Analysis of impurities in 99.99 % copper

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Boliden Rönnskär

- Boliden operates mines and smelters in Sweden, Finland, Norway and on Ireland.
- Main products are copper, zinc, lead, gold and silver.

- Rönnskär copper smelter outside Skellefteå
- Concentrates from mines and electronic scrap
- Produces copper, gold, silver and lead (plus a number of other by-products)
- 219,000 tonnes copper produced yearly

Laboratory at Boliden Rönnskär

- Process control (24-7)
- Raw materials and products
- Environmental analysis
- R&D samples

- 30 persons working with analysis
- Different instruments and classical techniques.
- New ICP-MS

Analysis of pure copper – requirements

- Important — Product – sell or discard
- Daily — Copper produced and shipped 365 days of the year
- Rapid — Samples arriving in the afternoon/evening, results finished the morning after sampling
- ppm level — Impurities in the ppm/sub ppm level in the solid sample
- Elements — Ag, As, Bi, Fe, Ni, Pb, S, Sb, Se, Te (and more…)

Different instruments for the analysis

1988 – 2013

DC-arc

Could run on solid samples.

Got too old and needed to be replaced

2011 – present

Spark-OES

Can run on solid samples

Fast and simple to use

Not sensitive enough for some elements (Bi, Sb, Te).

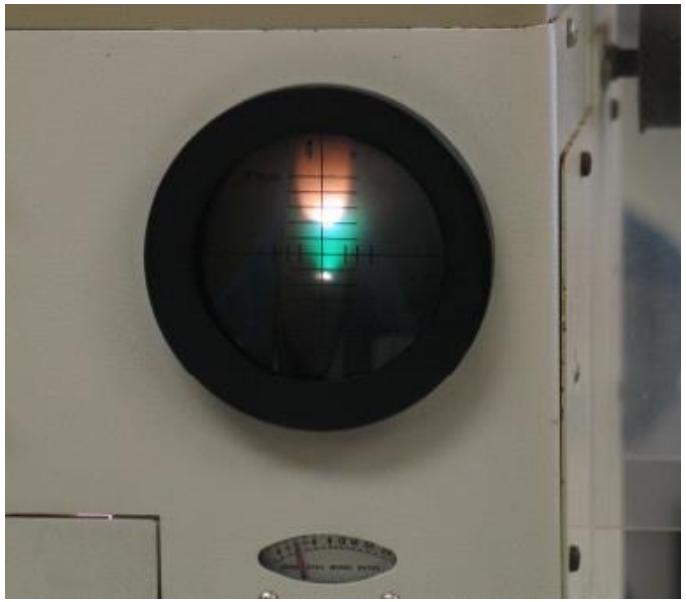
2014 – present

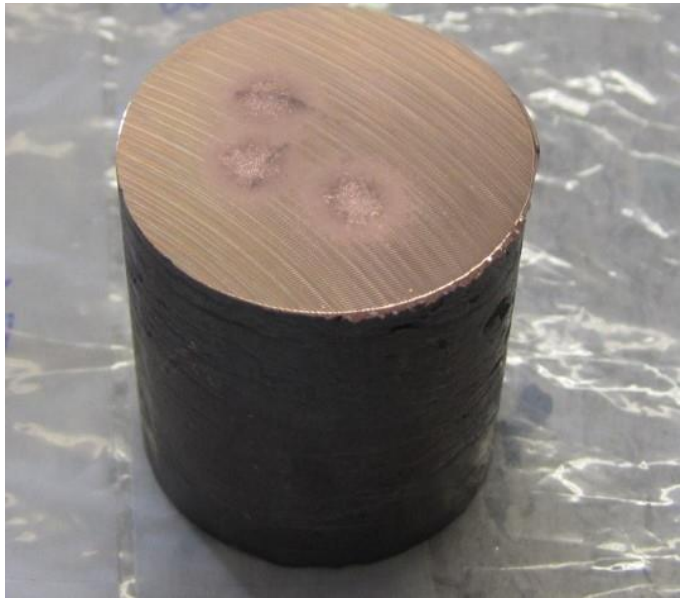
GFAAS for solid samples

Can run on solid samples

Too time consuming

Other issues





ICP-MS – advantages and drawbacks

Advantages

- Technique with low detection limit.
- Calibration from standard solutions, not depending on good solid reference material.
- Multi element technique with the possibilities to add new elements if required.
- Could be used as a backup for our spark-OES.
- Well established technique (but maybe not for our type of samples)

Drawbacks

- Dissolving the sample – takes time and risk for contamination.
- Advanced technique, not suitable for running on night shift with lots of different people involved.
- No experience of ICP-MS in the laboratory
- High matrix element (Cu) could be a problem?

