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Quantitative Analysis of Hydrocarbons in Sewage Sludge from Waste Water Purification Stations*

Introduction

Different methods have been used for the analysis of hydrocarbons. Of the well known techniques for quantitative determinations, namely, gravimetric (1), spectroscopic (2) and gas chromatographic (3) we have chosen the latter as it possesses a number of features that make it attractive: small samples of the order of a few grams are sufficient for analysis and the incorporation of an internal standard allows one to calculate the percentage recovery of hydrocarbons after each analysis.

Also the shape of the chromatograms can prove to be very useful in chromatographic analysis. Indeed a careful examination of our chromatograms showed that mostly each water purification station has a typical «fingerprint» chromatogram. Most important, however, is not this recognition but the fact that any departure from this «fingerprint» could indicate an illegal discharge of petroleum oils, or any other pollutant for that matter, to sewers.

Sludge samples vary enormously in their water content ranging from 40 to over 95% of water. The common practice using samples of high water content has been a direct extraction on a large volume of the sample, usually 500 to 1000 ml (4). With samples having high solids content, on the other hand, the Soxhlet extraction is preferred (5). We have in our method avoided the classical Soxhlet extraction step and have performed hydrolysis directly on the sludge samples irrespective of their solid content.

Following hydrolysis comes the usual clean up procedure by column chromatography and, after concentration, analysis by gas chromatography.

Working with 10 gram samples under these conditions we find that it is possible to obtain a percentage of greater than 95% of hydrocarbons. The use of an internal standard is an excellent control on the efficiency of the extractions. A number of chromatograms are shown illustrating the technique and demonstrating the advantage of this gas chromatographic technique.

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Origin of samples

The samples are received from 5 waste water purification stations in jars of $1^1/_2$ litre capacity.
The stations are coded as follows (fig. 1):

