# Analysis of total petroleum hydrocarbon and fractions in soil by two near infrared spectrometers

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## Introduction

The widespread use of petroleum hydrocarbons (PHCs) as fuels for transportation, heating and as lubricants has led to accidental spills, leakage or operational losses into the environment. Potential soil and water contamination poses health hazards to humans and animals. Policies and practices have been developed to assess sites for contamination, to apply remediation and to monitor recovery on an ongoing basis.

Near infrared (NIR) spectroscopy has been applied widely in the petroleum hydrocarbon and related industries for determination of such parameters as octane number, cetane, cloud point, vapour pressure, ethanol, lead, sulphur, aromatics, olefins and saturates content.<sup>1</sup> To date, few studies have reported results from applying NIR spectroscopy to determine petroleum hydrocarbons in contaminated soil.<sup>2-4</sup>

The purpose of this study was to examine the feasibility of using NIR spectroscopy for determining soil concentrations of total PHCs, three chain-length fractions and BTEX, as identified in the Canada Wide Standard for petroleum hydrocarbons in soil. BTEX is comprised of benzenes, toluenes, ethylbenzenes and xylenes. Conventional chemical analyses for PHCs are relatively costly, time-consuming, and laboratory-based. The delays involved in conventional soil sampling after an actual or suspected spill followed by the turnaround time required for the analyses by commercial laboratories can be prohibitively costly and can delay emergency response to a situation thereby endangering human and environmental health.

## **Materials and Methods**

#### Samples and analyses

A total of 70 bulk PHC-contaminated soil samples were collected from sites of former diesel powergenerating stations in three communities in Manitoba, Canada. From each bulk sample, 5 subsamples were taken in jars for chemical analysis. Immediately adjacent to each jar sample, 5 additional samples were collected in borosilicate vials for NIR spectroscopic analysis.

Three PHC fractions representing a range of molecular sizes were determined chemically using a standard gas chromatography method defined by the Canadian Council of Ministers of the Environment (CCME). Fraction 1 is a straight chain hydrocarbon of 5 to 10 carbon atoms; fraction 2, 10 to 16 carbons; and fraction 3, 16 to 34 carbons. The samples were divided into two groups on the basis of the predominant grain size of the soil. Samples with grain size > 75  $\mu$ m were coarse and those with grain size < 75  $\mu$ m were fine.

#### Near infrared spectroscopy

Samples in vials were scanned on a Foss NIRSystems Model 6500 spectrometer using the Rapid Content Sampler from 1100 to 2498 nm. They were also scanned on a Zeiss Corona 45 VISNIR spectrometer from 380 to 1760 nm using a custom-made vial adapter.

Calibrations were developed on 330 samples using PLS1 in The Unscrambler (v. 9.7; CAMO Software, Woodbridge, New Jersey). Spectra were smoothed and transformed to first or second derivative. Calibrations were developed for all of the samples for each constituent. These are termed global calibrations. Calibrations were also developed for each constituent separately for the coarse- and the fine-grained samples. Performance of calibrations was judged by criteria proposed for environmental samples.<sup>5</sup> Excellent calibrations are those with  $r^2$ >0.95, RPD >4 and RER>20. Successful calibrations have  $r^2$  of 0.90–0.95, RPD of 3–4 and RER of 15–20 while moderately successful calibrations have  $r^2$  of 0.8–0.9, RPD of 2.25–3 and RER of 10–15. Moderately useful calibrations have  $r^2$  of 0.7–0.8, RPD of 1.75–2.25 and RER of 8–10.

# **Results and Discussion**

#### Chemical composition of samples

Concentrations of BTEX and PHC fractions, including total petroleum hydrocarbons (TPH), in the 330 samples in this study are given in Table 1. There was no substantial correlation between moisture and any of the PHC constituents. This suggests that correlations to moisture will not be responsible for any favourable

calibration results. The concentration range for benzene in this data set is too small for effective evaluation of NIR calibrations for this constituent.

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Constituent	Mean <u>+</u> SD	Range					
Benzene (ppm)	0.0005 <u>+</u> 0.003	0-0.02					
Toluene (ppm)	0.019 <u>+</u> 0.34	0–1.70					
Ethylbenzene (ppm)	0.21 <u>+</u> 0.52	0–3.00					
M,p-Xylene (ppm)	1.33 <u>+</u> 3.05	0–15.00					
o-Xylene (ppm)	0.97 <u>+</u> 2.14	0–9.70					
CCME Fraction 1 (ppm)	76 <u>+</u> 100	0–430					
CCME Fraction 2 (ppm)	1949 <u>+</u> 2290	0–15000					
CCME Fraction 3 (ppm)	1156 <u>+</u> 1657	0–15000					
TPH (ppm)	3192 <u>+</u> 3838	0–30100					
Moisture (%)	15.79 <u>+</u> 7.02	0–27					

Table 1. Chemical composition of 330 PHC-contaminated soil samples in this study.

#### Calibrations

Spectra from two soil samples scanned with the Foss 6500 (left) and the Zeiss Corona (right) show that absorbance values are in the same range. The wavelength ranges of the two instruments are different from one another as shown by the position of the water band at 1400 nm.





**Figure 1A.** Spectra of two soil samples obtained with the Foss 6500. The arrow indicates a main water band at 1400 nm.

Figure 1B. Spectra of two soil samples obtained with the Zeiss Corona.

