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Standard Guide for
Determination of Chemical Elements in Fluid Catalytic Cracking Catalysts by X-ray Fluorescence Spectrometry (XRF)[1]

This standard is issued under the fixed designation D 7085; 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 guide covers several comparable procedures for the quantitative chemical analysis of up to 29 elements in fluid catalytic cracking (FCC) catalyst by X-ray fluorescence spectrometry (XRF). Additional elements may be added.

1.2 This guide is applicable to fresh FCC catalyst, equilibrium FCC catalyst, spent FCC catalyst, and FCC catalyst fines.

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 requirements prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:* [2]

C 982 Guide for Selecting Components for Energy-Dispersive X-ray Fluorescence (XRF) Systems

C 1118 Guide for Selecting Components for Wavelength-Dispersive X-ray Fluorescence (XRF) Systems

D 1977 Test Method for Nickel and Vanadium in FCC Equilibrium Catalysts by Hydrofluoric/Sulfuric Acid Decomposition and Atomic Spectroscopic Analysis

E 1172 Practice for Describing and Specifying a Wavelength-Dispersive X-ray Spectrometer

E 1361 Guide for Correction of Interelement Effects in X-ray Spectrometric Analysis

E 1621 Guide for X-ray Emission Spectrometric Analysis

E 1622 Practice for Correction of Spectral Line Overlap in Wavelength-Dispersive X-ray Spectrometry

3. Summary of Guide

3.1 The test specimen is prepared with a clean, uniform, flat surface. Two commonly used test methods of preparing test specimens are listed: briquetting a powder (Test Method A, Sections 8-15) and fusing a powder into a glass bead (Test Method B, Sections 16-23). This surface of the fused or briquetted specimen is irradiated with a primary source of X rays. The secondary X rays produced in the specimen are characteristic of the chemical elements present in the specimen. Two types of XRF instrumentation may be used to collect and process the X-ray spectra. Using a wavelength-dispersive X-ray spectrometer, the secondary X rays produced in the specimen are dispersed according to their wavelength by means of crystals or synthetic multilayers. The X-ray intensities are measured by detectors set at selected wavelengths and recorded as counts (number of X rays impinging on the detector per unit time). Concentrations of the elements are determined from the measured intensities using calibration curves prepared from suitable reference materials. Using an energy-dispersive X-ray spectrometer, the secondary X rays produced in the specimen are sent to a detector where the entire X-ray spectrum is electronically sorted according to the X-ray energy and processed into counts using a multichannel analyzer. The principal advantages of the wavelength-dispersive X-ray spectrometer are resolution and detection limit. The principal advantages of the energy-dispersive X-ray spectrometer are speed and a generally lower equipment cost.

4. Significance and Use

4.1 The chemical composition of fresh FCC catalyst and equilibrium FCC catalyst is a predictor of catalyst performance. The analysis of catalyst fines also provides information on the performance of the FCC unit and the fines collection device(s).

4.2 The chemical composition of equilibrium FCC catalyst is a measure of the hazardous nature or toxicity of the material for purposes of disposal or secondary use.

5. Apparatus

5.1 *X-ray Spectrometer*, wavelength or energy-dispersive system equipped with a vacuum sample chamber. Refer to Guide C 982, Guide C 1118, and Practice E 1172 for information on specifying XRF systems.

5.2 *Muffle Furnace*, capable of operating at 600°C.

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

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[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.

5.3 *Hot Plate*, capable of maintaining a constant 200°C.

5.4 *Porcelain Dishes*, of a suitable size for calcining 50-g sample aliquots.

5.5 *Vacuum Oven*, capable of maintaining 60°C. This is required only if catalyst fines are to be analyzed.

5.6 *Vacuum Desiccators*, useful for storing fusion beads or pressed pellets.

5.7 *Fusion Equipment*:

5.7.1 *Fusion Furnace or Fluxing Device*, capable of operating at 1100°C.

