



Standard Practice for Determination of the Six Major Rare Earth Elements in Fluid Catalytic Cracking Catalysts, Zeolites, Additives, and Related Materials by Inductively Coupled Plasma Optical Emission Spectroscopy¹

This standard is issued under the fixed designation D8088; 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 describes the analysis of fluid catalytic cracking catalysts, rare earth exchanged zeolitic materials, additive and related materials when analyzed by ICP-OES for the six most common rare earth elements.

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

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. See Appendix X3.*

2. Referenced Documents

2.1 ASTM Standards:²

- [C1109 Practice for Analysis of Aqueous Leachates from Nuclear Waste Materials Using Inductively Coupled Plasma-Atomic Emission Spectroscopy](#)
- [D1193 Specification for Reagent Water](#)
- [D3766 Terminology Relating to Catalysts and Catalysis](#)
- [D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance](#)
- [D6349 Test Method for Determination of Major and Minor Elements in Coal, Coke, and Solid Residues from Combustion of Coal and Coke by Inductively Coupled Plasma—Atomic Emission Spectrometry](#)
- [D7085 Guide for Determination of Chemical Elements in Fluid Catalytic Cracking Catalysts by X-ray Fluorescence Spectrometry \(XRF\)](#)

¹ This test method is under the jurisdiction of ASTM Committee D32 on Catalysts and is the direct responsibility of Subcommittee D32.03 on Chemical Composition.

Current edition approved Nov. 1, 2016. Published November 2016. DOI: 10.1520/D8088-16.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

Spectrometry (XRF)

[D7260 Practice for Optimization, Calibration, and Validation of Inductively Coupled Plasma-Atomic Emission Spectrometry \(ICP-AES\) for Elemental Analysis of Petroleum Products and Lubricants](#)

[D7442 Practice for Sample Preparation of Fluid Catalytic Cracking Catalysts and Zeolites for Elemental Analysis by Inductively Coupled Plasma Optical Emission Spectroscopy](#)

[E1479 Practice for Describing and Specifying Inductively-Coupled Plasma Atomic Emission Spectrometers](#)

2.2 EPA Standard:³

[Method 6010B Inductively Coupled Plasma-Atomic Emission Spectrometry](#)

3. Terminology

3.1 Definitions—see Terminology [D3766](#)

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *ICP-OES*—Inductively Coupled Plasma Optical Emission Spectroscopy

3.2.2 *FCC*—Fluid Catalytic Cracking

3.2.3 *Water*—Defined as ASTM Type I or highest quality available as defined in Specification [D1193](#).

4. Summary of Practice

4.1 Specimens are prepared using one of the three preparation techniques described in Practice [D7442-08a](#). The result should be a clear, dilute acidic solution suitable for ICP-OES. The final concentration should be 1.0 g of the test specimen prepared and diluted into a 250-mL volumetric flask. The test solutions are introduced into the plasma torch of the ICP instrument where excitation occurs. Characteristic atomic line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a high resolution grating and the intensities of the individual lines are measured.

³ Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, <http://www.epa.gov>.

By comparing emission intensities of the elemental lines in the test specimens with emission intensities measured in the standards, the concentration of the elements in the test specimens can be calculated. The internal standard will compensate for variations in test specimen introduction efficiency.

4.2 Details of the instrument components are given in Practice E1479. This Practice provides a good summary of instrument calibration and verification techniques.

4.3 Practice D7260, although primarily for non-aqueous applications, provides a good description of the basic components that make up an ICP-OES instrument.

4.4 This practice describes the analysis of the six major rare earth elements found in catalyst and related materials. It can easily be extended to any additional elements by following the protocols outlined in this Practice. Guide D7085 provides a list of the elements above 10 ppm commonly found in equilibrium fluid catalytic cracking catalysts. EPA Method 6010B is a good primer for those not familiar with the technique. It describes the analysis of water and waste water for numerous elements at low concentration.

5. Significance and Use

5.1 The chemical composition of catalysts 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 (1, 2, 3).

6. Reagents

6.1 All reagents should conform to American Chemical Society (ACS) specifications. 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 % (Refer to the Safety Information in Appendix X3).