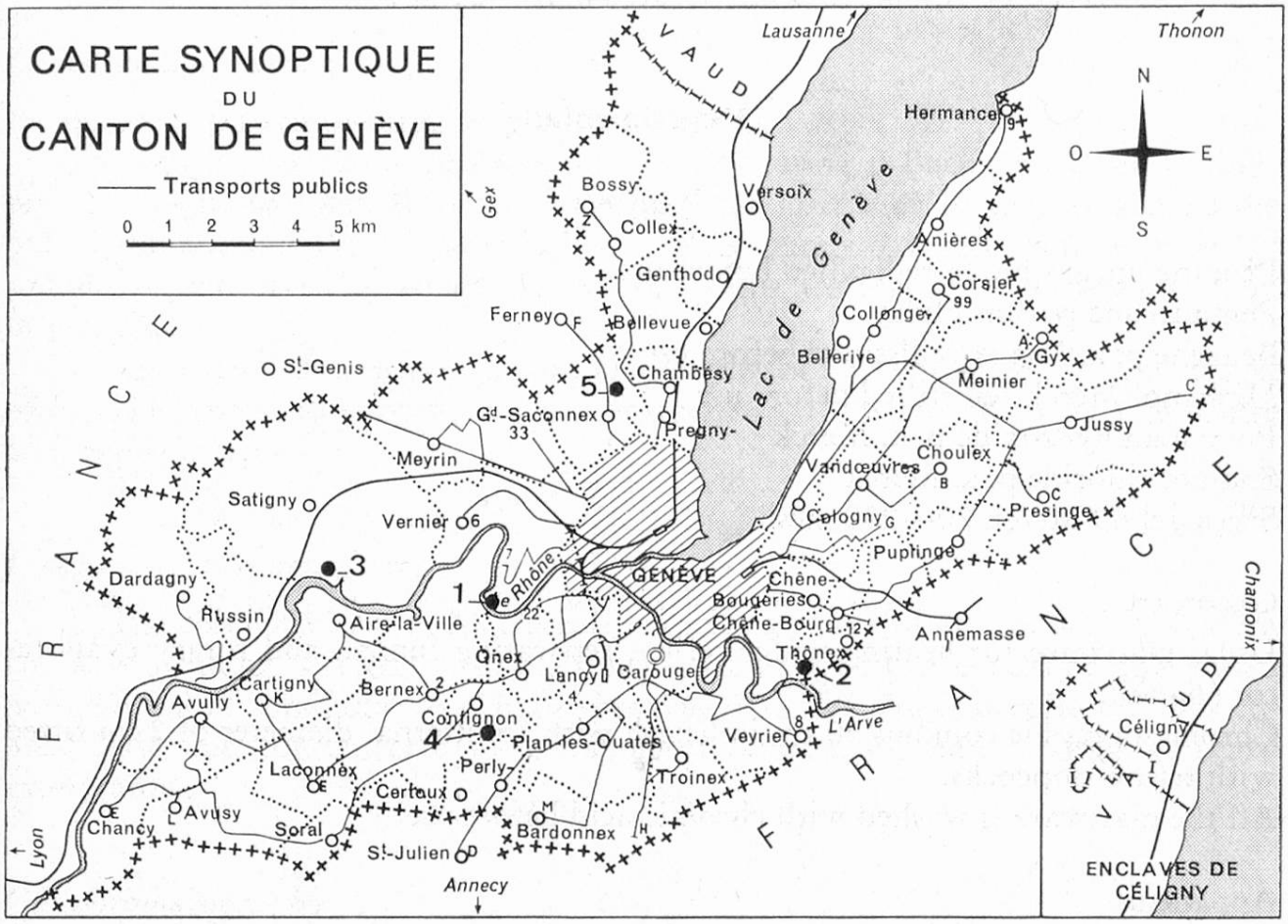

Fig. 1. Localisation of waste water treatment stations

1. Aïre
2. Villette
3. Nant-d'Avril
4. Plaine de l'Aire
5. Grand-Saconnex

AIR — Waste water of Aïre
A standard station with a primary decantation stage, an activated sludge basin, and a final decantation stage. The digestion is done in two stages.
Average volume of water treated daily 185 000 m³.

VIL — Waste water of Villette
A standard station similar to AIR.
Average volume of water treated daily 10 000 m³.

NAV — Waste water of Nant d'Avril
A standard station with only one stage of digestion.
Average volume of water treated daily 7 000 m³.

PLA — Waste water of Plaine de l'Aire
A standard station similar to NAV.
Average volume of water treated daily 3 000 m^3.

GDS — Waste water of Grand-Saconnex
This station has no preliminary decantation before the oxydation stage.
Average volume of water treated daily 900 m^3.

Experimental

Reagents

Pentane purum Fluka redistilled before use
Pentadecane purum Fluka
Benzene p. a. Merck redistilled before use
Methanol Merck redistilled before use
Potassium hydroxide p. a. Merck
Sodium chloride p. a. Merck
Silica gel 60 Merck 70—230 mesh

Glassware

Usual glassware for heating under reflux, separating funnel, and rotary evaporator (*Büchi*).
Chromatographic columns 30 cm in length with an internal diameter of 2 cm fitted with teflon stopcocks.
All the glassware is washed with chromic acid before use.

Apparatus

Carlo Erba gas chromatograph Model GI
Hewlett Packard gas chromatograph model 5730 A with automation system model 3385 A.

Procedure

Sampling

The whole of the samples are homogenised first by a high speed mixer and prior to weighing by vigorous shaking. Only 10 g samples are used for the analysis which is done in duplicate.

Hydrolysis

Samples extracted from sewage often contain fat and are cleaned up by saponification. Hydrolysis is performed directly on the sludge samples after weighing.

30 ml of a solution of methanolic potassium hydroxide, 0.25 m, are added to each of the two flasks for hydrolysis. Refluxing is carried on for $1^1/_2$ hour after

which the contents of the flasks are allowed to cool. To each of the flasks are then added 25 ml of pentane. To one lot of pentane is incorporated 0.25 µg of pentadecane as internal standard. After a further refluxing period of half an hour a clear layer of pentane rich in organic matter can be observed above the alcoholic-aqueous layer.

Filtration and extraction

Before filtration the organic phase is removed.

The aqueous alcoholic phase is then filtered using a Buchner funnel and applying a slight vacuum. In order to increase the efficiency of the extractions the pH of the aqueous layer is adjusted to approximately 2.5 and about 4 grams of sodium chloride are also added. Three extractions are performed each with 25 ml of pentane.

In the event of a strong emulsion the phases are separated by centrifugal force. The combined extracts are concentrated to a volume of about 1 millilitre on a rotary evaporator.

Liquid solid chromatography

A glass column 30 cm × 2.0 cm is filled with a slurry of 40 g of activated silica gel 60 in pentane. The concentrate (1 ml) is transferred to the column and eluted with 250 ml of a mixture of pentane-benzene 3:1. The eluate is collected in a conical flask and concentrated to a volume of between 0.2 and 1 ml on a rotary evaporator.

Gas chromatography

The chromatograph is equipped with a SE 30 silicone gum column.

Working conditions are as follows:

Detector F. I.	320°C
Injector	320°C

Temperature programme: Isothermal at 120°C for 4 minutes then increase in temperature at a rate of 8°C/minute to 320°C. The whole chromatogram lasts about one hour.

