Matrix effects in ionic emission lines of the elements ionized by charge transfer reactions with the working gas

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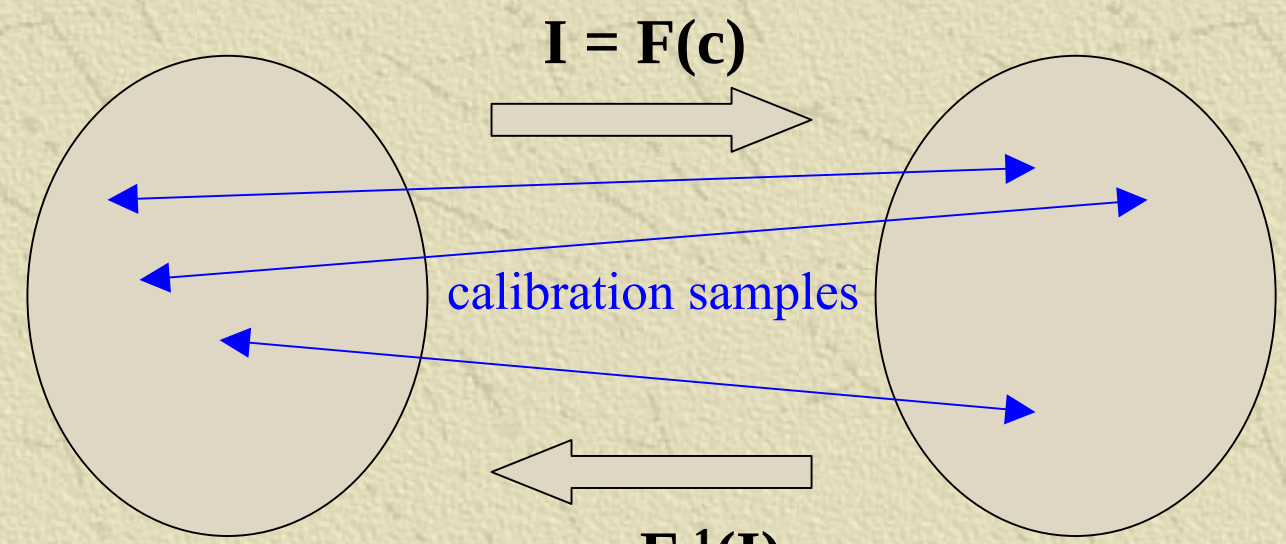
... why matrix effects in GD-OES ?

- accuracy : bulk- vs. surface / thin film analysis
- complex alloys, dissimilar matrices (coatings etc.)
- CCD-based instruments : multiple lines
- pragmatic approach / quest for explanations

relative methods: calibration and the analysis of the unknowns



composition of the material
(a vector space)

the signal response
(another vector space)

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the transformations **F** and $\mathbf{F^{-1}}$, their parameters, cal. model, cal. range

the standard calibration model in GD-OES :

