

Analysis of total content of petroleum products in water by using FTIR spectroscopy

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Abstract. Contamination of aquatic and terrestrial environment with oil products is a major problem in processes of extraction, transport and processing of crude oil. Derived organic compounds, resulting from fractional distillation of crude oil often end up in wastewater and surface water causing irreversible effects on aquatic ecosystems. Thus, it's necessary to identify and qualitatively determine the total content of petroleum products in water, by classical chemical, chromatographic and infrared spectroscopy methods. Gathering high-resolution spectral data was performed by a modern method, Fourier transform infrared spectrometry (FTIR), a relatively precise, high accuracy data method. The study's main purpose is to describe most important steps to be followed to obtain representative results for the use of FTIR spectrometry in determining total content of petroleum products in water. Steps described in the study involve drawing the baseline, calibrating the method with certified reference materials and estimating the uncertainty degree of the analysis method used. The study of total content of petroleum products is addressed especially to researchers in the field of analytical chemistry to update the methods used, environmental engineers to estimate the pollution degree of a body of water and (PhD) students who want to deepen the field of petroleum compounds analysis.

1 Introduction

Petroleum hydrocarbons are groups of chemical compounds of natural origin used in contemporary society for manufacturing oils and lubricants, synthetic plastics, bitumen and fuels for heating homes or operating internal combustion engines [1]. Development of the oil industry is accompanied by the phenomena of biotic and abiotic components' degradation, generating cumulative negative impacts on the environment and quality of human life.

In the current social context, petroleum hydrocarbons are common contaminants of extraction, transport, storage and refining sites of crude oil in useful products. Extracted crude oil (crude oil) is an extremely complex mixture of organic compounds (hydrocarbons) of different chemical structures and molecular masses, affecting the

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biochemical and chemical processes of the biotope with direct negative effects on terrestrial or aquatic ecosystems by increasing the degree of sensitivity to pathogens and pests.

In order to quantify analytical results and effects caused by petroleum hydrocarbons on water and the environment, they have been regulated as quality indicators of TPH methods (Total Petroleum Hydrocarbons) in European and national legislation [1, 2]. Total petroleum hydrocarbons are a generalized term that includes several hundred chemical compounds derived from crude oil, made up of carbon and hydrogen i.e., benzene, toluene, xylenes, hexanes, naphthalene, fluorene, jet fuels, mineral oils and so on [3]. From an environmental point of view, total content of petroleum hydrocarbons can infiltrate into the environment through accidents, from industrial emissions or as by-products of commercial or private uses, can be released directly into water by leaks, can form surface films, can sink into bottom sediments or decompose due to bacterial activity in the aquatic environment.

Population is exposed to moderate TPH contents as a result of handling substances with high TPH content, consumption of TPH - contaminated water, touching contaminated soil, living near an oil spill, inhalation of VOC vapours at gas stations, use of chemicals at home or at work or use of certain pesticides [3].

High TPH levels can affect the central nervous system and, as a cumulative effect, at high concentrations in the air one compound can cause headaches and dizziness and another compound can cause a nerve disorder called "peripheral neuropathy" or can cause effects on blood, immune system, lungs, skin and eyes [2, 3]. In this case, precise analysis of the total content of petroleum products is an important step in estimating the environmental impact for a given site.

The analysis method for the total content of petroleum products in water involves the extraction of non-polar substances from acid samples using organic solvents (cyclohexane, tetrachlorethylene) and measurement of absorbance, using an IR spectrometer at a wavelength of 2930 cm^{-1} , by the baseline method.

Quantification of the environmental impact is relative because of the structural and functional complexity of TPH components and impacts can be multiple, with cumulative effect, depending on the contaminated surface / environment, therefore the analysis methods according to the analysed matrix must be constantly updated, also taking into account objective assessment of the degree of uncertainty.

