Qualitative Analysis Blunders: the Perils of Automatic Peak Identification in EDS Analysis

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Automatic Qualitative Analysis (Peak ID)

• The critical first step in any EDS analysis: correctly identifying the elements responsible for the peaks

• Can we trust automatic qualitative analysis (peak identification) to always identify peaks of major constituents correctly?
  – **Major**: Concentration, $C > 0.1$ mass fraction (>10 weight %)
  – **Minor**: $0.01 \leq C \leq 0.1$ (1 to 10 weight %)
  – **Trace**: $C < 0.01$ (< 1 weight %)
Automatic Qualitative Analysis (Peak ID)

• Test automatic peak ID of commercial systems for the easiest case: major constituents
  – big peaks (high peak-to-background)
  – high counting statistics
  – no interferences
  – simple spectra

• Results on Peak ID of major constituents presented at M&M 2004, 2005, and 2006 conferences. Papers published:

Testing Automatic Peak Identification

Protocol

1. Select the pulse processing time constant to operate at optimum resolution for the particular EDS system.

2. Calibrate the EDS system (e.g., CuL and CuKα, preferably AlK and CuKα) and check the peak channel locations of some intermediate peaks, e.g., SiK, CaKα, TiKα, FeKα

3. Select a beam current to keep deadtime below 20%.

4. Obtain at least 1,000 counts in the peak channel for the peaks of interest.
KBr
E₀ = 10 keV
BrLα misidentified as AlKα
BrLl misidentified as AsLα

K vs. L vs. M bias in choosing from similar solutions
KBr
$E_0 = 20$ keV
BrL$\alpha$ still misidentified as AlK$\alpha$
despite correct identification of BrK$\alpha$-BrK$\beta$
BrL$\beta$ misidentified as AsL$\alpha$
Zircon

$E_0 = 20$ keV

26%DT

100 s

ZrL$\alpha$ misidentified as PtM$\alpha$
Niobium (element)  
$E_0 = 5$ keV 
$\text{NbL}\alpha$ misidentified as HgM$\alpha$  
$\text{NbL}\beta$ misidentified as Y L$\alpha$
KBr

$E_0 = 20$ keV

BrK$\alpha$ and BrL$\alpha$ correctly identified

K K$\alpha$ misidentified as U M$\alpha$

K K$\beta$ misidentified as SbL$\alpha$
KBr
$E_0 = 10$ keV
BrL$\alpha$ misidentified as YbM$\alpha$, despite previous success at $E_0=20$ keV
K K$\alpha$ misidentified as U M$\alpha$
K K$\beta$ misidentified as SbL$\alpha$
FeS\textsubscript{2} (pyrite, fool’s gold)

E\textsubscript{0} = 20 keV

FeK\alpha correctly identified

S K\alpha misidentified as PbM\alpha

Absence of Pb L lines is not considered when assigning PbM instead of S K!
Copper-Gold (NIST SRM 482)

$\text{AuM}_\alpha$ is misidentified as $\text{NbL}_\alpha$

$\text{AuM}_\zeta$ is misidentified as $\text{RbL}_\alpha$

$E_0 = 10 \text{ keV}$
Copper-Gold Standard Reference Material

AuMα is misidentified as NbLα

E₀ = 15 keV

Manufacturer #3

Intensity of this peak is still too low relative to noise threshold to identify

More than 2000 counts in AuM family
Copper- Gold Standard Reference Material

Correct assignments: With $E_0 = 15$ keV, the NbLα solution is put up initially, but as soon as the AuLα peak is detected (AuMα > 1500 counts/channel) and labeled, the NbLα solution is replaced by AuMα, the correct solution. Even so, the indicated RbLα peak is really AuMζ.

NbLα is the only solution given if $E_0 = 12$ keV or lower so that AuL cannot be excited.

Intensity (P/B) of this peak is now adequate for identification.
Possible Troublemakers
(Closely spaced K-L-M peaks; not necessarily a complete list!)

