Validation of Petroleum Hydrocarbons Determination in Wastewaters By FT-IR Spectroscopy

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ABSTRACT
Water contamination with petroleum hydrocarbons is one of the most challenging environmental problems, as crude oil continues to be the main source of energy and petrochemicals. This study presents the validation and the estimation of the measurement uncertainty for the determination of petroleum hydrocarbons in water samples by Fourier Transform Infrared Spectrometry (FT-IR). Method for petroleum hydrocarbons determination from water consist in the acidification of the sample (pH<5), extraction of 1 liter of water sample with 50 ml of carbon tetrachloride, removal of polar substances by Florisil column filtration and measurement of the IR absorption within the 3150-2750 cm$^{-1}$ range. The measurements were carried out using a Perkin Elmer Spectrum BX II FT-IR spectrometer. For the method validation detection limit and quantification limit, working range, trueness and precision were studied. The measurement uncertainty was evaluated based on the bottom-up approach. The detection limit was calculated to be 0.1 mg/l and the quantification limit 0.3 mg/l. Working range was set between 0.3 and 10 mg/l and samples with higher concentrations can be determined after appropriate dilution to fit within these limits. Relative standard deviation for repeatability was 6.4% for the 0.3-4 mg/l range and 6.0% for 4 – 10 mg/l range. The expanded uncertainty of this method is 13.5% for LQ-4 mg/l range and 12.5% for 4-10 mg/L range (at 95% confidence level, k=2).

Keywords: FT-IR spectroscopy, Method validation, Petroleum hydrocarbons, Water samples.

INTRODUCTION
Petroleum hydrocarbons is a term that covers a broad family of chemicals, from compounds of biogenic origin to mineral hydrocarbon constituents (Farmaki et al., 2007). These substances may enter the environment by leakage, spilling, improper storage or any other accident and pose a real danger for the ecosystem.

The major oil spill incidents include the one in Gulf of Mexico and the oil pipeline explosion in Dalian City, Liaoning Province, China (Tang et al., 2012).

Petroleum hydrocarbons effects on living organisms varies from destruction of algae and plankton, changes in feeding and reproduction of water life (plant, insect, and fish) (API, 2001, Clinton et al., 2009), to direct effects on human health, as fatigue, headache, nausea, drowsiness, and affect central nervous system, immune system, liver, spleen, kidneys and lungs (ATSDR, 2009).

Thus, a fast and relatively cheap method for petroleum hydrocarbon determination in wastewaters is a very useful tool for analytical laboratories dealing with this pollutant agent and FT-IR technique provide such an analysis method.

MATERIALS AND METHODS
Petroleum hydrocarbons determination from water is accomplished by extraction of 1 liter of water sample with 50 ml of carbon tetrachloride under continuous shaking, for 30 minutes. The sample must have pH value lower than 5 (obtainable using hydrochloric acid). The polar substances are removed by using Florisil column
filtration after the extraction and water excess is
removed by using anhydrous sodium sulphate.
The IR absorption spectrum is measured, within
the 3150-2750 cm\(^{-1}\) range, using a quartz cell of 1
cm length and a Perkin Elmer Spectrum BX II FT-
IR spectrometer ( ). All reagents were purchased
from Merck and were of p.a quality.

RESULTS AND DISCUSSION
For determination of detection and quantification limits, 10 independent blank
solutions have been spiked with 0.05 mg/l
TPH (1/1 diesel oil/ lubricating oil mixture
(BAMK010e, Federal Institute for Materials
Research and Testing, Germany) and their
absorbance recorded. Detection limit (0.1 mg/l)
was calculated using the three standard deviation
criteria (3s) and further on, quantification limit
(0.3 mg/l) was determined by the nine standard
deviation criteria (9s). The obtained value for
quantification limit was confirmed by preparing
10 solutions with a TPH concentration of 0.3 mg/l
and the obtained relative standard deviation was
below 5%, while the recovery were within 80-
120% of the theoretical value, thus validating the
value for the quantification limit.

