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The impact of different acid mixtures on total recoverable Iron analysis using microwave digestion

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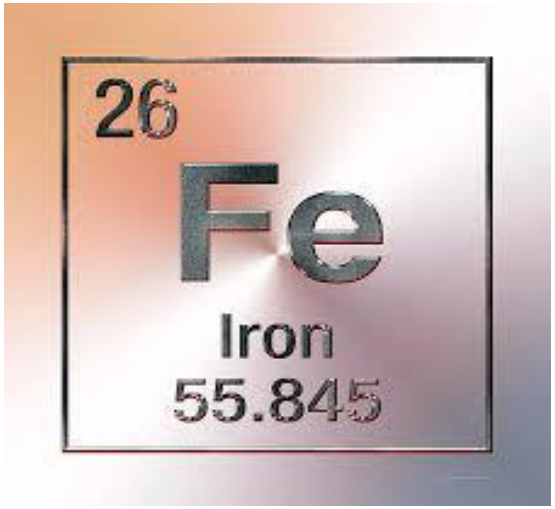
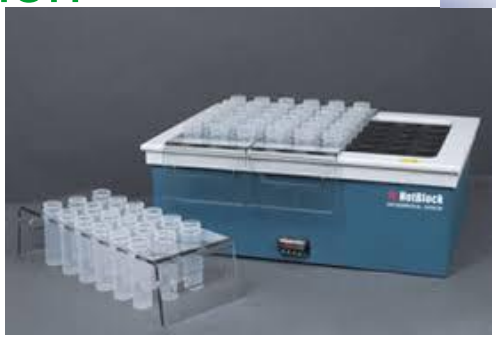
Outline

- Metals preparation methods for sludge, soil, and sediment analysis
  - SW-846
  - Different digestion methods
- Microwave Digestion
  - History
  - Pros and Cons
  - Microwave basics
- Appropriate acid mixtures
  - Impacts of different acid mixtures iron (Fe) and other metals
- Data Summary



Total recoverable vs total

- Many EPA prep methods available for use in SW-846 Chapter 2, Table 2-45
  - 3050B- total recoverable
  - 3051A- total recoverable
  - 3052-total decomposition
  - 3060-total (Cr(VI))
  - 3200-total Hg

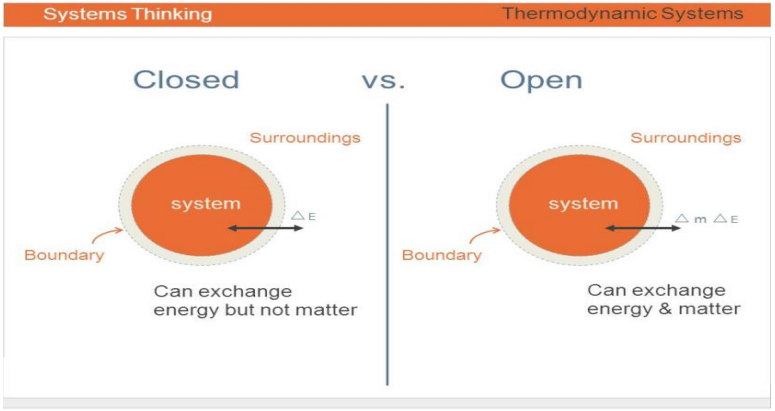


- Looking for what is recoverable…more environmentally available

Methods 3050B & 3051A

- Both EPA methods are appropriate
- Method 3050B
  - Conventional hot block leach/digestion method
  - Continuous heating, refluxing, and cooling over a long period of times (often two days)
  - Open vessel
- Method 3051A
  - Microwave leach/digestion method
  - Developed in the late 1980's as an alternative to 3050B

3051A Increasing popularity



- Pros: A Closed System!!!
  - Short Digestion time
  - Lower acid consumption
  - Less contamination
  - Volatile element loss prevented
  - Reproducibility
  - Safety
- Cons
  - Sample amount limited
  - No standardized acid mixture required

