

# Stabilità dei combustibili marina

CHIMEC S.p.A.

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# Olio Combustibile

Olio combustibile: miscela di idrocarburi

Residuo



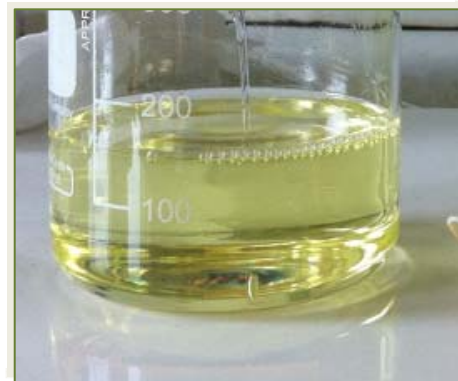
Flussante

Impianto di distillazione atmosferica

Tagli di prima distillazione

Impianto di conversione .....

Gasolio da cracking (LCO) ....



# Olio Combustibile

Olio combustibile: miscela di idrocarburi

Impieghi:

Combustibile per usi stazionari

uso industriale, elettrico, riscaldamento

Combustibile uso marina

# Qualità combustibile uso marina



INTERNATIONAL  
STANDARD

**ISO  
8217**

Fourth edition  
2010-06-15

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**Petroleum products — Fuels (class F) —  
Specifications of marine fuels**

*Produits pétroliers — Combustibles (classe F) — Spécifications des  
combustibles pour la marine*

## 1 Scope

This International Standard specifies the requirements for petroleum fuels for use in marine diesel engines and boilers, prior to appropriate treatment before use. The specifications for fuels in this International Standard can also be applicable to fuels for stationary diesel engines of the same or similar make and type as those used for marine purposes.

This International Standard specifies four categories of distillate fuel, one of which is for diesel engines for emergency purposes. It also specifies six categories of residual fuel.

# Tipologia combustibile uso marina

Table 2 — Residual marine fuels

Category ISO-F.

Category ISO-F.

Characteristic	Unit	Limit	Category ISO-F.										
			RMA	RMB	RMD	RME	RMG				RMK		
			10 <sup>a</sup>	30	80	180	180	380	500	700	380	500	700
Kinematic viscosity at 50 °C <sup>b</sup>	mm <sup>2</sup> /s	max.	10,00	30,00	80,00	180,0	180,0	380,0	500,0	700,0	380,0	500,0	700,0

Characteristic	Unit	Limit	Statutory requirements										Reference		
Sulfur <sup>c</sup>	mass %	max.													ISO 8754 ISO 14595
Flash point	°C	min.	60,0	60,0	60,0	60,0	60,0				60,0				see 7.3 ISO 2719
Hydrogen sulfide <sup>d</sup>	mg/kg	max.	2,00	2,00	2,00	2,00	2,00				2,00				IP 570
Acid number <sup>e</sup>	mg KOH/g	max.	2,5	2,5	2,5	2,5	2,5				2,5				ASTM D664
Total sediment aged	mass %	max.	0,10	0,10	0,10	0,10	0,10				0,10				see 7.5 ISO 10307-2
Carbon residue, micro method	mass %	max.	2,50	10,00	14,00	15,00	18,00				20,00				ISO 10370
Pour point (upper) <sup>f</sup>	winter quality	°C	max.	0	0	30	30	30			30				ISO 3018
	summer quality	°C	max.	8	8	30	30	30			30				ISO 3018
Water	volume %	max.	0,30	0,30	0,30	0,30	0,30				0,50				ISO 3733
Ash	mass %	max.	0,040	0,040	0,040	0,040	0,040				0,150				ISO 6245
Vanadium	mg/kg	max.	50	150	150	150	350				450				see 7.7 IP 501, IP 470 or ISO 14597
Sodium	mg/kg	max.	50	100	100	50	100				100				see 7.8 IP 501 IP 470

