



Standard Practice for Sample Preparation of Fluid Catalytic Cracking Catalysts and Zeolites for Elemental Analysis by Inductively Coupled Plasma Atomic Emission Spectroscopy¹

This standard is issued under the fixed designation D7442; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This practice covers uniform dissolution techniques for preparing samples of fluid catalytic cracking catalysts (FCC) and exchanged zeolitic materials for analysis by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). These techniques describe standardized approaches to well-known, widely used laboratory practices of sample preparation utilizing acid digestions and borate salt fusions. This practice is applicable to fresh and equilibrium FCC catalysts and exchanged zeolite materials.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Terminology

2.1 Acronyms:

2.1.1 *FCC*—Fluid Catalytic Cracking

2.1.2 *FCCU*—Fluid Catalytic Cracking Unit

2.1.3 *ICP-AES*—Inductively-Coupled Plasma-Atomic Emission Spectroscopy

3. Summary of Practice

3.1 Three preparation techniques are presented for converting solid, power samples into clear, dilute acid solutions suitable for analysis by ICP-AES. The three techniques presented are Perchloric Acid Digestion, Sulfuric Acid Digestion, and Lithium-Borate Fused Dissolution. Other techniques may be possible; however, these three approaches are established, widely used laboratory techniques for preparing FCC catalyst and catalyst-like samples.

3.2 Powder samples are heat-treated for 1 to 3 h to remove volatile components prior to further preparation by any of these three techniques.

3.3 The Perchloric Acid and Sulfuric Acid techniques involve dissolving small aliquots of heat-treated sample in the respective acid liquors and diluting the resulting solutions to the appropriate analytical volume. These techniques require boiling acid solutions in platinum or polytetrafluoroethylene (PTFE) labware and shall be used in appropriate fume hoods. The Perchloric Acid Digestion shall *never* be used in a standard fume hood.

3.4 The Lithium Borate Fused Dissolution technique involves dissolving small aliquots of heat-treated sample in a molten flux of lithium metaborate and lithium tetraborate salts, dissolving the resulting flux solution in a dilute nitric acid solution, and diluting the clear, concentrated specimen solution to an appropriate analytical volume. This technique must be performed in an operational fume hood and can be performed manually or may utilize the advantages of an automated fluxer. The optimal ratio of flux to sample, as well as fusion temperature needed, will vary depending on sample matrix.

4. Significance and Use

4.1 The chemical composition of catalyst and catalyst materials is an important indicator of catalyst performance and is a valuable tool for assessing parameters in a FCCU process. This practice will be useful to catalyst manufacturers and petroleum refiners for quality verification and performance evaluation, and to environmental authorities at the state and federal levels for evaluation and verification of various compliance programs.^{2, 3, 4}

4.2 Catalysts and catalyst type materials are difficult to prepare for analysis by ICP, and although the techniques presented in this practice are common, there is wide variation among laboratories in sample pretreatment and digestion

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² Dean, John R., *Practical Inductively Coupled Plasma Spectroscopy*, John Wiley, New York, 2005.

³ Gaines, Paul, "ICP Operations," at www.ivstandards.com/tech/icp-ops.

⁴ Segal, Eileen B., "First Aid for a Unique Acid: HF," *Chemical Health and Safety*, Vol 5, Sept/Oct 1998, p. 25.

*A Summary of Changes section appears at the end of this standard.

recipes. This practice is intended to standardize these variables in order to facilitate the utility of comparative data among manufacturers, refiners, and regulatory agencies.

5. Apparatus

- 5.1 *Muffle Furnace*—at 538 to 593°C.
- 5.2 *Analytical Balance*.
- 5.3 *Digestion Vessels*—platinum dish or PTFE beaker.
- 5.4 *Volumetric Flasks*—Class A glass, 250 mL.
- 5.5 *Automated Fusion Machine*—alternate to manual procedure.
- 5.6 *Crucible*—Pt_{95%}/Au_{5%} high-form.

