

LOSS ON IGNITION (LOI) FOR FRESH, REGENERATED, USED, AND SPENT CATALYSTS, CATALYST SUPPORTS, AND ADSORBENTS

UOP™ Method 954-03

SCOPE

This method is for determining the loss on ignition (LOI) in air, using a specified ignition temperature and time, for fresh, regenerated, used, and spent catalysts, catalyst supports, and molecular sieves of various shapes and sizes, including fines. This method is quantitative down to 0.1 mass-%. The method is not water specific; any components that volatilize at the selected ignition temperature, for example, carbon, chlorine, and fluorine, are also included in the LOI value. Some components, for example sulfates, may volatilize fully or partially depending on ignition time and temperature. Mass gains are possible with catalysts that contain reduced metals.

The criteria for selecting the temperature for the LOI are based on the volatility of components of materials. Examples are listed in *PROCEDURE, Table 1*. Length of time at temperature is dependent on the application of the LOI value. For example, it is important to drive off defined volatiles for the determination of platinum concentration.

REFERENCES

UOP™ Method 918, "Collection & Grinding of Adsorbents and Catalysts for Analysis,"
www.astm.org

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

OUTLINE OF METHOD

A representative sample is weighed into a crucible, warmed on a hot plate, and heated (ignited) in air at a specified temperature, typically 500, 700, 900, or 1000°C, for a specified period of time, typically 1 hour or 6 hours. After cooling, the sample is re-weighed and the mass loss is calculated as mass-% LOI.

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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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

Crucibles, Inconel, low-form, 45-mL capacity, with cover, B-J Scientific Products, Cat. Nos. 30-45LF and 30-45C, respectively (optional, see *NOTE 1*)

Crucibles, porcelain, low, wide-form, 30-mL capacity, with cover, Fisher Scientific, Cat. Nos. 07-955E and 07-970G, respectively

Desiccator, 250-mm ID, and porcelain plate, Fisher Scientific, Cat. Nos. 08-631B and 08-636F, respectively

Furnace, muffle, capable of operation at $1000 \pm 15^\circ\text{C}$, Fisher Scientific, Cat. No. 10-550-126

Gloves, lint-free nylon, VWR International, Cat. No. 32932-270

Hot plate, variable temperature to 250°C , Fisher Scientific, Cat. No. 11-497-2A

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

Tongs, crucible, 530- and 230-mm length, Fisher Scientific, Cat. Nos. 15-207 and -186, respectively

REAGENTS AND MATERIALS

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

Desiccant, molecular sieve, activated, moisture indicating, type 4A, 8-12 mesh, Cole-Parmer, Cat. No. M1373, or, Drierite, indicating, 8-mesh, Fisher Scientific, Cat. No. 07-578-3A

Grease, high-vacuum, Fisher Scientific, Cat. No. 14-635-5D

INTRODUCTION

There are a number of reasons for determination of the LOI. In some cases, the volatile component, typically water, is of interest. In other cases, the intent is to place samples at a baseline state so that some other analysis may be made, and comparisons to another material are thus made on the same basis. The criticality of the LOI value will impact the number of replicate samples analyzed. For general purposes, such as base metal determination, a single LOI determination is sufficient. For determination of noble metal on catalyst to meet specifications, duplicate LOI analyses are generally requested. Check the specific information for the material being analyzed to determine the LOI requirements before proceeding.

In all cases, the LOI must be performed with the sample in the appropriate physical state. For analysis of material to be shipped, the sample used to obtain the LOI must be in the same state as the sample when shipped: whole pill (sphere), whole extrudate, or powder; not ground. For noble metal analysis, since the noble metals are determined on a ground sample, the LOI must also be determined on a ground sample. Check the requirements or specifications of the material being analyzed, or any established method, standard operating procedure, or work instruction.

For analyses where the LOI is used to calculate the analysis results to a volatile free (VF) basis, always weigh the samples for LOI and elemental analysis at the same time. Where duplicate LOIs are stipulated, report the average of the two LOI values. If the expected LOI is greater than 5.0% and the two values differ by more than 0.3 mass-% absolute (or if the expected LOI is less than 5.0% and the two values differ by more than 0.2 mass-% absolute), rerun both the LOIs and the associated elemental analysis, since the sample may have gained or lost moisture during the interim.

Spent or used catalysts may ignite violently if introduced directly from the hot plate into the muffle furnace at 900°C, due to carbon or hydrocarbon combustion. For this application, the sample is warmed on a hot plate and then introduced into the muffle furnace set at 500°C. The furnace temperature is then ramped to 900°C, or other final temperature, over a period of time. The additional hardware required and the procedure are described in *APPENDIX A*. Materials that contain a high moisture level may be analyzed in the same manner.

For certain samples, or for experimental purposes, it may be desirable to measure an LOI to a constant weight. This procedure is described in *APPENDIX B*.

PROCEDURE

Typical LOI temperatures and times for various sample types are listed in Table 1. These are only examples. Specific conditions are to be established for individual applications. If desired, more than one sample can be placed, each in its own crucible, into the muffle furnace at one time. Each crucible must then be marked to prevent mix-up.

