

Laser Ablation ICPMS Methodology

Sarah Gilbert, Leonid Danyushevsky

Instrumentation

Laser Ablation

The CODES laser ablation analytical facility runs a New Wave UP-213 Nd:YAG Q-switched Laser Ablation System (Fig. 1). The MEOLaser 213 software controls all laser parameters including spot-size, laser energy, pulse rate, and the firing of the laser. The laser beam is fixed and the sample moved underneath by the motorised x-y-z stage (Fig.2). A digital video camera is mounted above the optical system, giving both real-time and still imagery of the sample.



Figure 1. The New Wave UP-213 Laser Ablation System.



Figure 2. The new sample chamber mounted within the motorised stage of the UP-213 Laser ablation system.

Samples are ablated in an ultra-high purity He atmosphere flowing through the sample chamber to entrain ablated material. Outside the chamber, He is mixed with Ar to aid the transport of ablated material, before flowing into the ICP-MS.

The response time is the time it takes for ablated material to reach the detector in the ICP-MS once the laser begins firing. It is controlled by the volume of gas within the sample chamber, the gas flow rate, and the length of tubing in the interface between the laser and the mass spectrometer. To reduce the response time, the chamber volume and tubing length need to be minimised, whereas the gas flow rate needs to be increased. A fast response time allows better interpretation of heterogeneities and inclusions within a sample and also improves washout times, leading to a faster throughput of samples. Additionally, the original sample chamber manufactured by MerkanteK was redesigned to significantly reduce the volume of gas between the sample and the upper glass window (Fig. 2). Response times of 1-2 seconds are now possible compared to ~10 seconds with the original chamber.

At low pulse rates (i.e. 5Hz or less), individual pulses of ablated material are measured by the ICP-MS, creating additional noise in the signal. By adding a mixing chamber between the laser and the ICP-MS, these discrete pulses can be smoothed into a continuous signal.

ICP-MS

The laser ablation system is used as the sampling tool for the Agilent HP4500 Quadrupole ICP-MS (Fig. 3).

The ICP-MS is tuned daily to optimise counts for the masses 45, 139 and 238, typically in the range $20\text{--}25 \times 10^4$ cps, and to minimise the production of oxides and doubly charged ions within the plasma (Table 1). For tuning, the international standard glass NIST612 is ablated with a $110\mu\text{m}$ wide line rastering at $3\mu\text{ms}^{-1}$ and 10Hz at $\sim 10\text{ Jcm}^{-2}$. Oxides are tuned to 0.4% ThO/Th and doubly charged ions to $<0.5\%$ Ce²⁺/Ce.



Figure 3. The Agilent HP4500 ICP-MS.

ICPMS Tuning Parameters

RF Power	1380 W
Carrier Gas (Ar)	1.23 L min ⁻¹
Auxiliary Gas (Ar)	1.00 L min ⁻¹
Plasma Gas (Ar)	15.0 L min ⁻¹
Blend Gas (He)	0.7 L min ⁻¹
Sampling Depth	6.5 mm
Sampling Cone	Pt 1.0 mm id orifice
Skimmer Cone	Pt 0.4 mm id orifice

Table 1. Typical ICP-MS tuning parameters.

Sample Preparation

The sample chamber holds a single 1-inch diameter epoxy mount. For sulphide analyses the mount contains a piece of rock sample set into the epoxy and polished with aluminium oxide powder (Fig. 4). Pressed powder pellets and grain mounts of separated mineral phases can also be ablated. Polished thin sections >100µm thick can be analysed if cut to fit a 1-inch round mount.

Sulphide grains of interest are identified under a petrographic microscope, circled with a fine marker and photographed under reflect light (Fig. 4).

Pyrites can be etched with nitric acid prior to analysis to enhance zoning and internal textures if present (Fig. 5). To etch the sample, the polished surface is covered with concentrated HNO₃ for 20-30 seconds, before thoroughly rinsing with water. The acid may attack other mineral phases however, such as carbonates and



Figure 4. A rock sample set into an epoxy mount.

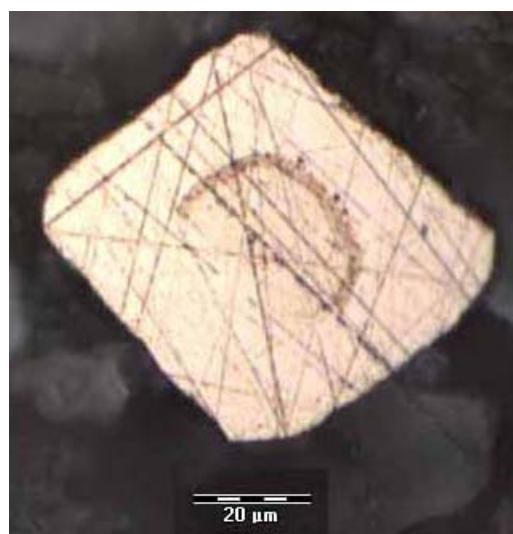


Figure 5. Etched pyrite grain exposing internal textures.

arsenopyrite, so if these phases are present in the sample mount and need to be preserved, adhesive tape can be placed over half the sample before etching.

Standards

Analyses of a primary standard are used to calculate concentrations of unknowns and also to correct for instrument drift, as the sensitivity of the ICP-MS gradually shifts during the day. To correct for drift standards need to be analysed every 1.5 hours. A secondary standard can also be used to correct for any matrix effects caused by compositional differences between the unknown mineral and the standard.

