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On controlled discharges of oil hydrocarbons from the Ekofisk field terminal platform

by

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1. INTRODUCTION

The purpose of this investigation was to get a qualitative and quantitative picture of the so called controlled discharges of oil hydrocarbons from the Ekofisk field terminal platform. The discharges were mainly sea water which had been in contact with the produced oil and therefore contained disolved or emulgated oil hydrocarbons. The water is discharged from two points, the Skimmer tank and the Sea sump.

The project was planned so that samples from these two discharge-points should be collected over a period of 24 hours, for analysis of oil hydrocarbons. The results of these analysis will be of use in the setting up of instructions concerning discharges from field terminal platforms.

2. COLLECTION OF SAMPLES

2.1 The Skimmer tank. Production water, water accompanying the produced oil, water from the oil and gas separators and other sources are drained to the Skimmer tank (Fig. 1). The oil collecting on the

surface of the skimmer tank is separated from the water and recycled to the oil production. The water is drained from the bottom of the tank and discharged into the sea.

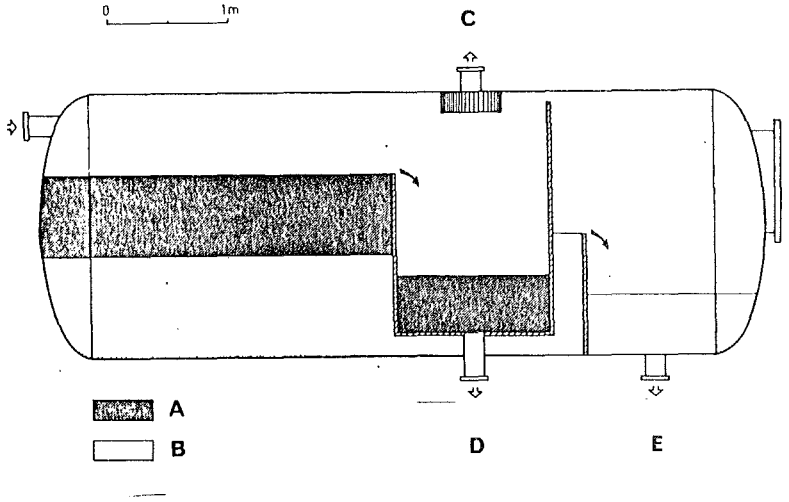

Fig. 1. Diagram of the skimmer tank at the EKOFISK field terminal platform. A = oil, B = water, C = gas to flare, D = oil to the second stage separator and E = water discharged to the sea.

Samples were collected six times in two 2 litre separating funnels and two 2.8 litre bottles from a tap situated in a side branch of the main drain (Fig. 1, E). Before the sample collection, the water was allowed to drain from the tap for some minutes to wash out the tube and tap. The water at this point had a temperature of 38 °C, a faint yellow colour and was cloudy due to suspended air bubles.

2.2 The sea sump is a 75 cm inner diameter tube extending from the lower deck on the field terminal platform down to 26 meter below normal sea surface level (Fig. 2).

The lower end of this tube is open but protected by a screen. A pump is situated within this tube at the normal sea surface level. Drains from the different decks and from the diesel storage tank leads to the sea via the sea sump. Oil accumulating on the top of the water in the sea sump is pumped back to the production system. The pump is started and stopped manually. There is no indication of the actual oil level in the sea sump.

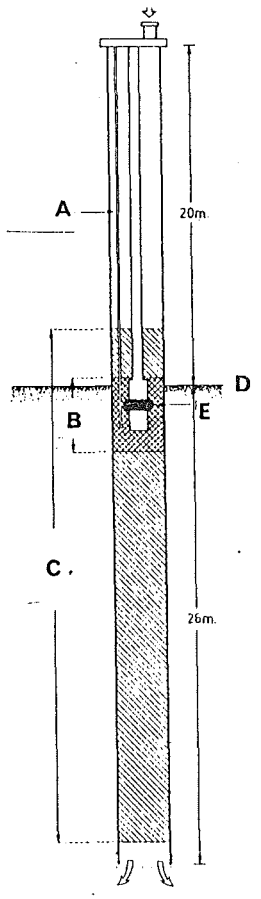

Fig. 2. Diagram of the sea sump at the EKOFISK field terminal platform. A = buble tube, B = minimum oil level, C = maximum oil level, D = sea surface and E = pump.