Microwave Digestion History

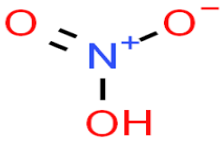
- Developed in the late 1980's
- Initial focus on oxide dissolution
- Improvements in temperature and pressure control enhanced dissolution
- Finding an appropriate digestion vessel was difficult
- As technology increased, so did the efficiency and control of microwave systems
- EPA methods became more flexible

Basics of microwave digestions

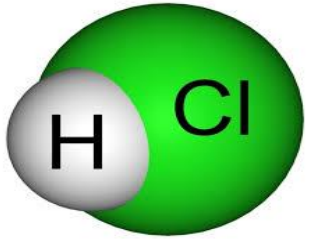
- Microwaves are electromagnetic waves in the range of 300 MHz (0.3 GHz) to 300 GHz, with a typical frequency of 2.450 MHz
- Microwave systems use dielectric heating, also known as electronic heating
- Microwaves promote the rotation of molecules, increasing molecular collisions, which increases temperature
- Temperature feedback control is very important
- Vessels are designed with pressure venting systems

Why different acid mixtures for different matrices

- Finding a good middle ground for our specific samples
- Consideration of the reference digestion procedures, and the reactivity of the acids for the analytes of interest are critical.
- Most digestions require a strong oxidizer



  - Nitric acid is an oxidizing acid that will dissolve most metals to form soluble metal nitrate
- Analyte stability, solubility, and complexing nature
  - Hydrochloric acid is often used



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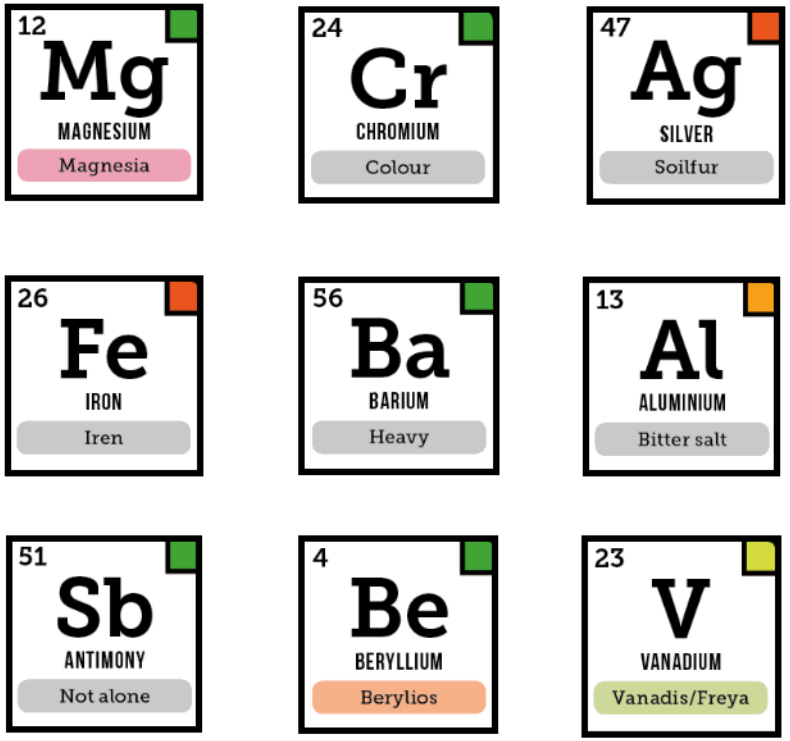
Consideration of Hydrochloric Acid

- 3051A states that certain target analytes require the addition of hydrochloric acid to achieve equivalent results to 3050B

