BE BOLD

2022 INORGANIC VENTURES WEBINAR SERIES

ANALYZING ZEOLITES

The general chemistry of silicon sample preparation where intended measurements are made by ICP.

THURSDAY, NOVEMBER 17
9:00–9:30AM EST

PRESENTED BY:

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Founder and Chair, BOD

The Analysis of Silicon

- **The Following Will Be Discussed:**
  - Background
  - Summarize Current Methodologies
  - Explain Chemistry
  - Compare Advantages and Disadvantages

The Analysis of Silicon– BACKGROUND

- Below are the 8 most common elements in the earth's crust:
  - Oxygen - 46.1%
  - Silicon - 28.2%
  - Aluminum - 8.23%
  - Iron - 5.63%
  - Calcium - 4.15%
  - Sodium - 2.36%
  - Magnesium - 2.33%
  - Potassium - 2.09%

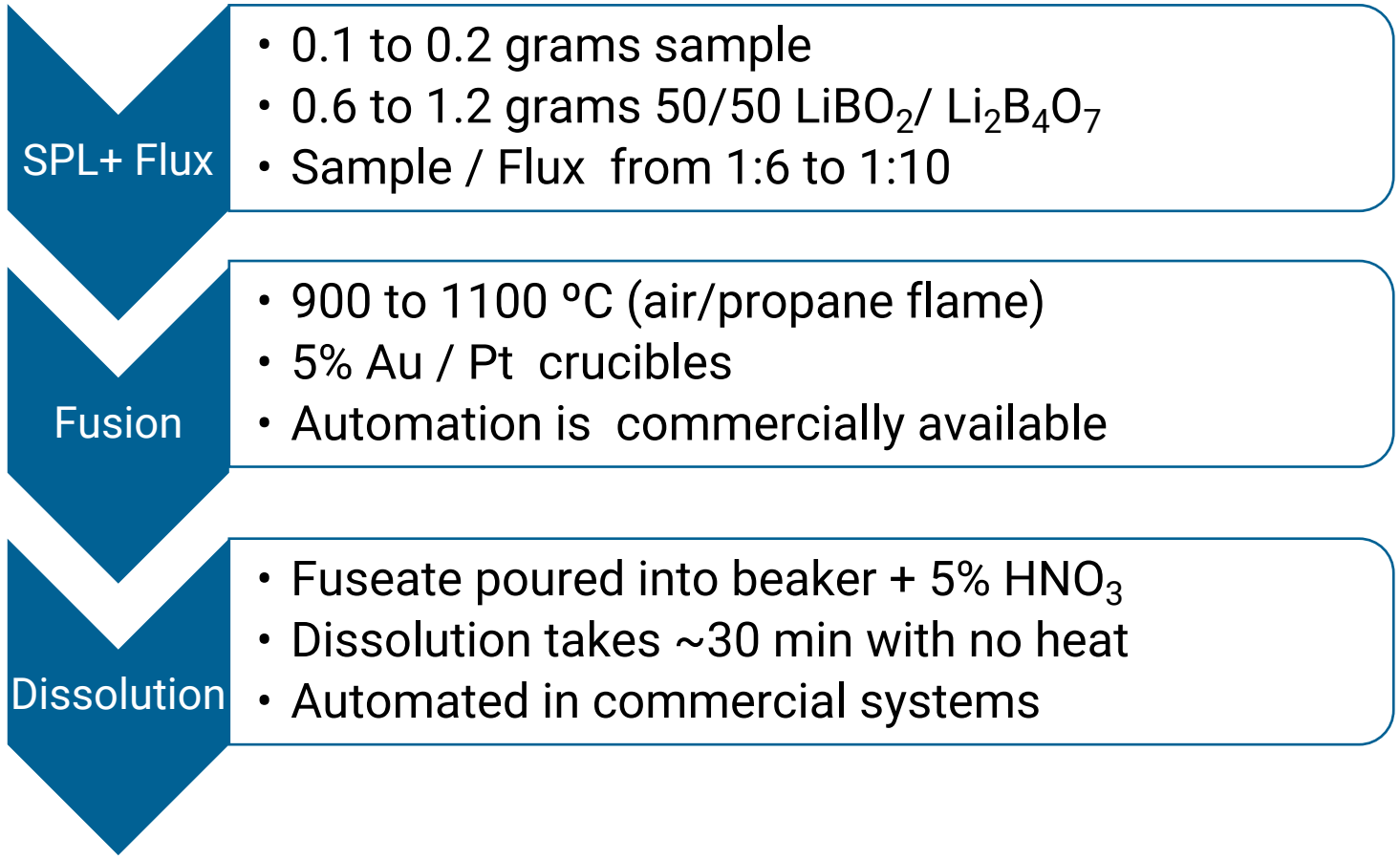
The Analysis of Silicon – BACKGROUND

- Si contamination problems are rarely not encountered
- Si is commonly found in laboratory glassware, oils and grease, plastics, and air particulates
- Methods developed for sample preparation use HF and alkali hydroxides and carbonates etc. corrosive chemicals that will attack/leach materials they come in contact with
- Special Laboratory apparatus and technique are required
- High levels of precision are required in the analysis of catalysts containing Si – typically Zeolites

