Quantitative Trace Metals Analysis using Hydrofluoric Acid Alternatives

Jane Ramsey and Tom Connell - E. I. du Pont de Nemours and Company
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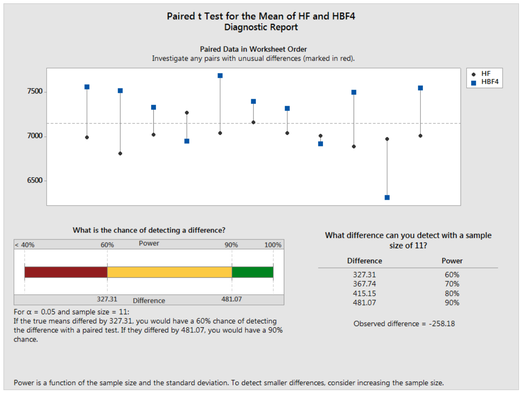
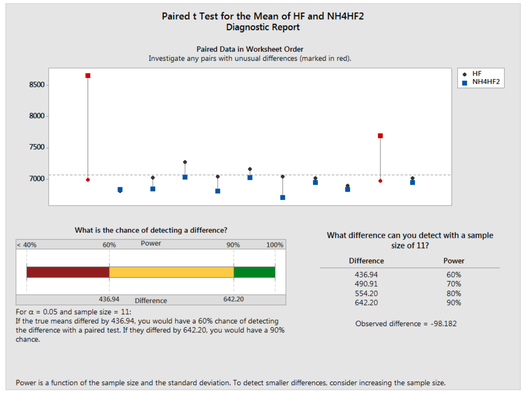
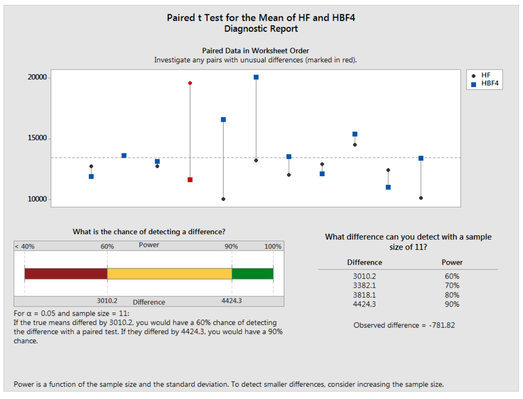
Researchers from CEM and DuPont have worked together to determine if it is possible to use a fluoride surrogate other than hydrofluoric acid (HF) in sample preparation. Total dissolution of a sample matrix is critical to ensure accurate data, and this study investigated two promising, commercially available HF alternatives. Our team used titanium dioxide with trace levels of aluminum and silicon as target analytes for this experiment. Ammonium bifluoride (NH_4HF_2) and fluoroboric acid (HBF_4) were chosen as fluoride sources and validated against digestions with HF. All samples were prepared with a MARS 6 microwave digestion unit and analyzed with a Perkin Elmer Optima 5300 ICP-OES.

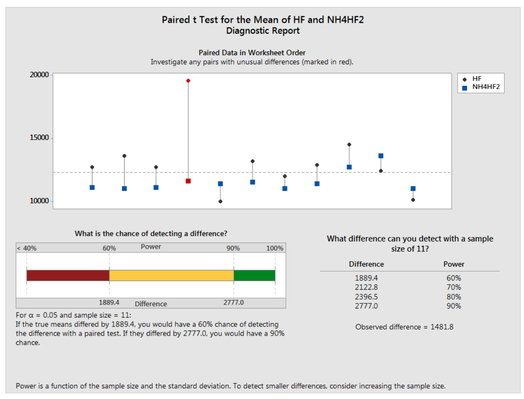
Trace Al in TiO_2



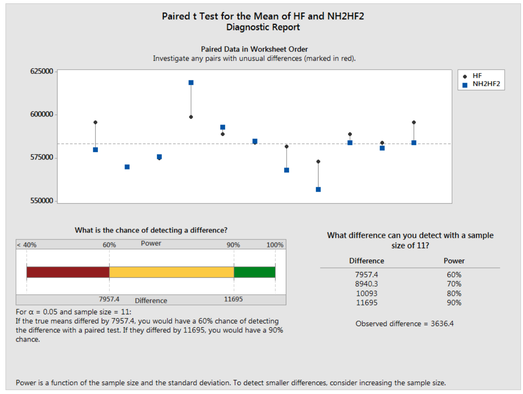


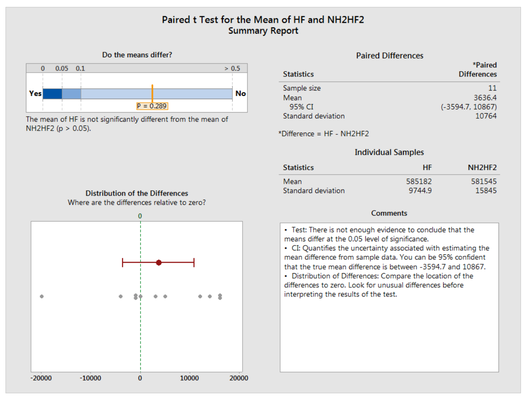
Trace Si in TiO_2





Bulk analysis of Ti





Experimental Design

Each sample was prepared and analyzed 12 times using HF, NH_4HF_2 and HBF_4 as the principal solvent. A MARS 6 Microwave Digestion System was used ramping to a temperature of 230°C and holding for 30 minutes.