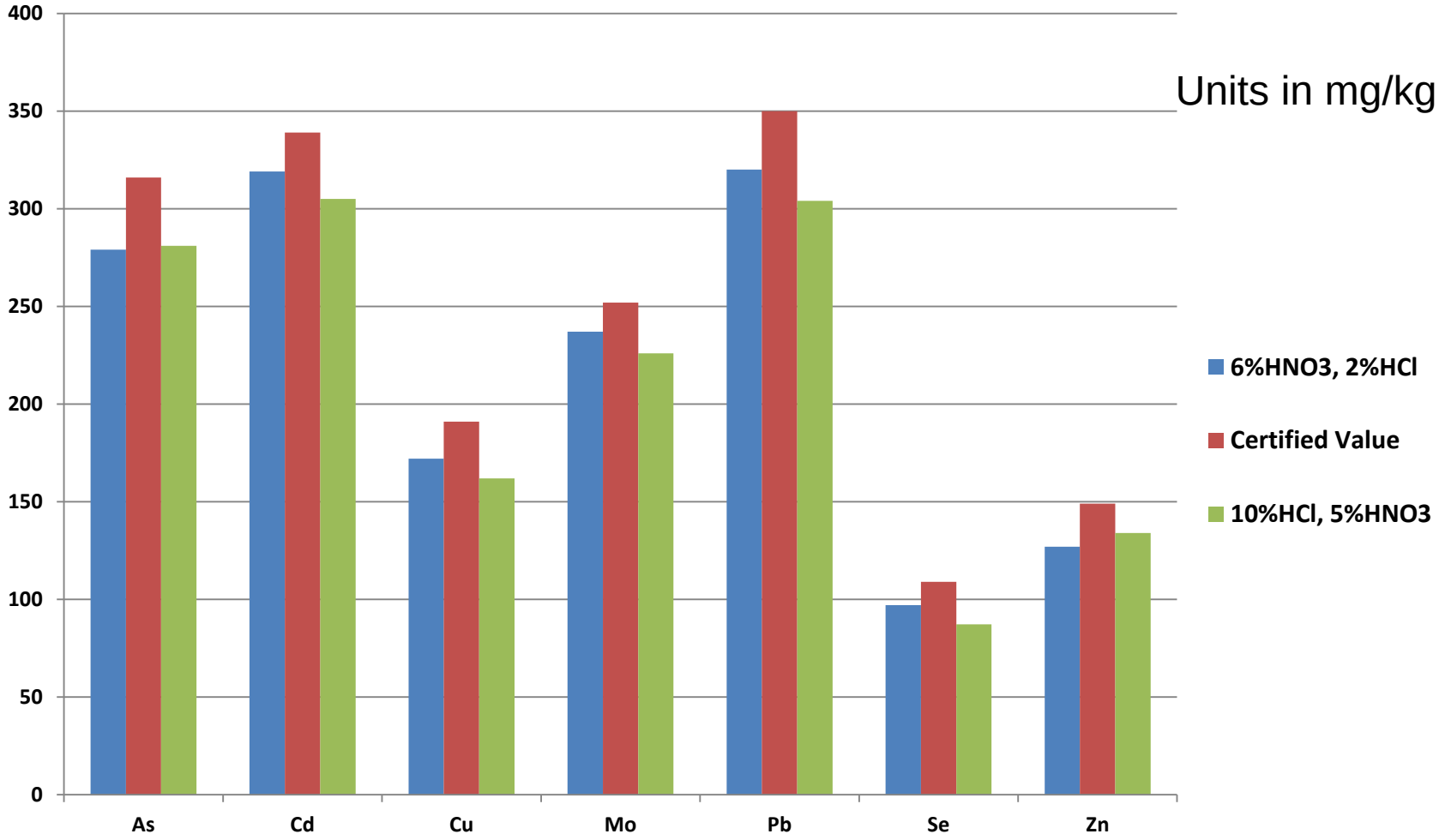


Using a targeted approach to assess acid mixtures

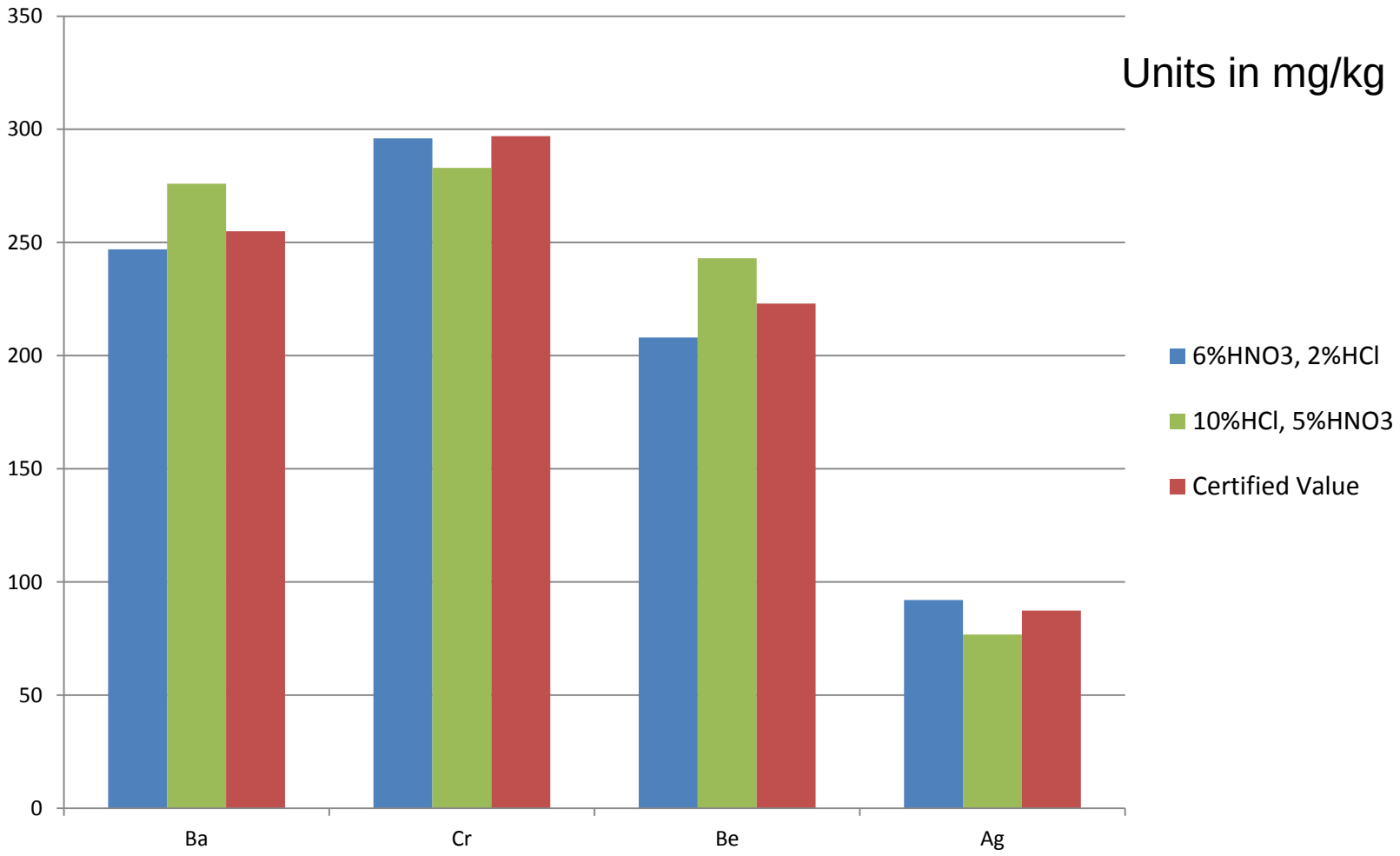
Acid mixture	Why test	Assessment
5%HNO3	A variation mentioned in 3051A (10%HNO3)	Bad recovery for Ag, Ba, Be
9%HNO3, 3%HCl	Method recommended	Too reactive
6%HNO3, 2%HCl	Same ratio as recommended	----------
5%HNO3, 10%HCl	Final acid mixture of 3050B digestion	----------

- 9%HNO3, 3%HCl is recommended (a ratio of 3:1)
  - We found this mixture to be very reactive
  - Many acid combinations were tested in succession