Attempts were made to take samples from the lower end of the sea sump (the water layer), using an aluminium bottle, open in the upper end and equipped with a valve allowing water to flow in at the lower end. The sampling bottle will then, when lowered, be washed through and when it is hauled the valve will close and the water sample from the wanted depth is taken. The purpose was to take samples from 3 meter above the lower open end of the sea sump and from a level 6 meters above. When the samples was hauled through the oil-layer in the sea sump, part of that oil remained on top of the water in the sampling bottle. This oil was carefully decanted off and the water sample drawn from the lower end through the valve and collected in 2.8 litre sample bottles. Each haul resulted in a 0.8 litre sample.

The sampling-bottle was trapped in the installations in the the third haul, so that further sampling from the sea sump

2.3. Condensate-Skimmer tank A drain tube from the bottom of this tank is connected to the drain from the main Skimmer tank so that water from this tank is also drained to the sea. It was difficult to obtain a satisfactory sample from the tap installed in the drain, possibly because oftoo little flow through the system. At the first attempt only a few hundred ml were obtained, of which only 10% was water. Later a greater volume was obtained of which approx 10% was an organic phase. This organic phase was separated in a separating funnel and stored for analysis. The water sample was drawn into a 2.8 liter sample bottle.

2.4. Production water. To get a representative sample of the water, which is produced with the oil, a sample was collected from the bottom of the first stage separator. This sample also contained oil. The oil and water sample was stored separately.

2.5 Sediment samples. Four attempts were made to sample sediments with a 13 kilogram gravity corer, but with no success, probably due to the nature of the bottom (gravel and pebbles) or from washing out of the sediment core during the hauling caused by the heavy wave action at the surface.

2.6 Crude oil. Two samples, each 100 ml of crude oil were taken from a tap in the production system after the third stage separator, for use as references in the analysis of the collected samples.

3. SAMPLE TREATMENT

3.1 Water samples in separating funnels. These samples were extracted, imediately after collection in a laboratory situated on the same deck as the skimmer tank. The extractions were

performed using 3 x 40 ml of dichloromethane. The separating funnel was shaken vigorously for 2 minutes. From the first 40 ml added only 10 ml were left partly, because of evaporation (high temperature) and solution of dichloromethane in the water phase. Of the next 40 ml portions added practically all remained as the dichloromethane phase, giving a total of 80 - 90 ml. The combined extracts were kept in 100 ml sample bottles with a teflon lined screw cap.

The efficiency of the extraction procedure was tested by extracting the sample again with 3 x 30 ml dichloromethane and keepin this extract separately for further analysis. Two blank samples were also performed shaking an empty separating funnel with 3 x 30 ml of dichloromethane. Before the analysis were started all the extracts were adjusted to the same volume (90 ml) and the samples dried using approx. 5 grams of dry sodium sulphate.

3.2 Water samples collected on 2.8 litre bottles. Immediately after collection of the samples approx. 10 ml of dichloromethane was added to prevent any biological activity. The bottles were provided with an aluminiumfoil lined screw cap before transportation to the institute. The samples from the skimmer tank was then extracted as described above. The samples of the production water and the water from the sea sump were extracted three times with 3 x 30 ml dichloromethane. This was done because the first set of extractions were strongly brown coloured and the second set of extraction had also a faint colour.

To enable a search for acidic components in the skimmer tank water the samples were acidified to pH = 1, using concentrated sulphuric acid (approx. 1 ml acid per litre of water) and then extracted according to the method already described above. The extracts were evaporated to approx 5 ml and then extracted with 3 ml of I N sodium hydroxide. During this procedure the acidic components will be extracted from the bulk of components in the dichloromethane extract. The alkaline solution was

acidified and extracted with benzen, evaporated and a solution of diazomethane in ethylether was added and allowed to react for 5 minutes at room temperature. The result of this treatment is methylesters of the acidic components, which enables a better gas chromatographic separation and analysis.

