



# Biodiesel - Evoluzione delle norme Europee

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Stazione Sperimentale Oli e Grassi



# Sommario

- 1 – Evoluzione della Norma EN 14214:20XX**
- 2 – Attività del GdL Monosat/SG**
- 3 - Specifica EN per il B30**
- 4 – Petroxy**
- 5 – Una vecchia conoscenza**
- 6 – Invito al prossimo EUROFEDLIPID Congress**

## Evoluzione della Norma EN 14214:20XX

Parametro	EN 14214:2008	prEN 14214:20XX
Fosforo totale (mg/kg)	4	4 (down to 2)
$\Sigma$ Na + K (mg/kg)	5	5 (down to 3,5)
$\Sigma$ Ca + Mg (mg/kg)	5	5 (down to 3,5)
StaboOX	6	8
Steryli glucosidi	--	Metodo
Monogliceridi saturi	--	Metodo
Filtrabilità	--	Discussione
Cold flow properties	CFPP	CFPP + CP

## Nuova EN 14214

### Divisione in classi secondo comportamento a freddo

<b>A1</b>	<b>B1</b>	<b>C1</b>	<b>D1</b>	<b>E1</b>
<b>A2</b>	<b>B2</b>	<b>C2</b>	<b>D2</b>	<b>E2</b>
<b>A3</b>	<b>B3</b>	<b>C3</b>	<b>D3</b>	<b>E3</b>

### Classi per monogliceridi, in assenza metodo per saturi

<b>Classe X1</b>	<b>→</b>	<b>0,8</b>
<b>Classe X2</b>	<b>→</b>	<b>0,5</b>
<b>Classe X3</b>	<b>→</b>	<b>0,3</b>

### Altri parametri considerati: CP e CFPP

## Tabelle MG/CP/CFPP CONCAWE Proposal

<b>Property</b>	Cloud point	12	7	3	0	-3
<b>Unit</b>						
<b>Test method</b>	<i>°C max</i> EN 23015					
	CFPP	10	5	0	-5	-10
	<i>°C max</i> EN 116					
Monoglyceride content	0,8	A1	B1	C1	D1	E1
	0,5	A2	B2	C2	D2	E2
% (m/m) max	0,3	A3	B3	C3	D3	E3
	EN 14105					

# Climate Classes

Table B

Continent	a	b	c	d	e	f
Suggested Area	SWISS MSZ	Northern Europe	Northern Europe (Atlantic)	Northern Europe (Continental)	Continental Europe (Western)	Continental Europe (Eastern)
45° N FAMS	A5	B5	C5	D5	E5	F5
47° N FAMS	A7	B7	C7	D7	E7	F7
49° N FAMS	A9	B9	C9	D9	E9	F9

	Mean Temp. °C	GDD (°C)				
		12	7	1	0	-3
		10	5	0	0	-12
Maximum Manufacturable Consum. %/day	0.0	*	*	*	E5 F4,F7	C5 D5,D7 E4,E7 F4,F7,F10
	0.5	*	F5	E5 F4,F7	C5 D4,D7 E4,E7,E10 F4,F7,F10	A5 B4,B7 C4,C7 D4,D7,D10 E4,E7,E10 F4,F7,F10
	1.5	E5 F5	D5 E4 F4	C5 D4,D7 E4,E7,E10 F4,F7,F10	A5 B4,B7 C4,C7	A4,A7 B4,B7,E10 C4,C7,D10



## Attività del GdL SG/ASG + Saturated Monoglycerides


- 1 – Primo RRT sui campioni distribuiti
- 2 – Proseguimento dell'attività
- 3 – Metodo monogliceridi saturi

