



**PROCEDURE FOR THE DETERMINATION OF NITROGEN IN FUELS BY
CHEMILUMINESCENCE**

SOP MV-FUELS-143
Version 2.1
Effective Date: December 1, 2019

Fuels Analysis and Methods Evaluation Section
Chemical Analysis and Emissions Research Branch
Mobile Source Laboratory Division

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1 Introduction

- 1.1 This procedure describes the determination of nitrogen content in diesel by chemiluminescence.
- 1.2 The Air Resources Board utilizes this procedure to analyze nitrogen content of diesel to determine compliance with the nitrogen specifications of California Clean Diesel regulations and to support various research projects requiring nitrogen analysis.
- 1.3 This method determines total nitrogen in liquid hydrocarbons with a boiling point range from approximately 50 to 400 degrees Celsius, with viscosities between approximately 0.2 and 10 cSt (mm/S) at room temperature. This procedure is applicable to naphthas, distillates, motor fuels and oils containing 0.3 to 500 mg/kg total nitrogen.
- 1.4 This procedure is based on American Society for Testing Materials (ASTM) D 4629-96.

2 Method

- 2.1 Fuel samples are injected into a high temperature combustion tube where the fuel is vaporized and organically bound nitrogen is converted to nitric oxide (NO) in an oxygen rich atmosphere. The water vapor, a product of the oxidation reaction, is removed from the combustion gases prior to measurement by the chemiluminescence detector.
- 2.2 The NO contacts ozone and is converted to excited nitrogen oxide (NO₂). The light emitted as the excited NO₂ decays is detected by a photomultiplier tube and the resulting signal is a measure of the nitrogen contained in the sample.
- 2.3 The data system identifies the peaks and quantifies the nitrogen content by integrating and comparing the areas of sample and calibration standard peaks.

3 Instrumentation and Apparatus

- 3.1 Furnace, electric, held at a temperature sufficient to volatilize and pyrolyze all of the sample and oxidize the organically bound nitrogen to NO. Furnace temperature(s) for petroleum substances shall be as recommended by the manufacturer (typically around 1100 degrees Celsius).
- 3.2 Combustion tube: The instrument must be equipped with a quartz

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combustion tube constructed to allow the direct injection of the sample into the heated oxidation zone of the furnace. The combustion tube must have side arms for the introduction of oxygen and carrier gas.

- 3.3 Flow controllers: The instrument must be equipped with flow controllers capable of maintaining a constant supply of oxygen and carrier gas.
- 3.4 Drier tube: The instrument must be equipped with a membrane drying tube for the removal of water vapor. The oxidation reaction products include water vapor which must be eliminated before the sample is measured by the detector.
- 3.5 Chemiluminescence detector: The chemiluminescence detector is a quantitative detector capable of measuring light emitted from the reaction between NO and ozone.
- 3.6 Microlitre syringe: The microlitre syringe that is used in the autosampler should be capable of accurately delivering 1 to 50 uL quantities. The needle should be long enough to reach the hottest portion of the inlet section of the furnace when injecting the sample.
- 3.7 Direct Injection autosampler, capable of automated injecting sample from 1 ul to 50 ul at a uniform speed of 0.2 to 1.0 ul/s with capacity of 50 or more positions.
- 3.8 Data system: The data system should provide autosampler control, sample identification, calculation, statistics, and disk storage of results for data manipulation.

4 Reagents and Materials

- 4.1 Solvent: Isooctane, Reagent grade.
- 4.2 Calibration Standards: Suggested compounds used to prepare the nitrogen standards are either one of the following:
 - Pyridine, FW 79.10, Reagent grade.
 - Carbazole, FW 167.21, Reagent grade.
- 4.3 Quality Control Sample: ASTM Round Robin diesel sample with a nitrogen range of 5 – 100 mg/kg (ppm).
- 4.4 Carrier gas: Argon or helium, ultra-high purity grade, 99.998% minimum purity.
- 4.5 Oxidizing reagent: Oxygen, ultra-high purity grade, 99.998% minimum purity.

