The GLADNET Catalogue of Glow Discharge Spectra: Part 1 finished !

(... almost)

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Marie Curie RTN GLADNET (2007-2011), Workpackage 5, project P16

the team working on the catalogue:

- LECO Plzeň, Czech Rep. - Zdeněk Weiss (P16 coordinator)
- London Metropolitan University, UK - Edward Steers
  - Viktoria Weinstein (now at EAG Labs., France)
- Imperial College London, UK - Juliet Pickering
  - Sohail Mushtaq (now at London Metropolitan Univ.)
- IFW Dresden, Germany - Volker Hoffmann
  - Varvara Efimova

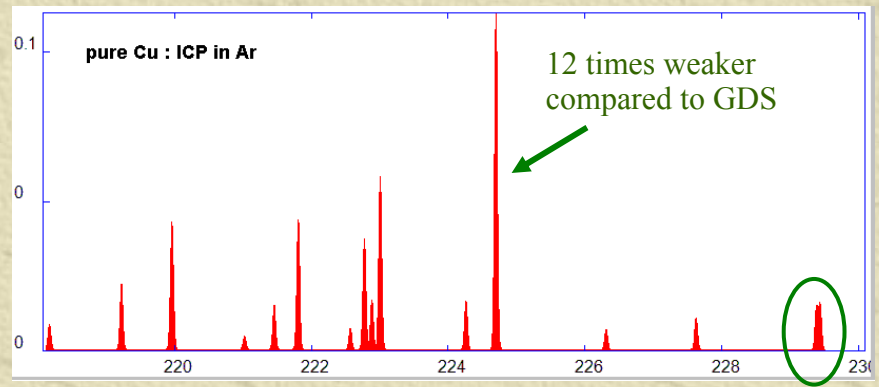
- Jovica Jovović, Univ. of Belgrade, Serbia
- Petr Šmíd, ŠKODA Výzkum, Czech R., (now at AQura GmbH., Germany)

instrument suport:

- Michael Analytis, Spectruma GmbH., Germany
- Patrick Chapon, Horiba Jobin Yvon, France

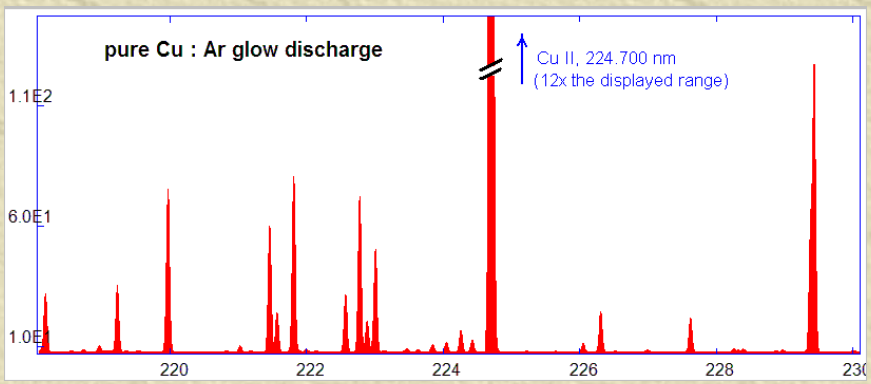
- 2007-2008 :
  - preliminary experiments with FTS and the GDS500A (LECO)
  - data processing strategies set and tested
  - Plasus SpecLine Spectroscopy software purchased
- 2009
  - paper in JAAS (*J. Anal. At. Spectrom.*, 2009, 24, 27–33)
  - 1st round of the FTS work: **Cu, Zn, Al, Mg**, (Fe) + alloys
- 2010
  - 2nd round of the FTS work: **Fe, Mn, Ni, Cr, Mo, V, W, Nb, Co, Ti, Zr, Ta**
- 2011
  - data processing, programming, further data from the GDS 500A (LECO)
  - monochromator data collected on the GD Profiler (Horiba Jobin Yvon)
  - measurements on the GDA650 (Spectruma), sputter rates measured at IFW
- 2012
  - 3rd round of the FTS work: (Fe, Mo, alloys), standard lamps
  - intensity calibration of FT spectra finished
  - part I of the catalogue – Fe, Zn, Cu (almost) prepared for publication

Why a separate catalogue for GD excitation ?



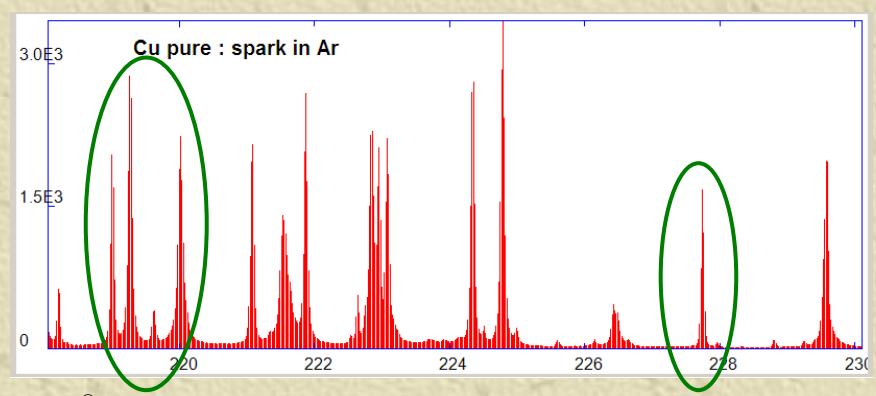
ICP spectrum of Cu

C. Shierle, A.P. Thorne,
Spectrochim. Acta 50B, 27-50 (1995)



GD spectrum of Cu:

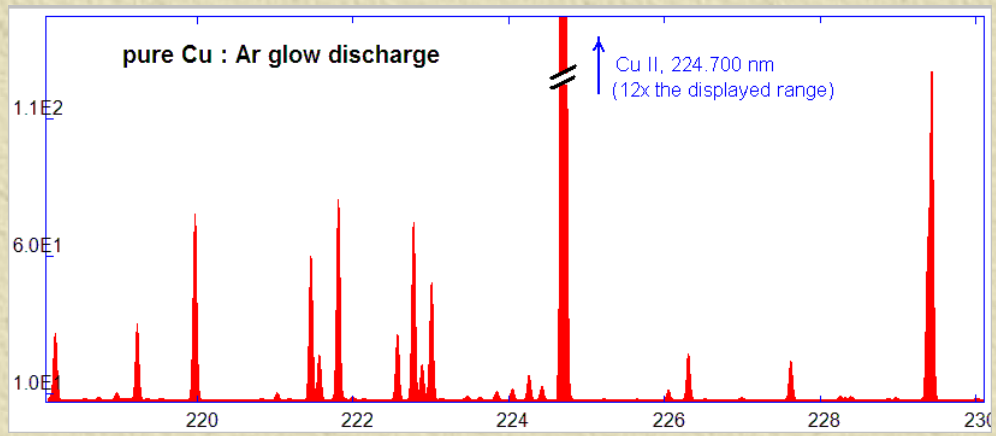
the Ar^+-ACT excited Cu II line at 224.700 nm is by far the strongest line in this region



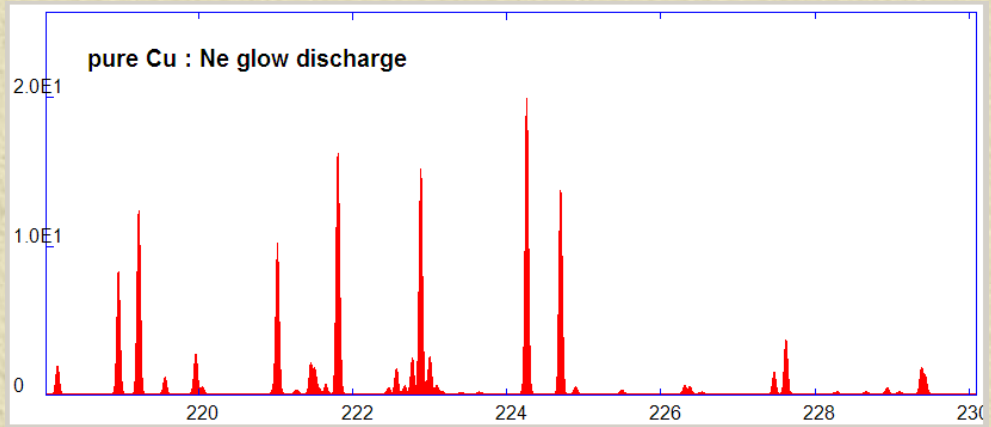
spark spectrum of Cu

emission spectra from different sources differ !

glow discharge spectra with different discharge gases



Cu in Ar

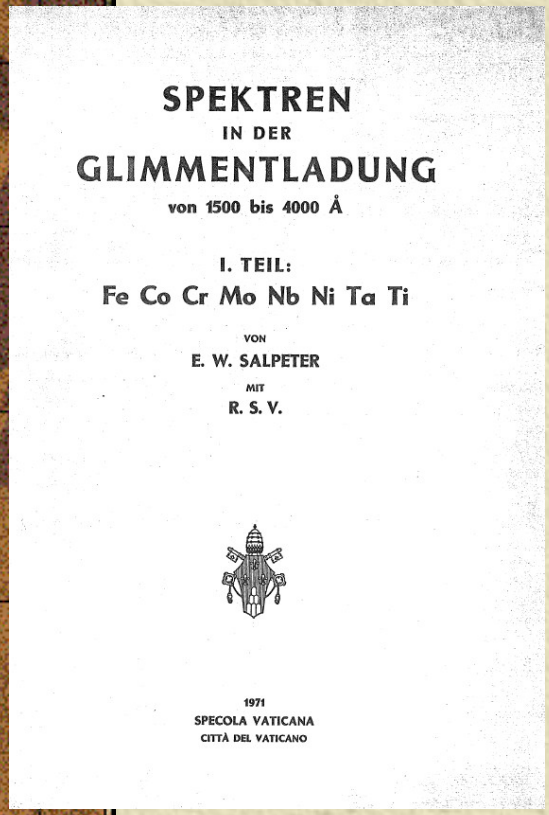


Cu in Ne

GD spectra with different discharge gases differ !

- relative intensities in a GD spectrum largely depend on interactions of the analysed element with species related to the discharge gas (ions, metastables)

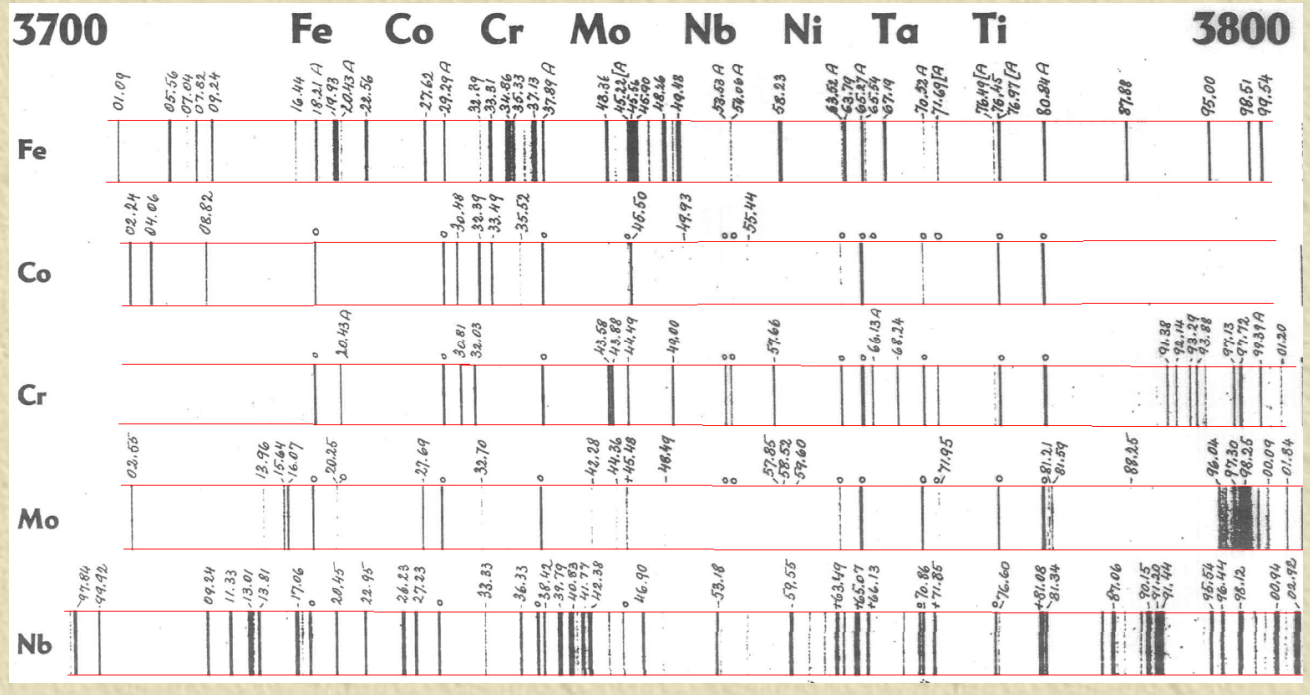
Existing reference sources for GDS


SPEKTREN
IN DER
GLIMMENTLADUNG
von 1500 bis 4000 Å

I. TEIL:
Fe Co Cr Mo Nb Ni Ta Ti

VON
E. W. SALPETER
MIT
R. S. V.