2 Materials and Methods

Analysis of the total content of petroleum products in water was performed by using an analysis system consisting of a Fourier-transform infrared spectrophotometer (Shimadzu IRTracer 100) and a digital unit for analysis, storage and processing of data obtained (fig. 1.).

The Fourier-transform infrared spectrophotometer measures an infrared spectrum by the Fourier transform of an interferogram obtained by using an optical system based on the use of a Michelson interferometer in which light, after passing through aperture, is transformed into a parallel beam by the collimator mirror and enters the light beam splitter [4]. A germanium film, deposited on a substrate of potassium bromide by evaporation, comprises the light beam splitter and divides the single beam into two beams, reflecting one towards the fixed mirror and transmitting the other towards the moving mirror.

Both mirrors reflect their rays back to the beam splitter and part of each returning beam is reflected and transmitted. Using the principle of overlap, the light transmitted from the fixed mirror and the light reflected from the moving mirror recombine and interfere with each other as they move towards the collector mirror.

In relation to the conventional dispersive spectrometer, that directly determines the light intensity at a certain wavelength, the FTIR detector draws the interferogram that must be Fourier - transformed to obtain the spectrum.

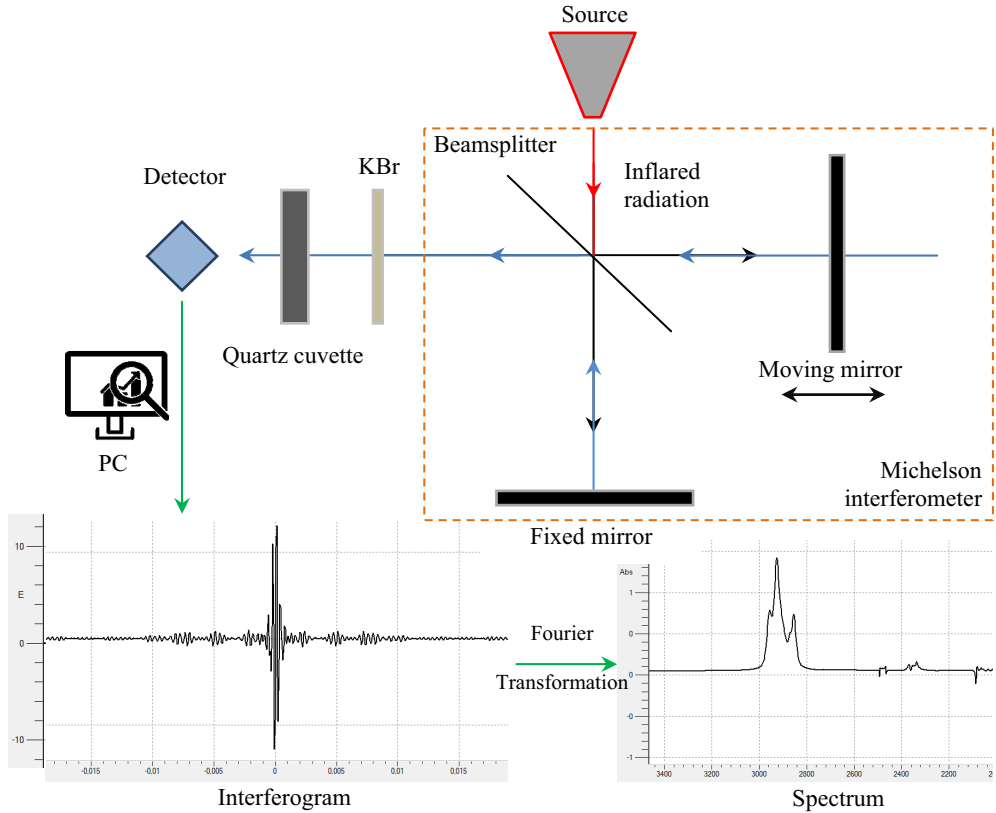


Fig. 1. Data analysis unit and FTIR spectroscopy measurement system.