Sulphides

The in-house standard STDGL2b-2 is used for sulphide analyses (Danyushevsky et al. 2003; 2004). It is comprised of powdered sulphides doped with certified element solutions and fused with lithium-borate into a glass disc. This standard was quantified using a combination of laser ablation analyses based on previous in-house standards (Norman et al. 2003) and NIST612, and solution ICP-MS.

Silicates

For silicate analyses the international standard NIST612 is used as the primary standard. It is a synthetic silicate glass, doped with elements at ~40ppm. The basaltic glass BCR-2 is used as a secondary standard.

Laser Analyses

ICPMS Parameters

The standard method for sulphide analyses contains the 26 elements: Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Zr, Mo, Ag, Cd, Sn, Sb, Te, Ba, La, W, Au, Tl, Pb, Bi, Th, U. In previous analyses V and Ge were also analysed, but these elements were removed after recent method development, due to polyatomic interferences in the ICP-MS. In the lithium-borate glass standard STDGL2b-2, ^{51}V has a large interference from $^{40}\text{Ar}^{11}\text{B}$, which prevents V concentrations from being quantified. However, this interference is not present when ablating sulphides, so calculated V concentrations are still comparable with the detection limits, although the absolute values are incorrect. ^{72}Ge has several interferences

from $^{40}\text{Ar}^{16}\text{O}^{16}\text{O}$, $^{56}\text{Fe}^{16}\text{O}$ and $^{40}\text{Ar}^{32}\text{S}$. These are present when analysing both the standard and sulphide unknowns, creating a significant over-estimation of the Ge concentrations.

The ICP-MS detector measures the number of 'hits' of a single ionic mass over a given period of time, then converts it to counts per second (cps). This integration time is user defined, typically 0.02 sec. The detector measures counts for one mass at a time, cycling through the selected list of elements with a dwell time of 0.02 sec for each, and a settling time of a few milliseconds between cycles. With 26 elements in the method this give approximately 175 data points per element over a 100 sec analysis.

If too many elements (>30) are selected for analysis, then there is a long period of time between successive analyses of a particular element ($0.02 \times 30 = 0.6$ seconds plus settling time). Apart from giving fewer data points over the 100 seconds, small variations in the sample may not be recorded if a spike is ablated between cycles.

The detector in the ICP-MS has two counting modes: Pulse and Analogue, which must be set for each element prior to analysis. Pulse counting is used for low count rates ($< 5 \times 10^6$ cps), and Analogue mode for high count rates ($> 5 \times 10^6$ cps).

Laser Parameters

The laser system is able to ablate spots from 8–110 μm in diameter, with sulphide analyses usually at 30–40 μm . The smaller the spot-size ($< 20 \mu\text{m}$ spots) the narrower the hole produced, which can cause a down-hole decrease in the signal intensity as it is harder for the gas flow to extract ablated material from the bottom of the hole. This is seen as a constant drop in counts towards the end of the analysis (Fig. 9).

The laser energy used is partially dependent on sample mineralogy, with easily ablated sulphides at 6–7 Jcm^{-2} compared to 12 Jcm^{-2} required for most silicates and carbonates. The pulse rate of the laser is set at 5–10Hz for analyses.

The laser can ablate samples as spot analyses (vertical holes) or as lines where the laser is rastered on a pre-defined course across the sample's surface. Spot analyses are predominantly used since

uncontaminated sub-surface material will be ablated. However, it is impossible to see if different mineral phases are being ablated below the surface. This means careful interpretation of the recorded spectra is crucial to determine if element variations are caused by inclusions, mineral zonation or drilling into a separate mineral phase.

By using line analyses it is possible to see what minerals will be ablated, and large inclusions can be avoided. However, the biggest consideration when ablating a line, is the potential for surface contamination. Contamination can occur from sample preparation and handling, but also from ablated material from nearby analyses settling on the sample surface. It is very difficult to identify contamination in a line analysis, so care must be taken. Unless there are textural constraints, such as a thin, shallow pyrite rim, spot analyses are recommended for *quantitative* analyses.

Lines are useful however for *qualitative* analyses. A line can be run over several zones or mineral phases to get a visual impression of element abundances.

Sample Analysis

When a target for analysis has been selected and laser parameters have been set, the surface of the sample is pre-ablated. The laser is fired at a low pulse rate (1-2 Hz) for a few seconds to remove any surface contamination. Pre-ablation is for spot analyses only, as surface contamination for lines cannot be removed by this method.

Most sulphide analyses are run for a total of 100 seconds, which includes an initial 30 seconds of analysing the gas background before commencing sample ablation (Fig. 6). The cps data for each analysis is recorded as a separate text file.

Data Reduction and Interpretation

Tabchart Interpretation

The analysis data is compiled and concentrations calculated using Microsoft Excel. First, the data is plotted as a line graph of counts vs. time and the integration times for the background and signal are selected for each analysis. This is straightforward for the analysis of standards which give a flat signal after an initial settling period of about 10 seconds (Fig. 6). The settling time is matrix dependent and in general is less than 10

seconds for sulphides. To calculate the signal intensity, the counts are averaged over the selected interval and the average background counts subtracted.