1971
SPECOLA VATICANA
CITTÀ DEL VATICANO



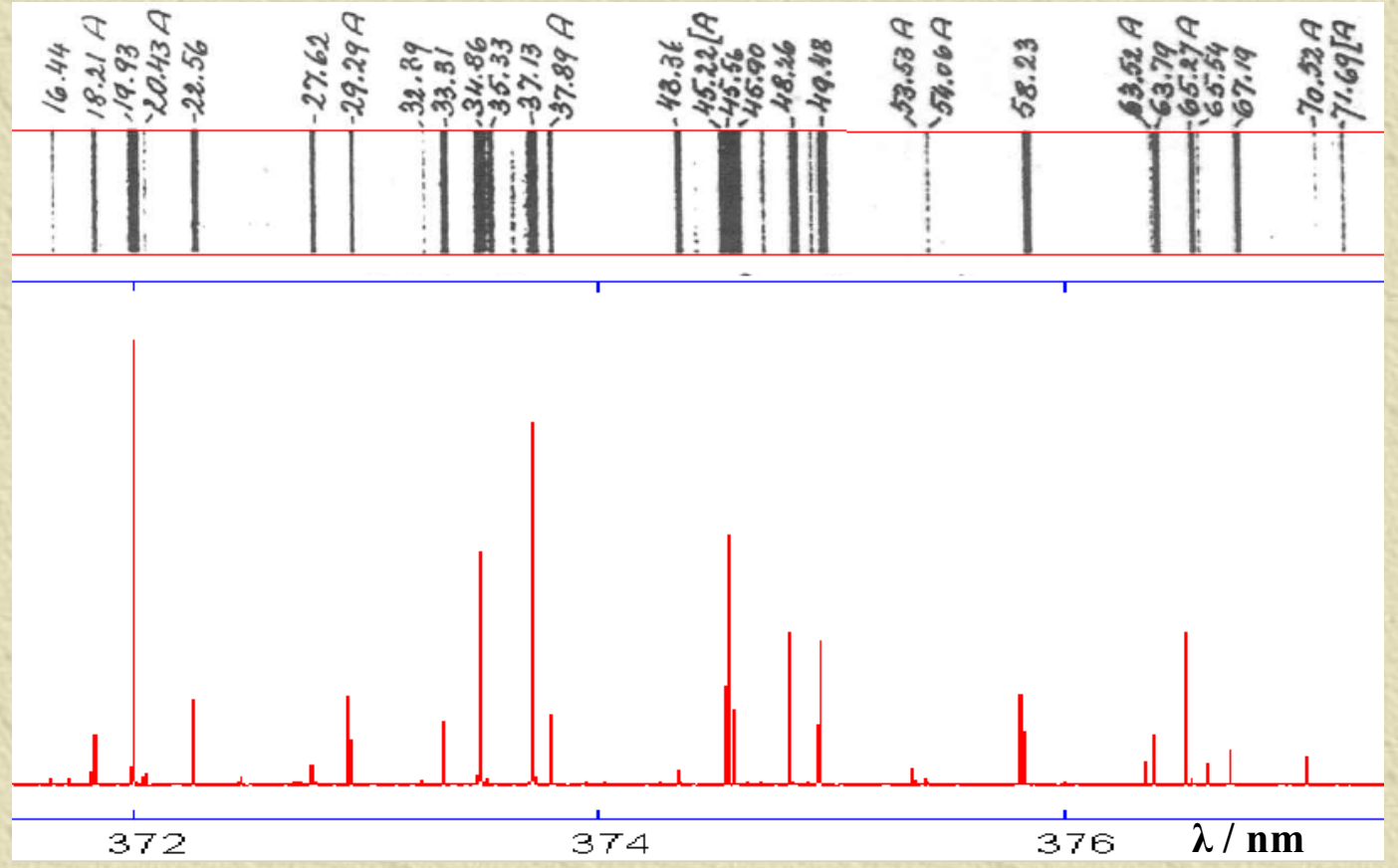
E.W. Salpeter: founder of *Spectrochim. Acta B*

- a collection of photoplates with GD spectra of elements from the early seventies
- reference data of different quality scattered in original papers
- general catalogues of atomic spectra

spectrum of Fe in Ar discharge (an example)

E.W.Salpeter
(1m Paschen-Runge spectrograph)

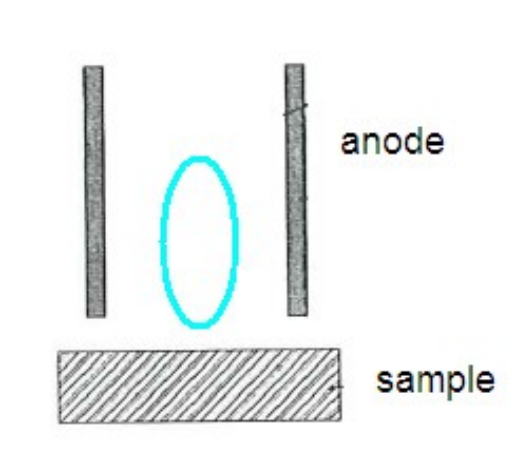
high res. FTS



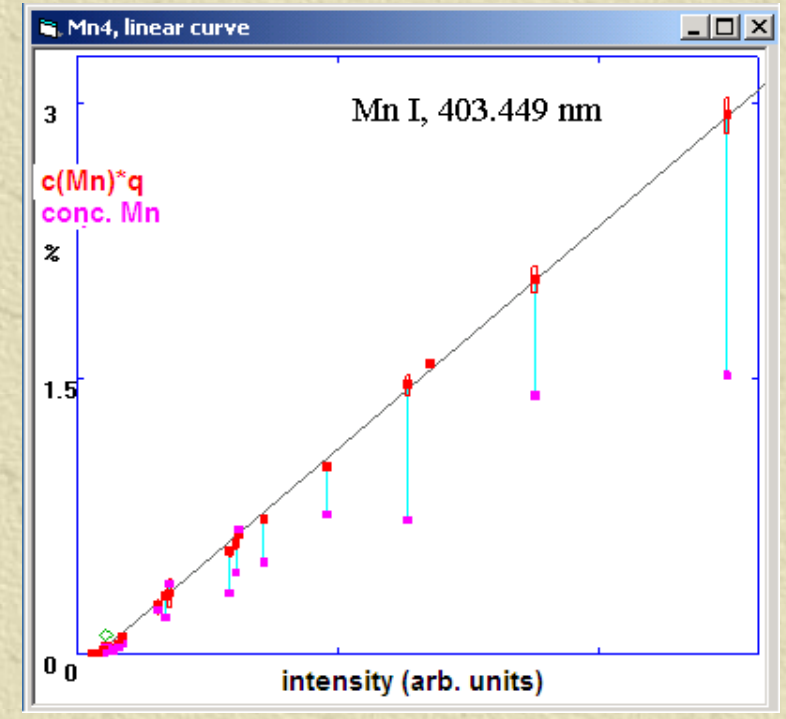
Content of the catalogue

- AES: line spectra (→ linelists)
  - completeness: all observable lines for a given element
  - observed strength of the line (as emission yield)
    - consistent over the spectral range
    - ... between elements
    - ... for both discharge gases
  - identification: atomic/ionic, energy of the upper level

  - flat cathode source (Grimm-type)
  - dc discharge at 700V, 20mA



Emission yields



different materials with different sputter rates q and different concentrations of Mn, c_{Mn}

λ stands for the line Mn I, 403.449 nm, I_λ for intensity of this line, R_λ for its emission yield :

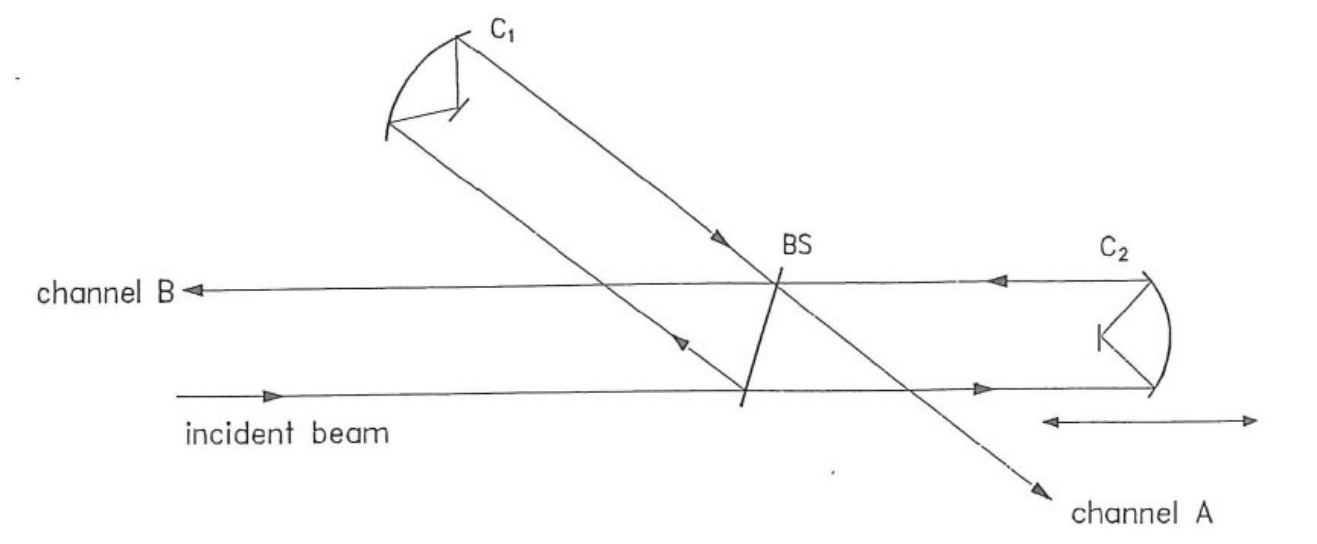
$$I_\lambda = R_\lambda \,.\, (c_{Mn}.q)$$

$$R_\lambda \sim 1 \,/\, (\text{slope of the cal. curve})$$

- weight / atomic concentrations : $R_{wt}(\lambda_E) = R_{at}(\lambda_E) \,.\, M_r(E)$
- to determine R_λ:
  - line intensity/intensities for a sample/samples
  - composition and sputter rate(s) of the sample(s)