HFTaged: < 0,10 mass%

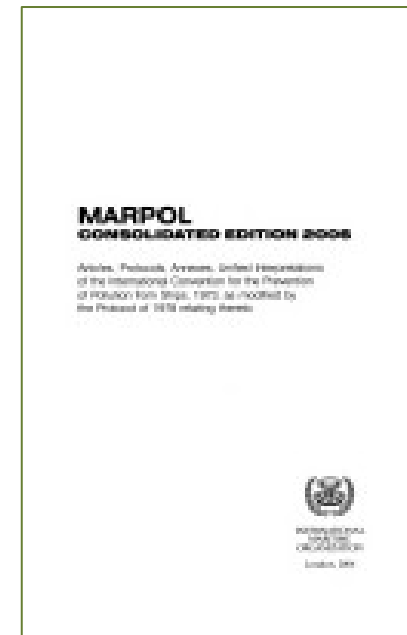
# Tipologia combustibile uso marina

Parametri critici:

- Densità
- Contenuto di acqua
- Sedimenti attuali e potenziali
- Contenuto di zolfo
- Contenuto di H<sub>2</sub>S

In prospettiva

- Contenuto di Azoto

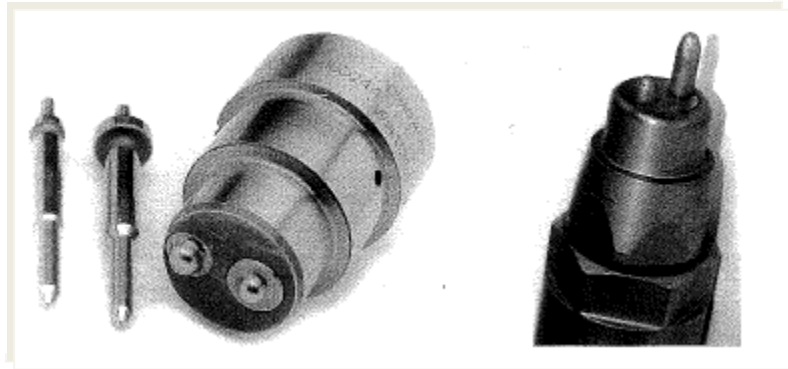




# Combustibile uso marina - sedimenti

## Inconvenienti

- Blocco funzionalità motore
- Fiamma non costante
- Blocco e sporcamento dei bruciatori
- Erosione dei bruciatori e delle parti meccaniche
- Sporcamento delle pale delle turbine



# Tecniche di laboratorio

Limite di specifica ISO 8217: HFT < 0,10%<sub>m</sub>

Metodo di controllo

- ISO 10307-2 (ASTM D 4870)

Hot Filtration Test - sedimenti potenziali

Metodi predittivi:

- ASTM D 4740 – Spot Test
- ASTM D 7157 – Evoluzione del PV
- ASTM D 7061 – Misure di trasmissanza