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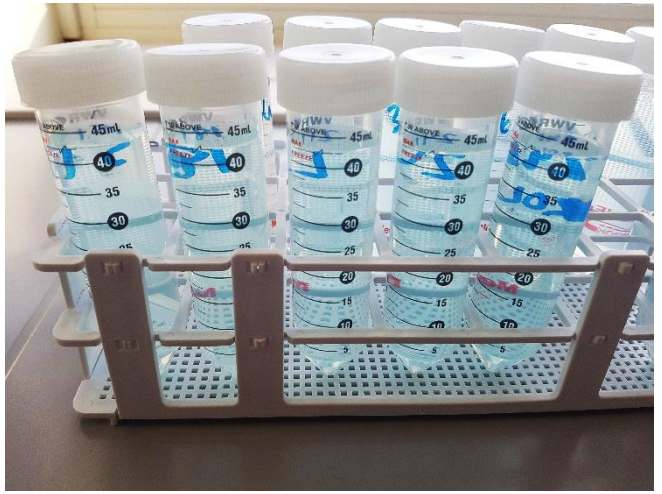
Sample preparation

- Easy to dissolve in nitric acid
- 50 ml metal free plastic tubes
- 0.04 – 0.05 g of copper chips
- 2.25 ml HNO_3 (5 %)
- Wait for a few minutes for the copper to dissolve and dilute to 45 ml.
- Dilution factor 1000 (1 ppb measured equals 1 ppm in the solid sample)



Method setup

- Nine elements
- Recommended masses, except for Se and Te
- All elements measured in KED mode
- Indium and iridium 5 ppb used as internal standard
- Calibration from 1000 ppm standard solution made in concentration of 0.5 – 1 – 5 – 10 – 20 and 50 ppb
- Priming with Cu-samples for stability

Element	Mass	Internal standard	Max. calibration
Ag	107	Ir	50 ppb
As	75	In	5 ppb
Bi	**209**	**Ir**	**5 ppb**
Fe	57	In	50 ppb
Ni	70	Ir	10 ppb
Pb	208	Ir	10 ppb
Sb	**121**	**In**	**10 ppb**
Se	78	In	5 ppb
Te	**130**	**In**	**5 ppb**

Validation set-up

- Linearity of calibration up to 50 ppb
- LOD and LOQ at least as good as our current instruments
- Precision, accuracy and measurement uncertainty
- BAM-M381, BAM-M382, BAM-M383 and BAM-M384 pure copper reference material analyzed a number of times