Fourier transform spectrometry

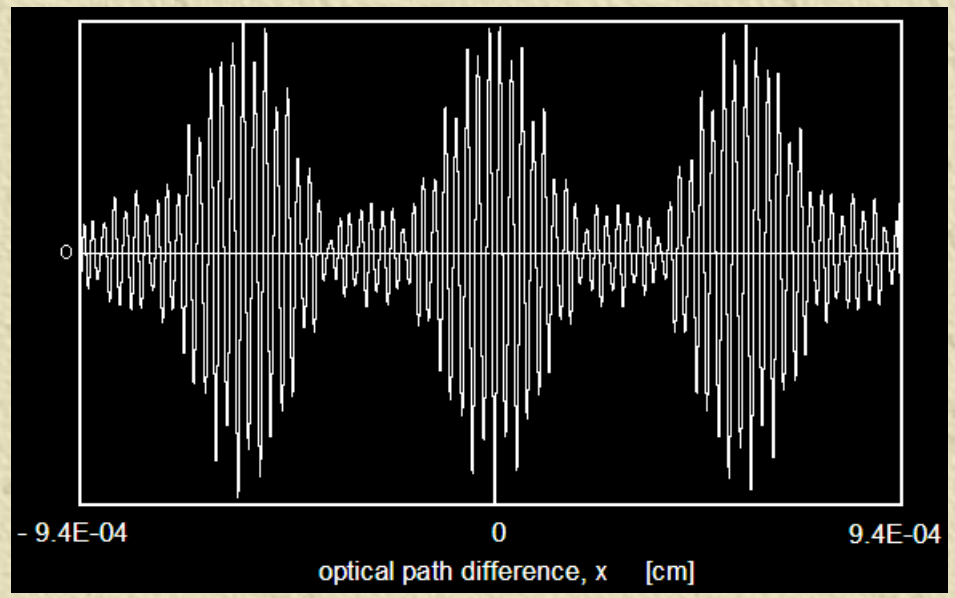
scanning Michelson interferometer



C. Shierle, A.P. Thorne, *Spectrochim. Acta* 50B, 27-50 (1995)

- BS – beamsplitter
- C_1 – fixed catseye
- C_1 – moving catseye

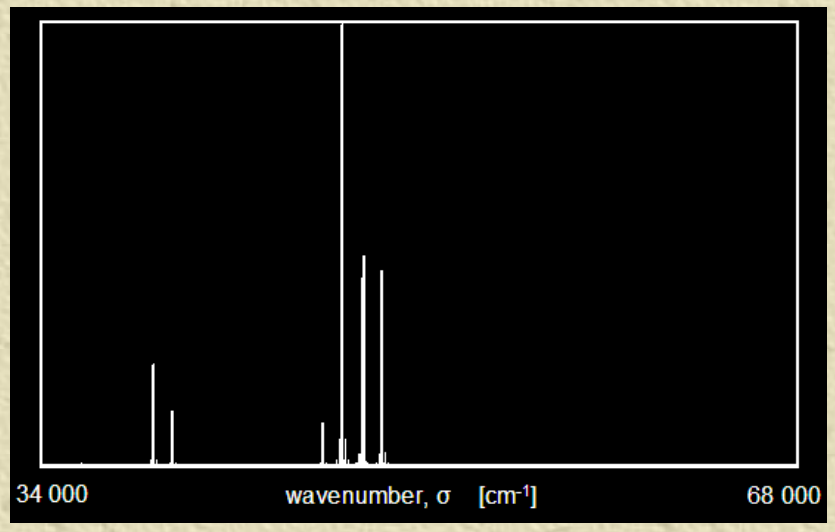
Fourier transform spectrometry



interferogram = cosine FT of the source distribution B(σ),

$$I(x) - \langle I \rangle = \int_0^\infty B(\sigma)\cos(2\pi\sigma x)\,d\sigma$$

σ = 1/λ is the wavenumber



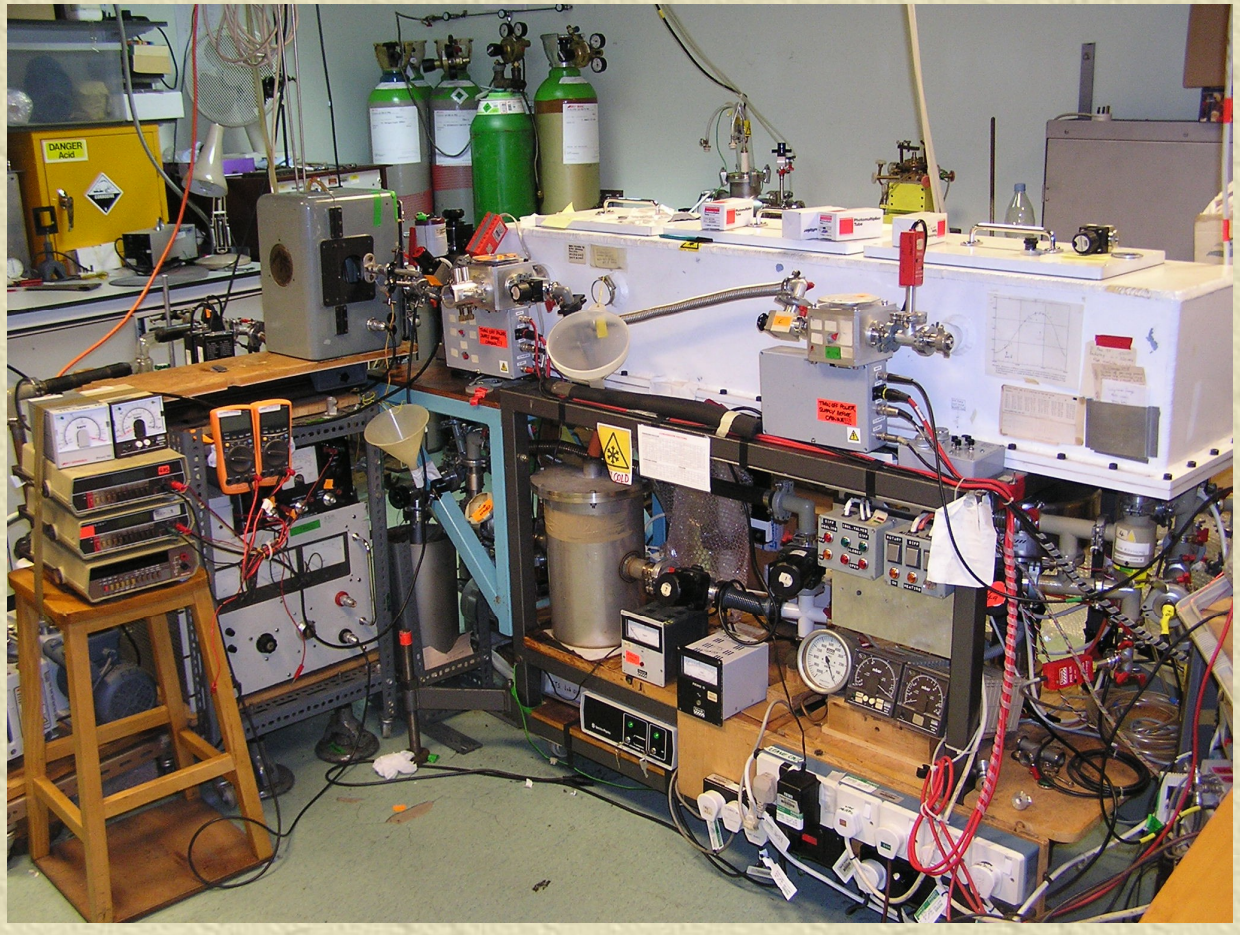
the spectrum B(σ) can be recovered by the inverse FT of the interferogram:

$$B(\sigma) = \int_0^\infty I(x)\cos(2\pi\sigma x)\,dx$$

pure Zn in Ne
147-294 nm
(nzn22b)

the FT500 high res. UV-VIS FT spectrometer (IC design) at Imperial College London

- down to VUV (MgF_2 beamsplitter, limit of ca 135 nm),
- 20 cm optical path: max. resolving power = $2x10^6$ at 200 nm, $1x10^6$ at 400 nm
- program GREMRIC2 to calculate the inverse FT transform



FTS: instrument function ('ringing')

- monochromatic light with a wavenumber σ_0 , path difference in the scan - L

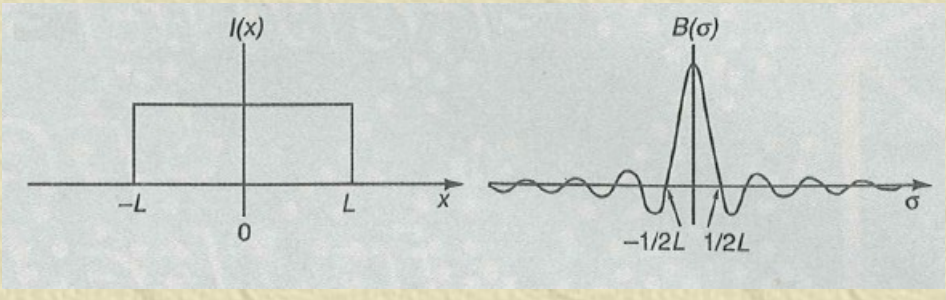
  the instrument function:

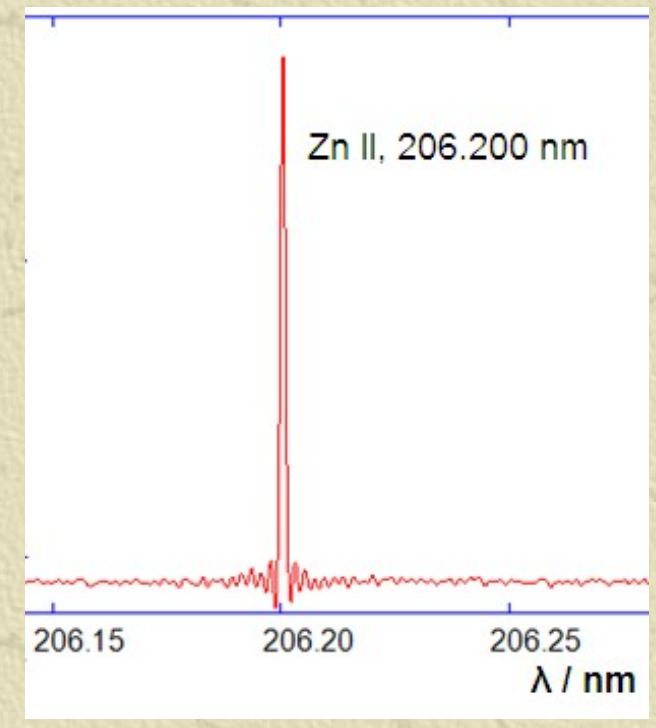
  $$f(\sigma) = \text{sinc } 2(\sigma-\sigma_0)L,$$

  where $\text{sinc } x = (\sin \pi x) / \pi x$

- the first zero of this function ... the resolution:

  $$\delta\sigma = 1/2L \quad [cm^{-1}]$$





FTS: aliasing and wavelength ranges

- discrete sampling → the spectrum B(σ), i.e., inverse FT of the interferogram, replicates itself at wavenumber intervals of $1/\Delta x$ (aliasing)
- i.e., the 'free spectral range' $\Delta\sigma = 1/2\Delta x$ [cm^{-1}]
- light from outside the alias used must be blocked to prevent foldback
- actual measurements: 3 regions, continuous coverage from 150 to 630 nm