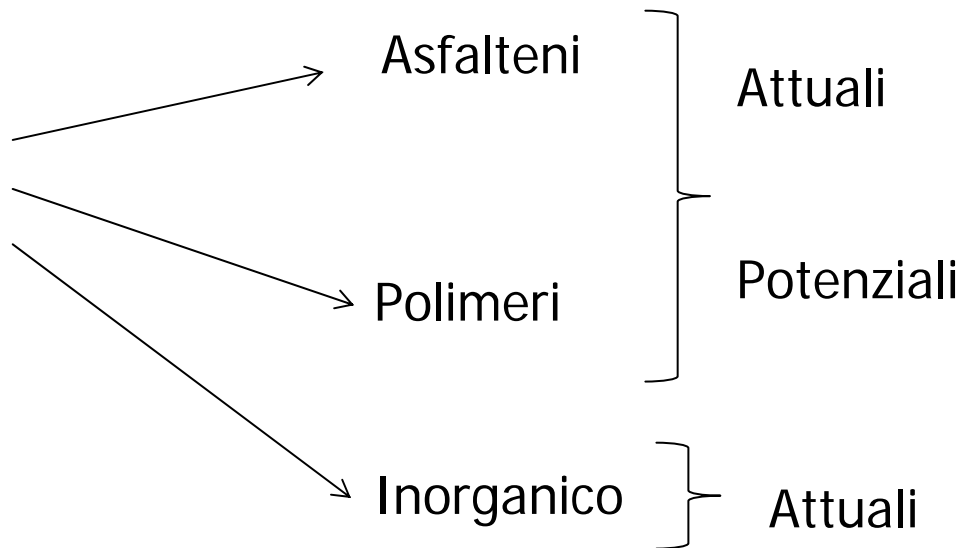
# Stabilità combustibili marina

ISO 10307-2



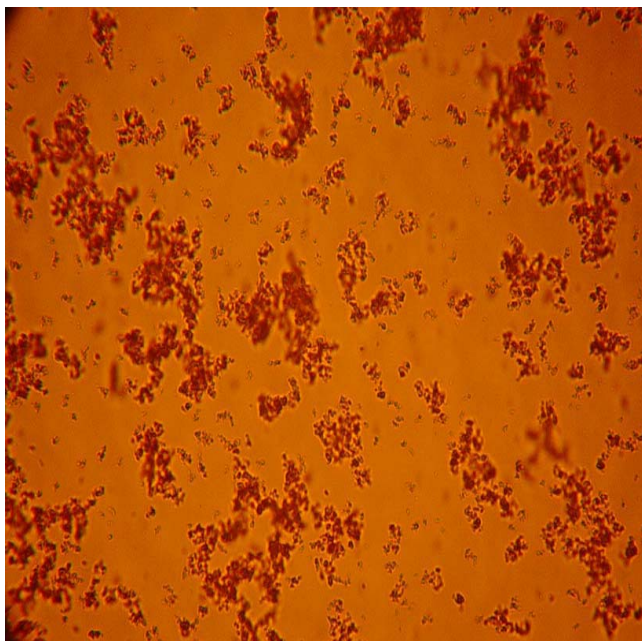
3.1.1 *total sediment*—the sum of the insoluble organic and inorganic material that is separated from the bulk of the residual fuel oil by filtration through a Whatman GF/A filter medium, and that is also insoluble in a predominantly paraffinic solvent.

Sedimenti  
Totali



# Stabilità combustibili marina

Gli asfalteni sono idrocarburi ad alto peso molecolare (mw:5000), stabilizzati in una sospensione colloidale da idrocarburi aromatici e resine. Sono determinati come la frazione insolubile in n-esano e solubile in solvente aromatico.



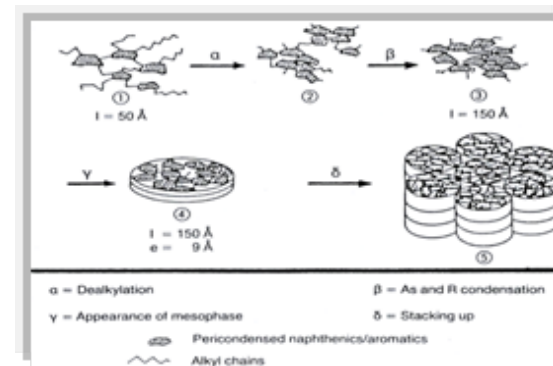
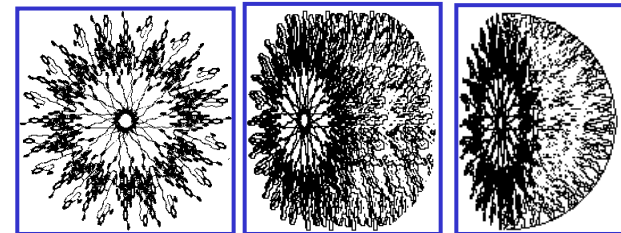
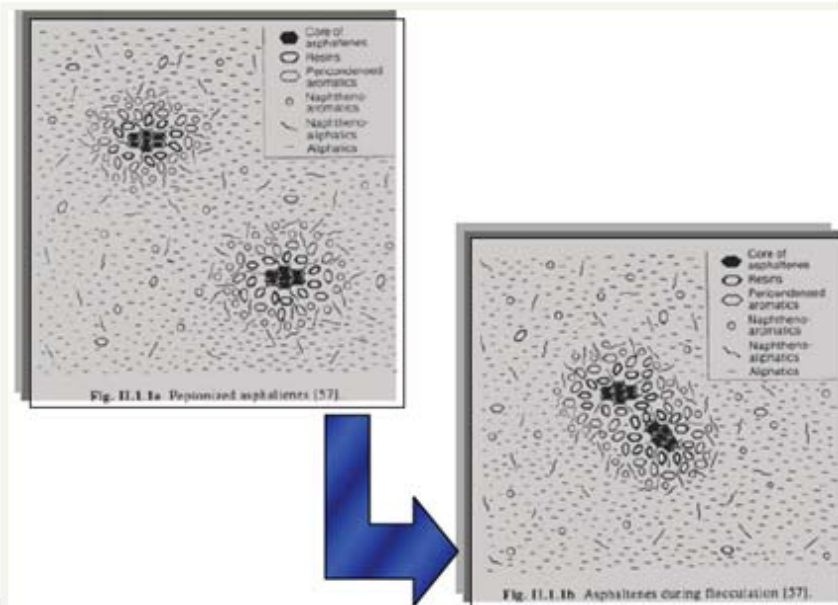
Promotori della instabilità degli asfalteni:

