

# Determination Of The Spectrum Of Soils Polluted With Hydrocarbons, Soil And Water Depollution Methodologies Based On Spectrophotometric Analysis

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## **Abstract:**

**Background:** Oil pollution is one of the most serious types of pollution, being in addition to an aggressive action on plants and microorganisms in the soil and being one of the most difficult actions to determine the type of pollutant and especially the polluter. This article aims to present the effects of oil pollution on the environment and also to present the types of photometric spectra of the main pollutants.

**Materials and Methods:** Oil biomarkers are shown and spectra are also shown.

**Results:** The results of oil fingerprinting are similar to other forensic analyzes (for example, blood typing), where oil fingerprinting techniques provide the data needed to prove that a sample does or does not match a suspect source.

**Conclusion:** Because petroleum is a very complex mixture of compounds that cannot be fully resolved by gas chromatography, a highly selective detector such as a mass spectrometer used in conjunction with a high-resolution chemical separation system, GC, leads to the determination specific target compounds from spilled oil and control oil.

**Key Word:** Oil pollution, biomarker, compounds,

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## **I. Introduction**

In the anti-pollution fight, the strategic objectives of protecting ecosystems and limiting the damage caused by petroleum products' accidental or non-accidental spillage are achieved by applying various theoretical methods and an adequate arsenal of technical means.

Before establishing the criteria according to which the person who carries out the de-pollution, faced with a concrete situation, will have to choose one or the other, let's see what they are and what application limits each one has.

There is an excellent diversity of ways a crude film can appear and evolve.

Both the methods and the means must take these particularities into account, not out of a simple desire for adaptability (a particular method should correspond to each situation - an ideal thing - but impossible to achieve in practice), but out of a requirement for flexibility (a method and related means to be used in a wide range of situations).

The polluting source's origin can be in the soil (the rupture of an oil pipeline, the transport by underground waters of the waste resulting from the washing of oil tanks, a major naval accident, and the pollution of the shore, etc.) or underground water [1].

Depending on the extent, pollution can take the form of incidents (for the solution of which simple means are sufficient, as a rule, mandatorily in equipping the potential polluting agent), accidents (when the spilled amount exceeds the possibilities of action of a single pollution control unit equipped accordingly, requiring the intervention of other similar units) or catastrophes (when all existing means in the area must come into operation, including those provided by neighboring riparian countries or other foreign companies, specialized).

The type of hydrocarbon also influences the method and means of work.

In fact, light hydrocarbons —distillates—pose fewer problems than heavy hydrocarbons—oil—which are more toxic for the environment and have a more complicated evolution over time.

Solid floaters in the film (typical case in underground waters) make recovering or neutralizing hydrocarbons even more difficult [2].

If we also add the particular circumstances of each pollution accident (for example, whether it is accompanied by fire or not, whether it threatens special areas or industrial installations of particular importance, etc.) and the fact that all of the above are variable over time, we will understand more easily why there is this great diversity of methods and means of intervention.

At the same time, the diversity we are talking about should not be understood as an exclusive type (either one or the other) but as a complementary type (both one and the other), the sequence or simultaneity of the application of several methods and means constituting the secret of a better organization in the tactical field.

Conventionally, the methods of combating hydrocarbon pollution are grouped into five major categories [3]:

- methods to limit the spread of hydrocarbons;
- methods of mechanical recovery of hydrocarbons;
- methods of physical-chemical and biological neutralization of hydrocarbons;
- washing and cleaning methods of adhering hydrocarbons;
- restoring the environment.

Of particular importance is the technical equipment of the existing installations that may or may not allow the elimination of the cause by timely detection of the accident and the isolation of the defective section.

In the case of soils, choosing the most appropriate pollution mitigation technology will use the information gathered during the investigation stages regarding [4]:

- The type of pollutants present and their concentration;
- The volume of polluted soil that requires treatment; its location, depth and accessibility;
- Soil characteristics;
- The objectives of the cleaning or the legal provisions and the time frame necessary to achieve them;
- Local regulations and available local arrangements that could prevent the application of certain remedial processes;
- The expected use of the site for the future;
- The ratio between the costs of different cleaning/remediation options;
- Risk assessment.

## **II. Properties Of Petroleum Pollutants**

Oil residues (we call them specific oil pollutants most often determined in ecological accidents in Romania) are complex mixtures of hydrocarbons with a relatively low content of impurities or polluting substances, such as oxygen, nitrogen, sulfur, and various metals.