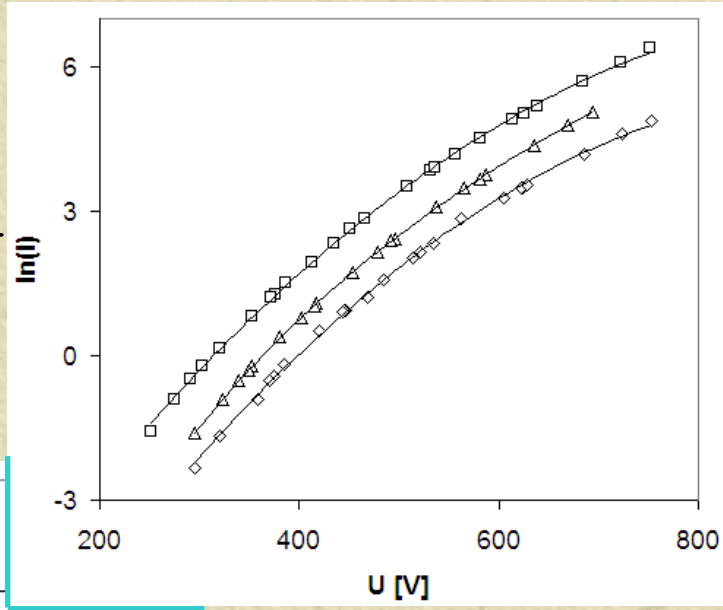
range	FSR	alias	alias range	'true' range	resolution	Filter	PMT
	cm^{-1}		σ, λ	nm	**)	transmits / nm	
VUV-UV	34 000	2	34 000 - 68 000 cm^{-1}		0.07 cm^{-1}		R1220: solar-blind, with MgF_2 window
			147 - 294 nm	147 - 250	0.15-0.44 pm		
intermediate	22 000	2	22 000-44 000 cm^{-1}		0.05 cm^{-1}	UG-5	1P28: standard PMT, 200-630 nm
			227 - 454 nm	250 - 365	0.31-0.67 pm	220 - 380	
visible	15 500	2	15 500-31 000 cm^{-1}		0.04 cm^{-1}	WG-320	1P28: standard PMT, 200-630 nm
			322 - 645 nm	365 - 632 *)	0.53-1.66 pm	> 320	

*) laser light at 632.816 nm

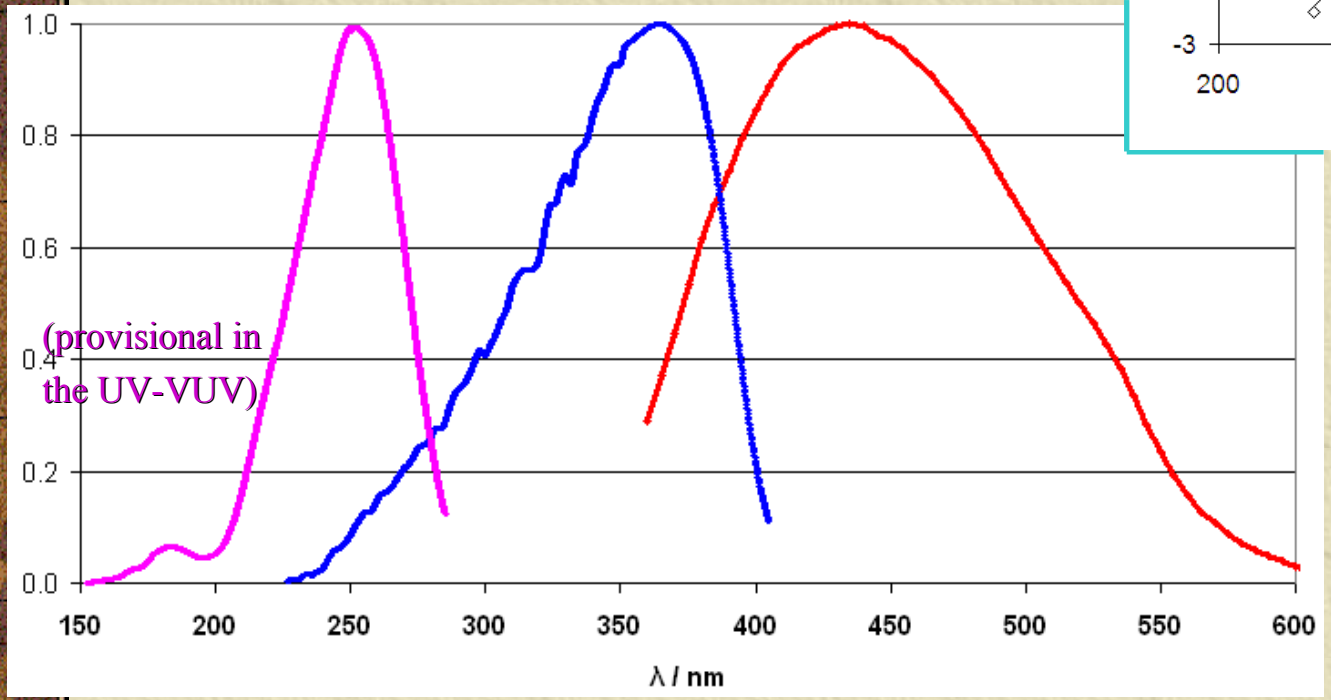
**) resolution in pm at the ends of the 'true' range

FTS: radiometric calibration

- observed intensity –vs – ‘true’ intensity (instrument response function)
- transmittance, reflectivity of opt. components, etc.
- standard lamps : W-halogen, D2 lamp
- calibrated Fe-Ar (Mo-Ar) spectra



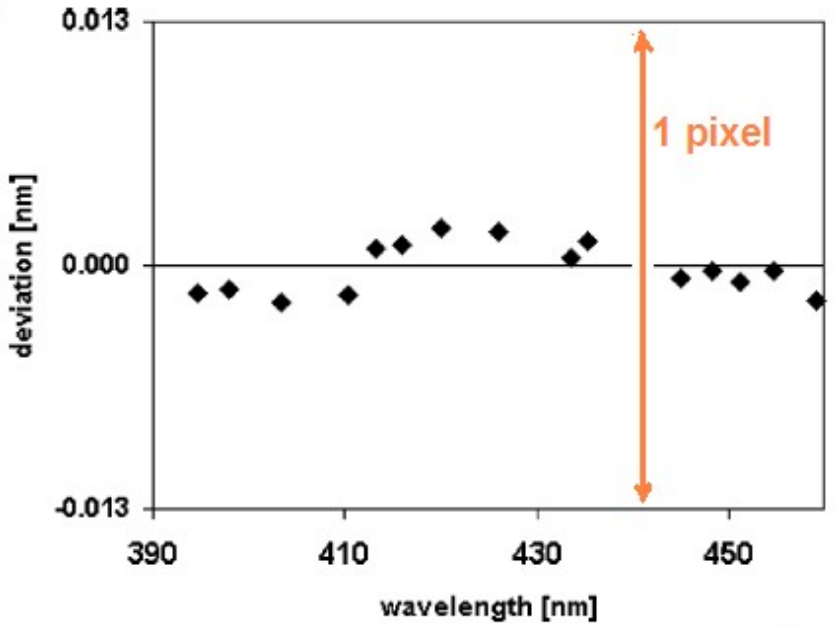
calibration of the PMTs



CCD spectrometers: wavelength calibration

- a set of 'clean' lines with a suitable intensity for a given matrix and a given spectral region

line	Wavelength/nm
Ar II	394.610
Ar II	397.934
Ar II	403.381
Ar II	410.391
Ar II	413.172
Ar I	415.859
Ar I	420.067
Ar I	425.936
Ar I	433.533
Ar II	435.220
Ar II	444.888
Ar II	448.181
Ar I	451.073
Ar II	454.504
Ar II	458.989



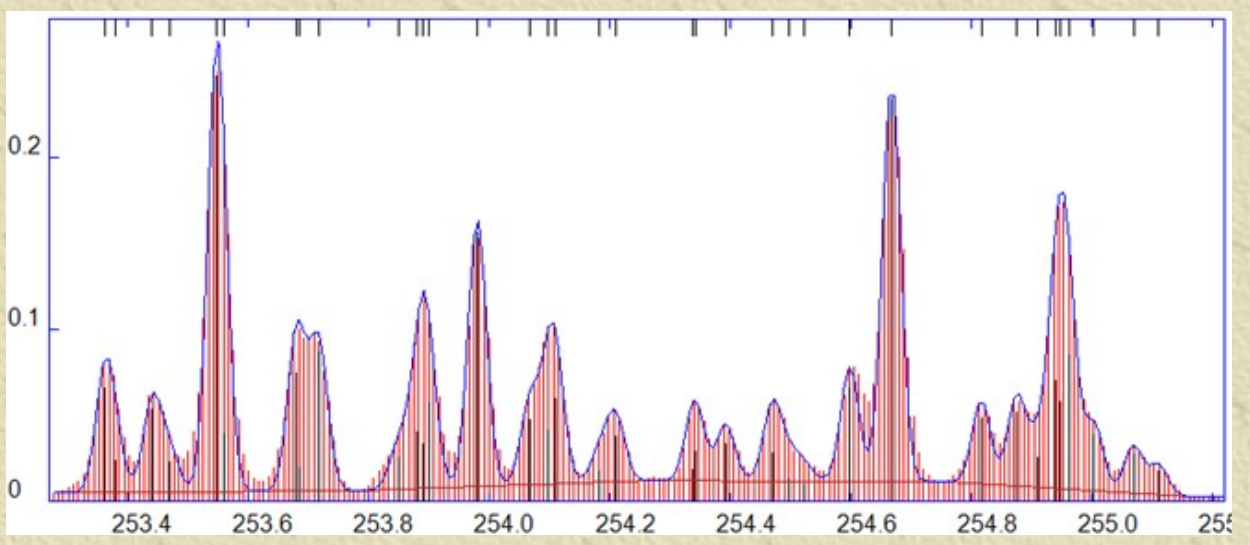
Deviations between the actual and predicted wavelengths.

LECO GDS500A, array 4

Z. Weiss, *J. Anal. At. Spectrosc.*, 20, 557 (2005)

Matching together the CCD- and the FT spectra

- ‘deconvolution’ of a CCD spectrum, based on the corresponding FTS linelist that is used as a template, assuming Gaussian ‘CDD line profiles’



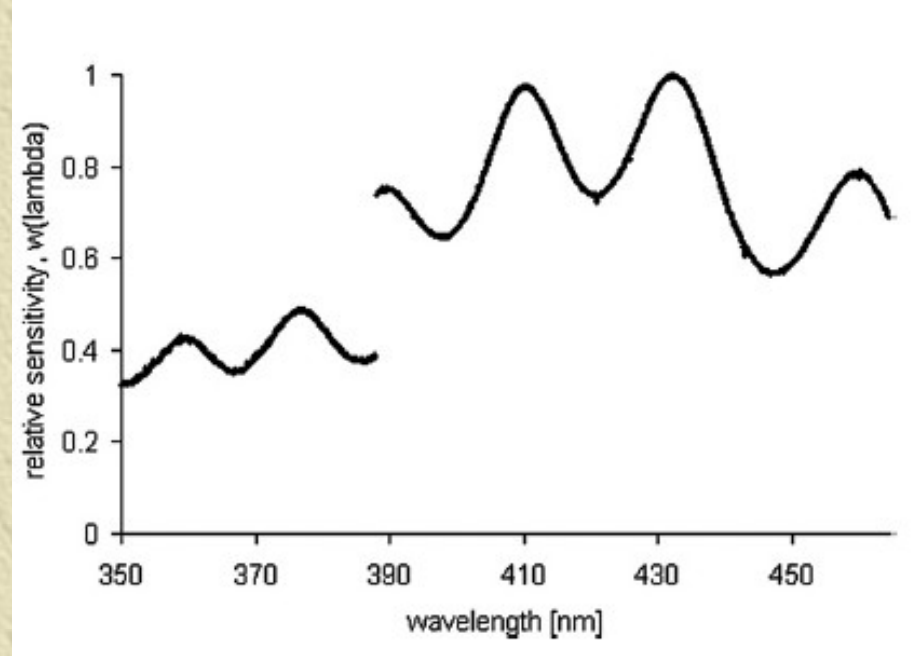
Spectruma GDA650:
- red lines: measured
- blue envelope: the fit

result: relative intensities of lines from the template, even if unresolved in the CCD spectrum

FTS (template)