The Analysis of Silicon – BACKGROUND

- Researchers synthesizing and evaluating new zeolites require accurate and precise elemental compositions such as Si/Al ratios
- Often established methodology gives insufficient precision
- A precision of ≤ ± 1% preferred instead of typical values of ± 4% to 5%
- Si/Al = ±3% / ±3% … the uncertainty of the ratio = $(3^2 + 3^2)^{1/2} = 4.2\%$

The Analysis of Silicon— FUSION

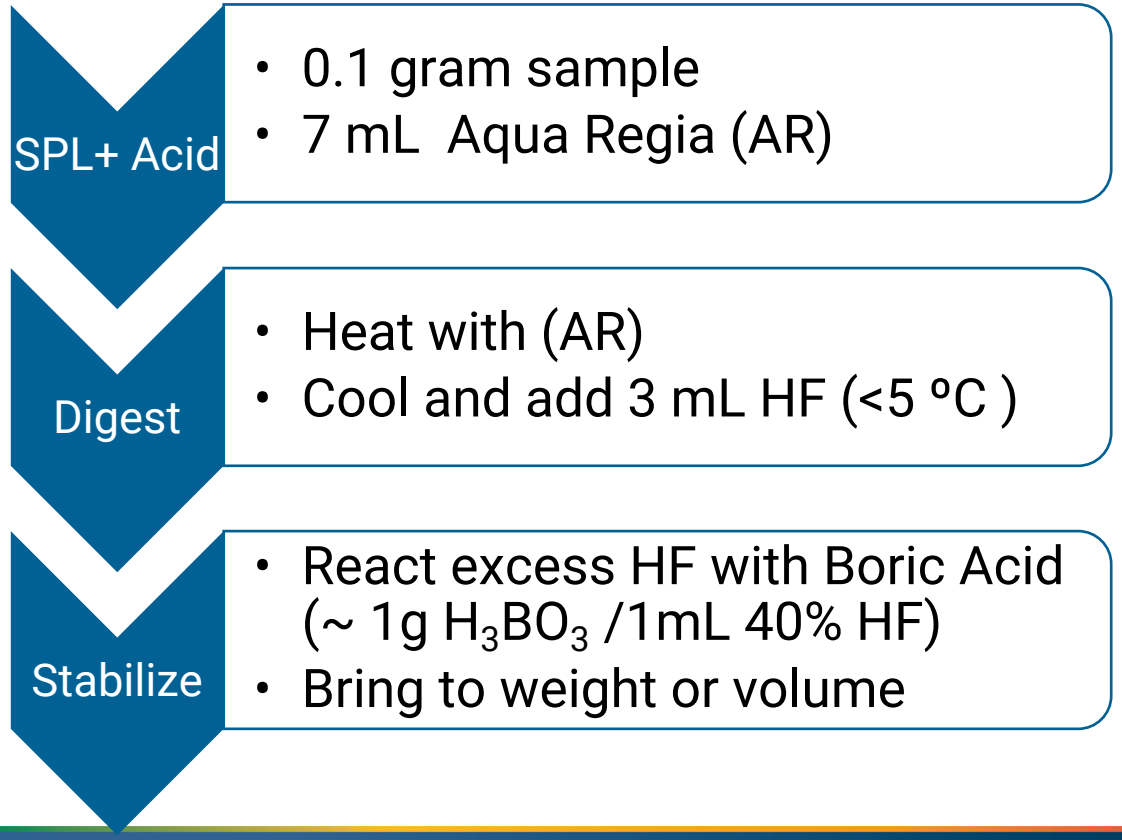


The Analysis of Silicon — FUSION

Very Popular Method Covering Broadest Range of Sample Types

- Does not require HF
- Can be automated
- Covers a very broad range of sample types
- Good for sample types resistant to acid dissolution
- Salting out is problematic causing drift and poor precision

The Analysis of Silicon—
NUMEROUS HF DIGESTION METHODS



The Analysis of Silicon

1. A short-term precision of 1% = 1.4% $(1^2 + 1^2)^{1/2}$ = 1.4% uncertainty in the ratio of two signals (Al/Si ratio). If we expand the uncertainty in the measurement, we include the weight of sample and sample solution and uncertainty of the calibration standard. If we are comparing samples using the same standard the limiting factor is short term precision and DRIFT (a systematic error) causing a BIAS
   in the data.