$$I_{\lambda(E),M} = R_{\lambda(E)}\, c_{E,M}\, q_M$$

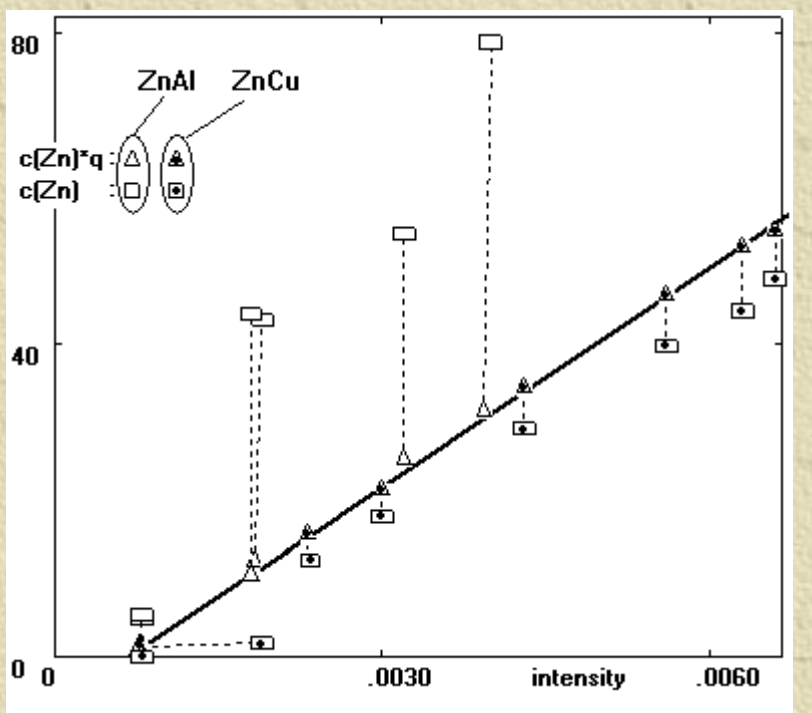
<u>matrix effect</u> : situation when the given *calibration model* is not describing the signal response accurately enough

<u>what we can do :</u>

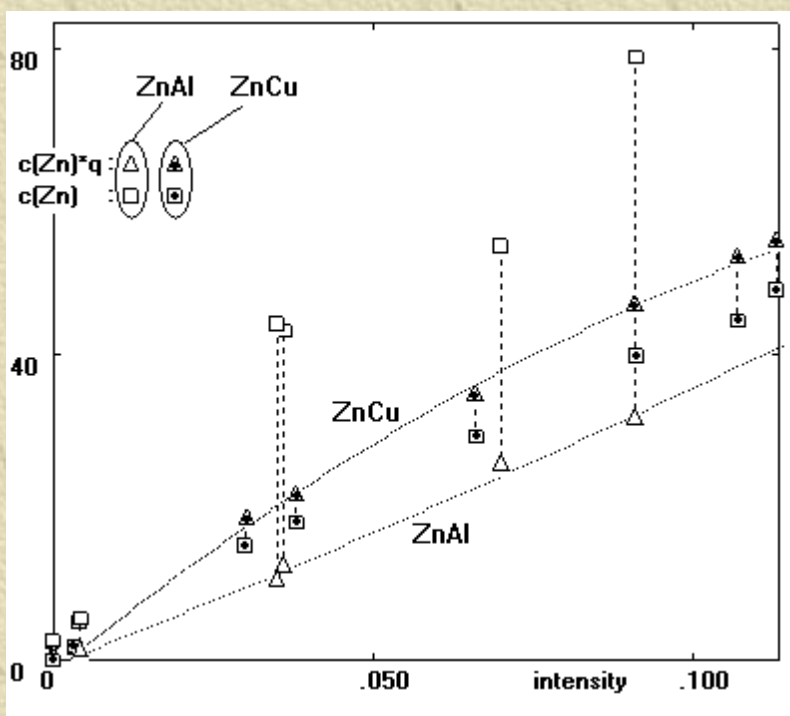
- reduce the calibration range
  - matrix-matched calibrations
  - the ‘type standardization’
- extend / change the calibration model
- claim that the results are OK anyway

the observed matrix effect

(mentioned first at WPC2005, Budapest)