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 tetra-borate or meta-borate, or both.

6.9 *Boric Acid Solution*, 3 %.

6.10 *Water*, Type I preferred, or highest quality available.

7. Preparation of Calibration Standards

7.1 Determine the method that will be used for the preparation of the test specimens. Determine the element that will be used as an internal standard. The sample test specimens should contain no appreciable amount of the element selected as an

internal standard. Common elements used as internal standards for catalysts and related materials are cobalt and scandium.

7.2 For the purpose of this discussion, we will assume a perchloric acid digestion with cobalt as the internal standard.

7.3 Prepare ten 250-mL volumetric flasks. Number each flask. Fill each flask half full with water and then into each flask add 20 mL of perchloric acid, 15 mL of 3 % boric acid solution, and 10 mL of hydrochloric acid.

7.4 Label flask number 1 “Reagent Blank.” Add 1 mL of internal standard. For this example, 1 mL of a 10 000 ppm solution of cobalt and dilute to volume with water.

7.5 Into flask number 2, add 25 mL of 10 000 ppm aluminum. Label flask number 2 “Sample Blank.” Add 1 mL of the internal standard solution and dilute to volume with water.

7.6 Into flask number 3, add 10 mL of a 1000 ppm lanthanum solution. Add 1 mL of internal standard solution and dilute to volume with water. Label “La Std.”

7.7 Into flask number 4, add 10 mL of a 1000 ppm cerium solution. Add 1 mL of internal standard solution and dilute to volume with water. Label “Ce Std.”

7.8 Into flask number 5, add 5 mL of a 1000 ppm neodymium solution. Add 1 mL of internal standard solution and dilute to volume with water. Label “Nd Std.”

7.9 Into flask number 6, add 5 mL of a 1000 ppm praseodymium solution. Add 1 mL of internal standard solution and dilute to volume with water. Label “Pr Std.”

7.10 Into flask number 7, add 5 mL of a 1000 ppm gadolinium solution. Add 1 mL of internal standard solution and dilute to volume with water. Label “Gd Std.”

7.11 Into flask number 8, add 2 mL of a 1000 ppm solution of samarium. Add 1 mL of internal standard solution and dilute to volume with water. Label “Sm Std.”

7.12 Into flask number 9, add:
 25 mL of 10 000 ppm aluminum solution,
 10 mL of 1000 ppm lanthanum solution,
 5 mL of 1000 ppm cerium solution,
 2 mL of 1000 ppm neodymium solution,
 5 mL of 1000 ppm praseodymium solution,
 3 mL of 1000 ppm gadolinium solution, and
 2 mL of 1000 ppm samarium solution.

7.12.1 Add 1 mL of internal standard solution and dilute to volume with water. Label “Check Std #1.”

7.13 Into flask number 10, add:
 25 mL of 10 000 ppm aluminum solution,
 5 mL of 1000 ppm lanthanum solution,
 10 mL of 1000 ppm cerium solution,
 5 mL of 1000 ppm neodymium solution,
 2 mL of 1000 ppm praseodymium solution,
 1 mL of 1000 ppm gadolinium solution, and
 1 mL of 1000 ppm samarium solution.

7.13.1 Add 1 mL of internal standard solution and dilute to volume with water. Label “Check Std #2.”

8. Preparation of Apparatus

8.1 Consult the manufacturer's instructions. Design differences between the various available units make it impossible to specify exact operating conditions.

8.2 Operating parameters should be established for the instrument in use. Method development will yield appropriate conditions for the following variables:

- 8.2.1 Torch configuration,
- 8.2.2 Nebulizer conditions,
- 8.2.3 Auxiliary gas,
- 8.2.4 RF power,
- 8.2.5 Nebulizer pressure,
- 8.2.6 Spray chamber type,
- 8.2.7 Plasma gas,
- 8.2.8 Mass flow to nebulizer, and
- 8.2.9 Emission line used.