Analyses of sulphide grains can be far more complex than the standards, and require careful interpretation of tabcharts and the selection of integration intervals. The following series of tabcharts (Figs. 6-12) represent typical features observed in sulphide analyses. Interpretations tend to be element dependent, based on the chemistry of the sulphide and knowledge of associated minerals in the sample.

Calculations

Once integration intervals have been selected for each analysis, the data is compiled in an Excel spreadsheet, where the counts are corrected for instrument drift and converted to concentration.

To be able to quantify an analysis the concentration of one element, the internal standard, needs to be known. For most sulphides, stoichiometric concentrations for Fe or Cu are assumed.

The drift is calculated by comparing the average cps, normalised to the intensity of the internal standard, of the two standards run at the beginning and end of a set of analyses. The unknowns are then corrected using a linear regression.

The average cps of the four standard analyses are used to calculate ppm. The relationship between the standards and the unknowns is described by the formula:

$$\frac{\left(\frac{\text{cps}}{\text{ppm}}\right)_{\text{Std}}^{\text{IS}}}{\left(\frac{\text{cps}}{\text{ppm}}\right)_{\text{Std}}^{\text{el}}} = \frac{\left(\frac{\text{cps}}{\text{ppm}}\right)_{\text{smp}}^{\text{IS}}}{\left(\frac{\text{cps}}{\text{ppm}}\right)_{\text{smp}}^{\text{el}}}$$

where: cps = counts per second
ppm = concentration
std = standard material
smp = unknown sample
IS = internal standard element
el = element analysed

When the concentration of the internal standard element is known in the sample, the formula can be rearranged to calculate the element concentration in the sample (in bold).

The detection limit (DL) is the lowest concentration that can be confidently measured above the background. It is based on the concentration formula above, where the cps term for the element in the sample is replaced by three times the error of the background signal:

$$DL = \frac{3\sigma \times \sqrt{\frac{1}{n_{BG}} + \frac{1}{n_{SG}}}}{\left(\frac{\text{cps}}{\text{ppm}}\right)_{\text{smp}}^{\text{IS}}} \times \frac{\left(\frac{\text{cps}}{\text{ppm}}\right)_{\text{Std}}^{\text{IS}}}{\left(\frac{\text{cps}}{\text{ppm}}\right)_{\text{Std}}^{\text{el}}}$$

where: σ = standard deviation of the background signal
 n = number of data points
 BG = background counts
 SG = analysis signal

The DL varies with spot size, being larger for small spots since there are less counts per ppm. For low level analyses the DL can be reduced by limiting the number of elements analysed. This creates more data points (n) over the time of the analysis.

The error on the element signal over a selected integration interval is calculated by:

$$\%Error = \frac{\sigma}{\sqrt{n}} \times 100$$

where: σ = standard deviation

The total analytical error (AE) for a particular element, expressed as a percentage of the concentration, is the combined error associated with each component of the concentration formula above, and can be expressed as:

$$AE = 100 \times \sqrt{\left(E_{\text{smp}}^{\text{el}}\right)^2 + \left(E_{\text{smp}}^{\text{IS}}\right)^2 + \left(E_{\text{Std}}^{\text{el}}\right)^2 + \left(E_{\text{Std}}^{\text{IS}}\right)^2}$$

$$\text{where } E = \frac{\sqrt{(BG_{\%Error})^2 + (SG_{\%Error})^2}}{\text{cps}_{SG}}$$

For a homogeneous sample or standard, the analytical error is an expression of the analytical noise. Whereas for an inhomogeneous sample, the analytical error expresses sample variability.

For elements close to or below the detection limit the analytical error is very high. This is mainly due to very low count rates (cps) in the sample and also to a higher signal error ($SG_{\%Error}$).

References and Method Development

- Danyushevsky L., Robinson P., McGoldrick P., Large R. and Gilbert S., 2004; Quantitative multi-element analysis of sulphide minerals by laser ablation ICPMS, 17th AGC, Hobart, p. 260.
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- Norman M., Robinson P., Clark D., 2003; Major- and trace-element analysis of sulphide ores by laser-ablation ICP-MS, solution ICP-MS, and XRF: New data on international reference materials, *The Canadian Mineralogist*, Vol. 41, pp293-305
- Yu Z., Norman M., Robinson P., 2003; Major and trace element analysis of silicate rocks by XRF and Laser Ablation ICP-MS using lithium borate fused glasses: Matrix effects, instrument response and results for international reference materials, *Geostandards Newsletter*, Vol. 27(1), pp67-89

