Multiple Digestions Are Sometimes Necessary

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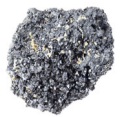
Abstract

Accurate data in trace metals analysis is essential for chemists and engineers to make critical decisions. Sample preparation plays a huge role since the analytical data can be no better than the prepared sample. Different acid combinations combined with multiple digestion methods are sometimes necessary to complete the analysis. A clear digest has always been the end goal in elemental analysis. The belief was that a clear digest meant that your elements of interest were in solution. With the wrong acid combination even though your sample is a clear digest, the element of interest will be biased low. This application note will provide examples of situations where the sample preparation influenced the final result.

Experimentation

Samples Prepared using Hydrofluoric Acid (HF) in the acid combination
Analysis of samples containing HF should consider additional preparation without HF when the element of interest is Ca, Mg, Sr, Y, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Pr, Sc, or Th. The digested sample with HF can form insoluble fluorides with the above mentioned elements. Even though the microwave digestion with HF is a clear solution and the digestion without HF required filtering prior to analysis, the difference in these results need to be considered; especially when it comes to the accuracy of your data.

In this study, iron oxide samples were digested in a MARS 6 Microwave Digestion System, **Figure 1**, utilizing two acid mixtures, one with and one without HF. Results of the analysis are shown in **Table 1**.



Titanium Ore Samples comparing microwave digestion vs lithium metaborate fusion
Solid samples with complicated matrices may require more than one digestion type to fully solubilize all elements of interest and destroy the matrix. Multiple digestions may have to be run and compared to determine which one is correct. You may use an Element Oxide Conversion chart to help determine which method may be correct.

For analysis of titanium ore samples, preparation by microwave digestion, using an acid mixture of HCl, HNO_3, HF, and H_2O, and lithium metaborate fusion were performed and comparative data is shown in **Table 2**.

Samples Prepared not using Hydrofluoric Acid (HF) in the acid combination
Acid combinations not containing HF may have a biased low result for certain elements, i.e. Si, Zr, and Ti. In the case of samples that require silicon analysis, fluoroboric acid can be substituted for HF, however, it is not effective for the other elements.

Eight different lots of gold powder were digested in a MARS 6 in Aqua Regia, Aqua Regia with HF, and Aqua Regia with HBF_4. Results are shown in **Table 3**.

Analysis and Results

Iron oxide samples were analyzed by ICP-MS, all other samples were analyzed by ICP-OES. The instrument was setup with various conditions, optimized for each sample introduced.

Table 1. Thorium recovery with and without HF

Iron Oxide	Microwave digestion w/ HF	Microwave digestion no HF
	Th (µg/g)	Th (µg/g)
1	18	28
2	15	114
3	7.71	35
4	16	32
5	11	73
6	4.97	32
7	23	28
8	13	79

Figure 1. CEM MARS 6

Table 2. Si, Ti, and Zr recovery comparison between microwave digestion and fusion

Titanium Ore	Microwave Data (µg/g)			Fusion data (µg/g)			% Difference		
	Si	Ti	Zr	Si	Ti	Zr	Si	Ti	Zr
1	62200	392000	3700	70900	441000	14600	14	13	295
2	59500	366000	4820	74000	414000	17500	24	13	263
3	44200	323000	8840	75500	420000	17700	71	30	100
4	52900	369000	5780	70800	416000	14000	34	13	142

Table 3. Si recovery with various HF and non HF digestions

Gold Powder	Aqua Regia no HF	Aqua Regia with HF	Aqua Regia with HBF_4
Lot#	Si, µg/g	Si, µg/g	Si, µg/g
1	150	805	811
2	196	721	738
3	257	854	839
4	185	792	770
5	211	1010	1015
6	127	675	692
7	150	648	666
8	111	590	608

Conclusions

Accurate data in trace metals analysis is essential for chemists and engineers to make critical decisions. Sample preparation plays a huge role since the analytical data can be no better than the prepared sample. Different acid combinations combined with multiple digestion methods are sometimes necessary to complete the analysis. Pay attention to the data that you produce from your prepared samples. Use all of the tools available to validate your data. In this study cross functional collaboration was utilized to help determine unknowns in the sample matrices, which was used to determine the most likely source of origin.

Thorium recovery from iron oxide was muted in the presence of HF due to formation of insoluble fluorides.

Titanium ore analysis requires multiple sample preparation methods in order to accurately quantify the elemental content within the complex matrix. In this study, microwave digestion was used for minor constituents while lithium metaborate fusion produced more accurate results on the major constituents that may be present in percent quantities.

Silicon is insoluble in non-fluorine containing acids and therefore must be digested either in the presence of HF or HBF_4 but care should be taken as Zr and Ti recovery may suffer if HBF_4 is used, as opposed to HF.

References

1. Gaines, Paul R, *ICP Periodic Table Guide*, Inorganic Ventures
2. MARS 6 Method Note Compendium (current version), *CEM Corporation*