

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

APPLIED SCIENCE & TECHNOLOGY DIVISION

LABORATORY SERVICES BRANCH

TECHNICAL REPORT

**ADDITIONAL REQUIREMENTS TO ASTM STANDARD TEST METHOD E 1868-10
LOSS-ON-DRYING BY THERMOGRAVIMETRY FOR RULE 1144
METALWORKING FLUIDS AND DIRECT-CONTACT LUBRICANTS**

VERSION 1.0

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1. Introduction

This technical report describes additional procedures required for determining the amount of volatile organic compound (VOC) content in metalworking fluids and direct-contact lubricants by ASTM Standard Test Method E 1868-10 (E 1868-10) Method A as required by South Coast Air Quality Management District (SCAQMD) Rule 1144.

2. Overview

2.1 Principle

Refer to E 1868-10 Section 4 (including Note 2).

2.2 Applicability

This technical report applies to the analysis of VOC content in metalworking fluids and direct-contact lubricants subject to SCAQMD Rule 1144.

2.3 Range

With respect to metalworking fluids and direct-contact lubricants, E 1868-10 quantifies VOC content from about 1% to 100% (approximately 10 g/L to 1000 g/L).

2.4 Interferences

Refer to E 1868-10 Section 6.

2.5 Safety

Refer to E 1868-10 Sections 1.6 and 8 and the following instructions:

2.5.1 Consult the Material Safety Data Sheet (MSDS) of each standard and sample for appropriate information prior to use (if available).

2.5.2 Handle standards and samples in a fume hood using non-permeable gloves.

2.6 Definitions

Refer to E 1868-10 Section 3.

2.7 Precision

Refer to E 1868-10 Section 14.1, with the exception of Table 3 (replace with Table 1 of this document).

Table 1: Precision Statistics

Material	Average	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	\bar{x}	s_r	s_R	r	R
E*	4.18	0.639	1.68	1.79	4.71
F	58.5	3.40	11.6	9.52	32.5
H	87.9	4.73	10.3	13.3	28.8
D	633	11.5	14.5	32.3	40.6
G	982	4.84	9.18	13.6	25.7

* Results from only 3 laboratories.

3. Equipment

Refer to E 1868-10 Section 7 and the following additional specifications.

3.1 Thermogravimetric Analyzer – Any commercially available thermogravimetric analyzer capable of continuously measuring and recording sample mass and temperature in a controlled atmosphere. At a minimum, the instrument shall consist of the following:

- 3.1.1 *Balance*, with a minimum sample capacity of 50 mg, a sensitivity of ± 1 μg , and the ability to continuously record mass changes. Performance to be verified in accordance with ASTM Test Method E 2040.
- 3.1.2 *Furnace*, with a minimum temperature range of 25 to 100°C, capable of a heating rate of 25°C/min which can be controlled to within $\pm 0.1^\circ\text{C}/\text{min}$, and the ability to maintain a set temperature isothermally to $\pm 1^\circ\text{C}$. Performance to be verified in accordance with ASTM Practice E 1582.
- 3.1.3 *Temperature Sensor*, with the ability to continuously record sample temperature to within $\pm 0.1^\circ\text{C}$ over the range from 25 to 100°C. If the system employs multiple temperature sensors or a movable temperature sensor, use the temperature sensor which is closest to the sample. Performance to be verified in accordance with ASTM Practice E 1582.

3.1.4 *Atmospheric Control*, two controls are required, one for purge flow and one for balance protection flow, each with the ability to supply purified grade nitrogen with an adjustable flow rate of 10 to 50 mL/min to within ± 5 mL/min.

3.1.5 *Timer*, with the ability to continuously record elapsed time up to 3 h to within ± 0.1 min. Performance to be verified in accordance with ASTM Test Method E 1860.

3.2 Sample Holders (*pans, crucibles, etc.*) – Sample holders must have flat bottoms and be capable of being placed or hung horizontally, such that the sample spreads evenly across the bottom of the pan.