Oxygen compounds are made up of naphthenic acids and phenols. Nitrogen compounds are derivatives of pyridine, quinoline, and pyrrole. Sulfur is found in crude oil in amounts from less than 0.08% to 1.5% in elemental sulfur, hydrogen sulfide, mercaptans, sulfides, and thiophene.

Oil residues are made up of hydrocarbons, which represent about 98% of the total. The elemental composition is expressed by the C/N ratio, which varies with the structure of the hydrocarbons.

The following classes of hydrocarbons are found in oil residues [5]:

- saturated acyclic hydrocarbons-alkanes;
- cyclic saturated hydrocarbons-cycloalkanes;
- mononuclear aromatic hydrocarbons;
- condensed polynuclear aromatic hydrocarbons.

The research shows that crude oil residues are complex mixtures of substances and that crude oil has not been separated into its components in the soil.

Table 1,2,3 presents the average composition of oil residues of interest through the global effect they determine. Analyzing these from the soil determines their total and sometimes fractional amounts.

The analytical methods used to determine oil residues consist of extracting them with a selective solvent (hot or cold), followed by separating the main phases through a silica gel column, eluting according to their polarity with the elutrope series hexane-benzene-benzene: methanol, and gravimetric dosing.

**Table 1. Minimum composition of oil residues [6]**

Component	Oil %	Gasoline %	Residue from refineries, %
Alkanes (paraffins) Hexadecane	15-30	25-68	21
Cycloalkanes (naphthenes) Cyclohexane	30-50	5-24	-
Aromatic (Benzene) Benzene	5-24	7-55	49
Asphaltenes (heterocyclic compounds with O, S	2-15	0,1	30

and N) Naphthalene			
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**Table 2.** Characteristics of oil residues [6]

Component	Specific density g/cm <sup>3</sup>	Nitrogen %	Carbon %	Sulph %	Carbon/Nitrogen %
Paraffins	0,81	0,01	85,1	0,07	8500
Asphaltenes	0,84	0,05	86,6	0,23	1730

**Table 3.** Properties of oil residues [6]

Grupe de poluanti	Exemple	Proprietati comune
Current petroleum hydrocarbons	Gasoline Diesel Fuel for heating Aviation fuel Crude oil	-easier than water - biodegradable - generally slightly soluble, but with possible solubility of some fractions -variable viscosity and absorption -volatile or holders of some volatile fractions
Heavy hydrocarbons	- heavy fuel -coal tars - petroleum tars -creosote	-variable density -reduced biodegradation -low solubility -low volatility - viscous - generally high adsorption
Aliphatic halogenated hydrocarbons	-tricloretilena -tetraclorotilena -diclormetan -cloroform -bromoform	- high density - low biodegradability -relatively soluble -volatile -low viscosity - generally weak adsorption
Oxygenated hydrocarbons	- glycols -alcohols -ketones phenols - furani - fuel additives	- very soluble - biodegradable -other variable properties
Cyclic halogenates	-numerous pesticides -polychlorodiphenyl -pentachlorophenol	- reduced volatility - non-biodegradable or slightly biodegradable

The properties of oil, the most important from the point of view of interaction with soil and water, are [7]:

- the state of aeration-mixture of liquid compounds in which solid and gaseous compounds are dissolved;
- hydrophobic character - repels water molecules, is immiscible in water, forms a superficial film;
- high content of organic carbon;
- very high C/N ratio.

### III. Intervention Guide For The Elimination Of Soil Pollution

Soil remediation techniques can be divided into two categories:

- ex-situ (requires excavation)
- in-situ (excavation is not necessary)

The main advantage of isolation and in situ remediation techniques is that they involve minimal displacement of the location and monitoring and, therefore, can be applied in congested places in operation.

The disadvantages of in-situ remediation include the need for a more in-depth site investigation, monitoring, and longer treatment times.

Identifying the achievement of objectives is more complex than in the case of ex-situ techniques.

Remediation options range from simple excavation and evacuation to more sophisticated techniques such as in situ bioremediation.

The applicability of these techniques depends to a large extent on the particularities of the location and on factors such as:

- a. the type, concentrations and distribution of pollutants;
- b. soil structure;
- c. hydrogeological conditions;
- d. infrastructural limitations (foundations, cables, pipes);
- e. the level of cleaning (purification) required and the time available;
- f. the cost.

Spectrophotometric and chromatographic analysis is performed to indicate the optimal depollution method depending on the pollutant.

Following the chromatographic analyses, the diesel fuel sampled has more than 200 chemical compounds, whose aliphatic chain varies from 10 to 30 carbon atoms, most of these compounds having a number of 14 carbon atoms.

Oils show a smaller range in terms of the diversity of their molecules, whose aliphatic chain varies between 20 and 40 carbon atoms, most compounds having a number of 28.