Carrier gas:	nitrogen:	30 ml/min
Fuel:	hydrogen:	30 ml/min
	air:	250 ml/min

The quantitative determination of total hydrocarbons from the chromatogram is made with reference to the peak corresponding to pentadecane.

Vigorous shaking prior to weighing is really important with samples of low solid content in order to avoid gross errors. 10 g samples are sufficient as bumping becomes important with larger samples especially those with high solid contents. The phenomenon of emulsion is another factor to be taken into consideration when working with larger samples. Strong emulsions are formed when experiments with larger samples, 20 or 40 g, are performed. With smaller samples than 10 g on the other hand higher sensitivity is required and baseline drift can be a severe problem during the temperature program in gas chromatographic analysis.

Because of the high percentage of water in the sludge samples, ranging from 40 to over 95%, the classical Soxhlet extraction step has been eliminated.

It is advisable, during hydrolysis to swirl, from time to time, the round bottom flasks as suspended matter tends to adhere to the walls of the flask.

The use of pentane at this stage of the analysis is to introduce the internal standard in the process. Refluxing with pentane also serves other purposes, for example, all the organic matter which has been deposited on the walls of the vessel is dissolved in the pentane layer, and a fair amount of extractible matter is present in the organic layer at the end of the hydrolysis, as evidenced by the highly coloured layer of pentane.

Suspended matter in the aqueous phase after hydrolysis is the most important source of difficulties in our procedure, yielding, after shaking, a supernatant layer of sludge instead of a clear layer of solvent. The samples therefore have to be filtered before extraction.

Pentane has been chosen as solvent because of its low boiling point and its low solubility in water. Pentane is about 30 times less soluble in water than dichloromethane and 20 times less soluble than carbontetrachloride. Additions of sulfuric acid and sodium chloride dramatically improves the extraction efficiency (6, 7).

Pentane alone is not strong enough an eluant to remove the more polar aromatic hydrocarbons from the column (8). Thin layer analysis indicates the presence of polycyclic aromatics in some samples.

Indeed experimenting with samples from AIR we found that 250 ml of pentane could only eluate the aliphatics and simple aromatics. After concentration of the eluate a colourless concentrate was obtained.

The polycyclic aromatics were not present in that concentrate as shown by the lack of fluorescence when viewed under UV light. Adding a percentage of benzene to pentane, however, eluted the more polar hydrocarbons giving a coloured concentrate which fluoresced when excited by UV light. A comparison of the elution power of pentane and a mixture of pentane-benzene 3:1 is shown in figure 2.

As low volatile compounds are not present in our samples and as resolution is not our aim the starting temperature is set at 120°C. Formerly the starting temperature was 70°C and programmation was done at a rate of 4°C/min (fig. 3).

Experience showed that the length of the chromatogram could be considerably shortened by changing the working conditions.