CCD spectra

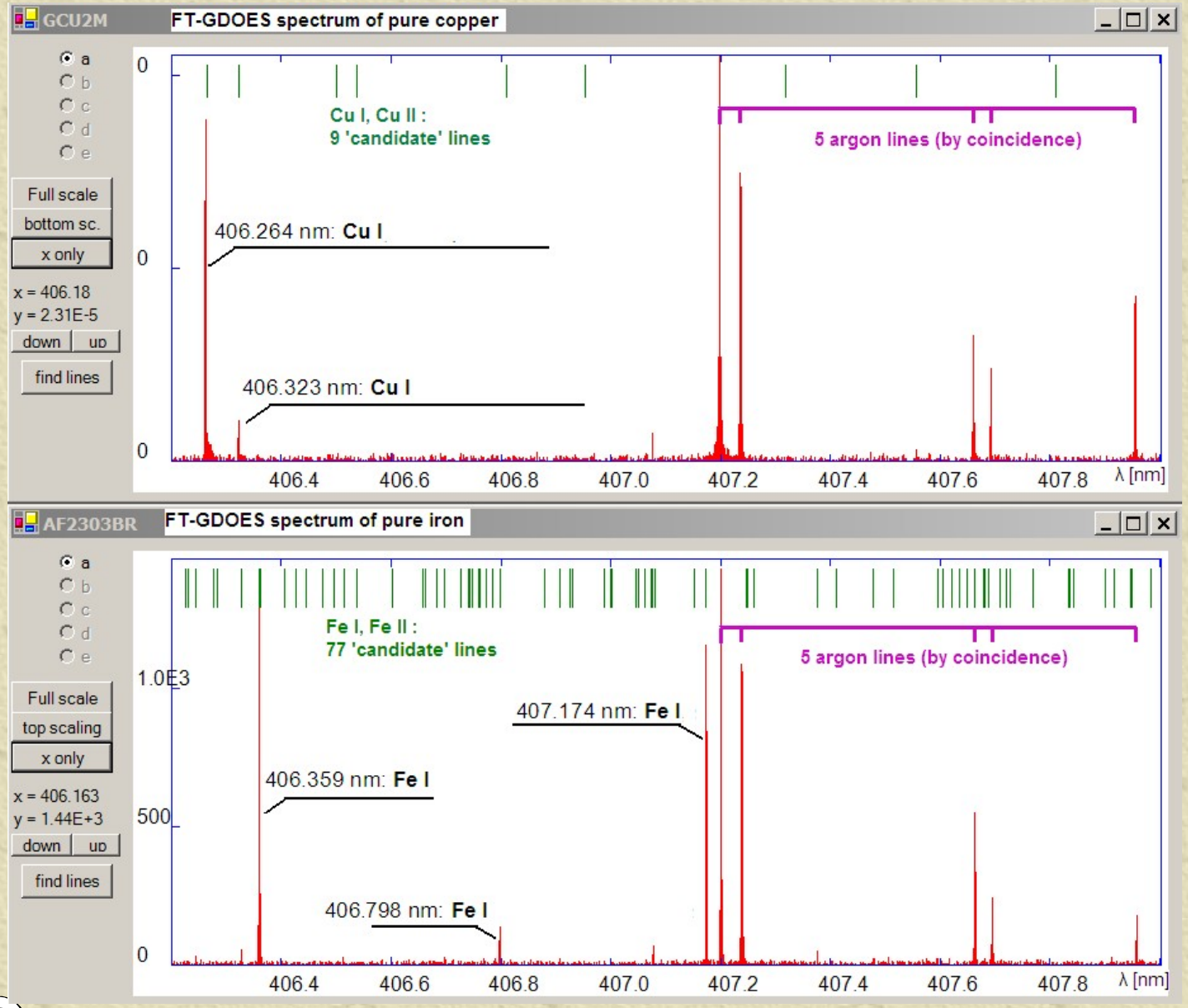
- 'pixelation' – typically few pixels per line width (resolution)
- blooming: strong lines produce signal in neighboring pixels
- intensity response curves in CCD instruments



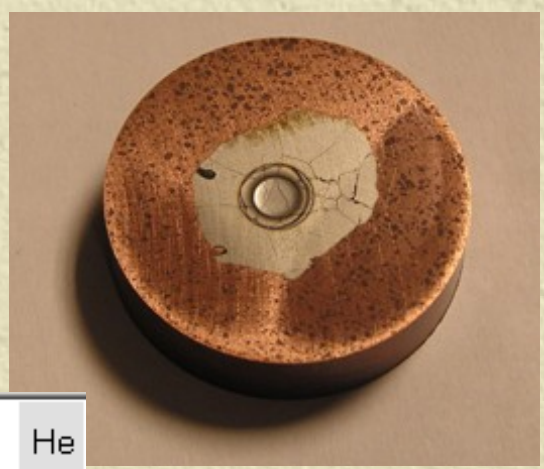
LECO GDS500A: response function, 3rd and 4th CCD array

Z. Weiss, E.B.M. Steers, P. Šmíd, V. Hoffmann, *J. Anal. Atom. Spectrom.* 24, 27-33, (2009)

Generating linelists (coincidences and exclusivity of lines in different spectra)



Elements measured



H	s^2											s^2p					He
Li	Be											B	C	N	O	F	Ne
Na	Mg									$d^{10}s$	$d^{10}s^2$	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		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt									
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

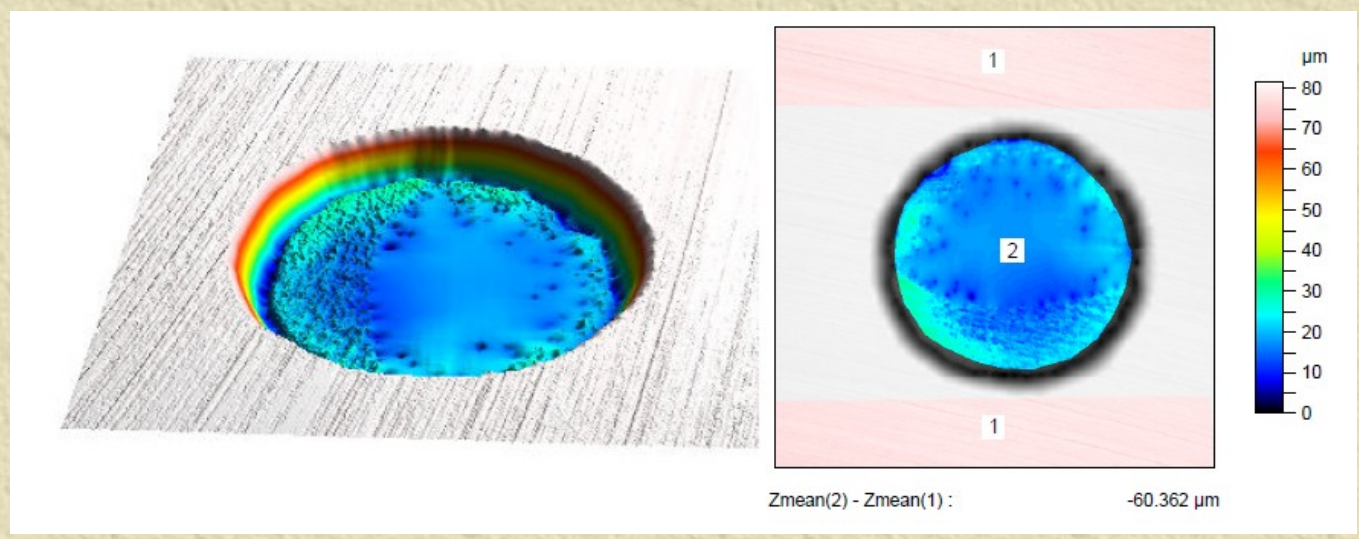
- matrix elements in real applications
- some ‘difficult to run’ samples – Mn
- transition elements with s^2 d^x configurations: complex spectra
- Salpeter’s ‘Teil 1’ : Fe, Co, Cr, Ti, Ta, Nb, Ni, Mo

Calculating emission yields

- sputter rate measurements:

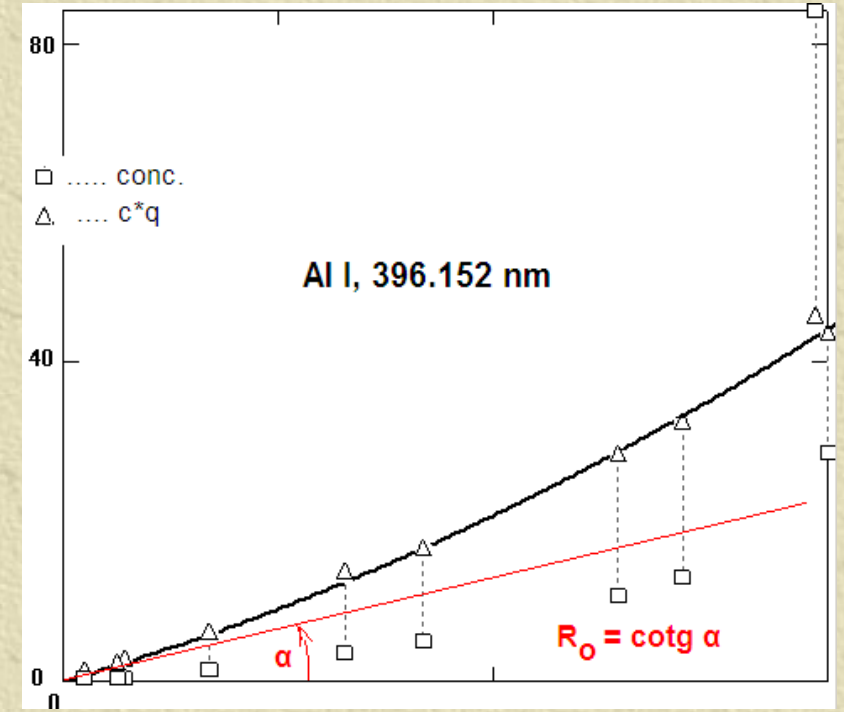
  q = crater volume * sample density / time of sputtering

