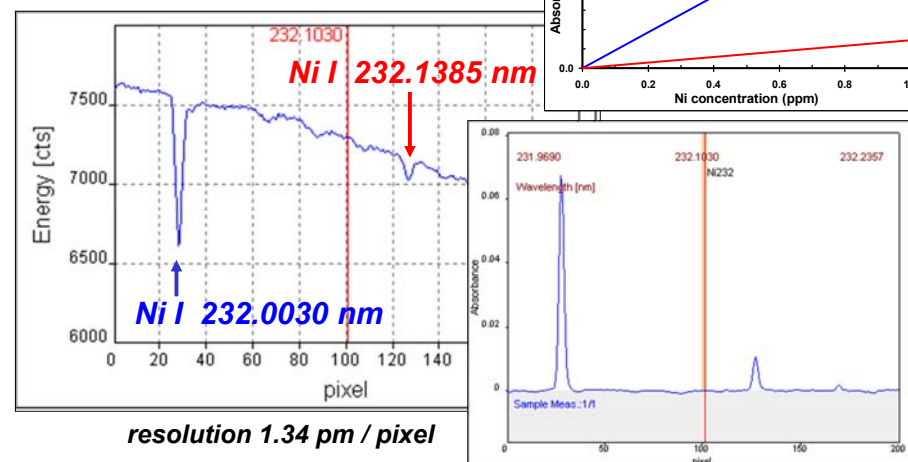


Absorption spectra

1 ppm Ni – 4" air-acetylene flame

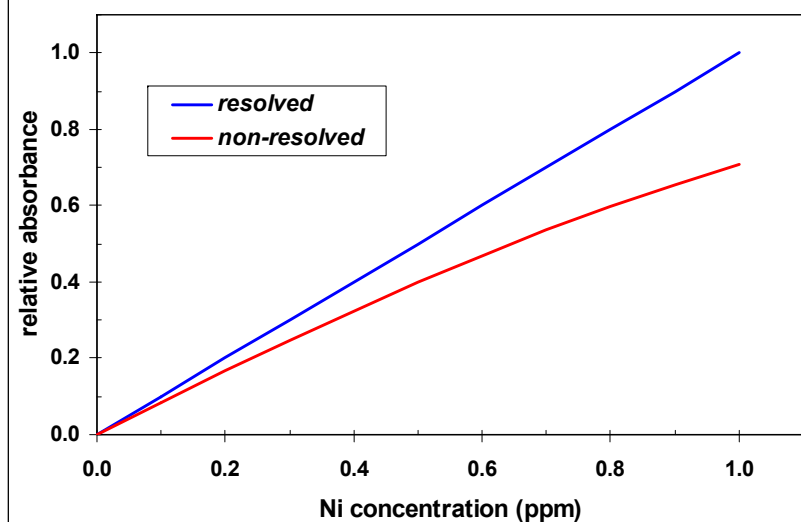
characteristic concentration

0.0236 and 0.1517 mg/L / 1 % abs. (3 pxls)



Calibration

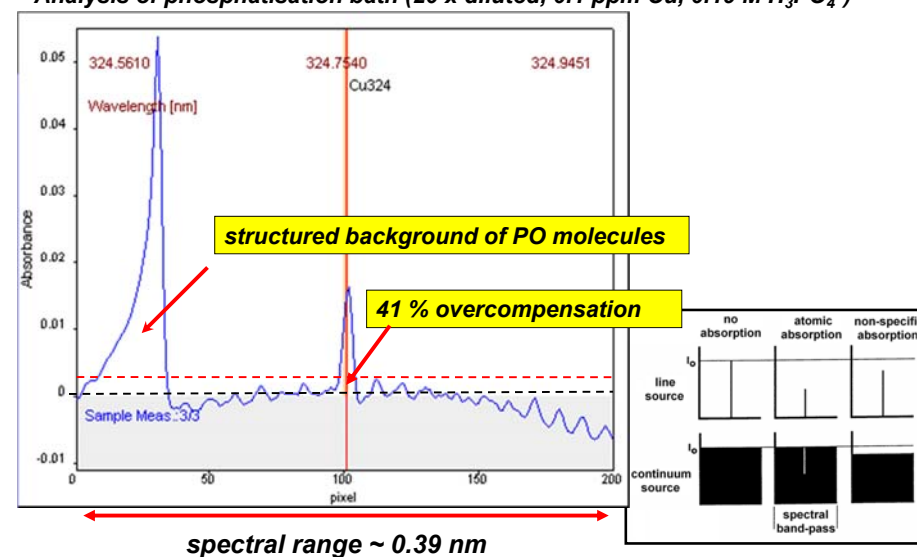
Influence of spectral resolution on response