5.7.2 *Fusion Crucibles and Molds*, graphite or platinum–5 % gold alloy, sized to match the specimen holder of the X-ray spectrometer.

5.8 *Pressed Pellet Equipment*:

5.8.1 *Grinders or Pulverizers*, manual (such as agate, mullite, alumina, tungsten carbide, or boron carbide mortar and pestle) or automated (typically with a tungsten carbide grinding vessel). Avoid steel grinding vessels.

5.8.2 *Mixer Mill*, useful for blending ground sample and binder prior to preparing a pressed powder specimen.

5.8.3 *Mixing Vials*, sized to match the mixer mill.

5.8.4 *Briquetting Press*, capable of maintaining a reproducible pressure of at least 25 000 psi. This is required only if the pressed powder method is utilized. Match mold size to the specimen holder of the X-ray spectrometer. Typical sizes are 25 to 40 mm.

6. Reagents

6.1 *Reagents for Fusion Techniques*:

6.1.1 *Fluxes*, lithium borates or carbonates or mixtures, of ultrahigh purity.

6.1.2 *Non-Wetting Agents*, such as lithium or ammonium iodide, are frequently added to the flux, as are oxidizing agents such as lithium, potassium, or ammonium nitrate. Take care that adding non-wetting or oxidizing reagents does not cause spectral interference with the analytes of interest.

6.2 *Reagents for Pressed Pellet Techniques*:

6.2.1 *Heavy Absorber*, barium or hafnium oxides are commonly used as heavy absorbers, if that technique is applied.

6.2.2 *Binders*, required for the pressed powder technique. These should not contribute any spectral interference. Microcrystalline wax or cellulose with negligible levels of sodium or potassium are suitable.

6.3 *Detector Gas*, for a wavelength dispersive system. The typical gas for the flow-proportional counter is P-10: 10 % methane and 90 % argon.

6.4 *2-propanol*, ACS reagent grade.

6.5 *Calibration References*, commercially available standard or certified reference materials or locally prepared mixtures from ultra high purity materials that include the elements of interest in the concentration ranges expected in unknown samples.

6.6 *Standard Solutions*, 10 000 µg/mL of nickel and 10 000 µg/mL of vanadium.

7. Procedure

7.1 Prepare specimens using either a pressed powder or a fusion technique.

7.2 Prepare calibration standards using the same techniques and reagents that will be used with the unknown samples.

7.2.1 Calibration standards can be prepared from previously analyzed samples where the accuracy and precision of the analysis is known. This is the typical calibration method for the pressed powder technique. Up to 100 analyzed standards may be required for a full range calibration for 29 elements using the pressed powder technique.

7.2.2 Synthetic standards can be prepared from reagent-grade chemicals, analyzed samples, and certified reference materials. This is the typical calibration method for the fusion technique.

7.3 Several tables, listed in Appendix X1, provide operating information on the requirements necessary to establish a pressed powder method for 29 elements in equilibrium FCC catalyst.

TEST METHODS

Test Method A—Pressed Powder

8. Scope

8.1 A test method example is provided for the analysis of nickel and vanadium in equilibrium FCC catalyst using either a wavelength or an energy-dispersive X-ray spectrometer and test specimens prepared by the pressed pellet technique.

8.2 This technique can be extended to other elements.

9. Significance and Use

9.1 In use, the FCC catalyst becomes contaminated with metals present in the feed oil. The levels of the contaminant metals, particularly the catalyst poisons nickel and vanadium, can be used to predict catalyst performance.

10. Hazards

10.1 Catalyst dust.

10.2 X-ray radiation.

10.3 Heat.

10.4 High pressure.

11. Preparation of Apparatus

11.1 Select the appropriate instrument for either a wavelength-dispersive or energy-dispersive technique. For these examples, use of energy-dispersive systems for analytes below 1000 ppm would prove difficult. Assuming the FCC catalyst contains rare earths, the difficulty increases because, by energy-dispersive X-ray fluorescence spectrometry (EDXRF), rare earths are poorly resolved and create significant matrix effects.