# SG – il primo RRT

SG [mg/kg]					Method used	sample purification	Standard	comment	Company
1	2	3	4	5					
-	-	-	-	-	GC	-	cholesteryl glucopyranoside	silylation of IS was not successful	Frauenhofer
18,8	9	17	8,2	7,7	GC-MS Uni Graz method	SPE	cholesteryl glucopyranoside	silylation of IS was not complete	Shell Global Solutions
25,1	12,2	25,5	11,6	11,2	GC-FID		cholesteryl glucopyranoside	-	Shell Global Solutions
26,5	11	25,5	14,5	13	HPTLC	SPE	cholesteryl glucopyranoside	external standard	ASG
25,8	11,3	20,4	11,4	9,7	GC-MS	SPE	cholesteryl glucopyranoside	Acetylation of SGs, internal standard	ASG
15,1	10,8	20,4	11,5	11	GC-MS	-	cholesteryl glucopyranoside	internal standard	Univerity Graz
26,6	12,7	26,6	20,9	16,2	A-SSOG method		cholesteryl glucopyranoside	-	SSOG
18	20,2	33,7	22,2	16,3	B-ITERG method		cholesteryl glucopyranoside	-	SSOG
-	-	-	-	-	GC		cholesteryl glucopyranoside	silylation of IS was not successful	ADM Research
23	7	26	22	15	GC SSOG method		a-cholestanol		OMV
33	9	43	38	-			cholesteryl glucopyranoside	80 °C, 1h	OMV
19	14	26	12	13	GC-MS	?	cholesteryl glucopyranoside	internal standard	SGS
16,7	5,1	13,1	6,7	6	GC-FID		cholesteryl glucopyranoside	silylation of IS was not complete	Repsol
30,9	12,7	41,6	30,2	22,3	GC-FID		a-cholestanol	external standard	Acciona Biocombustibles
92,5	61	67,5	63,5	91,5	GC-FID	ITERG Method	a-cholestanol	internal standard	ITERG
18,5	9	24	12,5	11	GC-FID	ASG Method	a-cholestanol	internal standard	ITERG
27,5	13,5	29	17	14	GC-FID	ASG Method	cholesteryl glucopyranoside	internal standard	ITERG
25,5	16	22	17	12,5	GC-MS Uni Graz method	no purification	cholesteryl glucopyranoside	internal standard	ITERG
20,2	11,8	336*	37,7	37,5	GC-FID	?		*matrix problems	Cargill
27	13,2	24,4	14,6	11,5	B-ITERG method	SPE	cholesteryl glucopyranoside		Bio-Oils Huelva, S.L
24,6	11,1	28	21,5	16,8	ITERG	SPE	cholesteryl glucopyranoside	internal standard, Acetylation o	BP Europe SE




## SG – I due metodi oggetto di studio

**ITERG** 

Working Draft


Determination of Steryl Glucosides content  
Revision no. 2 - Sept. 2010



**Fat and oil derivatives – Fatty Acid Methyl Esters (FAME)**

**Determination of Steryl Glucosides content**

**WORKING DRAFT**



**ASG**  
Analytik-Service  
Gesellschaft

**ASG Method**

15.10.2010 rev. 3

**Fat and oil derivatives – Fatty Acid Methyl Esters (FAME)**

**Determination of Steryl Glucosides content**

**WORKING DRAFT**

# SG Procedure in a glance

## *Sample preparation*

1 - Dissolve 2 g sample in 10 ml  $\text{CHCl}_3$

2 - Elute the solution on a microcolumn, discard eluate

3 - Elute with additional 10 ml  $\text{CHCl}_3$ , discard eluate



$\text{CHCl}_3$  Pre-conditioned  
690 mg silica  
microcolumn

4 - Elute with 10 ml MTBE, discard eluate

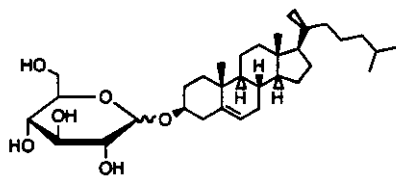
5 - Load on the top 100 micro-litres of a Pyridine soln of Cholesteryl glucoside

