COD AND TPH ANALYSIS IN SLOPS TREATMENT EXPERIMENTAL PLANTS: ISSUES IN ANALYTICAL PROCEDURES

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ABSTRACT

Oily wastewater generated by ships, mainly in engine rooms (bilge waters) and from tank cleaning (slops) exhibit high salinity levels (up to 25.000 mgL^{-1}) as well. Effective treatment of such wastewater prior to discharging is necessary [1]. As a part of a broader project concerning slops treatments, this work addresses issues related to the analytical methods of the COD and TPH parameters, chosen under the provisions of Italian Legislative Decree 152/06 and MARPOL 73/78 convention, that implements the European directives on environmental protection. In the COD analysis the greatest difficulty was the high chloride levels, which cause a positive interference in the measurement; this was investigated at various concentrations of mercury trying to minimize the use of this harmful reagent [2][3][4]. The major problems in TPH analysis laid in *i*) the marked attitude of the samples to form emulsions during the liquid-liquid extraction procedure and *ii*) in the correct setup of the gas chromatographic separation.
This study is part of STITAM European project, created with the aim to develop innovative technologies for the treatment of liquid wastes of navigation, in order to better safeguard marine environment.

INTRODUCTION

Chemical oxygen demand (COD) is the main parameter used to measure the organic content of water and wastewater. One of the major problems associated with the COD analysis regards high salinity water, as seawater. Chloride ions indeed cause a positive interference being oxidized by dichromate too, what that instead would not occur with oxygen. Reduction of the chlorides up to 2 g/L may be carried out by the addition of mercury salts. Above this threshold, the methods standards suggest various solutions, such as the lowering of the concentration of dichromate or the use of a ratio Hg/Cl higher (20:1) [6]. Total petroleum hydrocarbons (TPH) is a term used to describe a large family of several hundred chemical compounds that originally come from crude oil. It is not practical to measure each hydrocarbon separately, however, it is useful to measure the total amount of TPH at a site [5]. In this paper the focus is fixed on the diesel-range organics (DRO) fraction, which includes hydrocarbons between C10 and C40.

MATERIALS AND METHODS

In this work we used analytical grade reagents. Blank tests allowed checking and correcting any sources of contamination. A and AS class volumetric material and a calibrated analytical balance were used for relevant volumetric and gravimetric steps.