11.2 Read Guide E 1621, Guide E 1361, and Practice E 1622. These will provide a general knowledge of the function of a wavelength-dispersive X-ray spectrometer.

11.3 Set up the instrument using the vendor's manual. Modern X-ray spectrometers are equipped with software that guides the operator through the steps necessary to create an analytical program for a specific analysis. For this example, analysis of equilibrium FCC for nickel and vanadium, typical instrument conditions are given in Appendix X1.

12. Calibration and Standardization

12.1 *Preparation of Calibration Standards*:

12.1.1 Assemble a minimum of five catalyst samples with nickel and vanadium concentrations that cover the range of interest. This test method is specific for a single grade of catalyst and is limited to material where only the nickel and vanadium content varies.

12.1.2 Prepare each catalyst sample in duplicate in accordance with Section 13, saving a portion of the calcined and ground specimen for the next step.

12.1.3 Determine the nickel and vanadium content of the materials prepared in 12.1.2 using a comparative analytical technique such as Test Method D 1977.

12.2 Calibrate the instrument using the prepared standards following the vendor's recommended procedure.

13. Preparation of the Test Specimen

13.1 Heat approximately 50 g of specimen in a muffle furnace at 600°C with a bed depth less than 25 mm for a minimum of 1 h, if it is fresh catalyst, or up to 3 h to remove carbon from spent catalyst, equilibrium catalyst, or catalyst fines.

13.2 Grind approximately 20 to 30 g of the heated specimen to less than 30 µm. Homogenize the material if it was ground in several batches.

13.3 Combine the ground specimen with binder at a predetermined ratio into a mixing vial with mixing beads added to promote agitation. Typically, the binder is blended at a ratio of 1 part binder to 3 to 5 parts sample and chosen to give consistent and stable pellets.

NOTE 1—As an example, 1.5 ± 0.01 g of a micronized high molecular weight paraffin wax binder is mixed with 6.5 ± 0.01 g of the ground specimen.

13.4 Place the mixing vial into a mixing mill for 10 min to thoroughly mix/blend the specimen and binder.

13.5 Place the contents of the mixing vial onto a piece of weighing paper. Remove and discard the mixing beads.

13.6 Transfer the contents of the weighing paper to the briquetting press, which has been previously cleaned with 2-propanol, and spread evenly over the surface of the mold or optionally press into an aluminum cap.

13.7 Press the specimen at a ram pressure of between 25 000 and 60 000 psi. The pressure used will depend on the binder and binder/sample ratio and is usually determined empirically. For this binder example, a typical ram pressure is 30 000 psi for 10 ± 2 s for a 40-mm mold.

13.8 Attach an identifying label to the backside of the pellet. Typically, the top surface is the analytical surface. Avoid touching this surface when handling the briquetted pellet.

13.9 Store the pressed powder specimens in a vacuum desiccator to prevent moisture pickup or contamination prior to analysis.

14. Procedure

14.1 Analyze the prepared specimens following the vendor's recommended procedure using the calibration established previously in 12.2.

TABLE 1 Precision Values

	Mean Concentration, %	±2 σ (95 % C.I.)	%RSD
Al_2O_3	29.92	0.16	0.27
SiO_2	65.48	0.49	0.37
Ni	0.2332	0.0051	1.1
V	0.2417	0.0028	0.58
Fe	0.54	0.01	0.78
Cu	0.0045	0.0002	1.7
TiO_2	1.03	0.01	0.49
Mn	0.0040	0.0003	4.1
Co	0.0142	0.0006	2.0
Na	0.60	0.01	0.73
MgO	0.085	0.004	2.5
P_2O_5	0.340	0.009	1.2
CaO	0.16	0.005	1.7
SO_4	0.17	0.01	2.3
Sb	0.0862	0.0013	0.77
ZnO	0.0255	0.0007	1.4
Pb	0.0077	0.0002	1.4
Ba	0.030	0.002	3.3
La_2O_3	0.84	0.01	0.47
CeO_2	0.37	0.01	1.3
Nd_2O_3	0.42	0.01	0.93
Pr_6O_{11}	0.13	0.01	2.3
Sm_2O_3	0.01	0.001	6.0
Total REO	1.77	0.01	0.60
K_2O	0.10	0.002	0.92
Sr	0.011	0.001	2.9
Zr	0.009	0.001	6.0