8.3 Operating parameters should be designed for the particular on-board computer. Parameters to be included are element, wavelength (see [Table A1.1](#) for suggested wavelengths), background correction points, integration time, number of repeat integrations (two minimum), automatic internal standard correction, and re-calibration frequency. Analysis of a check standard every 5 test specimens is recommended.

8.4 Data tables should be developed in the computer for calibration curve coefficients and inter-element correction. Inter-element correction is very important to eliminate interferences and will guide the selection of emission line wavelengths.

8.5 Check all expected spectral interferences for the elements listed in [Table A1.1](#). Follow the manufacturer's instructions to develop and apply correction factors to compensate for interferences.

8.6 To properly apply interference correction factors, you must first establish the linear response range for each element.

8.7 Correct wavelength profiling is important and will reveal any spectral interference. Follow the manufacturer's instructions for wavelength profiling before proceeding with the calibration.

8.8 Spectral interferences can usually be avoided by selecting the proper emission line wavelength. When they cannot be avoided, computer software provided by the manufacturer can be used. If this is not available, then the empirical method in [Practice C1109](#) may be used.

8.9 When analyzing unknown materials, the analyst must always be alert to the presence of interfering elements. There are three basic types of interferences that require correction: spectral line overlap, matrix effects that either enhance or suppress the intensity of the element of interest, and a special form of matrix effect that occurs when it affects the background measurement.

8.10 [Appendix X2](#) includes a simple procedure that can be used to verify that the interference(s) have been properly compensated. The procedure is widely known as the Standard Addition Method (SAM).

9. Calibration

9.1 Prepare the equipment according to the manufacturer's instructions. Unless otherwise specified by the manufacturer, warm the instrument up for at least 30 minutes.

9.2 Perform wavelength profiling for each element of interest using the solutions prepared in [Section 7](#). The sample blank and all six rare earth standards should be analyzed at each analytical wavelength to determine if background or inter-element corrections are necessary. Do not analyze flasks 9 and 10 at this point. If spectral interferences are noted, follow the manufacturer's instructions.

9.3 In this example, we are using a simple two point calibration, the blank (zero) and a high standard. Many manufacturers systems will handle multiple calibration standards. This is usually preferable and will validate the linear range for each analyte.

9.4 Analyze the two "Check" standards to validate the linear range.

10. Procedure

10.1 Analyze the test specimen solutions in the same manner as the calibration standards.

10.2 The computer system will present the concentration of each analyte as micrograms per milliliter ($\mu\text{g/mL}$).

10.3 Re-analyze the check standards every 5 test specimens to verify the calibration.

10.4 Test specimens with analyte concentrations above the linear range will need to be diluted. Care must be taken to keep the internal standard concentration at the correct level. It is recommended that dilutions be done with the "Reagent Blank."

11. Calculation

11.1 Frequently, the calculation procedure can be set up in the on-board computer. In this situation, the results may be reported as the element or as the corresponding oxide. The manual calculations are:

$$\text{Mass \%} = \frac{C \times V \times D}{S \times (10^6 \mu\text{g/g})} \times 100 \% \quad (1)$$

where:

C = concentration $\mu\text{g/mL}$

V = volume, normally 250 mL

D = dilution factor, normally 1

S = actual mass of test specimen, nominally 1 g.

12. Calculation Example

12.1 1.0000 g of a test specimen was digested and diluted to 250 mL. The analysis of the solution revealed a lanthanum concentration of 30.0 $\mu\text{g/mL}$.

12.2

$$\text{Mass \%} = \frac{C \times V \times D}{S \times (10^6 \mu\text{g/g})} \times 100 \% \quad (2)$$

12.3

$$\text{Mass \%} = \frac{30.0 \mu\text{g/mL} \times 250 \text{ mL} \times 1}{1.0000 \text{ g} \times (10^6 \mu\text{g/g})} \times 100 \% \quad (3)$$

12.4

$$\text{Mass \%} = \frac{7500.0 \mu\text{g}}{10\,000.0 \mu\text{g}} \quad (4)$$

$$\text{Mass \%} = 0.75\% \text{ lanathum} \quad (5)$$

13. Keywords

13.1 catalysts; FCC; FCCU; fluid catalytic cracking; ICP; ICP-OES; inductively coupled plasma optical emission spectroscopy; rare earths

ANNEX

(Mandatory Information)

A1. RECOMMENDED WAVELENGTHS

A1.1 Detection limits are estimates for radial view. Axial view are generally an order of magnitude better.