Temperatura

Variazione equilibrio della sospensione colloidale

# Meccanismo di aggregazione degli asfalteni

1. Dealchilazione della molecola di asfaltene, formazione delle prime micelle
2. Condensazione delle molecole formate in strutture bidimensionali compatte difficilmente solvabili
3. Aggregazioni tridimensionali delle micelle con conseguente formazione di macromolecole



# Metodo ISO 10307-2 - ASTM D 4870-A



Designation: D 4870 - 88

An American National



Designation: 375/88

AMERICAN SOCIETY FOR TESTING AND MATERIALS  
100 Barr Harbor Dr., West Conshohocken, PA 19380  
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## Standard Test Method for Determination of Total Sediment in Residual Fuels<sup>1</sup>

This standard is issued under the fixed designation D 4870; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last approval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or approval.

This test method has been approved by the governing committee and accepted by the cooperating agencies in accordance with established procedures.

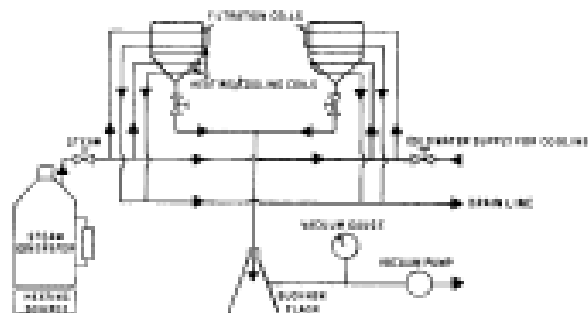


FIG. 2 Arrangement of Filtration Apparatus

## X1.8 Procedure A for Thermal Ageing

X1.8.1 Pour duplicate  $25 \pm 1$  g aliquots of the thoroughly mixed sample into each of two conical flasks, attach the air condenser by means of the cork stopper, and place the flasks in the air wells of the oil bath, maintained at  $100 \pm 0.5^\circ\text{C}$ , for  $24 \text{ h} \pm 15 \text{ min}$ .

X1.8.2 Remove the flask from the bath, replace the air condenser and cork stopper by the rubber stopper and shake vigorously until all the sludge has been uniformly suspended. Invert the flask and examine its bottom and wall for any sludge deposits. Remove stubborn deposits from the wall or bottom of the conical flask by scraping with the spatula. Shake again vigorously and initiate hot filtration in accordance with Test Method D 4870 within 1 min.



# Metodo ISO 10307-2 - ASTM D 4870-A

## 4. Summary of Test Method

4.1 A weighed quantity (10 g) of the oil sample is filtered through the prescribed apparatus at 100°C. After solvent washing and drying the total sediment on the filter medium is weighed. The test is to be carried out in duplicate.



Solventi utilizzati:

N-eptano

Toluene

Solvente di lavaggio: 85% n-eptano + 15% toluene

Commenti:

Preparazione filtri

Analisi in doppio

Operatore deve essere esperto

t: > 24 h + ca 2h



Riproducibilità e ripetibilità:

R:0,294  $\sqrt{x}$

r:0,089  $\sqrt{x}$

# Tecniche di laboratorio

Metodo di controllo

- ISO 10307-2 - ASTM D 4870

Hot Filtration Test - sedimenti potenziali

Metodi predittivi:

- ASTM D 4740 – Spot test
- ASTM D 7157 – Evoluzione PV
- ASTM D 7061 – misure di trasmittanza

} indice di stabilità



# Metodo ASTM D 4740

E' utilizzato come indice di garanzia da diverse raffinerie.