6 - Elute SG using 10 ml  $\text{CHCl}_3/\text{MeOH}$  2:1 blend, collect

7 - Remove solvents, dissolve in 2-5 ml MeOH, transfer in 10 ml tube, dry

## Attività del GdL SG/Monosat

### Cholesteryl-D-glucopyranoside Standard



purity: > 99%

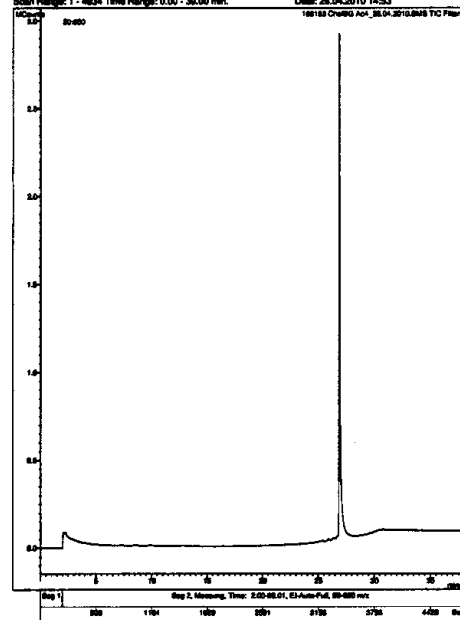
Il nuovo I.S.

