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 ($^{40}\text{Ar} + ^1\text{H}$) $\rightarrow$ $^{41}\text{K}$
  
  • 56 ($^{40}\text{Ar} + ^{16}\text{O}$) $\rightarrow$ $^{56}\text{Fe}$
  
  • 80 ($^{40}\text{Ar} + ^{40}\text{Ar}$) $\rightarrow$ $^{80}\text{Se}$

• 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 HNO₃ or H₂O₂, 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 H₂SO₄ changes the situation since Cl⁻ and S can be used to form polyatomic ions.
Sample Analysis Design – Polyatomic Interferences

• HCl matrix:

  • $^{35}\text{Cl} + ^{16}\text{O} = ^{51}\text{V}$
  • $^{37}\text{Cl} + ^{16}\text{O} = ^{53}\text{Cr}$
  • $^{40}\text{Ar} + ^{35}\text{Cl} = ^{75}\text{As}$
  • $^{40}\text{Ar} + ^{37}\text{Cl} = ^{77}\text{Se}$
Sample Analysis Design – Polyatomic Interferences

• $\text{H}_2\text{SO}_4$ matrix:

  • $^{32}\text{S} + ^{16}\text{O} = ^{48}\text{Ti}$

  • $^{32}\text{S} + ^{16}\text{O} + ^{16}\text{O}$, or $^{32}\text{S} + ^{32}\text{S} = ^{64}\text{Zn}, ^{64}\text{Ni}$

  • $^{34}\text{S} + ^{16}\text{O} = ^{50}\text{Ti}, ^{50}\text{V}, ^{50}\text{Cr}$

  • $^{33}\text{S} + ^{16}\text{O} + ^{16}\text{O} = ^{65}\text{Cu}$
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) HNO₃ 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 HNO₃
Sample Analysis Design –
Polyatomic Interferences

• The most serious polyatomic interferences are formed from the most abundant isotopes of $\text{H}, \text{C}, \text{N}, \text{O}, \text{Cl}$, and $\text{Ar}$

• 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 <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 ratio 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,

  • $MO > MO_2 > MO_3 > MO_4$
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
Sample Analysis Design

• PART III

• Spectroscopic interferences

• Matrix effects
Matrix Effects

• **Physical**
  • physical effects from dissolved or undissolved solids present in solution

• **Chemical**

• **Ionization**
  • suppression and enhancement effects
Matrix Effects

• *Physical*
  
  • variations in rate of atomization/ionization of samples and standards
  
  • samples and standards should have similar viscosities
  
  • matrix acid concentrations should be the same in samples and standards
Matrix Effects

• Chemical
  • properties of the solution may inhibit or suppress the formation of ions
  • high TDS, refractory species
  • typically increasing RF power or lowering nebulizer flow rates can reduce this type of interference
Matrix Effects

• Ionization
  • space charge effects
Matrix Effects

• Effects from high TDS

  • Significant sample drift observed when TDS is > 2000 ug/ml
  
  • 200 mg of sample in 100 ml of solute
Matrix Effects

• Ways to avoid high TDS effects:
  
  • most obvious - DILUTE
  
  • 2nd way - prime the system → most high TDS effects will cause signal drift until a lower (or sometimes higher) analyte signal is reached after that point, the change is minimal
Matrix Effects

• *Ion signal Suppression* and *Enhancement*

  • suppression more common than enhancement

  • suppression through space charge effects

  • in general, large concentrations of heavy elements will cause signal suppression through space charge effects

  • S, P – are classic ion signal suppressors
Matrix Effects

• Enhancement is more rare as ion signal increases over time are more likely the result of changing machine conditions than true matrix effects

• Overall - matrix effects caused by low mass elements are poorly understood
  
  • plasma dynamics? ion transfer changes? supersonic expansion?
Matrix Effects

• Matrix effects are difficult to quantify

• Corrections are typically quite error prone

• Hard to determine if signal degradation is due to instrumental drift or due to suppression/enhancement
Ways to overcome matrix effects?