▪ COD ANALYSIS

For chlorine recovery method [6] we used a system equipped with heating mantle, 250 ml flask (Fig1 "a"), reflux eight-bulb condenser, rubber and glass (Fig1 "b") connection, assembled as shown in Fig 1-2. For no chlorine recovery method [6] we used a six positions programmable temperature reactor, equipped with glass tubes, glass air condensers and glass bell jars with knob on the top. A 20 ml sample was treated with 35 ml solution of concentrated sulfuric acid with Ag_2SO_4 10,12 g/l, and 10 ml potassium dichromate 0,5N at 148°C for 2 hours.
For chlorine recovery, 200 ml distilled water with 2,5g potassium iodide and 5 ml glacial acetic acid, were placed in 250 ml cylinder (Fig 1 "c").
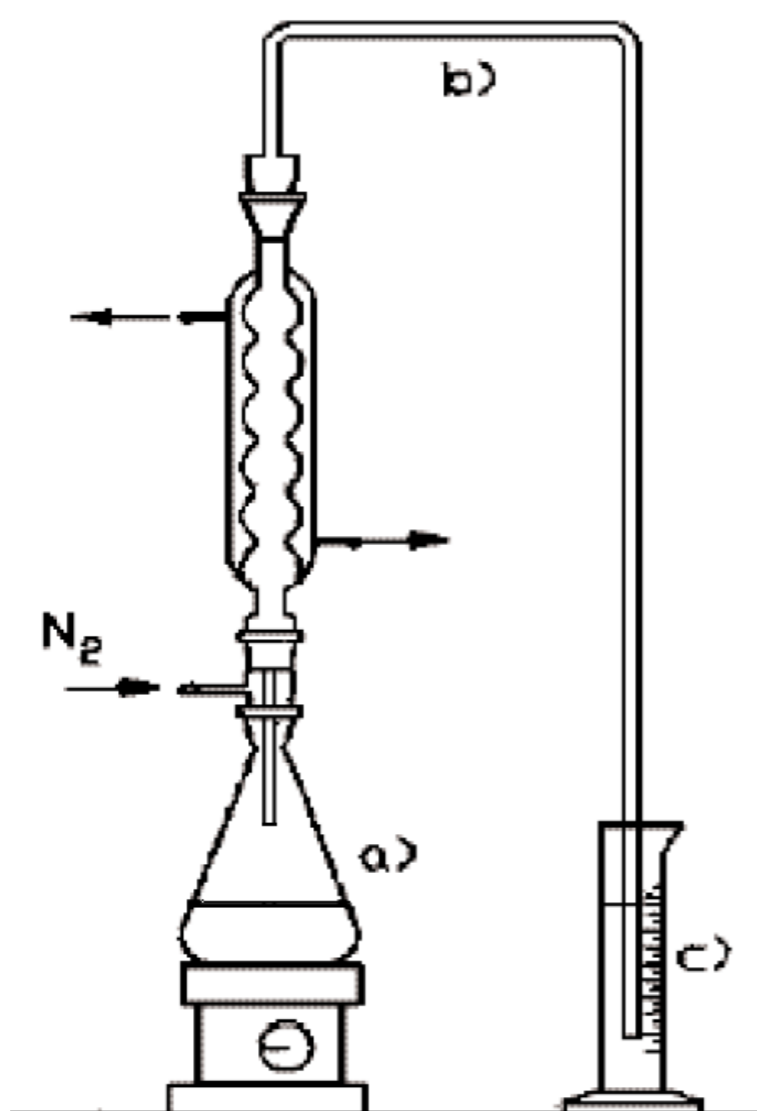
Emulsifying substances such as EPS, create a gelatinous layer which tends to obstruct the purification columns, making very difficult the extraction step and decreasing reaction yields.
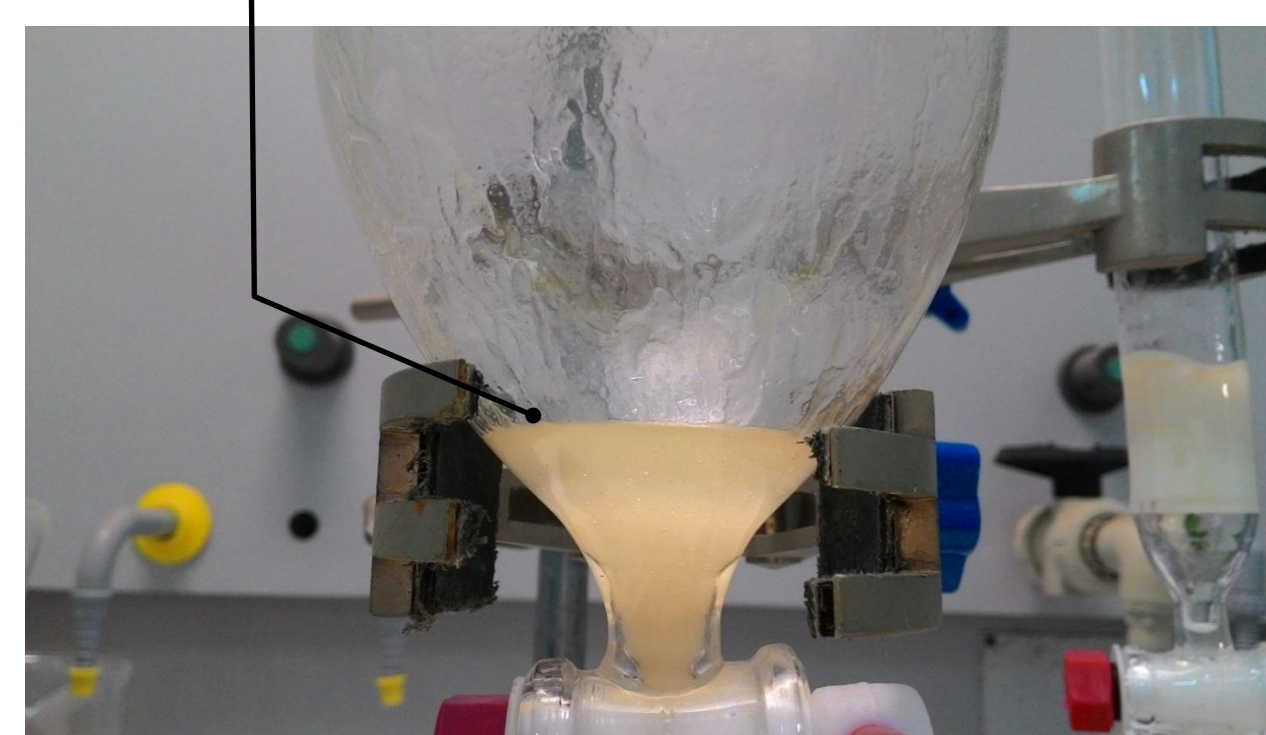