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5 Calibration Standards Preparation

5.1 NITROGEN STOCK SOLUTION, 1350 mg/kg (ppm) N

5.1.1 Prepare a stock solution gravimetrically by accurately weighing either 1.195 g of Carbazole or 0.565 g of Pyridine into a tared 100 mL volumetric flask. If using Carbazole, dissolve the Carbazole with approximately 50 mL isooctane. Add isooctane to the mark on the flask and weigh. This solution may be diluted to desired nitrogen concentrations.

5.1.2 Working standards should be prepared on a regular basis depending upon frequency of use and age.

5.2 CALIBRATION RANGE

5.2.1 Prepare a series of at least FIVE calibration standards by making dilutions of the stock solution to cover the range of operation. Calibrate the analyzer as per manufacturer's instructions using the average response of three injections for each standard. The calibration curve should be linear and the accuracy must be verified with a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) or a NIST traceable certified reference material (CRM), and a quality control (QC) sample (see Quality Control Section 8.3). The following is a table of the suggested calibration curves.

Curve I Nitrogen, mg/kg (ppm)	Curve II Nitrogen, mg/kg (ppm)
1.00	10.00
10.00	50.00
25.00	100.00
50.00	250.00
100.00	500.00
	1350.00
Suggested injection size 40 microliters	Suggested injection size 20 microliters

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6 Procedure

- 6.1 Fuel samples are collected in glass bottles or metal canisters and delivered to the laboratory.
- 6.2 The calibration standards and fuel samples are transferred into autosampler vials.
- 6.3 A typical calibration curve run on the instrument shall be similar to Curve II.
- 6.4 Sample injection size of 3 ul to 40 ul is acceptable. It is advisable that the size of injected sample be the same as the injected standards. All samples shall be run in triplicate to obtain the average value.
- 6.5 All samples are drawn from vials by the autosampler equipped with a clean microliter syringe, and injected into the heated combustion tube. The syringe should be pre-cleaned and flushed with the sample to be determined.
- 6.6 If the detected result of a sample is over the calibration range, it shall be diluted by the appropriate factor to get it within the range of the calibration curve.

6.7 INSTRUMENT OPERATING CONDITIONS

- 6.7.1 Analyzer Operating Conditions: Different manufacturer recommends different operating conditions. Follow the advice of the manufacturer of the analyzer for the optimum settings of temperatures and flow rates of gases.
- 6.7.2 Autosampler Operating Conditions: Different manufacturer recommends different optimum operating conditions. Follow the advice of the manufacturer of the autosampler for the operating conditions.
 - 6.7.2.1 Rate of injection is dependent on such factors as viscosity, hydrocarbon type, and nitrogen concentration. It is advisable that the injection speed be at a uniform rate 0.2 to 1.0 uL/s.

7 Calculation of Results

- 7.1 The nitrogen concentrations, given in mg/kg (ppm), are calculated by the data system using external multipoint calibration standards. The area count measured from the sample is compared to the area counts measured from the multipoint calibration.

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- 7.2 Check each run for proper integration of the nitrogen peak. If necessary, omit the outlier from the triplicate runs.
- 7.3 The result of the nitrogen concentration needs to be corrected for density. The densities of isooctane and of the sample are measured. The formula to calculate the corrected nitrogen concentration in mg/kg (ppm) is shown below:

$$\text{Nitrogen, mg/kg (ppm)} = A \times B / C$$

where: A = Average result from the triplicate runs
B = Density of isooctane
C = Density of the sample

8 Quality Control

8.1 BLANK ANALYSIS

- 8.1.1 A sample of isooctane is used as a blank and analyzed daily to check the analytical system for contamination. If the blank analysis shows an area count greater than the 1 ppm standard for the low-level nitrogen or 10 ppm standard for the high-level nitrogen, the blank analysis should be repeated.
- 8.1.2 If the blank still shows nitrogen content greater than 1 ppm or 10 ppm, the system should be checked for possible contamination or soot accumulation in the analyzer system. The contamination sources must be eliminated, and the blank shows nitrogen content is below the detection limit before any sample can be analyzed.