6. Reagents

6.1 All reagents should conform to American Chemical Society (ACS) specifications.⁵ Ultra high purity standards and reference materials are commercially available from recognized vendors.

- 6.2 *Perchloric Acid*, concentrated, 69 to 72 %.
- 6.3 *Hydrofluoric Acid*, concentrated, 48 %.
- 6.4 *Sulfuric Acid*, H₂SO₄, concentrated, 94 %.
- 6.5 *Nitric Acid*, HNO₃, concentrated, 65 %.
- 6.6 *Hydrochloric Acid*, 1:1 HCl (concentrated HCl, 38 %, diluted 1:1).
- 6.7 *Hydrogen Peroxide*, 3 %.
- 6.8 *Lithium Borate Fluxes*, lithium tetraborate, or metaborate, or both.
- 6.9 *Boric Acid Solution*, 2 to 3 %.

7. Preparation of Powder Samples

7.1 Catalysts and catalyst type sample powders contain small amounts of moisture and other volatile materials that must be removed to eliminate potential error in the analysis. Typically, 50 g of powder sample are heated in air in a laboratory furnace at 538 to 593°C for 1 to 3 h to remove volatile components prior to further preparation by any of these three techniques.

7.2 The bed depth of catalyst during the heat treatment should typically be 25.4 mm or less. The heat-treated specimen should be thoroughly blended upon cooling, since some particle size segregation normally occurs during the heat treatment step.

7.3 The heat-treated specimen should remain in a desiccator until use to prevent re-adsorption of ambient moisture.

8. Hazards

8.1 *Hazards Common to All Mineral Acids:*

8.1.1 Wear suitable gloves, eye protection, and proper protective clothing to protect in the event of splashes and spills. Dilutions shall be performed by adding acid to water, not the other way around. Limit quantities in storage to what is needed for the next few weeks.

⁵ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For Suggestions on the testing of reagents not listed by the American Chemical Society, see *Annual Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

8.1.2 Boiling acid solutions can be particularly dangerous, and the elevated temperature typically increases the severity of the hazardous properties. Particular care and advance preparation shall be given to work with tasks involving acid solutions under these conditions.

8.2 *Hazards Specific to Perchloric Acid:*

8.2.1 When not handled properly, perchloric acid can be a very dangerous reagent. Digestions with perchloric acid should be performed only in a fume hood specifically designed for its unique hazards and properties. This hood shall have a water washdown system, operated according to the manufacturer's specifications and instructions. This system is required to prevent buildup of explosive perchlorate salts in the duct work.

8.2.2 Solutions with perchloric acid shall never be boiled to dryness. Careful, attentive observation of techniques using perchloric acid is imperative for safe use.

8.2.3 Perchloric acid should not be mixed or used with organic materials if there is a possibility that the temperature will become elevated beyond ambient levels.

8.2.4 In the event of a perchloric acid spill, neutralize with soda ash or other appropriate neutralizing agent. Soak up with an inorganic based absorbent. DO NOT use rags, paper towels, saw dust, or any organic or oxidizable material, as such material may spontaneously ignite. An approved spill kit for perchloric acid is highly recommended.

8.3 *Hazards Specific to Hydrofluoric Acid (HF):*

8.3.1 Hydrofluoric acid is an extremely hazardous liquid and vapor that causes severe burns which may not be immediately painful or visible. It may also be fatal if swallowed or inhaled. The liquid and vapor can burn skin, eyes, and respiratory tract and cause bone damage.

8.3.2 Calcium gluconate ointment should be kept in the work area for application in the event of accidental contact with HF. In case of HF contact with any body parts, wash the affected area immediately with cold water and then liberally apply the calcium gluconate gel. Seek prompt medical treatment.

8.4 Molten fluxes have the potential of liberating and volatilizing hazardous respiratory agents. Work involving these molten solutions shall be done only in functional fume hoods with additional protection from skin contact and spattering.

8.5 Analysts should avoid the dust produced by samples. A ventilated balance area or a dust mask should be utilized when weighing large numbers of samples.

