Standard Operating Procedure for:

Analysis of Petroleum-Range Organics by GC-FID (FL-PRO-2018 Method)

DEPARTMENT OF ENVIRONMENTAL PROTECTION
CHEMISTRY SECTION
TALLAHASSEE FLORIDA

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

CONTENTS

1. SCOPE AND APPLICATION

2. SUMMARY OF THE METHOD

3. APPARATUS AND EQUIPMENT

4. REAGENTS AND CHEMICALS

5. SAMPLE PREPARATION PROCEDURE

6. SAMPLE ANALYSIS/QUANTITATION

7. RESULTS CALCULATION

8. REPORTING AND DOCUMENTATION

9. DATA ARCHIVAL

10. QUALITY CONTROL

11 SAFETY/HAZARDOUS WASTE MANAGEMENT

12. DETERMINATION OF METHOD DETECTION LIMITS:

13. REFERENCES

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

1. SCOPE AND APPLICATION

1.1 This method describes the analysis of Petroleum-Range Organics (FL-PRO-2018 Method, Ref 13.1). Extracts from water, sediment and waste samples (DEP SOP SV-004, ref. 13.2) are analyzed by GC-FID for the LIMS test ID: W-FL-PRO, S-FL-PRO, WAS-FL-PRO and SPLP-FLPRO.

1.2 In Florida Department of Environmental Protection's *Method for determination of Petroleum Range Organics* (FL-PRO-2018), the concentration of Petroleum Hydrocarbons of range C_8-C_{40} (normally gasoline through motor oil) is measured in water, soil/sediment and waste samples using Gas Chromatography with Flame Ionization Detection (GC-FID).

1.3 Petroleum Hydrocarbons: All chromatographic peaks, both resolved and unresolved, eluting between the peak start of n-octane (n-C_8) and the peak end after n-tetracontane (n-C_{40}). Quantitation is based on direct comparison of the area within this range to the total area of the Petroleum Hydrocarbon standard as determined from FID response using baseline - baseline integration.

1.4 Petroleum Hydrocarbon Standard: A 17-component mix of all even-numbered normal alkanes from C_8 to C_{40} (Table 1). This standard serves as a quantitation standard and a retention time window defining Petroleum Hydrocarbons. Other organic compounds, including chlorinated hydrocarbons, phenols, phthalate esters as well as biodiesel fuels are also measurable. As defined in the method, the Petroleum Range Organics method results include these compounds. Biodiesel fuels will typically elute shortly after the o-terphenyl surrogate, as a cluster of several sharp peaks.

Animal and vegetable oil and grease may also be partially measurable if the sample is not cleaned up before analysis, and the method prescribed integration window is applied. In those cases, the peaks that would typically elute in the C8 to C40 range are usually some minor impurities or decomposition products. Animal fats and vegetable oils are mixtures of fatty acid triglycerides, which have much higher boiling points than the TRPH range. They can only be eluted when using high temperature GC columns and injector/column temperatures as high as 380C. In order to eliminate false positives from these sources, **the silica cleanup (9.1.6) is a mandatory part of this procedure**. However, one needs to always consider the possibility that large concentrations of fats and oils may overwhelm the silica cleanup cartridge and still make it into the final extract. A variety of biogenic materials may also be extracted by the procedure. That includes various terpenes as well as plant oils and waxes that are often present in vegetation rich soils. Other natural organics that may be measured are long chain carboxylic acids (fatty acids), and steroids such as cholesterol. Lastly, not all petroleum range hydrocarbons always originate from petroleum products. Some background levels of various hydrocarbons are to be expected in certain organic rich formations like peat moss or other accumulations of partially decayed vegetation.

1.5 Petroleum Source / Petroleum Products Identification Standards: Various commercial petroleum products are used to qualitatively identify petroleum product types in the samples by direct visual comparison of chromatographic profiles. These standards may be purchased from vendors or obtained from commercial sources. If the sample is suspected to be a crude oil, the sample can be further analyzed, if necessary, by GC/MS analysis. Direct visual comparison of extracted ion chromatograms of reference oils or a known crude oil source may be compared to the spilled oil sample in GC/MS analysis (refer to DEP SOP SV-006, ref. 13.3).

