

NICKEL, TUNGSTEN, SODIUM AND ALUMINUM IN HYDROCRACKING CATALYSTS BY ICP-AES

UOP Method 924-00

SCOPE

This method is for determining nickel(Ni), tungsten(W), sodium(Na) and aluminum(Al) in fresh alumina or alumino-silicate supported catalysts by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The method is suitable for the determination of elements from the low ppm to high mass percent concentration ranges. The determination of Ni, W, Na and Al is described herein, however, many other elements which are brought into solution during the described sample decomposition can be also determined. Because of incomplete dissolution, catalysts containing *alpha*- or *theta*-alumina phases cannot be analyzed by this method, however, it can be applied if a modified sample dissolution technique, such as a TeflonTM lined pressure vessel (not described herein) is utilized.

This method can also be used for spent catalyst after suitable pretreatment.

OUTLINE OF METHOD

Samples are ground and dissolved using sulfuric and hydrofluoric acids. The digest is aspirated into an ICP-AES spectrometer equipped with a sample transport system that is resistant to hydrofluoric acid(HF). The concentrations of Ni, W, Na, Al and other metals of interest are determined by comparison to standards containing the same acid concentration as the sample solutions. Results are generally reported on a volatile-free basis; 500°C Loss on Ignition (LOI) is determined using UOP Method 412.

APPARATUS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Balance, readability, 0.1-mg

Beaker, Teflon, 250-mL, Fisher Scientific, Cat. No. 02-593-5B

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UOP Methods are available through ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken PA 19428-2959, United States. The Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

Beaker cover, Teflon, 80-mm., Fisher Scientific, Cat. No. 02-617-1G

Crucible, quartz, 20-mL, Fisher Scientific, Cat. No. 08-072C (for spent catalyst only)

Cylinders, graduated, polypropylene, 10- and 50-mL, Fisher Scientific, Cat. Nos. 08-570-21A and 08-570-21C, respectively

Fume hood, laboratory

Gloves, nitrile or neoprene

Hot plate, variable heat to at least 300°C

Inductively Coupled Plasma-Atomic Emission Spectrometer, Perkin–Elmer Optima 3000 or equivalent, equipped with a HF resistant sample transport system

Mill, coffee mill type, capable of grinding catalyst to <80 mesh. Proctor - Silex E160B, or equivalent, local supply

Muffle furnace, capable of operation to a minimum of 500°C (for spent catalyst only)

Pipets, glass, Class A, 5-, 15-, 50-mL, Fisher Scientific, Cat. Nos. 13-650,2F, -2M, -2S, see *NOTE*

Regulator, argon, two-stage, high purity, Matheson Gas Products, Model 3122-580

Regulator, nitrogen, two-stage, high purity, Matheson Gas Products, Model 3122-580

Sieve, wire cloth, brass frame, 8-inch diameter, 2-inch depth, U.S. standard sieve, No. 80, Fisher Scientific, Cat. No. 04-881W; with cover and pan, Fisher Scientific, Cat. Nos. 04-886A and B, respectively

Thermometer, electronic, with surface temperature probe, Omega Engineering, Cat. Nos. HH81 and 88108K, respectively

Volumetric flasks, Nalgene polymethylpentene, 500-mL, Fisher Scientific, Cat. No. 10-198-52F

REAGENTS AND MATERIALS

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Aluminum solution, 1000-µg/mL, Spex, Cat. No. PLAL1-2X

Argon, 99.995% minimum purity, ICP feed gas

Hydrofluoric acid, concentrated, Reagent ACS Grade, Fisher Scientific, Cat. No. A147-1LB

Nickel solution, 1000-µg/mL, Spex, Cat. No. PLNI-2X

Nitrogen, 99.99% minimum purity, water/oil free, ICP optics purge gas

Scandium solution, 1000-µg/mL, Spex, Cat. No. PLSC2-2X (to be used as an internal standard)

Sodium solution, 1000-µg/mL, Spex, Cat. No. PLNA1-2X

Sulfuric acid, concentrated, Certified ACS Plus Grade, Fisher Scientific, Cat. No. A300-212

Sulfuric acid, 1:1, Fisher Scientific, Cat. No. LC25640-3. Or, mix equal parts of concentrated sulfuric and water; slowly add the acid to the water.

