# A Safer Approach to Chromium Oxide Digestion

Natalie Polillo and Jane Ramsey (retired) - The Chemours Company FC, LLC
Sam Heckle, Elaine Hasty, Leanne Anderson - CEM Corporation

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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 $NaOH/KNO_3$, $NaOH/ Na_2O_2$

## 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, ug/g | $Cr_2O_3$ ug/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% |

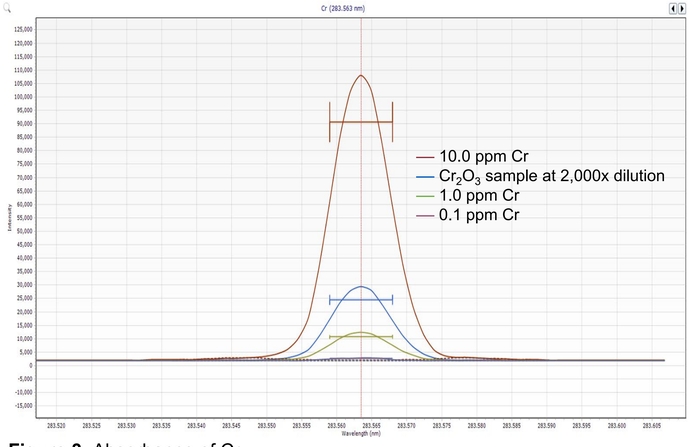


**Figure 3.** Absorbance of Cr

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