

Sample Analysis Design

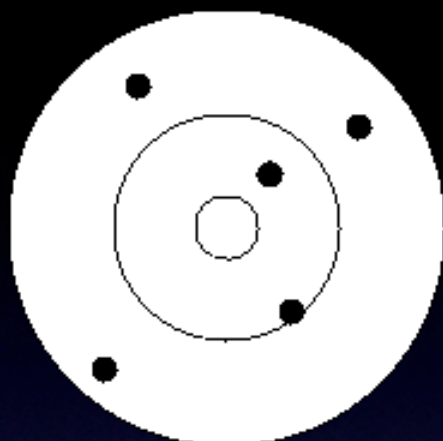
PART III

Sample Analysis Design

- Generating high quality, validated results is the primary goal of elemental abundance determinations
- It is absolutely critical to plan an ICP-MS analysis carefully
 - from sample gathering to final analysis on the ICPMS
- Always create and follow an analysis design that shall permit you to follow the procedure for future samples, AND know what you did when looking at old data

Sample Analysis Design

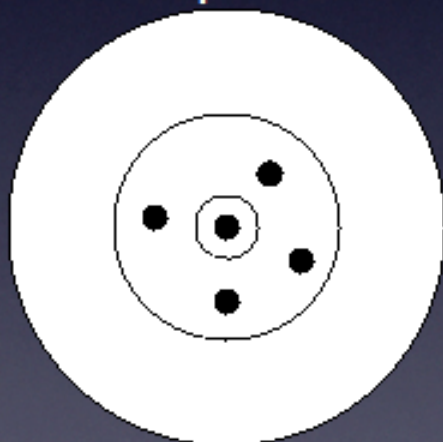
- **Goal**: high quality, validated, quantitative determination of elemental concentrations/isotope ratios
- This goal can be achieved by:
- ***Specificity*** - only detecting isotope(s) of interest, not interferences, OR making sure that matrix effects do not play a role
- ***Sensitivity*** - can we differentiate the isotope of interest from the background signal?
- ***Accuracy*** - does the analysis represent the real value?
- ***Precision*** - how repeatable is the value?



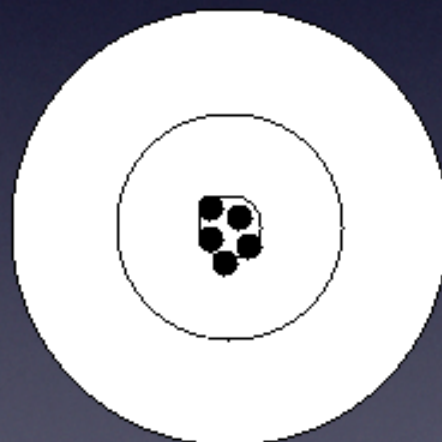
Not accurate
Not precise



Not accurate
Precise



Accurate
Not precise



Accurate
Precise

Sample Analysis Design

- ***Sensitivity*** and ***Precision***:
 - generally defined by how well the instrument is tuned (assuming dilution factor is appropriate)
- ***Specificity*** and ***Accuracy***:
 - generally governed by how well you prepare your sample and set up your analysis method/parameters

Sample Analysis Design

- Spectroscopic interferences
 - Matrix effects

Sample Analysis Design

- ***Interference*** – analytical artifact which causes the ion signal in a sample to vary from an idealized (true) signal
 - Interferences cause inaccurate analyses
- **Two main types:**
 - 1. Spectroscopic
 - 2. Nonspectroscopic

Sample Analysis Design

- **Spectroscopic Interferences** in ICP-MS
 - 1. Isobaric overlap
 - 2. Polyatomic ions
 - 3. Refractory oxides
 - 4. Doubly charged ions

Sample Analysis Design

- ***Isobaric Overlap***
- Two different elements having the same nominal mass
 - E.g., ^{40}Ca (96.9%) and ^{40}Ar (99.6%)
- Monoisotopic elements:
 - B, Na, Al, Sc, Mn, As, Nb, Y, Rh, I, Cs, Pr, Tb,
 - Ho, Tm, Au, Th
 - None have isobaric interferences