Interference effect of PO molecules in determination of Cu

AAS with HCL line source and D_2 -kompensation system

Analysis of phosphatisation bath (20 x diluted, 0.1 ppm Cu, 0.19 M H_3PO_4)



Flame atomic spectrometry

Emission vs. Absorption

air-acetylene flame, 4" burner head

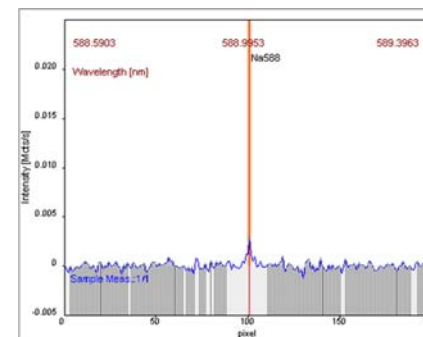
determination of Na in 3 - 4 mol/L concentrated solutions for dialysis requirement – accuracy and precision of results: RSD (%) = 0.3



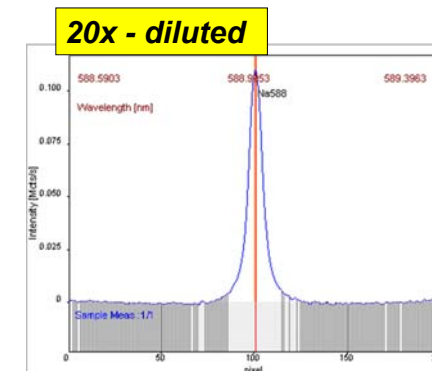
Flame atomic emission spectrometry

air-acetylene flame, 4" burner head

close to LOD at Na 589.0 nm line

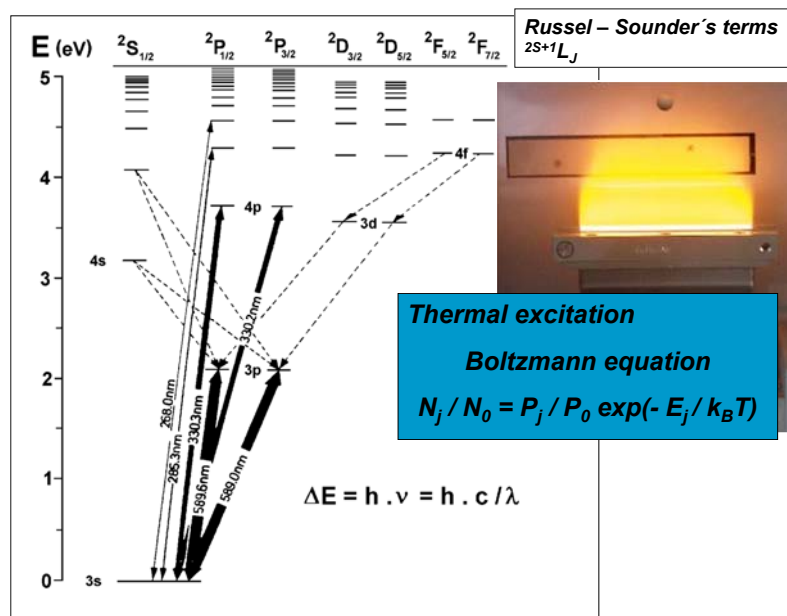


resolution 4.05 pm / pixel,
