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A method for extraction and determination of non polar, dissolved organic substances in sea water

by

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Summary

A method to extract sea water by sorbtion on Amberlite XAD is described. First the apparatus is explained, then sampling technic, working up procedure and determination by Gaschromatography. Recovery tests with DDT, DDE, Lindan, Aldrin, 2-Cl-biphenyl, Phenanthren, Pristan and n-Hexadecan demonstrates the applicability of the method for non-polar substances. The recovery ratios were about 80%. Gaschromatograms of two samples are shown.

Development of a method for extraction and determining of non polar, dissolved organic substances in sea water

Introduction:

The pollution by hydrocarbons, pesticide residues, PCB's and many other organic compounds has stimulated the development of analytical methods for dissolved organic compounds in the past last years. Previously emphasis was put on substances of so called natural origin, such as amino acids, fatty acids, and carbohydrates; now one would wish for more universally applicable methods to determine a great number of family of substances, even if they are only present in a trace range. If on takes into consideration that the sum of all dissolved organic substances in the sea water is in the ppm range, one should demand the following conditions for a method:

1)The concentrating factor should be sufficiently good, such that even individual substances in the ppt-range could be detected after seperating the pool with specific detectors or methods.

2)The working-up procedure should not change identity and content of the compounds.

3) Contaminants in the chemicals used in the methods, e.g. material, solvents etc. should not be accumulated in the adsorption analysis.

4.The inorganic salts, the content being 10^4 times greater than the organic substances, should be excluded from the concentrations.

Several methods had been developed to determine qualitatively and quantitatively dissolved organic compounds. Without concentrating a method had been elaborated to determine benzene in water with the aid of Laser-Raman Spectroscopy (1). Since the Raman spectrum of water is not very significant, pollutants with a characteristic Raman spectrum could be detected in water without a working-up procedure (e.g.Benzene 50 ppm (1)). In most cases a direct determination without separation and concentration is not possible. Two pricipal approaches to the problem of separation had been employed:

1) Sorption on a solid adsorbend (sometimes coated)

2) Solventextraction

Batchwise solvent extraction is usually restricted to only relatively small water masses. Although this method of extraction was methodically improved, (KAWAHARA et. al. (2) constructed a semiautomatic device to shorten the extraction time; SCHAFER et. al. (3) extracted 3.5 l sea water by quick stirring with 10 ml of hexan) the continuous solvent extraction is the more superior method. WERNER and WALDICHUK (4) modified a Scheibel-apparatus (5) with an interchangeable solvent circulation. KAHN and WAYMAN (6) constructed a three stage liquid - liquid extractor, in which non-polar substances were extracted up to 97 % by a strong circulating petrolether current (500 - 1100 ml/h). GOLDBERG et.al. (7,8) constructed a similar apparatus for solvents lighter than water (5 stage) and heavier than water (4 stage). With a water flow rate of 7 - 8 l/h they were able to recover up to 80 % of non-polar substances with 5 different solvents with a concentration factor of about 10^5. They pointed out that the efficiency of extraction depended on the difference of the dipole moments of solution and extracting solvent. A further improved apparatus was constructed by A.AHNOFF and B.JOSEFSSON (9), by which was avoided the renewing of the solvent by distillation. It was suitable for fieldwork because of it's good handling. They restricted the apparatus to one extraction vessel, specially constructed so that in a mixing chamber with a water flow of 2-5 litre/hour effective magnetic stirring resulted in a good mixing of water and solvent. Separation of emulsions was also achieved, resulting in low losses of the solvent in the waste water. The recovery of pesticides was nearly 90 %.

The limiting factor for all extraction methods is the distribution coefficient of the substances between the water and solvent. Especially for little more polar substances the factor for water/nonpolar solvent is not very good. The time for exchanging is often too short; the disadvantage could only overcome by several extraction in serie. Therefore the adsorption by an adsorbent fullfilled in a column has not these disadvantages.

