Towards an intelligent selection of analytical lines in GD-OES

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Outline

1. GD-OES instruments and GD-OES spectra
2. Instrumental factors: line interferences and sensitivity variations
3. Links between applications and fundamentals: methods, goals and motivation

GD-OES instruments and the nature of GD-OES spectra

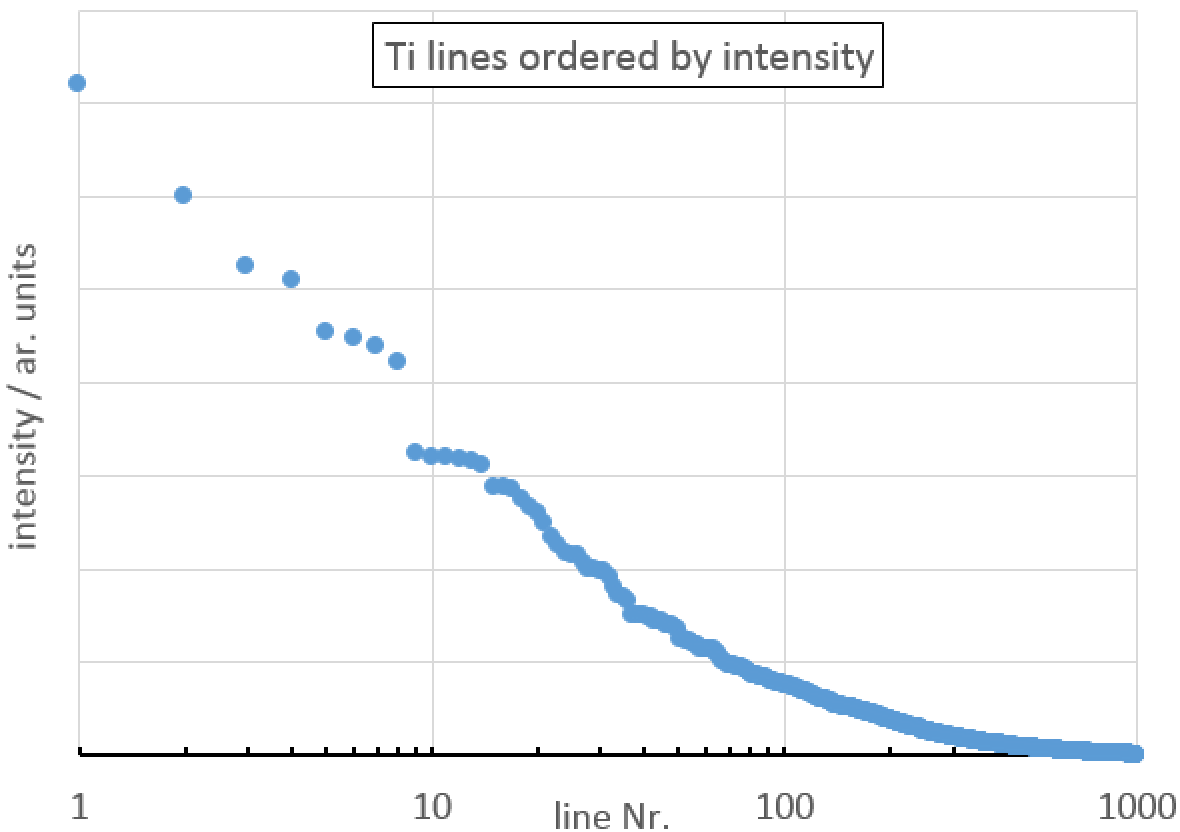
1. optical system: polychromators with PMTs, mono-chromators, CCD-based optics, less common instruments (Echelle systems, Fourier Transform Spectrometers)

2. Instrumental parameters:
   - resolution / resolving power
   - wavelength range
   - sensitivity / dynamic range
   - speed (sampling rate)

3. What the Mother Nature offers and how we can read it

A typical GD-OES spectrum: pure Ti in Ar discharge

the wavelength range: 160 nm to ≈560 nm



		the number of lines
TiAr_all		1 446
of which Ti lines		1 031
of which Ar lines		415
sorted:	Ti I	372
	Ti II	660
	Ti III	7
Ti unidentified		44
Ti blended *)		52

*) at resol. = 1 pm

111 Ti lines have **$I > I_{max}/10$** (≈20 are analytically important ?)

- all 1031 (1446) lines ... may interfere with other elements
- this range at a resolution of 50 pm ... 8000 "channels"

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Line interferences and analytical accuracy

1. Line interferences occur at common instruments and are frequent.
2. They can be corrected for in a calibration, but with inevitable trade-offs, on
   - precision,
   - sensitivity.
3. Matrix-specific selection of lines, incl. multiple lines for a single element

