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Preliminary quantitative determination of petroleum and petroleum products in contaminated soils by using dynamic thermogravimetry

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Abstract

Thermogravimetric (TG) method for the preliminary selection and rapid quantitative determination of petroleum and petroleum products in contaminated soils is described and tested. The influence of the analytical conditions, the kind and the amount of the pollutant on the temperature interval of separation, the accuracy, the reproducibility and the detection minimum of the determination were studied with model samples based on both the inert and soil carriers.

The results led to the conclusion that the dynamic thermogravimetry method offered significant advantages for the selection and the direct quantitative determination of petroleum and petroleum products with concentrations exceeding 10 g/kg. The corresponding analytical errors were found to be smaller or, at least, commensurable with those of the methods developed so far. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

No integrated standardized analytical methods for determination of pollution caused by petroleum (P) and petroleum products (PP) in soils have been developed so far. Moreover, the mere definition of the term petroleum products is somewhat conditional and includes the non-polar hydrocarbons predominantly. Thus, the more polar and toxic hydrocarbons have been excluded, possibly, because of the limited instrumental tools available for their determination. The latter are based on extraction methods followed by infrared spectroscopy (IRS) and gas chromatography (GC) predominantly [1–3]. The draft analytical standard for the determination of petroleum products in soils [3] has recognized the impossibility of evaluating the total concentration of these pollutants by using the indirect methods mentioned above, because of both the hampering influence of the polar substances on the IRS determination and losses of volatile components. The number of preliminary procedures for the sample treatment and the need of reactants of high purity result in slow and expensive methods of determination, and additional analytical errors. These methods are particularly inefficient with soils of high concentrations of the pollutants. Therefore, a preliminary evaluation of the concentration of the pollutants is necessary. Until now, the latter has been conducted gustatory in the open field, or, at best, by using the semi-quantitative luminescent capillary analysis only [4]. The latter, however, did not offer the advantages of high resolution at concentrations of the pollutants exceeding 1 g/kg soil [2].

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Recently [5], we have suggested the utilization of thermoanalytical methods such as dynamic thermogravimetry in order to resolve the problem more rationally.

Here we propose a TG method for both the preliminary selection and rapid quantitative determination of P and PP in contaminated soils.

To achieve the above-mentioned goals, the following analytical tasks were resolved:

1. By using model samples, the optimum conditions for the fast quantitative separation of the pollutants were determined.
2. The basic parameters such as the accuracy, reproducibility and detection minimum for the quantitative determination were established, depending on the concentration of pollutants. These parameters were compared to those obtained by using the IRS method.

2. Experimental

2.1. Starting materials

Inert carriers such as infusorial earth (kieselguhr) *HYPLO-super sel* (particle size 10–20 μm) treated thermally at 1200°C to ca. 0.5% humidity level prior to use and standard α-Al_2O_3 (MOM, Hungary) were employed for part of the model samples.

For another part of the latter, standard soil samples from the so-called *Horizon A* [6] were taken. The bigger particles were removed mechanically and then an average sample among forth ones in mass of ca. 30 g was air-dried and ground in agate mortar to pass a 0.25 mm sieve. Then, an average sample of 10 g was taken again, kept in a closed crucible and was stored in a desiccator. Before the thermal analysis, a smaller sample of 0.1–1 g was picked out for evaluation.

The model samples contained (P) and diesel oil (DO) in concentrations of 4, 35, 170 and 300 g/kg carrier, respectively. The pollutants were introduced into the sample matrix by pouring out drop by drop into the crucible for the thermal analysis immediately before the actual analytical experiment. For some of the soil samples, this was done by preliminary mixing of the components. For control analyses and to prepare reference (‘‘background’’) samples, extractions were performed with 1,2-dichloroethane (DCE) (*purum*) or tetrachloromethane (TCM) (p.a.) amounts of 5, 10, 20, 40 or 50 ml solvent per gram of soil sample, the extraction time being 15, 30, 60 min or 18 h.