Tungsten solution, 1000- $\mu\text{g/mL}$, Spex, Cat. No. PLW9-2X. This solution contains $(\text{NH}_4)_2\text{WO}_4$ in water, no HF. See *NOTE*.

Water, deionized

PROCEDURE

The analyst is expected to be familiar with the basic instrumentation and concepts of ICP-AES.

The method describes a beaker based sample dissolution of fresh catalyst. Other techniques, such as microwave, can be used for dissolution assuming equivalency.

All steps involving handling and heating of concentrated acids or acid solutions must be performed in a fume hood.

Preparation of Calibration Standards

A single standard containing the four elements of interest is used to calibrate the ICP. If the determination of additional elements is desired the analyst must check for line overlaps and select emission lines that are free of overlap. The concentration of elements in the calibration standards was made up assuming the following catalyst composition: W = 20%, Al = 20%, Ni = 6% and Na = <0.1%. The concentration of elements in the calibration standard may need to be changed for different catalyst types.

Prepare the ICP calibration solution as follows:

1. Add into two 500-mL plastic volumetric flasks, using a plastic graduated cylinder, 20 mL of 1:1 sulfuric and 4 mL hydrofluoric acids. Wash down the walls with water. Label one flask "blank = zero $\mu\text{g/mL}$ " and the other "calibration standard." *CAUTION:* Appropriate safety precautions must be taken when handling hydrofluoric acid.
2. Pipet into the "calibration standard" 500-mL volumetric flask:
 - a) 50 mL of 1000- $\mu\text{g/mL}$ tungsten solution (if HF is present use a plastic pipet)
 - b) 50 mL of 1000- $\mu\text{g/mL}$ aluminum solution
 - c) 15 mL of 1000- $\mu\text{g/mL}$ nickel solution
 - d) 2 mL of 1000- $\mu\text{g/mL}$ sodium solution
3. Wash down the walls with water.
4. Pipet into both volumetric flasks 5-mL of the 1000- $\mu\text{g/mL}$ scandium internal standard solution.
 - When diluted, both flasks will contain 10- $\mu\text{g/mL}$ Sc.
5. Dilute both flasks to mark with water, cap and invert to mix thoroughly.
 - The calibration standard will contain: 100- $\mu\text{g/mL}$ W, 100- $\mu\text{g/mL}$ Al, 30- $\mu\text{g/mL}$ Ni and 4- $\mu\text{g/mL}$ Na.
 - This standard is stable for 3 weeks.

Sample Preparation

A reagent blank is carried through the procedure analogous to the sample.

A quality control (QC) sample is to be prepared and analyzed with each group of samples.

- Typically, a large volume of a single sample is retained for use as a QC sample.
1. Grind the sample in a mill to a uniform powder (<80 mesh).
 - The grinding capability of the mill can be determined by pulverizing and then screening similar catalyst types prior to performing this method.
 2. For fresh catalysts, proceed to Step 4. For spent catalysts, weigh, to the nearest 0.1 mg, 0.20 g (± 0.02 g) of the catalyst into a quartz crucible, and ignite for 1 hr at 500°C in a muffle furnace.
 - Generally the results are reported on volatile-free basis, therefore, weigh a sample for a LOI @ 500°C, using UOP Method 412, at the same time as sampling for the acid decomposition.
 3. Quantitatively transfer the ignited powder into a Teflon beaker by rinsing with ~20 mL of water. Proceed to Step 6.
 4. Weigh, to the nearest 0.1 mg, 0.20 g (± 0.02 g) of the ground catalyst into a 250-mL Teflon beaker.
 - Generally the results are reported on volatile-free basis, therefore, weigh a sample for a LOI @ 500°C, using UOP Method 412, at the same time as sampling for the acid decomposition.
 5. Add, using a graduated cylinder, ~ 20 mL of water to the beaker. This is to wet the catalyst.
 6. Add, using a graduated cylinder, 20 mL of 1:1 sulfuric acid to the beaker, and swirl to mix the contents.
 7. Add, using a polypropylene graduated cylinder, 10 mL of concentrated hydrofluoric acid to the beaker and wash down the beaker walls with water.
 - Appropriate safety precautions must be taken when handling hydrofluoric acid.
 8. Place the beaker on a hot plate, ~150°C, and heat to mild boiling.
 9. Slowly increase the hot plate temperature and continue heating until the evolution of thick white fumes characteristic of sulfuric acid.
 - The heating in the presence of HF will volatilize silicon as SiF_4 from solution.
 - Do not fume excessively; this will volatilize additional sulfuric acid and will make it difficult to match the acid concentration in the sample solutions and the standards.
 - The hot plate temperature must not exceed 300°C as Teflon will soften and deform.
 10. Remove the beaker from the hot plate, cover with a Teflon cover and allow it to cool to room temperature.
 11. Partially uncover the beaker, slowly and carefully add, using a graduated cylinder, 20 mL of water.
 - Add the water carefully to avoid loss of sample due to splattering.
 - Inspect the solution for total decomposition, if undissolved matter is present, repeat Steps 7-11.