Table 1
Time at Specified Temperature

<u>Sample Type</u>	<u>Typical LOI Temperature, °C</u>	<u>Typical Time in Muffle Furnace, hours</u>
Catalysts with Tungsten or Molybdenum	500	1
Catalysts with Potassium	700	6¹
Catalysts	900	6¹
Molecular sieves	1,000	1
Spent or used catalyst	Ramp 500 to 900	12²
Calcined supports	700 or 900	1

¹The 6 hours specified is for samples to be analyzed for platinum.

²For convenience, this could be timed to be run overnight.

- Obtain a representative portion of the catalyst, catalyst support, or adsorbent to be analyzed.
 - Refer to UOP Method 918 for sampling procedures
- Ignite a porcelain crucible and a crucible cover by heating for 20 minutes in a muffle furnace at the specified LOI temperature for the catalyst or adsorbent.
 - The crucible cover needs to be heated only once per day.
 - An Inconel crucible and cover are also satisfactory as an alternative (see *NOTE*).

- The muffle furnace should be calibrated as per the lab's quality program.
 - Alternatively, the crucible and cover could be heated over a flame until they glow red hot.
3. Remove the crucible and cover from the furnace with tongs and place them in a desiccator containing a desiccant.
 - Discretion must be used regarding the number of crucibles placed in the desiccator at one time since an overheated desiccator may shatter.
 - When the top of the desiccant bed, or the indicator, turns from blue to pink, stir to redistribute.
 - The desiccant should be replaced when it is one-third spent, as indicated by the color change.
 - To minimize exposure to moist ambient air, the desiccator should be placed close to the balance.
 4. Allow the crucible and cover to cool to ambient temperature.
 - The cooling time will vary depending on the number of crucibles being cooled.
 5. Remove the crucible only from the desiccator and immediately weigh the crucible to the nearest 0.1 milligram.
 - The crucible cover remains in the desiccator.
 - The crucible must be handled with small tongs or lint-free gloves – not with bare hands.
 6. Weigh approximately 2 grams of the sample, to the nearest 0.1 milligram, into the ignited crucible immediately after completing Step 5.
 - Most catalysts and adsorbents are hygroscopic and should not be unnecessarily exposed to air.
 - Take samples for other analyses, if required, at the same time.
 7. Preheat the crucible containing the sample on a hot plate, having a surface temperature of 150 to 200°C, for approximately 20 minutes.
 - Fresh and regenerated whole-pill samples known to contain low volatiles do not require this pre-heating step.
 - A separate muffle furnace at a temperature of approximately 400°C may be substituted for the hot plate for catalysts and adsorbents which require LOI temperatures of 700°C or greater.
 8. Transfer the crucible containing the sample to the hot muffle furnace, which has been calibrated to the specified temperature, with the crucible tongs.
 9. Allow the sample to remain in the muffle furnace at the specified temperature for the specified length of time.
 - When multiple crucibles are placed in the furnace, additional time may be required for the furnace to return to the specified temperature.
 10. Remove the crucible from the muffle furnace with the crucible tongs, place it in the desiccator, and cover it with a crucible cover.
 11. Allow the crucible and cover to cool to ambient temperature.
 - The cooling time will vary depending on the number of crucibles being cooled in the desiccator, but is approximately one hour, or more.
 - Often, for convenience, the crucibles are left in the desiccator overnight.

12. Weigh the uncovered crucible and contents to the nearest 0.1 milligram.

- The crucible must be handled with small tongs or lint-free gloves – not with bare hands.

CALCULATIONS

Calculate the LOI at the specified temperature using Equation 1:

$$\text{LOI, mass-\%} = 100 \frac{A - C}{A - B} \quad (1)$$

where:

- A** = mass of ignited crucible and sample, before heating, g
- B** = mass of ignited crucible, g
- C** = mass of ignited crucible and sample, after heating, g
- 100** = factor to convert g/g to mass-%

REPORT

Report the LOI value to two decimal places when the value is below 5 mass-%, or to one decimal place when the value is above 5 mass-%, at the specified temperature in degrees Celsius.

State the mass-% gain in cases where oxidation has occurred.

Unless otherwise directed, report the average of the replicates.

NOTES

1. A porcelain crucible is commonly used for this analysis, however, there are special circumstances wherein an Inconel crucible may be preferred. There may be less of a tendency for some samples to stick to an Inconel crucible, so if the same sample is to be reused for further testing, Inconel may have an advantage. Also, samples containing high levels of fluoride may degrade a porcelain crucible during heating, where this may not occur with an Inconel crucible. Perform comparison tests before switching to an Inconel crucible.
2. Classical methods or Thermogravimetric Analysis/Mass Spectroscopy (TGA/MS) can be used to establish the fate of individual components upon heating.

PRECISION

The precision statements were determined using UOP Method 999.

