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Hällristning
Fiskare från bronsåldern

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Bronze age fishermen

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Hydrografiska avdelningen, Göteborg.

Determination of small amounts of non-polar hydrocarbons (oil) in sea water

by

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C. Bo Skarstedt Industrial Water and Air Pollution Control Company (Sweden)

December 1970

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C O N T E N T

Introduction

The need for methods of determination of small amounts of oil has increased during recent years. The main reason for this is the swiftly rising consumption of oil throughout the entire world. This means more and larger transports by land and sea and increased storage in big dumps and in smaller fuel-oil tanks spread out over all civilized areas.

The increased handling of oil results in increased oil-spillage, which today amounts to about one per cent of the oil consumption. The spillage of oil stems from leaking tanks and pipe-lines, over-loading and/or broken tubes when pumping, transport accidents, discharge of oil-polluted sewages from industries, cleaning of ship-tanks and dumping at sea.

The type of damage that primarily called for (and still dominates) the need for sensitive methods of determination of the existence of oil were damages on ground- and surface-waters used as supplies for drinking-water.

Very small amounts of oil in water are capable of causing deterioration of smell and taste. Melpolder et al. (1) claims 0.005 mg/l as a treshold concentration for gasoline and Gibbon (2) 0.2 mg/l for gasoline and 0.7 mg/l for fuel-oil. The National Institute of Public Health in Sweden gives the treshold concentrations 0.05 - 0.1 mg/l for fuel-oil no 1 as well as gasoline.

Several methods for isolation and determination of oil are described in the literature. Diethylether, petroleum spirit, chloroform and carbon tetrachloride have been used as extracting agents. For the quantitative determination have been used gravimetry, measurement of fluorescence, determination of specific weight, mass-spectrometry, thin layer- and gas chromatography. Simard et.al. (3) 1951 proposed a method with extraction by carbon tetrachloride and subsequent quantitative determination with infrared spectrophotometry. The absorption due to hydrocarbons is measured in the spectral range 3333 cm^{-1} - 2500 cm^{-1} (3-4 μ).

Oil consists of a mixture of hundreds of hydrocarbons, the proportions of which strongly vary with the type of oil. In order to overcome these difficulties, Simard et.al. (3) made a standard-mixture of

n-hexadecane (cetane), iso-octane, and benzene and compared the unknown samples with this standard. This standard is now commonly used in infrared analyses of oil.

In the extraction of the sample are isolated not only petroleum hydrocarbons but also organic substances of other origins such as humic compounds, lignin, animal and vegetable fats and oils and surface-active agents. Hence what is really determined is the total amount of carbon tetrachloride extractable substance.

C.G. Lindgren (4) has taken up this fenomenon and in his exellent article proposes chromatography through a polar column in order to remove these interfering organic substances from the petroleum hydrocarbons. The hydrocarbons passing the column are regarded as mineral oils and consist mainly of alkanes. This way of looking at the problem is now commonly accepted. As the polar compound in the column aluminium oxide is normally used.

An interesting and precise method for determination, involving thin layer chromatography has been worked out by Giebler et. al. (5). Stichting Concawe (6) has 1968 published some analytical methods for determination of oil in water and soil.

The analytical method described below is an attempt to put the finishing touches to, and adapt the techniques for determinations of small amounts of oil in sea-water on a routine basis and with a reasonable amount of effort.

Sampling equipment and techniques

Because of the risk to contaminate the sample it is essential that the equipment used should be of a construction that never needs lubrication. Hence Perspex, PVC, glass etc. are suitable construction materials.

After sampling, the water is transferred to glass bottles with grounded stoppers. Avoid touching the grounded surfaces !

All equipment used should be carefully washed and thoroughly rinsed with large amounts of ion-exchanged or distilled water. Whenever possible the different items should be rinsed with carbon tetrachloride after washing and rinsing.

