Experimental studies were conducted to establish the influence of the type of solvent on the degree of extraction of hydrocarbons from the soil samples contaminated with crude oil of unknown chemical composition, measurement concentration of TPH (total petroleum hydrocarbons) using two methods of IR analysis. On the same soil samples the TPH were determined by IR-NDIR spectroscopy using an agent extraction dimer/trimer chlorotrifluoroethylene and FTIR spectroscopy using as extraction agent tetrachloroethylene. For the soil samples which presented high concentration of TPH, over 8000 mg/kg dry matter, was performed also analysis of hydrocarbons by gas chromatography (GC-FID) using a column SIMDIST. Besides the global concentration of hydrocarbons, the concentration of the hydrocarbons between C12-C36+ could also be established. Total petroleum hydrocarbon concentrations measured by IR-NDIR showed lower concentration than the measurements in FTIR. From chromatographic analysis it can be observed that the hydrocarbons C12-C20 are in small concentration, towards the area of C27-C37+. The analysis of the concentration of hydrocarbons in soil can be used to establish more appropriate methods of extraction of hydrocarbons according to the fraction that predominates in the organic soil matrix.

Keywords: soil contamination, crude oil, TPH indicator, IR spectroscopy, dimer/trimer chlorotrifluoroethylene

Crude oil in soil is the results of activities where oil is used or transported. Leakage of pipelines can introduce large amount of crude oil in the environment. Soil is able to adsorb an amount of oil in pores and organic matter up to a residual concentration.

In time the organic hydrophobic pollutant suffered a series of physico-chemical transformations, through the “weathering” phenomenon [1].

The organic matter in soil may influence the adsorption capacity of soils. The chemical composition of crude oil is complex and change over time following its release into the environment [2]. Because crude oil is such complex mixtures, there is no single “best” method for measuring all types of hydrocarbons contamination. These factors make it difficult to select the most appropriate analytical methods for evaluating environmental soil samples [3].

The extraction of the soil matrix of hydrocarbons from the accidental leakage of crude oil, which is necessary for measuring the parameter TPH (total petroleum hydrocarbons), is a source of active research, intensely studied in a series of recent papers [4-9].

Any given method for the analysis of semi-volatile total petroleum hydrocarbons (TPH, C10-C36+) in contaminated soil is made up of a number of procedures each being able to be subjected to improvement or optimization [10].

There are two common practices for the measurement of TPH in soil samples: use of gas chromatography with flame ionisation detector (GC-FID) and use of infrared spectroscopy (IR).

The purpose of this research study is to determine the quantitative experimental of TPH (total petroleum hydrocarbons) content in soil from accidental pollution with crude oil.

**Experimental part**

To study the influence of the solvent type on the degree of extraction of hydrocarbons from the soil matrix and for determining the concentration of total petroleum hydrocarbons (TPH), the IR spectroscopy was used. Sets of samples of soil were collected and prepared from a soil profile at depths of 5 cm, 10 cm, 30 cm and 50 cm. The soil used in these experiments had: porosity 43 % and permeability 1.3 x 10^-4 m/s at 5 cm depth, porosity 42 % and permeability 7.9 x 10^-4 m/s at 10 cm depth, porosity 42 % and permeability 6.2 x 10^-3 m/s at 30 cm depth, porosity 43 % and permeability 1.9 x 10^-4 m/s at 50 cm depth.

Soil samples are contaminated with crude oil of unknown composition. For the same composition of soil samples the TPH concentration was determined using the two types of IR analysis, IR spectroscopy NDIR (Non Dispersive Infra Red), using as extraction dimer/trimer chlorotrifluoroethylene (S-316), on OCMA-310 spectrometer (Oil Content Monitor-HORIBA) spectrometer. To remove interferences organic extracts were purified with fluorisil (anhydrium magnesium silicate).

The OCMA-310 uses special S-316 solvent to extract the oil components from water samples and soil samples. The extract is measured using IR absorbance, a non-dispersive infrared spectrophotometric technique which is specific to hydrocarbons such as oil. The device characteristics are: field measurement is between 0-200 mg/L, resolution 100 to 200 mg/L and the ratio sample/solvent is 2:1.