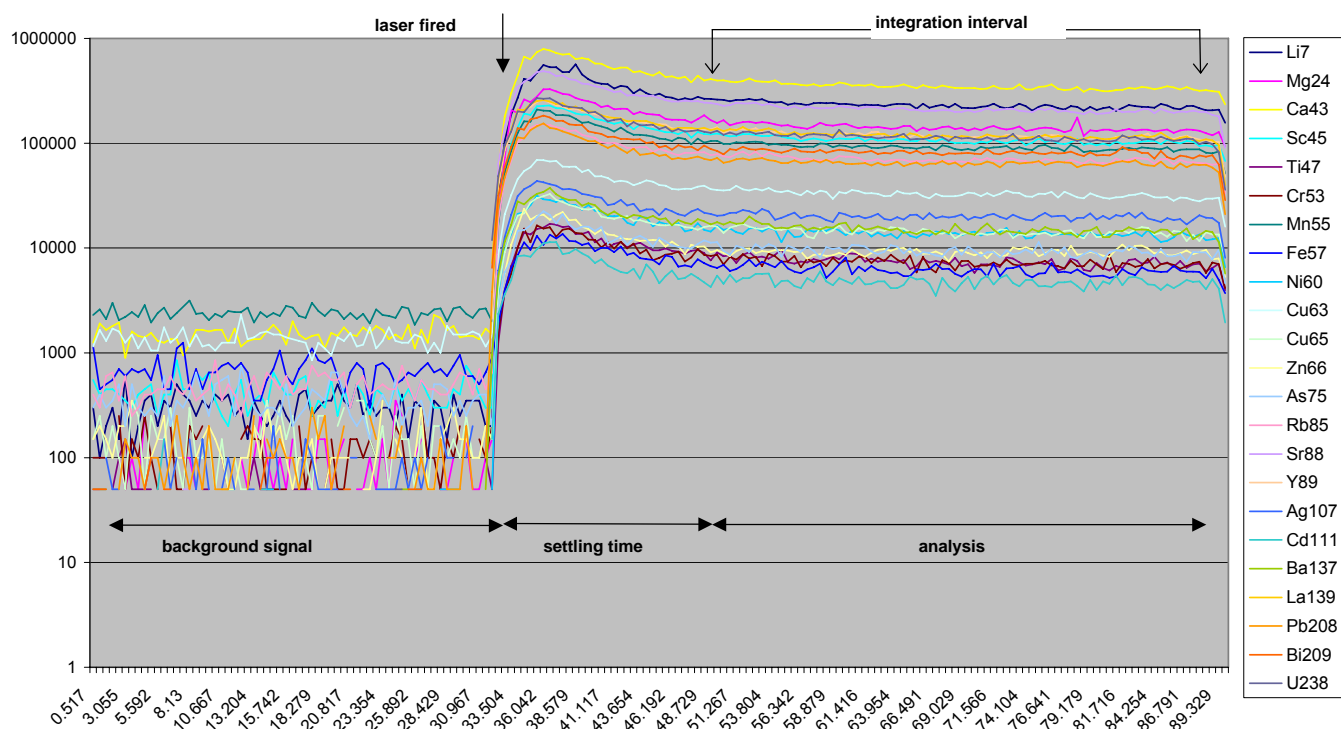


Figure 6. Analysis of the standard NIST612.