2. The goal is to achieve a short-term precision of ≤ 0.7% with no measurable drift. $(0.7^2 + 0.7^2)^{1/2}$= 1.0%

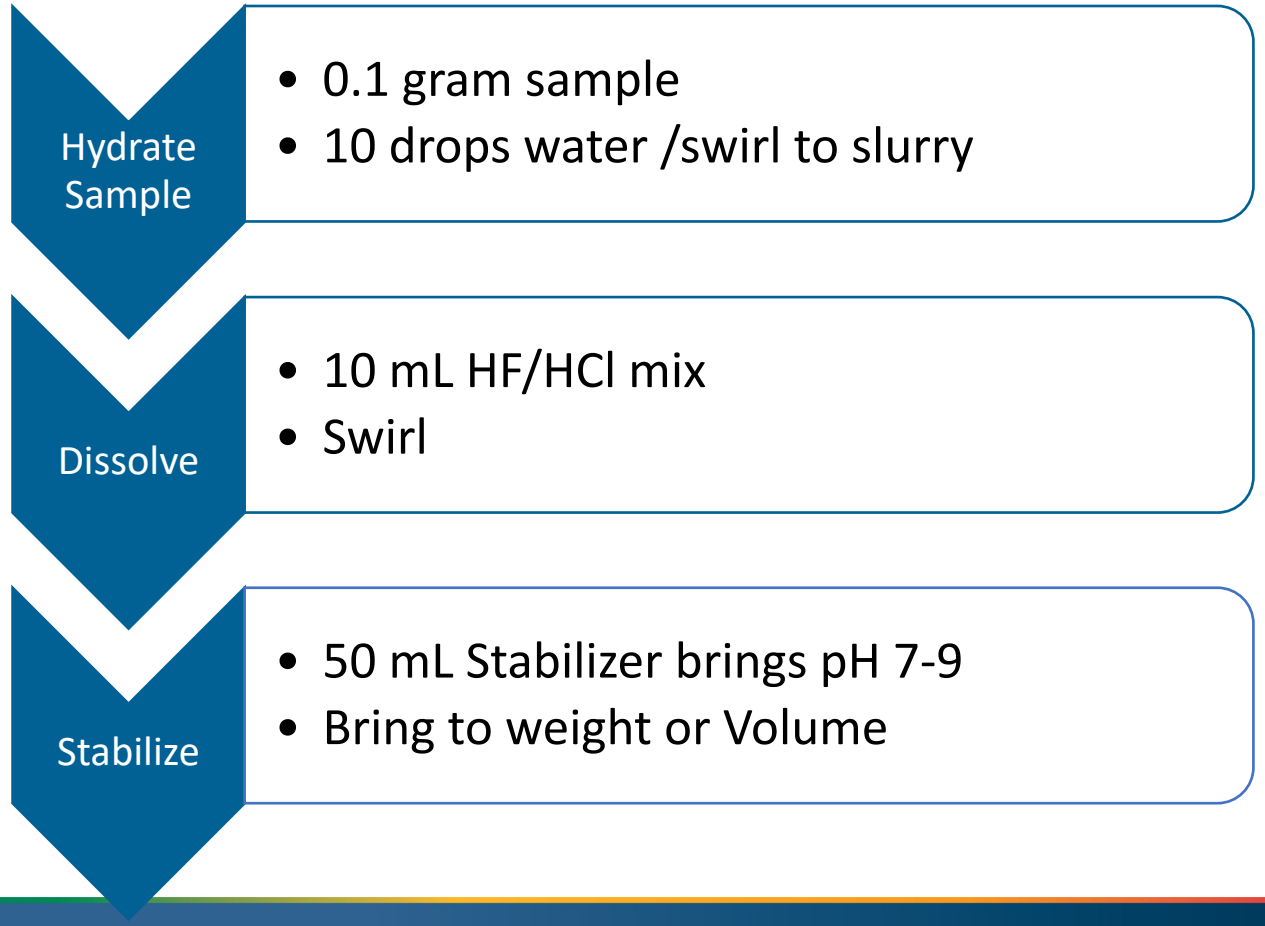
The Analysis of Silicon

- Both Methods had trouble with **salting out** (boric acid) causing **drifting** and **poor short-term precision** (~ 5%) using a fixed cross-flow nebulizer(Pt/Ir) with a Scott spray chamber