TABLE A1.1 Recommended Wavelengths

Element	Wavelength (nm)	Detection Limit ($\mu\text{g/mL}$)
Lanthanum	408.672	0.01
Cerium	418.660	0.05
Neodymium	406.109	0.10
Gadolinium	335.047	0.02
Praseodymium	414.314	0.04
Samarium	359.260	0.05
Cobalt	238.892	Internal Standard
Scandium	361.384	Internal Standard

A1.2 Recommended wavelengths are to be used for initial set-up. The ultimate choice of wavelength will depend on sample matrix and any interferences that may be encountered. [Appendix X1](#) lists alternate wavelengths and known interferences.

APPENDIXES

(Nonmandatory Information)

X1. ALTERNATE WAVELENGTHS WITH KNOWN INTERFERENCES

At. No.	Element	Wavelength (nm)	Known Interferences
57	Lanthanum	333.749	—
		408.672	Th
		412.323	Ce, Th
58	Cerium	413.765	Ce
		418.660	Zr
		453.975	—
		414.314	Ce
59	Praseodymium	417.939	Ce, Cr
		422.535	V, U
		401.225	Ti, Cr
60	Neodymium	430.358	—
		406.109	Ce
		359.260	W, Th
62	Samarium	442.434	Ce, Ca
		428.079	Ce, Cr
		342.247	Th, U
64	Gadolinium	336.223	Th, Ca
		335.047	Ce, Ca

X2. INTERFERENCES

X2.1 Several types of interference effects may contribute to inaccuracies in the determination of major and minor elements. The analyst should follow the manufacturer’s operating guide to develop and apply correction factors to compensate for the interferences. The interferences can be classified as spectral, physical, and chemical.

X2.1.1 Spectral interferences can be categorized as overlap of a spectral line from another element, unresolved overlap of molecular band spectra, background contribution from continuous or recombination phenomena, and background contribution from stray light from the line emission of high concentration elements. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multi-element instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array.

X2.1.2 Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies, especially in samples that may contain high dissolved solids or acid concentrations, or both. The use of a peristaltic pump is recommended to lessen these interferences. If these types of interferences are operative, they must be reduced by dilution of the sample or utilization of standard addition techniques, or both. Another problem that can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aerosol flow rate causing instrumental drift. Wetting the argon before nebulization, the use of a tip washer, or sample dilution have been used to control this problem. Also, it has been reported that better control of the argon flow rate, particularly nebulizer flow, improves instrument precision. This is accomplished with the use of mass flow controllers.

X2.1.3 Chemical interferences are characterized by molecular compound formation, ionization effects, and solute vaporization effects. Normally these effects are not pronounced with the ICP technique. However, if such effects are observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, matrix matching, and standard addition procedures. These types of interferences can be highly dependent on matrix type and the specific analyte element.⁴

X2.2 How do you determine if you have correctly compensated for all of the interferences in an unknown sample for an ICP-OES analysis? The most common method in ICP is to analyze each analyte at two wavelengths. A second method is

to analyze the unknown by a non-complimentary technique, which is a method that would not have the same type of interferences; XRF vs. ICP is a good example. ICP vs. AAS would be a bad example, since they operate on similar principles with similar instrumentation.

X2.2.1 A third method would be to use the Standard Addition Method (SAM) that was developed in 1951, long before there was a computer system available to de-convolute interfering lines. You would use this method to verify the accuracy of your analytical scheme. If the data you generated matches the data from the Standard Addition Method (SAM), then you can be fairly certain you have developed a robust method. SAM can be quite useful when you receive the occasional sample that does not fit in with the sample matrix of your general analytical procedure.