   (!! - gaps in the wavelength range, etc.)
4. ‘true’ matrix effects

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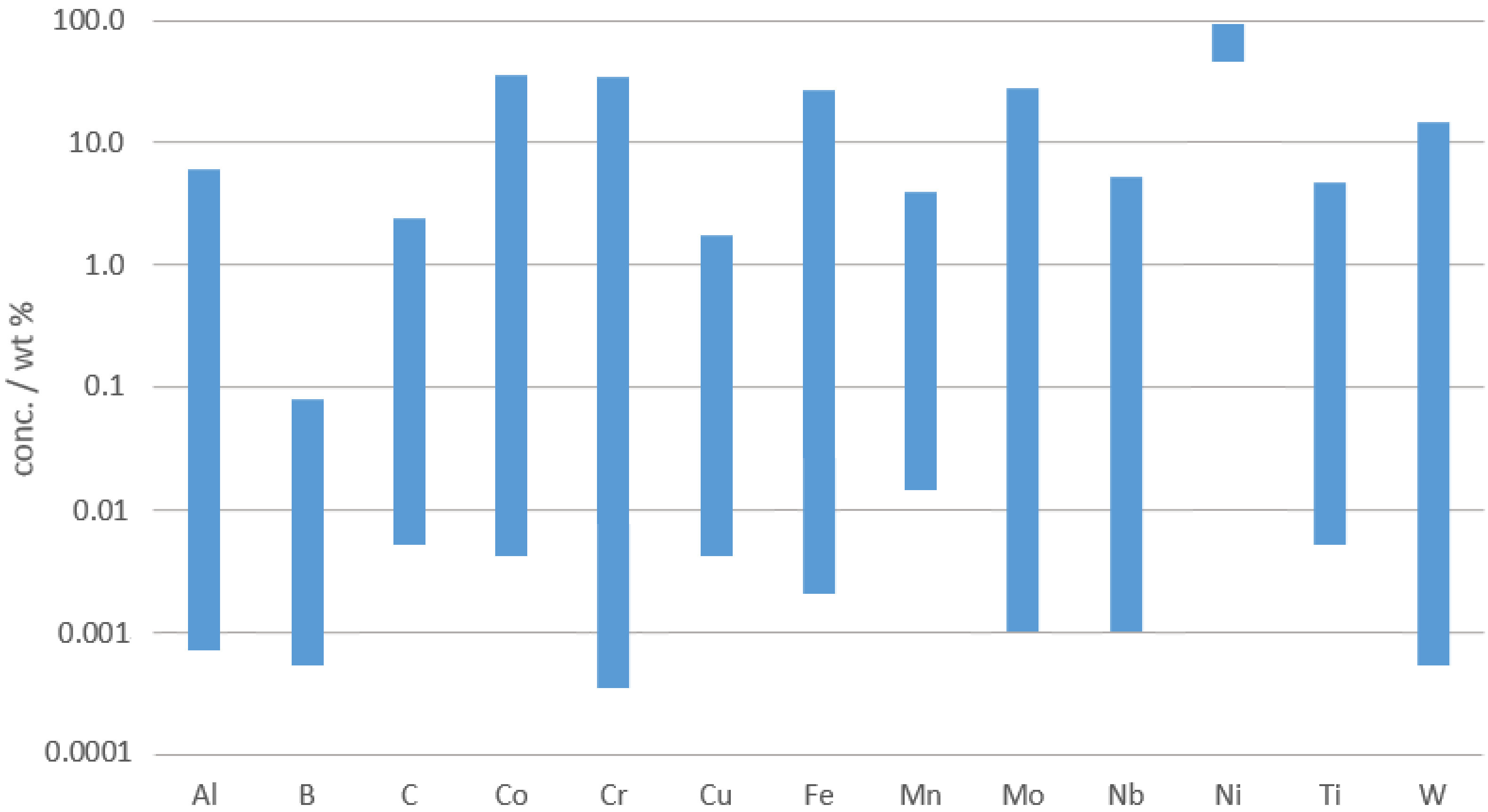
Example: analysis of Ni alloys on a CCD instrument



calibration ranges (some could be extended towards the ppm region)

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Ni alloys: the list of the standards used

composition / wt %		Al	B	C	Co	Cr	Cu	Fe	Mn	Mo	Nb	Ti	W
	max	6.00	0.080	2.44	35.6	34.0	1.74	26.9	4.00	27.48	5.19	4.74	14.90
	Grade												
55A	Haynes 242	0.24	0.0050	0.030	0.04	7.90	0.030	1.09	0.33	25.4	0.020	0.010	0.090
60A	RA 333	0.08	0.002	0.058	3.02	25.72	0.10	17.71	1.50	3.09	0.14	0.030	2.98
62A	Waspaloy	1.32	0.0050	0.039	13.34	19.36	0.020	1.08	0.02	4.33	0.040	3.05	0.11
63A	Hastaloy B-2	0.28	0.0005	0.005	0.09	0.55	0.050	1.47	0.19	27.48	0.005	0.005	0.175
66A	Hastaloy C-276	0.21	0.001	0.010	1.95	15.74	0.13	5.81	0.53	15.02	0.040	0.030	3.40
69A	Hastaloy X	0.19	0.0005	0.11	2.11	22.31	0.13	18.35	0.72	9.17	0.12	0.010	0.82
BS200-4	Ni 200	0.007	0.0037	0.11	0.091	0.13	0.049	0.29	0.31	0.002	0.002	0.019	0.0005
BS200A	Ni 200	0.029	0.0044	0.077	0.057	0.001	0.004	0.076	0.15	0.001	0.001	0.043	0.005
S-20	stainless st.			0.097		2.06	0.44	71.5	1.5	3.15	1.22	0.01	
S-22	stainless st.			0.014		1.00	0.02	68.8	0.34	0.82		0.13	
S-23	stainless st.			0.007		0.13	0.04	65.4	0.82	0.021			
BS617	Inconel 617	1.20	0.002	0.079	12.42	22.44	0.062	1.76	0.057	9.64	0.123	0.28	0.06
BS925	Inconel 925	0.17	0.002	0.011	0.34	20.82	1.74	26.92	0.50	3.00	0.23	2.20	0.47
NIRM-6	Ni-resist iron			2.44		1.07	0.10	62.53	4.00	0.45			
NIRM-7	Ni-resist iron			2.04		3.53	0.52	56.18	0.71	0.99			
BS718A	Alloy 718	0.57	0.0046	0.036	0.32	18.21	0.060	19.21	0.078	3.06	5.19	1.02	
SS345	IN 100	5.58	0.019	0.153	14.71	9.95				3.01		4.74	
SS350	IN 713	5.97	0.013	0.138	0.338	13.43		1.50	0.019	4.29	2.17	0.87	0.094
IMZ-180		6.00	0.017	0.107	9.95	7.98		0.073		5.93	0.025	1.02	0.05
IMZ-181		5.61	0.014	0.15	10.02	8.36		0.071		0.676	0.020	1.04	9.97
IMZ-182		5.69	0.013	0.169	13.52	8.63		0.040		3.10		4.69	
IMZ-183		3.51	0.010	0.10	8.32	15.87		0.046		1.81	0.92	3.34	2.66
IMZ-184		4.37	0.016	0.086	14.32	14.16				4.30	0.032	3.43	
IMZ-185		5.56	0.015	0.152	4.47	9.91		0.022		3.92		2.73	5.12
BS600-1	Inconel 600	0.26	0.0089	0.07	0.10	15.35	0.14	8.82	0.39	0.009	0.020	0.32	0.003
BS600-3	Inconel 600	0.09	0.0082	0.02	0.10	14.77	0.24	8.88	0.28	0.007	0.020	0.20	
256A	MP159	0.17	0.013	0.02	35.6	19.1	0.008	9.00	0.014	7.00	0.51	3.03	0.02
HC3-L	Hastelloy C	0.048	0.0093	0.102	0.903	17.48	0.254	5.02	0.698	18.0		0.087	4.42
1312		3.08	0.080	0.060	11.2	15.7		0.09		1.82	0.15	4.56	5.00
235		0.29		0.043		24.5		0.88	0.35	0.27		0.57	14.9
28		1.21	0.020	0.12	0.040	34.0		2.47		0.73	1.15	1.81	3.06

