

A Safer Approach to Chromium Oxide Digestion

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Abstract

Chromium Oxide (Cr_2O_3) catalysts play an important role in chemical manufacturing; however, it is difficult to oxidize Cr(III) to Cr(VI) in digestion and this presents itself with analytical challenges. Traditionally, this sample type was digested via hotplate with perchloric and sulfuric acids or by fusion. The use of perchloric acid poses safety issues as it is an extremely strong oxidizing agent that can cause an explosion in the presence of organics. Perchloric acid should be avoided if the chemist is unable to obtain the appropriate wash-down hood and PPE requirements for its use. Chemists at CEM and Chemours have been working together to develop a digestion method to safely digest this sample type without resorting to perchloric acid, thus significantly improving the workplace safety for the analyst. In this study samples were prepared using a CEM MARS 6 microwave coupled with the iPrep vessel design allowing for total digestion using sulfuric and nitric acids.

Traditional Preparations

- Sulfuric/perchloric acid hotplate digestion
- Fusion with KHSO_4 and extraction with hot KCl with the residue fused with Na_2CO_3
- Fusion with NaKSO_4 and NaF
- Fusion with sodium or potassium carbonates
- Fusion with Na_2O_2 or NaOH/KNO_3 , $\text{NaOH/Na}_2\text{O}_2$

Experimental Design

Five chromium oxide catalyst samples were sampled from different lots for comparison. The chromium oxide was crushed into fine particles using a mortar and pestle in the hood. Each sample was accurately weighed and transferred to an iPrep vessel. HNO_3 and H_2SO_4 (dropwise) were added to the vessel. The sample was allowed to predigest before sealing. A Classic Method was created on the MARS 6, see Figure 1, with ramp and hold times and temperature programmed per Table 1. The samples were allowed to cool before being quantitatively transferred to a tared 100 mL centrifuge tube and the final weight recorded.



Figure 1. CEM MARS 6 with iPrep Vessels

Table 1. Digestion Conditions

Microwave Digestion Method Conditions	
Sample weight	50 mg
Acid	10 mL HNO_3 & 3 mL H_2SO_4
Predigestion	15 min
Temp	250 °C
Ramp	35 min
Hold	120 min
Cool	15 min

Analysis and Results

An Agilent 5100 ICP-OES, with conditions set per Table 2, was used for analysis. Three wavelengths were monitored for analysis by ICP-OES: 205.552 nm, 284.325 nm, and 276.654 nm. The 284.325 nm line was chosen for quantitation. Cr_2O_3 calculations, in Table 3, are based on five lots of Cr_2O_3 samples compared against the theoretical calculation for total Cr_2O_3 using a factor of 1.4616.

Table 2. Instrument Conditions

Agilent 5100 ICP-OES Instrument Conditions	
Replicates	3
Pump Speed	12 rpm
Uptake	20 s
Rinse	30 s
Read Time	15 s
Viewing Mode	Radial, 8 mm viewing height
Nebulizer Flow	0.7 L/min
Plasma Flow	12 L/min
Auxiliary Flow	1 L/min

Table 3. Recovery of Cr and Cr_2O_3

Lot	Cr, $\mu\text{g/g}$	Cr_2O_3 $\mu\text{g/g}$	% Recovery
1	681,000	995,000	99.5%
2	680,000	994,000	99.4%
3	679,000	992,000	99.2%
4	682,000	997,000	99.7%
5	680,000	994,000	99.4%

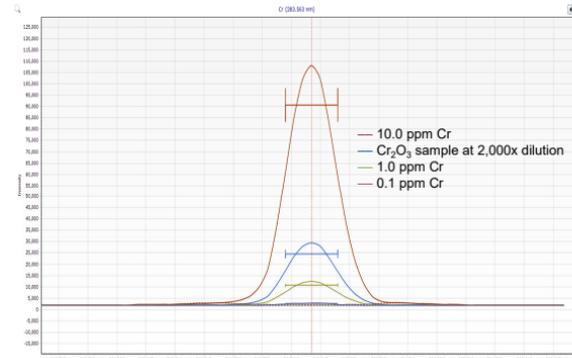


Figure 3. Absorbance of Cr

Figure 3 is an ICP-OES scan example of single-element Cr standards overlaid with a sample scan.

Conclusions

Workplace safety is of utmost importance even when faced with difficult to analyze samples. Chemours and CEM have collaborated on an alternate method with a focus on safety and efficiency. Using the CEM iPrep vessel design in conjunction with a mix of nitric and sulfuric acids, Chemours has successfully digested and quantified total Cr in 5 different lots of Cr_2O_3 with 99.2-99.7% recovery when compared to theoretical Cr_2O_3 . Furthermore, perchloric acid and fusions have been eliminated, improving laboratory safety.

Safety

- Inspect microwave vessels prior to use as Teflon vessels will degrade at the high temperature used in this digestion
- Take care when grinding the samples in the hood so that particles will not be ingested
- Wear appropriate PPE when handling Cr_2O_3 as chromium is highly toxic

References

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