- 0.390-0.395 keV  N K (0.392); ScLα (0.395)
- 0.510-0.525 keV  O K (0.523); V Lα (0.511)
- 0.670-0.710 keV  F K (0.677); FeLα (0.705)
- 0.845-0.855 keV  NeKα (0.848); NiLα (0.851)
- 1.00-1.05 keV    NaKα (1.041); ZnLα (1.012); PmMα (1.032)
- 1.20-1.30 keV    MgKα (1.253); AsLα (1.282); TbMα (1.246)
- 1.45-1.55 keV    AlKα (1.487); BrLα (1.480); YbMα (1.521)
- 1.70-1.80 keV    SiKα (1.740); TaMα (1.709); W Mα (1.774)
- 2.00-2.05 keV    PKα (2.013); ZrLα (2.042); PtMα (2.048)
- 2.10-2.20 keV    NbLα (2.166); AuMα (2.120); HgMα (2.191)
- 2.28-2.35 keV    S Kα (2.307); MoLα (2.293); PbMα (2.342)
- 2.40-2.45 keV    TcLα (2.424); BiMα (2.419)
- 2.60-2.70 keV    ClKα (2.621); RhLα (2.696)
- 2.95-3.00 keV    ArKα (2.956); AgLα (2.983); ThMα1 (2.996)
- 3.10-3.20 keV    CdLα (3.132); U Mα1 (3.170)
- 3.25-3.35 keV    K Kα (3.312); InLα (3.285); U Mβ (3.336)
- 4.45-4.55 keV    TiKα (4.510); BaLα (4.467)
- 4.90-5.00 keV    TiKβ (4.931); V Kα (4.949)

Directly observed
Peak ID for Minor (0.01 \leq C \leq 0.1 \text{ mass fraction}) and Trace (C < 0.01 \text{ mass fraction}) Constituents

- Things only get worse because of lower peak-to-background
- Round up the usual suspects (Table)
- Additional problems are found that lead to false positives
  - Not recognizing minor family members, L1, M_2N_4
  - Ignoring M-family solution (despite having data!)
  - Escape and sum peaks misinterpreted
Polystyrene 30%
Polymethylmethacrylate 70% with decabromodiphenyl ether (0.023)

$E_0 = 10 \text{ keV}$

Beam current = 2 nA

Time = 1000 seconds

BrLα misidentified as AlKα
Polystyrene 30%
Polymethylmethacrylate 70%
with decabromyldiphenyl ether (0.023)
$E_0 = 10 \text{ keV}$
Beam current = 1 nA
Time = 20 seconds
BrLα misidentified as AlKα
Polystyrene 30%
Polymethylmethacrylate 70%
with decabromyldiphenyl ether (0.023)
$E_0 = 10$ keV
Beam current = 1 nA
Time = 20 seconds

BrL\(\alpha\) correctly identified (approx. 1 in 10 times)

Instability of the Peak ID solution with low counting statistics.
LaB$_6$- 
$E_0 = 5$ keV 
$i_B = 2$ nA 
$t = 200s$

Complex M-families may be misinterpreted:
LaM$_\zeta$ as MnL
LaM$_{\alpha,\beta}$ as NiL
LaM$_\gamma$ as NaK
CeO$_2$
$E_0 = 5$ keV
$i_B = 2$nA
$t = 200$s

Complex M-families may be misinterpreted:
CeM$\zeta$ as F K
CeM$\alpha,\beta$ as GaL$
\gamma$
CeM$\gamma$ as GaL$\alpha,\beta$
Incorrect identification of sum peak by automatic qualitative analysis

Al K sum peak = 2.98 keV, exactly that of AgLα

Misidentification of Al + Al as AgLα
Incorrect identification of sum peak by automatic qualitative analysis

The sum peak can be diminished to a negligible level by operating at low deadtime.