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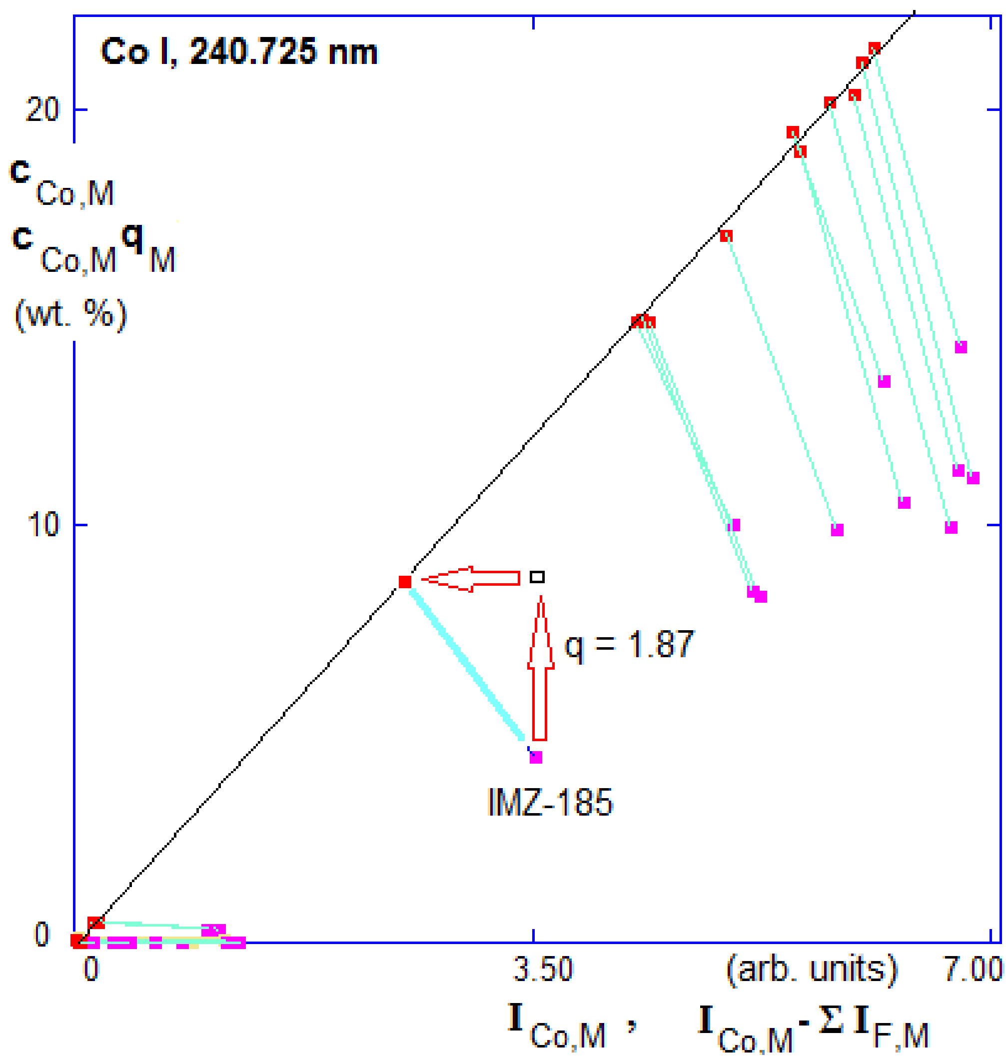
(combined with some steels and irons)

Cobalt in Ni alloys: calibration of the Co I line at 240.725 nm



LECO GDS500A: res. ≈75 pm

8 IECs, 15 degrees of freedom

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Z.Weiss, Calibration methods in glow discharge optical emission spectroscopy: a tutorial review, *J. Anal. At. Spectrom.*, 2015, 30, 1038–1049

3 more lines for cobalt, the IEC table for 2 instruments

LECO GDS500A : res. ≈75 pm

Co line λ [nm]	BEC [ppm Co]	IEC [ppm Co / 1 % interf.el.]								
		Fe	Mo	Nb	W	V	Cr	Ti	Ta	Ni
238.190	1 037	3 196	47	66	92				363	
240.725	1 257	378	76	128	69	132		87	52	247
340.512	728		70	251	13	136		47	14	
387.312	958	77	55	59	271	218	15	561	33	

LECO GDS900 : res. ≈40 pm

238.190	135	**3 156**	84	**43**	63				**472**	
240.725	431	104	**60**	54	42				23	50
340.512	1 057		**65**	**352**	**10**	**91**		18	31	
387.312	384	22	**38**		**230**	**167**		**597**	22	

e.g. INCONEL925 (BS 925): 0.34% Co, 2.20% Ti

if this line was not corrected for Ti:

we would get 0.47% Co ... there would be a 38% rel. error

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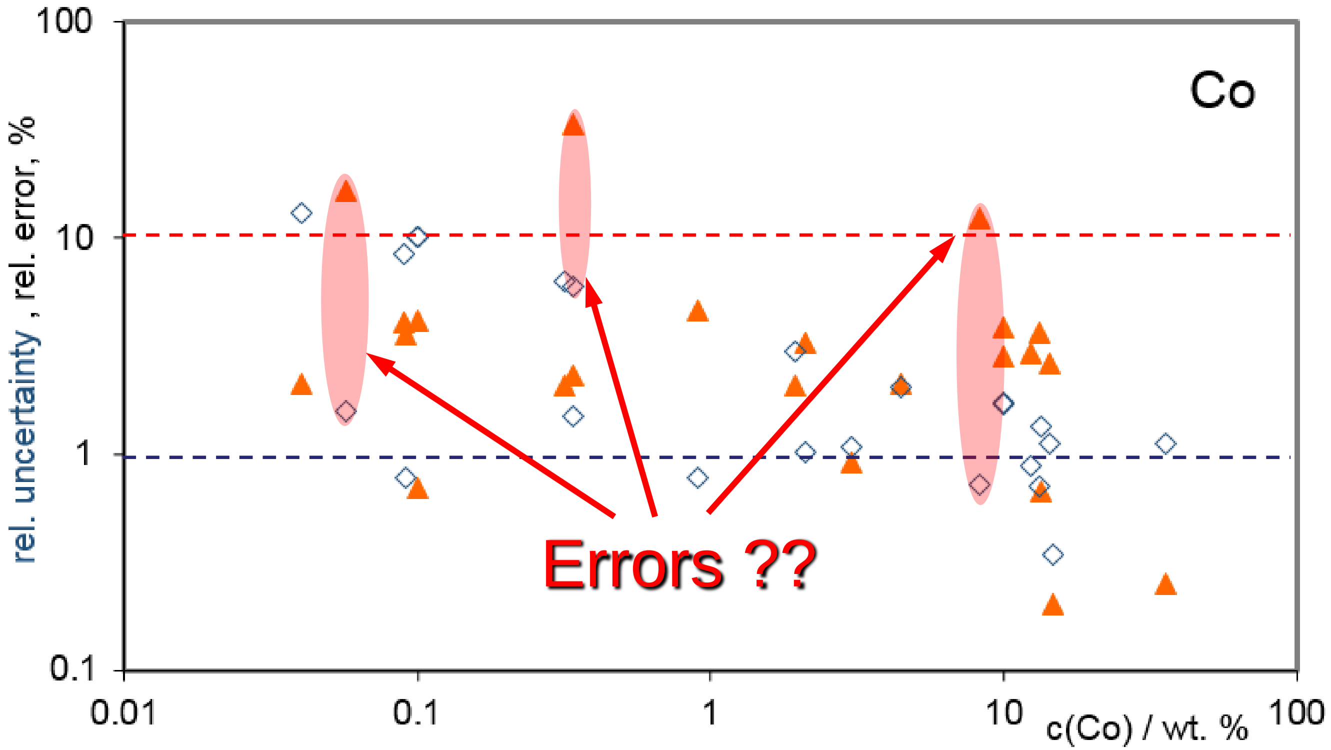
the accuracy achieved for cobalt

- I_{Co}/I_{Ni} –*versus*– c_{Co}/c_{Ni}), ref. line = Ni I, 460.500 nm, LECO GDS500
- line Co I, 240.725 nm, IECs: Fe, Mo, Ti, 22 degrees of freedom



◇ - declared relative uncertainties of the standards,

▲ - the magnitude of rel. errors

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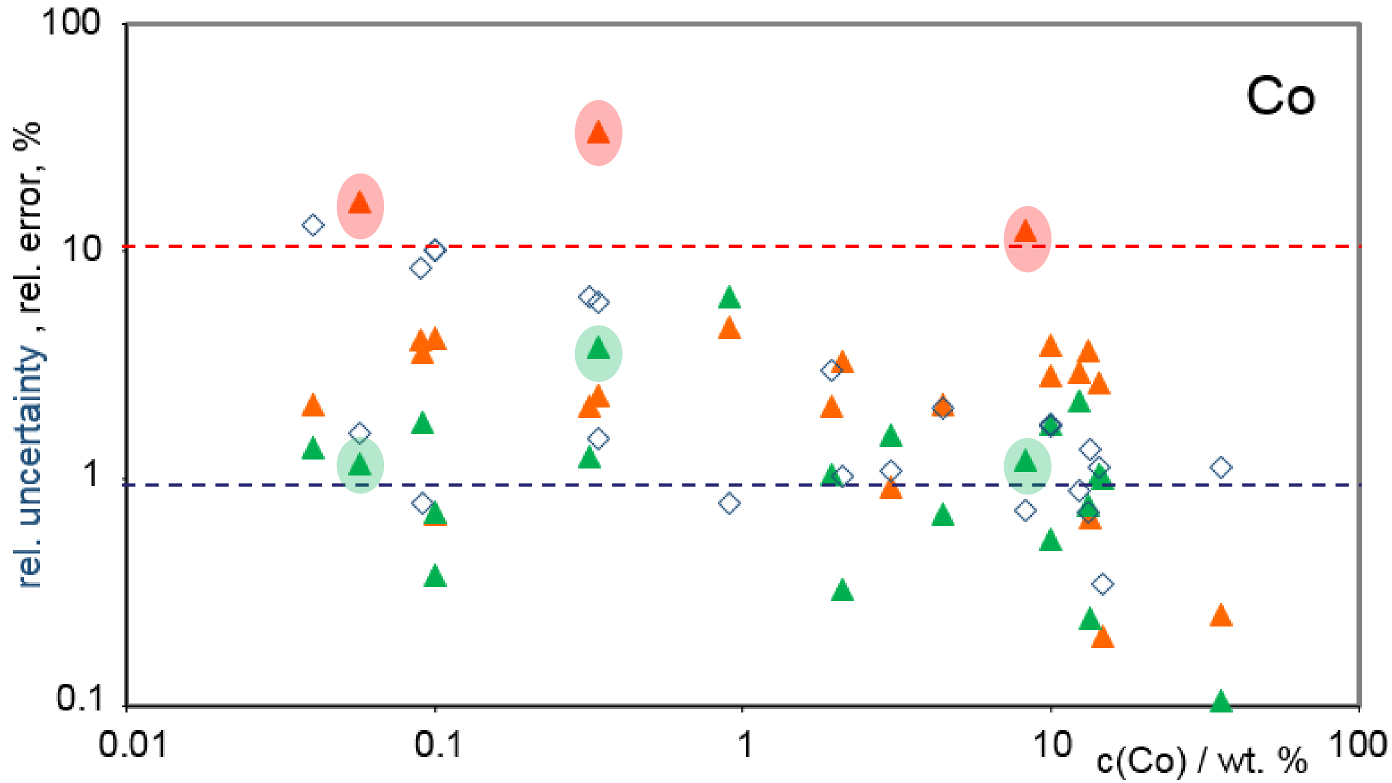
the ‘multi-line’ approach

cobalt, 5 lines combined: relative errors drop by a median factor of 2.8



◇ - declared rel. uncertainties of the standards,

▲ - the magnitude of rel. errors: ‘mode 3’, single line, Co I 240.725 nm

▲ - the magnitude of rel. errors: SR-corrected, 5 Co lines combined

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The applications and the fundamentals

- Two views of the reality: communication is needed in both directions
- The applications: how relevant are our empirical, though sometimes simplistic approaches ?
- The fundamentals:
  - real world is more complex than our selected examples for which we think we have explanations.
  - how to communicate our findings to get the message through ?