12. Rinse the Teflon cover and the beaker walls with water.
13. Add, using a graduated cylinder, 4 mL of concentrated hydrofluoric acid.
14. Cover the beaker with the Teflon cover and place on the hot plate, ~150°C, and bring to a boil.
15. Remove the beaker from the hot plate and allow it to cool.
16. Rinse the Teflon cover and the beaker walls with water.
17. Quantitatively transfer, with water, the contents of the beakers, sample and reagent blank, into 500-mL plastic volumetric flasks.
18. Pipet into the volumetric flasks 5 mL of the 1000-µg/mL scandium internal standard solution.
19. Dilute to mark with water, cap and invert to mix thoroughly.
20. The samples are now ready for ICP analysis.

Sample Solution Analysis

Set up the ICP-AES instrument according to the instrument manufacturer's guidelines. Table 1 lists the elemental wavelengths that are recommended in this method. Other wavelengths may be used if it can be shown that method precision and accuracy are not adversely affected. A HF resistant sample introduction system is required for use with hydrofluoric acid.

Table 1
Recommended Wavelengths

<u>Element</u>	<u>Wavelength, nm</u>
Ni	231.604
W	248.923
Al	396.152
Na	589.592
Sc	424.683

1. Standardize the instrument by aspirating the “zero µg/mL” standard, followed by the “calibration standard”. Allow sufficient wash-out time between aspirations.
2. Aspirate the reagent blank solution and examine the concentrations for elements of interest, especially Na, as it is present in trace amounts (~0.1 µg/mL in the sample solutions) and is prone to be a contaminant. The concentration (intensity) of Na in the reagent blank should be approximately the same as for the “zero µg/mL” solution. If not, clean the equipment again and repeat the procedure.
3. Re-standardize the ICP using the reagent blank as the “zero µg/mL” standard.
4. Analyze the sample and QC sample solutions.

5. To ensure ICP spectrometer performance, aspirate the calibration solution as a calibration check after every 4 - 8 sample solutions and after the last sample. The replication of the calibration solutions should be within 3% relative. If not, recalibrate the spectrometer and rerun the samples. If this does not help, investigate the sample transport system or other system performance parameters.

CALCULATIONS

Report the results to three significant figures at one mass-% and above, to two significant figures below one mass-%.

Calculate the concentration of elements in the catalyst on an as received (AR) basis as follows:

$$\text{Element, mass - \% (AR)} = \frac{10^{-4} CV}{W} \quad (1)$$

where:

C = concentration of element, µg/mL, in sample solution, from instrument printout
V = volume from *Sample Preparation* Step 17
W = weight of sample, from *Sample Preparation* Step 2 or 4
10⁻⁴ = factor to convert to mass-%

Calculate the concentration of elements in the catalyst on a volatile-free (VF) basis as follows:

$$\text{Element, mass - \% (VF)} = \frac{100A}{100 - \%LOI} \quad (2)$$

where:

A = concentration of element, mass-%, as received, oEq. 1
% LOI = from analysis of sample by UOP Method 412

If the results are to be reported as oxides, multiply by the appropriate gravimetric factor in Table 2.