spectral range ~ 0.81 nm



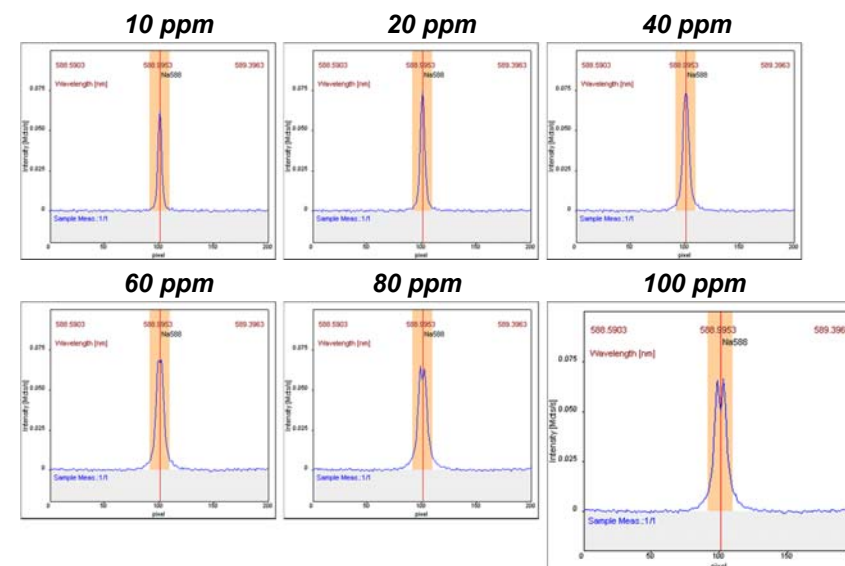
Korunní mineral water
(~ 103 mg/L Na)

Na – energy level diagram



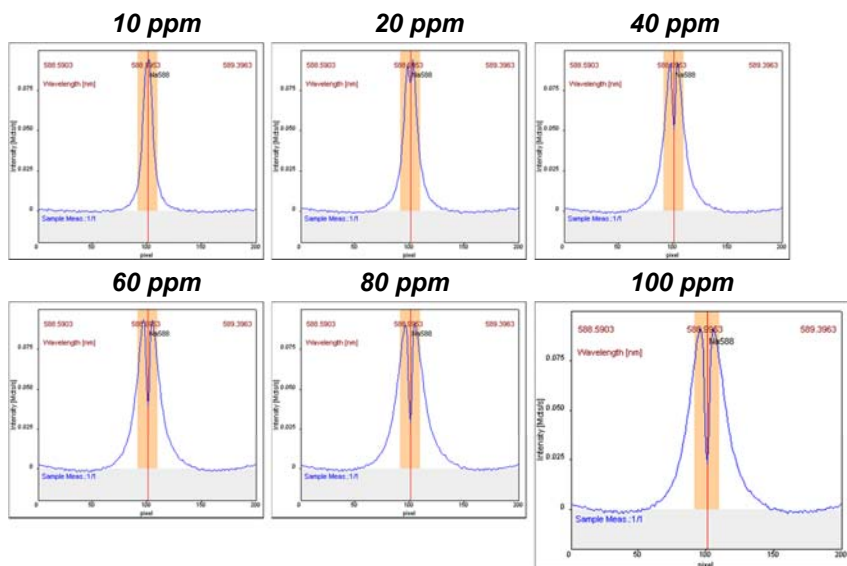
Flame atomic emission spectrometry

characteristics of air-acetylene flame – transversal view



Flame atomic emission spectrometry

characteristics of air-acetylene flame – longitudinal view



Flame atomic spectrometry

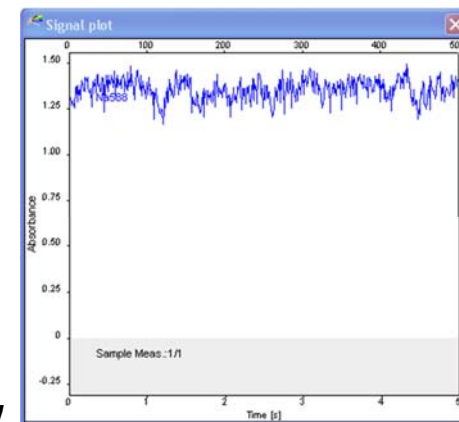
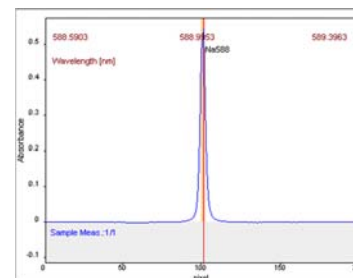
Emission vs. Absorption

air-acetylene flame, 4" burner head

determination of Na in 3 - 4 mol/L concentrated solutions for dialysis
1 ppm Na standard, read time 5 s, sampling frequency 0.01 s, 500 spectra