2. SUMMARY OF THE METHOD

2.1 For FL-PRO, 500 mL of water or 25 g of sediment or 1 g of waste sample is spiked with two surrogates, extracted with methylene chloride, and concentrated to 1 mL final volume for water or 2 mL final volume for sediments and waste samples. The entire extract for water and half of the extract for sediments/waste is cleaned up with silica gel to remove potential organic interference. A 1 µL aliquot of the final extract is injected onto a capillary gas chromatography instrument

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

equipped with a flame ionization detector (GC-FID). Quantitation of the sample extracts is based on the detector response compared to a series of normal alkane standards, using a baseline-to-baseline integration over the C_8 to C_{40} compound range.

3. APPARATUS AND EQUIPMENT

3.1 Bottles -- 25 mL, amber glass with Teflon-lined screw caps.

3.2 Auto sampler vials -- 2 mL, with Teflon-lined septa top, to fit the Agilent 7683 auto sampler.

3.3 GC-FID system: Gas chromatography, Shimadzu GC-2010 GC system (dual FID)

GC-FID Operating Conditions: (this serves as guideline only; different instrument may have different settings)

Parameter	Setting
Analytical Column	Restek - Rtx-5 30 m x 0.25 mm x 0.25 µm (or equivalent)
GC Oven Temperature Program:	50 °C for 3 min., to 320 °C at 22 °C /min. and hold for 14.73 min. Run Time = 30 min.
Inlet:	Temp: 275 °C; Mode: Splitless; Starting pressure 13.9 psi. Constant linear velocity 29 cm/s, 17.15 psi at 50 °C (1.6 mL/min); Purge Time ON: 2.0 min. Purge Flow: 50 mL/min. Purge Time OFF: 0.0 min. Injection Volume: 1 µL; Total Flow: 53.8 mL/min. Septum Purge: 2.0 mL/min. Gas saver: ON, Saver Flow: 25 mL/min.
Detector:	Temp: 250 °C; H2 at 40 mL/min., Air at 450 mL/min. & Aux Gas at 45 mL/min.

3.4 Helium, UPC grade, is the carrier gas in the gas chromatographs. The helium must be passed through an oxygen filter before entering the gas chromatographs.

3.5 Data system: A computer with chromatographic data system must be interfaced with the chromatographic detector. The chromatographic data system must allow continuous acquisition and storage of all chromatographic data obtained throughout the run sequence, and subsequent data processing. Shimadzu GC-2010 GC/FID data is collected using Shimadzu's LabSolutions software. The LabSolutions data is output in the .CDF format that is amenable to the Masshunter conversion. Those data files are converted using Agilent's GCMS Translator, using the AIA option ("translate ANDI/CDF files"). Converted data is then processed using the Masshunter software (GC version).

4. REAGENTS AND CHEMICALS

NOTE: Record Lot Numbers of all the reagents and solvents used in the Notebook

4.1 Solvent: methylene chloride (GC-Resolve grade), carbon disulfide (spectra-analyzed), and acetone (HPLC grade).

4.2 Stock Standard Preparations: Primary and secondary stock standards are available in pre-made mixtures.

5. SAMPLE PREPARATION PROCEDURE

5.1 Refer to TRPH Extraction SOP SV-004, Ref 13.2.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

5.2 All extracts must be analyzed within 40 days of extraction.

6. SAMPLE ANALYSIS/QUANTITATION

6.1 **Initial Calibration for FL-PRO**: Calibration standards are prepared in Methylene Chloride at following concentration levels: 425, 850, 1700, 2550, 3400, 5100, 6800 mg/L for TRPH and corresponding individual surrogate concentrations of 10, 25, 50 ,100, 150, 175, 200 mg/L. Calibration curve for surrogates is recommended, but not required. If the calibration curve for surrogates is not constructed, then the calibration response for surrogates must be established at the same concentration as the spiking level. (100 ppm for each surrogate). Freshly prepared calibration standards are given six months expiration dates. The external standard calibration technique is used for quantifying TRPH. The standard deviation for the response of the calibration standards must be within 20 % to ensure that the standard concentrations are within the linear range of the calibration curve. If the average response factor cannot be used, then a linear regression shall be calculated. The correlation coefficient shall be equal or greater than 0.995, 0.990 for quadratic fit. To use a quadratic fit a minimum of six calibration levels is required. In all cases, response of the standards must be determined by continuous integration of all responses (**excluding surrogates**) from a forced baseline beginning at a point prior to the elution of the compound C_8 to a point beyond the compound $C_{40.}$ **The selection of the time interval should be based on injection of appropriated pattern recognition standards and must be constant for all standards and samples.**