Fig.1 Scheme for COD analysis with chlorine recovery (IRSA, modified)

Fig.2 COD analysis configuration with chlorine recovery

Fig 3. Sludge formation during extraction step

▪ TPH ANALYSIS

For liquid-liquid extraction we used a 1 lt separating funnel, with hexane chromatographic grade as extraction solvent.
A 500 ml sample, put in separating funnel with 20 ml hexane, was extracted twice and the organic layer was percolated through a layer of anhydrous sodium sulfate and *florisil* 60-100 mesh for purification. The extract was evaporated until 2-3 ml reduced volume at low pressure and 40°C by means of a rotary evaporator, and the final volume was adjusted to 5 ml using hexane prior to gas chromatographic analysis.

An AGILENT 6890 GC-FID system with auto-sampler and a Parker gas generator 9090 for hydrogen supply was used for GC analysis, as shown in Fig. 4. We used the following parameters:
▪ Sample volume injection: 1 µl
▪ Injector temperature: 250 °C
▪ Carrier gas flow: 1 µl/min
▪ Ramp temperature: start at 45°C held 4 min; increased to 275°C at 10°C/min; held 10 min, then up to 300 °C at 6°C/min held for 5 min.
▪ FID temperature: 300°C.

Fig 4. Agilent 6890 GC-FID with Parker H$_2$ generator

RESULTS

The add of mercury sulphate reduces chloride interference when it is added with 10:1 Hg/Cl ratio, as reported in the analytical standards methods [6]. For samples containing chlorides at 5 g/L, the amount of mercury sulphate required should be 1,5 g/L. In order to limit mercury salts consumption, we carried out tests by reducing at 1/2 and at 1/3 the required quantities and by measuring the percentage reduction achieved for 5gCl/L and 10 gCl/L samples. Results are shown in Tab.1. Tab.1 shows that an amount of salt equal to 1/3 of that provided is sufficient to reduce over 80% of the interference, moreover, doubling the amount of mercury salt there is an almost negligible effect on reducing chlorides in both the proposed cases. The Tabs. 2-3 compare the results obtained with the two modified methods [6] used to analyze two standard solution containing potassium hydrogen phthalate in presence of chlorides. In both cases we obtained a good repeatability and accuracy.

Chlorides percentage reduction
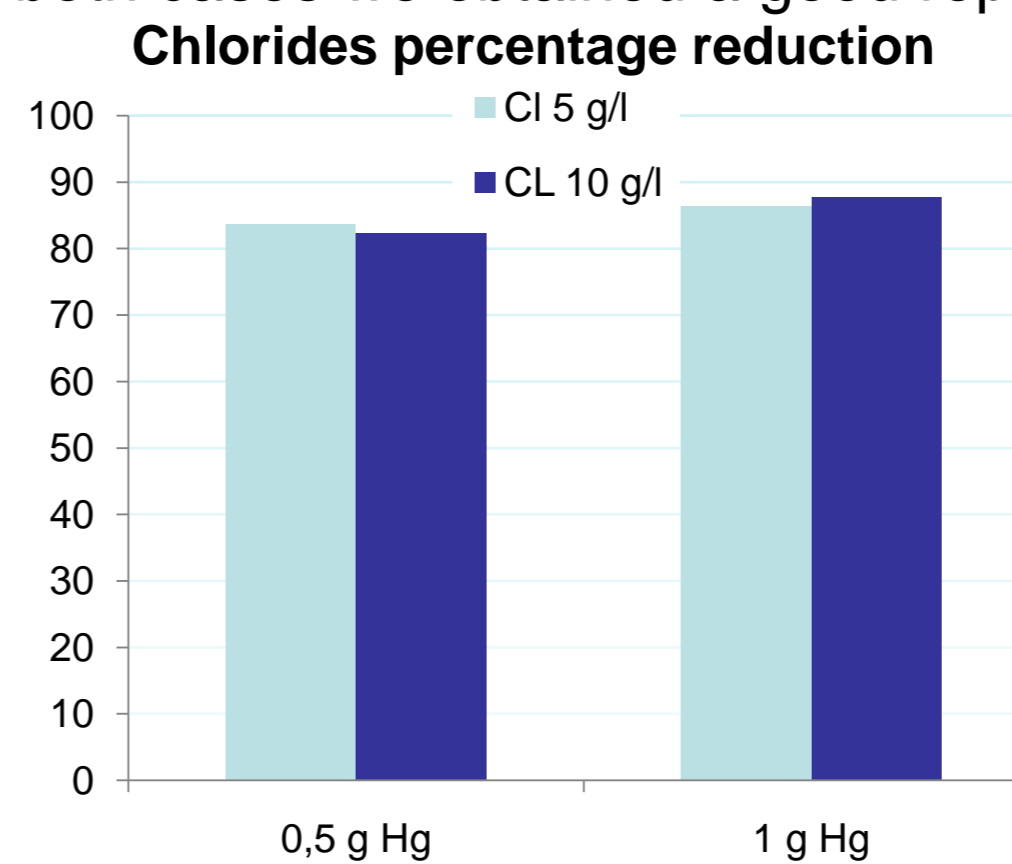
Tab.1 Chloride reduction as a function of mercury weight