3.3 Sample Containers

3.3.1 Wide-mouth glass jars with Teflon lined caps and 250 mL minimum volume.

3.3.2 Narrow-mouth metal cans with screw caps and 250 mL minimum volume.

3.4 Syringes (for filtering) – Sterile, single use, luer-lock tip

3.5 Syringe Filters – 1 μm Glass Fiber Membrane

3.6 Tweezers

4. Standards and Reagents

4.1 Cleaning Solvents – ACS reagent grade or equivalent

4.2 Nitrogen Gas – $\geq 99.9\%$ purity.

5. Sampling

5.1 For acidic, aqueous, unknown, and waste samples use glass jars as specified in 3.3.1.

5.2 For basic, neutral, and solvent-based samples use metal cans as specified in 3.3.2.

5.3 Fill sample containers to at least 85% full in order to reduce loss of volatiles.

5.3.1 Leave approximately $\frac{1}{2}$ inch of headspace in glass jars to prevent breakage due to thermal expansion.

5.4 Make sure that the collected sample is representative of the material in question.

5.5 Check for leaks by turning the container upside-down. If the sample leaks, re-tighten the cap until no more leakage occurs.

5.5.1 Once it is verified the container is leak free, wrap cap tightly with non-porous electrical (or similar) tape.

5.6 Label the sample uniquely.

5.7 Obtain an MSDS of collected sample when possible.

5.8 Protect the sample from heat and light.

5.9 Samples should be submitted to a laboratory for analysis as soon as possible to minimize loss of volatiles.

5.10 Samples may also be purchased off-the-shelf and submitted for analysis.

6. Sample Handling and Storage

6.1 Unless stated otherwise in accompanying analysis requests, store samples at room temperature.

6.2 Store samples away from heat and light.

7. Analysis

7.1 Calibration

Refer to E1868-10 Section 10 and the following additional specifications.

7.1.1 **Temperature** – Calibrate the thermogravimetric analyzer’s temperature signal every 3 months according to ASTM Practice E 1582. Use a heating rate of 1°C/min and a transition temperature close to, but greater than, 81°C.

7.1.2 **Mass** – Calibrate the thermogravimetric analyzer’s mass signal every week according to ASTM Test Method E 2040. Use a reference material with an approximate (but known) mass of 50 mg. If conformity is not better than 1%, calibrate the balance using the procedure described in the instrument manual.

7.1.3 **Time** – Calibrate the thermogravimetric analyzer’s time signal every 6 months according to ASTM Test Method E 1860.

- 7.1.4 **Flow** – Check each mass flow controllers' calibration annually. If the mass flow controller is not within calibration, calibrate according to manufacturer's instructions.

7.2 Preparation of Sample Holders

- 7.2.1 Always manipulate sample holders with tweezers; never handle sample holders.
- 7.2.2 Clean sample holders by soaking in acetone for 10 minutes, rinsing with distilled water, and then heating over an open flame until the platinum glows red.
- 7.2.3 Allow sample holders to cool down before use. If not being used immediately, store in a desiccator.

7.3 Determination of Density

- 7.3.1 Refer to ASTM Test Method D 1475 to determine the density of the sample.
- 7.3.2 Calculate and record the density of the sample (D_m) in g/mL.

7.4 Determination of Water Content

- 7.4.1 Refer to ASTM Test Method D 4017 to determine the water content of the sample.
- 7.4.2 Calculate and record the water content of the sample (W) in weight percent.

7.5 Determination of Exempt Compounds Content

- 7.5.1 Refer to SCAQMD Method 303 to determine the exempt compounds content of the sample.
- 7.5.2 Calculate and record the exempt compounds content (E_x) of the sample in weight percent.

7.6 TGA Procedure

- 7.6.1 Setup the thermogravimetric analyzer according to E 1868-10 Section 11.
- 7.6.1.1 Use Test Method A to terminate the experiment.

7.6.2 Analyze all blanks and samples under these instrument conditions.

7.6.3 Begin each 24-hour batch with a blank run.

7.6.4 Apply blank correction to all analyses.

7.7 Sample Preparation

Refer to E1868-10 Section 9 and the following additional instructions.

7.7.1 Samples shall not be thermally or mechanically treated.

7.7.2 9.2 and 9.3 are requirements and not recommendations.

7.7.3 Mix and/or stir the samples thoroughly prior to analysis to ensure that each sample aliquot is homogeneous and representative of the sample.

7.7.4 Filter samples containing solid particles. Use syringes and syringe filters as specified in Sections 3.4 and 3.5 of this document, respectively. Draw sample into the syringe until full. Secure the inlet of the syringe filter to the syringe. Hold the assembled syringe and filter vertically. Depress the syringe plunger gently. It is recommended that the first 0.25 to 0.50 mL of filtrate be discarded. If the back pressure ever increases significantly, change the filter as it may have plugged. Avoid pressing excessively as this could cause the filter housing to burst. Collect the filtrate in a suitable container such as a 2 mL vial with cap. Be sure to completely fill and immediately cap the container to minimize loss of volatiles.