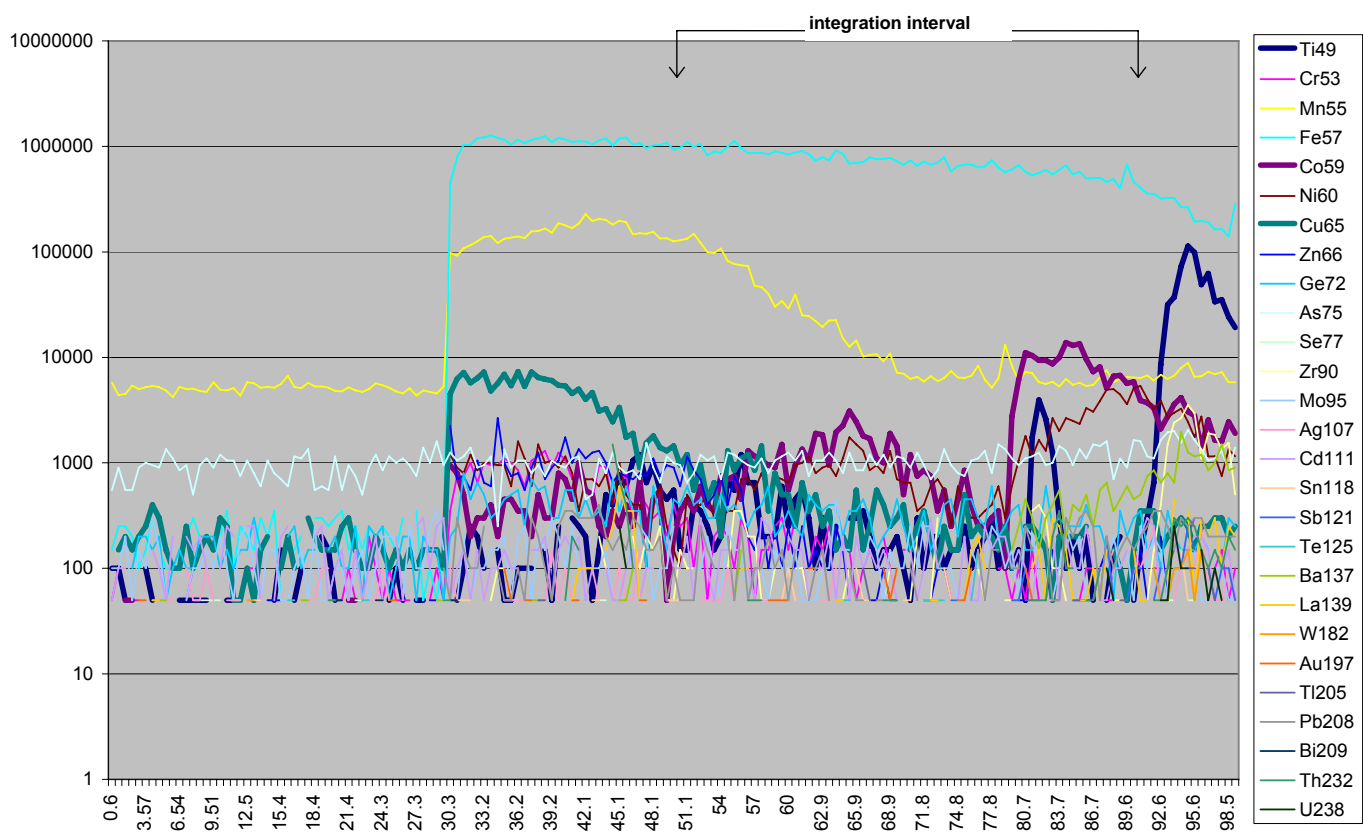


Figure 7. Example of a selective integration interval to avoid the possible Cu-rich (green) inclusion at the start and the Ti-rich (dark blue) inclusion at the end. The Co (purple) variations have been included, since this is likely to be internal variation within the pyrite rather than a separate mineral phase.

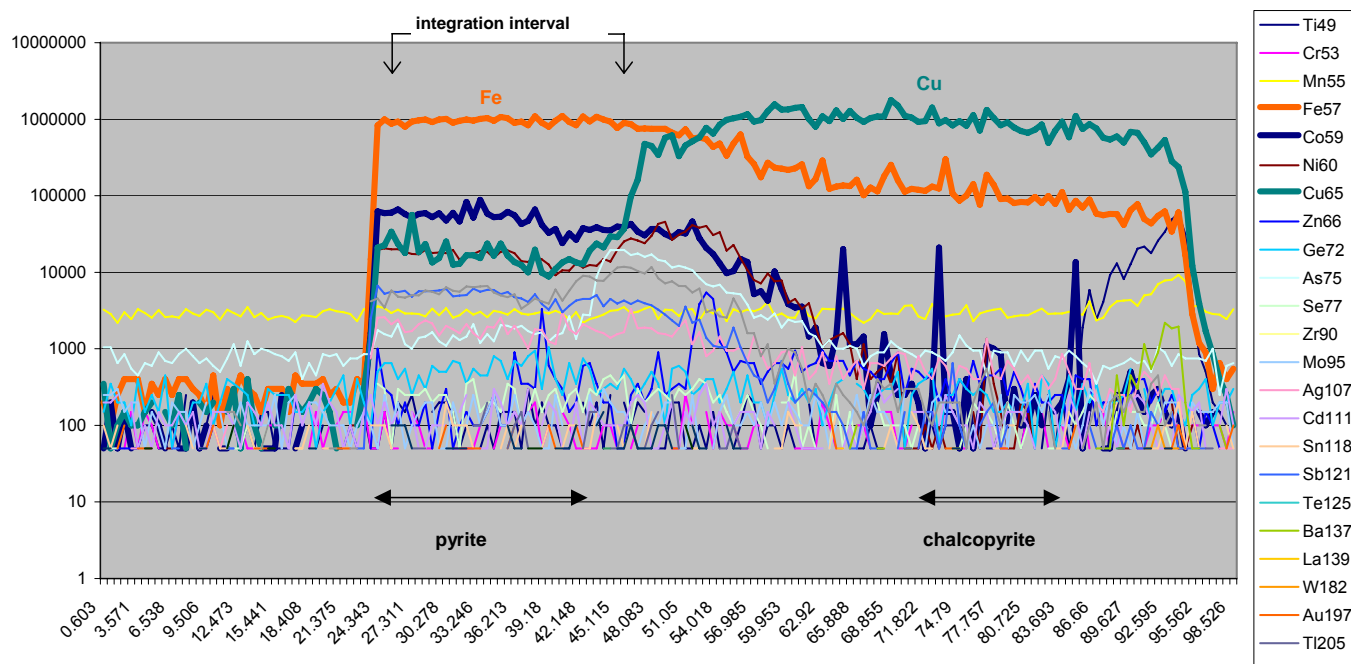


Figure 8. Example of gradually drilling through the surface pyrite into chalcopyrite below, as indicated by the changes in the major element counts. Also note the spikes in Co (navy blue) caused by drilling from a high Co zone into the low Co chalcopyrite. These spikes can be removed from the data when caused by poor washout, rather than small inclusions in the chalcopyrite.