A look round the corner: TRs and TR diagrams

- how strongly are excited different states of an atom or an ion and why ?
- collisional excitation, excitation-related matrix effects
- a way to deal with the complexity of GD excitation

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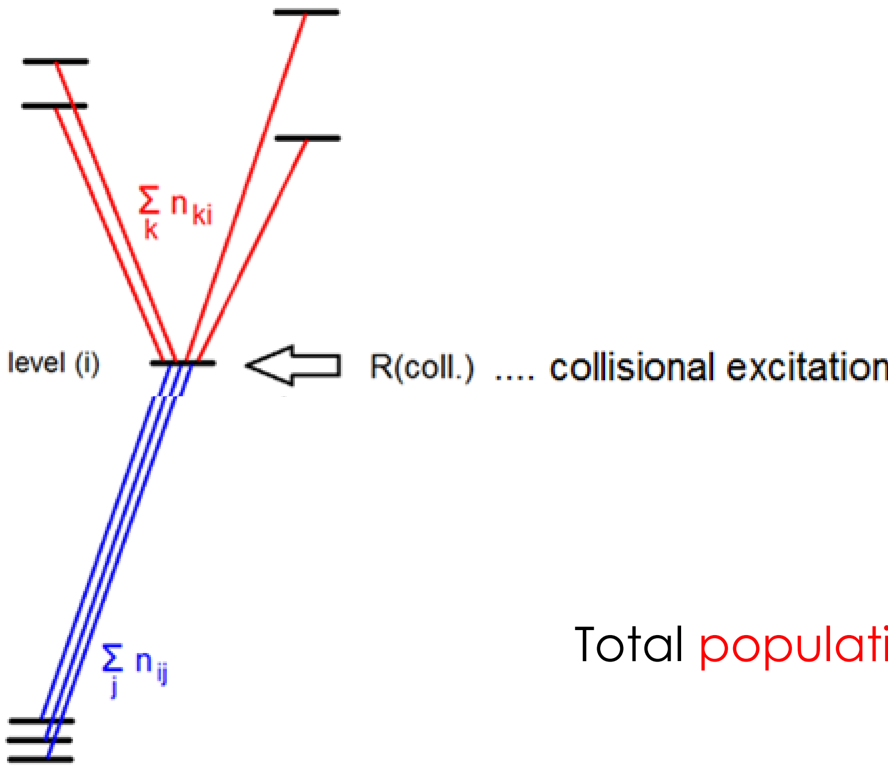
what is a TR diagram for an atom or ion:

radiative transition rate for ($i \rightarrow j$) : $n_{ij} \propto \lambda_{ij} I_{ij}$

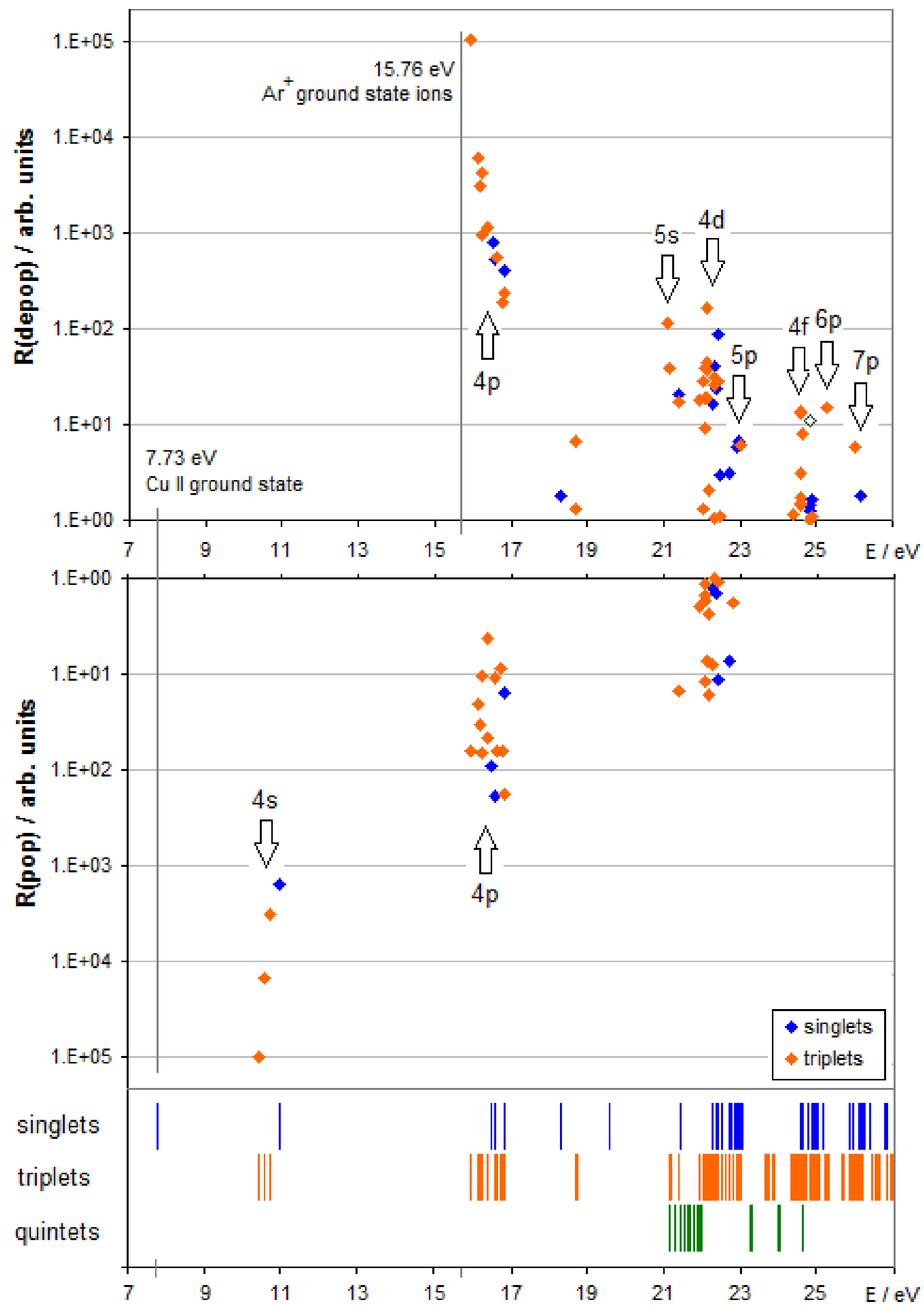


Total population /depopulation rate of a level:

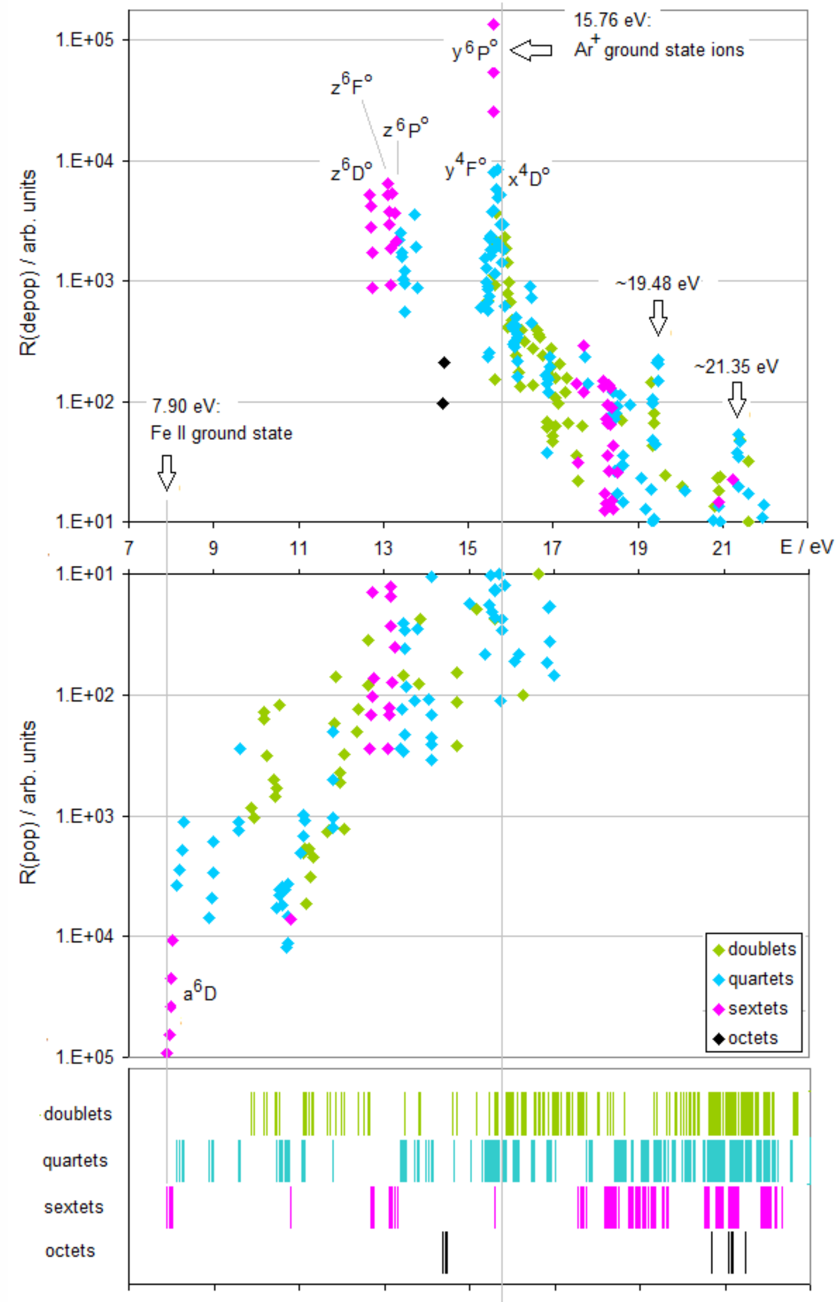
<u>steady state:</u>

$$R(\text{coll.}) = \sum_j n_{ij} - \sum_k n_{ki}$$

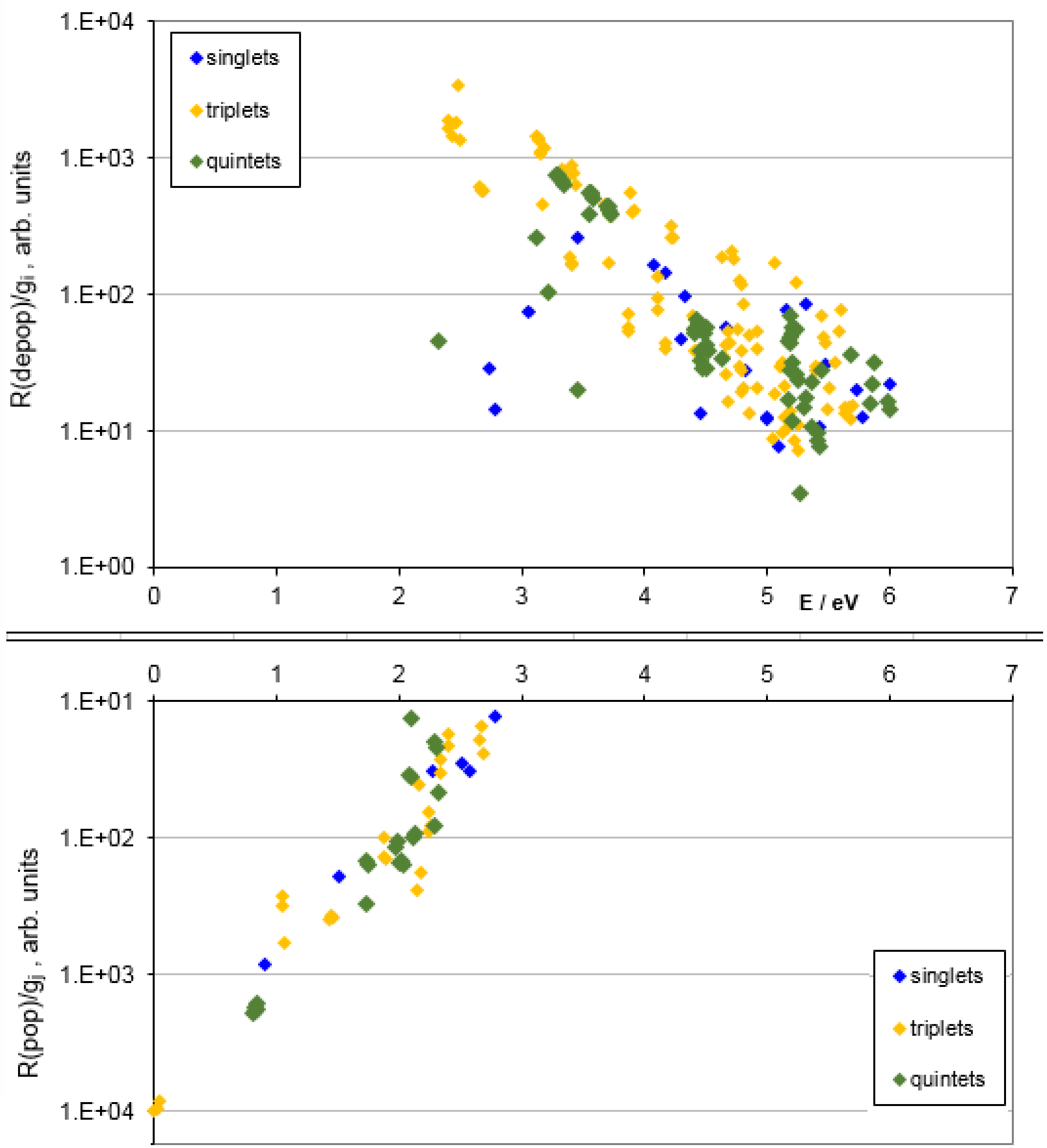
Cu II


R(depop) / arb. units
R(pop) / arb. units
15.76 eV
Ar+ ground state ions
7.73 eV
Cu II ground state
4p
5s
4d
5p
4f
6p
7p
4s
singlets
triplets
quintets
E / eV

Fe II


R(depop) / arb. units
R(pop) / arb. units
15.76 eV:
Ar+ ground state ions
7.90 eV:
Fe II ground state
y6P°
z6F°
z6P°
z6D°
y4F°
x4D°
~19.48 eV
~21.35 eV
a6D
doublets
quartets
sextets
octets
E / eV

Ti I: (TR/g) diagram in Ar discharge



there is no evidence for selective excitation

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What has been done so far

- 2013: TR diagrams for Mn
- 2014: TRs diagrams for Cu II, Fe II
- 2015: a review about TR diagrams

  Z. Weiss, E. Steers, J. Pickering, Transition rates and transition rate diagrams in atomic emission spectroscopy: A review , *Spectrochim. Acta Part B* 110 (2015) 79–90