FT 0,5 g/L + CL 5 g/L no chloride recovery method (APAT-IRSA 5130A)				
Sample	COD measures mg/l	Media mg/l	STD dev	Accuracy %
1	614			
2	653	604	±44	2,7
3	546			

FT 0,5 g/L + CL 5 g/L chloride recovery method (APAT-IRSA 5130B)				
Sample	COD measures mg/L	Media mg/L	STD dev	Accuracy %
1	595			
2	528	579	±37	1,5
3	615			

Tabs.2-3 Comparison between the methods used and verification of their repeatability and accuracy calculated on the expected theoretical COD value of 588 mgCOD/l. The methods 5130 A and B was conducted respectively without and adding 0.5 g of mercury salts.

Emulsions as that in Fig.6 are stable for long time, requires a lot of sodium sulphate for water removing and decrease reaction yelds to 70 %.
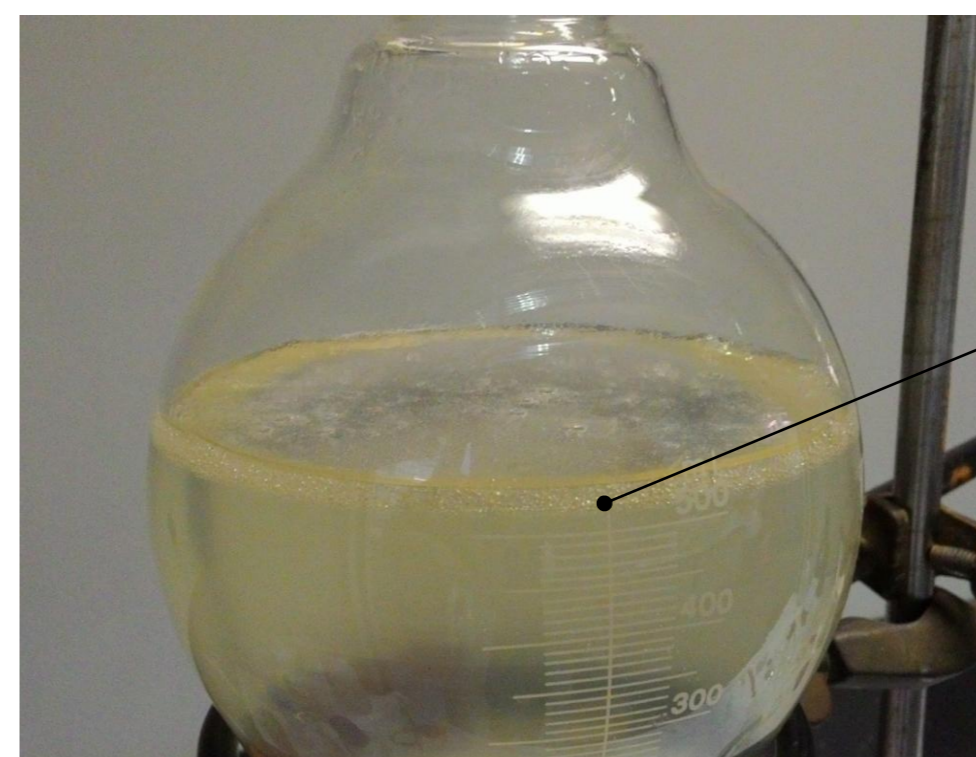
One of the major problems for TPH analysis was the sample complexity. During microbiological treatment of slops many extracellular polymeric substances (EPS) were produced, creating undesired emulsions in the extraction step with hexane, as shown in Figs.3-6. Furthermore the sample must be well emulsified and entirely used for the analysis, because it tends to quickly separate, as shown in Fig.7. DRO mix (Fig.8) was used as calibration standard, by summing all peaks in C10-C30 range[7].