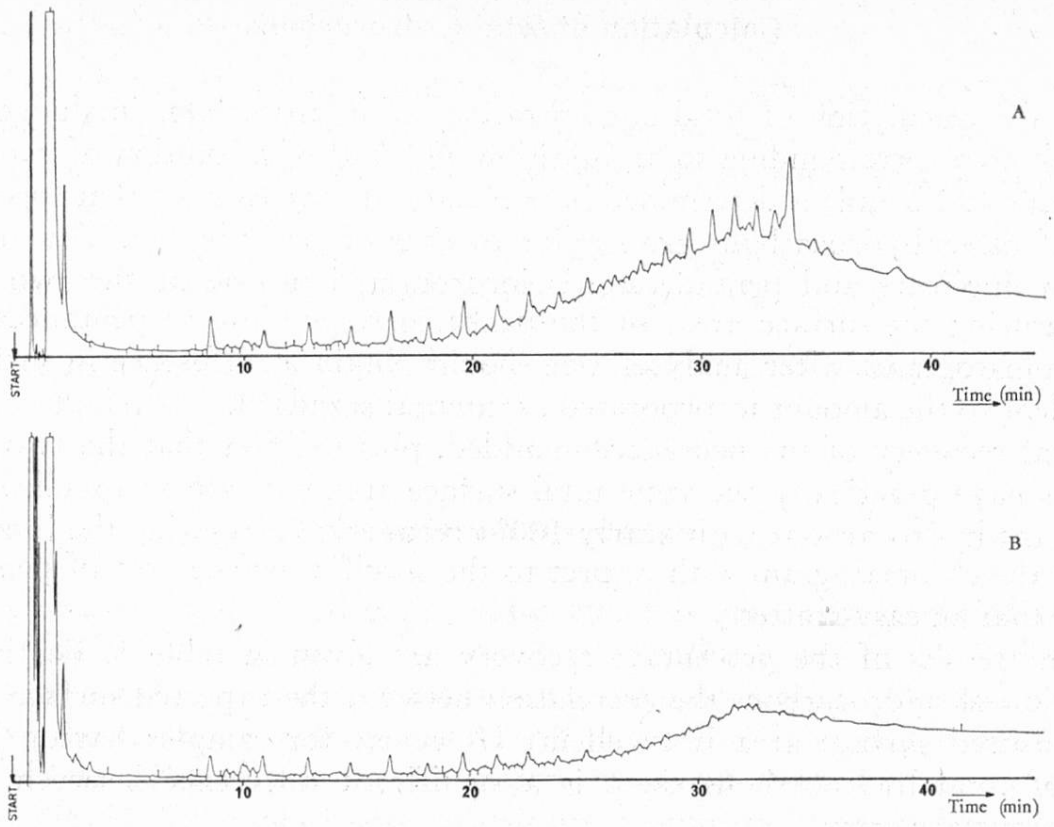

Fig. 2. Comparison of the elution power of
A 1 µl injection of the concentrate (200 µl) after elution with pentane-benzene 3:1
B 1 µl injection of the concentrate (200 µl) after elution with pentane

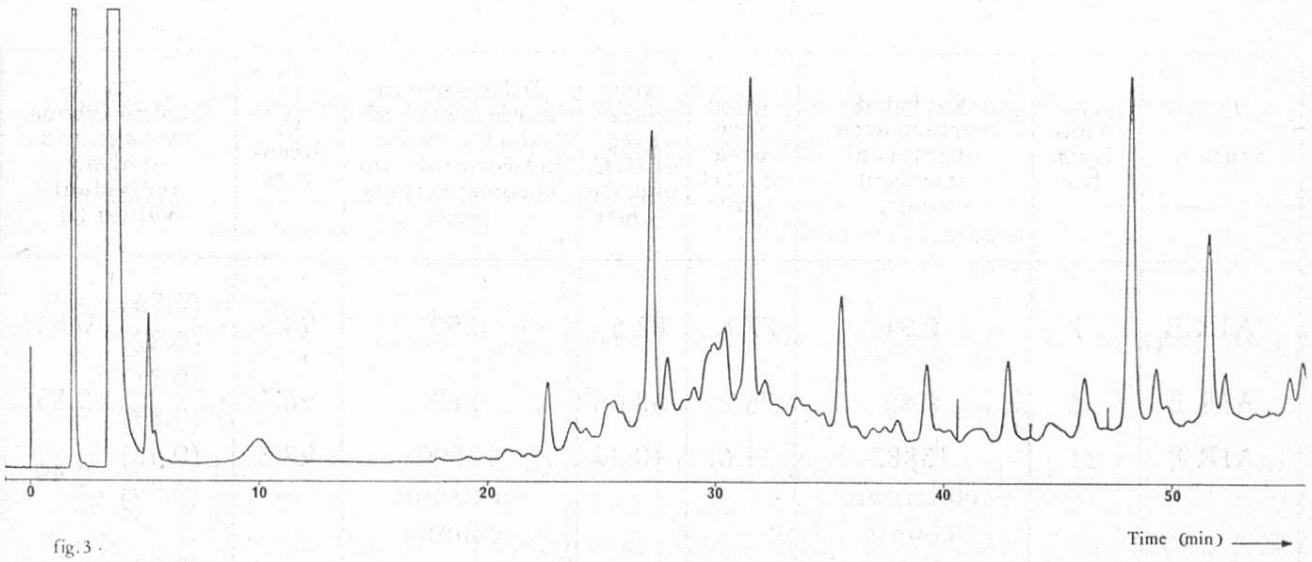

fig. 3 ·

Fig. 3. Chromatogram of a sample from NAV showing the absence of low volatile compounds, with operating conditions as indicated on page 100 starting temperature 70°C, temperature rate 4°C/min (only approx. half of the chromatogram is reproduced)

Calculation of total hydrocarbons

For the calculation of total concentrations of hydrocarbons in sludge samples the peak area corresponding to an injection of 1.0 µl of a solution of pentadecane in benzene (1.0 µl/ml) is determined in triplicate. It was assumed that specific peak areas of other hydrocarbons are similar to that of pentadecane. The analysis is done in duplicate and pentadecane is incorporated in one of the two samples. By measuring the surface areas of the peaks corresponding to pentadecane from the chromatograms, after analyses, one should obtain a difference in surface area equivalent to the amount incorporated as internal standard.

