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Determination of TPH Content in Soil by Portable Mid IR - ATR System

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Abstract

- The application of mid-infrared spectroscopy as a rapid screening tool for determination of the concentration of total petroleum hydrocarbons (TPH) in contaminated soils is discussed.

- We demonstrate use of ATR (attenuated total reflection) mid-infrared technique for TPH in soil using a handheld spectrometer with no solvent extraction or heating required.

- Partial least squares (PLS) and cross validation were used to develop correlation for estimation of TPH.

- From this preliminary study we show that mid IR-ATR can deliver promising results for field screening, providing real time in-situ TPH data.

Outline

- Introduction
  - Background
  - ATR (attenuated total reflection) technique
  - Field Methodology
- Applications
  - Site A
  - Site B
- Advantages, and limitation in deploying the FTIR-ATR
- Summary and Conclusion

Introduction

- Measurements of TPH in soils is obtained in analytical laboratories, typically using gas chromatography (GC) with a flame ionization detector (FID) after solvent extraction.
- Lengthy turnaround times of weeks to months can cause significant delays in field operations, e.g., during soil treatment processes.
- Currently, the field test kits typically require a solvent extraction and analysis by FTIR-ATR after removal for the solvent.
- Another commonly used field test kit uses DRIFT (diffuse reflectance) potable Near and Mid FTIR, but still required sample drying step which makes it time consuming and complicated to use in the field.
- We need rapid, field based method can speed site delineation, excavation decisions.

Spectroscopic Technique- Attenuated Total Reflectance (ATR)

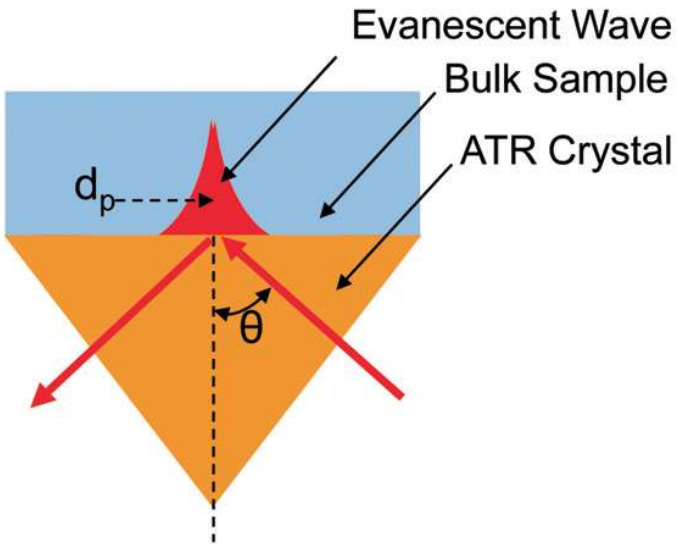


Image from PIKE Technologies

How ATR Work with Soil Samples

Infrared beam penetrates into a crystal and reflects from the internal surface of crystal and creates an evanescent wave, into the sample with intimate contact with the ATR crystal.

Some of energy of the evanescent waves is absorbed by the sample and the reflected radiation is returned to the detector.