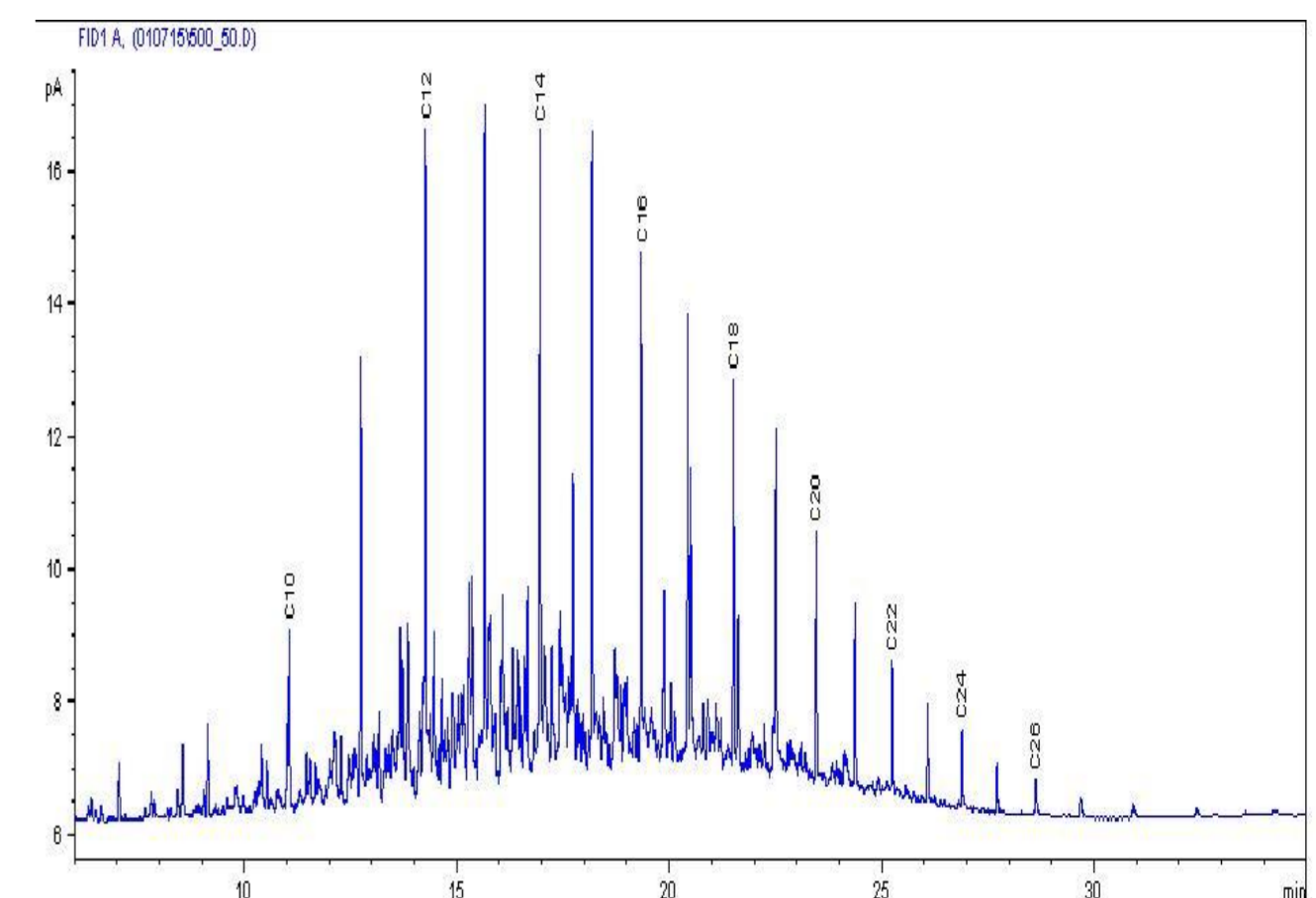

Fig.6 Emulsion formation during sample extraction step with hexane

Fig.7 Sample with clear phase separation, up hydrocarbons, down water

Fig.8 Calibration standard chromatogram, DRO mix, showing the classic bell curve.

CONCLUSIONS

The analysis of slops in experimental plants of treatment is challenging due to the complex sample matrix. The high salinity makes it difficult to measure the COD without appropriate precautions and modifications to standard methods. Some of these modifications allow, however, to avoid the addition of mercury salts, also for 20 mgCl/L samples. The presence of emulsifiers components makes difficult the extraction step during the analysis of the TPH, requiring longer time for the analysis, decreasing reaction yields. To avoid these problems, further studies might be conducted by changing the extraction technique with some more selective as solid phase extraction (SPE) and trying to change the extraction solvent.

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