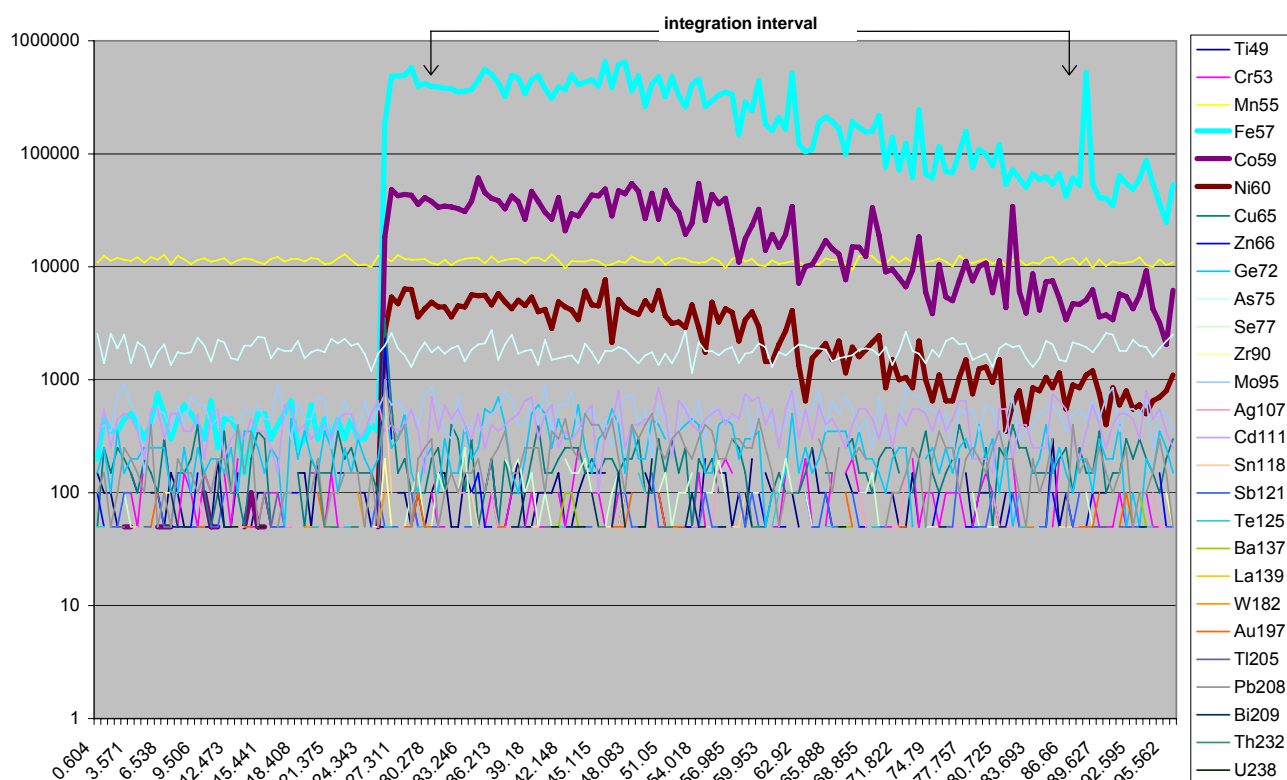


Figure 9. Down-hole decrease of signal intensity in small spot-sizes ($<20\mu\text{m}$). The slope for all elements is consistent, so the whole analysis can be used for integration.

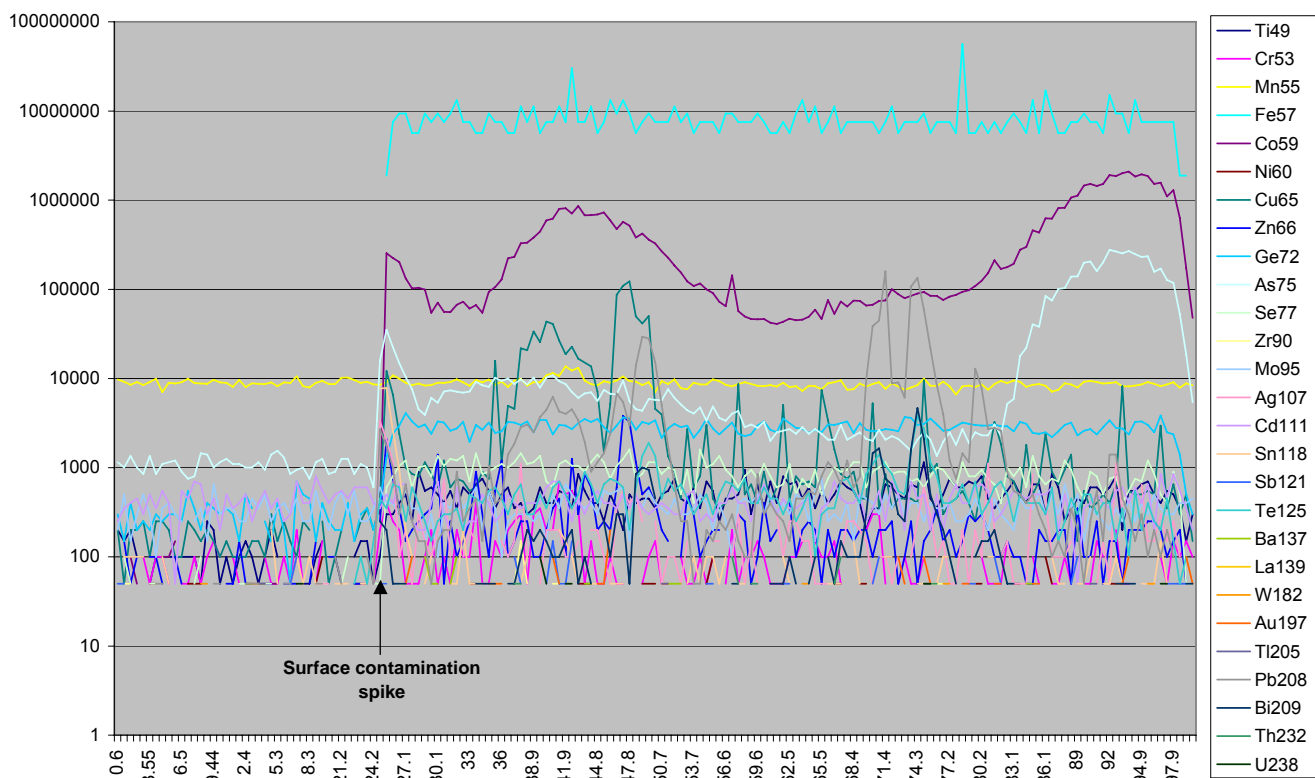


Figure 10. When the sample has not been pre-ablated surface contamination in a spot analysis is seen as an initial spike when the laser is first fired. This contamination should not be included in the integration interval.