6.2 **Calibration Factor for FL-PRO**: Determine the area response of the 17 hydrocarbon components and calculate the calibration factor for each level as the ratio of area of standard mix against the mass injected:

$$\text{Calibration Factor} = \frac{\text{Total PHS Area}}{\text{Total PHS mass injected (ng)}}$$

PHS: Petroleum Hydrocarbon Standard

PHS Area: Response as integrated in 6.1.

Total PHS: Refers to the sum of the concentration of the individual components.

6.3 **Initial and Continuing Calibration Verification**: The accuracy of the initial calibration must be verified by injecting a midpoint concentration standard (Initial Calibration Verification, ICV) solution that was obtained from a different source (different vendor). The calculated value shall be within +- 25% of expected value. Additionally, the working calibration factor or calibration curve must be verified on each working day before the analysis started (if the calibration curve is not established on the day) by the injection of a continuing calibration verification standard (CCV) at 2550 mg/L total TRPH concentration). This standard must be evaluated prior to the analysis of any samples.

6.3.1 If the response for this standard varies from the predicted response be more than ± 25%, a new initial calibration curve must be prepared and verified before samples are analyzed.

$$\text{Percent Difference} = \frac{(R_1 - R_2)}{R_1} \times 100$$

R_1: Average CF from the initial calibration curve or standard response from initial calibration curve

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

R_2: Calibration Factor from CCV or standard response from CCV

In addition, a calibration check standard (CCV) must be analyzed every 12 hrs or less and at the end of each analysis sequence. Evaluate the continuing calibration response. If the performance criteria fail, then the instrument must be recalibrated, and all of the samples injected after the failed check sample must be reanalyzed.

6.3.2 The retention time window for the surrogates and the compounds C_8 and C_{40} shall be within the established range. If they are out of the acceptance range, then a new initial calibration must be prepared and verified before samples are analyzed. Usually, after maintenance (e.g. cutting the injector end column, cleaning or changing detector jet) the retention times and sensitivity will change and will require that a new initial calibration curve be prepared.

6.4 Samples are analyzed by GC/FID using conditions established in 3.3.

6.5 A methylene chloride blank must be analyzed at the beginning of every analysis sequence to determine the area generated from normal background under the conditions used. The calculated concentration should be 5 times less than the MDL. Baseline subtraction is not necessary and is not recommended.

6.6 Qualitative Identification (Pattern Recognition): The laboratory may qualitatively identify the petroleum products when reporting data by direct comparison of sample chromatograms to retention times and peak patterns of known petroleum standards or a petroleum source. The experience of the analyst weighs heavily in the interpretation of the chromatogram. Because of weathering, the patterns may not be a perfect match; however, the characteristics of a petroleum hydrocarbon pattern must be present. Environmental samples may contain more than one type of product, and loss of light-end components may mean the product has been in the subsurface a longer period of time. Qualitative information may be reported on the final laboratory report. This information should include an alkane range. If possible, product identification should be included and may be based on the individual laboratory's chromatograms of commercial petroleum products (e.g., diesel fuel, motor oil, etc.). If the sample is suspected to be a crude oil, the sample can be further analyzed, if necessary, by GC/MS analysis. Direct visual comparison of extracted ion chromatograms of reference oils or a known crude oil source may be compared to the spilled oil sample in GC/MS analysis (refer to DEP SOP SV-006, Ref. 13.3).

7. RESULTS CALCULATIONS:

7.1 The integrated area for each component peak (including surrogates) eluting from n-octane through n-tetracontane shall be determined using a valley-to-valley integration baseline.