On the same soil samples the TPH was determined by FTIR using spectrometer Perkin Elmer, model Spectrum 2000, domain registration spectrum for compounds analyzed was 3100-2800 cm-1, using as extraction agent tetrachloroethylene. For removing polar compounds alumina was utilized. Samples were dried, homogenised and the hydrocarbon extraction was performed with tetrachloroethylene in a closed tube at a temperature of 100°C. Integration areas have been on the field -3000 ~ 2890 cm-1.
Methyl groups $CH_3$ and $CH_2$ methylene have 2 bands each in IR absorption in this area, at approximately 2958 and 2876 cm$^{-1}$, respectively. The solvent used (tetrachloroethylene) does not absorb IR from 3100 until about 2880 cm$^{-1}$.

Because the most intense bands of absorption are those from 2958 to 2924 cm$^{-1}$, it is convenient to use tetrachloroethylene as a solvent for determining the saturated hydrocarbons. Aromatic hydrocarbons which do not have saturated C-H links in their molecule do not absorb in this area, but can be measured with other absorption bands. For small concentrations of hydrocarbons a vat of quartz Infrasil was used, with an optical path of 10 mm. For high concentrations a KRS-5 (bromide / iodide thallium) vat was used, with an optical path of 0.31 mm.

For the soil samples which presented high global concentration of TPH (total petroleum hydrocarbons), over 8000 mg/kg d.m., the concentration of hydrocarbons with the same number of carbon atoms are determined by gas chromatography with flame ionisation detector (GC-FID) with Simdist column.

Instrument gas chromatograph was Perkin Elmer Clarus 500, with detector FID, with the frequency of reading 12.5 Hz, the domain 1 and attenuation 4. The SIMDIST (Simulated Distillation) column has a length of 12 m, an inside diameter of 0.53 mm, and a 0.1 micron film. The conditions were, as follows: He as carrier gas, the temperature of column from 55 to 380 °C, with 15 degrees per minute, original time of 1 minute, final time of 10 min, the constant rate of the carrier gas was 30 cm/s, and the temperature of the injector and detector was 400 °C. Samples were injected manually with a syringe of 2 μL. In order to determine the retention times, a mixture of normal alkanes was used, with a number of carbon atoms ranking from 19 to 40, in known quantities and analyzed by the same method. For the retention times of the other n-alkanes, a paraffin oil diluted in tetrachloroethylene was injected.

The integrations were performed by using the TotalChrom software of the instrument.

Results and discussion

The global TPH concentrations (mg /Kg dry matter) of soil samples are shown in figure 1.

From these results it can be observed that the tetrachloroethylene extracted more TPH than the S-316. The results of the samples soil analyzed by the CG and SIMDIST column (concentration of hydrocarbons with the same number of carbon atoms between components C12-C37) were calculated from peak areas and are presented in figure 2.

From these results it can be observed that the isoalkanes of range C12-C20 are in a small concentration compared with isoalkanes of range C27-C37 for all soil samples. The chemical composition of the crude oil is complex and may vary after the crude oil spills on the surface soil. Composition change influences desorption. The „weathering” phenomena make in the composition of the crude oil adsorbed on the soil’s organic mineral surface appear
heavy compounds from biodegradation that are extracted with difficulty from the soil. The following comments can be made:

- tetrachloroethylene extracted more pollutant than the S-316;
- mixtures of hydrocarbons are separated and partitioned in function of the molecular weight and structure of the compounds. Some persist, others fade, others migrate, and others adhere strongly to the particles of the soil. It is reasonable to believe that the compounds having a similar chemical character (aliphatic or aromatic) and those with close boiling points will behave similarly;
- the TPH measured by different analytical methods gives a single value, a global concentration of hydrocarbons which cannot be used in the risk criteria, since it gives a number which does not represent the concentration from a specific individual component about which chemical properties are known that can be helpful in determining the risk.

Conclusions

The fact that different results of TPH (total petroleum hydrocarbons) are obtained from the same soil samples emphasizes the necessity of reviewing the term of TPH, as it is required by the legal provisions currently in force. The "TPH" term could perhaps be replaced with the one of "extractable" hydrocarbons. These would include hydrocarbons between C_{10}-C_{40}, being extracted in varying amounts, depending on the solvent used and the determination method chosen.

Because the extraction degree of hydrocarbons differs depending on the method of determining chosen, for the same analyzed area different levels of pollution can be obtained.

TPH analysis is widely used as a general measure of the presence of crude oil in soils. TPH itself is not a direct indicator of the risk.

TPH measured depends on the ability of the solvent used to extract the hydrocarbons from soil. Solvents have different extraction efficiencies. The choice of solvents is determined by many factors such as cost, spectral qualities, method regulations, extraction efficiency, toxicity and availability.

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