8.2 CALIBRATION STANDARDS ANALYSIS

- 8.2.1 Calibration standards are prepared as needed. It is estimated that the standards will maintain a shelf life of about one year. This depends on how often the standards are uncapped. Working standards are stored in the refrigerator.
- 8.2.2 The nitrogen analyzer needs to be calibrated at least once a year and as needed when the NIST traceable CRM or QC samples are out of control. The calibration curve should be verified with a NIST traceable CRM and a QC sample. The r of least square fit of the calibration must be 0.995 or greater.

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- 8.2.3 If the NIST traceable CRM result fails its acceptable range, or r^2 falls below 0.995, the instrument system should be checked for possible malfunction and may require maintenance. The calibration should then be rerun.

8.3 CONTROL SAMPLE ANALYSIS

- 8.3.1 The QC sample shall be an ASTM round robin diesel sample that contains nitrogen at the appropriate level.
- 8.3.2 The QC sample is analyzed at the beginning of the sample set, after every ten samples, and at the end of the sample set. For the screening purposes with a single injection analyses the QC sample is analyzed at the beginning of the sample set, after every 25 samples and at the end of the sample set.
- 8.3.3 A control chart is maintained for the QC sample results. The upper and lower warning limits are set at two standard deviations ($\pm 2s$). The upper and lower control limits are at three standard deviations ($\pm 3s$).
- 8.3.4 A QC sample is out of control when the measured value of nitrogen exceeds the 3s limit or when two successive measurements of the control sample exceed the 2s limit.
- 8.3.5 If the QC sample is out of control, the instrument must be recalibrated.

8.4 REPLICATE ANALYSIS

- 8.4.1 A replicate analysis is performed at least once per day, after every ten samples, and/or at the end of the sample set when at least 5 samples are run. For a single injection screening analyses a replicate run is performed at least once per day, after every 25 samples, and/or at the end of the sample set when at least 10 samples are run. It is recommended to run the replicate immediately after the original sample. A control chart is maintained for the replicate analysis.
- 8.4.2 If the difference of replicate results is greater than 50% of the reproducibility specified in the ASTM Method D 4629-96, the replicate analysis should be repeated. If the closest two values of the three replicate analyses still show a difference greater than 50% of the reproducibility, steps should be taken to determine and correct the cause of the problem. All samples for the day from this instrument must then be reanalyzed.

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8.5 LIMIT OF DETECTION

8.5.1 The limit of detection (LOD) is determined annually from multipoint calibration data. The low level calibration curve is used to determine a linear regression.

$$\text{LOD} = (|b| + 3.3 \times s) / m$$

where: b = intercept
 s = standard deviation of the lowest concentration
 m = slope

8.5.2 The LOD must be less than or equal to 10.0 ppm.

9 Safety Precautions

- 9.1 Fuels and solvents may be harmful or fatal if ingested or inhaled.
- 9.2 All fuels and solvents should be treated as extremely flammable and explosive.
- 9.3 Prepare fuel samples and standards under a fume hood.
- 9.4 Wear safety glasses and disposable gloves when handling fuels or solvents.

10 References

- 10.1 ASTM D 4629-96, "Standard Test Method for Trace Nitrogen in Liquid Petroleum Hydrocarbons by Syringe/Inlet Oxidative Combustion and Chemiluminescence Detection"

11 Revision History

11.1 Revision No. 1.2 Effective:

Significant changes:

Section 8.4.1 modified to require replicate analysis only when more than 5 samples are run.

11.2 Revision No. 1.3 Effective: September 9, 2010

Significant Changes:

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8.5.2- modified to require LOD to be less than or equal to 10 ppm. Based on historic data and current regulation (CCR Title 13, Section 2282 g2), 10 ppm is appropriate.

11.3 Version 2.0 Effective: March 1, 2017

Significant Changes:

Removed all of the trade names of commercial products throughout the procedure.

11.4 Version 2.1 Effective: December 1, 2019

SOP format updated for ADA compliance