2.2. Methods

2.2.1. Thermal analysis

P and PP were determined by the evaluation of the thermogravimetric (TG) data only. DTA and DTG curves were recorded in order to obtain monitoring information. To determine the reproducibility of the methods, three instruments of different design, such as Derivatograph OD-102, Derivatograph Q and Derivatograph C (MO, Budapest, Hungary) were used. The corresponding temperature interval was within 20–900°C at heating rates of 6°C/min, 10°C/min and 20°C/min in air. Samples of initial masses 0.1, 0.2, 0.3, 0.5 and 1 g were used and both the platine and ceramic crucibles of internal diameter 9.5, 12.5 and 17 mm were employed, α-Al_2O_3 was chosen as reference sample.

2.2.2. IR spectroscopy

IR spectra of extraction samples taken from both the pure and contaminated soils were studied by using UR-20 and M-80 instruments (Germany). This independent method was employed to compare the results with those obtained from the TG determination and, Also, to verify the probability for the extraction of soil organics under the conditions of the reference sample preparation.

3. Results and discussion

3.1. Model experiments with inert carriers

Thermal analyses of model samples with inert carriers such as kieselguhr and α-Al_2O_3 mixed with the most common pollutants such as P and DO [2] were conducted. Here the direct determination of the amount of pollutant from the TG scans of the corresponding mixtures was believed to be possible (Fig. 1) and can be compared with that introduced preliminarily. Under the conditions of P concentration ranging between 1 and 300 g/kg carrier, heating rate of 10°C/min and sample mass of 0.5 g, almost the whole

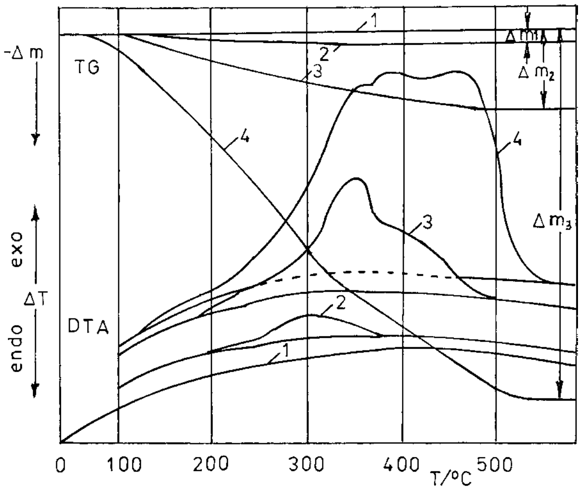

Fig. 1. Measured curves of model samples containing kieselguhr and P (heating rate 10 K/min, sample weight 0.3 g): kieselguhr (curve 1); kieselguhr and 4 g/kg P (curve 2); kieselguhr and 35 g/kg P (curve 3); kieselguhr and 170 g/kg P (curve 4).

amount of petroleum was found to be separated within the temperature interval of 40–620°C. The higher content of the pollutant in the sample resulted in extending the above-mentioned temperature range. Under these conditions, the actual time of analysis was 60–100 min and, at heating rate of 20°C/min, it was reduced to 40–65 min (Table 1, (a)). The optimum conditions for the quantitative determination of P and DO in inert carriers were within the following intervals: sample mass of 0.3–0.5 g; heating rate of 10°C/min; platinum or ceramic crucible of internal diameter 12.5 mm.

The crude P used in most of the experiments as pollutant contain volatile fractions which were separated within the widest temperature interval employed, i.e., between the room temperature and 620°C, Consequently. the analytical errors involved were expected to be the highest in the case of crude P, somewhat lower for DO (Table 2), and still lower for the remaining highly-boiling petroleum (i.e., mineral) oils.