Zn I, 268.416 nm



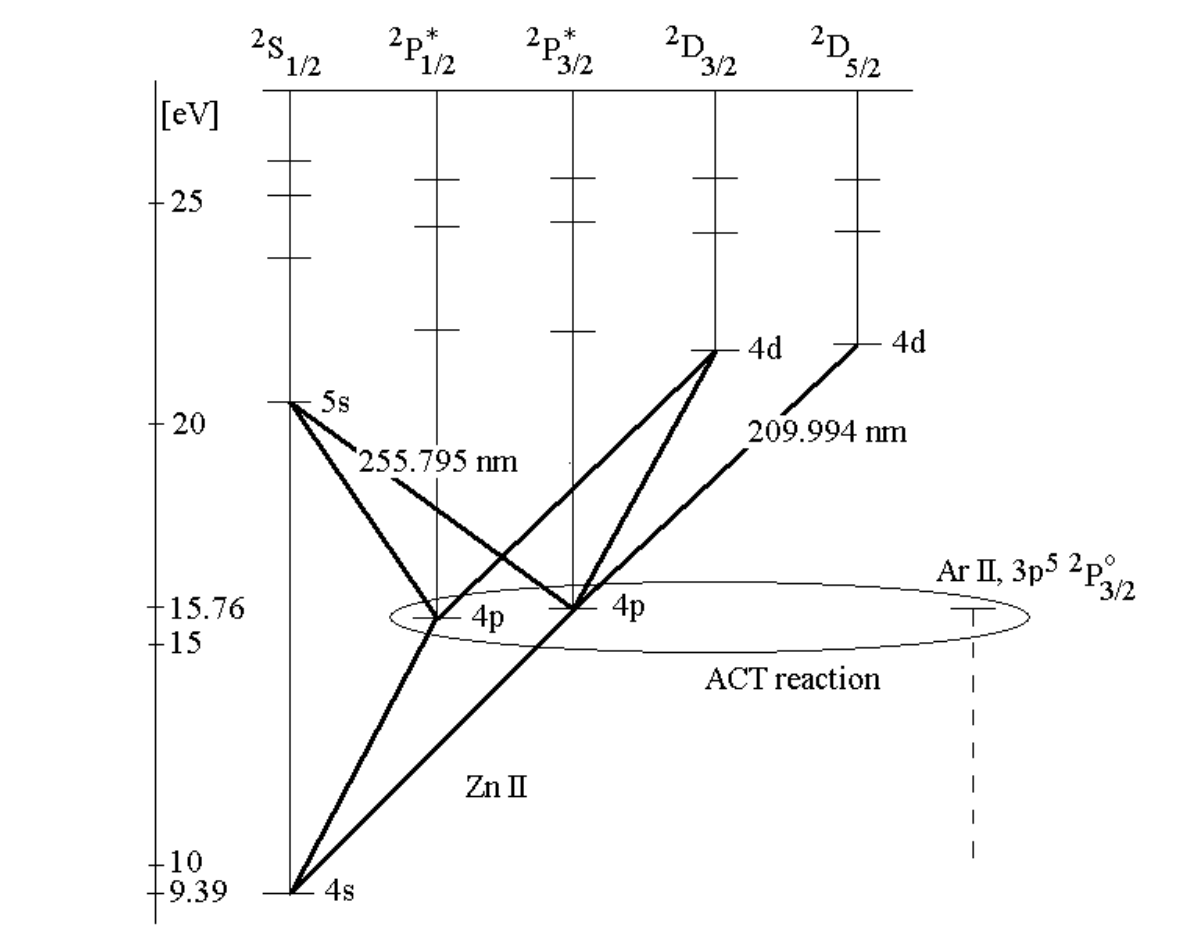
Zn II, 250.199 nm

and all other Zn II lines

a set of ZnCu, ZnAl alloys

DC discharge in Ar, 700V, 20mA, 4mm anode (LECO GDS500A)

Energy diagram of the zinc ion levels



proposed explanation :

(Z. Weiss, *J. Anal. At. Spectrom.*, 2006, **21**, 691-696)

$$Zn^0 + Ar^+ (3p^5\ {}^2P^o_{3/2}) \rightarrow Zn^{+*} (4p\ {}^2P^o) + Ar^0 + \Delta E$$

$$\Updownarrow$$

$$Cu^0 + Ar^{+*} (3p^5\ {}^2P^o_{1/2}) \rightarrow Cu^{+*} (4p\ {}^3P_2) + Ar^0 + \Delta E \qquad ^{1)}$$

Al II does not have any level with energy close to 15.75 eV ...
... no ACT with Ar^+, no reduction of the argon ionization degree