For quantitative analysis of the total content of petroleum products in water, the Fourier-transform infrared spectrophotometer uses the Beer-Lambert law of absorption spectrometry which relating band intensity to concentration [5].

$$A = \varepsilon \cdot l \cdot c \quad (1)$$

Where: A – absorbance;
 ε – absorptivity;
 l – Pathlength;
 c – concentration.

Absorbability is the constant of proportionality between concentration and absorbance that differs from one wavelength to another and from molecule to molecule. However, for a given molecule and wavenumber of absorbance, the absorptivity is a fundamental physical property of the molecule. The units of ε are usually given in $(\text{concentration} \times \text{pathlength})^{-1}$, so the absorptivity cancels the units of the other two variables in Beer's law [6, 7]. For quantitative analyses, it is absolutely necessary that infrared spectra be represented in

absorbance and not in transmittance, because absorbance is linearly proportional to concentration, and transmittance and concentration are linked by an inverse algorithm.

Standard solutions with concentrations of 12.5 mg/l, 25 mg/l, 50 mg/l, 100 mg/l and 200 mg/l of TOG/TPH in one litre of solution were used to represent the absorbance spectra. Measuring bottles and glass droppers were also used for preparing calibration standards and optical path quartz cuvettes were used for analysis of working standards in the FTIR spectrometer 99.8% pure tetrachlorethylene and isopropyl alcohol were used as chemical reagents to clean any traces of water inside the quartz cuvettes.

Drawing calibration curves was performed according to ASTM D7066-04, ASTM D7678-11 and SR 7877-2 / 1995 [8, 9, 10] and identification of the method's uncertainty sources was performed according to The Fitness for Purpose of Analytical Methods A Laboratory Guide to Method Validation and Related Topics [11, 12].

3 Results and Discussion

The presence and concentration of total content of petroleum products in water is of concern to the public because of its deleterious aesthetic effect and its impact on aquatic life. Nowadays regulations and standards have been established that require monitoring of total content of petroleum products in water, thus for analytical analysis of TPH in water by using Mid-IR laser Spectroscopy is required the use of a Fourier transform infrared spectrometer which can provide high-resolution spectral data based on wavelength of absorbance.

Quantifying the total content of petroleum products in water using FTIR spectroscopy involves plotting the calibration curve according to the absorbance value measured at a certain wavelength for a specific certified reference material or standard calibrator prepared in the laboratory.

In order to improve the accuracy of the water TPH analysis method, it is recommended to power the FTIR spectrometer in normal operation at least 24 hours before drawing the absorbance spectra. Recording the absorbance spectra for plotting the calibration curve, but also for analysing water samples in order to quantify the TPH content in water, involves the following steps:

- 1) cleaning quartz cuvettes of any impurities and traces of water;
- 2) filling a quartz cuvette with 5 ml of solvent (Tetrachloroethylene) and recording the background interferogram on the same solvent sample (P - 0);
- 3) after recording the background interferogram, a scanning on the same sample (P - 0) is performed and the resulting absorption spectrum (fig. 2.) is recorded as point "zero" on the calibration graph.

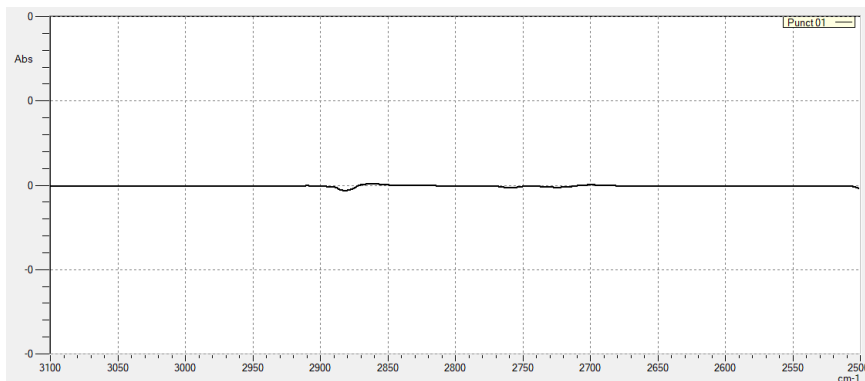


Fig. 2. Infrared spectrum recording for point "zero".