Print Date: 28 Apr 2010 17:43:01

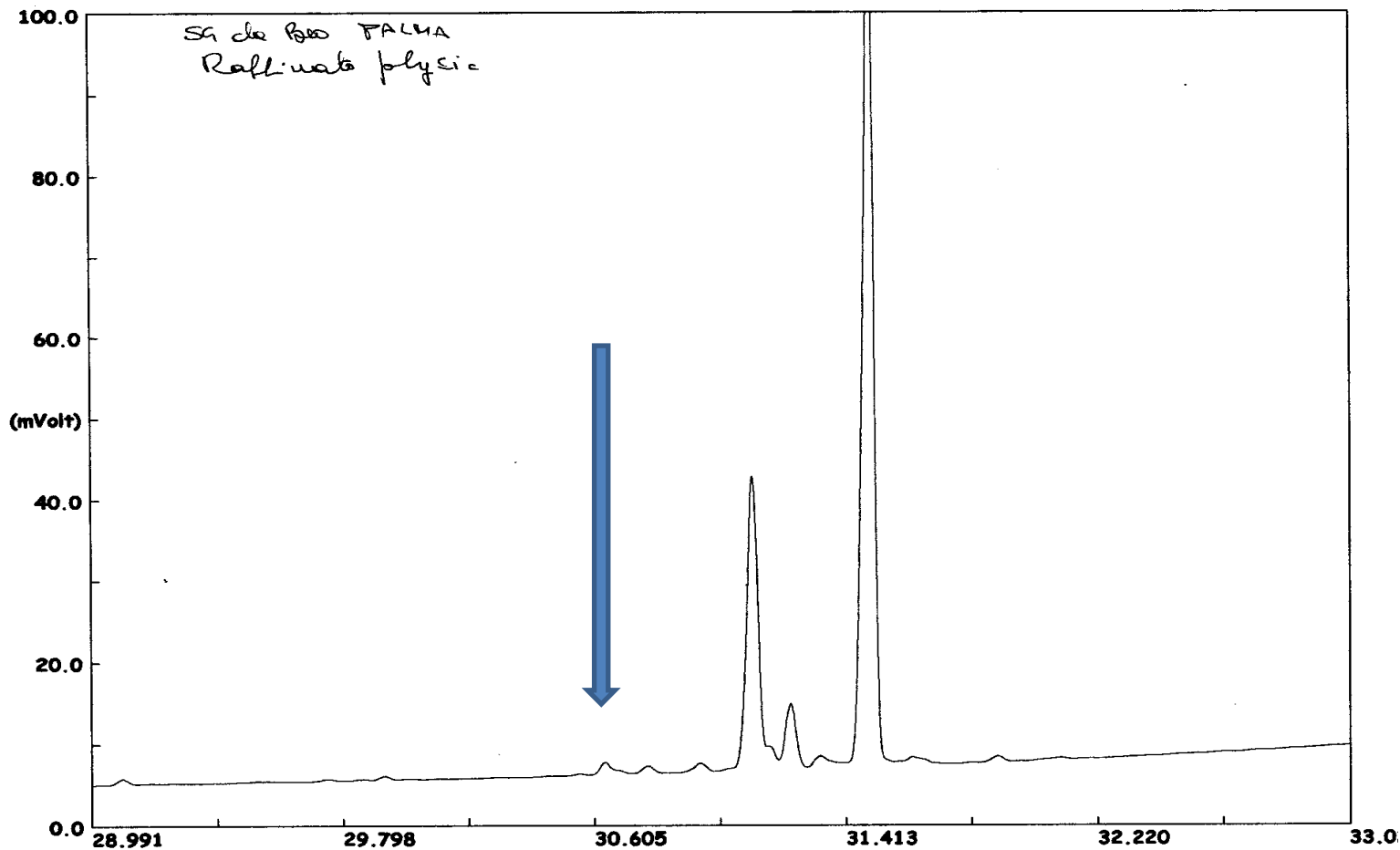
#### Chromatogram Plot

File: c:\vialen\midas\021\0ap\0160153 choleq ac4\_28.04.2010.ms  
Sample: 160153 CholSG Ac4  
Scan Range: 1 - 4854 Time Range: 0.00 - 30.00 min.

Operator: KY  
Date: 28.04.2010 14:53



## Attività del GdL SG/Monosat



## Sviluppo metodica per Steryl Glucosidi

Decisioni prese:

- 1 – Primo RRT su sei laboratori per verificare la intercambiabilità dei metodi
- 2 – Scelta del metodo da utilizzare per il RRT ufficiale
- 3 – Realizzazione del Round Robin
- 4 – Metodo EN per Steryl Glucosidi in biodiesel

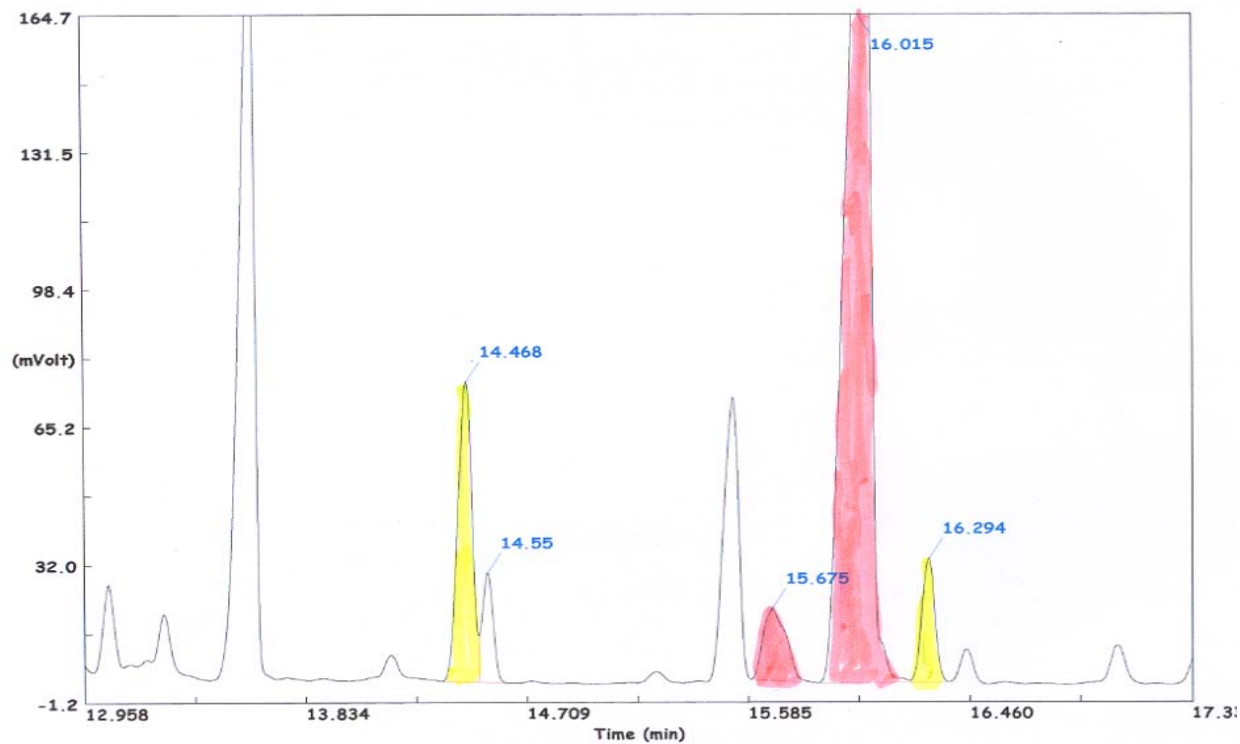


## **Attività del GdL SG/Monosat Saturated Monoglycerides**

Decisioni prese:

- 1 – Modificare EN 14105:2010 per calcolo monogliceridi saturi
- 2 – Recupero risultati RRT del 2008, rielaborazione in vista calcolo MonoSat
- 3 – Bondioli prepara testo e invia lettera per il ricalcolo a tutti I partecipanti
- 4 – Se risultati sono incoraggianti si farà un RRT

## Saturated Monoglycerides



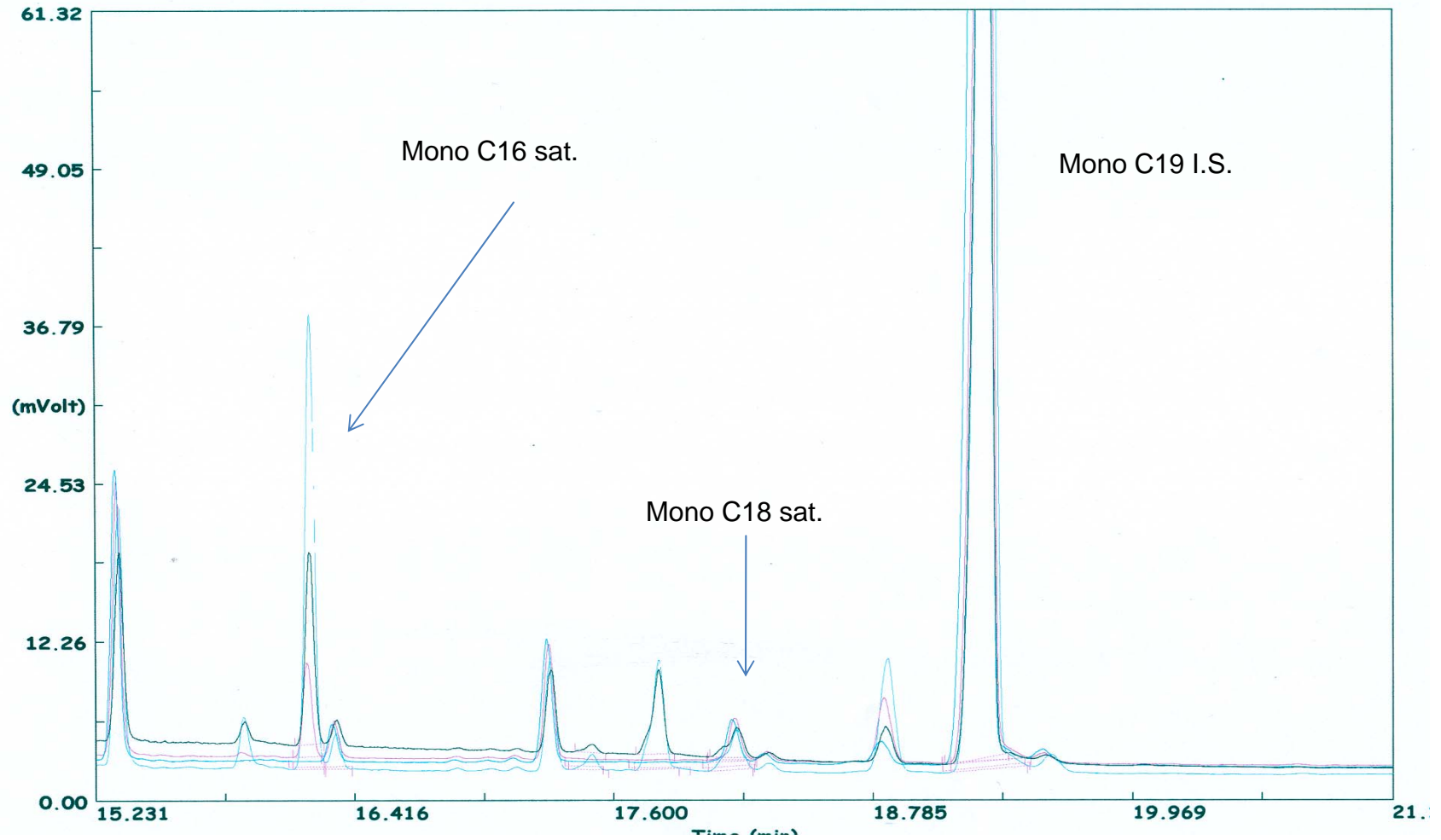
$$\text{Saturated Monoglycerides (\% m/m)} = \frac{\sum (\text{Area MONOP} + \text{Area MONOS})}{\text{Area Mono C19}} \times \frac{M_{\text{MonoC19}}}{m} \times 100$$