We have used a bucket (10 litres) of stainless steel to obtain the surface samples. This sampling of the sea-surface is always made from the moving ship, just before it stops at a sampling station. This method seems sufficient to prevent contamination from the ship itself. The samples from the deeper water-layers we have obtained with TPN (Total Plastic Nansen) water--bottles from Hydro-Bios Apparatebau GmbH, Kiel, W. Germany. The TPN is never fastened on the hydrographic wire but on a nylon rope attached to the wire and about 5 metres below the end of the wire. The TPN is messenger-operated. This is performed with help of a common messenger-operated water-bottle, placed so it overlaps the joint between the wire and the rope.

The water is poured into (2.5 litres) glassbottles. To prevent biological activity in the sample we add 1.5 ml of saturated mercuric chloride solution ($HgCl_2$) per sample.

Equipment

A. Reagents

A1. Hydrochloric acid, certified. The concentrated acid is diluted with an equal volume of distilled water.

A2. Carbon tetrachloride. It is not important to use expensive spectroscopic or certified grades. It is important that the quality used should be free of any significant absorption-maximum in the infrared region 3333 cm^{-1} to 2500 cm^{-1} (3-4μ). The same quality is used through all steps in the analysis, from cleaning of equipment to spectrophotometric determination. For the present we use carbon tetrachloride BP 1953 grade from Albright and Wilson.

A3. Aluminium oxide, neutral, activity step 1 due to Brockman. We have found that type 507 C from Fluka (Switzerland) is quite suitable.

A4. n-Hexadecane (cetane), certified.

A5. iso-Octane, certified.

A6. Benzene, certified.

B. Glass-ware and apparatus

B1. We extract the samples in the glass bottles mentioned above. To collect the carbon tetrachloride after extraction we replace the stopper with a TS-cone provided with a stopcock (e.g. Quickfit Stopcock Adapter MF11 Fig. 1 d).
Thus the bottle acts as a separatory funnel. (When extracting with 25 ml it is not necessary to provide the adapter with air-inlet.)
NB! The presence of any kind of (fatty) lubricant, except the sample itself will disturb the analysis, giving high, positive values. Therefore we recommend the use of stopcock keys made of PTFE.

B2. Shaking-machine with a reciprocating motion. We use an apparatus from Edmund Bühler AG, Tübingen, W. Germany, model no Sm 2.
The speed used is about 180 strokes (5-6 centimetres) per minute.

B3. Chromatography columns. Easily made from glass tube 10 mm inner diameter, 150 mm long, formed to a narrow neck at one end, (Fig.1 b).

B4. Glass woll.

B5. Filtering paper. Munktell no OOR or equivalent.

B6. Funnels for filtering. To reduce the losses of carbon tetrachloride due to evaporation a high, narrow type should be used. We suggest Pyrex no 3960 (Adapters for Gooch Crucibels) or similar, (Fig. 1 c).

B7. Centrifuge. Capacity 50 ml in each tube and 3000 rpm.

B8. Infrared spectrophotometer (IR-photometer). Any low- or medium ost instrument will do if it has double-beam operation and capacity for 40 mm cells. Anyhow an instrument with a grating monochromator is preferred.

B9. Cells 40 mm Infrasil or equivalent quartz material.

Extraction

To the sample (approximately 2 litres) add 2 ml hydrochloric acid 1+1. Check that the pH is about 3 or less. From a measuring glass add 25 ml carbon tetrachloride. Stopper the bottle and shake it by hand for a few seconds. Open the bottle and re-stopper it again. Repeat this procedure until the sample is totally de- gassed.

Place the bottle (bottles) in the shaking-machine and shake for 60 minutes. (The Bühler machine is capable of shaking four 2.5 litres bottles at a time).

After the extraction stand the sample aside to let the phases separate. If an emulsion has formed or if the phases haven't separated completely after two hours it is necessary to centrifuge.

Replace the stopper with stopcock adapter described above. Secure it to the bottle with a clamp or rubber band. Invert the bottle and place it in a stand. (For instance an ordinary laboratory stand with a big - upper - ring around the body of the bottle, and one smaller - lower - ring around the neck of the bottle Fig, 1 a). Draw off the organic phase directely into the narrow filtering funnel. The filtering paper should previously have been washed with 10-15 ml carbon tetrachloride. The filtered sample is collected in a 25 ml conical flask with a grounded stopper.