Absorption (588.9953 nm)

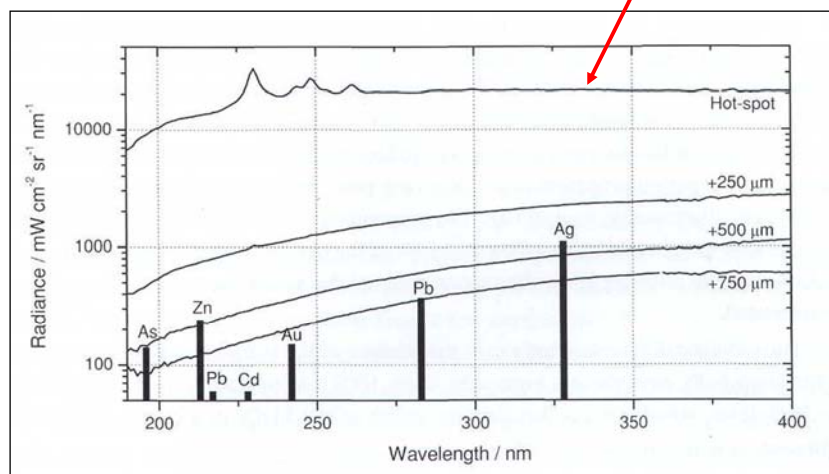
final fluctuation RSD (%) = 0.19



! dilution factor 100,000 !

Xe hot-spot discharge vs. HCL

short Xe - discharge



B.Welz, H.Becker-Ross, S.Florek, U.Heitmann: High-Resolution Continuum Source Atomic Absorption Spectrometry, Wiley-Verlag Chemie, Weinheim 2005 (ISBN 3-527-30736-2)

Flame atomic spectrometry

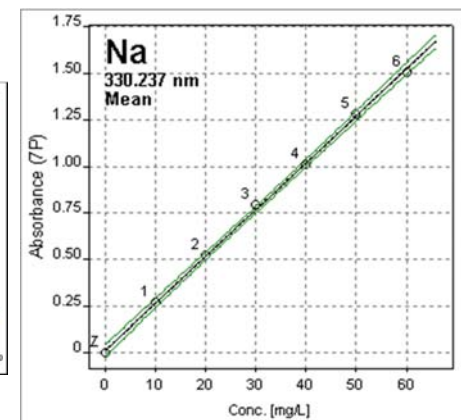
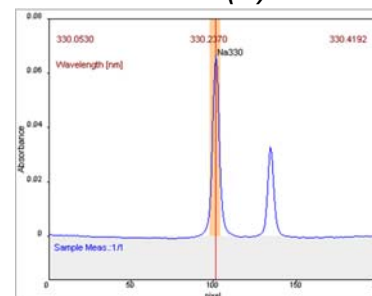
Emission vs. Absorption

air-acetylene flame, 4" burner head

determination of Na in 3 - 4 mol/L concentrated solutions for dialysis
0 - 60 ppm Na standards, read time 5 s, 6 replicates, 7 pxls

Absorption (330.237 nm)

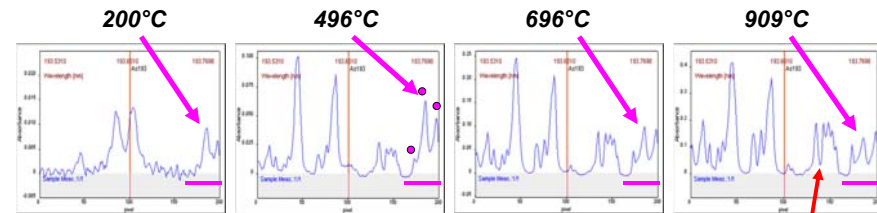
final fluctuation RSD (%) = 0.15



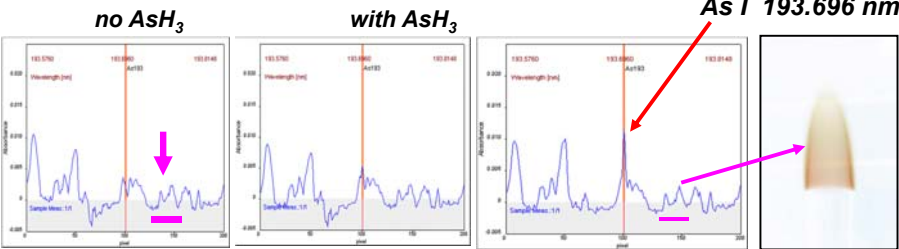
! dilution factor 1,000 x !