The number of carbon atoms that form the aliphatic chain has a direct effect on physico-chemical characteristics of carbide.

In infrared, the differentiation of carbons is done by measuring the absorption of C-H bonds, as a result of the applied vibrations.

For an aromatic carbide, the absorption due to the C-H bond occurs for a wave number corresponding to a  $\nu$  value greater than  $3000\text{ cm}^{-1}$ .

In the ultraviolet, aromatic carbides are the only ones that absorb chromomorphous chemical groups, that is, those groups that have free electrons or PI orbitals.

As in the previous case, we made the ultraviolet spectra of different carbides.

These U.V. spectra give aromatic absorptions for wavelength values of 230 and 260 nm respectively. Their quantitative analysis shows that, for an identical concentration of hydrocarbons of  $100\text{ mg.l}^{-1}$ , there is an important variation of the absorbance at the value of the wavelength of 230 nm.

Thus, residual oil contains five times more aromatic products than motor oil. This, of course, in the assumption that the hydrocarbons have identical properties (the specific molar absorption coefficient  $E$  is identical).

This aspect must still be viewed with a certain reserve since, for the two situations, the spectra are different. In particular, there is no 260 nm absorption band for residual oil.

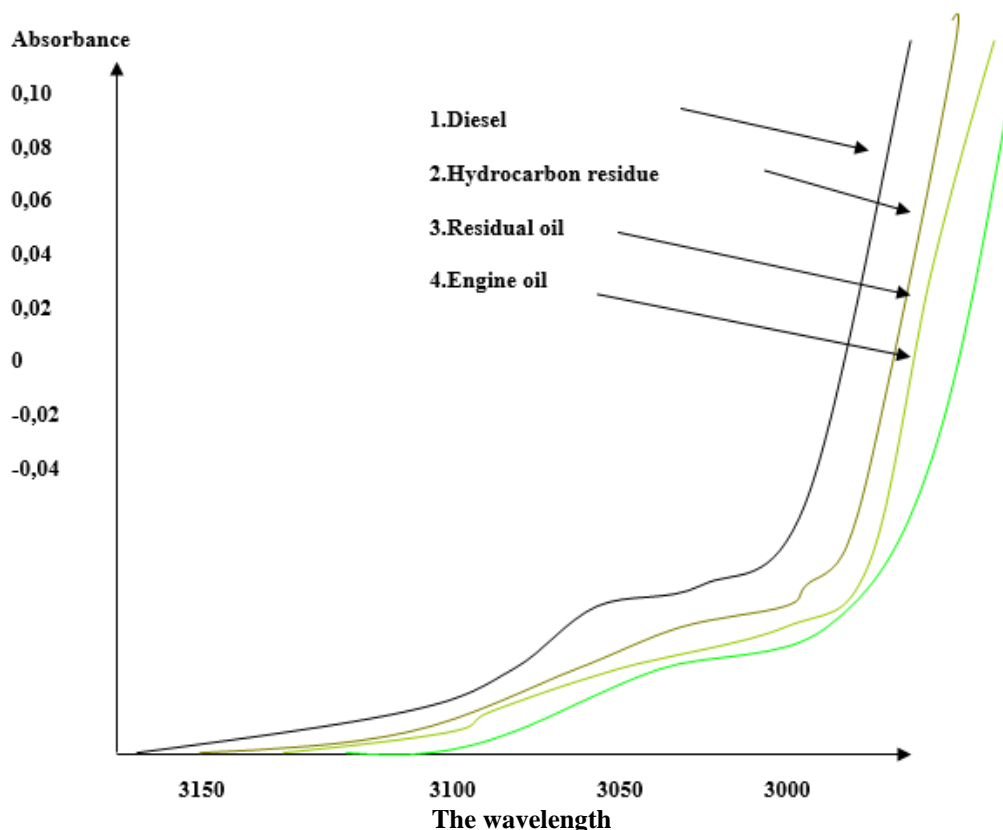
This reserve is confirmed, in addition, by the absorbance ratio  $a/b$  corresponding to the three petroleum products, for wave values of 230 nm and 260 nm, respectively.

For diesel fuel and hydrocarbon residue, the values of these ratios are very close, a fact that confirms, once more, the results obtained in infrared.

On the other hand, motor oil and waste oil have totally different profiles.

Analytical methods for the identification of oil in a marine environment should perform the following tasks:

- detects the presence of oil;
- provides and quantifies the target compound from petroleum compounds and provides applicable source fingerprinting data.