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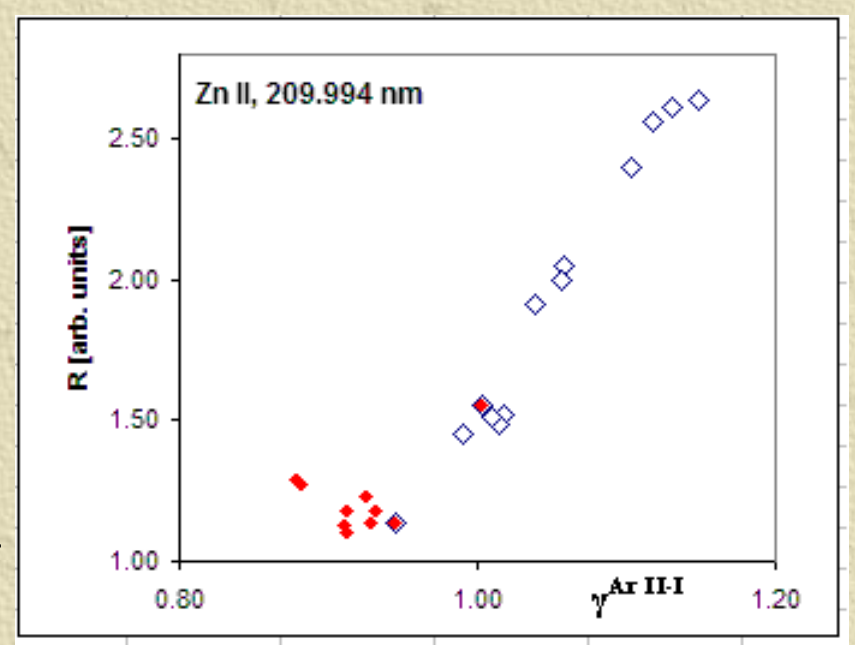
[1]) E.B.M. Steers, R.J. Fielding, *J. Anal. At. Spectrom.*, 1987, **2**, 239-243