4. ANALYSIS

4.1 Identification. Dichloromethane was removed from five ml portions of the extracts using a stream of dry nitrogen, the residues were then dissolved in a controlled volume of carbondisulphide. Samples of the resulting solutions were analysed using a computerized gac chromatograph-mass spectrometer; Finnigan 3200 E-6100 equipped with a 20 meter OV-1 glas capillary column. The mass spectra of the separated peaks in the gas chromatograms were used for identifications. The results are given in Table 1.

Table 1. Identified hydrocarbons in water samples from the Skimmer tank at 20.30 hours, November 18th, 1975.

Components	Amount in mg/l
Benzene	
Toluene	
Xylene	
Trimethylbenzenes	3
Tetramethylbenzenes	0.6
Naphthalene	
Methylnaphthalenes	
Dimethylnaphthalenes	0.7
Trimethylnaphthalenes	
Phenanthrene	0.004
Phenol	
Methylphenoles	2
Dimethylphenoles	
Trimethylphenoles	
Alkanes C_{13} - C_{29}	0.9
Fatty acids	
Benzoic acids	

4.2 Quantification. The quantification was performed in the three following ways:

4.2.1 The volatile components benzene, toluene and the xylenes were dominating. The quantification of these components were performed by gas chromatography of 2.0 µl of the total extracts using a OV-1 packed column. An example of such a chromatogram is shown in Fig. 3. The three isomeric xylenes, ortho, meta and para were not properly separated on this column, the meta and para xylenes are overlapping each other. The amount of each of the components in the samples was calculated from the area of the peaks in the respective chromatograms. From a calibration curve, based on accurately weighed benzene and toluene a response factor was found for both components to be 27.5 area units per µg injected component. The same respons-factor was used for the xylenes. The results are given in Table 2.

Table 2. Hydrocarbonconcentrations (mg/l) in water samples from the Skimmer tank, Sea sump and after the first stage separator. Samples taken the 18th - 19th November 1975 on the Ekofisk field terminal platform.

	Benzene	Toluene	Xylene	Others
Skimmer tank				
1500 hours	28	21	8	8
1730 "	45	40	14	20
2030 "	81 (83)	64 (63)	21 (21)	
0030 "	35	33	10	
0600 "	62	54	17	
1145 "	31 (38)	29 (32)	10 (12)	
Seasump				
1500 hours			1100	
1. stage sep.				
2200 hours			500	

The values in brackets represent samples collected in 2.8 litre sample bottles, which were extracted at the Institute of Marine Research.

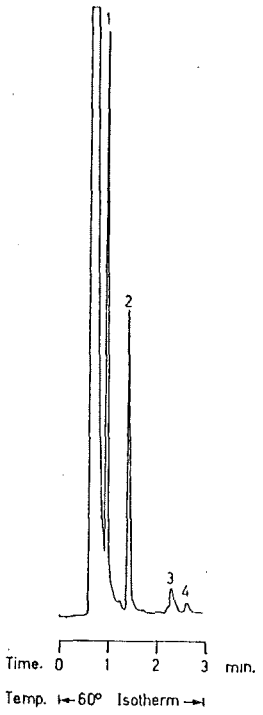

Fig. 3. Gas chromatogram of the most volatile aromatic hydrocarbons from an extract of water from the skimmer tank. The chromatographic peaks 1, 2, 3 and 4 represents benzene, toluene, meta-xylene and para-xylene and ortho-xylene respectively. The gas chromatogram was obtained on a Perkin-Elmer 900 gas chromatograph equipped with a flame ionization detector. A glas column, 3 m x 2 mm packed with 3% OV-1 on 80/100 gas-chrom Q and nitrogen, 15 ml per minute, was used as a carrier gas.