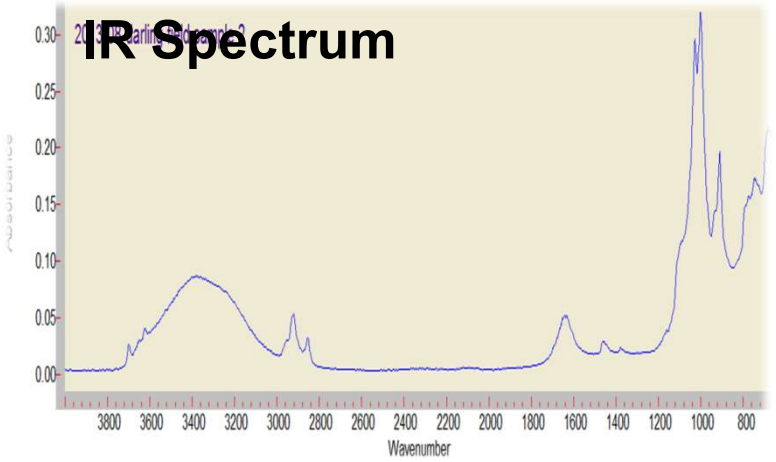
Collect information from ATR surface

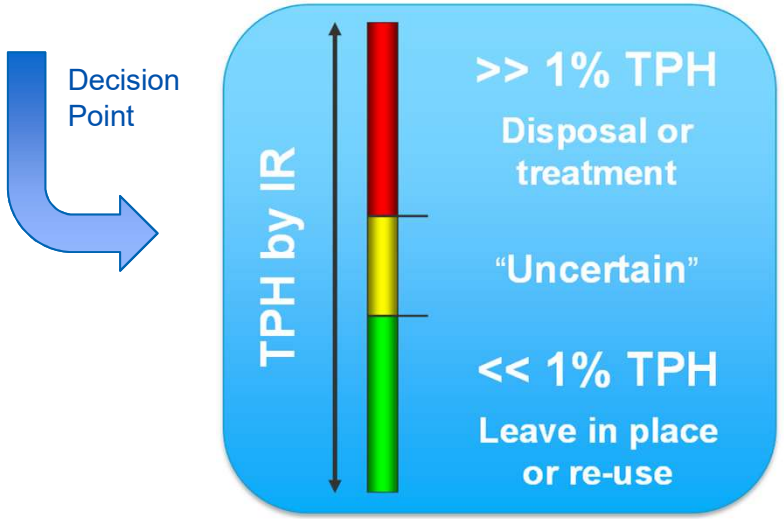
Achieve a good sample contact with the ATR crystal to ensure the evanescent wave penetrate into the sample.

5

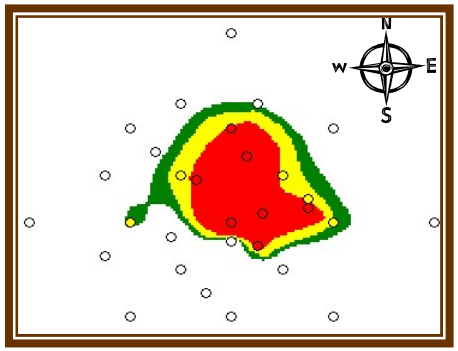
Workflow for Quick Screening of TPH in the Field

- IR spectra reflect complex molecular vibration patterns
- Modeling correlates spectra from calibration samples with known TPH concentrations
- Field data can indicate if TPH concentration in soil is significantly above or below a cleanup level
- A field IR-ATR measurement takes less than 30 sec