Working range was set between 0.3 – 10
mg/l, which can be further extended using
dilution. For linearity domain verification,
a number of 5 solutions were prepared, with
concentration of 0.01, 0.02, 0.05, 0.1 and 0.2 mg/
ml, using a mix of Diesel and mineral oil (1:1), BAM-
K010e certified reference material. The squared
ratio of standard deviation between the highest
and the lowest point on the calibration curve was
determined to be below 5, which proves that the
domain was correctly chosen and its linearity is
ensured.

Repeatability was verified by using aliquot
samples for two levels of concentration within
the work domain and the relative standard
deviation was below 10% for both cases. Further
on, intermediary repeatability was verified,
by measuring a stable, certified sample over a
period of 10 days. The NG 11 filter (polystyrene
traceable reference material Perkin Elmer
PE08280) was chosen for this task and the
relative standard deviation found 10 days was
0.072%.

Reproducibility was checked by participating
in Proficiency Test Scheme (Aquacheck, LGC
Promochem, UK). The Z-score value is within -1
and +1 interval, which indicates a good agreement
with indicative values.

A number of two samples were spiked with
2.3 mg/l and 6.4 mg/l petroleum products, in
order to determine the recovery. The results for
the recovery value were 82%, respectively 83%.

Tab. 1. Measurements of 10 independent samples for detection limit and quantification limit
determination, in both mg/ml (as determined by reading the sample directly) and mg/l (the final
result, after considering the volume of the sample and flasks)

<table>
<thead>
<tr>
<th>Result (mg/ml)</th>
<th>Results (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0015</td>
</tr>
<tr>
<td>2</td>
<td>0.0016</td>
</tr>
<tr>
<td>3</td>
<td>0.0015</td>
</tr>
<tr>
<td>4</td>
<td>0.0010</td>
</tr>
<tr>
<td>5</td>
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<tr>
<td>6</td>
<td>0.0008</td>
</tr>
<tr>
<td>7</td>
<td>0.0006</td>
</tr>
<tr>
<td>8</td>
<td>0.0008</td>
</tr>
<tr>
<td>9</td>
<td>0.0016</td>
</tr>
<tr>
<td>10</td>
<td>0.0023</td>
</tr>
<tr>
<td>s</td>
<td>0.00064</td>
</tr>
<tr>
<td>LD (3s)</td>
<td>0.002</td>
</tr>
<tr>
<td>LQ (9s)</td>
<td>0.006</td>
</tr>
</tbody>
</table>

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The uncertainty budget comprised of various sources: purity of reference material, weighting uncertainty, volume of liquid use in standard preparation, sample volume, FT-IR instrument uncertainty, calibration curve uncertainty and aliquot sample repeatability (visually described in Fig. 1).

All these were taken into account and calculation was made according to Eurachem guide (Ellison et al., 2012). Extended uncertainty for of petroleum hydrocarbons determination in wastewaters using the described method was found to be 0.702 mg/l which translates to a 12.5% relative extended uncertainty.

**CONCLUSION**

The detection limit for the determination of petroleum hydrocarbons in soil was found to be 0.1 mg/l and the quantification limit 0.3 mg/l. The working domain was found to be linear between 0.3 and 10 mg/l, but solutions with higher concentrations can be analyzed after dilution. Recovery (%) of petroleum hydrocarbons in water samples calculated in spiked wastewater was 82±10%. Relative standard deviation for repeatability was 6.4% for the 0.3-4 mg/l range and 6.0% for 4-10 mg/l range. Reproducibility was determined by measuring a certified filter supplied by vendor and the relative standard deviation obtained was 0.07. Z-score for inter-laboratories studies was -0.59. The expanded uncertainty of this method is 13.5% for 0.3-4 mg/l range and 12.5% for 4-10 mg/l range (at 95% confidence level, k=2).

The FT-IR method for the determination of petroleum hydrocarbons in water samples was validated. The method’s figures of merit were studied, the main uncertainty components were identified and the measurement uncertainty budget was estimated. The FT-IR method allows the accurate determination of petroleum products from water samples.

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**REFERENCES**

3. Clinton HI, Ujagwung GU, Horsfall M (2009). Evaluation of total hydrocarbon levels in some aquatic media in an oil