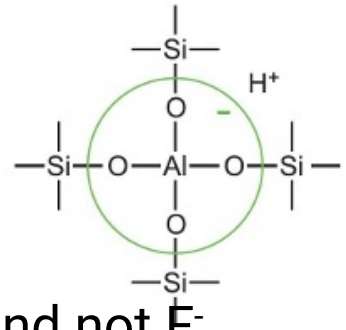
- Using a concentric glass nebulizer/cyclonic spray chamber improved precision but salting out was still problematic and short-term precision still ~ 2%

- Drifting by > 3% over 4 hours was problematic

Dissolution of Aluminosilicates — UniSolv HF Digestion — Developed for Zeolites



Some Chemistry –
HCl Helps by Shifting HF Equilibrium

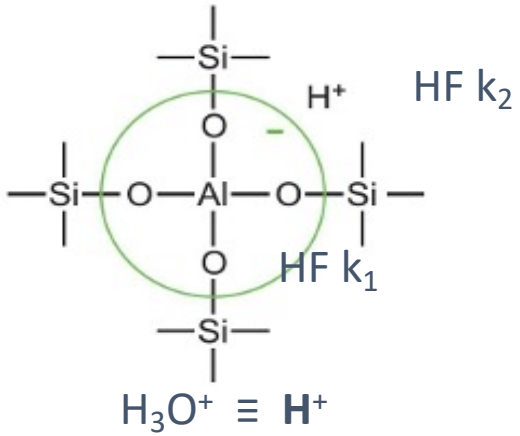


It is the HF molecule that reacts with the Si — O bond and not F^-

$HF \rightleftharpoons H^+ + F^-$ @ $K_a = 10^{-4}$ and adding HCl pushes equilibrium to the HF

1. $Si - OH + HF \longrightarrow Si - F + H_2O$ (HF not F^{-1})
2. $Si - O - Al + HF \longrightarrow Si - F + \{H - O - Al$ and/or $F - Al + Si - OH\}$
3. $M^{+2} + F^- \longrightarrow MF_2\downarrow$ (fluoride ppt discouraged)

Some Chemistry – (cont.)



- Rxn 1 = Surface - O — Si-$(OH)_3$ + H — F ⟶ Surface —O— H + F — $Si(OH)_3$
  @ rate = k_1
- RXn 2 = --Al-O — Si-$(OH)_3$~**H^+** Cl^- + H—F ⟶ Al—O—H~ **H^+** Cl^- + F —$Si(OH)_3$
  @rate = $k_2 > k_1$

This is a surface (two phase) reaction
The reaction is catalyzed by HCl

Changes in the Digestion Composition for Different Sample Types — Zeolites and Silica Gel

- HF : HCl is 8:2 v/v for “normal zeolites” or alumino silicates which require no heating and dissolution appears diffusion controlled (<1 second after acid addition).
- The greater the silica the greater the ratio of HF : HCl
- For example – Si/Al > 8 zeolites and Silica Gel is 9:1 HF : HCl

Changes in the Digestion Composition for Different Sample Types – Coal Fly Ash, Limestone

- Hard to digest samples like coal fly ash need H_3PO_4 to promote reaction by complexing transitions, group II and III elements, etc. with H_3PO_4 using a ratio of 4.0/3/3 of HCl/HF/H_3PO_4
- Zeolites containing high levels of the alkaline earth and rare earth elements use a 4.0/0.7/5.3 ratio of HCl/HF/H_3PO_4 this ratio is also used for limestone.
- HF does not ppt. Group II and III elements but F^- does
- The relative amount of HF : F^{-1} is increased along with the addition of a complexing acid to help keep groups II and III in solution

Changes in the Digestion Composition for Different Sample Types – Limestone, Aluminosilicates Containing Alkaline, Rare Earth and % Levels of Transitions