The tetrachlorethylene solution was considered the zero point of the calibration graph because the extraction of nonpolar compounds had been made with tetrachlorethylene that separates petroleum products and nonpolar compounds from water and other chemical species.

After recording the “zero” spectrum, standard solutions with concentrations of 12.5 mg/l, 25 mg/l, 50 mg/l, 100 mg/l and 200 mg/l of TOG/TPH were prepared by successive dilution of a certified calibration standard with a concentration of 2000 mg/l TOG/TPH from a High Range Calibration set (AMETEK) Tetrachloroethylene TOG / TPH with Product No: 403-1078 and Lot No 110641.

4) For each calibration solution obtained, 5 absorbance spectra were recorded (Fig. 3), each representing a point on the calibration graph of the method for quantifying the total oil hydrocarbon content;

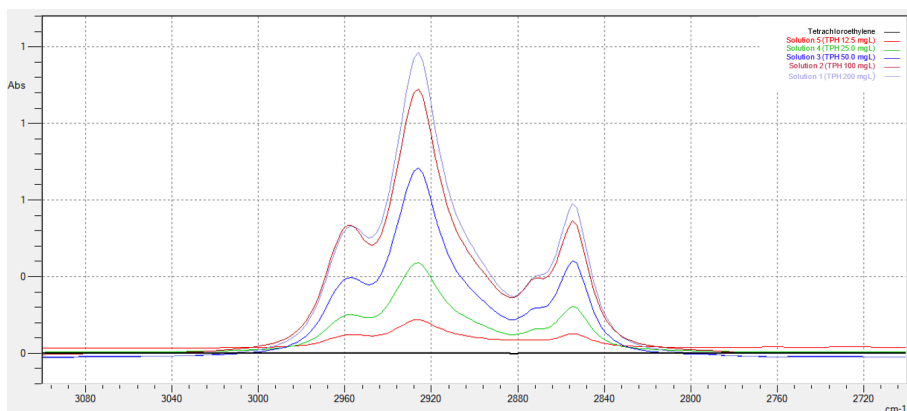


Fig. 3. Infrared recording spectrum of standard solutions.

For each calibration spectrum obtained after scanning the standard TPH solutions using the IR spectrometer, the absorbance value (Table 1) is calculated at a wavelength of 2930 cm^{-1} , a wavelength corresponding to the total content of petroleum products.

Table 1 Absorbance value for standard solutions.

No	Component	Concentration (mg/l)	Absorbance
1.	Tetrachloroethylene	0	0.303
2.	Solution 5	12.5	0.575
3.	Solution 4	25	0.770
4.	Solution 3	50	0.944
5.	Solution 2	100	1.288
6.	Solution 1	200	1.548

Quantification of the TPH content in water using FTIR spectroscopy was performed by measuring the intensity of substance absorbance at a single point, i.e., at 2930 cm^{-1} with autozero spectrum processing according to each background interferogram determined before each measurement. The height or area of a peak in an absorbance spectrum is directly proportional to concentrations of the analyte in infrared beam. For each determined IR radiation spectrum, no instruments such as: Spectral Subtraction, spectral derivatives, peak deconvolution, smoothing and curve fitting were used to improve the appearance of the spectrum in order to extract more information from the spectrum.