Activated charcoal is very suitable for adsorption (10) (11), but it is difficult to elute the adsorbed substances completely, and furthermore there is the possibility that chemical changes will occur (12).

AUE et al. (13, 14) used silicons chemical bonded to chromosorb G to adsorb chlorinated hydrocarbons from fresh water with good success. ITO (15) used alkylchlorsilanes chemically bonded to celite, with less sussess for the adsorption of pesticides. For the extraction of PCB's GESSER et al. (16) used porous polyurethanefoam, UTHE et al. (17) used a polyurethanefoam coated with selective adsorbents with better results. For the extraction of sea water AHLING and JENSEN (18) used carbowax 4000 together with n-undecane on chromosorb DMCS, the particulate material were removed first by precipitating with $Al_2(SO_4)_3$. The recovery of of pesticides and PCB's was 80 - 100 % depending on experimental conditions. First RILEY et al. (19) used crosslinked polymers like styrene-divinyl-copolymers of Amberlite XAD-Typ to extract ^{14}C-DDT from sea water. BURNHAM et al. (20) applied the resin in different typs (XAD-2 and XAD-7) to extract phenols, amines, ketones and sulfonates from fresh water with good success and G. HARVEY (21) for the extraction of DDE, DDT and dieldrin from sea water. We have refined the separation method of the precious workers and have found it to perform satisfactorly for the analysis of non-polar substances from sea water.

Apparatus: (Fig. 1)

The apparatus consist of a double-pistonpump (Fa. Bran und Luebbe, Hamburg, Typ Simplidos) which is connected with a teflon tube by a quick closing clamp. The piston stroke is continous adjustable, so that every flow rate of 3 - 70 l/hr can be regulated. After a pulsation-damper connected to an excess-pressure valve the water flow is filtered. On the filter device is a pressure-gauge, which anables one to measure the pressure on the filter up to 2 atmosphere.

After filtering the water flow is divided and directed parallel to six columns, each disconnectable by a stop-cock. One adsorption column (Fig. 2) is composed of a cylindric glasbody, 9 cm in length, 2.3 cm i.d., which has two screw-threads at each end and a glass-sinterplate inside at one end. The tube for influx and outflow are connected by fittings to a teflon body, which distributes equal the water flow over a teflon-gauze all over the column transverse. The teflon-body is tightened to the glass-cylinder by a nut. The water outflows are combined and the extracted sea water is determinded and afterwards discarded.

Sampling procedure and working up: (Fig.3)

The sea water is directly pumped on board ship through the previously described apparatus. To avoid contamination by the ship, a little buoy with the suction inlet is about 50 m away from the ship and connected by a teflon tube to the apparatus. It is possible to attach vertical teflon tubes of different length to the buoy, so that one can sample water from different depths.

The absorption material in the columns is Amberlite XAD-2, each column is filled with 65 ml aqueous slurry, thus all contain 390 ml. The flow rate is about 1.4 Bedvolumes/min, equivalent to 2.0 $ml/min/cm^3$. After sampling the apparatus and the columns are washed with 2 l distilled water. The connections are screwed off, the columns are washed outside with methanol and directly extracted in a Soxhlet with 150 ml methanol plus 100 ml distilled water per column for 8 hrs. (in the same time it is possible to process another sample with a second set of columns.) After extracting, each column is washed free of methanol with 50 ml distilled water in the Soxhlet, so that it is ready for the next sampling procedure. The combined methanol-water extracts are reextracted with 3 x 25 ml of n-hexane in a separating funnel, the hexane is dried with anhydrous Na_2SO_4 and either made up to 100 ml (high substance content) or evaporated under reduced pressure to 0.5 ml using a water bath (low substance content). In the same manner the filters from one sample are extracted and the extract are worked up. An aliquot is then injected into the G.C.

Instrumentation:

The G.C. is a Varian 2740 with a FID and ECD.