**Figure 1.** Comparison of infrared spectra of four products [8]

**Table 4. Quantitative analysis of U.V. spectra. for four petroleum products [8]**

Products	Concentration Mg.l <sup>-1</sup>	Absorbance 230 nm	Absorbance 260 nm
Hydrocarbon residue	44,44	0,658	0,133
Diesel fuel	61,38	1,505	0,307
Engine oil	159,70	0,993	0,307
Residual oil	14,24	0,397	0

The petroleum components selected for analysis in the GC laboratory are shown in Table 5.

**Table 5. Petroleum components selected for analysis in the GC laboratory [9]**

Component	Quantification ion	Abbreviation
alkanes	85	
naphthalene	128	NAPH
C-1 naphthalene	142	C-1 NAPH
C-2 naphthalene	156	C-2 NAPH
C-3 naphthalene	170	C-3 NAPH
C-4 naphthalene	184	C-4 NAPH
Fluorene	166	FLU
C-1 Fluorene	180	C-1 FLU
C-2 Fluorene	194	C-2 FLU
C-3 Fluorene	208	C-3 FLU
Dibenzothiophene	184	DBT
C-1 Dibenzothiophene	198	C-1 DBT
C-2 Dibenzothiophene	212	C-2 DBT
C-3 Dibenzothiophene	226	C-3 DBT
phenanthrene	178	PHEN
C-1 phenanthrene	192	C-1 PHEN
C-2 phenanthrene	206	C-2 PHEN
C-3 phenanthrene	220	C-3 PHEN
C-4 phenanthrene	234	C-4 PHEN
Fluoranthrene	202	FLANT
pyrene	202	PYR
C-1 pyrene	216	C-1 PYR
C-2 pyrene	230	C-2 PYR
C-3 pyrene	244	C-3 PYR
C-4 pyrene	258	C-4 PYR
chrysene	228	CHRY
C-1 chrysene	242	C-1 CHRY
C-2 chrysene	256	C-2 CHRY
C-3 chrysene	270	C-3 CHRY
C-4 chrysene	284	C-4 CHRY
Benzo (b) Fluoranthene	252	B(b)F
Benzo (k) Fluoranthene	252	B(k)F
Benzo (e) Pyrene	252	B(e)P
Benzo (a) Pyrene	252	B(a)P
perylene	252	PERYL
Indeno (g,h,i) Pyrene	276	INDPYR
Dibenzo (a,h) Anthracene	278	DIBENZ
Benzo (1,2,3-cd) Perilen	276	BENZP
<u>Horani (191 familie)</u>	191	
<u>Sterani (217 familie)</u>	217	

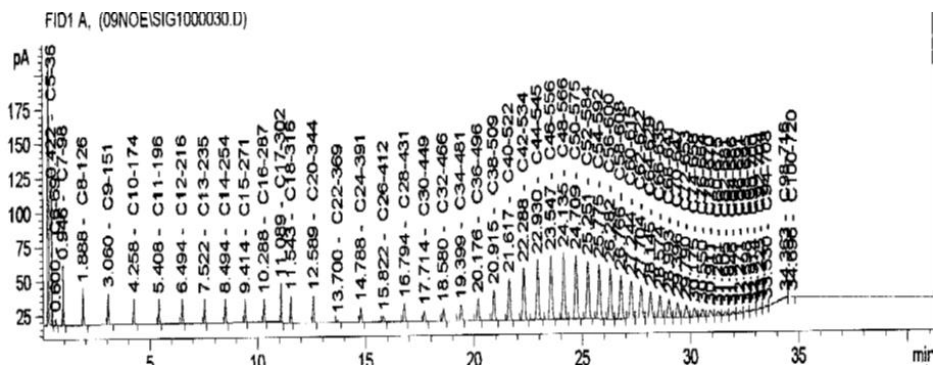


Figure 3. Analysis of a crude oil



Figure 2. GC-MS technique [8]

#### IV. Result

Because petroleum is a very complex mixture of compounds that cannot be fully resolved by gas chromatography, a highly selective detector such as a mass spectrometer used in conjunction with a high-resolution chemical separation system, GC, leads to the determination specific target compounds from spilled oil and control oil.

#### V. Conclusion

The target of our research is the polycyclic aromatic hydrocarbons (PAHs) listed in Table 5, since they represent less than 5% of the oil composition by weight.

This list of aromatics is extremely useful in differentiating crude oil from products from burning fuels.

This is possible because incomplete combustion of fuels produces PAHs, which are characterized by 3, 4, 5 ring aromatics, compounds with several substituted alkyl counterparts.

For example, fluoranthene, chrysene, and benzopyrene are more common in source combustion pollution than oil pollution.

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