Observations:

- A Paired t Test was used to determine if the data was the same or different from the HF results.
- The experiment worked with the NH_4HF_2 and HBF_4 . The data suggest that the all digested samples are statistically the same.
- HF out performed the other solvents in some cases.

Conclusions:

- HF is still the best solvent for total dissolution of titanium dioxide.
- HBF_4 works well for trace metals recoveries for Al and Si.
- NH_4HF_2 works as a suitable replacement for the total dissolution of titanium dioxide for trace metals analysis.

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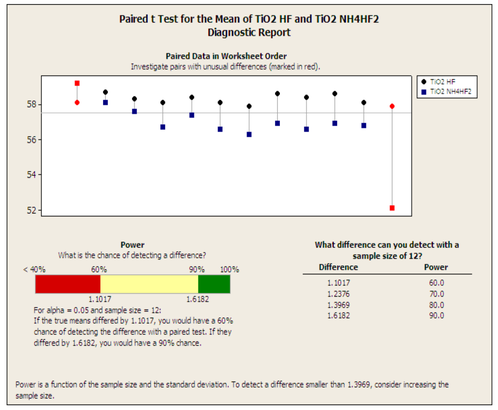

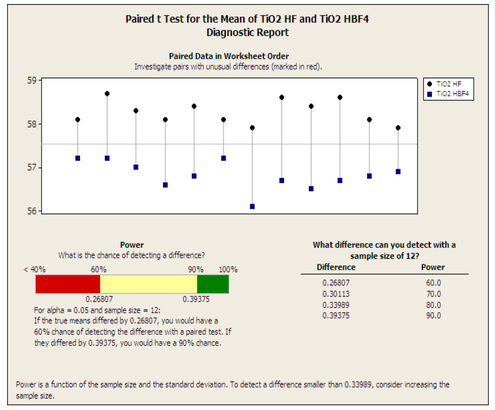

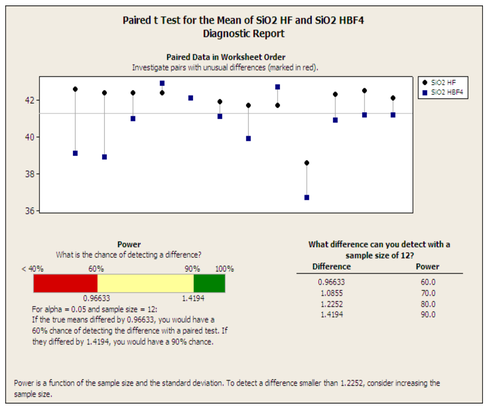

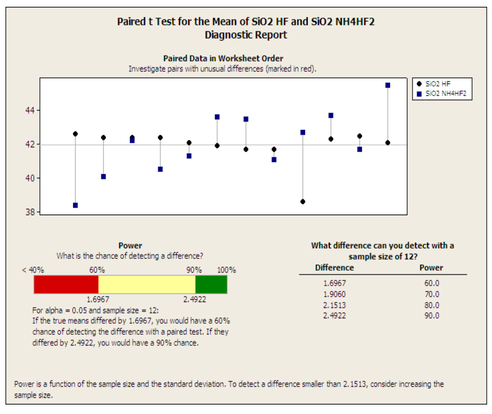

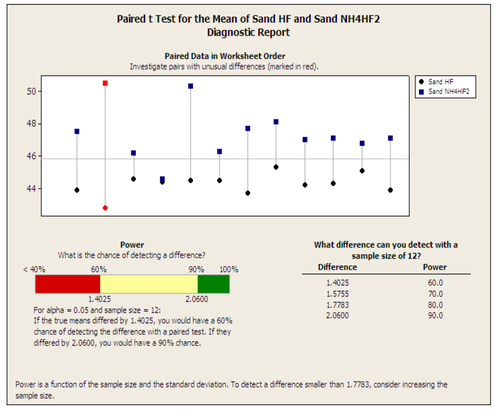

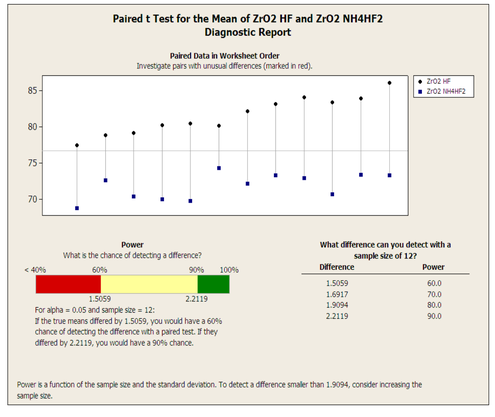

Experimental Design

Each sample was prepared and analyzed 12 times using HF, NH_4HF_2 and HBF_4 as the principle solvent. A MARS 6 chemical microwave was used ramping to a temperature of 210°C and holding for 30 minutes.