In case it is necessary to centrifuge the emulsion and organic phase, draw these off directly into the centrifuge tube. After centrifugation, collect the organic phase with a pipette. After this the filtering sometimes might be avoided. Now the extract is ready for column chromatography.

NB! If the oil content of the sample is very high it may be necessary to extract twice or more.

Column chromatography.

This step is necessary in order to remove the polar hydrocarbons from the sample.

A small piece of glass wool is placed in the bottom of the column and the aluminium oxide is poured above this to a height of about 10 cm. NB! Don't tap on the column or make any other attempt to settle the powder, because this will inevitably result in an extremely slow-running column! Place a small piece of glass wool atop of the oxide. This will prevent the powder from whirling up when pouring in the sample.

Now saturate the column with carbon tetrachloride and let approximately 6 ml flow out. This is about equal to the volume retained by the oxide. When the column has stopped dripping, carefully pour a part of the sample on the column. When another 6 ml has passed out (use measuring glass!) collect the remaining part of the sample as it passes the column. Grounded 25 ml conical flasks are very suitable for this purpose.

Infrared spectrophotometric determination

The reference- and sample cells are carefully cleaned with carbon tetrachloride, filled up with the same liquid and the zero-absorption is checked up in the region 3333 cm^{-1} - 2500 cm^{-1} (3-4μ). Then the sample cell is filled up with the sample and the spectrum is recorded in the region mentioned above. If the absorption of the sample appears to be higher than suitable due to the calibration curve, the sample is diluted with pure carbon tetrachloride and the spectrum is recorded once again.

If the absorption of the sample is measured directly after extraction and filtering, the quantity measured is the total amount of carbon tetrachloride extractable organic substance. If however the absorption of the sample is measured after the chromatography the quantity measured is the total amount of carbon tetrachloride extractable non-polar hydrocarbons. "oil".

Calibration and evaluation of results

Obviously the most correct way to make the calibration curve is to add known amounts of the standard mixture to a series of water samples (1 litre , synthetic sea-water or distilled water) and extract the samples, followed by the column chromatography.

We have simplified that procedure to a great extent. From a solution with a known concentration of standard-mixture (37.5 % n-hexadecane, 37.5 % iso-octane, 25 % benzen) in carbon tetrachloride, we prepared a series of dilutions in 25 ml measuring flasks. Thus the concentrations (in mg/25 ml) of these solutions corresponds to the concentrations of samples in mg/l if one litre of water is extracted. (E.g. 0.34 mg/25 ml = 0.34 mg/l sample). The correctness of this calibration procedure was confirmed by application of this method when analyzing effluents from some factories. The concentrations of oil in these samples were so high that we had to dilute them about 100 times. In parallell we made gravimetric determinations on several of the extracts after IR-photometric determination.

The following figures are representative for the results we obtained:

Industry	Oil mg/l IR-photometric	Oil mg/l gravimetric
A	324	319
B	138	140
C	142	142

Thus the simplified procedure might be regarded as sufficient.

Lindgren (No 4) made a lot of experiments with the extraction procedure and found that generally one extraction was sufficient to recover 93-99 % of the oil, (where 93 % is for gasoline).

To evaluate the spectra obtained a straight line is drawn between the two absorption minima (that means about 100 % transmission) surrounding the region 3000 - 2800 cm^{-1}. See figure no 3. This line is normally horisontal, it is not unusual however that a slight absorption remains in the region of 2500 cm^{-1} even if the recorded curve there is a straight line. This due to increasing absorption in the carbon tetrachloride and the cells. In a case like that a horisontal line is drawn from the minimum in the 3300-3000 cm^{-1} region. From the straight line the absorption maximum at 2930 cm^{-1} is measured. Most instruments are graduated in per cent transmission and in that case the transmission value obtained is converted into absorption value with means of a standard table or the formula:

$$A = \log \frac{I_o}{I}$$

where

A = absorption

I_o = intensity of incident radiation (100 %)

I = intensity of the radiation passing the sample (in per cent)

To make a general formula for calculating the final concentration of oil, it is suitable as mentioned above to make a calibration curve with absorption plotted versus mg oil/25 ml carbon tetrachloride (figure no 2) and regard this as a result of an extracted 1-litre sample.