- 2016: Effects of O, N, H - description by TRR diagrams
- pending: TR diagrams for Ti I, Ti II

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Matrix effects caused by oxygen, nitrogen, hydrogen

- different elements behave differently
- different lines/excited levels of an element behave differently
- no sound ‘general’approach to handling these effects is in sight yet
- but something can be done, after all
- example: the effects on GD-OES spectra of Cu^+ ions in Ne discharge caused by O, N, H
- TRR diagrams: instead of bare TR-s, on the ordinate are their ratios:

$$\frac{TR(with\ the\ light\ element\ present)}{TR(without\ any\ light\ element\ present)}$$

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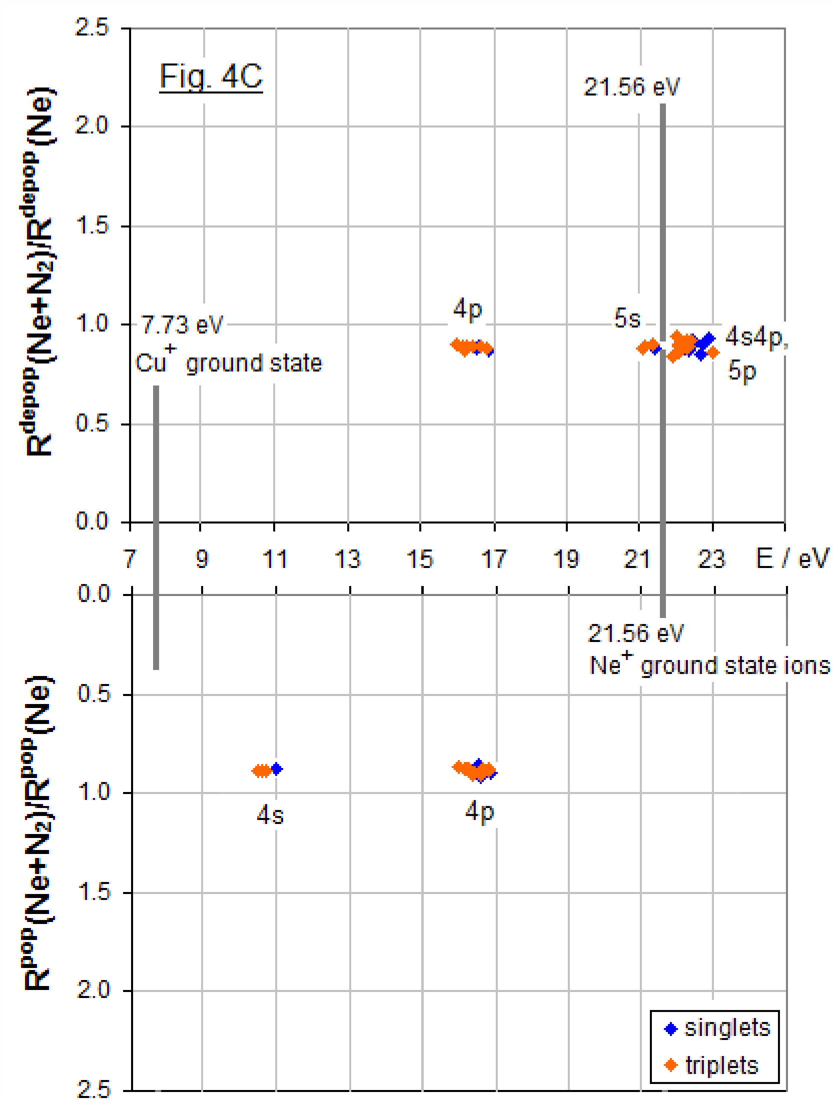
addition of nitrogen: nothing happens