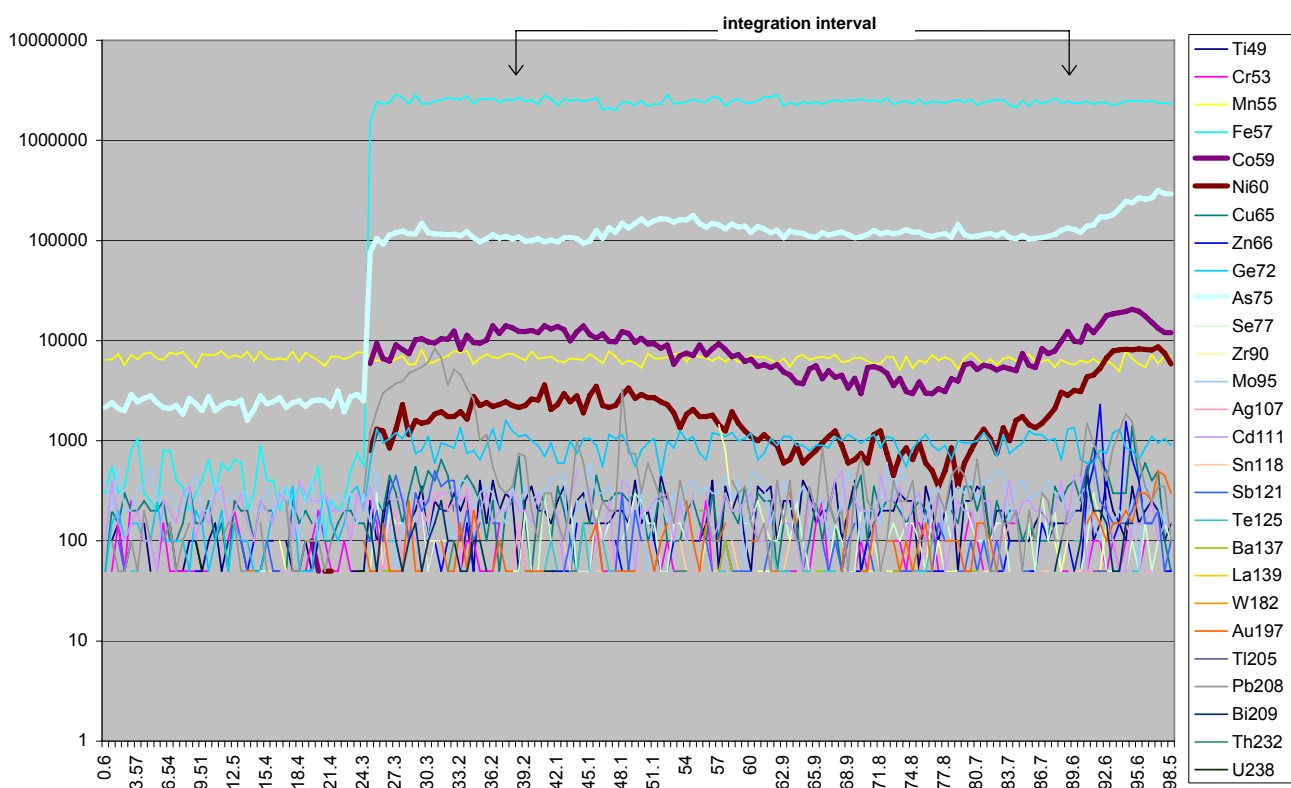


Figure 11. Possible zoning of Co (purple) and Ni (brown) in pyrite.