Total recovery of the pentadecane added, plus the fact that the two chromatograms have practically the same total surface area indicate an excellent extraction of the hydrocarbons with nearly 100% recovery. Computing the total surface area of the chromatogram with respect to the specific surface area of pentadecane is after that an easy matter.

Some results of the percentage recovery are given in table 1. For high concentration of hydrocarbons the correlation between the expected surface area and the measured surface area is excellent. However, for samples having less than 0.1% of total hydrocarbons there is a significant difference between expected and real surface areas.

Table 1

Comparison of percentage recovery from samples having different solids content

AIR B: Aïre. Solids content greater than 50%
GDS: Grand-Saconnex. Solids content 2—3%
VIL: Villette. Solids content around 4%

Station	Analysis No	Expected surface area of internal standard (cm^2)	Surface area of G. C. (cm^2)	Surface area of G. C. plus C_{15} (cm^2)	Difference in surface area of the C_{15} peaks between the two chromatograms (cm^2)	% Recovery	% Hydrocarbons average of 2 analysis individual values ( )
AIR B	7	0.91	77.8	82.5	0.90	98.9	(0.85) (0.82) 0.84
AIR B	6	0.85	76.2	68.66	0.82	96.0	(0.81) (0.89) 0.85
AIR B	11	13887 electronic counts	34.6	40.36	13590 electronic counts	97.8	(0.48) (0.49) 0.49
GDS	9	1.45	18.22	16.26	0.86	60.0	(0.036) (0.040) 0.038
VIL	7	0.75	22.43	24.63	0.48	64.0	(0.096) (0.104) 0.10

Reproducibility and errors

The reproducibility of the analyses depends on homogenisation to a great extent. Analyses performed on 5 g and 10 g samples have shown that with these amounts the method works well. The values obtained for a sample from AIR are:

for a 5 g sample 0.494% of hydrocarbons
for a 10 g sample 0.480% of hydrocarbons.

Significant errors, of the order of 10%, can be made when measuring the surface areas especially those of pentadecane.

Results and discussion

Biodegradable organic matter in waste water is generally classified in three categories: carbohydrates, proteins and fats. Synthetic detergents are finding their way into sewers in increasing quantities from both household and industry. These have the effect of destroying bacteria and other living organisms. Approximately 20 to 40% of the organic matter in waste water appears to be non biodegradable (9). Saturated hydrocarbons are a problem in treatment because of their physical properties and resistance to bacterial action.

The results obtained show that the percentage recovery is a function of the total solids and hydrocarbon contents of the samples. The values of hydrocarbons increase in direct relationship with the percentage of solid matter. The volume of water treated daily on the other hand bears no relationship to the concentrations of hydrocarbons found (table 2).

A close examination of the chromatograms displayed shows that each station has a «fingerprint» chromatogram. The samples are received every month and the

Table 2

Results of total hydrocarbons in sludge samples from various waste water purification stations

Stations	Approximate volume of water treated daily (m^3)	Average % of solid matter	% total hydrocarbons								
			July 1976	Sept.	Oct.	Dec.	Jan. 1977	Feb.	March	April	May
AIR A	185.000	3.0	0.10	0.07	0.37	0.20	0.13	0.18	0.19	0.15	0.12
AIR B	185.000	55.0	0.15	1.68	1.76	0.60	0.33	0.85	0,85	0.87	0.77
GDS	900	2.5	0.10	0.02	0.07	0.02	0.30	0.02	0.09	0.06	0.04
NAV	7.000	5.0	0.06	0.11	0.06	0.06	0.11	0.11	0.08	0.22	0.12
PLA	3.000	10.0	0.11	0.19	0.07	0.03	0.34	0.13	—	—	—
VIL	10.000	4.0	0.13	0.18	0.08	0.28	0.48	0.17	0.11	0.09	0.09