ASTM and UOP Repeatability

A nested design was carried out for determining LOI of six different catalysts with two analysts in each of four or five laboratories. Each analyst carried out two tests on each of two separate days. The total number of tests performed was 224. Using a stepwise analysis of variance procedure, the within-day estimated standard deviation (esd) was calculated and is listed in Table 2. Two tests performed by the same analyst on the same day should not differ by more than the ASTM allowable difference shown in Table 2 with 95% confidence. 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 2 with 95% confidence.

The data in Table 2 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 LOI of six different catalysts with two analysts in each of four or five laboratories. Each analyst carried out two tests on each of two separate days. The total number of tests performed was 224. Using a stepwise analysis of variance procedure, the within-lab and between-lab estimated standard deviation (esd) was calculated and is listed in Table 2. Two tests performed by different analysts in different laboratories on different days should not differ by more than the allowable difference shown in Table 2 with 95% confidence.

Table 2
ASTM and UOP Repeatability and Reproducibility, mass-%

<u>Sample</u>	<u>Temp, °C</u>	<u>Time, hours</u>	<u>LOI, Mean</u>	<u>ASTM</u>		<u>UOP</u>		<u>Reproducibility</u>	
				<u>Within- Day esd</u>	<u>Allowable Difference</u>	<u>Within- Lab esd</u>	<u>Allowable Difference</u>	<u>Within- Lab and Between- Lab esd</u>	<u>Allowable Difference</u>
Whole pill	700	1	0.82	0.040	0.12	0.068	0.21	0.094	0.30
Ground	700	5	4.44	0.040	0.12	0.076	0.24	0.113	0.38
Whole pill	900	1	1.63	0.043	0.13	0.065	0.19	0.129	0.45
Whole pill	900	1	4.77	0.049	0.15	0.122	0.36	0.119	0.35
Ground	900	5	1.99	0.028	0.08	0.103	0.31	0.241	0.84
Whole pill	900	1	3.95	0.041	0.12	0.075	0.22	0.099	0.30

TIME FOR ANALYSIS

The elapsed time for one analysis is 0.5 hour in addition to the time in the muffle furnace and cool-down time. The labor requirement is 0.5 hour.

SUGGESTED SUPPLIERS

B-J Scientific Products, Inc., 173 Queen Ave. SE, Albany, OR 97321 (503-976-8383)

Cole-Parmer Instrument Company, 625 East Bunker Court, Vernon Hills, IL 60061 (847-549-7600)
www.coleparmer.com

Fisher Scientific Co., 711 Forbes Ave., Pittsburgh, PA 15219-4785 (412-490-8300)
www.fishersci.com

Omega Engineering, Inc., One Omega Drive, Stamford, CT 06907 (203-359-1660)
www.omega.com

VWR International, 1310 Goshen Parkway, West Chester, PA 19380 (610-431-1700)
www.vwr.com

APPENDIX A

Analysis of Spent and Used Catalysts

APPARATUS

The following item is required in addition to, or as an alternative to, that listed in the body of UOP Method 954-03.

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

Furnace, muffle, programmable, capable of operation at $1000 \pm 15^\circ\text{C}$, Fisher Scientific, Cat. No. 10-650-126 (replaces furnace 10-550-126)

PROCEDURE

1. Follow Steps 1 through 7 under *PROCEDURE* in the body of the Method.
2. Program the muffle furnace to the desired program. Example programs are shown in Table A, and are specified or experimentally determined for each sample type. Allow the furnace to equilibrate at the initial temperature.

Table A

Examples of Furnace Temperature Program Times, hours

<u>Temperature setting</u>	<u>Program I</u>	<u>Program II</u>	<u>Program III</u>
500°C ^A	0.5	1	1
600°C	-	1	1
700°C	0.5	1	1
800°C	-	1	1
900°C	4	8	20

^AHighly coked catalysts may require a starting temperature of 400°C or lower.

3. Transfer the crucible containing the sample to the muffle furnace with the crucible tongs and start the temperature program.
4. Allow the sample to remain in the muffle furnace at the specified temperature for the specified length of time.
5. When the temperature program is finished, remove the crucible from the muffle furnace with the crucible tongs, place it in the desiccator and cover it with a crucible cover.
6. Reduce the furnace temperature to the initial setting.
7. Continue with Steps 11 and 12 under *PROCEDURE* in the body of the Method.

APPENDIX B**LOI to a Constant Weight****PROCEDURE**

1. Follow Steps 1 through 12 under *PROCEDURE* in the body of the Method.
2. Repeat Steps 8 through 12 until the weight (**C**), under *CALCULATIONS*, no longer trends in one direction.

CALCULATIONS

Calculate the LOI at the specified temperature using Equation B1:

$$\text{LOI, mass-\%} = 100 \frac{A - D}{A - B} \quad (\text{B1})$$

where:

A = mass of ignited crucible and sample, before heating, g

B = mass of ignited crucible, g

D = average mass of ignited crucible and sample, after the last two heatings, g

100 = factor to convert g/g to mass-%

NOTE

An alternative means of determining LOI to a constant weight is Thermogravimetric Analysis (TGA).

TIME FOR ANALYSIS

The elapsed time for one analysis is 2 hours in addition to the times in the muffle furnace and the cool-down times. The labor requirement is 2 hours.