Observations:

- A Paired t Test was used to determine if the data was the same or different from the HF results.
- The experiment worked with the NH_4HF_2 and SiO_2. The data suggest that the two digested samples are statistically the same.
- Zr did not go into solution with the HBF_4.
- The TiO_2 data comparing the three solvents showed that the NH_4HF_2 and HBF_4 data compared to one another however they were both lower that the HF data.
- HF out performed the other solvents in every case.

Conclusions:

- HF is still the best solvent for total dissolution of titanium, zirconium and silicon.
- We pushed the limits of the solvents by using the most concentrated source of the element of interest, further testing is needed.

Path Forward:

- Repeat the experiment using samples where Ti, Zr and Si are at a much lower level..
- Lengthen the microwave program from a hold of 30 minutes to 45 to see if that makes a difference

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Experiment #1 – Focus on an all inclusive method

- TiO_2, ZrO_2, SiO_2 and Silica Gel were prepared as follows:
  - 0.7 g NH_4HF_2, 6 mL H_2O, 3 mL HCL, 1 mL HNO_3
  - 15 mL HBF_4, 3 mL HCL, 1 mL HNO_3
  - 3 mL HF, 3 mL HCL, 1 mL HNO_3
  - Each set of 12 were ramped to 210°C and held for 30 minutes.
    - Experiment Failed
    - HF provided the best recovery in every case

Experiment #2 – Focus on an all inclusive method

- Repeat Experiment #1 using less sample (0.1g) and a longer digestion time (60 minutes)
  - Experiment failed
  - HF provided the best recovery in every case

Experiment #3 – Focus on an all inclusive method

- Repeat Experiment #2 and increase microwave temperature to 230°C, keeping sample size and length the same.
  - Experiment failed
  - HF provided the best recovery in every case

Experiment #4 – Focus on ZrO_2

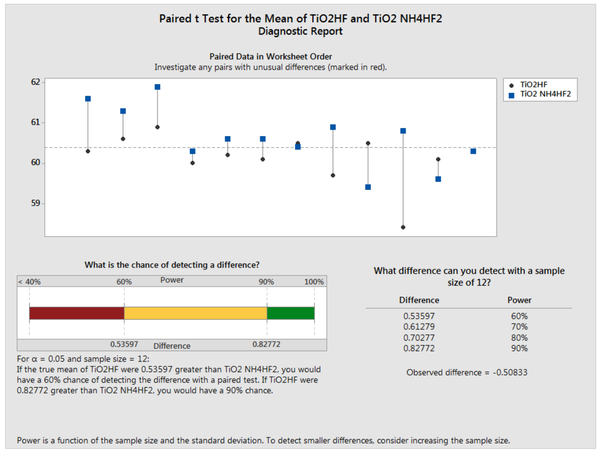
- Increase NH_4HF_2 to 1 g, keep temperature at 230°C for 30 minutes
  - Experiment failed
  - $ZrO_2 + NH_4F.HF \Rightarrow (NH_4)ZrF_7 + H_2O$
  - Ammonium hepafluorozirconate decomposes at 250°C
  - One set of sample was digested at 260°C and Zr recoveries were comparable to the HF digestion

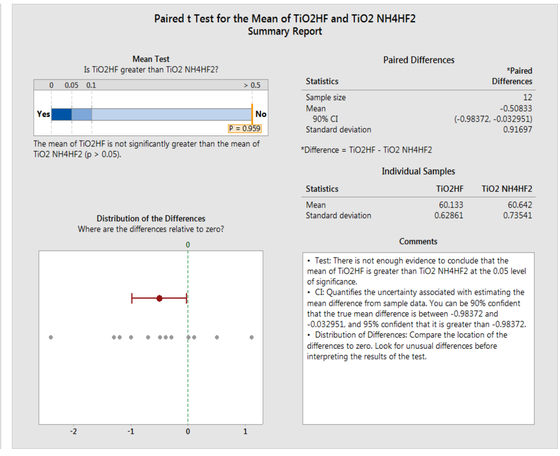
Experiment #5 – Focus on TiO_2

- Increase NH_4HF_2 to 1 g, temperature at 230°C for 30 minutes
- Increase HBF_4 to 20 mL, temperature at 230°C for 30 minutes
  - Experiment failed
  - NH_4HF_2 and HBF_4 compared well to each other, however HF had the best recovery.

Experiment #6 - Focus on TiO_2

- Increase NH_4HF_2 to 3 g, temperature at 230°C for 30 minutes
  - Success! HF and NH_4HF_2 compared favorably





Conclusion and Path Forward

- ZrO_2 does not work with NH_4HF_2 or HBF_4
- Good recovery on TiO_2 with NH_4HF_2 – repeat using 24 samples vs 12 to confirm findings.
- Continue to work on SiO_2 and Silica Gel with the HF alternatives