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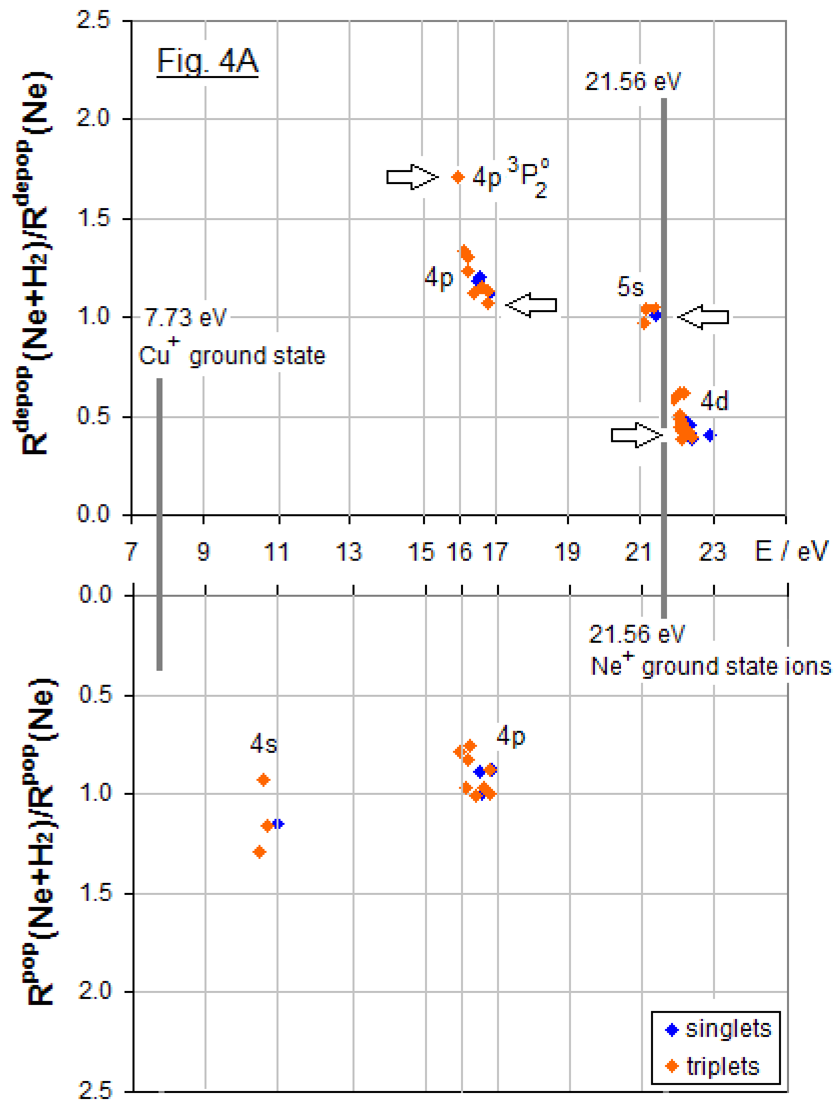
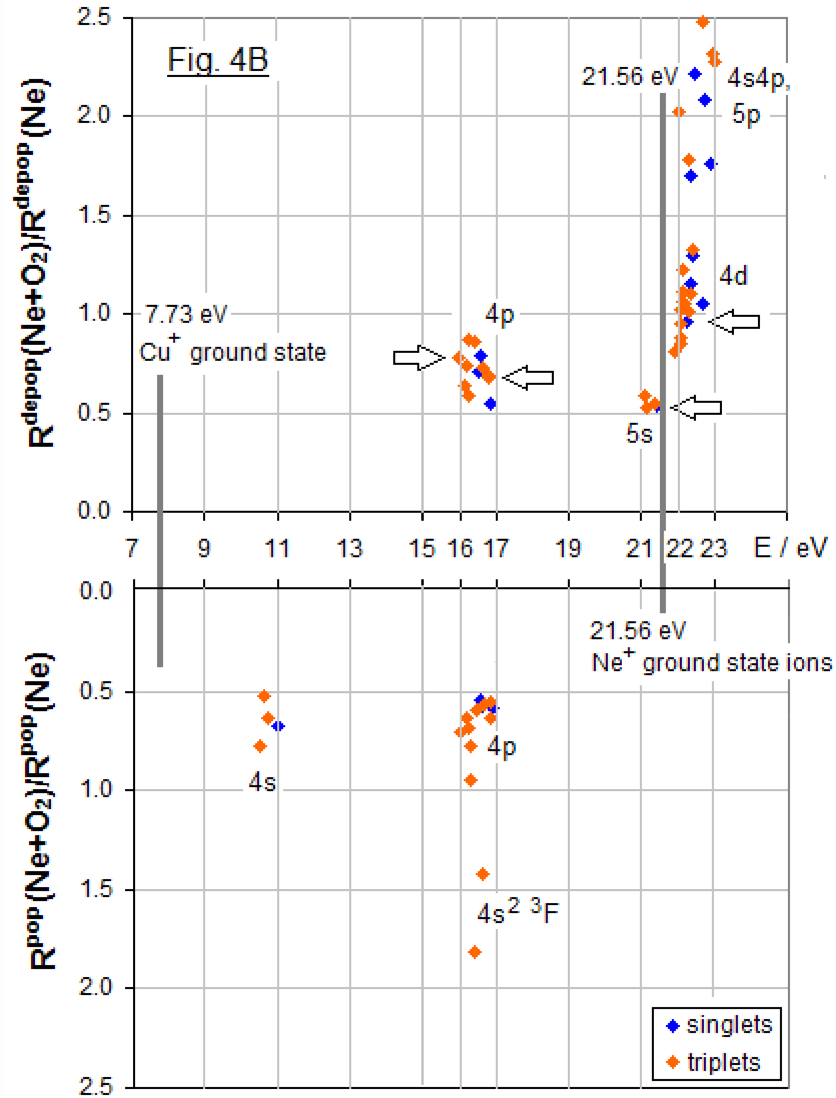
addition of H_2 or O_2:





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some explanations have been proposed:

Z. Weiss et al., Spectrochim. Acta Part B 118 (2016) 81-89

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Acknowledgments:

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Thank you for attention.

Danke für die Aufmerksamkeit !