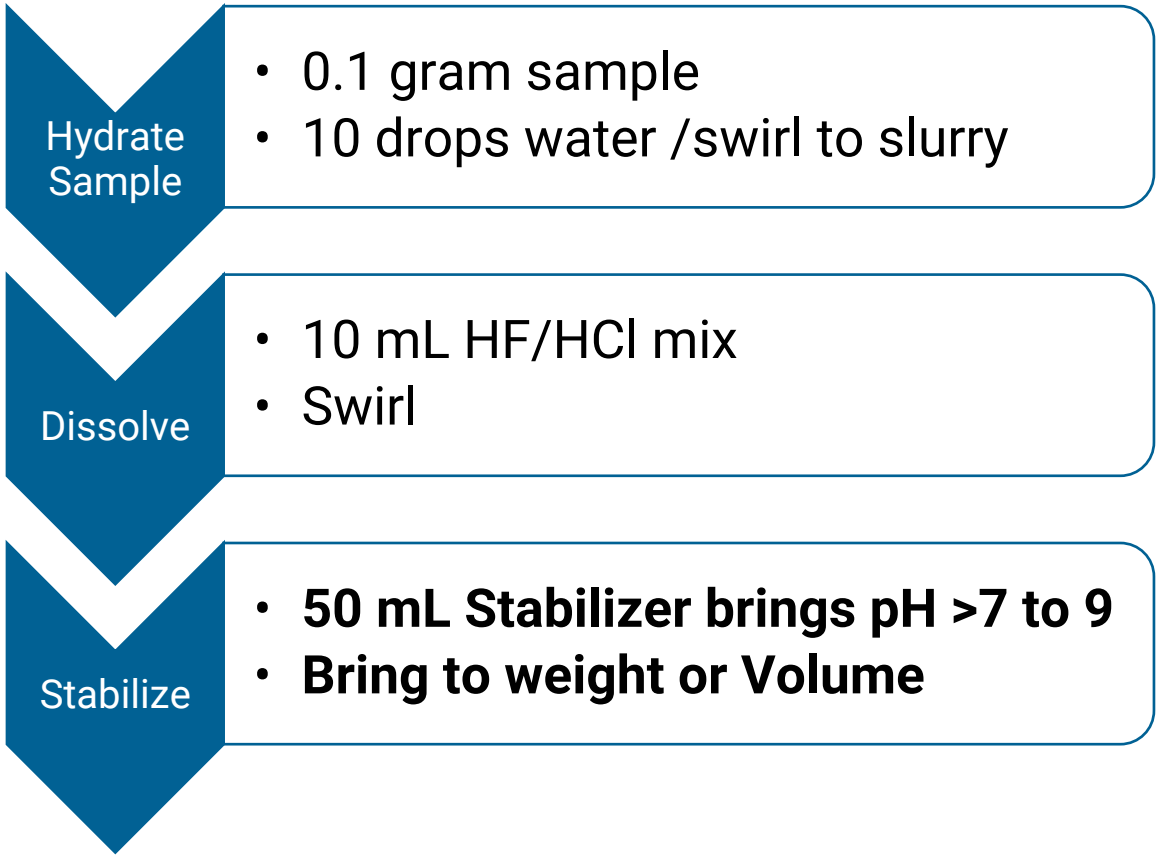
The relative amount of HF is increased along with the addition of a complexing acid

$HF \rightleftharpoons H^+ + F^-$ @ $K_a = 10^{-4}$ and adding HCl pushes equilibrium to the HF

$\equiv Si - O - Ca - O - H + H^+ / HF / H_2PO_4^- \longrightarrow \equiv Si - F + [Ca\ PO_4]^{-1} + 2H_2O$

$HCl/HF/H_3PO_4 = (4.0/0.5/5.5)$

Dissolution of Aluminosilicates — UniSolv HF Digestion — Developed for Zeolites



The UniSolv Stabilizer Helps with the Fusion Method

- Salting out eliminated — By adding TEA to pH ~8 to the sample fuseate solution or HF/boric acid digestion method salting out is eliminated.
- Concentric glass nebulizer with cyclonic spray chamber performs at ≤ 0.7 % short term precision — can now use with all methods.
- Eliminating HF and Salting Out makes Fusion Very Attractive for a broad sample scope.

Advantages of Using UniSolv Stabilizer with the Fusion Method —

- Safe for instrument and analyst — No Si blank using an all-glass introduction system and quartz tourch.

- Fusion Method does not use HF therefore safety is not an issue as with methods using HF.

- Fusion gives a broader range of sample types and is the only viable method for the more refractor sample types (carbides, nitrides, ignited oxides, chromite, etc.)

Advantages of Using UniSolv Stabilizer with the Fusion Method –

- If you already have a fusion capability then you have a broader sample type capability and cost effectiveness on a daily use basis is good.
- UniSolv's net advantage is lower precision if you are analyzing zeolites.
- Other sample types generally require digestion.

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