• DILUTE
• internal standarization
• instrument optimization
• matrix matching standards and samples
• standard addition
• matrix separation
Sample Introduction Systems

SOLID – LASER ABLATION
Save the Date: June 8-11, 2021

NAWLA 2021

The 4th North American Workshop on Laser Ablation

at the UNIVERSITY OF NOTRE DAME
Laser ablation

• Benefits:
  • spatial resolution of < 10 um
  • little to no sample preparation required

• Drawbacks:
  • transient signal
  • reduced precision/accuracy relative to solution mode
What is a laser??

• **LASER** = light amplification by stimulated emission of radiation

• beam of coherent monochromatic light (i.e. characterized by one wavelength)
Types of lasers

• carbon dioxide
• Nitrogen
• Ruby
• Nd:YAG
• excimer = excited dimer (e.g. ArF gas)
Laser – general principles

• a flash tube supplies photons for amplification through the gain medium

• atom in gain medium absorbs energy to become excited

• the excited atom is hit by another photon to become “doubly excited” and will release 2 photons of the same wavelength

• light produced reflects back and forth between mirrors

• one of the mirrors is typically partially transparent and the beam of light is emitted through this mirror
Laser ablation system – general configuration

Figure 3.39 Schematic diagram of a laser ablation system. (Revised from Reference 538, with permission.)
Fig. 2-4 Optical layout and trigger scheme used for the visualization of aerosols during their initial stage of expansion (a) and transport period (b).

Günther & Koch (2008)
Laser Ablation

• The most versatile solid sampling technique for ICP spectrometry

• Sufficient energy in the form of a focused laser beam is directed onto the sample, material from the surface is sputtered and vaporized

• The plume of vapor and particulate matter is transported in a He carrier gas to the plasma for ionization
Laser Ablation

- The laser beam is steered in the direction of the laser ablation cell (sample) using mirrors and/or prisms and then focused onto the sample using a lens

- Aperatures along with other optics may be inserted into the beam path in order to improve beam homogeneity
Laser Ablation

• We require an optical system to observe the sample while it is being ablated – however, this typically consists of a video system to protect the eyes of the operator from potentially damaging laser energy.
Laser Ablation

• **Laser**
  • A minimum power output is required – in the vicinity of 1 mJ per pulse
  • Most commonly used laser energies are based upon the **Nd:YAG** (Neodymium: Yttrium Aluminum Garnet) laser
  • Solid state laser in which the garnet rod is excited using a flash lamp (similar to flash lamps used in photography).
Laser – Nd:YAG

• Fundamental energy output is at a wavelength of 1064 nm – near Infrared spectrum

• Using suitable crystals, the frequency of the laser output can be multiplied
  • e.g. doubled – 532 nm
    • tripled – 355 nm
    • quadrupled – 266 nm
    • quintupled – 213 nm
Laser

• $f = \frac{c}{\lambda}$
• $f$ – frequency
• $c$ – speed of light (299,792,458 m/s)
• $\lambda$ – wavelength

• $f = \frac{E}{h} \ ; \ E = \frac{h \cdot c}{\lambda}$

• $E$ – photon energy
• $h$ - Planck’s constant $(6.62606896(33) \times 10^{-34} \text{ J} \cdot \text{s})$
## Laser Ablation Systems