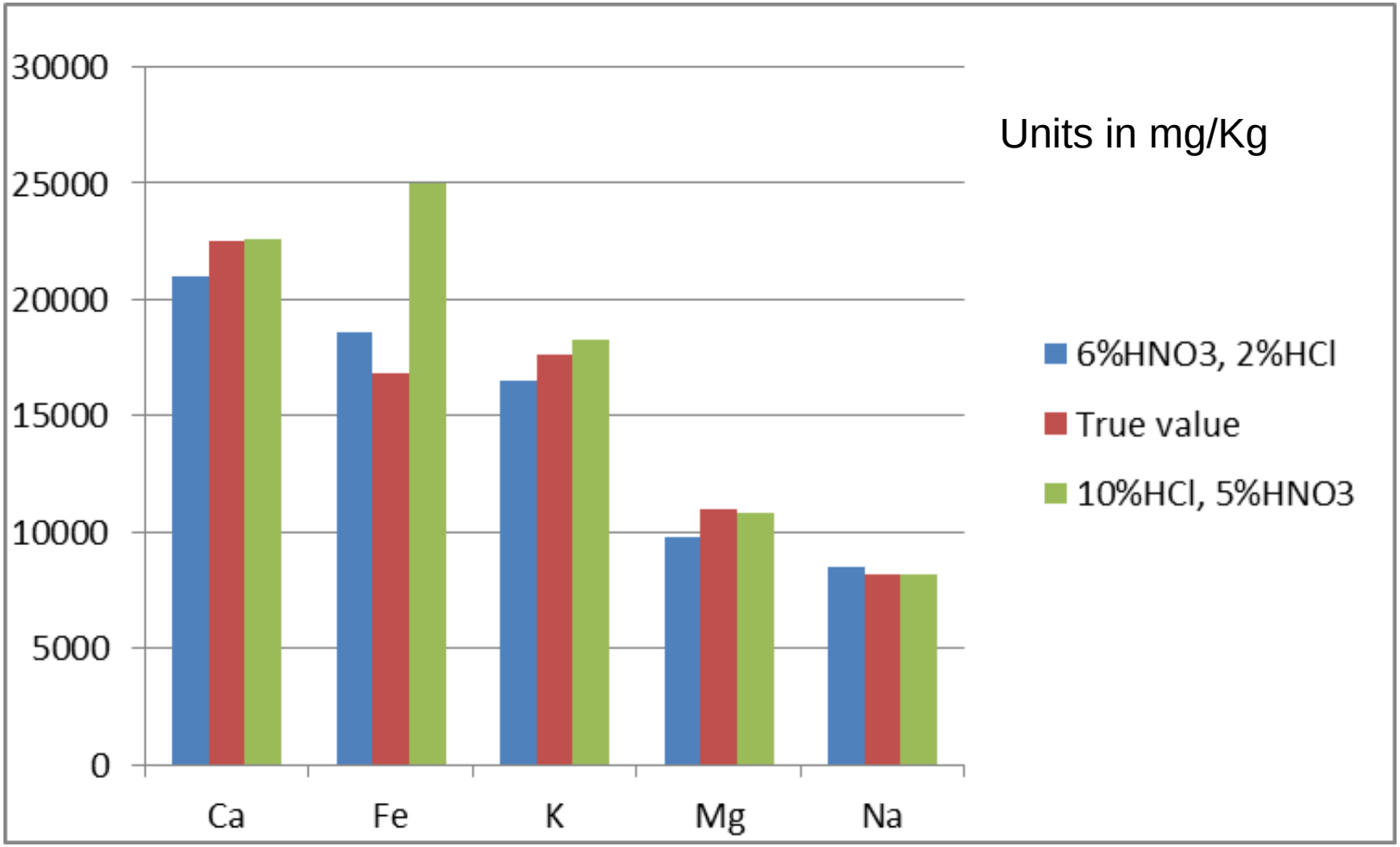
Recoveries for target analytes



Recovery for problem analytes mentioned

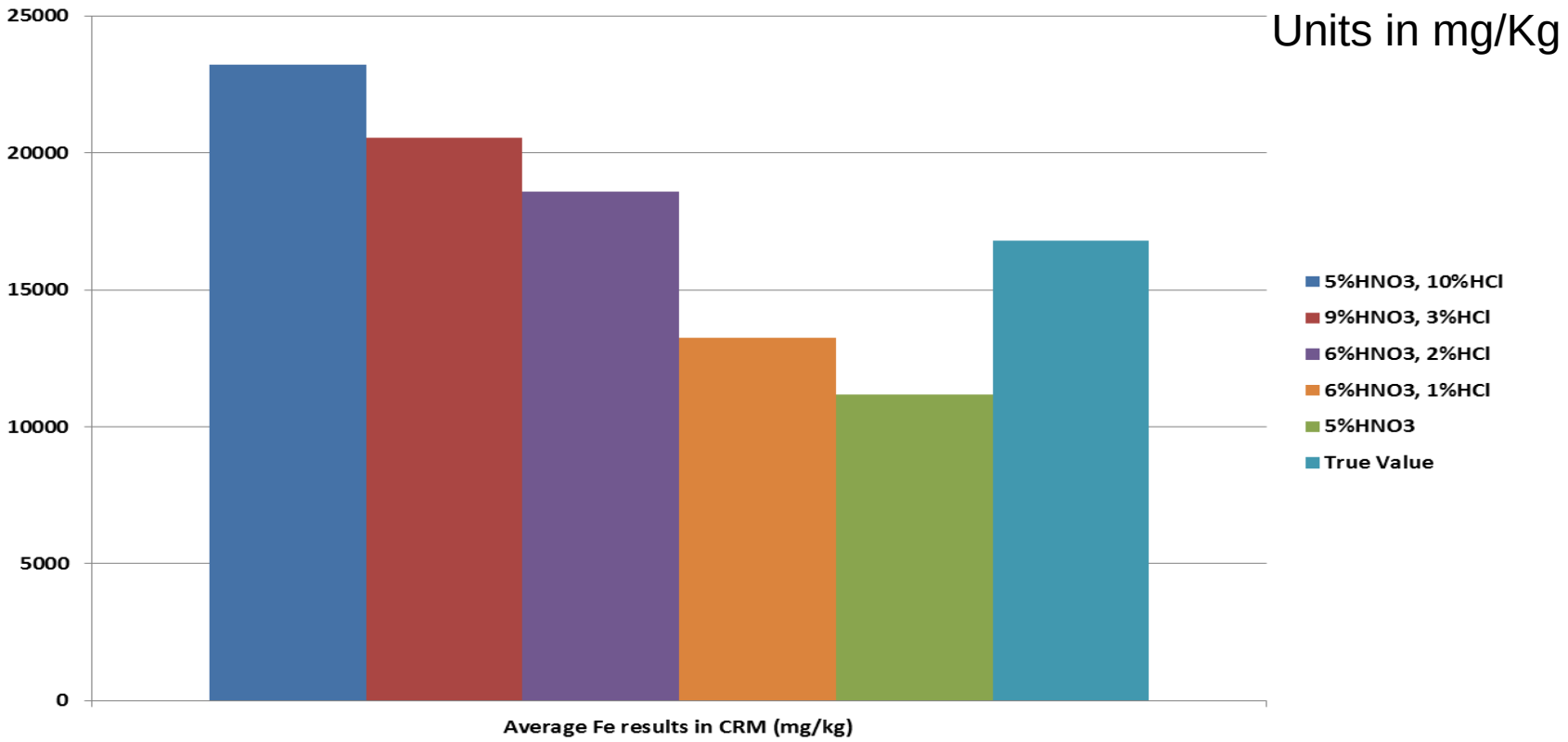


Recovery of more target analytes



Acid combination testing

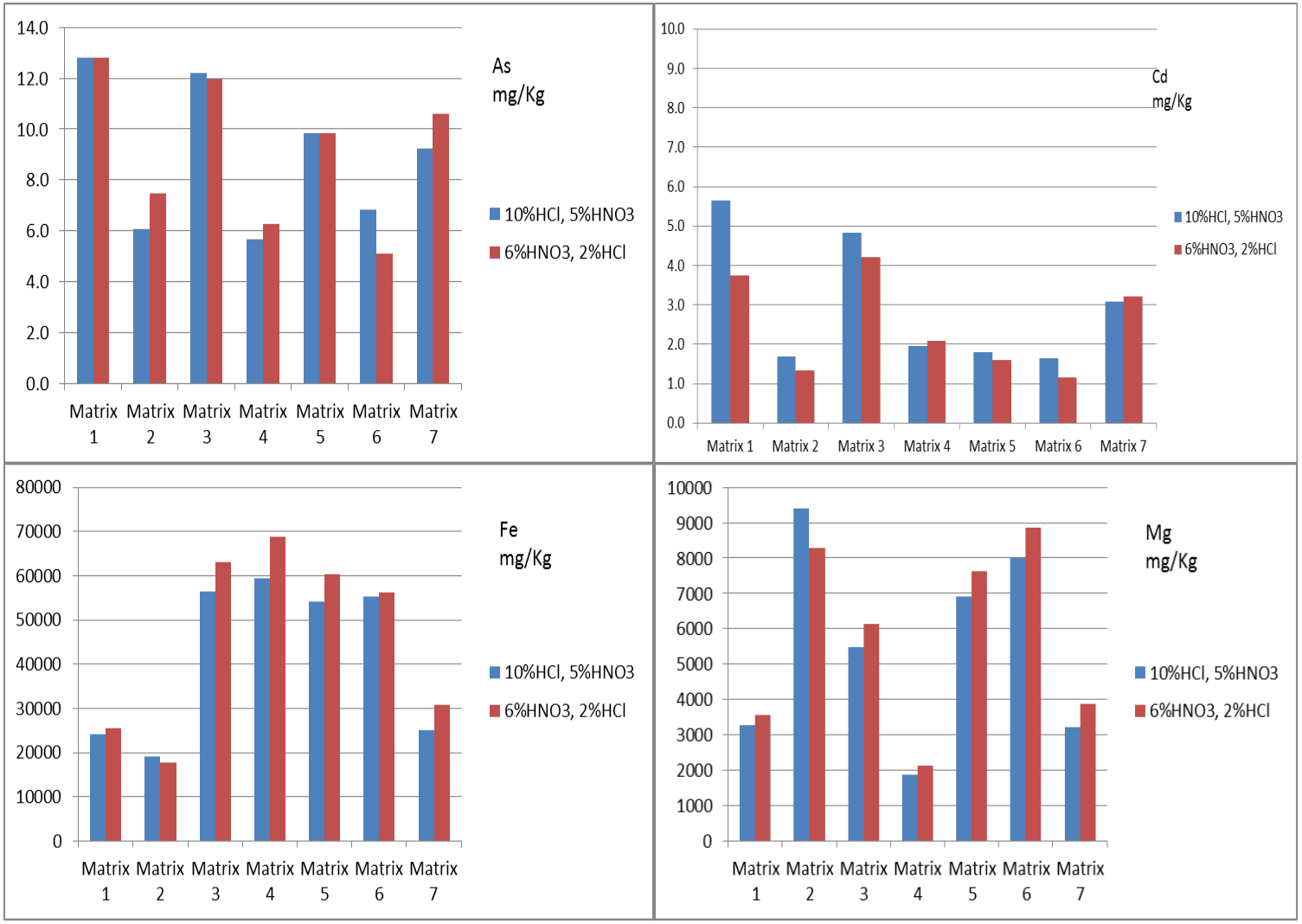
- The ratio of Nitric acid to Hydrochloric acid affects the percent recovery of Fe



Why is iron affected so much?

- Hydrochloric acid's complexing nature allows for complete dissolution of numerous metals, such as Fe(II) and Fe(III) complexing to form $[FeCl_4]^{-2}$ and $[FeCl_4]^{-}$
- Hydrochloric acid can completely dissolve some metals
- When you increase Hydrochloric acid, pressure in your vessel will increase too

Real world matrix comparisons



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6%HNO3, 2%HCl	Same ratio as recommended	Good recoveries for all target analytes
5%HNO3, 10%HCl	Final acid mixture of 3050B digestion	Good recoveries for most target analytes, but not all

Conclusions

- The ratio of nitric acid: hydrochloric acid greatly affects volatility, reactivity, solubility, complexation, stability, and catalytic effects of target analytes
- During our testing, a nitric: hydrochloric ratio of 3:1 yielded the best quality data
- We chose to move forward with 6%HNO3, 2%HCl acid mixture
  - same 3:1 ratio recommended but less reactive

Thank you
Questions?

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