In that case the formula will be:

$$C = \frac{a \cdot \text{ml } CCl_4}{25} \cdot \frac{1000}{b} \cdot d$$

where

C = mg/l hydrocarbons, oil

a = mg/25ml from the calibration curve

ml CCl_4 = total volume of carbon tetrachloride used for the extraction (or multiple extractions).

b = ml sample used

d = possible dilution factor in the photometric step

Precision and accuracy

For the time being we regard 0.05 mg/l standard mixture to be lower limit for the method.

Because different types of oil have different specific absorptivities ranging from 1.75 to 2.99 $l \cdot g^{-1} \cdot cm^{-1}$ for lubricating oil, drilling oil and fuel oil respectively (Scholl and Fuchs, No 7 they would give calibration curves with different steepnesses. Obviously the standard mixture method is a (good) compromise between the extremes mentioned. The specific absorptivity of this mixture is 2.37 $l \cdot g^{-1} \cdot cm^{-1}$ and thus the resulting accuracy is $\pm$26 %. This value can of course be improved if it is known what type of oil is present in the sample and the calibration is made with the same or a similar product.

Acknowledgment

Thanks are due to Doctor Stig H. Fonselius (Fishery Board of Sweden) for valuable discussions and for stimulating us to write this paper.

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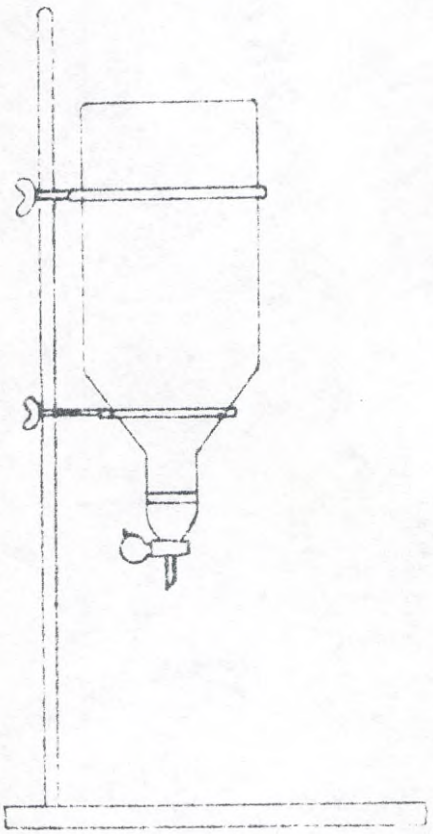

Fig. 1a Glass bottle with stopcock adapter in the stand with rings

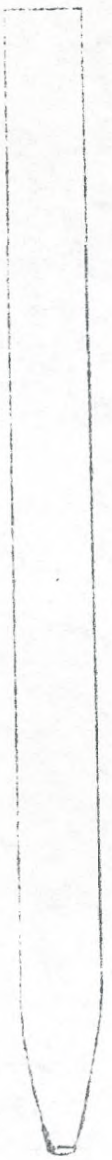

Fig. 1b. Chromatography column (actual size)