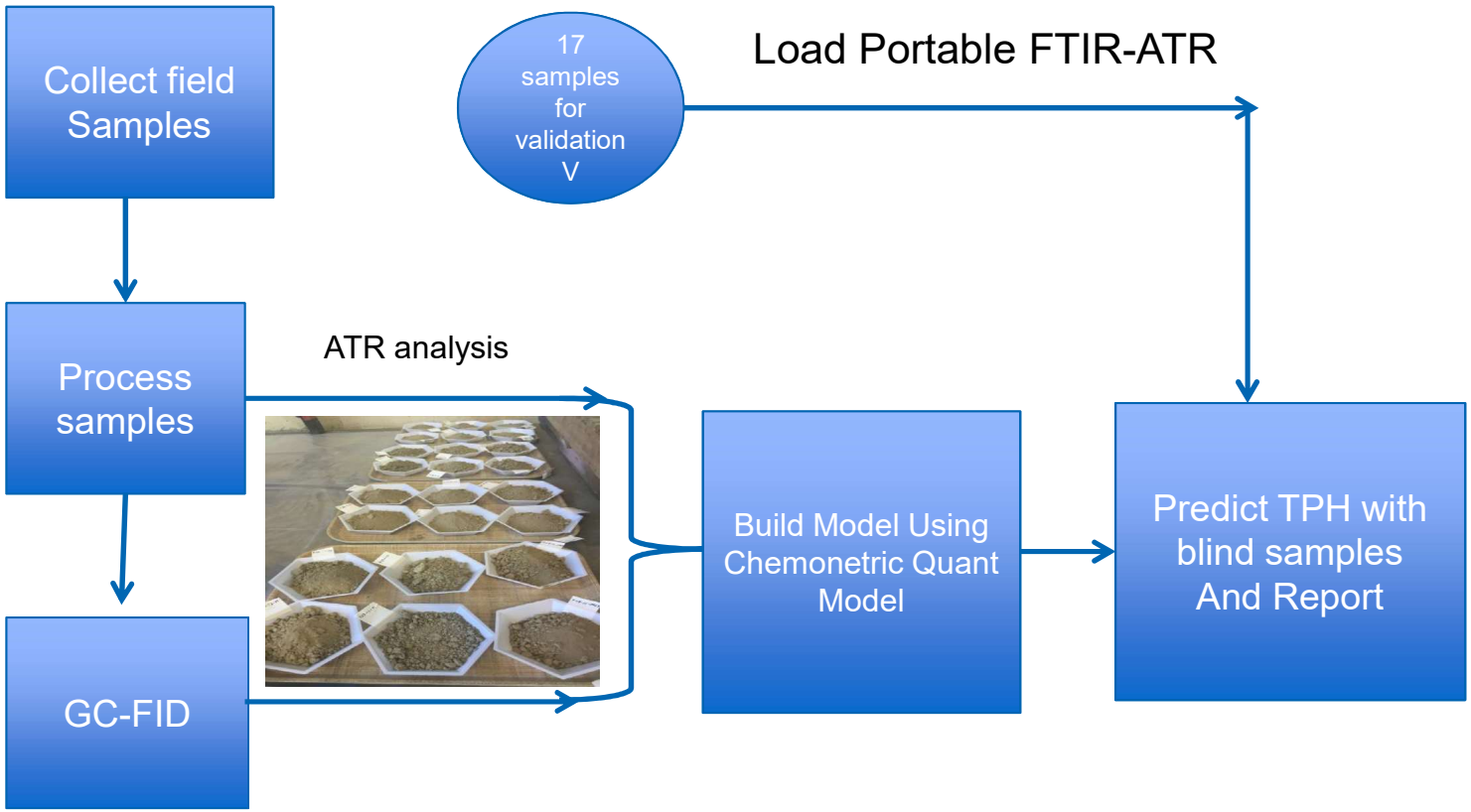


Example contaminated site sample points

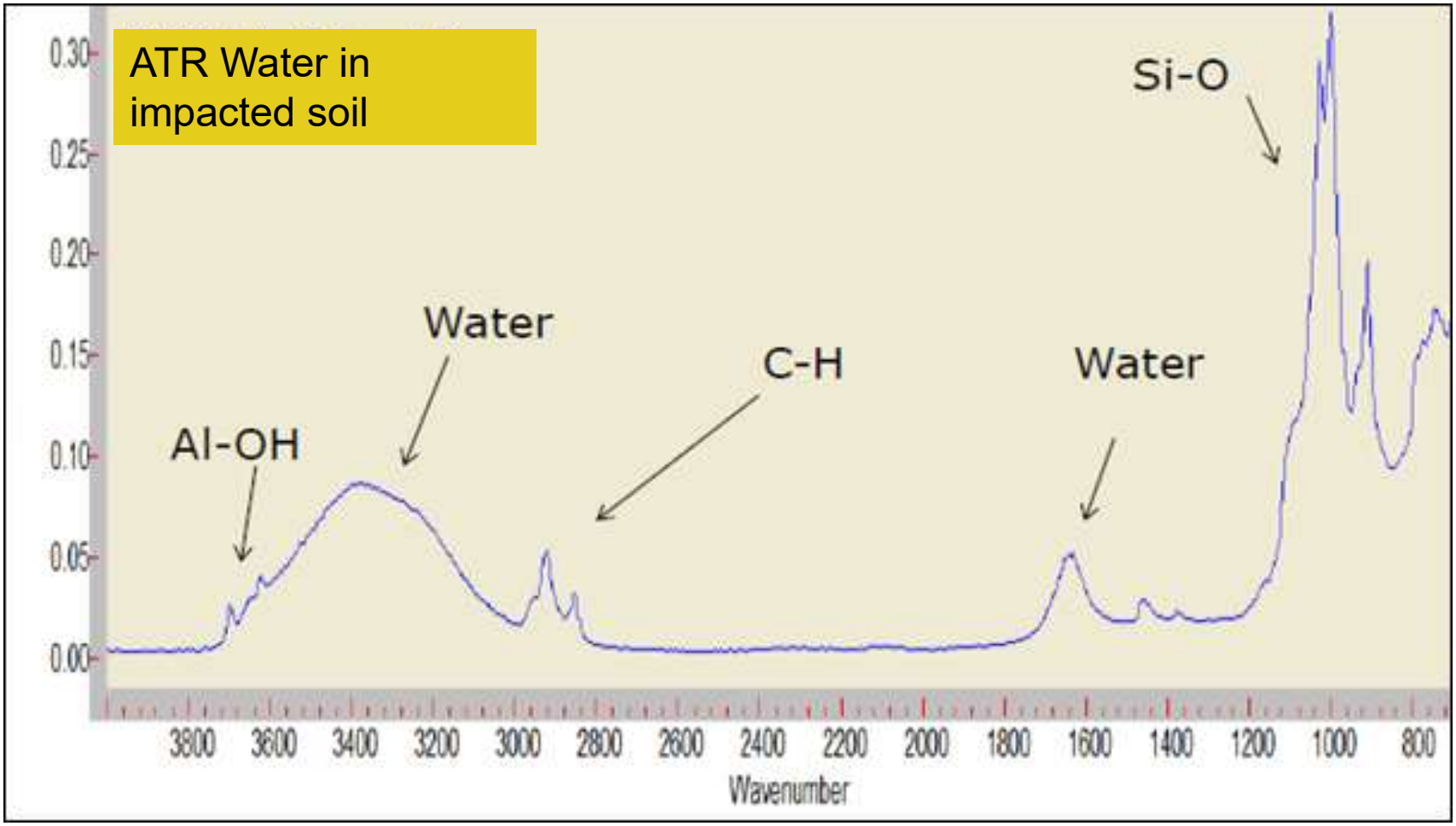


6

Field Trial Approach



ATR with Water band



Pilot Trial - Site A

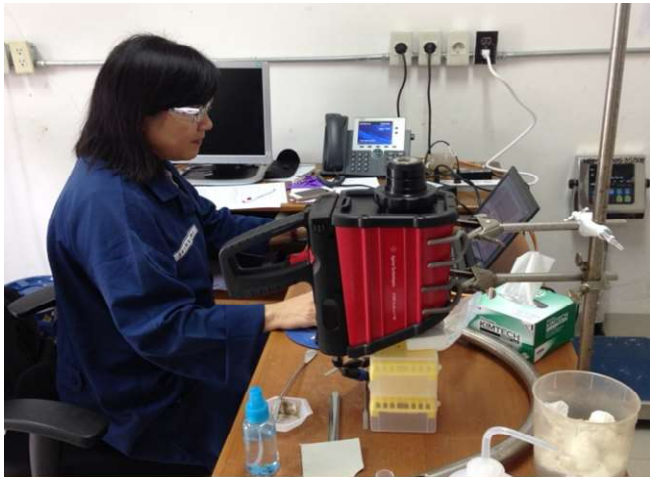
Methodology used:

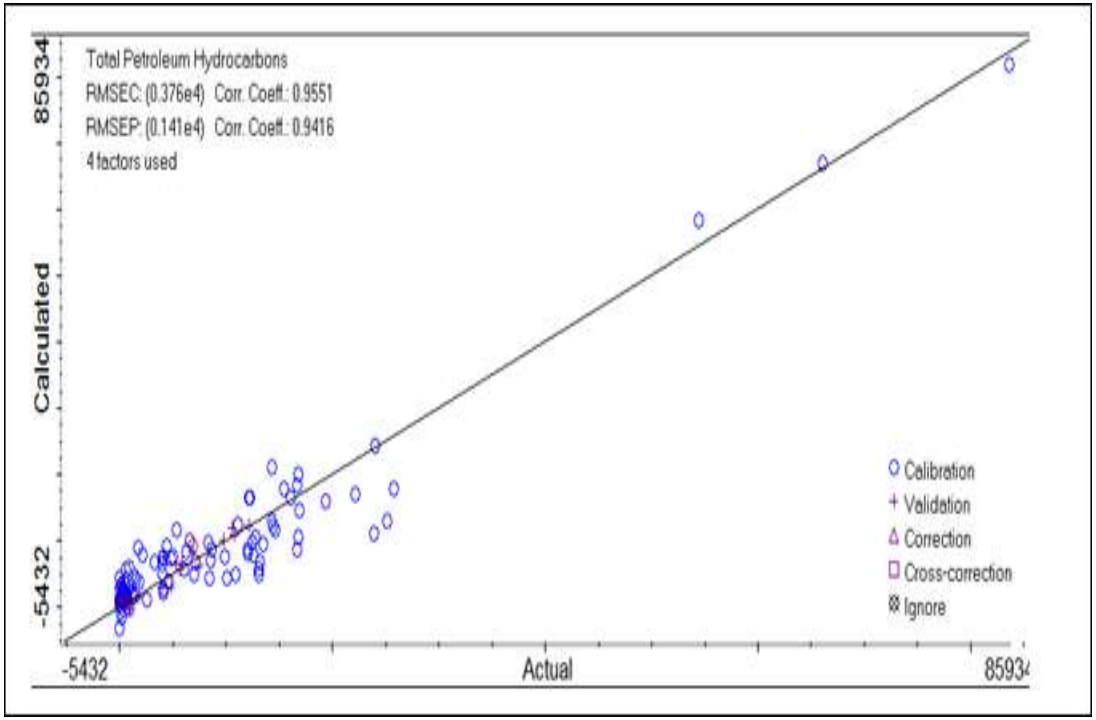
1) Collected 100 soil samples from multiple sites;
    1) 25% selected for model validation
    2) 75% selected for calibration
    3) Created additional 10 calibration samples around 1% TPH

2) Homogenize the samples; and screen the sample (sample size < 2mm);