Column: i.D. 2 mm, 2 m length, glass
2.5 % QF-1 and 2.5 % DC 11 on chromosorb
WHP 100 - 120 mesh

Caries gas: N_2: 30 ml/min

Injection: 270°C

Detector: 225°C

Temperatureprogram: 180° - 200°C : 6°C/min
and: 100° - 180°C : 8°C/min.

The eluat is split 1 : 1 and measured simultaniously on an FID and ECD. So it is possible to determine hydrocarbons and chlorinated hydrocarbons with one injection. The identification of the peaks was done by comparing Rf-values with standards in the recovery tests, with unknown substances it is possible to use a coupled GC-MS-system. The quantitative determination was done at the FID-side by comparing peak area with known amounts, on the ECD-side an automatic integrator was used with a calibration curve (Integrator units/mg sample weight.) It is recommended to repeat calibration very often, for the sensitivity of the ECD changes very often.

Materials:

The construction of the apparatus allows the sea water coming in contact only with teflon, stainless steel or glass.

All glassware is carefully cleaned with Detex$^{(R)}$, rinsed with water, methanol and hexane and heated in an oven for at least 12 hrs at 200 °C.

Methanol: The solvent is distilled before use with a distillation column, 1 500 mm in length and each batch is tested by G.C.

n-hexane: The solvent is boiled for 3 hrs with sodium and distilled like methanol.

Dist.water: Ion exchanged water is boiled with $K_2S_2O_8$ for 4 hrs and then distilled.

Amberlite XAD-2: The commercial material is several times suspended in water and decanted to remove the subtle particles and then extracted in a Soxhlet with methanol for at least 24 hrs.

Filters: Glassfiberfilter No. 6, Schleicher & Schüll, heated at 450°C for 24 hrs.

Recovery tests:

To determine the specifity and accuracy for non polar substances, we conducted recovery tests. A definite amount of test substances is dissolved in 10 ml acetone and this solution is put into 100 l sea water and shaken for a short time. Immediately after shaking,the water was pumped over the columns. The sea water was either "preextracted", that means it had already once been filtered and extracted by the apparatus and was therefore free of most of particles and dissolved substances or it was "not preextracted", that means it was natural sea water from the Baltic.

The following substances were tested:
DDT, DDE, Aldrin, Lindan: pesticides
2-Cl-Biphenyl (PCB-2): PCB's
n-Hexadecan, Pristan,Phenanthren: hydrocarbons

The concentrations ranged from 10 ug/kg max. to 0.01 ug/kg for the chlorinated hydrocarbons and from 100 ug/kg max to 0.1 ug/kg for the hydrocarbons.

Results and discussion:

The construction of the apparatus enables one to extract large amounts of sea water aboard a ship. Contamination is minimized by avoiding the contact of sea water with plastic material except teflon. It is not necessary to store and preserve water samples. The concentration ratio is 1 : 10^5 by a water sample of 100 l. It is possible with larger water samples to increase the concentration ratio. With two sets of columns a continously sampling and working up at the same time is possible.

If one column is damaged, the sampling must not be interrupted, for this column could be blocked out and the remaining five columns are capable to extract the sea water at the same flow rate. The adsorption capacity is such that 1 000 l of sea water with a content of about 1 mg/kg dissolved organic material can be extracted without any exhaustion. The flow rate is limited first by the pressure arising from the filter: it should not exceed 1 at. to avoid a too great damage of living cells, for this would increase the content of the dissolved organic material. Secondly the water should be exposed to the adsorbent for sufficient time to allow the partition to occur. For our purpose a flow rate of 1 - 2 bedvolumes/min was sufficient to extract hydrocarbons and chlorinated hydrocarbons dissolved in sea water in a range of 0.01 - 100 ug/kg/substance.

As shown by the recovery tests, Amberlite XAD-2 is suitable to separate hydrocarbons and chlorinated hydrocarbons from inorganic salts even in a range of 1 ug/kg. With the exception of Lindan the recovery of all substances were about 80%. At the flow rate used, Amberlite XAD-2 adsorbs polar substances too; for this reason the elution in the Soxhlet was done with a polar solvent (methanol) so that the columns are fully regenerated for the next sampling. In the next step the non-polar substances are extracted into the hexane layer whereas the polar substances remain in the methanol-water layer.