9. Procedures

Perchloric Acid Digestion Procedure

9.1 Accurately measure 1.0 g of sample into a clean, dry digestion vessel (5.3).

9.2 Add 20 mL of perchloric acid (HClO₄) and 25 mL of hydrofluoric acid.

9.3 Heat on a hot plate in a perchloric acid fume hood until heavy fumes are visible.

9.4 Cool and add 15 mL boric acid solution (H₃BO₃), and heat to fumes again. This step is required to completely eliminate residual HF, as subsequent steps utilize glass vessels.

9.5 Remove from heat and assess the condition of the solution; a clear solution without undissolved sample solids is desired. If digestion is complete, proceed to 9.8.

9.6 If a clear solution does not exist, transfer the solution to a 400-mL beaker.

9.7 Carefully add 100 mL of deionized (DI) water and 10 mL of hydrochloric acid (HCl). Cover with a watch glass, and boil on the hot plate until full digestion is complete.

9.8 Cool to ambient temperature, and quantitatively transfer to a 250-mL volumetric flask.

9.9 Add internal standard aliquot, if required.

9.10 Mix well and dilute to volume. Submit for ICP analysis.

Sulfuric Acid Digestion Procedure

9.11 Accurately measure 1.0 g of heat-treated sample into a clean, dry digestion vessel.

9.12 Add 10 mL of sulfuric acid, 10 mL of nitric acid, and 25 mL of hydrofluoric acid.

9.13 Heat on a hot plate in a fume hood, and evaporate to near dryness.

9.14 Cool to near ambient temperature, and quantitatively transfer solution to a 400-mL digestion vessel.

9.15 Add 20 mL of 19 % hydrochloric acid and 30 mL of 3 % hydrogen peroxide.

9.16 Cover with watch glass and heat on hot plate in fume hood to boiling until all of the salts are dissolved.

9.17 Cool to ambient and quantitatively transfer to a 250-mL volumetric flask.

9.18 Add internal standard aliquot, if required, and 10 mL of hydrochloric acid.

9.19 Mix well and dilute to volume. Submit for ICP analysis.

Lithium Borate Flux Dissolution Procedure

9.20 Accurately measure 0.1 to 1.0 g of heat-treated sample into a clean, dry crucible (5.6).

9.21 Add 5.0 g of lithium borate flux to the sample. The optimal ratio (flux:sample of 5:1, 10:1, 20:1) and temperature needed for successful fusion will vary depending on sample matrix; adjust sample size to appropriate ratio. Keep the weight of borate flux used constant, and adjust the weight of sample to obtain optimal ratio.

9.22 Thoroughly mix sample and flux using a platinum wire as a stir rod.

9.23 Heat for 20 min in a 950°C muffle furnace.

9.24 Cool to ambient temperature in a desiccator.

9.25 Heat a solution of 100 mL deionized water and 10 mL concentrated nitric acid in a suitable laboratory beaker, to simmering on a hot plate in a fume hood.

9.26 Transfer the fused sample plug to the beaker with attentive care to avoid splashing the hot acid solution.

9.27 Continue heating, with occasional stirring, until the entire fused plug is dissolved.

9.28 Cool to ambient and quantitatively transfer to a 250-mL volumetric flask.

9.29 Add internal standard aliquot, if required.

9.30 Mix well and dilute to volume. Submit for ICP analysis.

10. Precision and Bias

10.1 This practice purports only to standardize the approach to sample preparations and does not provide for quantitative determination of any sample characteristics. As such, there are no parameters measured, and it is not possible to determine statistical precision or bias of the techniques discussed herein.

11. Keywords

11.1 acid decomposition; atomic spectroscopy; fusion; catalyst; fluid catalytic cracking; hydrofluoric acid; inductively-coupled plasma emission spectroscopy; perchloric acid; zeolites

SUMMARY OF CHANGES

Committee D32 has identified the location of selected changes to this standard since the last issue (D7442-08) that may impact the use of this standard.

(I) Modified 6.9.

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