3.2. Model experiments with soil samples

The thermal effects of the pollutants present in these samples are superimposed on the inherent effects of the soil carrier. For the different kinds of soils, these effects were similar and could be subdivided, approximately, into three groups [5,7] (Figs. 2 and 3): (1) humidity below 200°C, (2) soil organics between 200°C and 600°C, (3) carbonates from 600°C to 850°C. With agricultural soils, the second and the third group of effects were shown to be rather conservative [5,8] and, for a given land, did not change significantly. This made it possible, with the approximate accuracy up to 1%. to use the same sample as a reference (i.e., "background sample") for the quantitative TG determination of P and PP in soils.

The degree of extraction of PP with TCM in order to prepare background sample, in most cases, was below 80%. Particularly, with highly contaminated soils [9].

Table 1
Optimum conditions for the quantitative TG determination of P and PP depending on the concentration of pollutants

Thermoanalytical parameters	Concentration of pollutants (g/kg)							
	1–10		10–100		100–200		>200	
Maximum temperature of the pollutants separation (°C) (heating 10°C/min)	400[a]		500[a]		580[a]		620[a]	
	600[b]		620[b]		700[b]		750[b]	
Initial mass of the sample (g)	0.5–1[a,b]		0.3–0.5[a,b]		0.1–0.5[a,b]		0.1–0.3[a,b]	
Duration of the determination in minimum at heating rates:								
6°C/min	80[a]	120[b]	100[a]	120[b]	120[a]	140[b]	120[a]	140[b]
10°C/min	60[a]	80[b]	70[a]	80[b]	80[a]	100[b]	100[a]	100[b]
120°C/min	40[a]	70[b]	50[a]	70[b]	65[a]	80[b]	65[a]	80[b]

[a] For the samples with inert carriers.
[b] For the samples with soils.

Table 2
Statistical variance characteristics obtained by TG determination of P and PP in inert carriers

Characteristics	Pollutant	Concentration of pollutants (g/kg)			
		1–10	10–100	100–200	>200
Average absolute error X (g/kg)	P	2.0	1.5	2.5	4.0
Average relative error ΔX (%)	P	30.0	5.0	3.0	3.0
	DO	10.0	3.0	1.5	1.5
Standard deviation S_x (g/kg)	P	0.9	0.14	0.13	0.24
	DO	1.1	0.07	0.03	0.05
Variation coefficient V (%)	P	45.0	10.0	5.0	6.0
Detection minimum (g/kg)	P and PP	0.5	1.0	2.0	4.0
Number of excerpt		10	10	10	6

The most complete and the most rapid extraction of P, DO and mineral oils was conducted by using DCE as solvent. For example, the degree of extraction of 100% in the presence of 20 ml solvent per gram of soil sample was achieved for 15 min only, provided the pollution level did not exceed 100 g/kg soil. The procedure was conducted with air-dried soil samples at room temperature and under agitation [10]. The treated sample was left for 30–60 min in air to evaporate the solvent.

Biologically pure *humus sample* was treated with DCE for 15, 30 and 60 min and, also, for 18 h. This

