Designation: D7085 – 04 (Reapproved 2010)$^{\varepsilon 1}$

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 D7085; 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.

ε^1 NOTE—Updated Scope and text to reflect the use of ppm and SI units editorially in April 2010.

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

1.3.1 The units of ppm (mg/kg) are used instead of wt% in Tables X2.3-X2.5 for reporting concentration of certain elements because of industry convention and because most of these elements are present at trace levels.

1.4 *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]

C982 Guide for Selecting Components for Energy-Dispersive X-Ray Fluorescence (XRF) Systems (Withdrawn 2008)[3]

C1118 Guide for Selecting Components for Wavelength-Dispersive X-Ray Fluorescence (XRF) Systems (Withdrawn 2011)[3]

D1977 Test Method for Nickel and Vanadium in FCC Equilibrium Catalysts by Hydrofluoric/Sulfuric Acid Decomposition and Atomic Spectroscopic Analysis

E1172 Practice for Describing and Specifying a Wavelength-Dispersive X-Ray Spectrometer

E1361 Guide for Correction of Interelement Effects in X-Ray Spectrometric Analysis

E1621 Guide for X-Ray Emission Spectrometric Analysis

E1622 Practice for Correction of Spectral Line Overlap in Wavelength-Dispersive X-Ray Spectrometry (Withdrawn 2006)[3]

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.

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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.

Current edition approved April 1, 2010. Published May 2010. Originally approved in 2004. Last previous edition approved in 2004 as D7085–04$^{\varepsilon 1}$. DOI:10.1520/D7085-04R10E01.

[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.

[3] The last approved version of this historical standard is referenced on www.astm.org.

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 C982, Guide C1118, and Practice E1172 for information on specifying XRF systems.

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

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 0.1 wt% 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 E1621, Guide E1361, and Practice E1622. 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 D1977.

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.

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

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.

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 0.1 wt% 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 E1621, Guide E1361, and Practice E1622. 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 0.05 wt% Ni.

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 0.05 wt% 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 0.5 wt% 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 non-homogeneous 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, 1.0 wt% 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
% Nickel = 100 × (0.06363 × 0.78584) / (25.0600 − 20.0000)
= 5.0003 / 5.0600
= 0.9882 wt% Ni

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 the solid solutions prepared in 20.3.9 to increase the concentration of one or more analytes.

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

21. Preparation of the Test Specimen

21.1 Calcine approximately 3 to 8 g of specimen at 600°C for a minimum of 1 h, if it is fresh catalyst, or up to 3 h to remove carbon from the spent catalyst.

21.2 Mix the calcined specimen with flux at a predetermined ratio. Typically, the flux is blended at a ratio of 1 part specimen to 3 parts flux to a ratio of 1 part specimen to 10 parts flux and chosen to give consistent and stable beads. The flux and specimen shall be accurately weighed into the fusion crucible and have a total mass compatible with the capacity of the mold.

21.3 If a heavy absorber is being used, add it at this point with the mass equivalent to the specimen mass.

21.4 Add the non-wetting agents and any oxidizing agents.

21.5 Fuse the sample mix at approximately 1100 ± 100°C (do not exceed 1250°C) in a fusion furnace or a fluxing device. Shake or swirl the crucible and adjust the time to allow complete dissolution and a uniform melt.

TABLE 2 Precision Values

	Mean Concentration, %	±2 σ (95 % C.I.)	%RSD
Al_2O_3	51.86	0.34	0.33
SiO_2	40.89	0.42	0.51
NiO	0.175	0.01	3.1
V_2O_5	0.30	0.008	1.3
Fe_2O_3	2.5	0.17	3.5
CuO	0.017	0.0008	2.6
TiO_2	1.19	0.016	0.67
CaO	0.19	0.014	3.6
Na_2O	0.5	0.12	11.5
MgO	0.136	0.024	8.7
P_2O_5	0.325	0.01	1.5
BaO	<0.003	N/A	N/A
SnO	0	0	0
Sb_2O_3	0.055	0.008	6.6
Bi_2O_3	0	0	0
PbO	0.028	0.002	4.2
La_2O_3	0.835	0.01	0.63
CeO_2	0.17	0.004	1.3
Nd_2O_3	0.117	0.006	2.8
Pr_6O_{11}	0.119	0.004	1.8
Gd_2O_3	<0.003	N/A	N/A
Sm_2O_3	0.013	0.004	12.6
Total REO	1.25	0.022	0.86
K_2O	0.071	0.008	3.4

21.6 Cast the fusion melt into a mold and cool. Select the mold size to correspond with the specimen holder of the X-ray spectrometer, which has typical diameters between 25 mm and 40 mm. Thickness should be a minimum of 2 mm to avoid breakage. If the disk is to be analyzed directly, the analytical surface shall be smooth and flat. Avoid touching the analytical surface, as this will contaminate the surface.