7.2 Calibration factor for FL-PRO:

$$Cs = \frac{(Ax)\,(Ve)\,(D)}{(CF)\,(Inj)\,(Vs)}$$

Where:

Cs = Concentration of Petroleum Hydrocarbons (mg/L or mg/kg)

Ax = Response for the Petroleum Hydrocarbons in the sample (baseline to baseline integration subtracting the area of surrogates), units in area

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

Ve = Volume of final extract (mL)

D = Dilution factor, if dilution was performed on the sample prior to analysis. If no dilution was made, D = 1, dimensionless

CF = Average Calibration Factor from initial calibration (See 6.2)

Inj = Volume of injected sample (µL)

Vs = Volume of sample extracted in ml or weight of sample in grams

7.3 Dry weight determination:

$$\text{mg/dry kg PH} = \frac{Cs}{1 - (\%\text{moisture}/100)}$$

Where:

Cs = Concentration of Petroleum Hydrocarbons (mg/L or mg/kg)

7.4 Calculation of recoveries (FL-PRO):

7.4.1 The surrogate, Lab Fortified Blank (LFB) and Matrix spikes recoveries in each sample must be calculated. The peak areas obtained should be based on a valley-to-valley integration.

7.4.2 If the surrogate, LFB or Matrix spike recovery is outside of established limits, then the results must be flagged, and a comment provided.

7.4.3 A comment must be added to the qualified data in the final report explaining any deviation from the routine limits whenever the spikes or surrogates are out of range (DEP SOP LB-027, Ref.13.4).

7.4.4 Check the method blank for any interfering contaminants. The MDLs may have to be elevated if the blank(s) indicate contamination.

7.5 Determination of recovery limits.

To determine the acceptance accuracy limits for surrogates, LFBs and Matrix spikes the following procedure should be used :

(1) for each sample/QC sample analyzed, calculate the percent recovery for each QC type in the sample,

(2) once a minimum of twenty data points (preferably more) of the same matrix has been analyzed, calculate the average percent recovery (p), and standard deviation of the percent recoveries (s), for each of the QC types,

(3) for a given matrix, calculate the upper and lower control limit for method performance for each QC type as follows:

Upper Control Limit (UCL) = p + ts
Lower Control Limit (LCL) = p – ts

where “t” stands for Student’s coefficient for n-1 degrees of freedom (n = number of measurements), 99% confidence level, two-sided statistics.

Compare the calculated recovery limits with the tables below. If the calculated limits are more stringent than the limits given in the tables, use the calculated limits to assess

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

recoveries in routine samples. However, if the calculated limits are not as stringent as the limits in the tables, then the table limits apply.

Compound & Matrix	Acceptance limits %
Ortho-Terphenyl - Water	66-139
Nonatriacontane_Water	40-129
Ortho-Terphenyl_Soil	66-136
Nonatriacontane_Soil	36-132
Ortho-Terphenyl_Waste	61-138
Nonatriacontane_Waste	27-141

Compound & Matrix	% Rec	RPD
TRPH_LFB_Water	–66-119	< 20
TRPH_LFB_Soil	–65-119	< 25
TRPH_LFB_Waste	70-114	<25
TRPH_MS_Water	65-123	< 20
TRPH_MS_Soil	39-181	< 25
TRPH_MS_Waste	14-197	<25

The control limits are supposed to be checked and updated at least once per year if enough measurements have been conducted.

8. REPORTING AND DOCUMENTATION

8.1 When analysis is complete, the QC Manager is used to download the final sample results into the Laboratory Information Management System (LIMS). If a sample has been diluted, then make sure that the information was entered properly into the QC Manager.

8.2 Add the appropriate qualifiers and comments to the sample data in the QC Manager after performing a complete review of the sample data and QC data. Follow DEP SOP GC-001, Ref. 13.5, for details of data review and reporting. See DEP SOP LB-027, Ref. 13.4, for guidelines for qualifying data when quality control results are outside established control limits and re-analysis is not a viable or desired option.

8.3 Definitions of the available qualifying codes are listed in DEP SOP LB-027.

8.4 All quantitation reports for samples and QC should be placed in a results folder labeled with the job number, the sample numbers, and the type of analysis.