7.8 Sample Analysis

7.8.1 At a minimum, analyze all samples in duplicate.

7.8.1.1 Additional analyses will be required if quality control requirements are not met.

7.8.2 Refer to Section 9 of this document for Quality Control Requirements.

8. Calculations

8.1 When performing these calculations, retain all available decimal places in the measured value and in intermediate values in the calculations. Only the final report value should be rounded in accordance with the established precision of the test.

8.2 Percent Mass Loss (m)

$$m = \frac{(m_I - m_F)}{m_I} \times 100 \quad (\text{Equation 1})$$

where:

m = percent mass loss (%),
m_I = initial mass (mg), and
m_F = final mass, mass at the time of the termination of the
experiment (mg).

$$m_{avg} = \frac{1}{n} \sum_{i=1}^n m_i \quad (\text{Equation 2})$$

where:

m_{avg} = average calculated percent mass loss (%),
n = number of runs, and
m_i = calculated percent mass loss of run i (%).

8.3 VOC Content (VOC)

$$VOC = (m_{avg} - W - E_x) \times D_m \times 10 \quad (\text{Equation 3})$$

where:

VOC = VOC Content (g/L),
m_{avg} = average calculated percent mass loss (%),
W = weight percent water (%) [Section 7.4.2],
E_x = exempt compounds content by mass (%) [Section 7.5.2],
and
D_m = density (g/mL) [Section 7.3.2].

8.4 Standard Deviation (s)

$$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (m_i - m_{avg})^2} \quad (\text{Equation 4})$$

where:

s = sample standard deviation (%),
n = number of runs,
m_i = calculated percent mass loss of run i (%), and
m_{avg} = average calculated percent mass loss (%).

8.5 Relative Standard Deviation (RSD)

$$RSD = \frac{s_m}{m_{avg}} \times 100 \quad (\text{Equation 5})$$

where:

RSD	=	relative standard deviation of multiple runs (%)
s_m	=	standard deviation of VOC Content (%), and
m_{avg}	=	average calculated percent mass loss (%)

9. Quality Control (QC)

The control limits cited in this method are the maximum allowable QC limits. If any QC requirement is not met, perform corrective action and bring the instrument back into control. Repeat invalid analyses according to the recommendations below. If any of the QC criteria is not met but the data must be reported (i.e. insufficient sample size to reanalyze), identify all out of control QC criteria in the laboratory report.

9.1 Calibrations

9.1.1 Instrument output signals (temperature, mass, time, and flow) must be calibrated according the frequency specified in Section 7.1 or any time major changes are made to the system.

9.2 Batch Time

9.2.1 *Requirement:* A batch begins with a valid blank run. All analysis associated with a batch must be completed within 24 hours of the blank run's start time.

9.2.1.1 *Corrective Action:* If the batch cannot be completed within the method batch time allowed, the analysis should be separated into smaller batches.

9.2.2 *Reminder:* Auto-samplers are not to be used.

9.3 Multiple Analyses

9.3.1 *Requirement:* The RSD of multiple analyses must be $\leq 5\%$ VOC content or the absolute difference between multiple analyses must ≤ 20 g/L VOC content, whichever requirement is greater.

9.3.1.1 *Corrective Action:* Troubleshoot the instrument and analyst technique, paying particular attention to instrument signal output and sample preparation. Repeat the affected analyses.

9.3.2 *Requirement:* Multiple analyses must be run in separate batches.

10. Reporting

Refer to E1868-10 Section 13 and the following additional instructions.

10.1 A complete identification and description of the material being tested,

10.1.1 Include any sampling issues and holding time violations,

10.2 A description of the temperature, mass, and time calibrations,

10.3 QC results,

10.4 Any deviations from the method, and

10.5 Density, water content, and exempt compounds content results.

11. References

Refer to E1868-10 Section 2 and the following additional references.

11.1 ASTM Documents

RR:E37-1039 Interlaboratory Study to Establish Precision Statements for ASTM E1868-10, Standard Test Method for Loss-On-Drying by Thermogravimetry

11.2 South Coast Air Quality Management District

Method 303 – Determination of Exempt Compounds

Rule 1144 – Metalworking Fluids and Direct-Contact Lubricants

11.3 Other

Pino, J., Barry, T., and Rose, J., *Estimation of Volatile Emission of Pesticides by Thermogravimetric Analysis*, California Environmental Protection Agency, 1020 N Street, Room 161, Sacramento, CA 95814-5624.