Sample Analysis Design – Isobaric Overlap

- A few multi-isotope elements have no interference free isotopes:
 - E.g., **In** - $^{113}\text{In} \rightarrow ^{113}\text{Cd}$, and $^{115}\text{In} \rightarrow ^{115}\text{Sn}$
- Usually possible to choose an interference free isotope or one that is unlikely to be interfered upon strongly (either due to very low natural abundance of interfering element (isotope) or the interfering element (isotope) is not present in sample)

Sample Analysis Design – Isobaric Overlap

- IF an isobaric interference is unavoidable, you can correct for it by measuring the counts on a non-interfering isotope of the interfering element
 - $$\text{CPS}_{\text{analyte}} = \text{CPS}_{\text{total}} - \text{CPS}_{\text{interferent}} * (X_a/X_b)$$
- X_a = abundance of interfering isotope
- X_b = abundance of non-interfering isotope

Sample Analysis Design – **Polyatomic Interferences**

- More serious than isobaric interferences
- Result from possible, short-lived combination of atomic species in the plasma or during ion transfer
- Common recombinants are Ar, H, and O
- Dominant elements in reagents also form polyatomic interferences - N, S, and Cl

Sample Analysis Design – Polyatomic Interferences

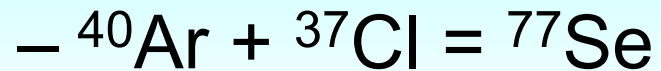
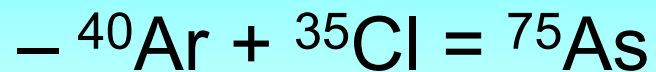
- Analyzing deionized water with ICP-MS instrument – we have solely **H** and **O** present (within the ‘matrix’)
- Thus, peaks would be visible at masses:
 - **41** ($^{40}\text{Ar} + ^1\text{H}$) \rightarrow ^{41}K
 - **56** ($^{40}\text{Ar} + ^{16}\text{O}$) \rightarrow ^{56}Fe
 - **80** ($^{40}\text{Ar} + ^{40}\text{Ar}$) \rightarrow ^{80}Se
 - As well as other minor peaks from the minor isotopes of Ar and O

Sample Analysis Design – Polyatomic Interferences

- If you acidify the deionized water with HNO_3 or H_2O_2 , these behave in the same manner as deionized water
 - these acids are considered “ideal matrices” as they don’t add unnecessary polyatomic interferences
- Acidification with HCl or H_2SO_4 changes the situation since **Cl** and **S** can be used to form polyatomic ions

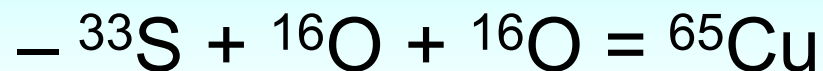
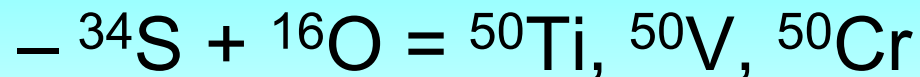
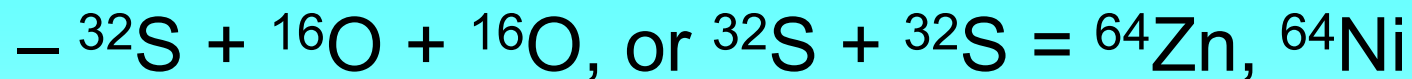
Sample Analysis Design – Polyatomic Interferences

- HCl matrix:



Sample Analysis Design – Polyatomic Interferences

- H_2SO_4 matrix:



Sample Analysis Design

- These interferences will be present just from the gas and solvent
- Therefore, if possible, solutions should be prepared with a weak (1-5% v/v) HNO_3 acid matrix
- Why not deionized water?
 - acid helps keep elements from sticking to sides of test tubes and tubing during transport
 - ionization efficiency is significantly lower relative to HNO_3

Sample Analysis Design – **Polyatomic Interferences**

- The most serious polyatomic interferences are formed from the most abundant isotopes of **H, C, N, O, Cl, and Ar**
- So, if polyatomic interferences are present in plain deionized water with no other ions present, what happens in natural (complex) samples/matrices?