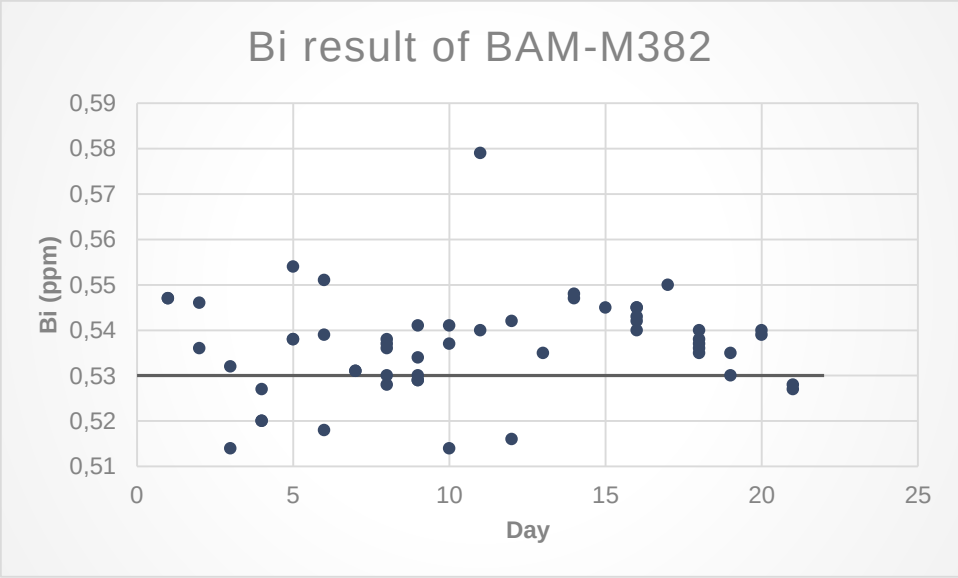
LOD/LOQ

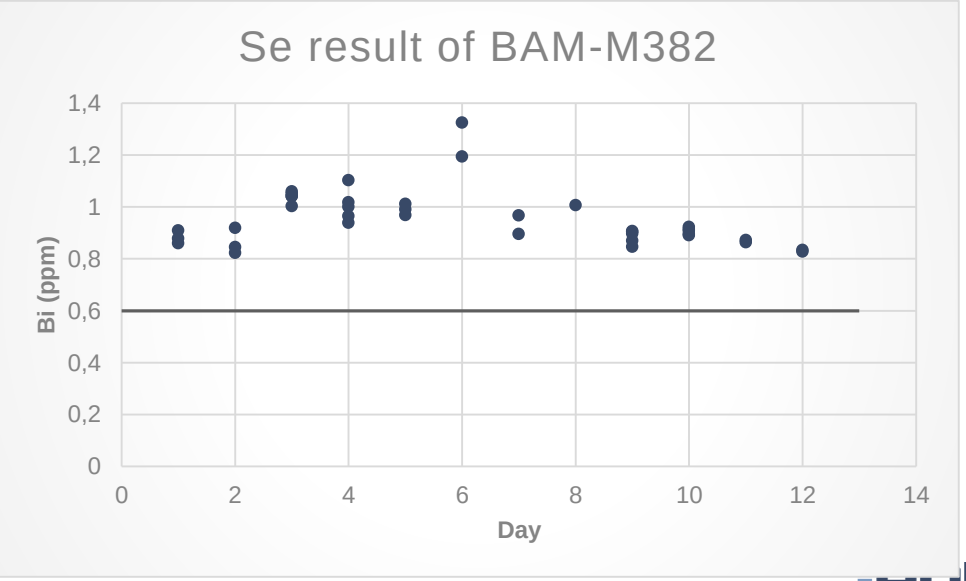
Element	LOD (ppm)	LOQ (ppm)	Requirement LOQ (ppm)
Ag	0.014	0.048	1.0
As	0.013	0.043	0.5
Bi	0.001	0.002	0.1
Fe	0.22	0.75	2.0
Ni	0.040	0.13	0.3
Pb	0.008	0.028	1.0
Sb	0.002	0.007	0.2
Se	0.042	0.14	0.5
Te	0.004	0.012	0.2

Precision & Accuracy

- Precision typical between 2 and 10 %
- A little higher (20-40 %) for some concentrations below LOQ (0,2 ppm and lower)

- Recovery of reference material typically between 80 and 120 % for all elements except Se
- Recovery for Se:
  160 % at 0.6 ppm
  130 % at 1.2 ppm
  93 % at 4.2 ppm