**FALSE POSITIVE**

\[
A_1 \\
E_0 = 20 \text{ eV}
\]
CaF$_2$

$E_0 = 10$ keV

Escape peak misidentified as trace constituent

FALSE POSITIVE

P = 275 counts

$3B^{1/2} = 45$

CaK$_\alpha$

CaK$_\beta$

YL$_\alpha_1$

C K  F K

$\text{CaK}_\alpha = \text{CaK}_\alpha - \text{SiK}_\alpha$

$= 3.690 - 1.740$

$= 1.950$ keV

YL$_\alpha_1 = 1.922$

Pho$$

\text{ton Energy (keV)}$

km - 0.5 - Ca
Choosing a higher threshold for the “Spectral sensitivity” (P/B noise) setting may suppress this identification of false peaks.
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Peak ID for Low Voltage Microanalysis ($E_0 \leq 5$ keV)

- $E_0 = 5$ keV is the lowest energy for which the entire Periodic Table (except H, He, Li) is accessible by EDS, although some elements are just barely detectable, e.g., Cs, Ba
- Operating with LVSEM conditions ($E_0 \leq 5$ keV) eliminates K- and L- shell information critical for robust peak ID obtained from peaks with photon energies $> 5$ keV.
- Unfamiliar L- and M- shells must be used instead.
- The fluorescence yield of these low photon energy L- and M- shell peaks is often very low, resulting in low P/B, even from pure elements
- The intensity relationships among family members may behave in unexpected ways.
- As $E_0$ is reduced below 5 keV, significant portions of the Periodic Table become inaccessible by EDS, even for pure elements
Titanium

$E_0 = 5 \text{ keV}$

Useful P/B for TiL-family, but O K is very close
**BaCO₃**  
**E₀ = 5 keV**  
Very poor P/B for BaM-family, and unexpected intensity relationships.
Why does automatic Peak ID fail?

• Apparent reliance on the “single channel” solution
What is going on here? Basic Peak ID finds the peak channel only and then proceeds to a look-up table!

KBr

$E_0 = 20$ keV

NIST DTSA

Auto peak ID

Peak finding algorithm
Basic single channel Peak ID is vulnerable to convolution of family members

KBr
E₀ = 5 keV
BrLα misidentified as AlKα
On a peak channel basis, AlKα is actually A better fit than BrLα!
KBr
$E_0 = 5$ keV
BrL$\alpha$ misidentified as AlK$\alpha$
On a peak channel basis, AlK$\alpha$ is actually a better fit than BrL$\alpha$!
Niobium (element)

$E_0 = 5$ keV

$\text{NbL}_\alpha$ misidentified as $\text{HgM}_\alpha$
A more robust approach: multiple linear least squares (MLLS) fitting

- Locate candidate peak
- Determine possible elemental families, e.g., AlK, BrL, YbM for $E = \sim 1.5$ keV
- Fit the peak reference over the full range of channels necessary to span family
- Test and compare residuals after fitting
KBr
$
E_0 = 5 \text{ keV}
$
$
i_B = 5 \text{ nA}
$
$
t = 10 \text{ s}
$
BrL fit with BrL
KBr
$E_0 = 5$ keV
$i_B = 5$ nA
$t = 10$ s
BrL fit with AlK
KBr

$E_0 = 5 \text{ keV}$

$i_B = 5 \text{ nA}$

$t = 10 \text{ s}$

BrL fit with YbM
1/10 of the dose of the previous example

BrL with AlK reference
1/10 of the dose of the previous example

BrL with BrL reference
Summary of blunders observed with Automatic Peak Identification under conventional beam energy conditions ($10 \leq E_0 \leq 30$ keV)

- It is estimated that if the entire Periodic Table (except H, He, and Li) is in play, about 3% to 5% of automatic peak IDs of major elements result in blunders (e.g., SiK instead of TaM; AlK instead of BrL).
- These blunders are not random mistakes. The same element/peak in different systems will be consistently misidentified, e.g., AlK for BrL in various Br-compounds.
- These blunders occur despite high counting statistics.
- In some EDS systems, identifying a high energy K or L peak does not eliminate the blunder on the corresponding low energy L or M peak; e.g., ZnK-ZnL (NaK)
- Poor EDS calibration makes the problem much worse!!
- The problem is worse for minor and trace constituents
- The problem is worse for low voltage ($E_0 \leq 5$ keV) microanalysis