3) Develop a site specific model

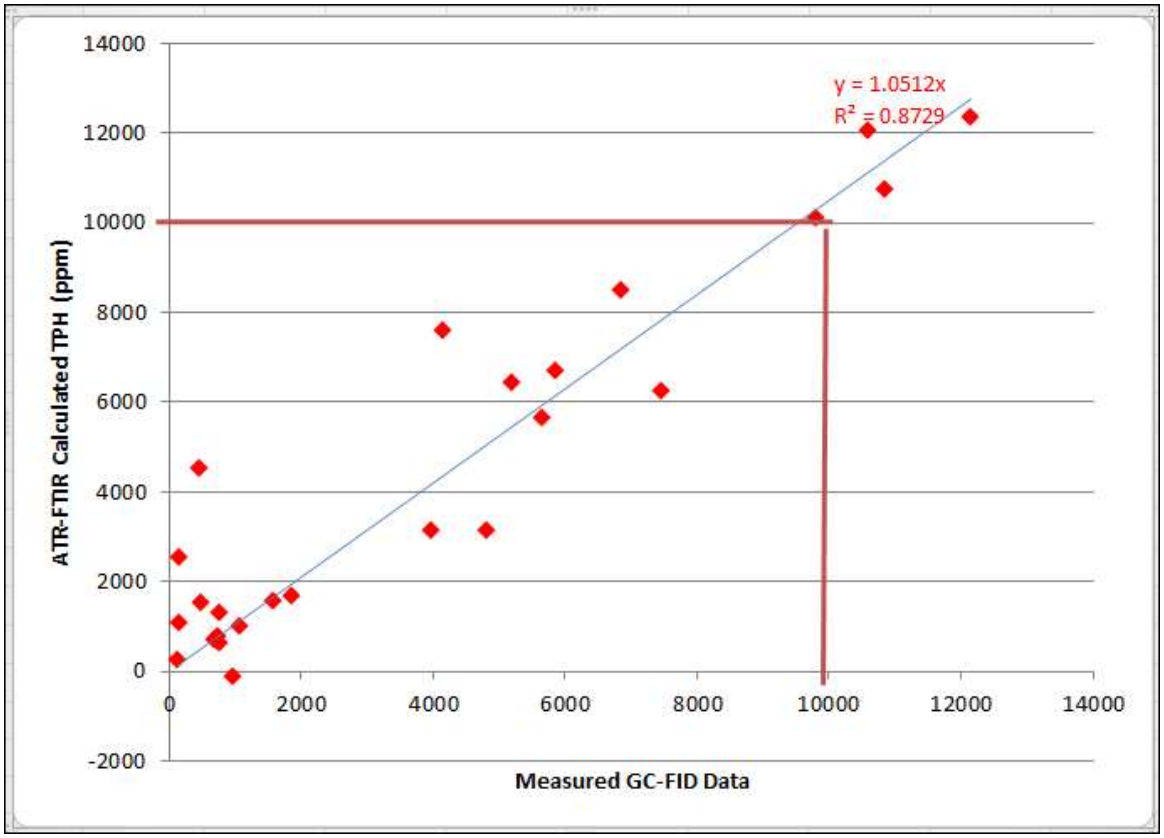
Developing a Site-specific Model





- The model with 100 calibration, 25 validation and with 4 factors developed.
- Correlation coefficients **0.9551**
- Root Mean Standard Error of Prediction (RMSEP)= **0.1500 wt.%**

Validation Accuracy



The Chemometric data shows good correlation with GC-FID data.

11

Moisture Content Impact

Table 1: Moisture content impact study with measurement of C-H Stretch vibration band

Sample ID	Moisture content (%)	C-H Stretching Peak Height	C-H Stretching Peak Height with Water Signal Baseline	CH Stretching Peak Area with Water Signal Baseline
Sample A				
1	13.04	0.03	0.01	0.59
2	28.58	0.03	0.01	0.51
3	21.36	0.03	0.01	0.54
4	23.60	0.02	0.01	0.60
5	33.19	0.03	0.01	0.52
Sample B				
1	15.82	0.02	0.01	0.47
2	20.69	0.02	0.01	0.79
3	24.37	0.03	0.01	0.43
4	29.87	0.03	0.01	0.43
5	33.22	0.03	0.01	0.67

Water signal does not impact the C-H stretch IR signal up to 30% water

12

Significance of these Results for site A

- 100 soil samples were used for developing the model and 25% for the model validation.
- Shows good agreement with GC-FID data with an R^2 of 0.96.
- Evaluation of the **root mean square error** suggests that the lower detection threshold for the site specific model was approximately 0.2 wt%, indicating that concentrations reported below this threshold are not valid.