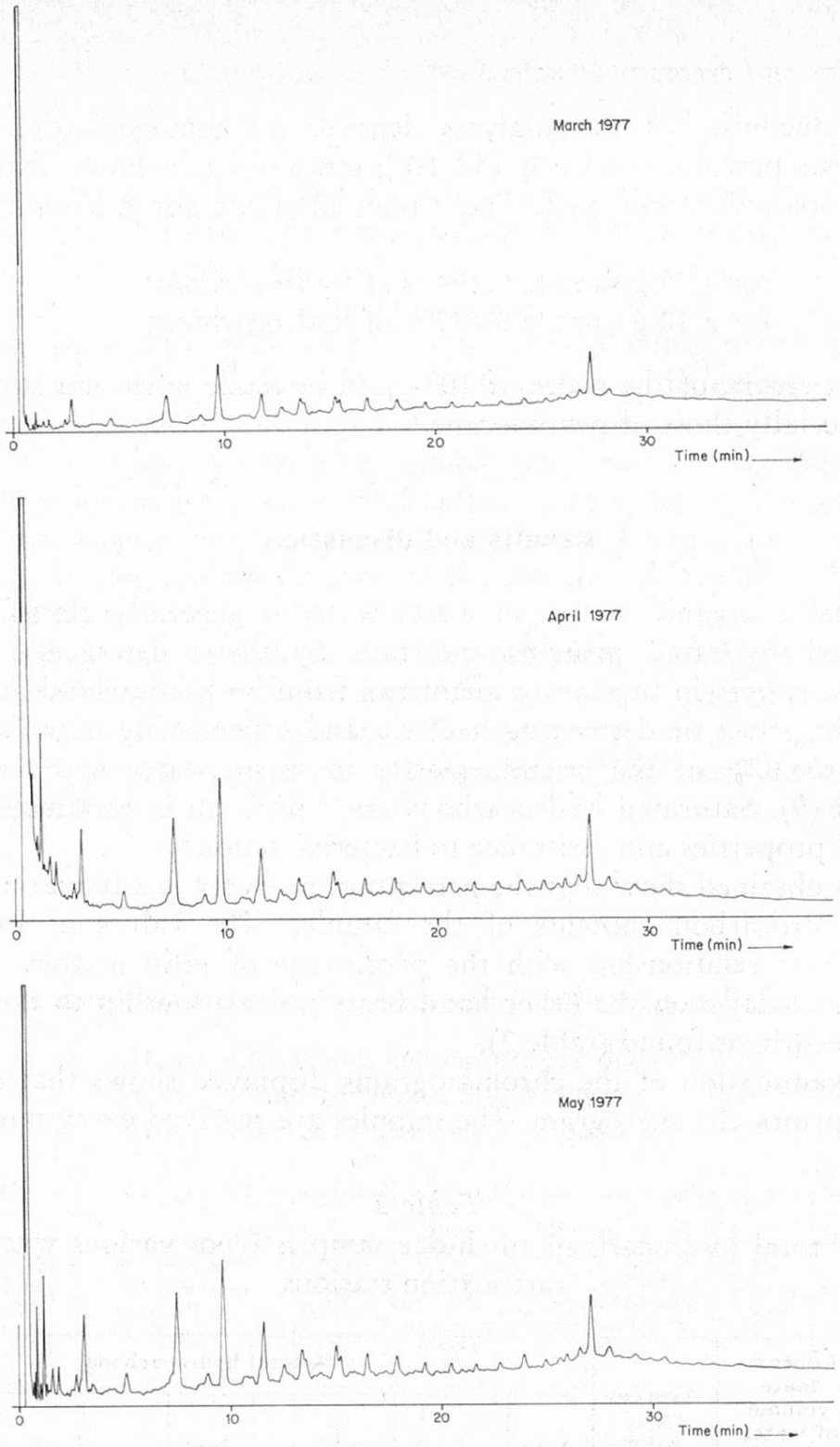

Fig. 4. «Fingerprint» chromatogram of VIL

chromatograms for three consecutive months are displayed for VIL, NAV and AIR (figs. 4, 5 and 6). The chromatograms from VIL are characterised by the presence of compounds of varying boiling points extending over the whole chromatogram. Chromatograms from NAV on the other hand are distinguished by the presence of a fair percentage of low boiling compounds. This mass of compounds appears before the pentadecane peak. Chromatograms from AIR, especially AIR B with high solids content, have a predominance of high boiling com-