Absorption spectra of oxygen – effect of temperature

QTA - 100 ml /min Ar + 20 ml /min O₂



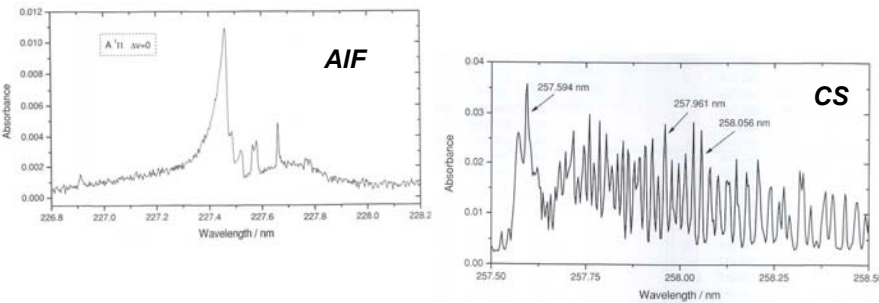
miniature hydrogen diffusion flame



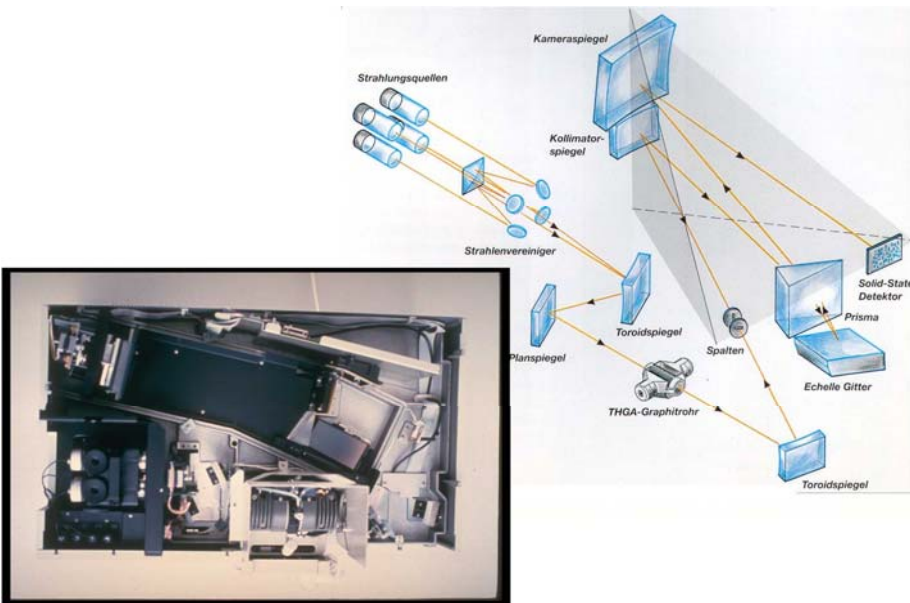
Determination of non-metals by AAS – molecular absorption structures