8.5 Retrieve the field folders (containing the field sheets) and check the data against the field sheets to see if it makes sense (i.e., does the equipment blank contain a hit while an effluent sample does not?) If anything looks suspicious, further research is necessary before posting results.

8.6 Enter the results for each sample in the analysis results form. Print out QC results from the QC Manager. Include a copy of dilutions page if any. Also include a printout of sample positives from the data review and file it in the data folder.

8.7 Submit the result folder to the GC group section supervisor. The supervisor will review results and then authorize the sample. The supervisor will then file the folders in the GC group lab.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

9. DATA ARCHIVAL

9.1 For the GC-SHIMADZU-FID systems:

9.1.1 Move the data files soon after collection from the hard disk of the instrument computers to the network drive \\FLDEP1\dear\labs\lab3\chemdata\organic\GC\BACKUP_GC-SHIMADZU-FID3 or SHIMADZU-FID4. Raw data files on the hard disk of each instrument may be deleted after 3 to 4 months or they are no longer in need.

9.1.2 Copy the Masshunter upload file into \\FLDEP1\dear\labs\lab3\chemdata\organic \GC\UPLOAD_GC-SHIMADZU-FID3 or SHIMADZU-FID4 to convert in QC Manager for reporting in LIMS.

9.1.3 The archived data may be retrieved by making a request to the Data Group or the GC supervisor. Make sure when setting up an injection sequence to write down the name of the data files with the associated sample information in the injection log.

10. QUALITY CONTROL

10.1 See DEP SOP GC-001, Ref 13.5 for detailed information on quality control, definitions and interferences. See DEP SOP LB-027, Ref. 13.4, for guidelines for qualifying data when quality control results are outside established control limits and re-analysis is not a viable or desired option.

11. SAFETY/HAZARDOUS WASTE MANAGEMENT

11.1 The toxicity and carcinogenicity of each reagent used in this method has not been precisely defined. All of the chemicals used in this method should be treated as a potential health hazard. Please review the relevant Material Safety Data Sheets.

11.2 Wear gloves and safety glasses at all times when working with standards. The lower petroleum range compounds and solvents are particularly volatile and must be handled in a hood. Carbon disulfide has a very unpleasant odor. Use care when handling all standards and solvents.

11.3 Please refer to the safety SOP OG-001, Ref. 13.6, for specific details on safety and hazardous waste management.

12. DETERMINATION OF METHOD DETECTION LIMITS:

12.1 **Determination of Method Detection Limits and Demonstration of Capability**

Refer to the SOP **LB-007, Ref. 13.7** and refer to SOP **LB-031, Ref. 13.8** for specific procedural details

The LOD and Demonstration of Capability (DOCs) shall be determined for each main quality system matrix group identified by NELAP (air, drinking water, non-potable water, biological materials and solids/chemical materials). These groups represent the minimum matrix distinctions for LOD determinations and DOCs where there is evidence that the method performance will not be affected by sub-matrix distinctions within these group, Otherwise LODs and DOCs shall be determined separately for the quality system matrix sub-groups listed below. Where a suitable matrix cannot be found for preparing samples for LOD determinations or DOCs, another similar matrix type may need to be used or samples may need to be prepared in the absence of a matrix (e.g. method blanks). Reasons for matrix substitution may include (but are not limited to): inappropriate background analyte levels in the matrix for the intended

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

study, no analyte-free matrix is available for method blanks, no reference materials are available for a matrix, etc,

12.1.1 Quality System Matrices:

- Aqueous – all aqueous samples excluding drinking water (see below) and salt or estuarine waters;
- Drinking Water – water from a designated potable source;
- Saline/Estuarine – an aqueous sample from an ocean or estuarine. The effects of this matrix type may vary from analysis to analysis and with salt content. Therefore, the decision to what extent if any this matrix has on the LOD and what salt levels may affect the LOD is left to the discretion of experienced supervisory staff;

12.1.2 MDL Determination Procedures

12.1.2.1 The MDLs were established using procedures given in EPA Chapter 40 Part 136, Appendix B of the Federal Register. Also refer to **Reference 13.7 and 13.8.**

12.1.2.2 Seven method blanks and seven spikes (spiked near the MDL) are prepared on at least three different days and analyzed by spreading among all instruments considered identical for the purpose of this analysis. The method MDL is set, at least, to the higher value of the MDL based on blanks and the MDL based on spikes. MDL is the concentration of analyte at which there is analyte present with 99% confidence.