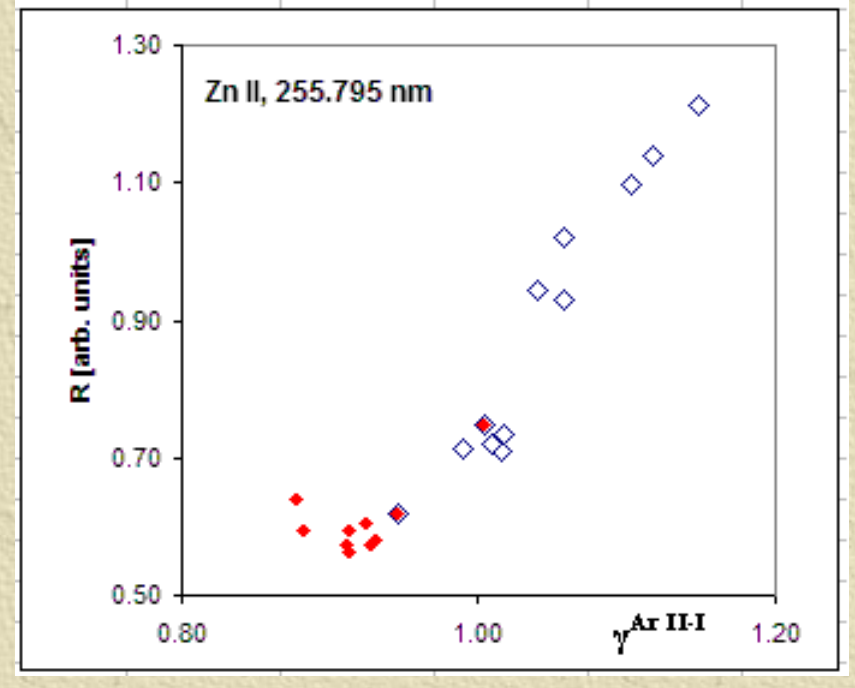
argon lines

10 Ar I lines, 10 Ar II lines :

$$\gamma^{Ar\,II-I}(M) = \left\{ \frac{I^{Ar\,II}(M)}{I^{Ar\,I}(M)} \right\}$$

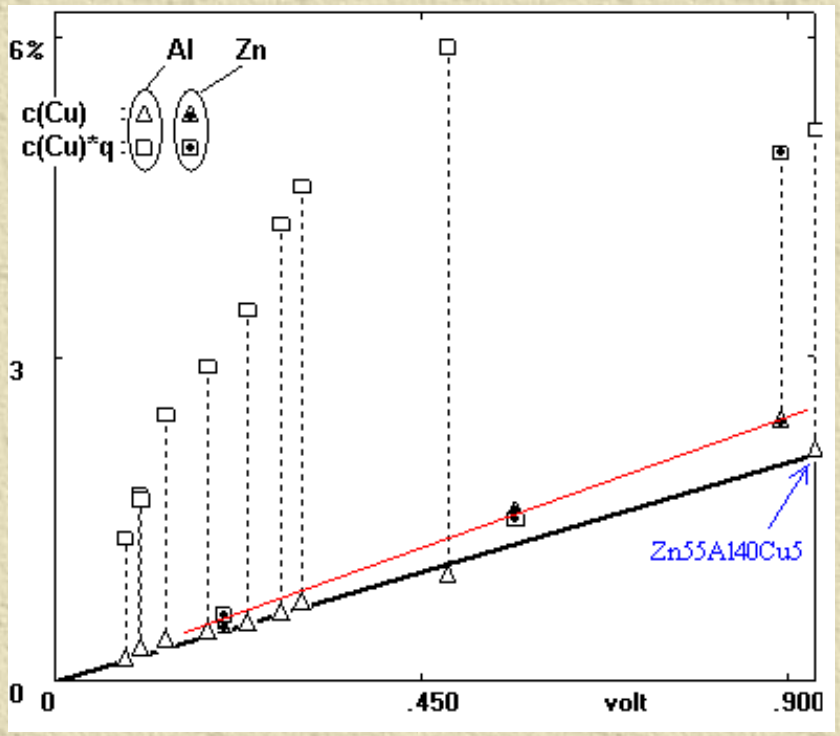
$\gamma^{Ar\,II\text{-}I}(M)$ reflects in some way the ionization degree of argon