Fig. 1c. Adapter for Gooch Crucibles

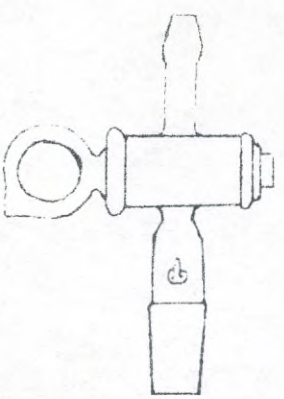

Fig. 1d. Stopcock Adapter

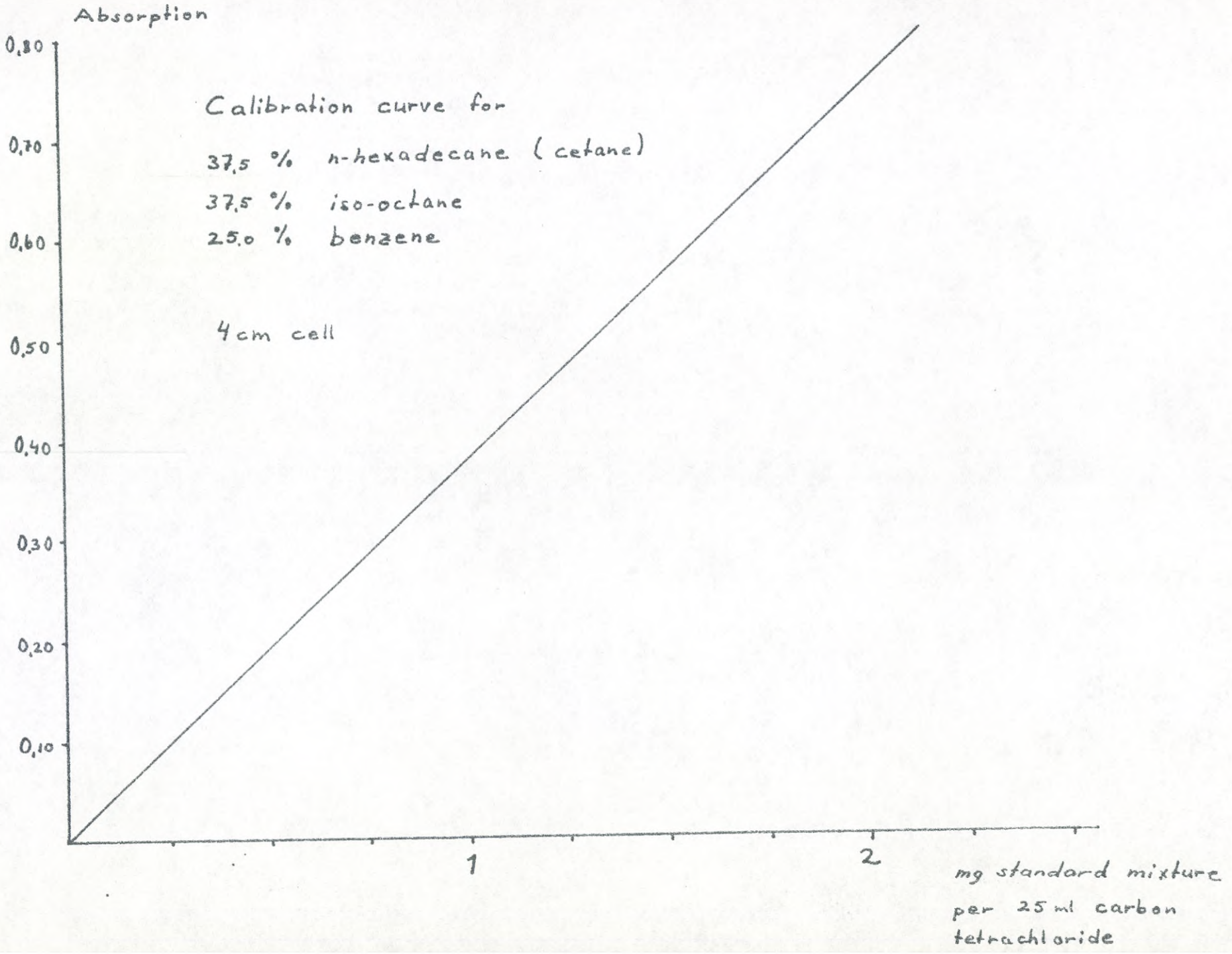
Absorption
0,80
0,70
0,60
0,50
0,40
0,30
0,20
0,10
Calibration curve for
37,5 % n-hexadecane (cetane)
37,5 % iso-octane
25.0 % benzene
4 cm cell
1
2
mg standard mixture
per 25 ml carbon
tetrachloride