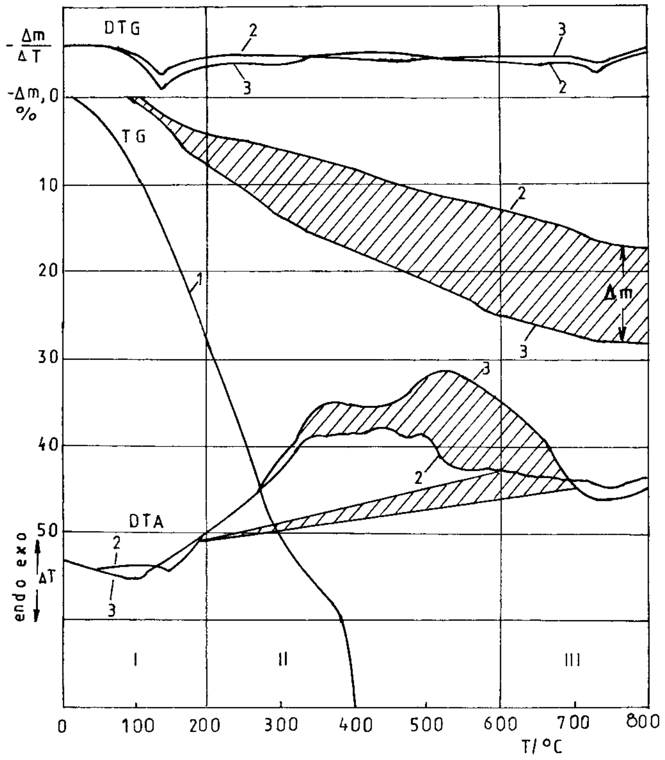

Fig. 2. Measured curves of model samples containing soil carriers and P (heating rate 10 K/min; sample mass 0.3 g): P (curve 1); initial soil from the region of the town of Bourgas (curve 2); model sample containing 120 g/kg P (curve 3).

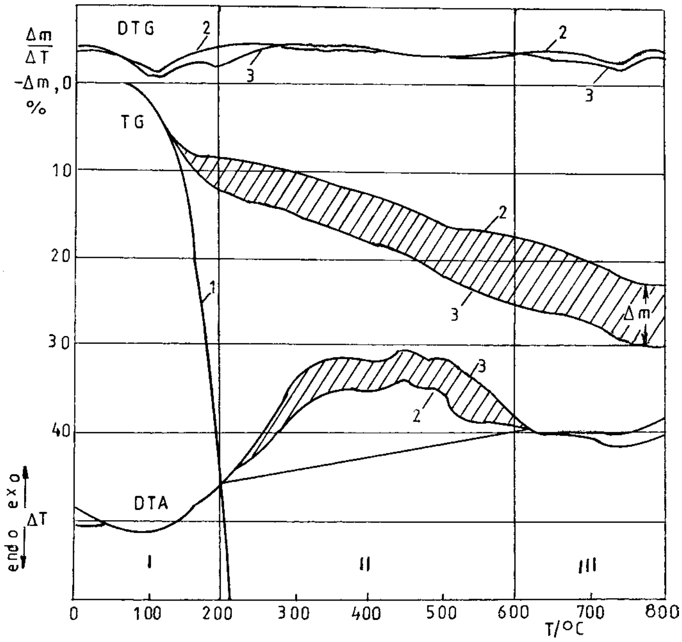

Fig. 3. Measured curves of model samples containing soil carriers and DO (heating rate 10 K/min; sample mass 0.3 g): DO (curve 1); initial soil of the region of the town of Bourgas (curve 2); model sample containing 70 g/kg DO (curve 3).

was done in order to check whether under the selected conditions of preparation of the background sample, DCE would extract some soil organics in concentrations which are commensurable with the detection minimum and thus would hamper the analytical determination. The extracts so obtained were subjected to IRS. No absorption bands corresponding to organic products of concentrations which were commensurable with the detection minimum of the methods employed (0.5 g/kg) were registered (Table 2).

Three series of model mixtures based on humus were studied. The first one was collected after biological purification, whereas the other two were taken from randomly selected parcels of land in the regions of the towns of Bourgas and Yambol, respectively. The results showed that, under the optimum conditions of the thermoanalytical experiments, the complete extraction and registration of the pollution derived from the presence of P and PP in soils was possible. These conditions did not significantly differ from that established with the inert carriers. The separation (i.e., the removal) of the pollutants was shifted towards the higher temperatures, probably, because of sorption interactions with the soil organics and diffusion limitations (Table 1, (b)), and the duration of the analytical determination was longer. For pollution levels below 10 g/kg, the sample weight should be greater (0.5–1 g), whereas, the higher pollution levels would require smaller samples (0.1–0.3 g).