## 4. Summary of Test Method

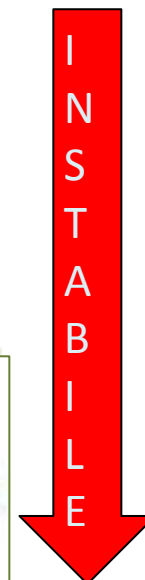
tempo: < 3h

4.1 *Cleanliness Procedure*—A drop of the preheated and thoroughly mixed sample is put on a test paper and placed in an oven at 100°C. After 1 h, the test paper is removed from the oven and the resultant spot is examined for evidence of suspended solids and rated for cleanliness using the D 4740 Adjunct Reference Spots.

4.2 *Compatibility Procedure*—A blend composed of equal volumes of the sample fuel oil and the blend stock is tested in the same way as described in 4.1 and rated for compatibility against D 4740 Adjunct Reference Spots.

**TABLE 1 Reference Spot Description**

Reference Spot No.	Characterizing Features
1	Homogeneous spot (no inner ring)
2	Faint or poorly defined inner ring
3	Well-defined thin inner ring, only slightly darker than the background
4	Well-defined inner ring, thicker than the ring in reference spot No. 3 and somewhat darker than the background
5	Very dark solid or nearly solid area in the center. The central area is much darker than the background



# Peptization Value

## PV 1

L'instabilità di un olio viene determinata aggiungendo alla miscela olio/toluene il minimo contenuto di n-eptano necessario alla flocculazione degli asfalteni. La lettura avviene, dopo trattamento termico, attraverso lo spot test

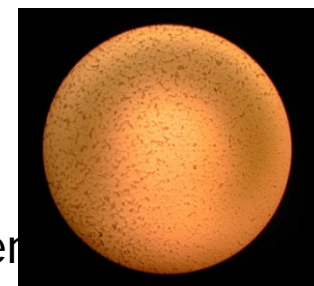
	Toluene (mL)	Residue (g)
Mix 1	1	3
Mix 2	2	2
Mix 3	3	1



tempo: < 3h

## PV 2

L'instabilità di un olio viene determinata aggiungendo la minima quantità di n-cetano capace di provocare la flocculazione degli asfalteni. La lettura avviene, dopo trattamento termico, attraverso un microscopio



## Risultato

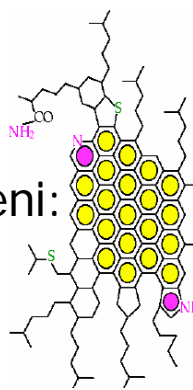
$$P = 1 + X_{\min}$$

dove  $X_{\min}$  è la diluizione necessaria alla flocculazione degli asfalteri

# Metodo ASTM D 7157

Standard Test Method for Determination of Intrinsic Stability of Asphaltene-Containing Residues, Heavy Fuel Oils, and Crude Oils

La stabilità intrinseca di un olio è legata alla stabilità degli asfalteni:



S value: stabilità del campione  $S = 1 + X_{min}$   
 $S_0$ : forza di peptizzazione del mezzo  
 $S_a$ : capacità dell'asfaltene a rimanere nella dispersione colloidale