15. Precision and Bias

15.1 The precision values listed in Table 1 were obtained from one sample of equilibrium FCC catalyst, prepared and analyzed 16 times. The % relative standard deviation (RSD) is defined as:

$$\%RSD = (\sigma / \text{mean concentration}) \times 100$$

Test Method B—Fused Bead

16. Scope

16.1 A test method example is provided for the analysis of nickel and vanadium in equilibrium FCC catalyst using either a wavelength or an energy-dispersive X-ray spectrometer and using test specimens prepared by the fused bead technique.

17. Significance and Use

17.1 In use, the FCC catalyst becomes contaminated with metals present in the feed oil. The levels of the contaminant metals, particularly the catalyst poisons nickel and vanadium, can be used to predict catalyst performance.

18. Hazards

18.1 Catalyst dust.

18.2 Flux dust.

18.3 Heat.

18.4 X-ray radiation.

19. Preparation of Apparatus

19.1 Select the appropriate instrument for either a wavelength-dispersive or energy-dispersive technique. For these examples, use of energy-dispersive systems for analytes below 1000 ppm would prove difficult. Assuming the FCC catalyst contains rare earths, the difficulty increases because, by EDXRF, rare earths are poorly resolved and create significant matrix effects.

19.2 Read Guide E 1621, Guide E 1361, and Practice E 1622. These will provide a general knowledge of the function of a wavelength-dispersive X-ray spectrometer.

19.3 Set up the instrument using the vendor's manual. Modern X-ray spectrometers are equipped with software that guides the operator through the steps necessary to create an analytical program for a specific analysis. For this example, analysis of equilibrium FCC for nickel and vanadium, typical instrument conditions are given in Appendix X1.

20. Calibration and Standardization

20.1 *Preparation of Calibration Standards*—Calibration with the fused bead test method for only one or two elements is generally simpler than with the pressed powder test method. If analyzed standard samples are available, they can be used. Usually this is not the case, and standards are prepared from synthetic materials. Two ways of preparing synthetic standards are provided.

20.2 *First Method for Preparing Fused Bead Standards*:

20.2.1 Obtain 50 g of the fresh FCC catalyst and heat at 600°C with a bed depth less than 25 mm for at least 2 h in a muffle furnace. Cool and store in a desiccator.

20.2.2 Prepare two standard solutions at 1000 and 10 000 µg/mL of nickel and two standard solutions at 1000 and 10 000 µg/mL of vanadium.

NOTE 2—NIST traceable solutions of this type are commercially available and sold as standards for atomic absorption or ICP analysis.

20.2.3 Weigh into a clean, dry fusion crucible 1.00 ± 0.01 g of calcined catalyst and 5.00 ± 0.01 g of flux; thoroughly mix the sample and flux.

NOTE 3—In this example, use Pt/5 % gold alloy crucibles and a commercially available fluxer. Other flux to sample ratios like 5:2 and 10:1 can be used. A suitable flux is 49.75 % lithium metaborate, 49.75 % lithium tetraborate, and 0.50 % lithium bromide. The flux can be prepared from pure materials or purchased commercially.

20.2.4 Prepare ten identical crucibles in accordance with 20.2.3.

20.2.5 Determine the range of standards that shall be prepared. This example prepares a standard that contains 500 ppm nickel.