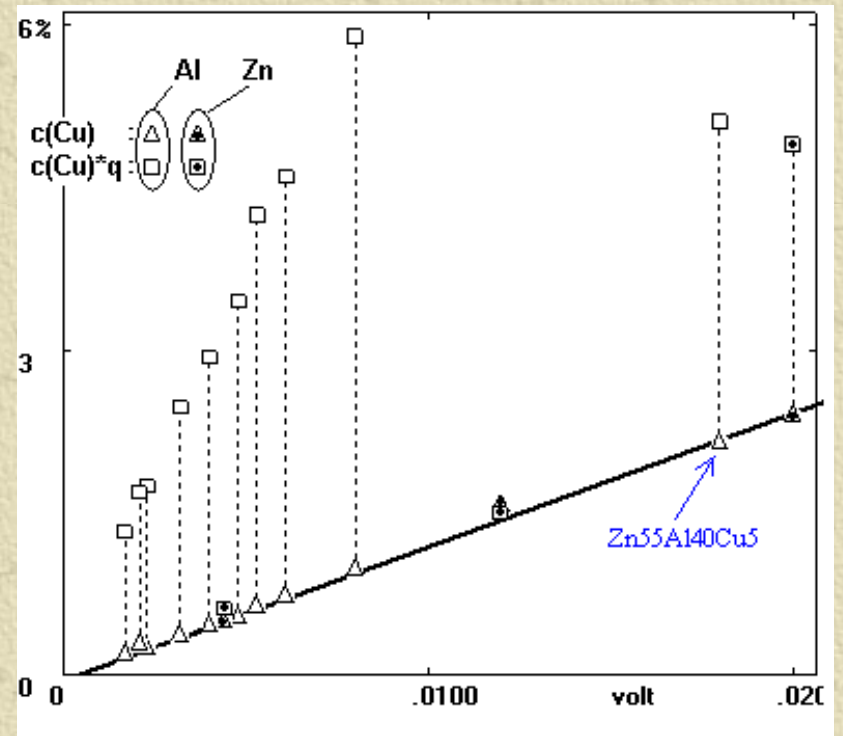


the reverse situation: effect of zinc on copper

small concentrations of copper in the Zn and Al matrices



Cu II, 224.700 nm

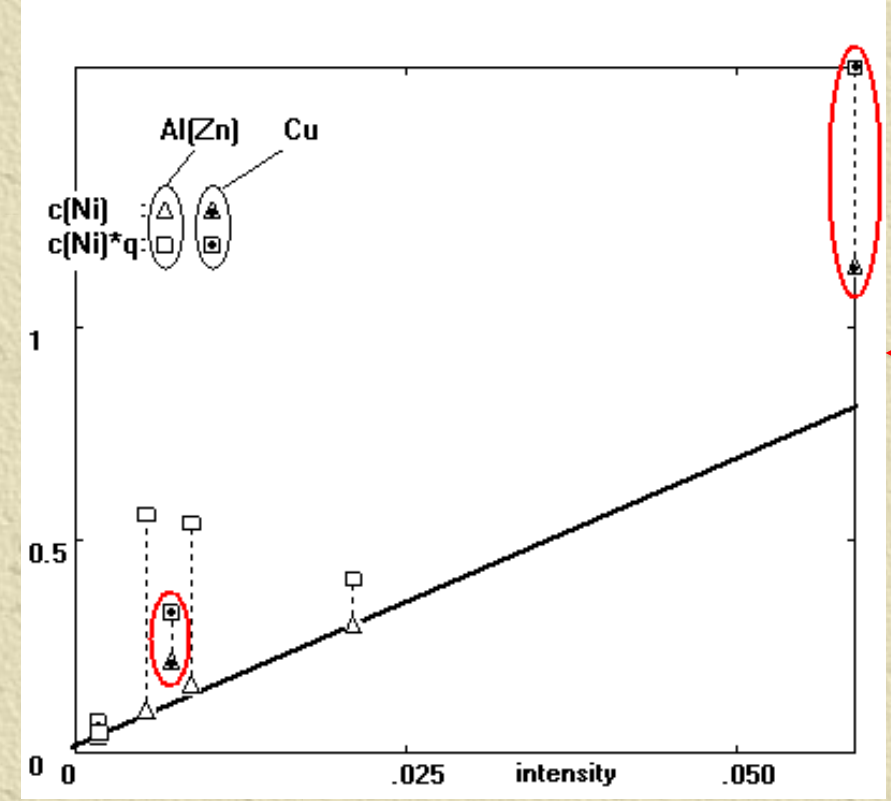


Cu I, 406.263 nm

can any other elements be affected as well ?

search for a matrix effect of this type in the copper matrix :

a Ni II level ... $3p^6\ 3d^8\ (3F)\ 4p\ \ ^2F^o_{7/2}$, E = 14.72 eV



2 lines from this level :

- Ni II, 229.655 nm
  _ (the plot on the left)
- Ni II, 237.542 nm

Δ E ≈ 1 eV ... isn't it too much for ACT ?

further remarks

- effect of hydrogen on the spectrum of zinc [1]) :
  - suppression of Zn II relative to Zn I
  ... H kills the Ar^+ ions
- are there any consequences for GD-MS ?
- this is just one class of matrix effects ...
  ... there are others, waiting for exploration

[1]) Z. Weiss, E.B.M. Steers, P. Šmíd, *J. Anal. At. Spectrom.*, 2005, **20**, 839-846

thank you for attention