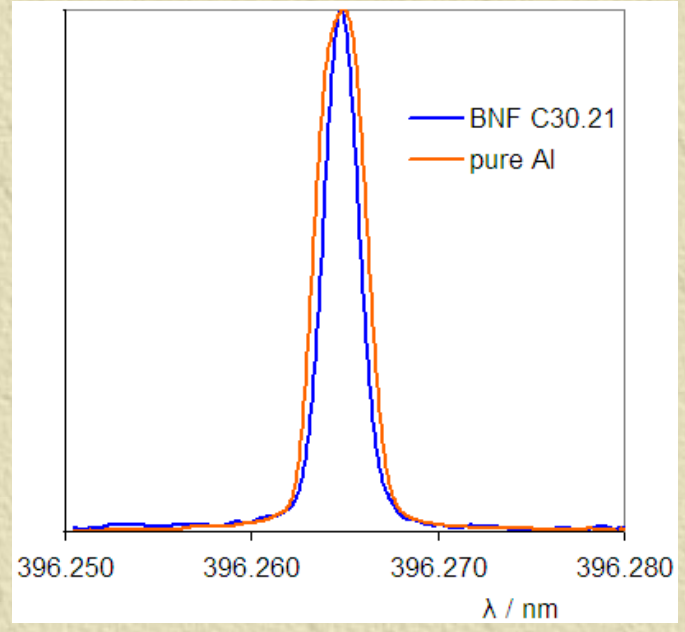
  $R = I / (c*q)$



Mg-in-Ar, 700V, 20 mA, 265 s : depth of the crater = ca 60 µm

Selfabsorption, nonlinear intensity-vs-(c.q) relations



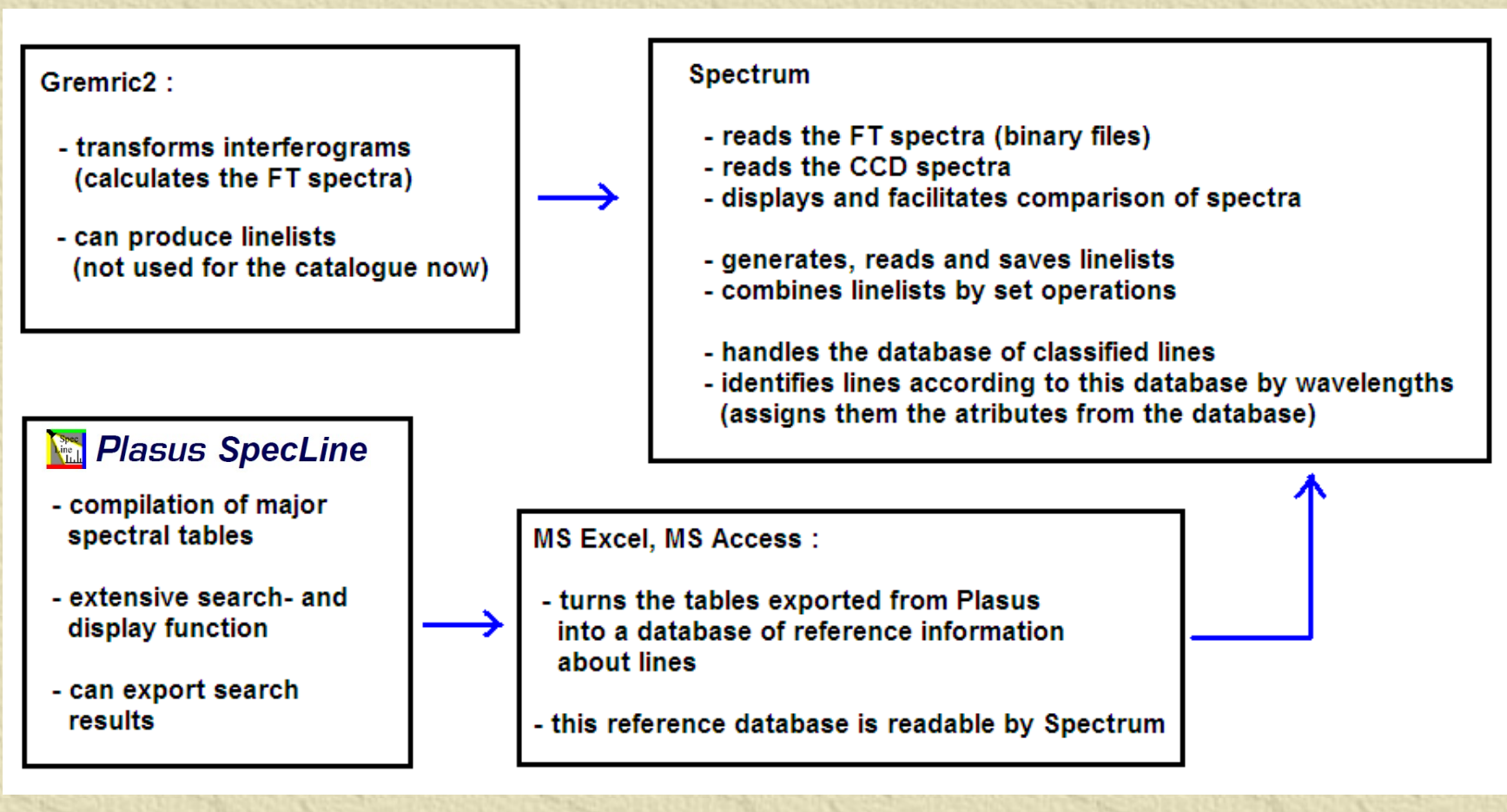


$$\frac{c_{Al}q(C30.21)}{c_{Al}q(pure\ Al)} = 0.16 \qquad \frac{R_{Al}}{R_{C30.21}} \approx 0.5$$

em. yield at low concentrations > em. yield for pure metal

in the catalogue: for self-absorbed lines, both values (R, R_0)

Data processing



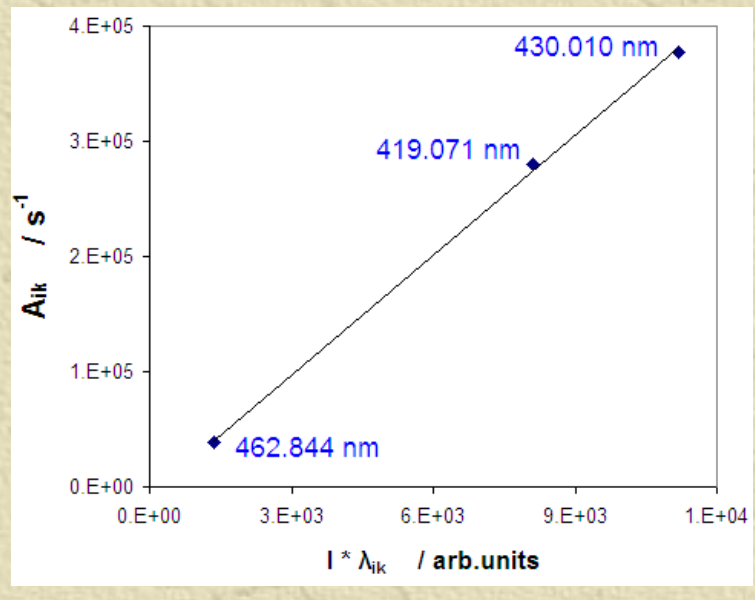
Branching ratios

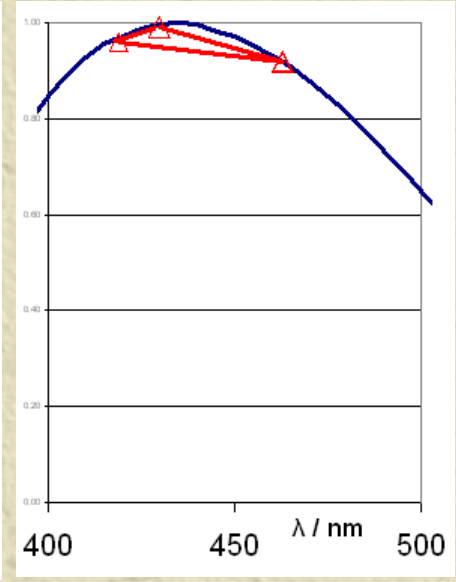
(lines with known transition probabilites)

Ar I: $3s^2\ 3p^5\ (^2P^\circ_{1/2})\ 4s\ ^2[1/2]^\circ_1$ - **$3s^2\ 3p^5\ (2P^\circ_{3/2})\ 5p\ ^2[5/2]_2$**

$3s^2\ 3p^5\ (^2P^\circ_{3/2})\ 4s\ ^2[3/2]^\circ_1$ -

$3s^2\ 3p^5\ (^2P^\circ_{3/2})\ 4s\ ^2[3/2]^\circ_2$ -

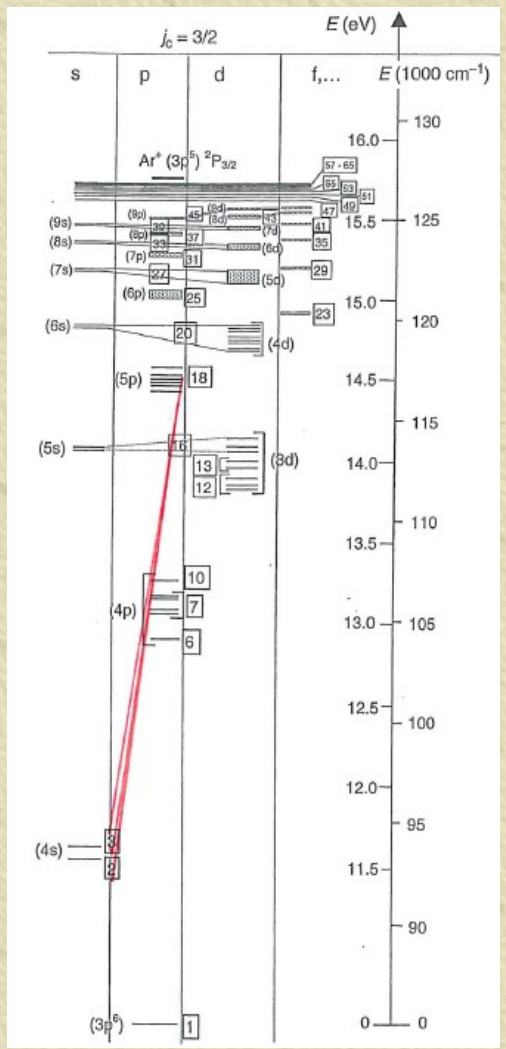




response function, FTS-visible region

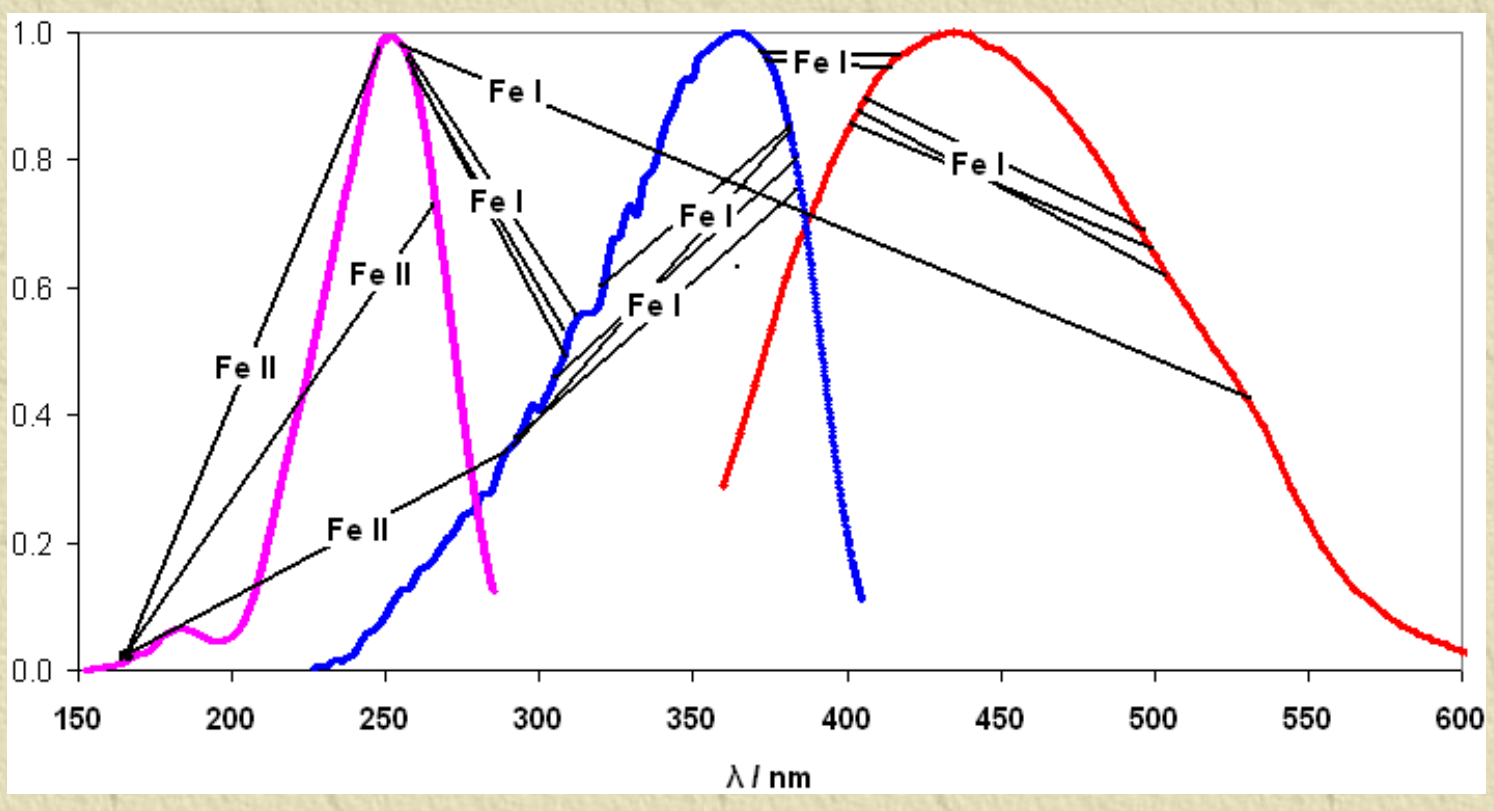
$$\frac{I_{ki}}{I_{kj}} = \frac{w(\lambda_{ki})}{w(\lambda_{kj})}\frac{A_{ki}}{A_{kj}}\frac{\lambda_{kj}}{\lambda_{ki}}$$

ratios of intensities of lines from the same upper level are <u>independent of level populations</u>