<table>
<thead>
<tr>
<th>Nd:YAG solid state</th>
<th>1064 nm</th>
<th>Fundamental wavelength, used for bulk sampling.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>266 nm</td>
<td>Good compromise between ease of use, durability, and cost. Applicable for a large number of sample types.</td>
</tr>
<tr>
<td></td>
<td>213 nm</td>
<td>Better compromise, but more expensive than a 266 nm and requires more maintenance. Applicable for a larger number of sample types than the 266 nm.</td>
</tr>
<tr>
<td></td>
<td>193 nm</td>
<td>Obtained using OPO (Optical Parametric Oscillator) optics. Allows the advantage of a solid state laser, with the disadvantage of more complicated optics. Most general applicability.</td>
</tr>
<tr>
<td>ArF Excimer gas</td>
<td>193 nm</td>
<td>Higher cost, but uses fundamental wavelength, eliminating the need for frequency multiplying crystals and their maintenance and alignment. Most general purpose wavelength.</td>
</tr>
</tbody>
</table>

Longerich (2008)
Laser ablation systems – new developments

• Recently developed \textit{femtosecond} (fs = 10^{-15} \text{ seconds}) laser systems (e.g. Horn, 2008)

• Characterized by a much shorter pulse width (10,000 times) compared to Nd:YAG and ArF excimer systems since these are characterized by pulse widths in the \textit{nanoseconds} (10^{-9} \text{ seconds})
Laser ablation systems – new developments

• Why is pulse width important??

  • The much shorter pulse width limits the phenomenon of sample melting at the ablation site.

  • However, much higher cost compared to other laser ablation systems and ‘no-turn key’ femtosecond model is available
Laser ablation systems

• Variable power output control is an absolute must!
  • This is required in order to achieve a suitable sampling rate, which is dependent on the sample matrix and laser beam size.

• E.g. an analysis using a ‘pit’ or laser beam diameter of 60 microns, an ablation lasting 60 seconds results in a pit 60 microns (@1 Hz) deep (sampling rate of 1 micron/second)
Laser pits

- Optimal geometry consists of a symmetrical pit and flat bottom
- These can only result from a homogenized beam energy profile
Laser ablation systems

• In order to maintain reproducibility, *energy meters* are installed

• Energy meters are either placed in the beam path, or laser beam is split so that a known fraction is directed towards the meter while the remainder is focused onto the sample
Fig. 2-1 Interaction and optimization scheme for the most influential parameters in LA-ICP-MS analyses for quantitative analysis. The intensity of the grey shading for wavelength, pulse width and fluence indicate increasing performance. Dark grey indicates no significant influence. However, UV-fs will always increase the performance with respect to precision and accuracy.
Laser ablation systems – New Wave Research (Division of ESI)

UP213 nm

UP193 nm
193 nm laser systems

Analyte 193H

Resonetics – 193 nm
Laser Ablation Systems – Applied Spectra

RESOlution-SE
Compact 193nm excimer laser ablation system, offering the Laurin Technic sample cell and GeoStar μGISTM software.

- On-sample fluence 20 J/cm²
- Laser pulse width of 5ns
- 32 mask wheel aperture positions as standard; optional 40 positions with beam expander
- Spot size range of 2μm to 100μm; up to 300 μm with optional beam expander
- Industry leading S155 sample cell; dual volume, constant volume
- Smoothing SQUID device included
- Flexible mounting options with nine (9) sample holders to choose from
- Compatible S155 fast and ultrafast transfer kits available for imaging and mapping
- Split Stream ready
Laser Ablation Systems – Applied Spectra

RESOlution-LR

High energy, 193nm excimer laser ablation system, offering Laurin Technic sample cell and pioneering GeoStar μGISTM software.

- On-sample fluence: 45 J/cm²
- Laser pulse width of 20ns
- 40 mask wheel aperture positions as standard
- Spot size range of 2 μm to 380 μm
- Industry leading S155 sample cell; dual volume, constant volume
- Smoothing SQUID device included
- Flexible mounting options with nine (9) sample holders to choose from
- Compatible S155 fast and ultrafast transfer kits available for imaging and mapping
- Split Stream ready
Laser Ablation Systems – Applied Spectra

S155 Laurin Technic laser ablation cell

- Movement range of 155mm x 105mm
- Mount up to 20 standard 1” mounts
- Mount up to 6 full-size thin section slides