Determination of non-metals by air-acetylene flame AAS

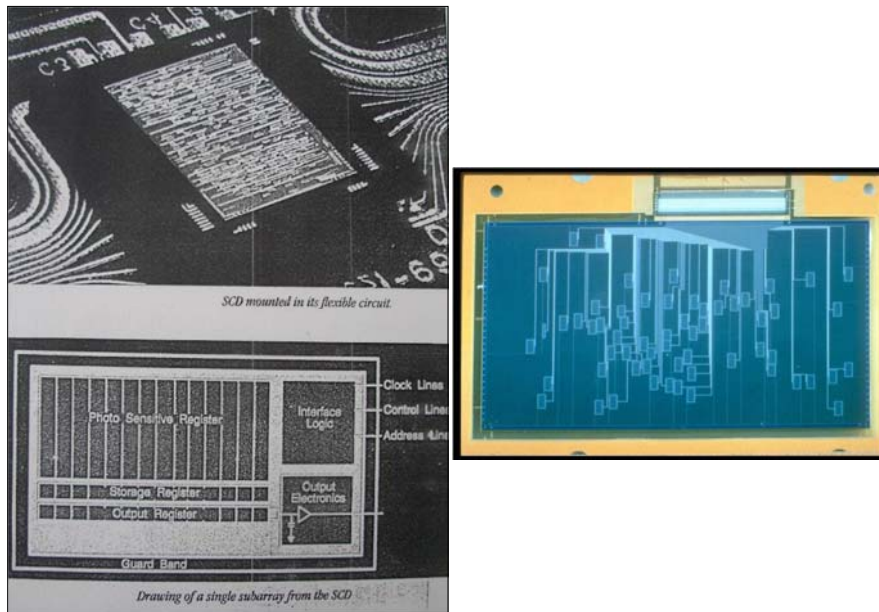
element	molecules	λ (nm)	LOD (ppm)
P	PO	325	2.6
S	CS	258	2.4
F	GaF, AlF	211, 227	1
Cl	InCl	267	3



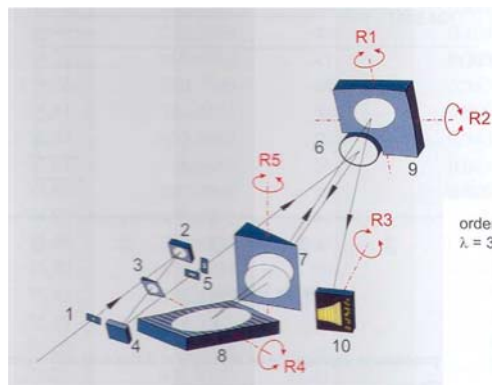
Line Source Simultaneous Multielement AAS (P-E SIMAA 6000)



Segmented „solid state“ detectors in AAS

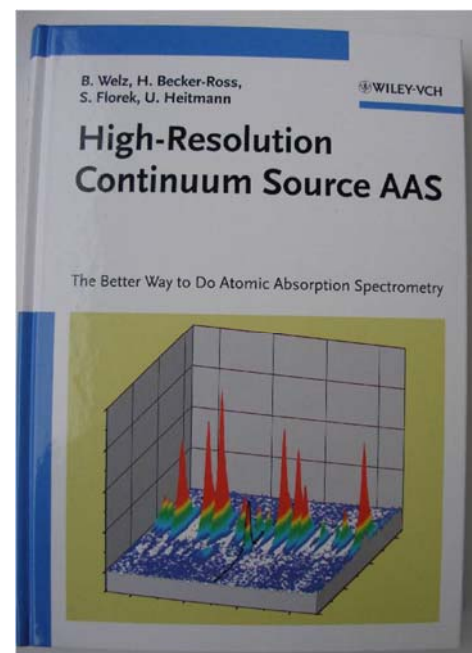
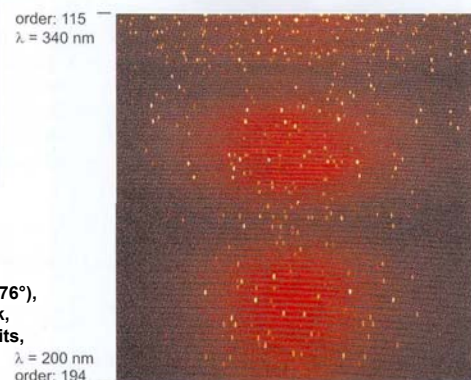


ARES – prototype of simultaneous HR CS AAS (ISAS, Berlin)



- 1 – entrance slit,
- 2-5 – dispersive slit illumination,
- 6 a 9 – spherical mirrors,
- 7 - prism,
- 8 - echelle grating (50 grooves/mm, blaze angle 76°),
- 10 - array CCD-detector (1024x1024 pixel) Kodak,
- R1-R5 – piezo-electrically controlled rotation units,
- resolution $\lambda/80000$

Echelle spectrum



B. Welz, H. Becker-Ross, S. Florek,
U. Heitmann:

*High-Resolution Continuum Source
Atomic Absorption Spectrometry*

Wiley-Verlag Chemie, Weinheim 2005
(ISBN 3-527-30736-2).



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