From the results shown in Table 1 - 4, one can ascertain two facts: First: Sea water, already once filtered and extracted by the apparatus (= sea water preextracted) did not give such good recoveries than natural sea water; secondly: The "dissolved fractions" (= extracted from the Amberlite) are higher than those retained by the filter in the recovery tests with "sea water preextracted". This fact is especially demonstrated by the hydrocarbons. The reverse is found in the case of the recovery tests with "sea water not preextracted". From these results one could conclude that the substances used for spiking were adsorbed on small particles as soon as they came into the water and that they are not truely dissoved. This could explain the higher recoveries with natural seawater, for the retention of particles is likely to be more efficient than the sorption of material from solution. In the "sea water preextrated" the "dissolved fraction" of course is higher because most of the particles are removed . One must keep in mind that glassfiber filters have not a definite pore size but filter by a process of random contact, also they have great surface area for sorbtion, so that it is very difficult to decide if the filters operate as an collector for small particles or as an adsorber for real dissolved substances. Our results suggest that both processes occur but that the first one is more efficient if particles are present. Additional from our results it is evident that substances with a better solubility in water (Table 5), that is Phenanthren, Lindan and PCB's, are mostly recovered in the dissolved-portion, whereas the more insoluble substances, which adsorb obviously faster on particles, are mostly recovered in the filter-portion. It is not possible to predict simply from laboratory experiment to natural conditions, for it is well known that particles or other substances (hydrotrophy) will change solubility of substance, normally insoluble in pure water. BORNEFF and KNERR (22) equilibrated 1.2.5.6-Dibenzanthracen for two years with distillated water and found nothing in the range of 0.01 µg/l, whereas the substance in this range is soluble in natural waters. ANDELMAN and SUESS (23) confirmed that the solubility in water of polynuclear aromatics could be increased by organic acids like lactic- or butyric acid. But if one looks for the "dissolved non polar substances" in sea water, it is necessary to look for the small particles, for most of the non polar substances will be adsorbed on them.

Gaschromatograms of two samples demonstrate the applicability of the apparatus and method. The first sample derives from the inner part of the Kieler Förde, a polluted area, the other from Schönberger Strand, an area not directly exposed to any sewage or other pollution sources. They were taken from surface water (50 cm depth).

Although the identification of single peaks has not been undertaken, the filter extract from the Kieler Förde sample has the typical pattern of gaschromatograms of a mixture of alkanes, whereas in the other sample no substances, sensitive to the FID, could be detected, but some ones sensitive to the ECD with identical Rf-values of pesticides.

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Table 1

	Sea water not preextracted 3)			Sea water preextracted 4)		
	dissolved1)	Filter2)	total	dissolved1)	Filter2)	total
Phenanthren	61,8	-	61,8	24,4	11,7	36,1
Pristan	-	62,5	62,5	34,6	20,3	54,9
n-Hexadecan	-	58,8	58,8	35,8	12,4	48,2

Recoveries from sea water that was spiked with 100 ug/kg substance.

Table 2

	Sea water preextracted 4)		
	dissolved1)	Filter2)	total
Aldrin	58,5	34,0	92,5
Lindan	39,8	-	39,8
DDE	49,2	51,8	101,0
DDT	47,6	40,8	88,4
PCB-2	95,2	-	95,2
Phenanthren	42,5	59,5	102,0
Pristan	64,9	32,4	97,3
n-Hexadecan	43,2	40,3	86,4

Recoveries from sea water that was spiked with 10 ug/kg substance

Table 3

	Sea water not pre-extracted			Sea water pre-extracted		
	dissolved1(	Filter2)	total3)	dissolved1)	Filter2)	total
Aldrin	23,7	61,1	84,8	38,6	44,7	83,3
Lindan	23,7	-	23,7	5,3	-	5,3
DDE	21,5	67,0	88,5	56,4	27,5	83,9
DDT	15,2	80,3	95,5	71,4	30,9	102,3
PCB-2	86,3	-	86,3	93,7	-	93,7
Phenanthren	57,0	-	57,0	25,1	9,3	34,4
Pristan	-	86,0	86,0	17,5	30,9	48,4
n-Hexadecan	-	69,0	69,0	15,0	28,7	43,7

Recoveries from sea water that was spiked with approximately 1 ug/kg of the substances mentioned.

