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, monochromators, 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

111 Ti lines have \( I > I_{\text{max}} / 10 \) (≈20 are analytically important ?)
- all 1031 (1446) lines ... may interfere with other elements
- this range at a resolution of 50 pm ... 8000 “channels”
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
Example: analysis of Ni alloys on a CCD instrument

calibration ranges (some could be extended towards the ppm region)
Ni alloys: the list of the standards used (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

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

LECO GDS500A : res. \(\approx 75\) pm

<table>
<thead>
<tr>
<th>Co line [(^\text{nm})]</th>
<th>BEC [ppm Co]</th>
<th>IEC [ppm Co / 1% interf.el.]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Fe   Mo   Nb   W   V   Cr  Ti  Ta  Ni</td>
</tr>
<tr>
<td>238.190</td>
<td>1 037</td>
<td>3 196 47  66  92</td>
</tr>
<tr>
<td>240.725</td>
<td>1 257</td>
<td>378  76 128  69  132  87  52 247</td>
</tr>
<tr>
<td>340.512</td>
<td>728</td>
<td>70   251 13  136 47   14</td>
</tr>
<tr>
<td>387.312</td>
<td>958</td>
<td>77   55  59  271 218 15  561 33</td>
</tr>
</tbody>
</table>

LECO GDS900 : res. \(\approx 40\) pm

<table>
<thead>
<tr>
<th>Co line [(^\text{nm})]</th>
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<tr>
<td>240.725</td>
<td>431</td>
<td>104  60  54  42  23   50</td>
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<td>1 057</td>
<td>65   352 10  91  18   31</td>
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<tr>
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<td>384</td>
<td>22   38  230 167 597  22</td>
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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
the accuracy achieved for cobalt

- \( \frac{I_{Co}}{I_{Ni}} \) versus \( \frac{c_{Co}}{c_{Ni}} \), 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
the ‘multi-line’ approach

cobalt, 5 lines combined: relative errors drop by a median factor of 2.8
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
what is a TR diagram for an atom or ion:

radiative transition rate for \((i \rightarrow j)\) : 

\[
\frac{n_{ij}}{I_{ij}} \propto \lambda_{ij} I_{ij}
\]

Total population /depopulation rate of a level:

steady state:

\[
R(\text{coll.}) = \sum_j n_{ij} - \sum_k n_{ki}
\]
Ti I: (TR/g) diagram in Ar discharge

there is no evidence for selective excitation
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
- **2016**: Effects of O, N, H - description by TRR diagrams
- pending: TR diagrams for Ti I, Ti II
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:

$$\frac{TR(\text{with the light element present})}{TR(\text{without any light element present})}$$
addition of nitrogen: nothing happens
addition of H\textsubscript{2} or O\textsubscript{2}:

some explanations have been proposed:

Acknowledgments:

The TR diagrams are based on high-res. FTS spectra measured at Imperial College, London, UK, in 2010, under the RTN Gladnet, Project P16.

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Thank you for attention.
Danke für die Aufmerksamkeit!