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Industrial pollution

ANALYTICAL INVESTIGATION OF MINERAL OIL CONTENT IN SOIL DURING THE REMEDIATION PROCESS

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Abstract. An analytical investigation of mineral oil content from Ploiesti area was performed for monitoring the soil remediation process. Mineral oil hydrocarbons are among the most widespread contaminants in soil. Refineries, petrol stations, tank depots, pipelines and waste disposals are typical sources of this kind of contamination. The distribution of mineral oil hydrocarbons in soil is very heterogeneous depending on the depth and soil composition, particle size distribution, the content of organic matter, the mineral composition of clay fraction, pH. Investigation of contaminated soil, assessment of treatment processes and environmental monitoring of soil remediation require rapid analytical control which can be performed by GC, IR or gravimetric method function of the concentration level of the pollutants. Analyses were carried out on standard solutions and samples of soil contaminated with different kinds of commercial hydrocarbons. Gas chromatographic technique was used both for qualitative determination of mineral oil composition and for the qualitative evaluation of the pollution level, after preliminary pretreatment of the soil samples by extraction with acetone – hexane and clearing-up with Florisil. Soil samples were collected from 2 selected points from the polluted area and after the chemical and biological treatment. The analytical results offered the possibility to characterise the polluted site and to conduct the remediation process.

Keywords: mineral oil, remediation, gas chromatographic method, analytical investigation, dry matter.

AIMS AND BACKGROUND

High toxicity and carcinogenic potential of some organic compounds impose analyses and monitoring of these pollutants from various water and soil categories, even if they are presented in traces.

Petroleum products represent the most frequently found category of pollutants both in water and in soil, the main sources of pollution being accidental spillages and dischagees from industrial plants (refineries, gas stations, etc.) and transport vehicles. These types of pollution produce damages of agricultural soil, leisure areas, beaches and induce bad taste and smell of water, putting in danger the life of aquatic or terrestrial organisms.

Environmental legislation, through Order No 756/97[1], sets the normal values and the alert and intervention levels for all important classes of high toxic potential organic compounds from soil. For petroleum products the limits are

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below 100 mg/kg dry matter (d.m.) for normal values, in the range 200-1000 mg/kg d.m. for alert levels and between 500-2000 mg/kg d.m. for intervention levels.

EXPERIMENTAL

Selection of optimum analytical method for soil samples mainly depends on the chemical structure of organic compounds and their concentration level. Three different analytical techniques can be used for testing petroleum products: gravimetry, IR spectroscopy and gas chromatography (GC)[2]. All these methods respond at least to one of the following essential characteristics:

- the pollutant can be analysed at low concentrations;
- the pollutant can be analysed in the presence of interfering compounds;
- presents a good precision and accuracy.

In Tables 1 and 2 are presented the advantages and disadvantages of using the above mentioned analytical methods.

Table 1. Advantages of the three analytical techniques used

Gravimetry	IR spectroscopy	Gas chromatography
• Simple and cheap • No special equipment is used • No equipment calibration is necessary • Can be used in any laboratory	• quick analytical response • high precision result • detection level 20 mg/kg d.m.	• halogenated solvents are not used for extraction • quantitative analyses of petroleum product fractions • high precision results • detection limit 5 mg/kg d.m.

Table 2. Disadvantages of the three analytical techniques used

Gravimetry	IR spectroscopy	Gas chromatography
• Quantitative analysis only for the global content in petroleum products • Halogenated solvent needed for the extraction of samples • Detection limit 50 mg/kg d.m.	• quantitative analysis only for the global content in petroleum products • halogenated solvent needed for the extraction of samples	• needs of modern equipment and high-qualified personnel • needs calibration and high-purity reagents

The most used method from the above mentioned three is gas-chromatography because of its low detection limit (5 mg/kg d.m.) it permits also detection of the petroleum product nature.

a. Primary processing was performed if the granulation of the soil sample was higher than 2 mm and pollutants were heterogeneously distributed. It consists of removal of various objects (vegetation, glass, metals, etc.) followed by chemical drying. The operation of chemical drying was performed through contact of equal quantities of soil and anhydrous sodium sulphate. The mixture was kept at cold temperature for 12-16 h and periodically mixed in order to avoid formation of agglomerates.

b. Liquid-liquid extraction was applied as separation method using acetone and hexane as extraction solvents.

c. Purification of the compounds was realised by liguid-solid adsorption chromatography which consists of the separation of different category of compounds as a function of their distribution and retention between a solid stationary phase (Florisil) and a liquid mobile phase which must have the following properties:

- good solubility for the components of the mixture;
- different density from water;
- no reactivity with the substances which will be purified.

d. Concentration by evaporation at low pressure was performed using a rotaevaporator. The advantage consists in the fact that the evaporation of the solvents is realised at low temperatures in order to impede pollutant's losses.