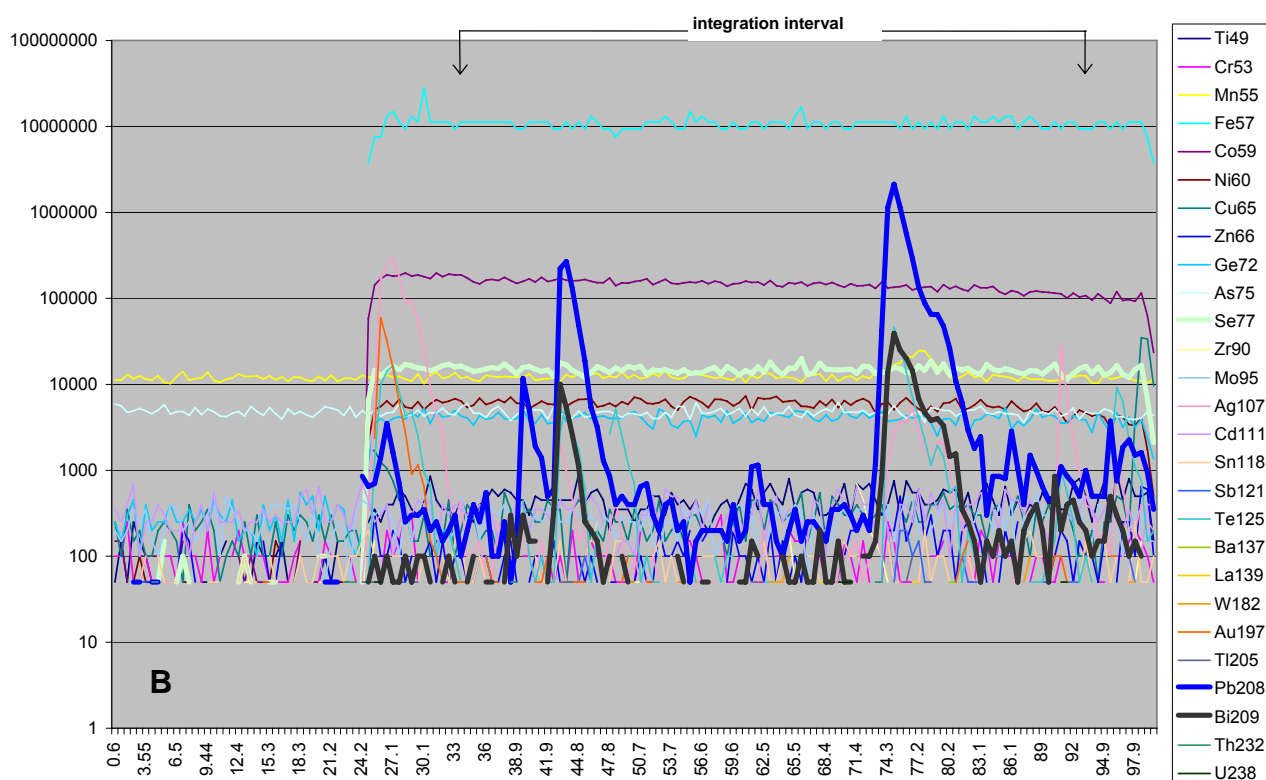
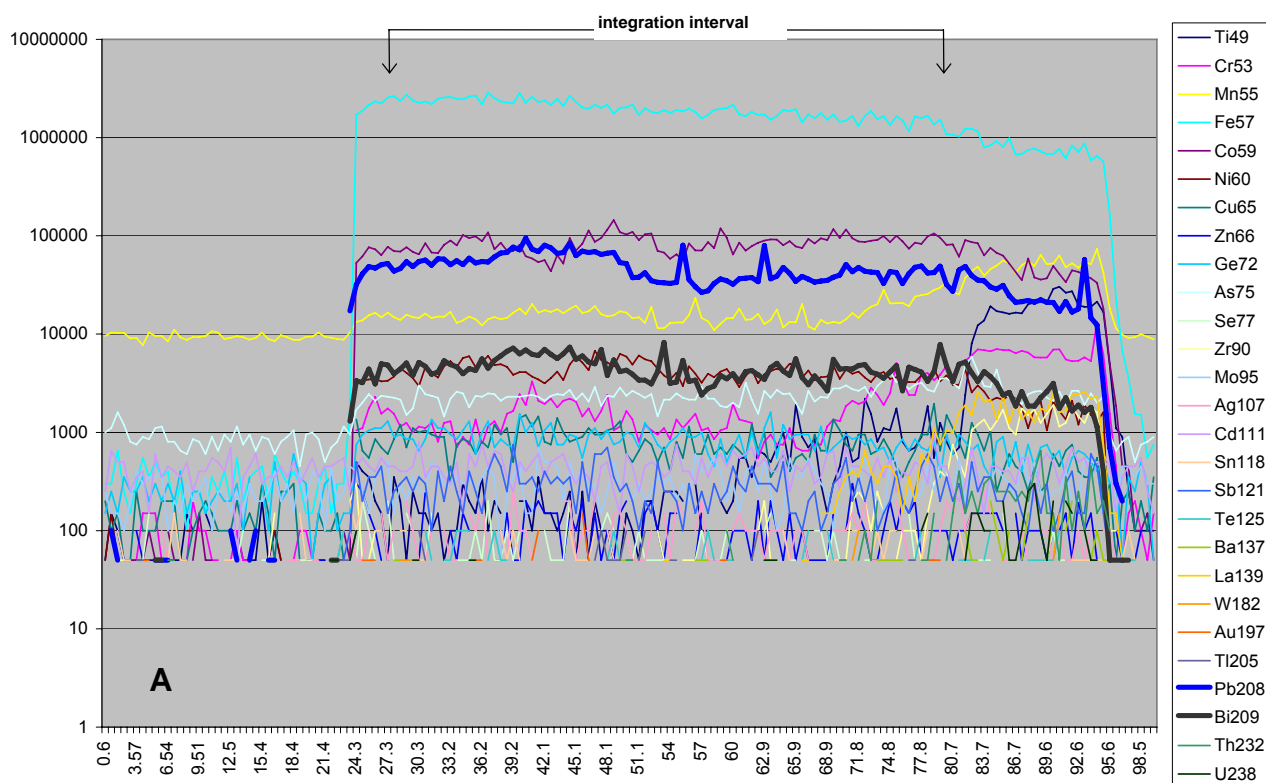


Figure 12. The trend of Pb (blue) and Bi (black) in analysis A may be interpreted as zoning. However, when coupled with analysis B from the same sample, where Pb and Bi occur as discrete galena inclusions, then the high counts in A can be attributed to the presence of evenly distributed micro-inclusions of galena.