NOTE 5—Beads can be cleaned with absolute ethanol.

22. Procedure

22.1 Analyze the prepared specimens following the vendor's recommended procedure and using the calibration established previously in 20.6.

23. Precision and Bias

23.1 The precision values listed in Table 2 were obtained from one sample of equilibrium FCC catalyst, prepared and analyzed eleven times. This is not the same sample analyzed by the pressed powder test method in Section 15. The %RSD is defined as:

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

24. Keywords

24.1 catalysts; fluid catalytic cracking (FCC); X-ray fluorescence spectrometry (XRF)

APPENDIXES

(Nonmandatory Information)

X1. EXAMPLE INSTRUMENT CONDITIONS, WAVELENGTH DISPERSIVE X-RAY SPECTROMETER

X1.1 Analyte—Nickel

X1.1.1 *X-ray Tube*—Rhodium anode at 60 kV and 66 mA for a 4-kW tube.

X1.1.2 *Path*—Vacuum.

X1.1.3 *Sample Spinner*—On.

X1.1.4 *Detector*—Duplex, with both scintillation counter and flow proportional counter in use.

X1.1.5 *Analysis Line*—Nickel K-alpha.

X1.1.6 *Crystal*—LiF200.

X1.1.7 *Angle*—48.6450.

X1.1.8 *Collimator*—300 micron.

X1.1.9 *Counting*—20 s.

X1.2 Analyte—Vanadium

X1.2.1 *X-ray Tube*—Rhodium anode at 47 kV and 85 mA for a 4-kW tube.

X1.2.2 *Path*—Vacuum.

X1.2.3 *Sample Spinner*—On.

X1.2.4 *Detector*—Duplex, with both scintillation counter and flow proportional counter in use.

X1.2.5 *Analysis Line*—Vanadium K-alpha.

X1.2.6 *Crystal*—LiF200.

X1.2.7 *Angle*—76.9636.

X1.2.8 *Background*—78.1040.

X1.2.9 *Collimator*—300 micron.

X1.2.10 *Counting*—20 s.

X2. EXAMPLES OF INSTRUMENT PARAMETERS FOR PRESSED PELLET ANALYSIS

X2.1 See Tables X2.1-X2.5 for examples pertaining to pressed pellet analysis.

TABLE X2.1 Example of Operating Conditions for a Wavelength Dispersive X-ray Spectrometer

XRF vacuum lock time (s):	7
XRF delay time (s):	0
XRF analysis medium:	Vacuum
Collimator mask (mm):	30
Priority:	5: Bottom
X-ray tube:	Rh
Spinner:	On
Flow detector window:	1 micrometre

TABLE X2.2 Example of a Line Library for a Wavelength Dispersive X-ray Spectrometer

Ch.	Line	Crystal	Collimator	Det.	Flit.	KV	MA	Angle	Bg1	Bg2	PHS1 LL	PHS1 UL
Al	KA	PE002	150 µm	Flow	None	32	125	144.9250			22	78
Ba	LA	LiF200	300 µm	Flow	None	37	108	87.1818	1.3322		29	71
Bi	LA	LiF200	300 µm	Scint	None	60	66	32.9700	-1.6000	1.6000	19	78
Ca	KA	LiF200	300 µm	Flow	None	32	125	113.1304	-0.9158		28	71
Ce	LA	LiF200	300 µm	Duplex	None	47	85	79.0450			30	70
Co	KA	LiF200	300 µm	Duplex	None	60	66	52.7922	-0.5000	0.6000	19	67
Cu	KA	LiF200	300 µm	Duplex	None	60	66	45.0020	0.7606		20	70
Fe	KA	LiF200	150 µm	Duplex	None	57	70	57.5136			15	70
K	KA	LiF200	300 µm	Flow	None	32	125	136.6930	-1.3512		27	74
La	LA	LiF200	300 µm	Flow	None	42	95	82.9362			30	70
Mg	KA	PX1	700 µm	Flow	None	32	125	22.2722	-0.8000	0.8910	23	85
Mn	KA	LiF200	300 µm	Duplex	None	57	70	62.9750	-0.9390		15	72
Mo	KA	LiF200	150 µm	Scint	None	60	66	20.2866	-0.5000	0.5000	25	75
Na	KA	PX1	700 µm	Flow	None	32	125	26.9218	-2.1684	1.9352	21	78
Nd	LB1	LiF200	300 µm	Duplex	None	57	70	65.1298	0.6124		15	70
Ni	KA	LiF200	300 µm	Duplex	None	60	66	48.6450			19	69
P	KA	Ge111	300 µm	Flow	None	32	125	140.9576	-1.2698	2.6310	22	78
Pb	LA	LiF200	300 µm	Scint	None	60	66	33.9024	0.7630		18	72
Pr	LB1	LiF200	300 µm	Duplex	None	57	70	105.0006	0.8612		12	69
S	KA	Ge111	300 µm	Flow	None	32	125	110.6618	1.9098		11	78
Sb1	KA	LiF200	300 µm	Scint	None	60	66	13.4078	-0.5000		29	75
Si	KA	PE002	150 µm	Flow	None	32	125	109.1046			24	78
Sm	LB1	LiF200	300 µm	Duplex	None	57	70	59.5042	0.5296		15	76
Sn1	LA	LiF200	300 µm	Flow	None	32	125	126.8242	-1.5000		29	70
Sr	KA	LiF200	300 µm	Scint	None	60	66	25.1050	-0.6224		22	77
Ti	KA	LiF200	300 µm	Flow	None	37	108	86.1750			30	70
V	KA	LiF200	300 µm	Duplex	None	47	85	76.9636	1.1404		30	70
Zn	KA	LiF200	300 µm	Scint	None	60	66	41.7650	-0.7550		15	77
Zr	KA	LiF200	300 µm	Scint	None	60	66	22.4968	-0.7000	0.7000	24	75