The operating parameters are presented in Table 3 together with the equipment used and the solutions for calibration curve.

Tabel 3. Equipment and operating parameters

Equipment – gas chromatograph FISONS 6000 with FID detection	
Operating parameters	
Stationary phase	Mobile phase pressure/flow of gas
• CP-Sil- 5CB	• hydrogen
• L=30 m	• column pressure – 40-45 kPa
• i.d. = 0.25 mm	• detector pressure – 65 kPa
• Φ = 0.25 μm	• gas flow
	o column – 3-4 ml/min
	o top valve – 3-4 ml/min
	o bottom valve – 15 ml/min
Temperature programme	
• injector 280°C	
• detector 275°C	
• column15°C/min 60°C (5 min) – 300°C (30 min)	
Calibration curve: Solutions prepared from mixture of diesel oil and oil without additives	

A sampling plan was developed for a highly affected with petroleum products area (Ploiesti area). In order to monitor the chemical and biological remediation process of soil, M11, C11, B11, M21, C21, B21 were sampled from 0.3 m depth, and M12, C12, B12, M22, C22, B22 samples from 3 m depth at various points of the polluted area.

2 polluted soil samples and also 2 soil samples after each stage of chemical and biological treatment were taken in accordance with the requirements of ISO 10381/1-94 standard[3].

RESULTS AND DISCUSSION

After analytical investigations the following global and also on fractions (C_{10}-C_{14}; C_{14}-C_{20}; C_{20}-C_{26}; C_{26}-C_{34}; C_{34}-C_{40}) results were obtained for all the samples (Tables 4 and 5).

Table 4. Results obtained before and after the chemical and biological treatment of M11 sample

	M11 (0.3 m)		C11 (0.3 m)		B11 (0.3 m)
629	C_{10}-C_{14} 35%	95	C_{10}-C_{14} 40%	24	C_{10}-C_{14} 35%
mg/kg	C_{14}-C_{20} 50%	mg/kg	C_{14}-C_{20} 50%	mg/kg	C_{14}-C_{20} 55%
d.m.	C_{20}-C_{26} 10%	d.m.	C_{20}-C_{26} 10%	d.m.	C_{20}-C_{26} 10%
	C_{26}-C_{34} 5%		C_{26}-C_{34} <5%		C_{26}-C_{34} <5%
	C_{34}-C_{40} <5%		C_{34}-C_{40} <5%		C_{34}-C_{40} <5%
	diesel oil		diesel oil		diesel oil trace

Table 5. Results obtained before and after the chemical and biological treatment of M22 sample

	M22 (3 m)		C22 (3 m)		B22 (3 m)
175	C_{10}-C_{14} 40%	45	C_{10}-C_{14} 55%	11	C_{10}-C_{14} 45%
mg/kg	C_{14}-C_{20} 40%	mg/kg	C_{14}-C_{20} 35%	mg/kg	C_{14}-C_{20} 50%
d.m.	C_{20}-C_{26} 15%	d.m.	C_{20}-C_{26} 10%	d.m.	C_{20}-C_{26} 5%
	C_{26}-C_{34} 5%		C_{26}-C_{34} <5%		C_{26}-C_{34} < 5%
	C_{34}-C_{40} <5%		C_{34}-C_{40} <5%		C_{34}-C_{40} <5%
mixture of oil and diesel oil		mixture of oil and diesel oil		mixture of oil and diesel oil trace	

From the results of the analytical tests (Table 4) and the chromatograms (Fig. 1) for samples M11, C11, B11 (0.3 m) can be observed that the main type of petroleum product present in all the soil samples consists in diesel oil product. The following comments can be made:

- removal of the petroleum product from soil using chemical treatment process was performed in proportion of 80% in case of surface soil. It shows the reduction of petroleum products at amounts lower than 100 mg/kg d.m.;
- during biological stage which involves microorganisms, the yields of removal of petroleum products are lower than those obtained in chemical stage for the same soil sample;