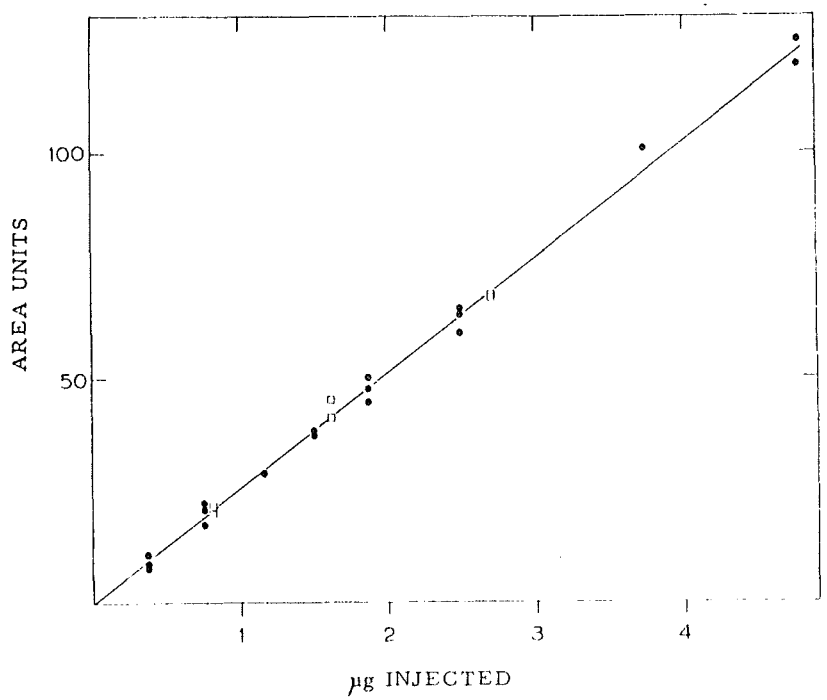

Fig. 4. Calibration curve for the area of the gas chromatographic peaks based on known amounts of benzene (●) and toluene (□).

4.2.2 The main portion of the other aromatic components were quantified using GC/MS. An internal standard, namely fluorene, was added to each of the total extracts. Then the dichloromethane was removed by a stream of dry nitrogen and the residues taken up in a measured volume of carbon-disulphide and aliquotes injected on the GC/MS. Mass fragmentograms based on the molecular ion of the different components were then recorded using the GC/MS.

The amount of the different components was calculated by comparing the area of the fragmentograms of a known amount of fluorene. The results are given in Table 1.

4.2.3 Apart from the components present in concentration high enough to show up as peaks in the chromatograms, the unresolved components show up as an envelope (Fig. 5). This is due to the fact that the separation power of an ordinary gas chromatografic column do not separate all the branched alifatics, cyclic alifatics, aromatics and the other components present in oil.

To measure the total content of oil hydrocarbons in the samples, however, this envelope must also be quantified. The dichloromethane was therefore removed from 5 ml portions of the extracts as described above (4.1) and the residues dissolved in 200 µl dichloromethane and 2.0 µl aliquotes of this solution was then chromatographed. A 1 ml solution of 15.2 mg of the crude oil-reference (2.6) was made and 2.0 µl of this solution (30.4 µg crude oil) was chromatographed under the same condition giving the result; 1 µg crude oil = 18.5 area units. The calculation of total oil hydrocarbons in the samples can thus be done (MEDEIROS and FARRINGTON, 1974). The areas were determined by cutting and weighing. The results are shown in Table 2.

The content of hydrocarbons in the extracts from the sea sump and production water were high enough to be chromatographed