Table 4

	Sea water not preextracted			Sea water preextracted		
	dissolved1)	Filter2)	total	dissolved1)	Filter2)	total
Aldrin	34,5	55,2	89,7	50,2	29,5	79,7
Lindan	36,4	-	36,4	29,3	-	29,3
DDE	22,3	71,4	93,7	53,4	29,5	82,9
DDT	22,6	68,6	91,2	48,5	38,2	86,7
PCB-2	87,5	-	87,5	84,2	-	84,2

Recoveries from sea water that was spiked with approximately 10 ng/kg substances as mentioned before.

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1) dissolved - which is extracted from the Amberlite
2) Filter - which is extracted from the filter
3) Sea water not preextracted - natural sea water, sampled in 25 litre glassbottles and spiked in the laboratory
4) Sea water preextracted - water once pumped through the apparatus on board the ship, sampled in 25 litre glass-bottles and spiked in the laboratory
5) Recoveries in percentage

Table 5

Aldrin	(24)	0,05
Lindan	(24)	7,3
DDE		0,25
DDT	(24)	0,0012
Clophen A-30		0,3 - 1,5
Phenanthren	(25)	1,6
Pristan	(26)	0,01
n-Hexadecan	(26)	0,01

Solubilities of the used substances in water at 25°C in mg/kg

Fig. 1 EXTRACTION APPARATUS FLOW DIAGRAM

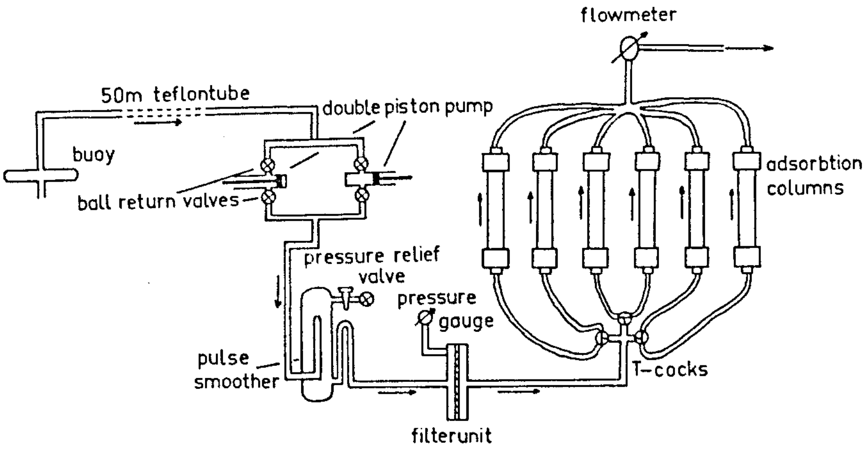


Fig. 2 ADSORBTION COLUMN

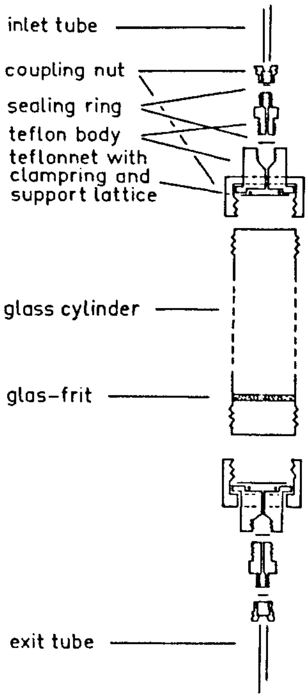
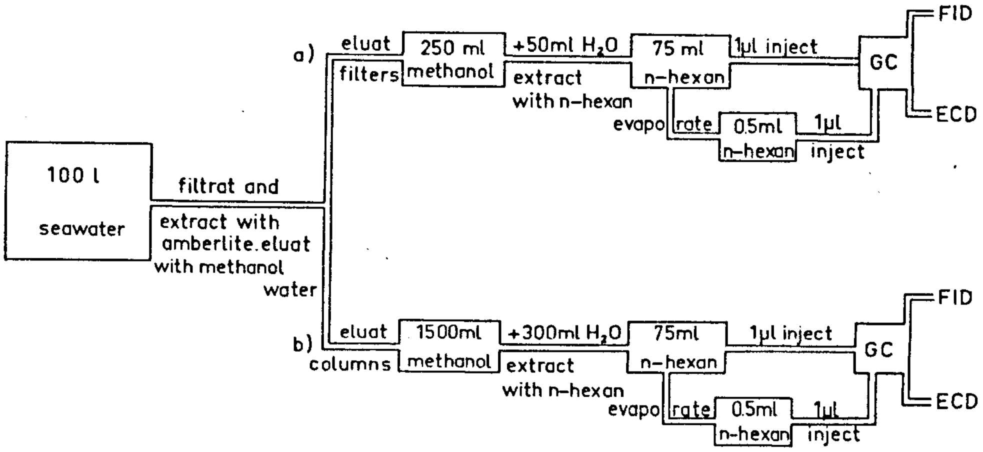