A.Bogaerts, R.Gijbels, J.Vlček, *J. Appl. Phys.* 84, 121, (1998)

Branching ratios: Fe I, Fe II



- an independent check of the instrument response curve
- they link together corrected intensity ratios of different lines, i.e., ratios of the instrument function for different pairs of wavelengths

Transition probabilities:

Fe I: L.J.Curtis, S.R.Federman, S.Torok, M. Brown, S.Cheng, R.E.Irving, *Physica Scripta* 75 (2007) C1-C7

Fe II: J. C. Pickering, S. Johansson, P. L. Smith, *Astronomy and Astrophysics*, 377, (2001) 361-367

Intensity ratios in Ar and Ne (another check)

- 'Ar/Ne'-intensity ratios of lines of element X from the same upper level are the same and equal to the ratio of populations in Ar and Ne at that level

Cu II:

λ [nm]	raw emission yields in Ar,	in Ne	E exc. [eV]	Ar/Ne	avg.	deviation %
224.700	150	37	15.9613	**4.02**	**3.94**	2
229.437	12	2.9	15.9613	**4.10**		4
235.664	0.87	0.23	15.9613	**3.83**		-3
248.965	1.4	0.37	15.9613	**3.79**		-4
221.811	7.1	45	16.1470	**0.16**	**0.16**	-1
227.626	1.4	9.6	16.1470	**0.15**		-9
240.012	0.25	1.4	16.1470	**0.18**		10
214.898	0.56	7.0	16.2129	**0.081**	**0.074**	8
219.227	2.6	35	16.2129	**0.075**		1
236.989	0.50	7.4	16.2129	**0.067**		-9
208.531	0.007	0.84	16.3890	**0.008**	**0.009**	-12
212.604	0.30	37	16.3890	**0.008**		-11
217.941	0.83	73	16.3890	**0.011**		23
201.690	0.004	0.36	16.5906	**0.011**	**0.010**	14
205.498	0.11	12	16.5906	**0.009**		-3
210.480	0.092	11	16.5906	**0.008**		-12
221.027	0.27	28	16.5906	**0.010**		1

The catalogue data (example):

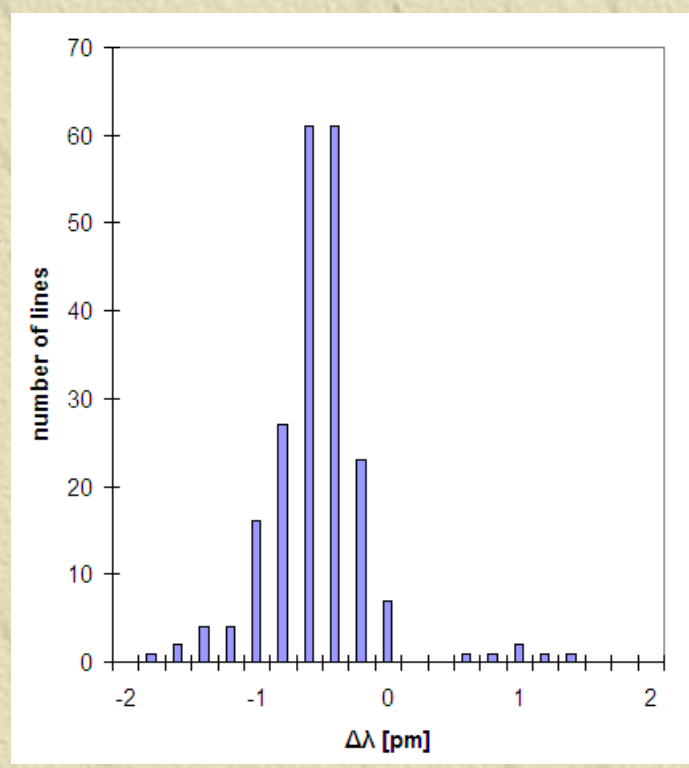
- 155 to 540 nm
- in Ar and Ne discharge
- Part 1:
  - Fe: 2 554 lines (of 34 853 ... Fe I, II)
  - Cu: 315 lines
  - Zn: 85 lines

emission yields are normalized so that average E.Y. in a set of 259 Fe lines in Ar, observed in the range 230 nm < λ < 250 nm, is equal to 1.00

λ / nm	line	E_i / eV	R^{wt}_{Ar}	R^{wt}_{Ne}
160.5278	Fe II	15.7088		**0.23**
160.8454	Fe II	15.6107	**251**	**12**
161.0923	Fe II	15.8311		**0.48**
161.2820	Fe II	15.8224	**1.1**	**3.4**
161.3757	Fe II	20.9463		**0.6**
161.7187	Fe II	20.7907		**0.16**
161.8470	Fe II	15.6107	**80**	**3.3**
161.9342	Fe II	20.8479		**0.31**
162.0149	Fe II	15.5955		**7**
162.1689	Fe II	20.8441	**103**	**0.17**
162.3080	Fe II	15.8425	**0.5**	
162.4536	Fe II	18.7558		**0.07**
162.5912	Fe II	15.6107	**15**	
162.7020	Fe II	20.8118		**0.4**
162.9162	Fe II	15.5955	**70**	**3.2**
163.0189	Fe II	20.7969		**0.23**
163.1132	Fe II	15.5864	**26**	**0.7**
163.3990	Fe II	19.9694		**0.7**
163.4350	Fe II	15.5955	**24**	
163.5403	Fe II, II		**2.9**	**1.0**
163.6320	Fe II	15.5864	**45**	**4.4**
163.7399	Fe II	15.7066	**3.0**	
163.7774	Fe II, II		**0.4**	
163.9404	Fe II	15.5864	**32**	**3.7**
164.0130	Fe II, II			**1.0**
164.1043	Fe II	21.9420		**0.16**
164.1780	Fe II	19.3430	**1.8**	
164.2480	Fe II, II			**0.25**
164.3570	Fe II	15.7473	**1.9**	

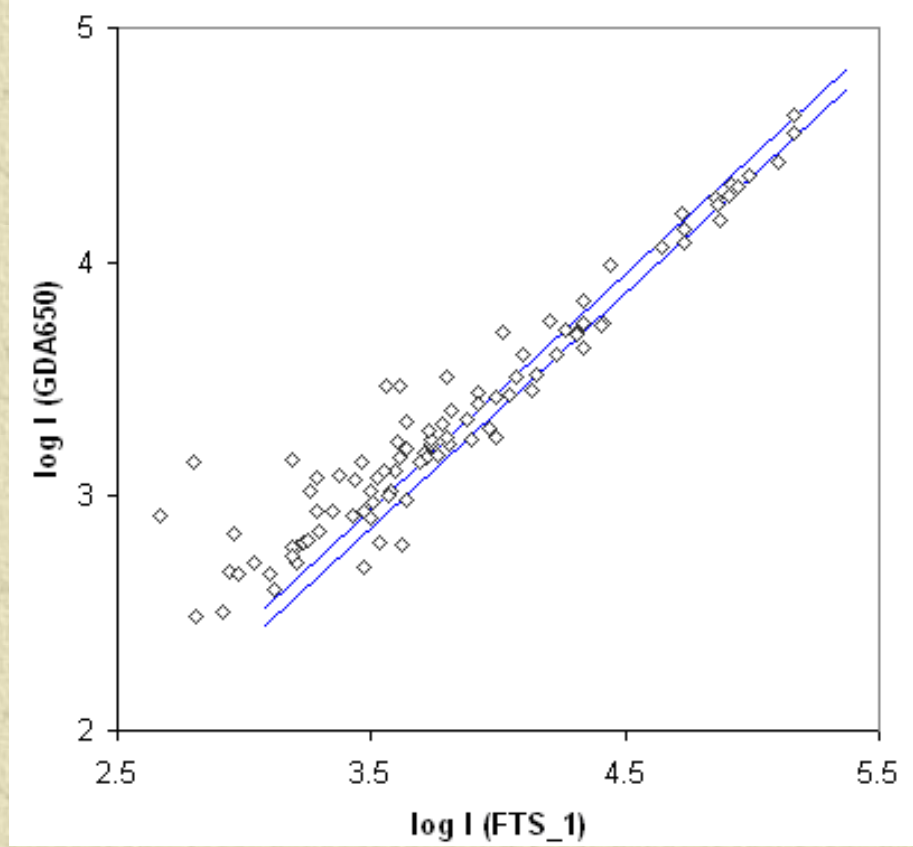
FTS: wavelength accuracy / tolerance for line identification

- 212 unambiguously identified Fe lines in the visible region (330-546 nm):
- mismatch between the tabulated- and measured wavelengths, according to Plasus 2.1
- histogram of the differences (each class is 0.2 pm wide)
- systematic mismatch of ca - 0.6 pm
- wavelength calibration can be made

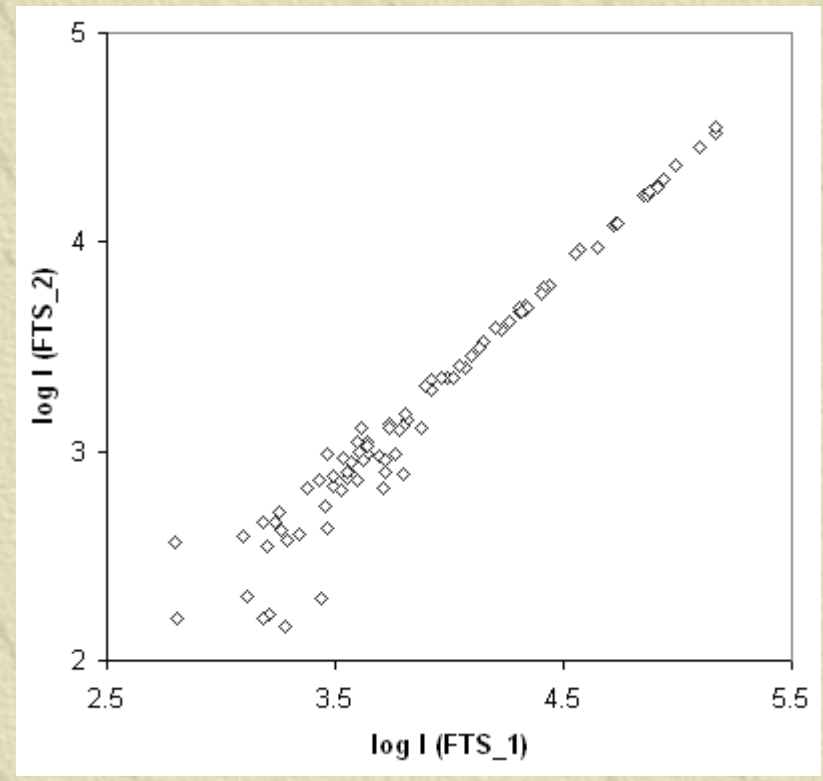


Comparison of intensities: FTS – vs – GDA650

- 164 lines from 248-258, Fe-in-Ar
- the 2 parallel lines: tolerance interval of ± 20%



