

Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 Method

Addendum 1

This addendum is posted as a draft subject to revision based on the results of the CCME multi-lab validation study being conducted by member labs of the Canadian Association for Environmental Analytical Laboratories.

Please revise Section 2 third bullet to read as follows:

- F4 result, C34 to C50 hydrocarbons, are determined by integration of all area counts from the apex of the nC34 peak to the apex of the nC50 peak. The average response factor for nC10, nC16 and nC34 hydrocarbons is used for primary calibration. The GC response factor of the nC50 must be no less than 70% of the average response for the three compounds nC10, nC16 and nC34 hydrocarbons. This result gives fraction F4 **provided** that the chromatogram descends to baseline by the retention time of nC50. **Note** that only half of the nC10 and half of the nC50 peaks are included in these analyses. Similarly, the nC16 and nC34 peaks are each split between two fractions.

Please revise Section 4 last paragraph in to read as follows:

To avoid losses in the C6 to C10 fraction, carry out the methanol extraction of the samples within 48 hours of sample receipt and analyse as soon as possible but within 40 days. Samples must be kept cold (approximately 4 degrees) and must be sealed. For the C10 to C50 fractions, again holding times should be minimized but they should be extracted no later than 14 days of sample receipt and analyse as soon as possible but within 40 days. Again, samples must be kept cold (approximately 4 degrees) and must be sealed (e.g., in a screw topped vial sealed with a Teflon liner.)

Footnote: If possible, establish maximum holding times and/or use a surrogate to establish stability. nC11 has been suggested as a surrogate for Fraction F1. Methyl nonane has been suggested as a possible surrogate for Fraction F2 and 5- α -androstane for Fractions, F2, F3 and F4.

Please revise Section 5 last paragraph to read as follows:

Collect soil samples in a manner that minimizes sample handling and agitation. If possible, do not collect samples from soil exposed to direct sunlight. This may mean removing some surface soil to obtain a fresh sample. The use of specially designed airtight collection samplers is recommended. All soil must be removed from the threads of jars and vials to ensure an adequate

seal. Samples must be placed on ice immediately after collection and shipped as soon as possible. Until analyzed, they must be kept at approximately 4°C or below. Freezing may cause glass sample bottles to break, thus rendering the samples useless. Ship samples to the laboratory as fast as possible. Several references are recommended for developing suitable standard operating procedures for collecting samples [5-8].

Please revise Section 8 last paragraph in to read as follows:

The following quality control criteria are mandatory and must be demonstrated before and during analysis:

Method Detection Limits (MDLs) must be met as follows:

Laboratories must achieve either an MDL that is 20% of the applicable soil type as described in the CWS PHC or the following *whichever is higher*.

- F1, C6 to C10 hydrocarbons **12 mg/kg**
- F2, C10 to C16 hydrocarbons **3.9 mg/kg**
- F3, C16 to C34 hydrocarbons **9.0 mg/kg**
- F4, C34 to C50 hydrocarbons **8 mg/kg**
- F4G (gravimetric) based on motor oil **290 mg/kg**

The average or mean for F2, F3 and F4 from these results is 7 mg/kg

Please revise Section 11.1 third bullet to read as follows:

- Mandatory instrument performance criteria for C10 to C50 are that nC50 response factor must be no less than 70% of the average of nC10, nC16 and nC34 response factors and the nC10, nC16 and nC34 response factors must be within 10% of the average response for the three compounds. This performance criterion must be met by any injection system used for hydrocarbon analysis and confirmed on a daily basis.

Please revise Appendix 3, third paragraph, second bullet to read as follows:

- For the F2 C10 to C16 and F3 C16 to C34 fractions, the MDL determination is done using soil contaminated or spiked with weathered diesel fuel at a concentration of 20 to 100 mg/kg. For the F4 C34 to C50 fraction the determination must be done using SAE 30 weight motor oil. The results for the three fractions are summed and that result is applied to each of the three fractions. This approach is practical, although not accurate for each fraction. The same MDLs shall be applied to the F2-PAH and F3-PAH fraction.

Please replace Appendix 5 with the attached version.

This change reflect the change in the MDL for F1 and some other typographical errors

APPENDIX 5 – SINGLE LABORATORY METHOD VALIDATION

A validation of the method was conducted in the Emergency Science Division laboratory of the Environmental Technology Centre, during the fall and winter of 2000/01*. The purpose of this study was to estimate precision of several aspects of the method, determine method detection limits, and verify that standards were stable over a reasonable length of time. This information is provided to assist individual laboratories as they implement the CWS PHC method.

The main findings from this study are summarized as follows:

1. Linearity Study

Excellent linear relationship between the concentrations and GC responses are clearly demonstrated for the target compounds of Fractions 1 (C6-C10), 2 (C10-C16), 3 (C16-C34), and 4 (C34-C50) in the studied concentration range.

2. Precision Estimation Study

(1) Precision Estimation for Standards: for Fraction F1, the target compounds (benzene and toluene) demonstrated reasonable reproducibilities with the relative standard deviation (RSD) being around 12% at 0.05 ppm and 7.5% at 0.2 ppm, respectively.

The RSDs obtained from 8 determination of the C8-C30 standard were under 4%. The RSD for C50 (n = 8) was determined to be 7.3% at 25 ppm.

(2) Precision Estimation for Complete Method (gasoline spiked soil): The average recoveries were determined to be 82% at 50 ppm and 88% at 400 ppm of gasoline, respectively. The method precision from 8 measurements was determined to be 7.5% (RSD) at 50 ppm and 8.4% (RSD) at 400 ppm of gasoline, respectively.

(3) Precision Estimation for Complete Method (diesel and motor oil spiked soil): The relative standard deviations were determined to be 5.0% for F2, 3.4% for F3, and 3.5% for F4 of diesel and motor oil spiked soil samples, respectively.

3. Method Detection Limit (MDL) for F1 Using Gasoline-spiked Soil

The MDL determination was done using a spiked soil at a concentration of 50 mg/kg soil. The SD and RSD from 8 replicate analyses were determined to be 3.4% and 8.6%, respectively. Therefore, the MDL for whole gasoline is determined to be 3.7×3.14 (the appropriate one-sided 99% t-statistic) = 12 µg/g soil or 12 mg/kg., based on a 5g sample

4. Method Detection Limit (MDL) for F2, F3, and F4 Using Diesel-spiked Soil

The MDL were determined to be 3.9, 9.0, and 8 mg/kg soil for F2, F3, and F4 (10.0 g of soil was spiked with 0.5 mg of diesel), respectively, again based on a 5g sample.

5. Determination of Method Detection Limit (MDL) for F4G (Motor Oil-spiked Soil) Using Gravimetric Method

The MDL ($MDL = t_{(n-1, \alpha=0.99)} s$) by gravimetric method was determined to be 0.29 mg/g soil or 290 mg/kg soil (5.0 mg of motor oil was added to 5.0 g of soil, equivalent to 1000 mg/kg of soil).

6. Stability Study

* Lab Validation Study Results for the “Reference method for the Canada Wide Standard for Petroleum Hydrocarbons in Soil-Tier 1 Method”, Zhendi Wang and Ken Li, Environmental Science and Technology Division, Environmental Technology Centre, Environment Canada, Ottawa K1A 0H3, March 2001, revised April 2002.

Around 100% and 85% of recoveries for all target compounds in the C6-C10 range were demonstrated at 7 days and at 38 days, respectively.

Excellent stabilities were demonstrated for the standard C10-C50 in 62 days period with the RSDs (4 measurements at 4 different dates) being under 4%.