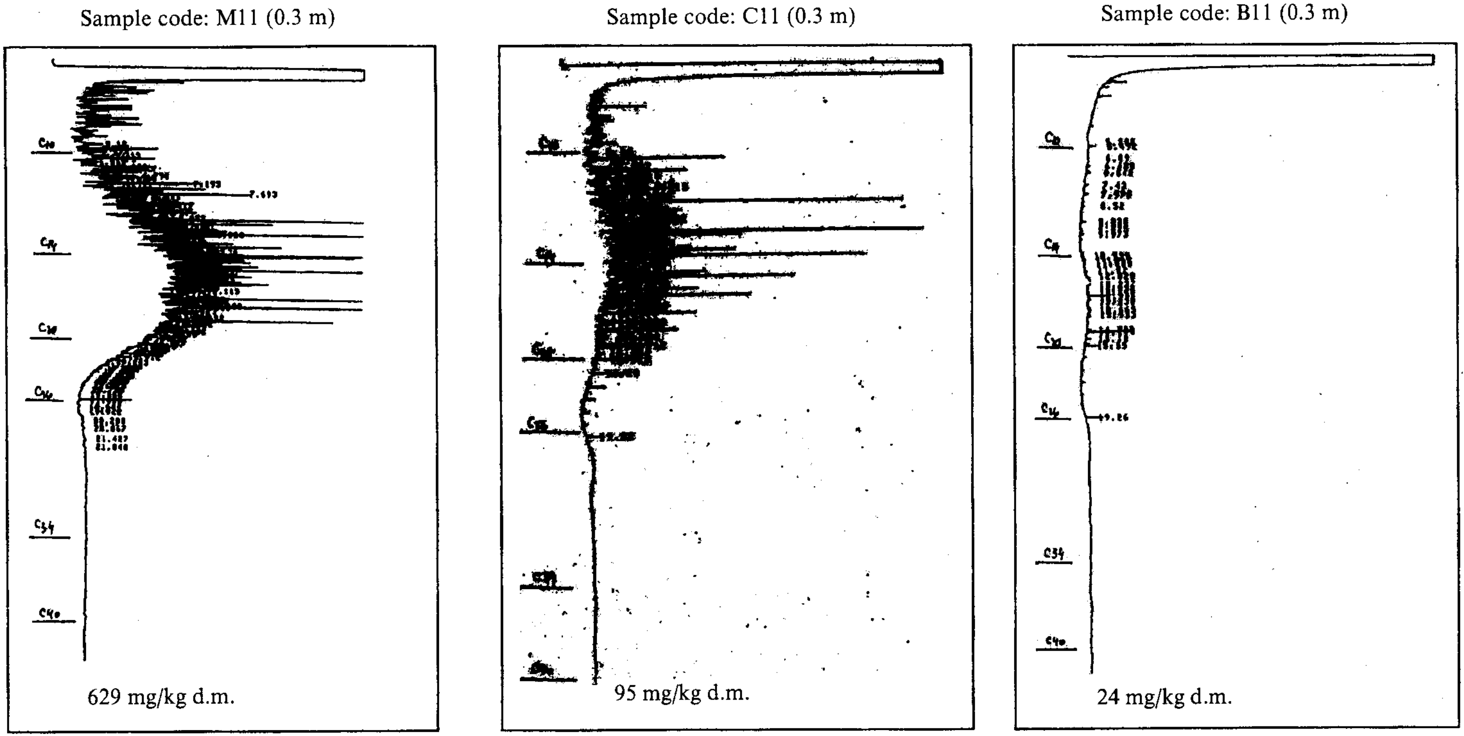
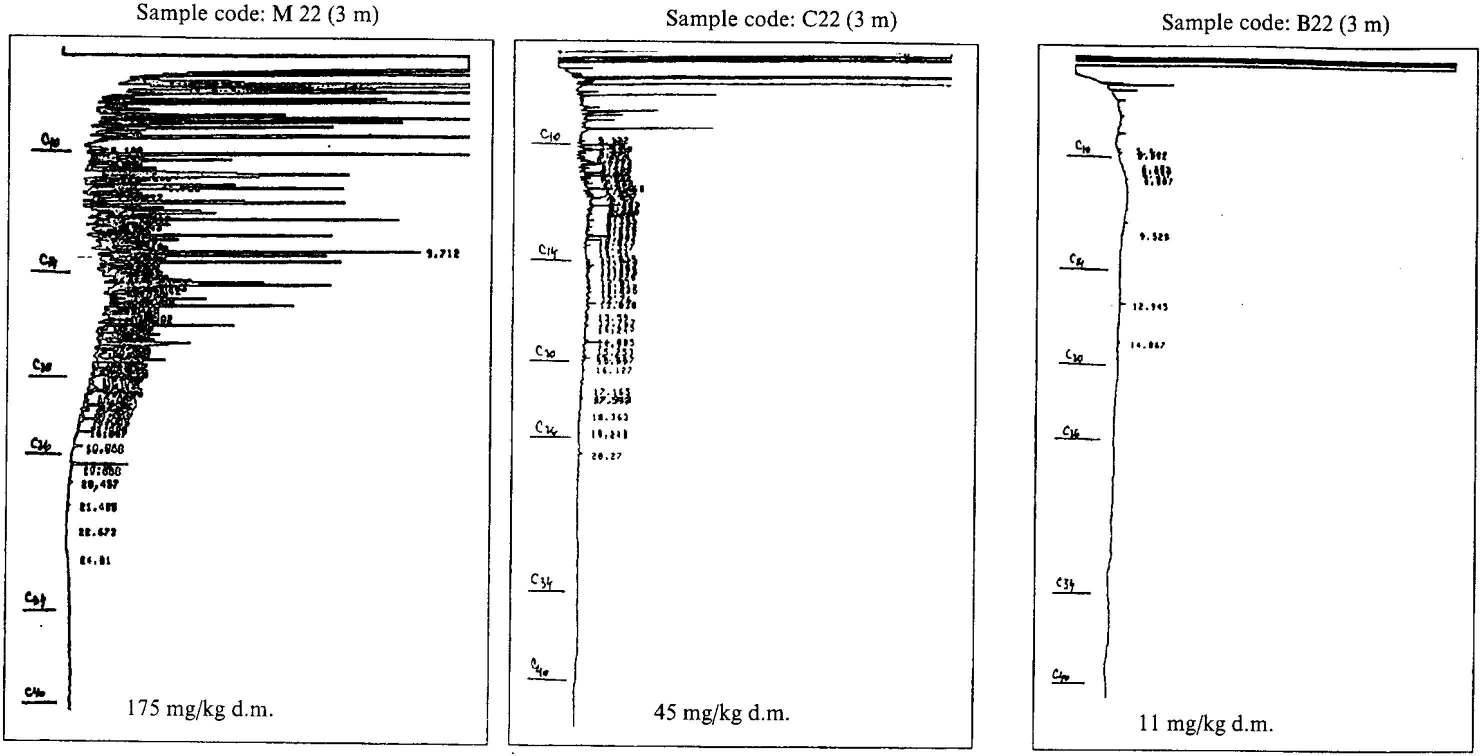