Figure no 2

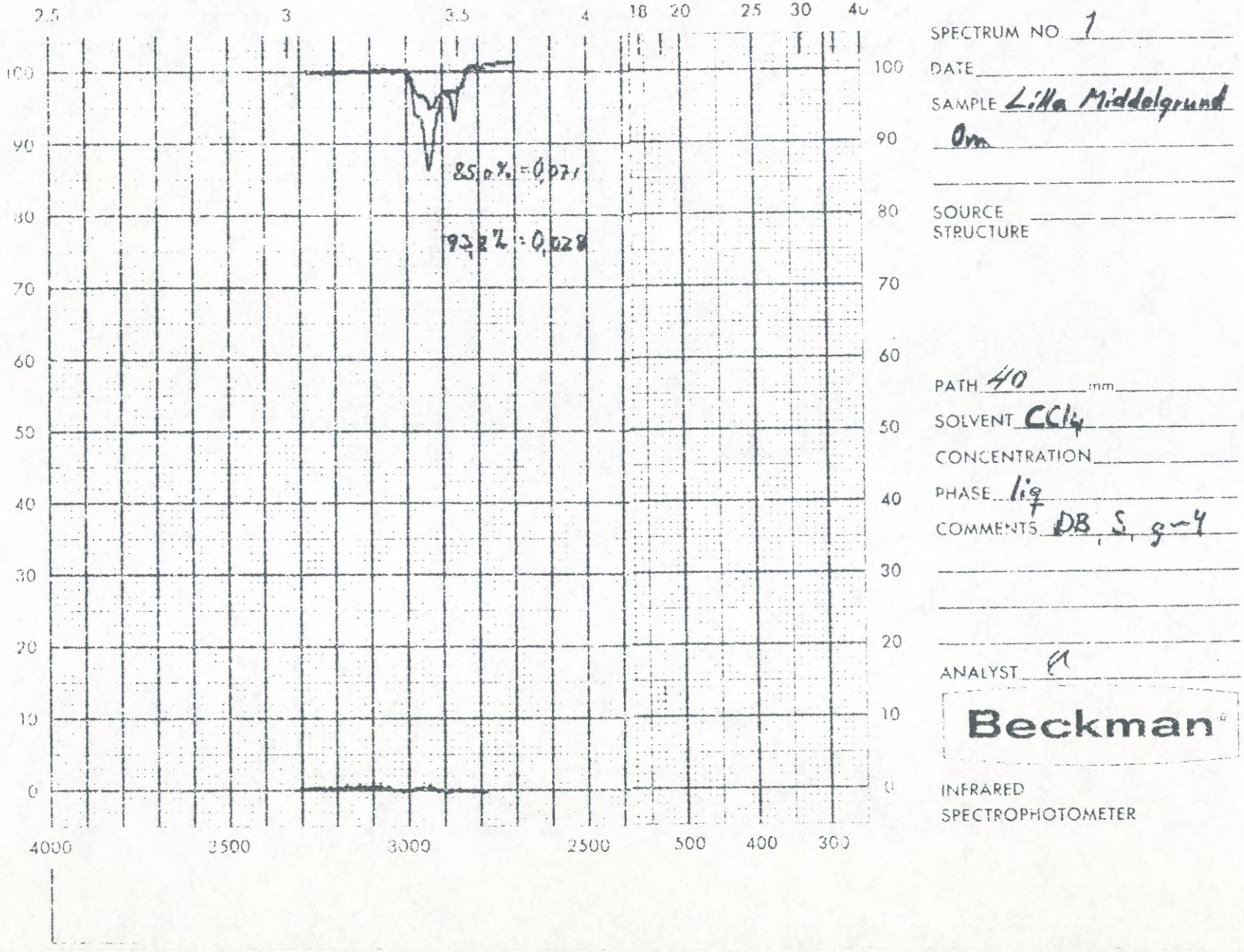
2.5
3
3.5
4
18
20
25
30
40
100
90
80
70
60
50
40
30
20
10
0
85,0 % = 0,071
93,2 % = 0,028
4000
2500
3000
2500
500
400
300
SPECTRUM NO 1
DATE
SAMPLE Lilla Middelgrund
Om
SOURCE
STRUCTURE
PATH 40 mm
SOLVENT CCl4
CONCENTRATION
PHASE liq
COMMENTS DB, S, g-4
ANALYST
Beckman
INFRARED
SPECTROPHOTOMETER

Figure no 3