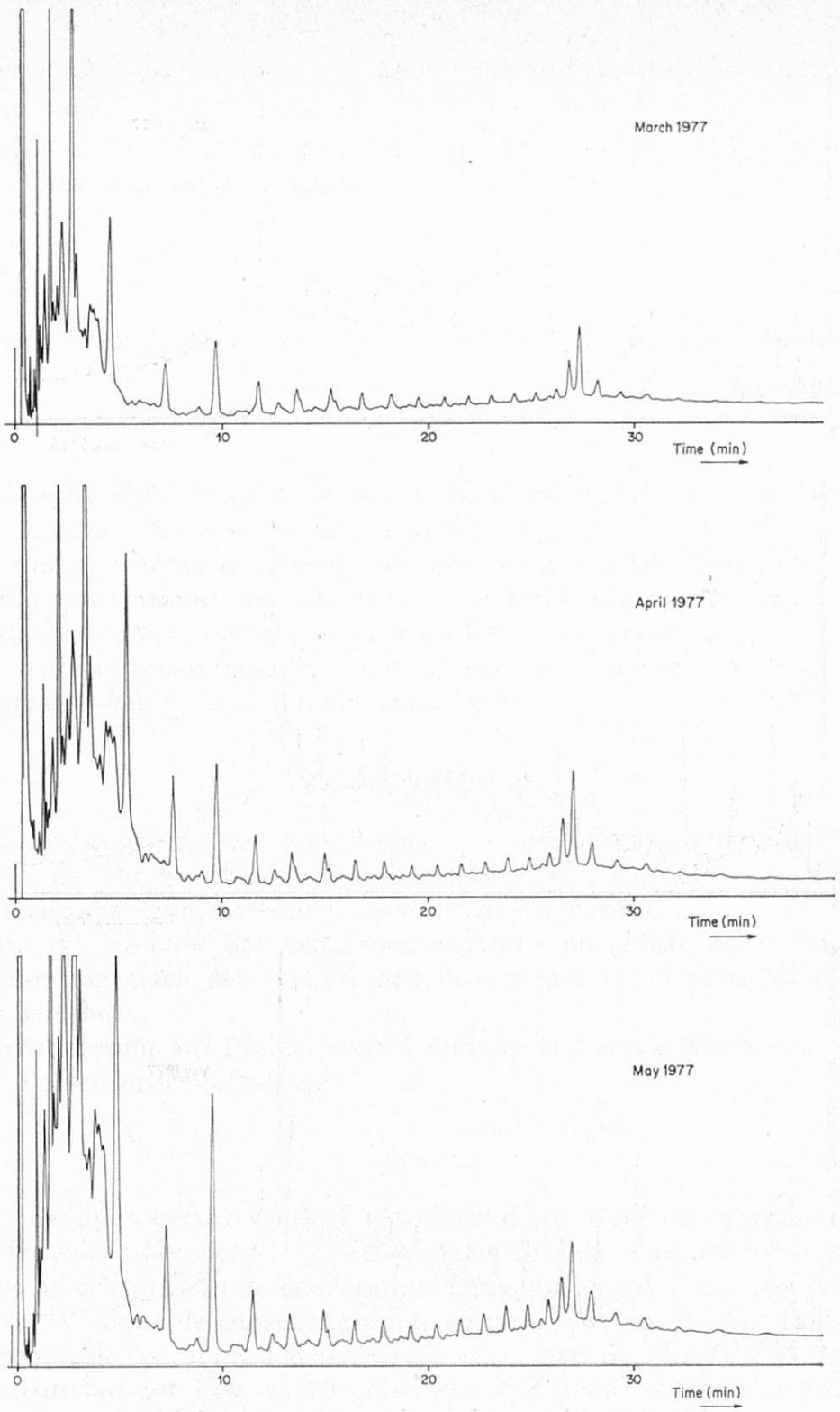

Fig. 5. «Fingerprint» chromatogram of NAV

pounds. These, by thin layer analysis and observation under UV light, have been shown to be fluorescent compounds. This technique of analysis by virtue of the chromatograms should allow an excellent control from the point of view of environmental pollution. For example analysis of sewage water from nearby garages and trade effluents can give indications on the pollutants that are illegally discharged. Waste water analysis in conjunction with air analysis should prove in the future efficient means of fighting the pollution problem.