Sample code: M11 (0.3 m)
Sample code: C11 (0.3 m)
Sample code: B11 (0.3 m)

Fig. 1. Chromatograms for mineral oil for M11 sample before and after the chemical and biological treatment


Sample code: M 22 (3 m)

Sample code: C22 (3 m)

Sample code: B22 (3 m)

Fig. 2. Chromatograms for mineral oil for M22 sample before and after the chemical and biological treatment

- no major changes occur, taking into consideration percentage content of hydrocarbons fractions from the petroleum mixture;
- residual content in petroleum product from contaminated soils after each chemical and biological stage are below the maximum admissible value (<100 mg/kg d.m.).

From the results of the analytical tests (Table 5) and the chromatograms (Fig. 2) for samples M22, C22, B22 (3 m) can be observed that the main type of petroleum product present in all the soil samples consists in mixture of oil and diesel oil product. The following comments can be made:

- removal of the petroleum product from soil using chemical treatment process was performed in proportion above 75% for ground soil (3 m). It shows the reduction of petroleum products at values lower than the normal values imposed by Order No 756/97;
- after biological stage the removal yields for petroleum products is performed in proportion above 75% for ground soil (3 m);
- no major changes occur, taking into consideration percentage content of hydrocarbons fractions from the petroleum mixture;
- residual content in petroleum product from contaminated soils after each chemical and biological stage are below the maximum admissible value (<100 mg/kg d.m.).

CONCLUSIONS

1. The application of GC method for analysis of petroleum products offers the following advantages:
   - high sensibility (detection limit 5 mg/kg d.m.), accuracy and precision;
   - possibility to identify petroleum product type after fractions separation.
2. Decontamination processes for soils polluted with petroleum products applied to a polluted site from Ploiesti area assures:
   - good efficiency of removing the pollutants till the limits imposed by actual norms;
   - no modification in the composition of residual petroleum products.
3. Biological stage can be applied *in situ* for improving quality of soils polluted with petroleum products and must be realised after chemical treatment stage.

REFERENCES

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