The use of a hand-held mid-infrared spectrometer for the rapid prediction of total petroleum hydrocarbons in soil

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1. Background
TPH Background

- Complex mixture of aliphatic hydrocarbon chains ($C_{10}^{-} \text{ to } C_{36}$) derived from crude oil
- Major environmental pollutant: spills from production, storage and distribution
- Impacts: soil, sediment, water, biology and humans
- Risk assessment and remediation needs to be quick and is expensive
TPH traditional analysis

- Traditional approaches
  - Laboratory: Supercritical fluid extraction followed by silica clean-up and gas-chromatography with flame ionization detector (GC-FID)
  - Field: IR method (ATR) which requires extraction prior measurement
- We need a reliable, quick, cheap and “in situ” technique
We propose diffuse reflectance mid-infrared spectroscopy together with partial least squares as an alternative for the “in situ” prediction of TPH (C_{10}^{-C_{36}}).

Advantages

- **Rapid**
- **No sample pretreatment**
- **In situ**
- **Multiple analytes prediction**
Our hand-held spectrometer

- Full FT-IR Hand-held (Agilent)
- 6000-650 cm\(^{-1}\)
- 15 s scan and 8 cm\(^{-1}\) resolution
- ~3 kg
- Blue-tooth PDA with PLS software
- Battery
TPH peaks

- Mid-infrared sensitive to C-H bonds

- ~2950 cm\(^{-1}\) (-\(\text{CH}_3\))
- \(-\text{CH}_2\)
- ~2730 cm\(^{-1}\) (-\(\text{CH}_3\))

NIR (5000-4000 cm\(^{-1}\)) and MIR (4000-1200 cm\(^{-1}\)) spectra of liquid diesel, crude oil and n-hexane

Forrester et al. 2013 (SSSAJ 77, 450-460)
The PLSR model

- Selection of optimal spectral range and PLSR development in Forrester et al. 2013 (SSSAJ 77, 450-460)
- n = 199 TPH contaminated soils from Australia (0-15,000 mg/kg)
- Air-dried
- Partial least squares and trained by cross-validation

<table>
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<tr>
<th>4540-4120</th>
<th>3000-2600</th>
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<tr>
<td>PCs</td>
<td>R²</td>
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<tr>
<td>9</td>
<td>0.84</td>
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<td>(4330, 4260)</td>
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Commercialisation of the technique

- 2008-2009: collaboration project with Ziltek Pty Ltd (South Australia)
- 2012: Method patented in Australia
- 2013: method patented in USA
- 2013: Ziltek Pty Ltd. releases the technology as REMSCAN
- 2013: Publication in SSSAJ describing the patented method (Forrester et al., 2013)
Challenges

- Presence of moisture: leave the sample drying, software cut-off
- Soil heterogeneity: repeated scans, mixing the sample
- Sample entering into the cone nose: instrument squared to the surface and sample tamped flat

![Graph showing absorbance vs. wavenumber with labels TPH, Moist sample, and x-axis labeled Wavenumber (cm^-1) ranging from 1000 to 5000]
Challenges

- Soil type (TPH spread in sandy soils vs “shielding” effect in clay soils): site specific or local models. Local models:
  - Spectral library divided in clusters linked to textural classes
  - Unknown spectra allocated to the correspondent model
  - Within each model, 5 TPH range concentrations models: final model dependent on the TPH value predicted
2. Examples of field uses
Case study 1: Western Australia

- Diesel leaked from a storage facility and captured in an emergency bund area
- Site specific calibration to quantify diesel in the bund area and monitor remediation works
- Remediation work completed in 4 days (200 samples/day)
- 19 ‘blind’ samples sent for analysis

Comparison of RemScan data to lab data for TPH (C_{10} - C_{36})

\[ R^2 = 0.997 \]
Case study 2: South Australia

- Ageing power transformer removed. Oil contamination in the footings.

- RemScan “guided” the remediation work: pit declared “clean” < 1000 mg/kg.

- Samples from walls and floor sent to reference laboratory.

- Reference analysis confirmed TPH predictions.

\[ R^2 = 0.994 \]
Case study 3: South Australia
Final remarks

- DRIFT-PLSR using a hand-held spectrometer is suitable technique for the rapid, cheap and accurate prediction of TPH
- RemScan commercially used
- On-going work
  - Inclusion of new soils in the global calibrations
  - Inclusion of additional contaminants
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