X2.3 Here is how you would proceed to analyze one analyte in one unknown sample:

X2.3.1 Determine an approximate concentration of the analyte. Say for example we get a rough value of 4.6 µg/mL of cerium.

X2.3.2 Set up six 25-mL volumetric flasks.

X2.3.3 Add 10 mL of the unknown sample solution to each flask.

X2.3.4 If you are using an internal standard, add it now.

X2.3.5 Prepare a standard solution to contain 1.0 µg/mL of cerium.

X2.3.6 In various flasks, add 0, 1.0, 2.0, 3.0, 4.0, and 5 mL of the standard solution.

X2.3.7 Dilute to the mark.

X2.3.8 Analyze with your standard conditions.

X2.3.9 Prepare a plot of the data, plotting concentration added vs. signal intensity.

X2.3.10 Example Data:

Flask Number	Amount Added	Intensity
1	0.0	100.0
2	1.0	150.0
3	2.0	200.0
4	3.0	250.0
5	4.0	300.0
6	5.0	350.0

X2.3.11 Determine the negative intercept of the plot, which is 2.0 µg/mL. Multiply this by the dilution factor = 2.5 to get the final result of 5.0 µg per mL in the original sample solution. It is not actually necessary to make a plot. You can enter the data into an Excel spreadsheet and use “Formulas,” “More functions,” “Statistical” menu to select “Intercept” to calculate the negative intercept after a linear regression analysis.

X2.3.12 In the case where this is series of samples with an unusual matrix, the data can be rescaled to read the final result directly on the remaining samples in the series.

⁴ Sections X2.1 – X2.1.3 were excerpted from Section 5 of Test Method D6349.

CERIUM

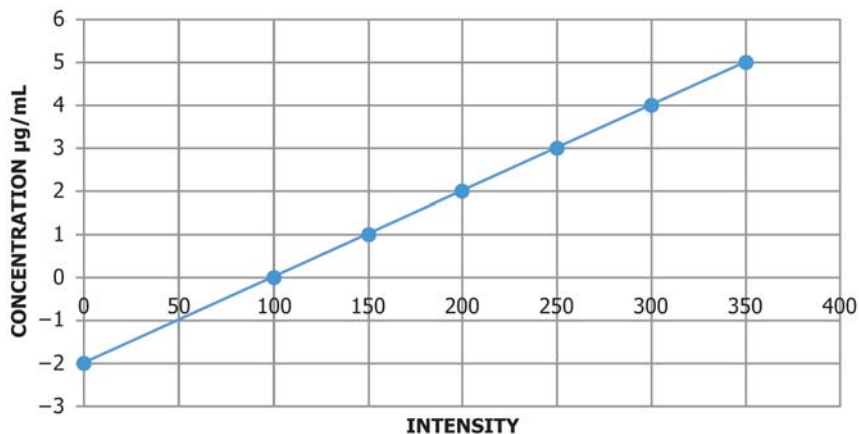


FIG. X2.1 Sample Data Plot

X3. SAFETY INFORMATION

X3.1 It is recommended that prior to the first use of hydrofluoric acid (HF), that the “HF Exposure Treatment Guide” be downloaded from the website: <http://www.honeywell-hfacid.com/safety-handling>.

exposure is so specialized and differs significantly from the treatment of other acid exposure, it is recommended that the neutralizing chemicals recommended in the treatment guide be available in the laboratory before the first use of HF.

X3.2 Because the medical treatment of hydrofluoric acid

REFERENCES

- (1) Chow, T. J., Thompson, T. G., “Flame Photometric Determination of Strontium in Sea Water,” *Analytical Chemistry*, Vol. 27, 1955, pp. 18–21.
- (2) “Optimization of the Standard Addition Method (SAM) Using Monte Carlo Simulation,” NIST, October 1, 2006.
- (3) Kelly, W. R., MacDonald, B. S., Guthrie, W. F., “Gravimetric Approach to the Standard Addition Method in Instrumental Analysis,” *Analytical Chemistry*, Vol. 80, No. 16, 2008, pp. 6154–6158.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; <http://www.copyright.com/>