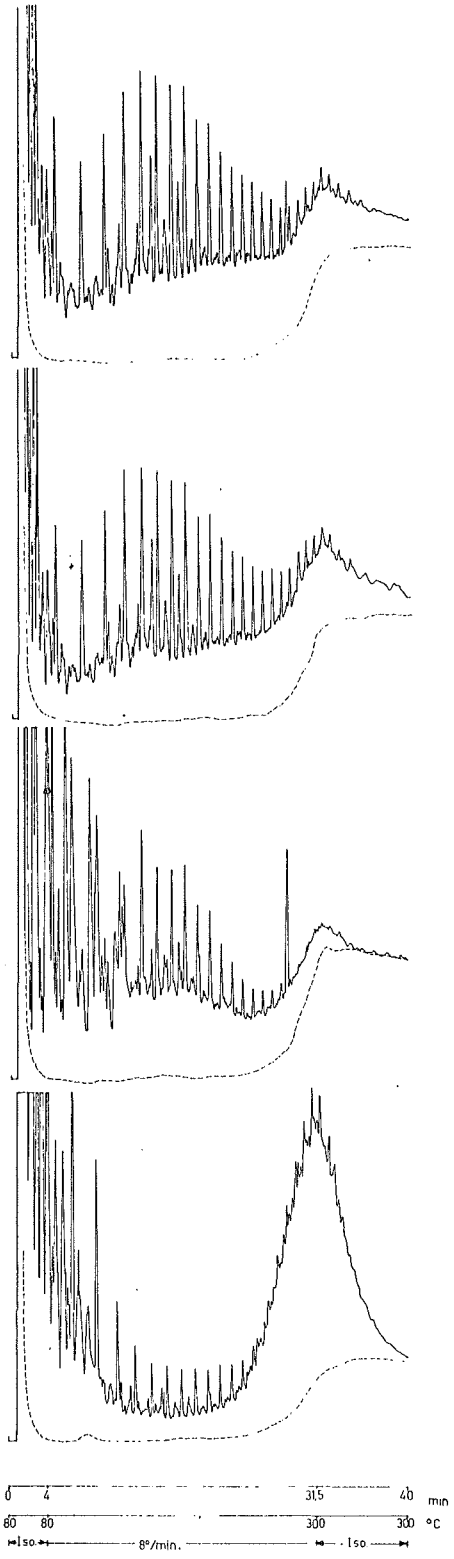

Fig. 5. Gas chromatograms of, from the top; EKOFISK crude, extract of production water from the first stage separator, extract of water from the skimmer tank and extract of water from the slop sump. The broken line represents the baseline of the chromatograms found by chromatography of pure solvent under identical conditions.

without any preconcentration before the quantitation of the envelope.

4.3 Sources of error. The quantitation of benzene, toluene and xylene was based on chromatography of two paralells of each extract. The mean deviation between two paralells was approx 2%. Each sample was taken in duplo (2.1), thus resulting in two extracts. The mean deviation calculated on the basis of these four determinations was approx. 5%. In addition to this the respons factor 27.5, which was used to calculate the concentrations (4.2.1), have some degree of uncertainty because the chromatographic condition used, did not give a baseline-separation.

The values for benzene, toluene and xylene given in Table 2 is therefore belived to have a maximum error of 10%.

The rest of the values, based on mass fragmentography (4.2.2) and area determination of the envelope (4.2.3) is believed tohave a mean deviation slightly more than 10%, allthough no systematic investigation on the accuracy has been performed.

5 DISCUSSION

The samples from the skimmer tank were extracted with 3 x 40 ml dichloromethane, as described under 3.1, which quantitativly removed benzene, toluene and xylene from the water phase. Repeated extractions with 3 x 30 ml dichloromethane only gave insignificant amounts of these components, The production- and sea sump water samples, however, had to be extracted twice. The second extraction, using 3 x 30 ml, gave about 10% of the amount from the first extraction.

The analytical methode used gave a quantitativ recovery of benzene. Tests were performed to show this by dissolving 174 mg benzene, using a calibrated 200 ul Carlsberg pipet in 2.2 litre of sea water, i.e. concentration of 79 mg/l. This sample was prepared and analysed according to the described method and gave a recovery of 83 mg/l benzene, e.g. 105%, which is within the accuracy of the method used.

The 2.8 litre water samples (3.2) which were brought back to the Institute and extracted in the laboratory gave the same results as those extracted in the field laboratory (Table 2). Extractions in future control activity could therefore be performed on the sampling site.

Benzene, toluene and xylene are the dominating hydrocarbons in the water discharged from the skimmer tank. The other hydrocarbons accounted for only approx. 10%, both for the sample with the lowest content, (at 15 00 hours) and the sample with the heighest content, (at 20 30 hours) see Table 2.

A routine check on the hydrocarbon content of discharge water could therefore be limited to the analysis of benzene, toluene and xylene.

The relatively high content of hydrocarbons in the discharged water could perhaps indicate that gravimetric analysis should be the most proper analytical method to use. Since, however, benzene, toluene and xylene are very volatile, they would partly or totally disappear, during the evaporation of the extraction solvent, even if the very volatile dichloromethane is used. A gravimetric analytical method is therefore not recommendable in this connection.

For these volatile components gas chromatography has proved to be a suitable analytical tool. Benzene, toluene and xylene have very little retention time on the column-material used,

OV-1, which makes it difficult to get a complete separation of benzene from the solvent used. In future investigations another column material, giving higher retention times for the low boiling aromatic hydrocarbons, will be chosen.