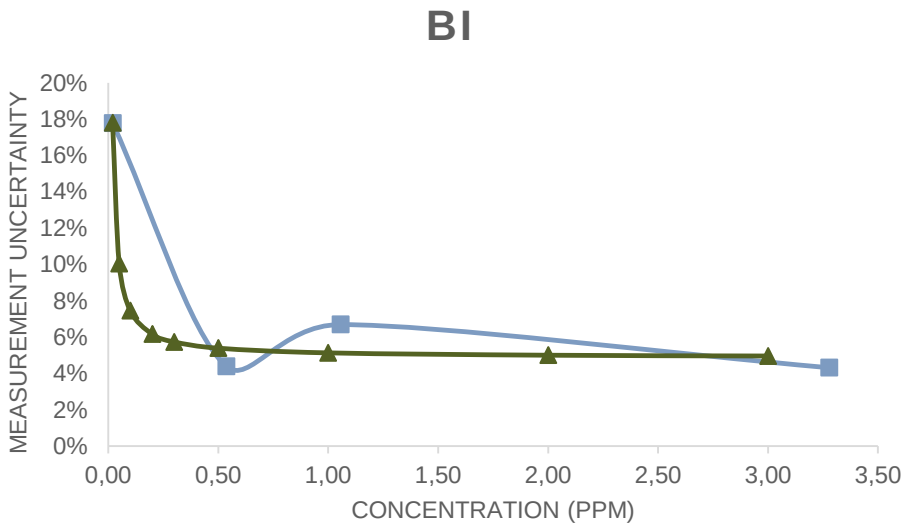


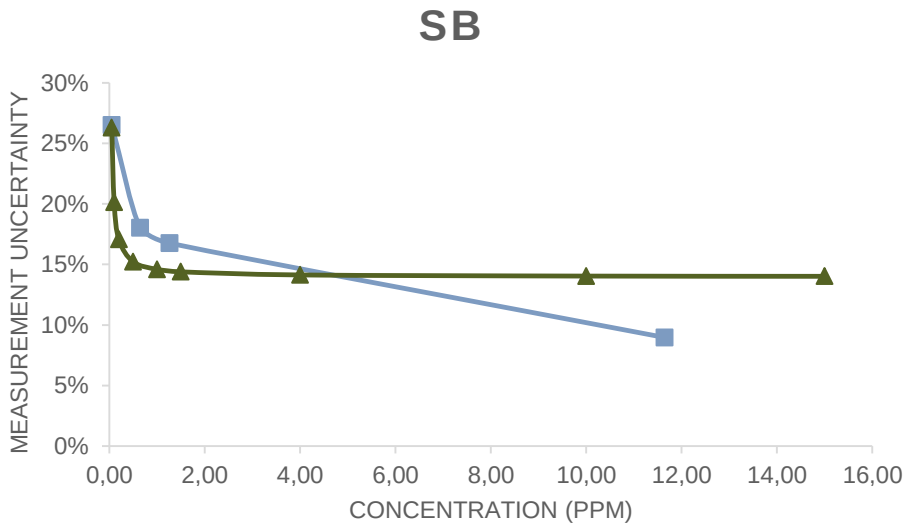


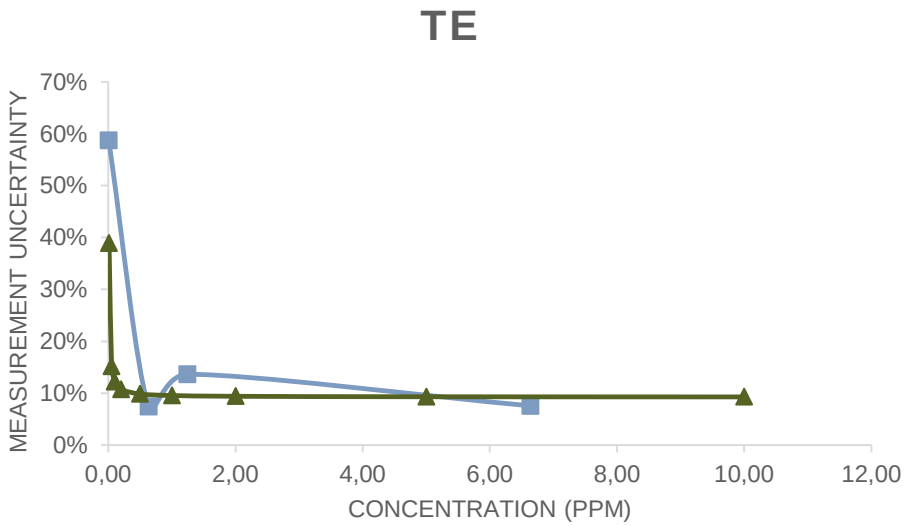
Selenium

- Need accurate results down to 0.5 ppm
- Calibration standards OK, but not Cu samples
- Adding about 5 % ethanol to the internal standard suggested by instrument supplier (article from Journal of Analytical Atomic Spectrometry)
- Still good precision for Se
- The recovery for the reference material is between 94 and 114 % for Se, which is good.
- The other elements are also ok with ethanol in the internal standard
- Not as a routine