$S < 1,3$   
 $S_0 < 1,0$   
 $S_a > 0,5$

} instabilità

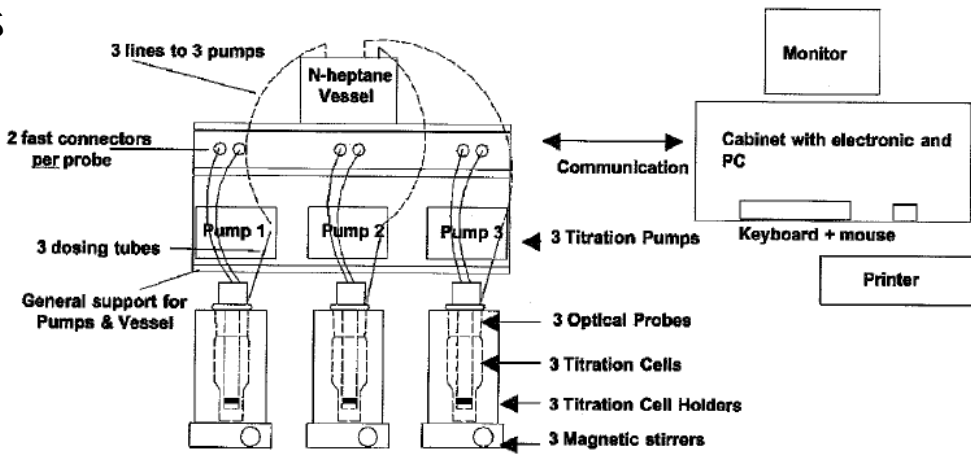


FIG. 1 Schematic Drawing of the Integrated Automated Stability Analyser System

tempo: < 3h

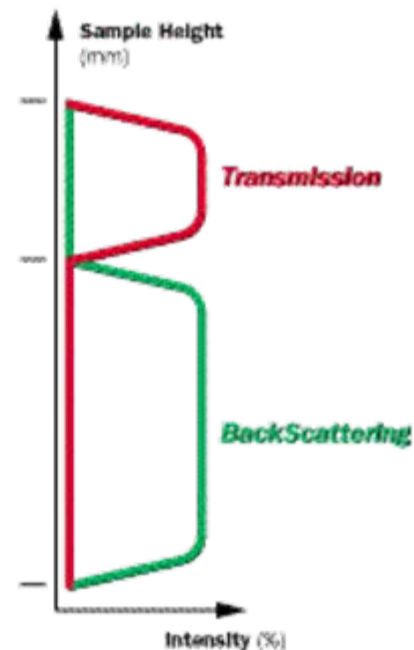
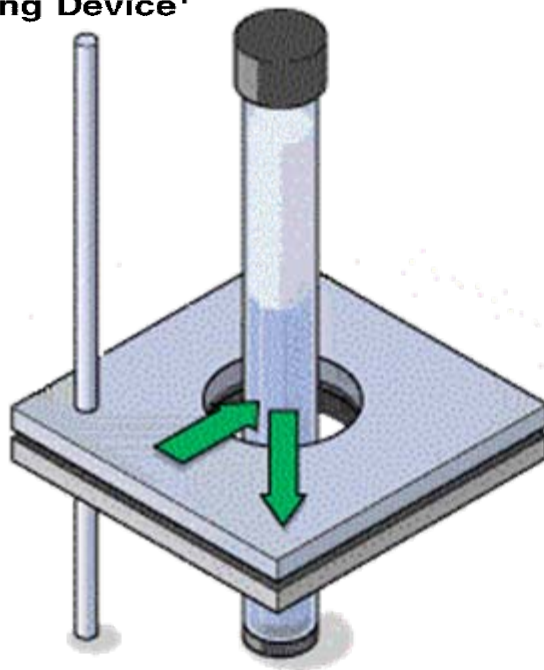
**TABLE 2 Repeatability (r) and Reproducibility (R) for  $S$ ,  $S_a$ , and  $S_0$**

	$S$	$S_a$	$S_0$
Repeatability (r)	$0.064 \cdot (X + 1.2)$	0.03	$0.15 \cdot X$
Reproducibility (R)	$0.1 \cdot (X + 1.2)$	0.04	$0.22 \cdot X$

where:  
 $X$  = the average of two results

# Metodo ASTM D 7061 -TURBISCAN

Standard Test Method for  
Measuring n-Heptane Induced Phase Separation of  
Asphaltene-Containing Heavy Fuel Oils as Separability  
Number by an Optical Scanning Device<sup>1</sup>





# Metodo ASTM D 7061

Misura la capacità di un olio di rimanere stabile dopo la miscelazione con gasolio