13

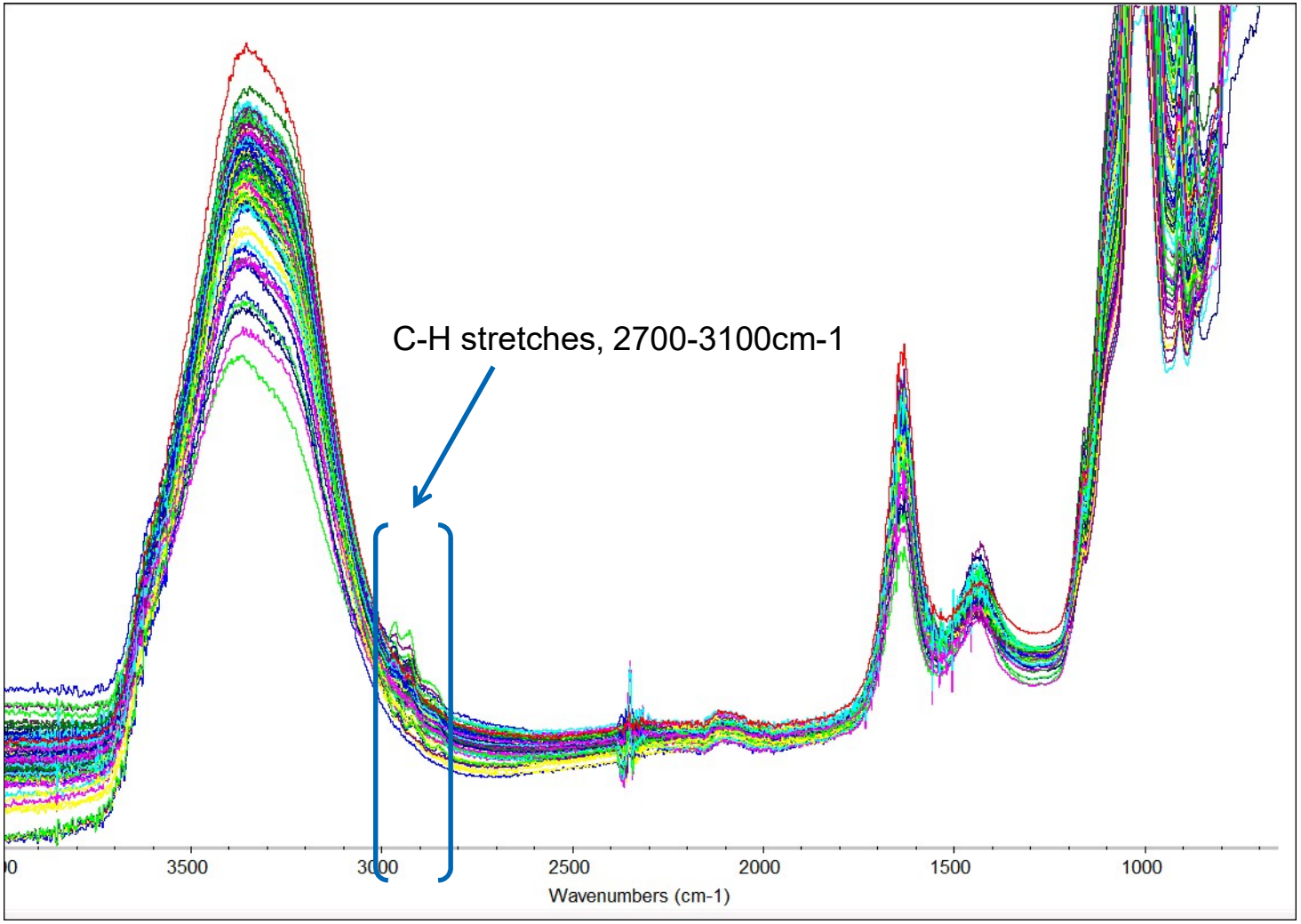
Pilot Trial – Site B with Heterogeneity

The soils were homogenized in the lab.

- ATR Sampling Techniques:
  - 5 Replicate measurements for each sample.
  - Use of little moisture on the soil and moderate pressure to create good contact with the ATR window.