Fig. 3 ANALYSIS DIAGRAM



concentration: $10^5 : 0.5$

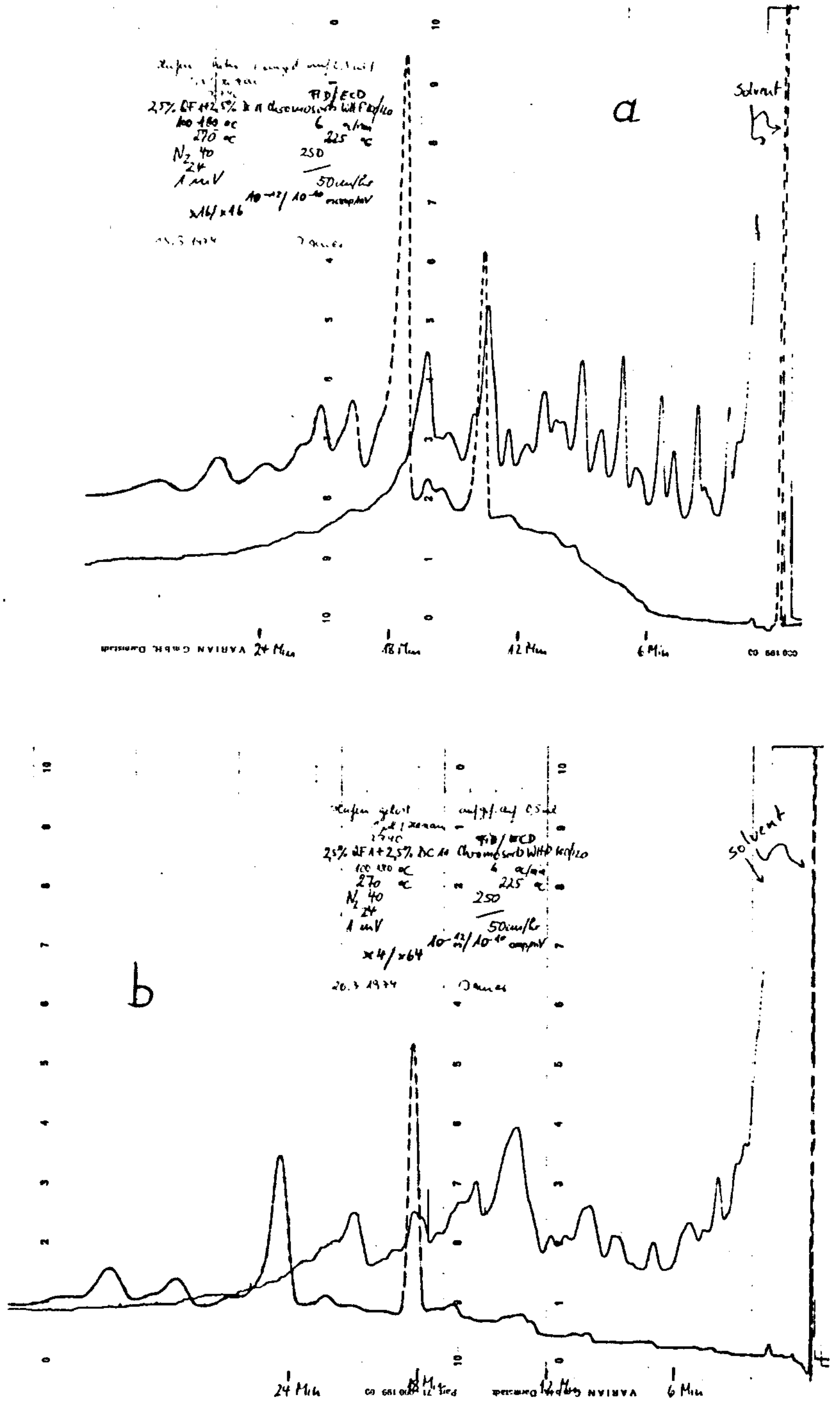


Fig. 4 Gaschromatograms ----ECD —— EID

a Extract filter Kieler Jnnenförde

