

California Environmental Protection Agency
 **Air Resources Board**

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

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FUEL ANALYSIS AND METHODS EVALUATION SECTION
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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 100 mg/kg total nitrogen.
- 1.4 This procedure is based on ASTM D 4629.

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 in an oxygen rich atmosphere. The water produced during the sample combustion is removed and the sample combustion gases are then exposed to ultraviolet (UV) light.
- 2.2 The NO contacts ozone and is converted to excited nitrogen oxide. 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-- Mitsubishi model TS-100V, or equivalent, should be equipped with an electric furnace capable of a maximum temperature of 1100 degrees Celsius.
- 3.2 Combustion tube--The instrument must be equipped with a quartz 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 Detector--The chemiluminescent detector is a qualitative and quantitative detector capable of measuring light emitted from the reaction between NO and ozone.
- 3.6 Microlitre syringe--Mitsubishi model TS-100V or equivalent-- The microlitre syringe that is used in the autosampler should be capable of accurately delivering 25 to 40 uL quantities. The needle should be 50 mm (+/- 5 mm) long.
- 3.7 Direct Injection--Mitsubishi model ASC-150L Autosampler, or equivalent.
- 3.8 Data system--Mitsubishi TS-100V Software or equivalent. System should provide autosampler control, sample identification, concentration, 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 are Pyridine, FW 79.10 or Carbazole, FW 167.21.
- 4.3 Quality Control Sample—ASTM Diesel samples with a nitrogen range of 5 – 100 ppm.
- 4.4 Carrier gas--Argon or helium, high purity grade (chromatography or zero grade), 99.998% minimum purity.
- 4.5 Oxidizing reagent--Oxygen, high purity grade (chromatography or zero grade), 99.75% purity.

5 Calibration Standards Preparation

- 5.1 NITROGEN STOCK SOLUTION, 1350 ppm N
 - 5.1.1 Prepare a stock solution gravimetrically by accurately weighing either 1.1 g of Carbazole or .53 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.

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

5.2 CALIBRATION RANGE

5.2.1 Calibration Range for Mitsubishi TS-100V or equivalent.

5.2.1.1 Prepare a series of 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 for each standard. This curve should be linear and the instrument performance must be checked with the Q.C. sample (see Quality Control Section 8.3). The following is a table of the suggested calibration curves.

Curve I Nitrogen, ppm	Curve II Nitrogen, ppm
1.00	10.00
10.00	50.00
25.00	100.00
50.00	250.00
100.00	500.00
	1350.00
Injection size 40 microliters	Injection size 40 microliters

6 Procedure

- 6.1 Fuel samples are collected in bottles or metal canisters and delivered to the laboratory.
- 6.2 The calibration standards and fuel samples are transferred into autosampler vials.
- 6.3 The initial calibration curve run on the instrument shall be similar to Curve II.

- 6.4 Samples shall be run in triplicate to obtain the average value.
- 6.5 If the average value of a sample is above that dictated by its predictive value, it shall be diluted by the appropriate factor to get it within the range of Curve I. The instrument shall be recalibrated using Curve I and the diluted sample shall be run in triplicate to obtain the average value.
- 6.6 A sample is drawn from the vial by the autosampler and is run in triplicate to obtain the average value.

6.4 TYPICAL INSTRUMENT OPERATING CONDITIONS

- 6.4.1 Typical Instrument Operating Conditions—Mitsubishi TS-100V or equivalent:
 - Furnace Temperature (Inner): 1075 C
 - Furnace Temperature (Outer): 850 C
 - Main Oxygen Setting: 400 mL/min.
 - Main Argon Setting: 350 mL/min
 - Auxiliary Oxygen Setting: 150 mL/min.
 - Auxiliary Argon Setting: 150 mL/min.
 - Ozone Setting: 350 mL/min

Calibration Curve I or similar – Sensitivity set at High

Calibration Curve II or similar – Sensitivity set at Low

6.5 TYPICAL AUTOSAMPLER OPERATING CONDITIONS

- 6.5.1 Typical Autosampler Operating Conditions—Mitsubishi TS-100V
 - Syringe drive: 1.2 uL/s
 - Sample injection volume is 40 uL.

7 Calculation of Results

- 7.1 The nitrogen concentrations, given in 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.
- 7.2 Check each run for proper quantification 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 concentration in ppm is shown below:

$$\text{ppm} = \frac{A \times B}{C}$$

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 5 ppm standard for the high-level nitrogen, the blank should be repeated. If the blank still shows nitrogen content greater than 1 ppm or 5 ppm, the contamination sources must be corrected before analyzing samples. The system should be checked for possible saturation or soot accumulation.

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. The calibration is run as needed and should be linear. The r of least square fit must be 0.999 or greater. If it falls below 0.999, the calibration should be rerun and/or the instrument should be checked for possible malfunction or required maintenance.

8.3 CONTROL SAMPLE ANALYSIS

- 8.3.1 The control 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 control sample is analyzed at the beginning of the sample set, after every 20-25 samples and at the end of the sample set. A control chart is maintained for the control sample. 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 ($\pm 3s$).
- 8.3.2 A control 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. If the QC sample is out-of-control, the calibration and QC sample must be

rerun. If the control sample continues to be out-of-control, determine the cause of the problem before analyzing any samples.

8.3.3 The QC sample shall be an ASTM round robin diesel sample that contains nitrogen at the appropriate level.

8.4 REPLICATE ANALYSIS

8.4.1 A replicate analysis is performed after every ten samples and/or at the end of the sample set when at least 6 samples are run. For a single injection screening analyses a replicate run is performed at least once per day and after every 20-25 samples. It is recommended to run the replicate immediately after the original sample. A quality control chart is maintained for the replicates.

8.4.2 If the difference is greater than 50% of the reproducibility specified in the method D 4629 the sample should be repeated. If the closest two values of the three analyses still show a difference greater than 50% of the reproducibility, all samples for the day from this instrument must be reanalyzed. Steps should be taken to determine the cause of the problem.

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.

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

where:

b = intercept

m = slope

s = standard deviation of the lowest concentration

8.5.2 The L.O.D. must be less than or equal to 10.0 ppm.

9 **Safety Precautions**

9.1 Prepare fuel samples and standards under a fume hood.

9.2 Wear safety glasses and disposable gloves when handling fuels or solvents.

9.3 Fuels and solvents may be harmful or fatal if ingested or inhaled.

9.4 All fuels and solvents should be treated as extremely flammable and explosive.

10 References

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

11 Revision History

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

11.2 Revision No. 2 Effective: 9/9/2010

Significant Changes: 8.5.2- modified to require L.O.D. 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.