Measurement uncertainty



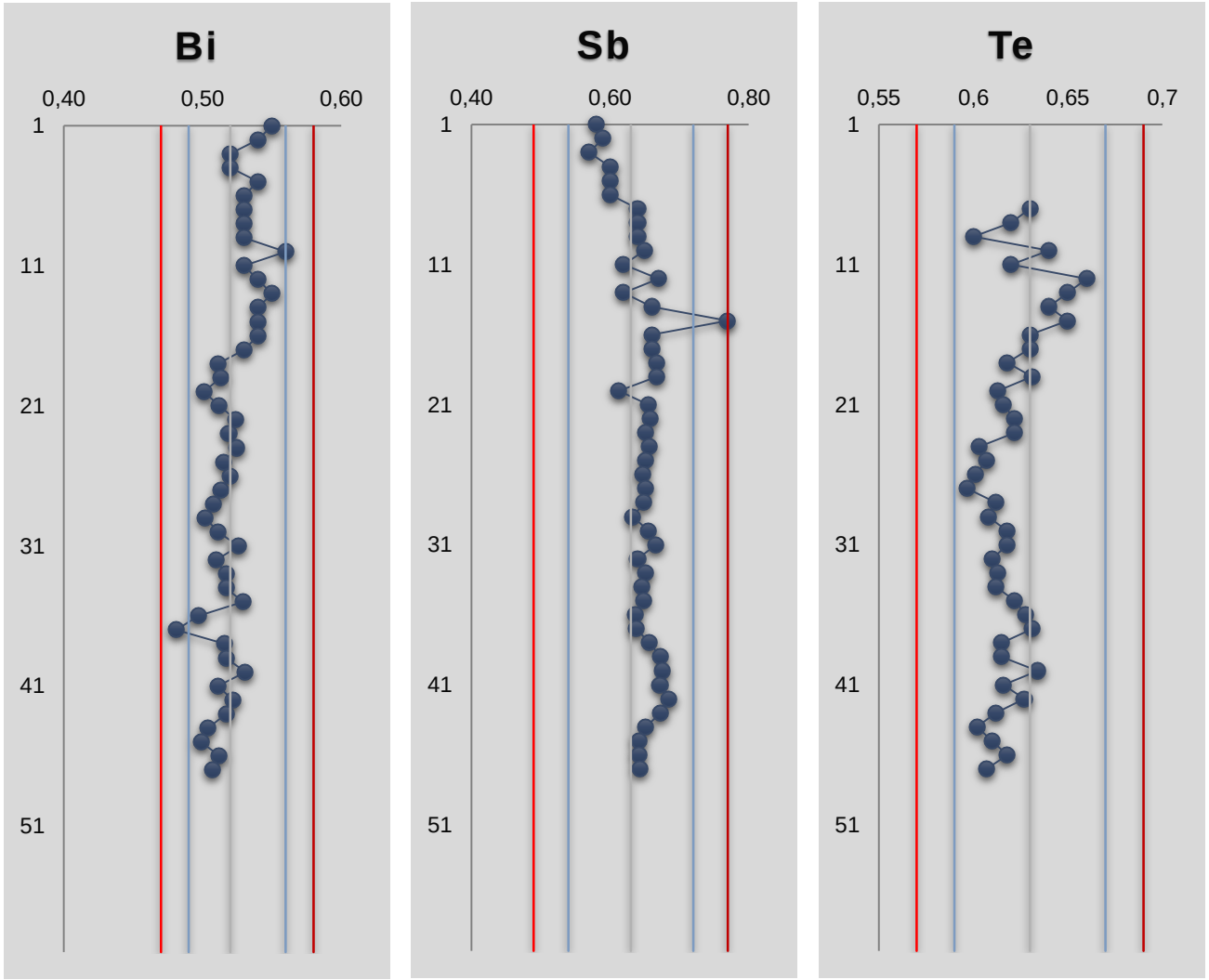




- Calculated from the precision and accuracy with a factor 2
- Blue graph shows the measurement uncertainty calculated for each reference material
- Green graph shows the fitted line to these points.