The absorbance corresponding to the quantity of petroleum products for the standard solutions corresponds to the points of the calibration curve (Fig. 4) of the method for analyzing the TPH content in water, this was drawn using 6 calibration points by the 2nd

order multipoint method with the correlation coefficient R2 and a value of $r = 0.967$ according to equation 2.

$$\text{Abs} = -4,944e^{-5} \times \text{Conc}^2 + 1,627e^{-2} \times \text{Conc} + 2,516e^{-1} \quad (1)$$

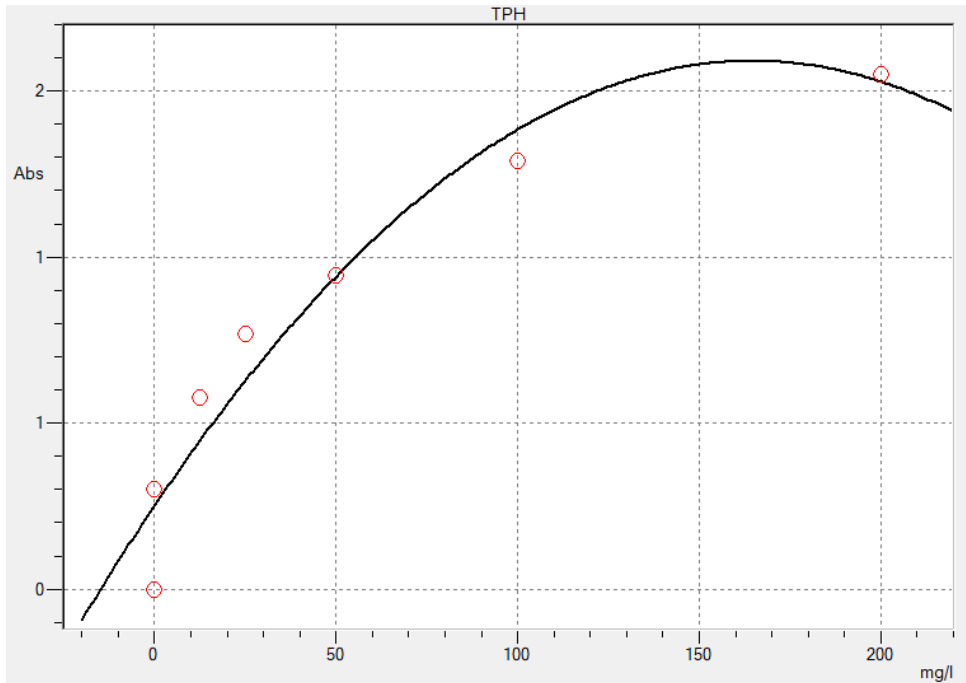


Fig. 4. Calibration curve of the total content of petroleum hydrocarbons in waters.

5) identifying sources of uncertainty in order to establish the uncertainty budget.

Measurement uncertainty as a parameter associated with the measurement results that characterizes the dispersion of values that can be reasonably attributed to the measured quantity [13]. The qualitative estimation of uncertainty involves the estimation of accuracy based on the estimation of the precision and trueness of the method which adds total error composed of systematic error and random error [14]. The quantitative estimate of the uncertainty is quantified statistically spread under values under specified conditions, bias and the qualitative estimate of the uncertainty of the method [13, 14].

The quantitative uncertainty of a test or a work procedure is a range of values that contains the true value and takes the form of an interval of values and is classified depending on the mode of expression as standard uncertainty, combined standard uncertainty, extended standard uncertainty and relative uncertainty.

In this case, the most significant uncertainty components related to the analysis of the total content of petroleum products in water can be approximated: preparation of the standard solution, the uncertainty of calibration standards, calibration curve, the uncertainty of the equipment, uncertainty of the environment and uncertainty of technician (operators) will be taken into account.

Thus, identifying sources of uncertainty for the analysis of total content of petroleum hydrocarbons in water by using FTIR spectroscopy is shown in Fig. 5.