The performance of global calibrations showed that the results were similar between the instruments (Tables 2A and 2B). The calibrations for moisture were judged to be successful with  $r^2$  of 0.9 and RPD of greater than 3. Those for the remaining constituents were mostly judged to be useful, with CCME 3 being moderately successful.

from 1100 to 2500 nm.				
Constituent	SEP	r <sup>2</sup>	RPD	RER
CCME F1 (ppm)	52	0.73	1.9	8.3
CCME F2 (ppm)	1171	0.74	2.0	12.8
CCME F3 (ppm)	603	0.87	2.7	24.9
TPH (ppm)	1742	0.79	2.2	17.3
Moisture (%)	2.25	0.90	3.1	12.0

 Table 2A. Calibrations developed on 330 samples scanned on the Foss 6500

 from 1100 to 2500 pm

Table 2B. Calibrations developed on 330 samples scanned on the Zeiss Corona.

Constituent	SEP	r <sup>2</sup>	RPD	RER
CCME F1 (ppm)	55	0.70	1.8	7.8
CCME F2 (ppm)	1175	0.74	1.9	12.8
CCME F3 (ppm)	689	0.83	2.4	21.8
TPH (ppm)	1798	0.78	2.1	16.7
Moisture (%)	2.10	0.91	3.3	12.9

Calibrations developed for the 6500 and the Corona for the PHC fractions in fine-grained soil ranged from not useful to moderately successful for both instruments (Tables 3A and 3B). The conclusion was the same for the BTEX constituents.

Reference paper as: D. Malley and P. Warburtoni (2012). Analysis of total petroleum hydrocarbon and fractions in soil by two NIR spectrometers, in: Proceedings of the15th International Conference on Near Infrared Spectroscopy, Edited by M. Manley, C.M. McGoverin, D.B. Thomas and G. Downey, Cape Town, South Africa, pp. 272-275.

Table 3A. Calibrations developed on fine-grained samples scanned on the Foss 6500.

Constituent	Ν	Range	SEP	r <sup>2</sup>	RPD	RER
CCME F1 (ppm)	88	0–78	12.8	0.64		6.1
CCME F2 (ppm)	89	0–5500	764	0.77		7.2
CCME F3 (ppm)	90	0–3500	325	0.83		10.8
Toluene (ppm)	82	0–0.05	0.007	0.56		7.1
Ethylbenzene (ppm)	96	0–0.36	0.042	0.40		8.6
Xylene (ppm)	79	0–0.21	0.028	0.69		7.5

Table 3B. Calibrations developed on fine-grained samples scanned on the Corona.

Constituent	Ν	Range	SEP	r <sup>2</sup>	RPD	RER
CCME F1 (ppm)	94	0–120	17.4	0.57		6.9
CCME F2 (ppm)	80	0–5500	758	0.75		7.3
CCME F3 (ppm)	88	0–3500	352	0.80		9.9
Toluene (ppm)	73	0–0.06	0.007	0.67		8.6
Ethylbenzene (ppm)	69	0–0.36	0.025	0.81		14.4
Xylene (ppm)	83	0–0.21	0.032	0.61		6.6

Tables 4A and 4B report the calibration results for the coarse-grained samples. Unlike for fine-grained samples, calibrations for these are judged excellent for one PHC fraction with the 6500 and successful for the other fractions for both instruments. Calibrations for the BTEX were also generally superior to those for finegrained soils, being moderately successful to successful.

Table 4A. Calibrations developed on coarse-grained samples scanned on the Foss 6500.

Constituent	Ν	Range	SEP	r <sup>2</sup>	RPD	RER
CCME F1 (ppm)	80	0–420	34	0.93	2.9	12.4
CCME F2 (ppm)	144	0–15000	648	0.93	3.5	23.1
CCME F3 (ppm)	87	0–15000	428	0.96	3.9	35.1
Toluene (ppm)	78	0–1.2	0.164	0.81		7.3
Ethylbenzene (ppm)	96	0–0.36	0.042	0.40		8.6
Xylene (ppm)	63	0–20.3	1.62	0.94		12.5

Table 4B. Calibrations developed on coarse-grained samples scanned on the Corona.

Constituent	Ν	Range	SEP	r <sup>2</sup>	RPD	RER
CCME F1 (ppm)	103	0–400	33	0.92	3.0	12.1
CCME F2 (ppm)	133	0–15000	761	0.90	3.0	19.7
CCME F3 (ppm)	116	0–15000	672	0.90	2.5	22.3
Toluene (ppm)	82	0–1.3	0.160	0.85		8.1
Ethylbenzene (ppm)	36	0–1.7	0.175	0.90		9.7
Xylene (ppm)	78	0–20.5	2.45	0.87		8.4

# Conclusion

The major result of this study was that excellent calibrations could be achieved with coarse-grain soils but not generally with fine-grained samples. This may be a result of the movement of hydrocarbons through soil and not necessarily an interaction between NIR spectroscopy and grain size. Coarse soils allow a more even distribution of the hydrocarbons in the matrix and therefore more representative sampling and NIR analysis. Movement of hydrocarbons through fine soils may be more along cracks and slickensides. Thus, in fine soils, it may be more difficult than in coarse soils to ensure that the sample scanned and the sample analysed in the chemical laboratory are identical. More attention to this important aspect of NIR spectroscopic analysis may improve the results for fine-grained soils.

Generally, the calibration results were similar between the Foss 6500 benchtop instrument and the fieldportable Corona. This is despite the difference in wavelength range scanned. It is favourable that a portable instrument such as the Corona achieves excellent calibration results since it can be deployed in the field for on-site analysis. Thus, the detection and delineation of hydrocarbon spills in soils can potentially be performed much more quickly, with less cost and less sample storage and handling than is presently the case. Nonetheless, benchtop NIR instruments in a commercial analytical laboratory could greatly save time and costs compared with the conventional analytical methods.

Reference paper as

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