Sample Analysis Design – **Polyatomic Interferences**

- Need to know the most abundant elements present in sample
 - Is (are) there any one (or more) elements present that are in very high abundances?
- If so - then it's likely interferences could be formed from such abundant element(s)
- E.g., rock samples - high Si

Sample Analysis Design – **Polyatomic Interferences**

- Typically, most polyatomic interferences are only present below mass 82 - since Ar, H, and O are by far the most abundant isotopes in the plasma, they form most interferences
- Counteractive measures:
 - Proper machine settings (especially nebulizer flow rate and RF power) can minimize formation

Sample Analysis Design – **Polyatomic Interferences**

- If a polyatomic interference is unavoidable, then a correction equation like the one for isobaric interferences can be used (assuming you are certain of the ‘species’ of the interference)

Sample Analysis Design – Refractory Oxides

- **Refractory Oxides**
- Occur because of incomplete sample dissociation or from recombination
- Always occur as an interference as an integral value of 16 mass units above the interfering element
- MO , MO_2 , or MO_3 where M is the interfering element

Sample Analysis Design – Refractory Oxides

- Elements with *high oxide bond* strength are most likely to form refractory oxide interferences
- Severity is expressed as MO/M as a percentage
- MO/M should be as low as possible, typically <3-5%
- MO/M minimized by adjusting nebulizer flow rate, z-axis position, and RF power

Sample Analysis Design – **Refractory Oxides**

- Si, Ce, Zr, Ti, Sm, Mo, and P all form strong oxide bonds and may have severe oxide interferences
- Usually monitor the CeO/Ce or BaO/Ba ratios to make sure it's below 5%

Sample Analysis Design – Refractory Oxides

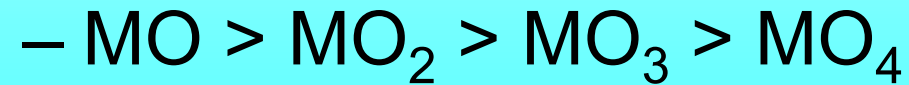
- Examples:
- LREE on the HREE
- BaO on Eu
- MoO on Cd

Sample Analysis Design – **Refractory Oxides**

- Again, correction equations can be applied but these lead to increased error, especially if the interference is large
- Oxide formation tends to not be stable and the corrections accumulate error quickly
- If there is a severe oxide interference, it's usually better to try to separate the interference from the analyte

Sample Analysis Design – Refractory Oxides

- Typically,



Sample Analysis Design – Doubly Charged Ions

- Form when the 2nd ionization potential is less than the first ionization potential of Ar
- Typical of alkaline earths, a few transition metals, and some REE
- Low nebulizer flow rates increase doubly charged ion formation
- Interference signal is always $M/2$ where M is the element becoming doubly charged

How to avoid spectral MS interferences?

- Attempt to 'dry' solutions prior to introduction to plasma - remove O and H gets rid of many polyatomic species (i.e. use a desolvating introduction system – e.g. DSN 100)
- Optimize instruments settings so that formation is minimized and corrections are not severe
- Use simple matrices whenever possible
- Process samples prior to analysis to isolate elements of interest or remove potential interfering elements; e.g. ion exchange chromatography

How to avoid spectral MS interferences?

- Alternatively - use higher mass resolutions, MR – medium resolution or HR – high resolution
- Most overlaps are not exact using medium and high resolution modes
- Can completely separate the isotope of interest from interfering species
- However, consequence is loss of sensitivity