20.2.6 Select a crucible and record the number. Form a small indentation in the center of the flux/sample mixture.

20.2.7 Select the 1000 µg/mL nickel standard and add using a micropipet, exactly 0.500 mL of solution.

20.2.8 Place the crucible in a ventilated oven or on a hot plate and dry at 250°C for 30 min. (**Warning**—The solutions may contain nitric or hydrochloric acid and fumes may be emitted on drying.)

20.2.9 The calculations are straightforward. Add 500 µg of nickel to the crucible that contained 1.00 g of sample. This is equivalent to 500 ppm of nickel in the sample.

20.2.10 As a second example, take another crucible and add 0.500 mL of the 10 000 µg/mL vanadium standard. This calculates out to 5000 µg of vanadium per 1.00 g of sample, which is equivalent to 5000 ppm of vanadium in the sample.

20.2.11 Determine the desired calibration range for the nickel and vanadium. Using the examples above, prepare five crucibles for nickel and five crucibles for vanadium.

20.2.12 Fuse the mixture at 1100 ± 100°C in a fusion furnace or a fluxing device for about 8 to 10 min to obtain a homogeneous melt.

NOTE 4—An incomplete dissolution or nonhomogeneous melt will have a cloudy appearance.

20.2.13 After the mixture has completely melted and is uniform, cast into the mold and allow to cool.

20.2.14 The bottom surface touching the mold is the analytical surface. Affix a label to the top surface and store in a desiccator.

20.3 *Second Method for Preparing Fused Bead Standards*—Standards can be prepared from pure powders of oxides, nitrates, or organometallic compounds. Avoid carbonates, since they introduce gas bubbles into the fusion beads.

20.3.1 In this example, prepare a standard without the catalyst, for example, 10 000 ppm of vanadium in the pure flux. Use a five-place balance if it is available.

20.3.2 Select a clean and dry crucible. Record the tare weight of the crucible. Add approximately 2.5 g of flux, and record the weight.

20.3.3 Weigh in precisely 0.06363 g of ultrahigh purity nickel oxide (78.584 % nickel). If another source of nickel is used, calculate the nickel content and adjust the weight accordingly.

20.3.4 Add in approximately an additional 2.5 g of flux. Mix the contents with a Teflon rod, being careful to keep all of the material in the crucible.

20.3.5 Fuse the mixture at 1100 ± 100°C in a fusion furnace or a fluxing device for 8 to 10 min to obtain a clear and homogeneous melt.

20.3.6 Remove the crucible from the heat source, and cool in a desiccator.

20.3.7 Reweigh the crucible, and melt to obtain the final weight of nickel and flux, which will be approximately 5 g.

20.3.8 *Calculation Example*:

Final weight of crucible and melt = 25.0600 g
Tare weight of crucible = 20.0000 g
Weight of nickel oxide = 0.06363 g

$$\begin{aligned}\%\ \text{Nickel} &= 100 \times (0.06363 \times 0.78584) / (25.0600 - 20.0000)\\ &= 5.0003 / 5.0600\\ &= 0.9882\ \%\\ &= 9882\ \text{ppm Nickel}\end{aligned}$$

20.3.9 Place the fusion bead into a heavy-duty plastic bag, and seal tightly. Break the fusion pellet into pieces by striking the bag with a hammer.

20.4 Prepare standards by following 20.2.3 through 20.2.14. The standards prepared in 20.3.9 are substituted for the solutions prepared in 20.2.2. Wherever the instructions say to add a liquid solution, weigh in the solid solution prepared in 20.3.9 instead. The standards prepared in 20.3.9 are mostly flux. Remember to include the weight of the flux in your calculations.

20.5 This can be a particularly useful technique for extending the calibration curve for a particular element if analyzed samples were used for the initial calibration. Fusion beads can be prepared from the analyzed standards and then *spiked* with