b Extract dissolved Kieler Jnnenförde

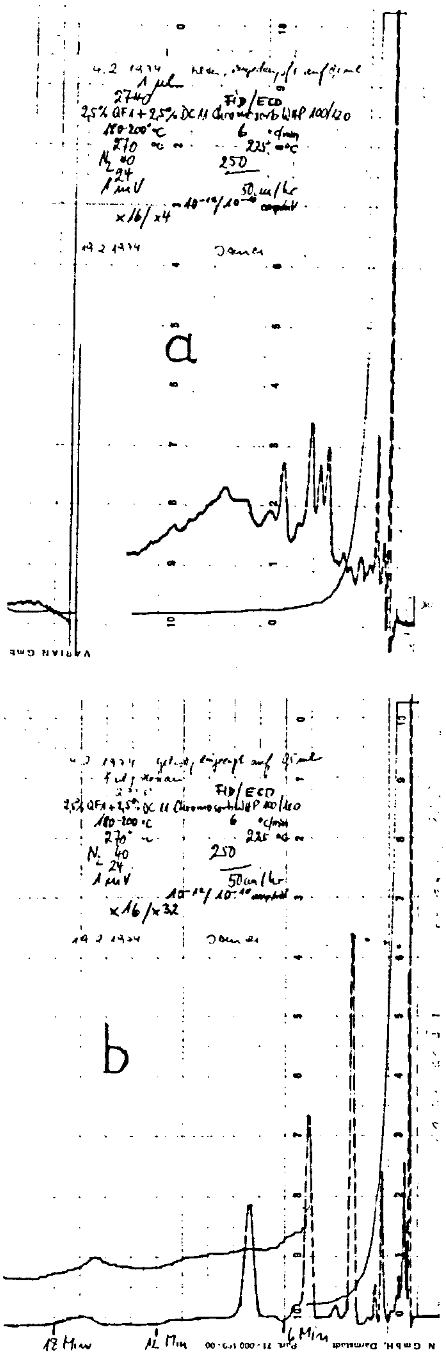


Fig. 5 Gaschromatograms ---- ECD —— FID

a Extract filter Schönberger Strand

b Extract dissolved Schönberger Strand