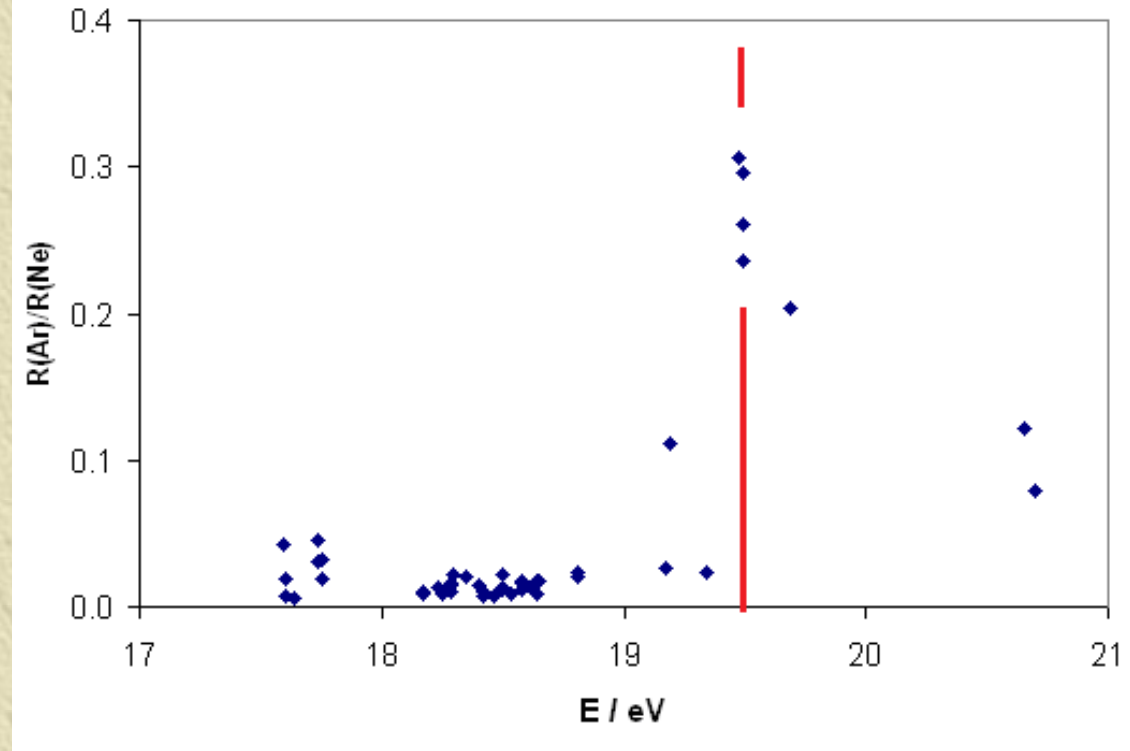
FTS: day-to-day reproducibility



- the same spectrum as in the previous slide

Some newly reported features/phenomena found in the spectra

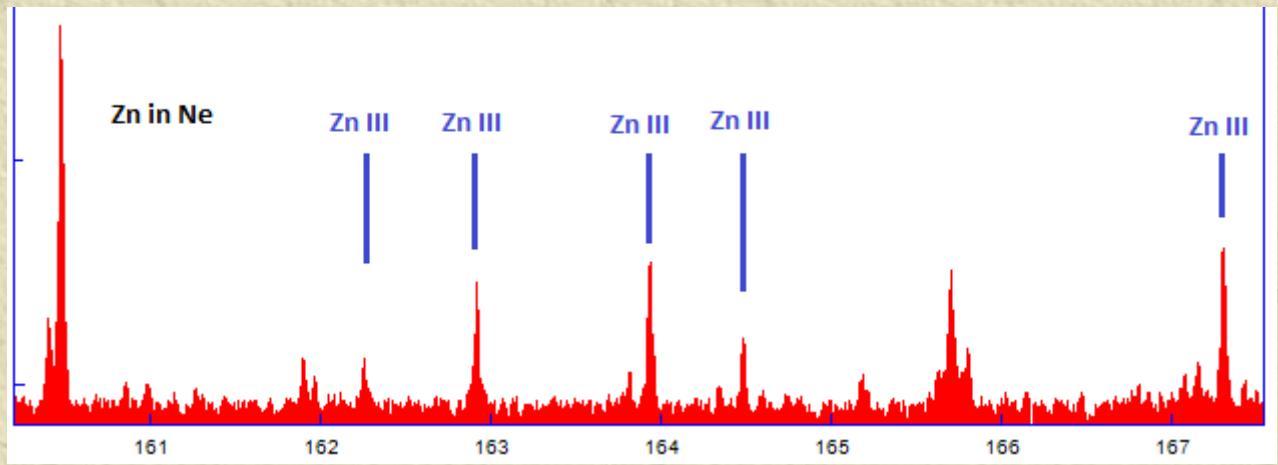
- Fe II: Penning excitation by Ar metastables:
- Ar/Ne ratios – enhancement of Fe II lines with exc. energy 11.57-11.59 eV relatively to the Fe II ground state



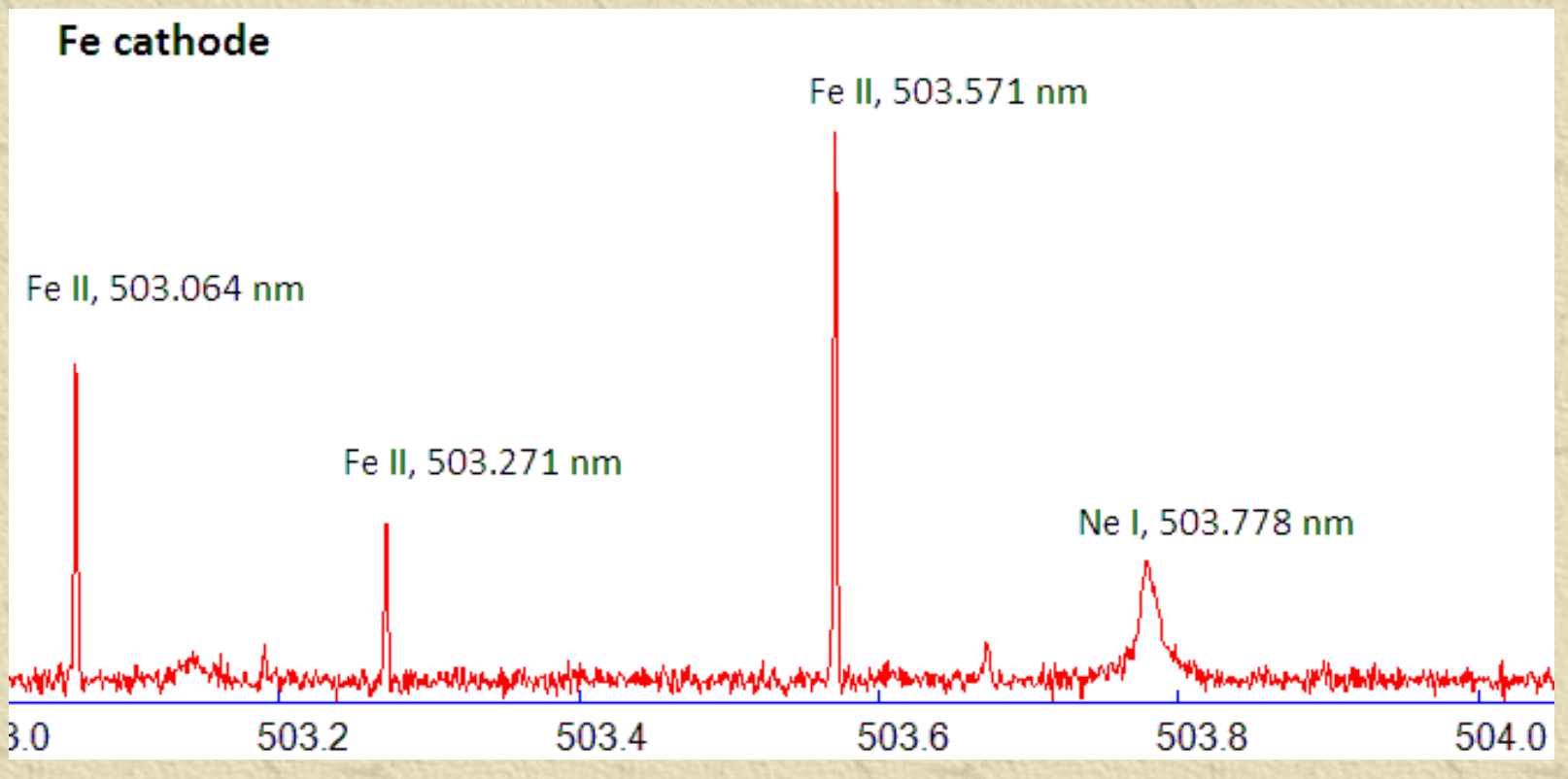
Zn III lines were observed in the zinc spectrum

- a high excitation energy,
- similar EYs in Ar and Ne (unlike Zn II)

λ / nm	line	E_i / eV	R^{wt}_{Ar}	R^{wt}_{Ne}
158.959	Zn I	7.7999	7.2E-01	1.4E+00
162.251	Zn III	45.0243	7.3E-03	6.9E-03
162.919	Zn III	44.7976	1.8E-02	2.3E-02
163.933	Zn III	45.2745	2.4E-02	2.2E-02
164.482	Zn III	44.7252	9.9E-03	9.7E-03
167.305	Zn III	44.4518		2.0E-02
174.712	Zn II	24.2673	7.2E-03	4.2E-02
196.939	Zn II	22.2517	6.6E-03	1.4E-02
201.192	Zn II	23.3313	2.1E-02	2.6E-02
202.548	Zn II	15.5135	8.7E+00	7.7E+02



Some extremely wide Ar and Ne lines were observed



Ar	Fe-Ar	Al-Ar	FWHM / pm		red shift			
λ [nm]					Δλ [nm]			
506.014	very weak		14-18		0.006			
515.141	very weak	very weak	7		0.002			
522.132		is there	13		**0.005**			
525.285	very weak, if existing		16		**0.006**			
Ne	**Fe-Ne**	**Al-Ne**	width /pm		**red shift**	z	v [km s-1]	E [eV]
λ [nm]					Δλ [nm]			
470.443		is there	14		0.003	7.4.E-06	2.2	519
470.889			18					
471.540		is there	18		0.006	1.2.E-05	3.5	1 275
475.283			21					
495.711			22					
503.778		**is there**	26		**0.003**	5.8.E-06	1.7	311
508.042		**is there**	24		**0.003**	6.9.E-06	2.1	445
512.233	very weak	is there	19		-0.002			
514.497		**is there**	26		**0.003**	6.4.E-06	1.9	386
515.200	very weak, if existing		38		0.004	7.4.E-06	2.2	510
520.395		is there	33		0.005	1.0.E-05	3.1	1 009
534.112		is there	38		0.003	4.9.E-06	1.5	222

- ?? Doppler broadening / Doppler shift in the cathode fall ?
- but why only these lines ?
- interpretation of this data is unclear

Applications

- simulation of spectra from instruments with a given resolution
- selection of analytical lines for a given application:
  - estimating magnitude of line interferences
  - excitation mechanisms / matrix effects
- semiquantitative analysis without calibration: known emission yields
- analysis using multiple lines for a given element
- selection of lines for fundamental studies

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the standard cal. model
with a line interference:

$$I_{\lambda,M} = R_{\lambda(E)}\, c_{E,M} q_M \left(1 + \alpha_{EF}^{\lambda} \frac{c_{F,M}}{c_{E,M}}\right)$$

magnitude of the interference:

$$\alpha_{EF}^{\lambda} = \eta(\Delta\lambda_{EF}) \frac{R_{\lambda(F)}}{R_{\lambda(E)}}$$

$\eta(\Delta\lambda_{EF})$ ... the 'overlap factor'

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thanks for attention