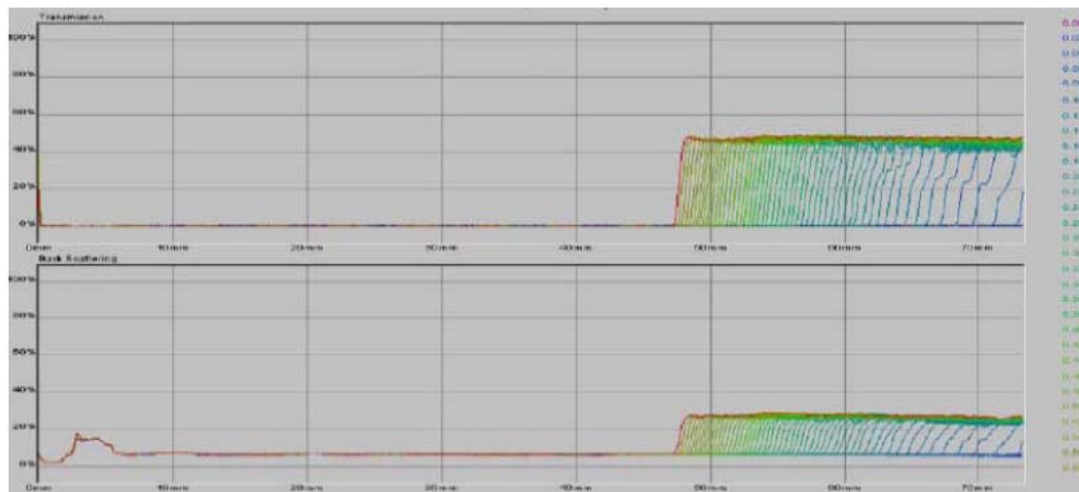
Permette di effettuare una caratterizzazione ottica della dispersione liquida e quindi di verificare la velocità di sedimentazione delle molecole asfalteniche disperse nell'olio.

4.2 The oil is first diluted with toluene in ratios that depend on the oil type (Annex A1). Mix 2 mL of the oil/toluene solution with 23 mL of heptane. Transfer 7 mL of the oil/toluene/heptane mixture into a glass vial that is inserted into an optical scanning device.

## 5. Significance and Use

5.1 This procedure describes a rapid and sensitive method for estimating the stability reserve of an oil. The stability reserve is estimated in terms of a separability number, where a low value of the separability number indicates that there is a stability reserve within the oil. When the separability number is between 0 to 5, the oil can be considered to have a high stability reserve and asphaltenes are not likely to flocculate. If the separability number is between 5 to 10, the stability reserve in the oil will be much lower. However, asphaltenes are, in this

Mean of Separability Number (%)	Standard Deviation (%)	95 % Confidence Interval (%)
0.3	0.02	0.01
6.9	0.6	0.4
17.0	0.4	0.3



$$\text{Separability number} = \sqrt{\frac{\sum_{i=1}^n (X_i - X_T)^2}{n - 1}}$$

tempo: < 2h

# Stabilità combustibili marina

Criteri per stabilizzare un olio combustibile

1. Utilizzo flussante ad alta aromaticità

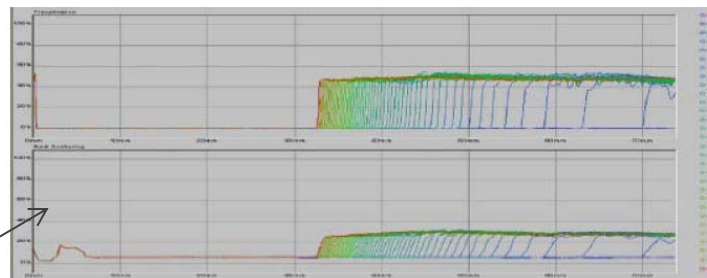
2. Impiego additivi stabilizzanti



# Stabilità combustibili marina – efficacia additivo

ISO 10307-2

Campione ca 50°E	HFT mass %
O.C. tal quale	0,04
O.C. tal quale ASTM D 4870 -A	0,18
O.C. + Additivo ASTM D 4870-A	0,05

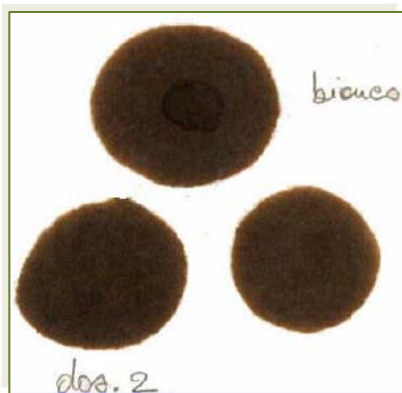


ASTM D 7061



Specifica HFT  
 $< 0,10\%w/w$

Campione a specifica



ASTM D 4740

# Stabilità combustibili marina – efficacia additivo

ISO 10307-2- ASTM D 7061 – ASTM D 4740

- L'additivo deve essere in grado di portare a specifica di HFT il campione di olio combustibile affetto da problemi di instabilità
- L'efficienza dell'additivo si deve mantenere nel tempo
- L'additivo deve contenere e contrastare l'aumento delle dimensioni delle macromolecole presenti nell'olio combustibile