12.1.2.3 The MDL verification spikes are collected on quarterly basis at a frequency of at least one per quarter per each instrument. At least annually, the results are tabulated, for both spikes and blanks, and the MDLs are recalculated. The last 24 months (if available) is included in the calculations. If the new calculated MDL is within a factor of two of the old MDL, the MDL may be kept unchanged. Otherwise it needs to be adjusted to the new calculated MDL.

TABLE 1: Components in Petroleum Hydrocarbon Standard (FL-PRO)

Octane (C_8)	Hexacosane (C_{26})
Decane (C_{10})	Octacosane (C_{28})
Dodecane (C_{12})	Triacontane (C_{30})
Tetradecane (C_{14})	Dotriacontane (C_{32})
Hexadecane (C_{16})	Tetratriacontane (C_{34})
Octadecane (C_{18})	Hexatriacontane (C_{36})
Eicosane (C_{20})	Octatriacontane (C_{38})
Docosane (C_{22})	Tetracontane (C_{40})
Tetracosane (C_{24})	
Surrogates	
Nonatriacontane (C_{39})	ortho-Terphenyl (OTP)

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

TABLE 2: MDLs and PQLs for FL-PRO method

	Water mg/L		Sediment/waste mg/kg	
Analyte	MDL	PQL	MDL	PQL
TRPH	0.45	1.8	35/880	140/3500

13. REFERENCES

13.1 Method for Determination of Petroleum Range Organics. Florida Department of Environmental Protection. FL-PRO-2018; 11-2-2018.

13.2 DEP SOP SV-004. Extraction of Petroleum Range Organics from Waters, Sediments and Wastes (FL-PRO-2018)

13.3 DEP SOP SV-006. Analysis of Base/Neutral/Acid Extractables by Gas Chromatography/Mass Spectrometry

13.4 DEP SOP LB-027. Reporting Qualified Data and Correcting Quality Control Problems.

13.5 DEP SOP GC-001. Quality Assurance/Quality Control and Data Review/Authorization in the GC pesticides Laboratory.

13.6 DEP SOP OG-001. Safety and Waste Management Practices in the Organic Analysis Groups (Volatile, Semi-Volatile and Pesticide Laboratories).

13.7 DEP SOP LB-007 Procedure and Policy for Demonstration of Capability for Methods, Instruments and Laboratory Staff. .

13.8 DEP SOP LB-031Method Detection Limit Verification.

Appendix of Significant Changes

08/06/2010 Elaborated MDL determination in section 12.1 to include different matrices and supporting references in section 13.

11/17/2010 Added sections 1.3 to 1.5 and 6.11 to include details on pattern recognition.

11/29/2011 Specified calibration standards concentration. Elaborated on calibration fit requirements. Added surrogate recovery limits table. Other editorial changes.

10/09/2014 Network directory changes for backup and upload files.

10/07/2015 Network directory changes for backup and upload files, added matrix spikes control limits in 7.5.3. The difference between ICV and CCV clarified in section 6.6.

09/21/2017 Enviroquant software replaced with Masshunter. MDLs updated.

09/10/2018 Removed long defunct Massachusetts Method and the related tests. Added Shimadzu GC-FID. Updated calibration levels and MDLs. Updated the MDL procedure.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.

01/07/2019	Updated to FL-PRO 2018 method.
04/22/2019	Agilent FID retired. Second Shimadzu FID added. Soil MDL updated.
04/20/2020	Shimadzu FID2 retired. Shimadzu FID3 added. CCV TRPH concentration changed to 2550 mg/L. EZchrom sopftware replaced with LabSolutions for data acquisition.
09/16/2020	CCV frequency changed to every 12 hrs, based on 2018 FL PRO method.
09/08/2021	MDLs updated. Shimadzu-FID removed. Shimadzu-FID4 added. References updated.

The OFFICIAL COPY is the on-line version. All other copies are considered unofficial and uncontrolled.