TABLE X2.3 Example Listing of an Analysis Program for a Wavelength Dispersive X-ray Spectrometer

Quantitative Program								Application Compounds		
Ch.	Time, (s)	CSE, (%)[A]	Drift Corr.	BG Factor	Bg const. (kcps)	Bg of Channel	Use Polynom.	Reporting Name	Units	Dec.
Al	6	0.067	Yes				No	Al_2O_3	%	2
Ba	6	0.210	Yes				No	Ba	%	3
BaBg1	2			1.0000						
Bi	12	0.358	Yes				No	Bi	ppm	0
BiBg1	6									
BiBg2	6									
Ca	8	0.823	Yes				No	CaO	%	3
CaBg1	4			1.0000						
Ce	6	0.349	Yes				No	CeO_2	%	3
Co	60	0.150	Yes				No	Co	ppm	0
CoBg1	30			0.5455						
CoBg2	30			0.4545						
Cu	12	0.439	Yes				No	Cu	ppm	0
CuBg1	6			1.0000						
Fe	4	0.110	Yes				No	Fe	%	3
K	10	0.576	Yes				No	K2O	%	3
KBg1	6			1.0000						
La	6	0.435	Yes				No	La_2O_3	%	3
Mg	50	0.100	Yes				No	MgO	ppm	0
MgBg1	20			0.5269						
MgBg2	20			0.4731						
Mn	8	0.176	Yes				No	Mn	ppm	0
MnBg1	4			1.0000						
Mo	40	0.200	Yes				No	Mo	ppm	0
MoBg1	20			0.5000						
MoBg2	20			0.5000						
Na	16	0.248	Yes				No	Na	%	3
NaBg1	8			0.4716						
NaBg2	8			0.5284						
Nd	6	0.670	Yes				No	Nd_2O_3	%	3
NdBg1	2			1.0000						
Ni	4	0.154	Yes				No	Ni	ppm	0
P	16	0.140	Yes				No	P_2O_5	%	3
Pb	16	0.417	Yes				No	Pb	ppm	0
PbBg1	8									
PBg1	6			0.6745						
PBg2	6			0.3255						
Pr	20	1.632	Yes				No	Pr_6O_{11}	%	3
PrBg1	10			1.0000						
S	20	0.109	Yes				No	SO_4	%	3
Sb1	20	0.223	Yes				No	Sb	ppm	0
Sb1Bg1	10			1.0000						
SBg1	10			1.0000						
Si	6	0.059	Yes				No	SiO_2	%	2
Sm	8	1.800	Yes				No	Sm_2O_3	%	3
SmBg1	4			1.0000						
Sn1	30	0.541	Yes				No	Sn	ppm	0
Sn1Bg1	10			1.0000						
Sr	6	0.150	Yes				No	Sr	%	3
SrBg1	2			1.0000						
Ti	6	0.185	Yes				No	TiO_2	%	3
V	6	0.215	Yes				No	V	ppm	0
VBg1	2			1.0000						
Zn	6	0.233	Yes				No	ZnO	ppm	0
ZnBg1	2			1.0000						
Zr	6	0.274	Yes				No	Zr	%	3
ZrBg1	2			0.5000						
ZrBg2	2			0.5000						

[A] CSE, (%), RSD of the count rate, in percent.