Benzene, toluene and xylene are strongly concentrated in the skimmer tank water compared to the composition found in the crude oil. A gas chromatographic - mass spectrometric analysis of the crude oil sampled at the third stage separator (2.6) showed a content of approx. 0.15% benzene and 0.5% toluene. The relative content of benzene and toluene in the hydrocarbons extracted from the production water, sampled from the first stage separator (2.4), showed to be corresponding. The gas chromatogram of the production water extract could be mistaken for the gas chromatogram of the crude oil (Fig.5), which indicates that the hydrocarbon content in the production water is an emulsion of crude oil in the water.

The chromatogram of the skimmer tank water extract (Fig.5) is essentially different from the chromatogram of the crude oil, in that it contains higher concentration of the more volatile components, early in the chromatogram, such as benzene, toluene and xylene. This indicates that these components in the skimmer tank water do not originate from the production water, but rather from the water from the gas scrubber system, which ends up in the skimmer tank. Due to the relative high temperature of the produced oil, the most volatile hydrocarbons will be present as gas. The gas is separated from the oil in the separator and led through a separate cleaning and drying system. Since these components belong to the most water soluble hydrocarbons, they will be dissolved in the water during this process and this water drains to the skimmer tank.

It is essential for the calculation of the total discharge of oil hydrocarbons from a skimmer tank that a flow meter is installed in the drain tube from the tank.

The salinity of the production water was very high, 49 o/oo, compared with the sea water, 35 o/oo. Water samples from the Skimmer tank varied between 37 and 42 o/oo, there was, however, no correlation between salinity and hydrocarbon content.

Water samples from the sea sump had a hydrocarbon content exceeding 1000 mg/l, mostly less volatile components, which are eluted from the gas chromatographic column as the characteristic envelope at about 300 °C (4.2.3). These components have most probably been in suspension in the water rather than in solution. It should be noted that the high value is based on one sample only and that the conditions during the sampling was not satisfactory, since the sample was hauled through the oil layer in the sea sump. Precautions was taken though, to prevent any of this oil to contaminate the water sample during the transfere to the sample bottle (2.2).

The sea sump seems not to be suitable for its purpose, even if it goes down to 26 meters below normal sea surface level. The wave action sets up a rather big vertical movement of the water/oil column within the sea sump, which was evident during the sampling from the strong current of air going in and out through the sampling hole. This will reduce the separation of the oil from the water phase and increase the dissolution and emulsification of oil in water. An installation of a proper sampling system is nessessary before a clear picture of the oil hydrocarbon content of the discharged water through the sea sump can be established.

Benzene and benzene derivatives are of the most volatile and most soluble fractions in crude oil. The relative high solubility in water render them more available for the marine organisms, they belong to the more toxic components and therefore more harmfull to the marine ecosystem.

Laboratory experiments has shown that 35 mg/l of benzene or toluene was lethal to freshwater fish (PICKERING and HENDERSON 1966). For salmon fry 10 mg/l of benzene had a narcotic effect (BROCKSEN and BAILEY 1973). A starting concentration of 40 mg/l of benzene reduced to 10 mg/l within the next 24 hours had a 50% lethal effect on herring eggs, but half the concentration had the same effect on herring fry. (STRUHSAKER, ELDRIDGE and ECHEVERRIA 1974). It has also been shown that less than 50 mg/l benzene, toluene or xylene has a 100% lethal effect on a few weeks old salmon fry in 48 hours (MORROW, GRITZ and KIRTON 1975). These components will also have a harmful effect on marine organisms in lower concentration. It is much more complicated to find out at which level sublethal effects start. Observations indicate that values down to 50 µg/l of oil hydrocarbons affects the photosynthesis in phytoplankton. (GORDON and PROUSE 1973).

As a guideline can be suggested that the concentration of oil hydrocarbons under no curcumstances should exceed one thousandth of the level found to have a lethal effect.

Because of the high volatility of benzene and its derivatives, it is to be expected that they will evaporate relatively rapid from the water in which they are dissolved. It has been found that up to 75% of dissolved benzene was evaporated from stagnant water at 12 °C during 24 hours (STRUHSAKER, ELDRIDGES and ECHEVERRIA 1974).

The present investigation should be extended to an analysis of the distribution of petroleum hydrocarbons in the water around the Ekofisk field and to an analysis of eventual hydrocarbons in the tissue of marine organisms in the area.

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