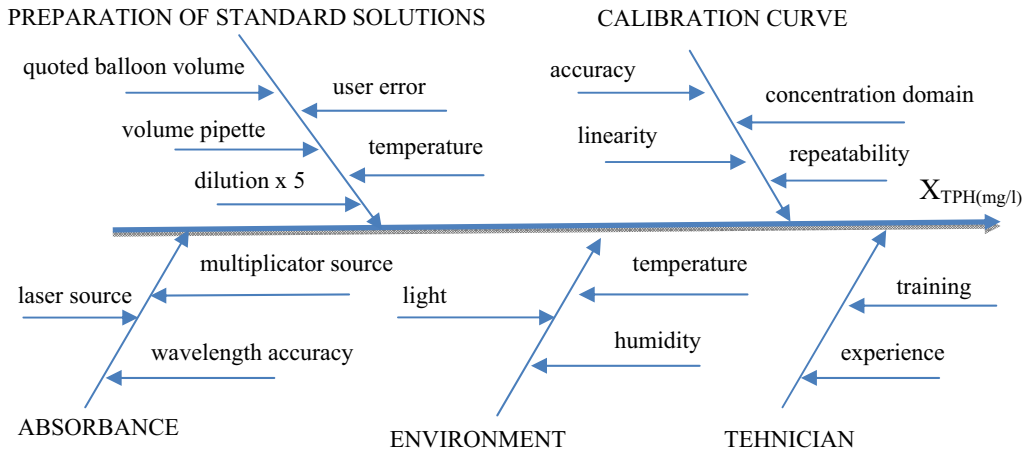


Fig. 5. Uncertainty budget for THP quantification method with FTIR spectrometer.

The quantification of the TPH measurement uncertainty in waters can be achieved in the first step by evaluating the standard uncertainty (Type A and B) followed by the calculation of the compound standard uncertainty and the calculation of the extended compound standard uncertainty. Usually, the expanded composite standard uncertainty is calculated by multiplying the composite standard uncertainty calculation by an expansion coefficient k ($k = 2$; for a 95% confidence level).

4 Conclusion

Calibration of the method for analysis of total content of petroleum products (TPH) in water by using FTIR spectroscopy carried out by plotting the calibration curve for 5 known concentrations of the total content of petroleum products. The equation of the calibration curve for determining the content of TPH in water can also be used in order to determine the concentration of TPH from the soil if the solid-liquid extraction is performed with Tetrachloroethylene. The reduction of signal noise in order to increase the wavelength accuracy is recommended the usage of high purity solvents and properly clean cuvettes. The absorbance spectra for the determination of the Background spectrum (Tetrachloroethylene) and the calibration concentration were processed by correcting the baseline (zero) adjustments and the temperature.

To reduce de uncertainty budget is recommended to use certified reference materials (CMRs) for each point of calibration in order to eliminate uncertainty given by the dilution of one certified reference material into 5 samples. Also, in this regard Horwitz Equation can be used as a known parameter of evaluation in systematic and random error can be followed by laboratory methods under this scope.

From the observations regarding the estimation of the uncertainty budget for the purpose of estimating the measurement uncertainty, it was found that there are always limits to knowledge, the observations vary from the measurement method used, the accuracy of the results obtained and the stability of the instruments and references is limited.

The pollution of soil from the environmental point of view with total petroleum hydrocarbons on oil exploitation sites, for which the level of groundwater contamination

risk could be moderate and high, it is recommended to apply risk mitigation measures, which may include the addition of substances that may neutralize the crude oil content of soil or replacing hazardous chemicals with safer alternatives, if other substances with a high potential for groundwater contamination are identified. From the toxicological point of view, in short term, the human body is not decisively affected by ingestion of food in which these volatile organic compounds have bioaccumulated or by consumption of contaminated water, because these compounds are not metabolized by the human body, being eliminated from the body in a reduced time through the urinary tract.

This paper was developed within the Nucleu-Programme, carried out with the support of MCI, Program Nucleu EXT0X 2, entitled “Modernization of the research infrastructure for complete investigation of both physical and chemical parameters of environmental components’ quality in situ within landfills as well as in work environments in order to increase the degree of safety and health”.

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