TABLE X2.4 Example of Concentration Limits of Analysis

Analyte	Lower Limit	Upper Limit
Al_2O_3 %	20	60
Ba %	0.005	1.500
Bi ppm	1	2000
CaO %	0.04	1.00
Co ppm	5	1000
Cu ppm	10	300
Fe %	0.10	1.50
MgO ppm	400	25000
Mo ppm	5	500
Na %	0.10	1.00
Ni ppm	40	4000
P_2O_5 %	0.04	4.00
Pb ppm	10	1000
REO %	0.10	5.00
Sb ppm	10	2000
SiO_2 %	25	75
Sn ppm	10	1000
SO_4 %	0.010	4.000
Sr %	0.005	0.100
TiO_2 %	0.40	3.00
V ppm	40	5000
ZnO ppm	20	1000
Zr %	0.00	0.10

TABLE X2.5 Example of Precision on 20 Repetitive Analyses of a Sample by a Wavelength-Dispersive X-ray Spectrometer

NOTE 1—%RSD values are high for some analytes due to the trace concentration of these analytes in this sample. At higher concentrations %RSD values will improve.

Analyte	Units	Mean Concentration	σ	RSD
Al_2O_3	%	29.92	0.08	0.3 %
Ba	%	0.0261	0.0012	4.6 %
CaO	%	0.0996	0.0011	1.1 %
CeO_2	%	0.369	0.003	0.8 %
Co	ppm	142.3	2.8	2.0 %
Cu	ppm	45.2	0.7	1.7 %
Fe	%	0.546	0.006	1.1 %
K_2O	%	0.1024	0.0007	0.7 %
La_2O_3	%	0.840	0.005	0.6 %
MgO	ppm	851	22	2.5 %
Mn	ppm	40.8	1.6	3.8 %
Na	%	0.605	0.004	0.7 %
Nd_2O_3	%	0.420	0.005	1.1 %
Ni	ppm	2333	26	1.1 %
P_2O_5	%	0.343	0.002	0.7 %
Pb	ppm	77.1	1.1	1.4 %
Pr_6O_{11}	%	0.133	0.004	3.4 %
REO	%	1.770	0.010	0.6 %
Sb	ppm	862.4	6.7	0.8 %
SiO_2	%	65.5	0.2	0.4 %
Sm_2O_3	%	0.01	0	0.0 %
SO_4	%	0.168	0.004	2.3 %
Sr	%	0.011	0	0.0 %
TiO_2	%	1.029	0.007	0.7 %
V	ppm	2417	14	0.6 %
ZnO	ppm	255.1	3.6	1.4 %
Zr	%	0.009	0	0.0 %

%RSD = (σ / mean concentration) × 100

X3. DISCUSSION

X3.1 The detection limit of the pressed powder method is 0.004 wt% (40 ppm) nickel and 0.0040 wt% (40 ppm) vanadium. The detection limit is defined as the concentration at which the X-ray peak intensity is three times the background intensity. Another way to say this is that the peak–to–background ratio equals 3. The detection limit of the fused bead technique would be expected to be higher because the specimen is being diluted. If you triple the counting time for fused beads, then the detection limits are about comparable for the two techniques.

X3.2 The precision of the pressed powder technique has a σ of 0.0025 wt% (25 ppm) nickel for a sample with 0.25 wt% nickel or an RSD of approximately 1 %. Vanadium has a σ of 0.0014 wt% (14 ppm) at the 0.25 wt% level for an RSD of approximately 0.6 %. The precision data is based on twenty trials of the same sample. The fused bead technique would be expected to be as good or better provided sufficient X-ray counts are accumulated.

X3.3 The examples given in Test Methods A and B should only be regarded as typical for this special type of analysis. This is a special case that analyzes one catalyst type, and the only components that vary are the two analytes of interest, nickel and vanadium. The analytical system employed, X-ray tube anode, crystals and angles, does not require any correction for spectral interference or any interelement corrections. This is not normally the case. As more analytes are added into the analysis, the level of difficulty increases.

X3.4 The ASTM standards listed in the Referenced Documents, Section 2, provide a good foundation for those new to the XRF technique. New users should pay particular attention to the publications concerning X-ray radiation safety. In addition, there are several good books on specimen preparation. See Buhrke, et al for a practical guide.[4] It provides tables of vendor names and addresses, instrument-specific operating instructions, and a very complete bibliography.

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[4] Buhrke, V., Jenkins, R., and Smith, D., *Preparation of Specimens for X-ray Fluorescence and X-ray Diffraction Analysis*.