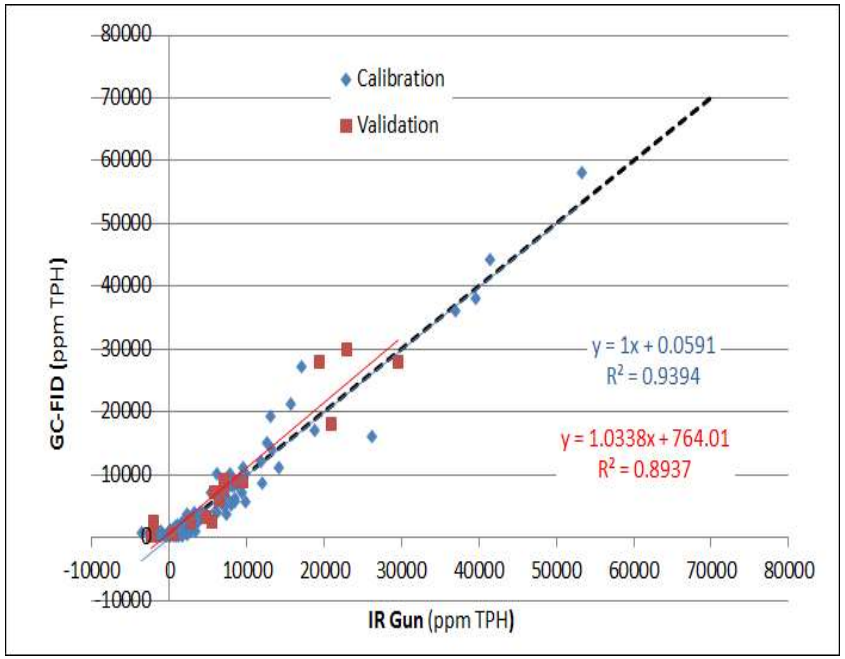
14

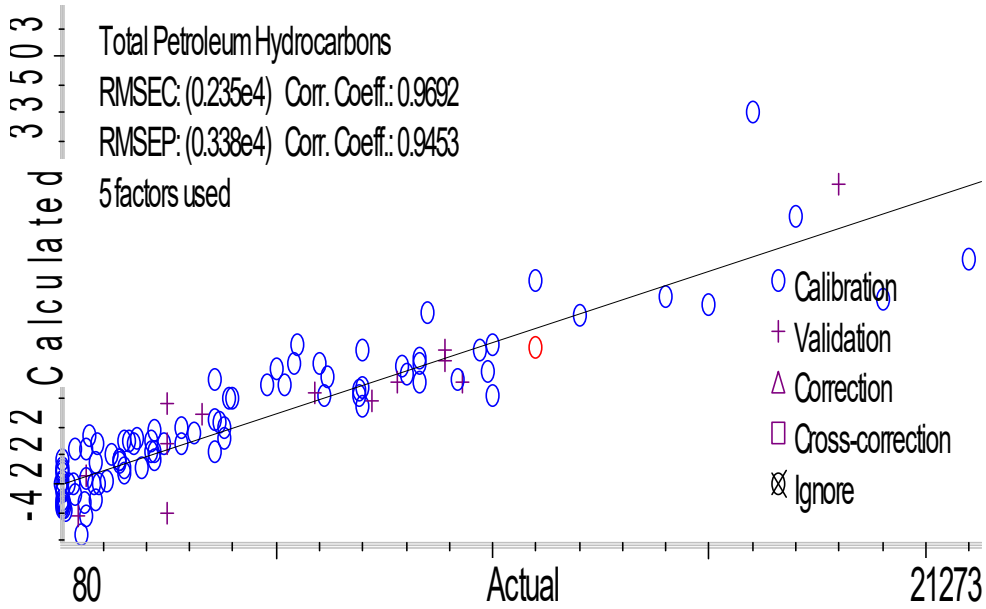
ATR Spectrum



15

Site B FTIR- ATR Model with the 0-5.5 wt% TPH Range

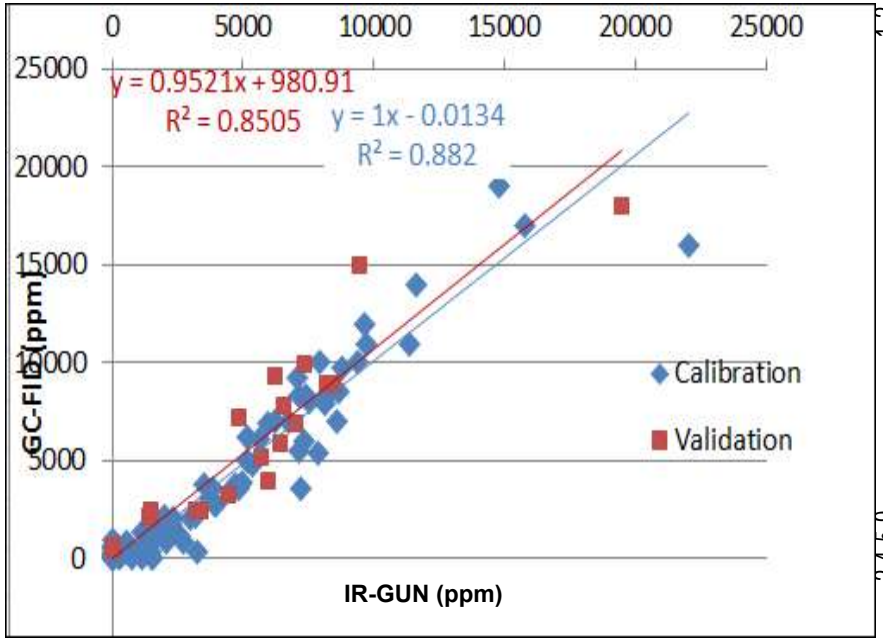


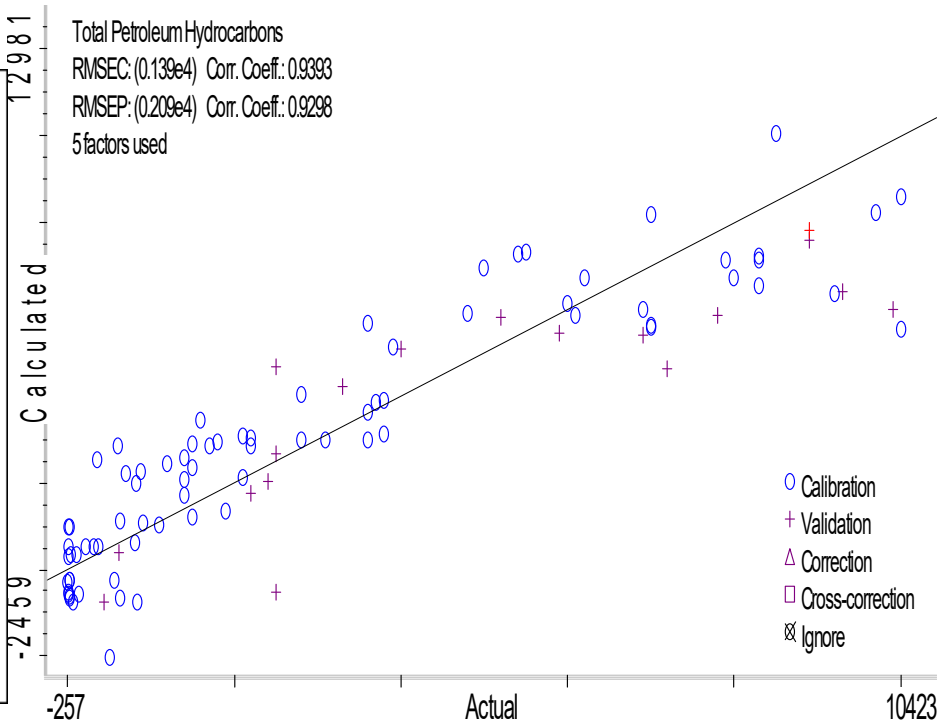


- The model with 97 calibration, 16 validation and with 5 factors used.
- Correlation coefficients **0.9453**
- Root Mean Standard Error of Prediction (RMSEP)= 3380 **ppm**
- ATR Model predictions vs GC-FID data; Correlation coefficient **0.8937**

16

Site B ATR Refined Model with the 0-2.2 wt% TPH range





- The model with 80 calibration, 17 validation and with 5 factors used.
- Correlation coefficients **0.9298**
- Root Mean Standard Error of Prediction (RMSEP)= 0.21 wt%
- IR-ATR Model predictions vs GC-FID data; Correlation coefficient **0.8505**

17

Accuracy for Calibration and Validation samples

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Accuracy for Various for calibration samples	
Range mg.kg TPH	RMSD
0-3,000	704
3,000-5,000	1223
5,000-15,000	2083
Accuracy for various for Validation samples	
range mg/kg TPH	RMSD
0-3,000	795
3,000-5,000	1594
5,000-15,000	2344

Accuracy of each data set was calculated as the difference ATR and GC-FID data

18

Significance of the Results for Site B

- Two FTIR-ATR calibration models were built using the C-H stretch (3100 to 2700 cm^{-1}):
  - for the initial model developed 0 to 5.5 wt% range of TPH.
  - for refined ATR model covers 0 to 2.2 wt% range of TPH.

- An composite spectrum (5 replicated samples) was used to build the chemometric model

- Refined model covers the range of 0 to 2.2wt%. Root mean standard error of prediction (RMSEP) is 2000ppm.

19

Conclusions and Summary

The results of those trials have clearly demonstrated:

- Portable field FTIR with ATR method enables time and cost efficiency for screening soils with TPH or individual petroleum components in the field .
- The models generated are site specific.
- Good correlation between FTIR-ATR and GC-FID concentration at 1 wt% with and RMSEP of 0.2 wt%, suggesting that the method requires confirmatory analysis of the estimated concentration falls between 0.8 and 1.2 wt.%.
- The method can be used for field screening purpose to make a quick decision at 1 wt.% with the moisture content up to 30%.
- The device has been tested at multiple field sites.

20

Conclusions and Summary

However:

- Further refinement of the chemometric model could improve the detection limit and model accuracy.
- For ATR analysis of soil, due to relatively small window size, samples need to be analyzed in replicate to improve data quality.

21

Acknowledgements

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Questions?

23