Table 2

Gravimetric Factors

<u>To Convert</u>	<u>Multiply By</u>
Ni to NiO	1.272
W to WO ₃	1.261
Na to Na ₂ O	1.348
Al to Al ₂ O ₃	1.889

NOTE

Ensure that the 1000- $\mu\text{g/mL}$ tungsten calibration standard does not contain any hydrofluoric acid (HF). If a calibration standard containing HF must be used, use plastic pipet and volumetric flasks, avoiding contact with glass.

PRECISION

Precision statements were determined using UOP Method 999.

ASTM Repeatability

A nested design was carried out for determining tungsten, nickel, aluminum and sodium in catalysts in four laboratories. In each laboratory, two analysts carried out tests on two separate days, performing two tests each day. The total number of tests performed was 32 for each element. Using a stepwise analysis of variance procedure, the within-day estimated standard deviation (esd) was calculated and is listed in Table 3. Two tests performed by the same analyst on the same day should not differ by more than the ASTM allowable difference shown in Table 3 with 95% confidence.

UOP Repeatability

A nested design was carried out for determining tungsten, nickel, aluminum and sodium in catalysts in four laboratories. In each laboratory, two analysts carried out tests on two separate days, performing two tests each day. The total number of tests performed was 32 for each element. Using a stepwise analysis of variance procedure, the within-lab standard deviation (esd) was calculated and is listed in Table 3. Two tests performed in one laboratory by different analysts on different days should not differ by more than the UOP allowable difference shown in Table 3 with 95% confidence.

The data in Table 3 are a short-term estimate of repeatability. When the test is run routinely, a control standard and chart should be used to develop a better estimate of the long-term repeatability.

Reproducibility

A nested design was carried out for determining tungsten, nickel, aluminum and sodium in catalysts in four laboratories. In each laboratory, two analysts carried out tests on two separate days, performing two tests each day. The total number of tests performed was 32 for each element. Using a stepwise analysis of variance procedure, the within-lab and between-lab standard deviation (esd) was calculated and is listed in Table 3. Two tests performed in different laboratories by different analysts on different days should not differ by more than the allowable difference shown in Table 3 with 95% confidence.

Table 3
ASTM and UOP Repeatability and Reproducibility, mass-%

Element	Mean Value	ASTM Repeatability		UOP Repeatability		Reproducibility	
		Within-Day esd	Allowable Difference	Within-Lab esd	Allowable Difference	Between-Lab esd	Allowable Difference
W	18.2	0.15	0.4	0.14	0.4	0.23	0.8
Ni	5.28	0.040	0.12	0.062	0.19	0.060	0.18
Al	16.2	0.14	0.4	0.18	0.6	0.18	0.6
Na	0.022	0.0016	0.005	0.0021	0.006	0.0023	0.007

TIME FOR ANALYSIS

The elapsed time for analysis on VF basis is about 4 hours. The labor requirement, including the LOI, for a single sample is about 1.75 hrs.

REFERENCES

UOP Method 412, "Loss on Ignition of Catalysts at 500°C"

UOP Method 999, "Precision Statements in UOP Methods"

SUGGESTED SUPPLIERS

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-562-8300) www.fishersci.com

Matheson Gas Products, Inc., 932 Paterson Plank Road, P.O. Box 85, East Rutherford, NJ 07073 (201-933-2400) www.mathesontrigas.com

Omega Engineering, Inc., One Omega Dr., P.O. Box 4047, Stamford, CT 06907 (203-359-1660) www.omega.com

Perkin-Elmer Inc., 761 Main Ave., Norwalk, CT 06859-0001 (203-762-4003) www.perkinelmer.com

Spex Certiprep, Inc., 203 Norcross Ave., Metuchen, NJ 08840 (732-549-7144) www.spexcsp.com