

# EPA Method 8270D—Calibration Curve Development and DFTPP Tuning by GC-TOFMS

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**Key Words:** Pegasus® HT, GC-TOFMS, Linearity, DFTPP abundance criteria

## 1. Introduction

EPA Method 8270D for the analysis of semivolatiles presents demanding challenges in method compliance, sensitivity, and productivity for environmental laboratories. Stringent guidelines are set for the DFTPP Tune abundance criteria and daily calibration verification. This study demonstrates the ability of the LECO Pegasus® HT GC-TOFMS instrumentation to meet tuning criteria and calibration curve linearity requirements. A fast analysis runtime of 10.1 minutes is achieved, while maintaining a sensitive and robust linear calibration concentration range from 200 pg to 160 ng. The 80 compound calibration standard mixture contains 10 calibration check compounds (CCC's), 6 internal standards, 8 surrogate standards, 4 system performance check compounds (SPCC's), and 52 analytes. This application illustrates the advantages of using GC-TOFMS and the advanced LECO ChromaTOF® software for semivolatiles analysis in environmental laboratories.

## 2. Instruments and Methods

This application was conducted with a LECO Pegasus HT time-of-flight mass spectrometer (TOFMS). The Pegasus HT TOFMS was equipped with an Agilent 6890 gas chromatograph and autosampler. LECO ChromaTOF software was used for all instrument acquisition, calibration curve development and data reduction.

A 10 m x 180 µm id. x 0.18 µm film thickness, Restek Rtx 5-SilMS capillary column was used for the chromatographic separation. The GC was operated with Helium carrier gas at a constant flow of 2 mL per minute. A 1 µL split mode injection for each standard was made at a 50:1 split ratio. The chromatographic temperature program was made at an initial temperature of 40°C for 0.10 minutes then ramped at 30°C per minute to 340°C with no hold time for a total analysis runtime of 10.1 minutes. The MS transfer line temperature was set to 280°C. The MS mass range was set from 35 to 500 amu with an acquisition rate of 20 spectra per second. The ion source chamber was set to 250°C. The detector voltage was at 1650V and the electron energy at -70eV.

The samples were prepared from Restek EPA Method 8270 environmental standards. Serial dilutions were performed to make 10 calibration standards which were injected at 200 pg, 500 pg, 1 ng, 5 ng, 10 ng, 20 ng, 50 ng, 80 ng, 100 ng, 120 ng, and 160 ng on column.

The acquired data was automatically processed through ChromaTOF software using a user defined Data Processing Method. Data review was performed on a midpoint standard and subsequently the Calibration Table was developed in the Calibration portion of the ChromaTOF software. All peak assignments, integrations,

minimum average response factors, and percent standard deviation values of relative response factors were examined to meet EPA criteria.

The linearity and low end activity EPA requirements are:

- Minimum Average RF of 0.050 for the System Performance Check Standard (SPCC's) (Method 8270, section 7.3.4.2)
- Percent Relative Standard Deviation of the Relative Response Factor for Calibration Check Compounds (CCC's) less than 30% (Method 8270, section 7.3.5.2)
- Percent Relative Standard Deviation of the Relative Response Factor for all target analytes is less than 15%. (Method 8270, section 7.3.5.2)

A Decafluorotriphenylphosphine (DFTPP) tune was conducted on the Pegasus HT that meets the LECO recommended manufacturer specifications for abundance criteria in compliance with section 11.3.1.2 of Method 8270D. A 1 µL injection of DFTPP at 10 ng is shown in the results section as a ChromaTOF Tune Report.

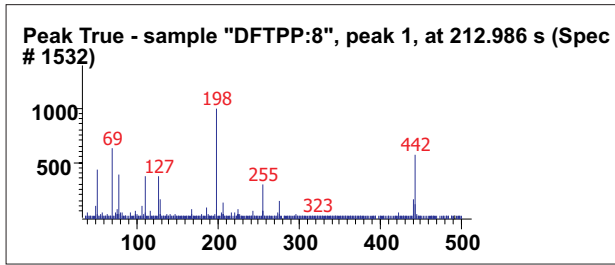
## 3. Results

The goals of this application were to meet the rigorous guidelines set by EPA Method 8270 for the DFTPP Tune and Calibration criteria. The DFTPP Tune utilizes the LECO recommendations for primary tuning acceptance criteria. The DFTPP tune criteria are accepted by EPA through an alternative test procedure (ATP\*) for LECO GC-TOFMS instruments. Method 8270D states in section 11.3.1 that the mass spectrometer system must be hardware tuned by injection of 50 ng or less of DFTPP which meets the manufacturers specified acceptance criteria. The DFTPP Tune Report Table and mass spectrum shown below illustrates that the Pegasus HT TOFMS effectively passes the mass abundance requirements.