Again, the values of the statistical variance characteristics regarding the quantitative determination of P and PP in soils were found to be of the same order of magnitude and, actually, almost coincided with those presented in Table 2 for inert carriers. The average relative error for the TG analysis (Δx) is known to be within 0.5–1%. The higher results for this analytical parameter obtained in some cases can be explained by the influence of random factors. Non-homogeneity resulting from the relatively small samples used, as a source of analytical errors could only be avoided by employing TG-DTA-EGA analyzer particularly designed for ecological studies [11].

The statistic variance characteristics of the analytical determinations based on the data obtained from the TG scans were compared with those from the IRS, according to two independent sources [2,9] (Table 3). As seen from the table, pollution levels exceeding 10 g/kg soil were determined more accurately by

Table 3
Comparative data of the accuracy and reproducibility of the analytical determination of P and PP in soils using IRS and TG

Characteristics	Pollutants	Concentration of pollutants (g/kg)								
		1–10			20–50			>50	50–200	>200
		IRS[a]	IRS[b]	TG	IRS[a]	IRS[b]	TG	IRS[b]	TG	TG
X (g/kg)	P			2.0			1.5		1.5–2.5	4.0
	PP	2.77	8.80		69.5	30.0		80.4		
ΔX (%)	P	4.10		30.0	2.6		5.0		5.0–3.0	3.0
	DO			10.0			3.0		3.0–1.5	1.5
S_x (g/kg)	P			0.9			0.14		0.14–0.13	0.24
	PP	0.28	1.15		4.4	4.43		7.04		
	DO			1.1			0.07		0.07–0.03	0.05
V (%)	P			45.0			10.0		10.0–5.0	6.0
	PP	10.1	13.1		6.3	14.6		8.8		
Number of except		30	30	10	25	14	10	14	10	6

[a] Ref. [2].
[b] Ref. [9].

employing TG and the reproducibility of the results was better.

The similarity of the data obtained with the quantitative determination of P and PP in both the inert carriers and real soils represents an evidence that, under the selected optimum conditions of TG, P and PP can be completely separated from the soil and analyzed quantitatively, regardless of the soil organics present. This can be done by ‘‘depositing’’ on each other and then ‘‘subtracting’’ the two TG scans, corresponding to the contaminated and the ‘‘background’’ soil samples. The studies conducted with soil samples contaminated under the real conditions and at different stages of the pollution indicated that, regardless of the kind of soil and the time of the actual presence of the pollutant in the soils, ranging between 5 days and 2 years, no measurable differences in the parameters of thermal destruction, the completeness of extraction, the accuracy and reproducibility of the TG determination were observed. Consequently, the probability of chemical interaction or any other mode of ‘‘trapping’’ of PP from the soil organics which would hamper the analytical determination by TG can be considered as insignificant [12].

The method can be utilized for the determination of the complete content of P and PP in soils. No limitations regarding the temperature of evaporation of the pollutants exist, since the analysis can be conducted directly and continuously and only the necessary minimum of the preliminary procedures are involved. To eliminate the effect of random factors such as a sudden change in the humidity of air, solvent residues, etc. on the results obtained. It is preferable to conduct the corresponding calculations on the basis of the solid residue left after the third ‘‘step’’ indicated on the TG scans, i.e., up to the maximum temperature of 850°C (Figs. 2 and 3).

4. Conclusions

The optimum conditions for the rapid and direct quantitative analytical determination of petroleum and petroleum products in contaminated soils have been proposed. The basic analytical parameters such as the detection minimum, the accuracy and the reproducibility of the determination, depending on the concentration of the pollutants, were established. The dynamic thermogravimetry had certain advantages over the methods employed so far, particularly, with respect to the preliminary selection of samples and the rapid quantitative determination of pollutants concentrations, which were close or exceeded the hazardous level. Moreover, the analytical errors for the determination were smaller or commensurable with those, accompanying the methods utilized previously.

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