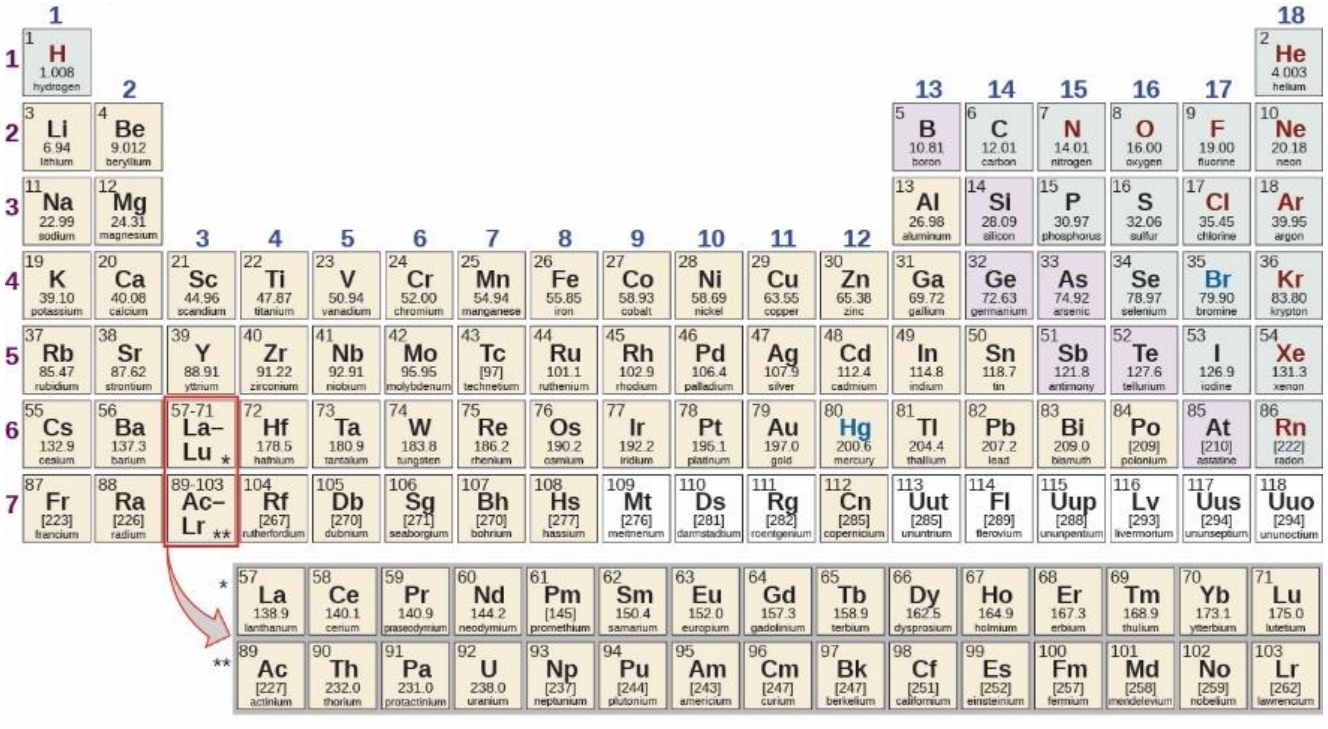
Instrument in use

- Instrument in daily use since 2018-02-07
- Results finished normally about 1h 20 min earlier than before
- Good agreement with the spark-OES
- Some problems with contamination of Fe and Pb, look over the routines



Future

- Evaluate how the instrument is working over a longer period of time
- Want to be able to analyze sulfur in the future
- New elements could be of interest



Thank you for your attention