### DFTPP TUNE CHECK REPORT

Sample Name: DFTPP: 8      Date: 8/29/07  
Time: 2:11:51PM      Result: Passed

Mass	Criteria	Relative Abundance	Pass/Fail
51	>10.00% and <85.00% of Base Ion	43.42	Passed
68	<2.00% of mass 69	1.68	Passed
70	<2.00% of mass 69	0.48	Passed
127	>10.00% and <80.00% of Base Ion	37.05	Passed
197	<2.00% of mass 198	0.43	Passed
198	Base Ion	100.00	Passed
199	>5.00% and <9.00% of mass 198	6.83	Passed
275	>10.00% and <60.00% of Base Ion	13.93	Passed
365	>0.50% of mass 198	1.22	Passed
441	<150.00% of mass 443	133.81	Passed
442	>30.00% of mass 198	56.81	Passed
443	>15.00% and <24.00% of mass 442	21.12	Passed

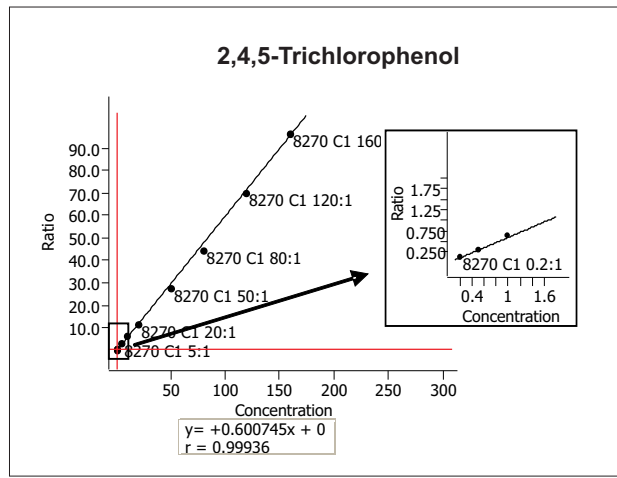


Calibration curve development utilized ChromaTOF software which automatically calculates the AvRF (Average Response Factor), and %RSD RF (Percent Relative Standard Deviation of the Average Response Factor). Excellent linearity was obtained from the %RSD of the RF's calculated in the ChromaTOF software. All Calibration Check Compounds (CCC's) met the <30% RSD of the criteria as stated in Method 8270 (section 7.3.5.2) at the full calibration concentration range of 200 picograms to 160 nanograms. The percent RSD RF values for all CCC's exceeded EPA criteria with % RSD RF's of less than 20%. This validates the high integrity of the chromatographic system.

Minimum system performance was determined for the four active compounds specified in Method 8270 as System Performance Check Compounds (SPCC's). The average RRF value for each component must be greater than 0.05. All components listed below exceed the limits set in the method.

SPCC	Average RRF
N-nitrosopropylamine	1.023
Hexachlorocyclopentadiene	0.452
2, 4-Dinitrophenol	0.199
4-Nitrophenol	0.447

All target analytes maintained excellent linearity meeting EPA percent RSD requirements of less than 15% as stated in section 7.3.5.2 of Method 8270. Shown below is an example of a calibration curve for 2,4,5-Trichlorophenol generated by ChromaTOF in the Calibration portion of the software. The linearity of the calibration curve is observed with a correlation coefficient of 0.99936 over a dynamic concentration range of 200 pg to 160 ng.



#### 4. Conclusions

The analytical study conducted on the LECO Pegasus HT TOFMS clearly demonstrates a fast, robust GC-TOFMS method for the analysis of EPA Method 8270D. All of the linearity and tune requirements for EPA methodology were completely met or exceeded. Environmental laboratories experience rigorous challenges for meeting the demands of increasing productivity. This application shows that the Pegasus HT TOFMS can provide a faster analysis, higher acquisition rate, rugged system integrity, increased linear dynamic range, and user efficient software for EPA Method 8270D semivolatiles analysis.

*\*Alternative Test Procedure (ATP letter 2-9-05) (ATP case numbers D04-002 and N04-002). [See EPA APPROVAL LETTER at [www.leco.com](http://www.leco.com)]*

*\*\*This application was conducted to meet and exceed the requirements of the current EPA Method 8270D and previous version EPA Method 8270C.*