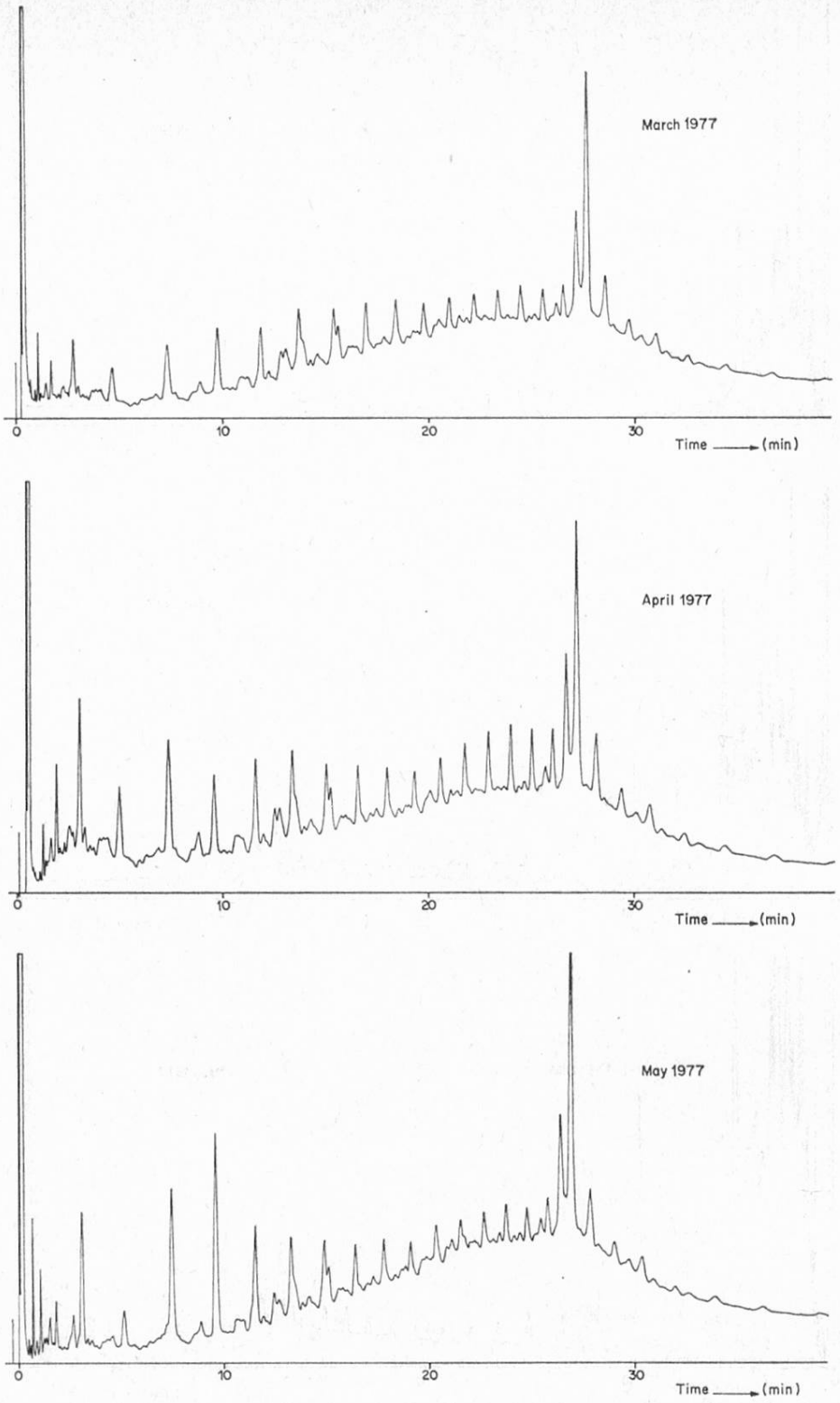

Fig. 6. «Fingerprint» chromatogram of AIR

Conclusion

The method as used in this study allows the quantitative determination of hydrocarbons in sewage sludge samples. The method being more efficient the greater the solids content of the sludge samples. However, the disadvantage for samples of low solids content is not a serious handicap as an internal standard is used.

There seems to be an increasing tendency these days to use compacted sludge as a land fertilizer.

Oour study shows that the greatest concentration of polycyclic hydrocarbons will be found in the compacted sludge.

Acknowledgement

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Summary

Sewage sludge samples from waste water treatment stations vary enormously in their hydrocarbons content. We describe here a method whereby it is possible to treat all the samples in a similar manner irrespective of their water content. Using the gas chromatographic technique with the incorporation of an internal standard in the sample allows us to calculate the percentage recovery of hydrocarbons after analysis.

Working with 10 gram samples we find that it is possible to have a percentage recovery of greater than 95% of total hydrocarbons.

Zusammenfassung

Der Kohlenwasserstoffgehalt von Proben von gereinigtem Abwasser, das die Kläranlage verläßt, ist sehr verschieden. Wir beschreiben hier eine Methode, die erlaubt, alle Proben gleich zu behandeln, unabhängig von ihrem Wassergehalt.

Wenn man die Technik der Gaschromatographie mit Hilfe einer inneren Referenz anwendet, kann man nach der Analyse den Prozentsatz des wiedergewonnenen Kohlenwasserstoffes berechnen.

Unsere Arbeit beruht auf Proben von 10 Gramm und ergab Werte von mehr als 95% der gesamten Kohlenwasserstoffmenge.

Résumé

La teneur en hydrocarbures des échantillons d'eau d'égouts provenant des stations d'épuration des eaux usées est très variable. Nous décrivons ici une méthode qui permet de traiter tous les échantillons de manière identique sans égard à leur teneur en eau.

Utilisant la technique de chromatographie en phase gazeuse et avec l'aide d'un étalon interne, on peut calculer après l'analyse le pourcentage de récupération des hydrocarbures. Travaillant sur une base de 10 grammes, nous avons obtenu des pourcentages de récupération supérieurs à 95%.

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Raumisomere Alkensäuren in teilhydriertem Sonnenblumenöl

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