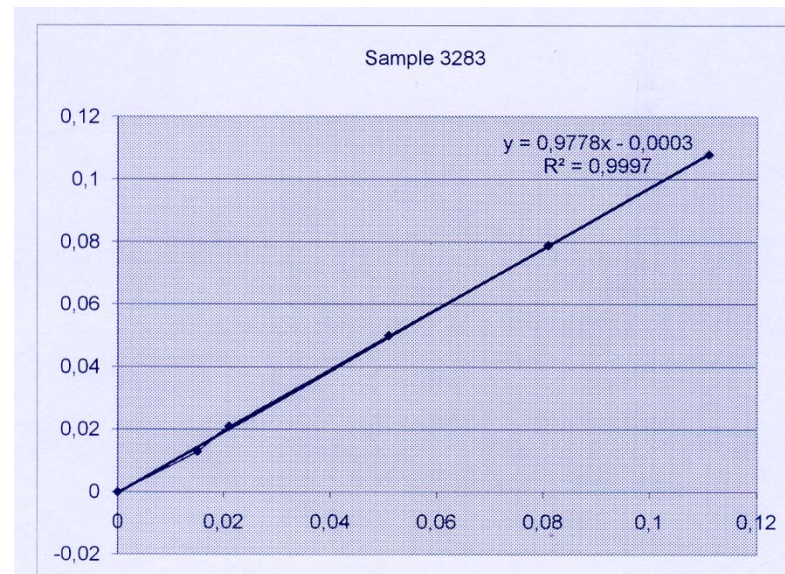
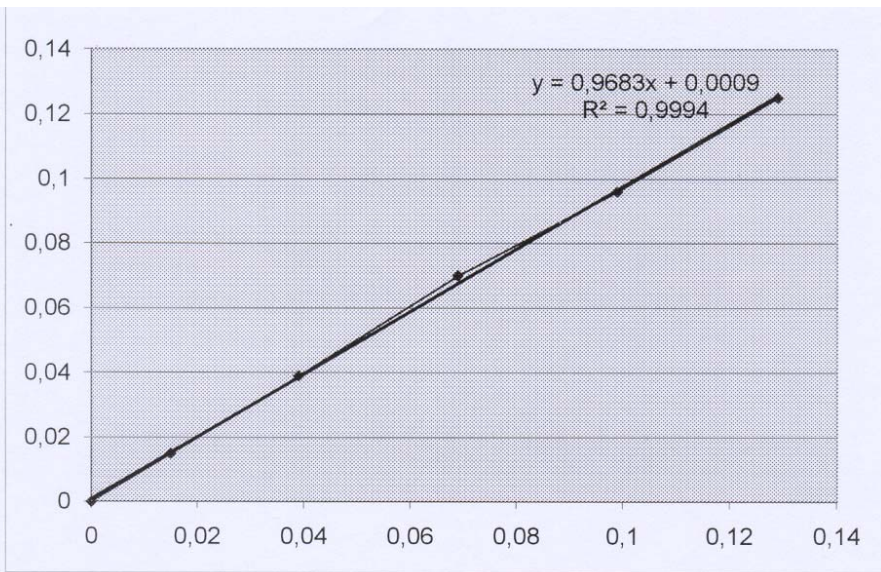
Berlino, 9 Settembre 2010  
Riunione TC 19 WG 1 +  
**Saturated Monoglycerides**

Decisioni prese:

- 1 – Modificare EN 14105:2010 per calcolo monogliceridi saturi
- 2 – Recupero risultati RRT del 2008, rielaborazione in vista calcolo MonoSat
- 3 – Bondioli prepara testo e invia lettera per il ricalcolo a tutti I partecipanti
- 4 – Se risultati sono incoraggianti si farà un RRT

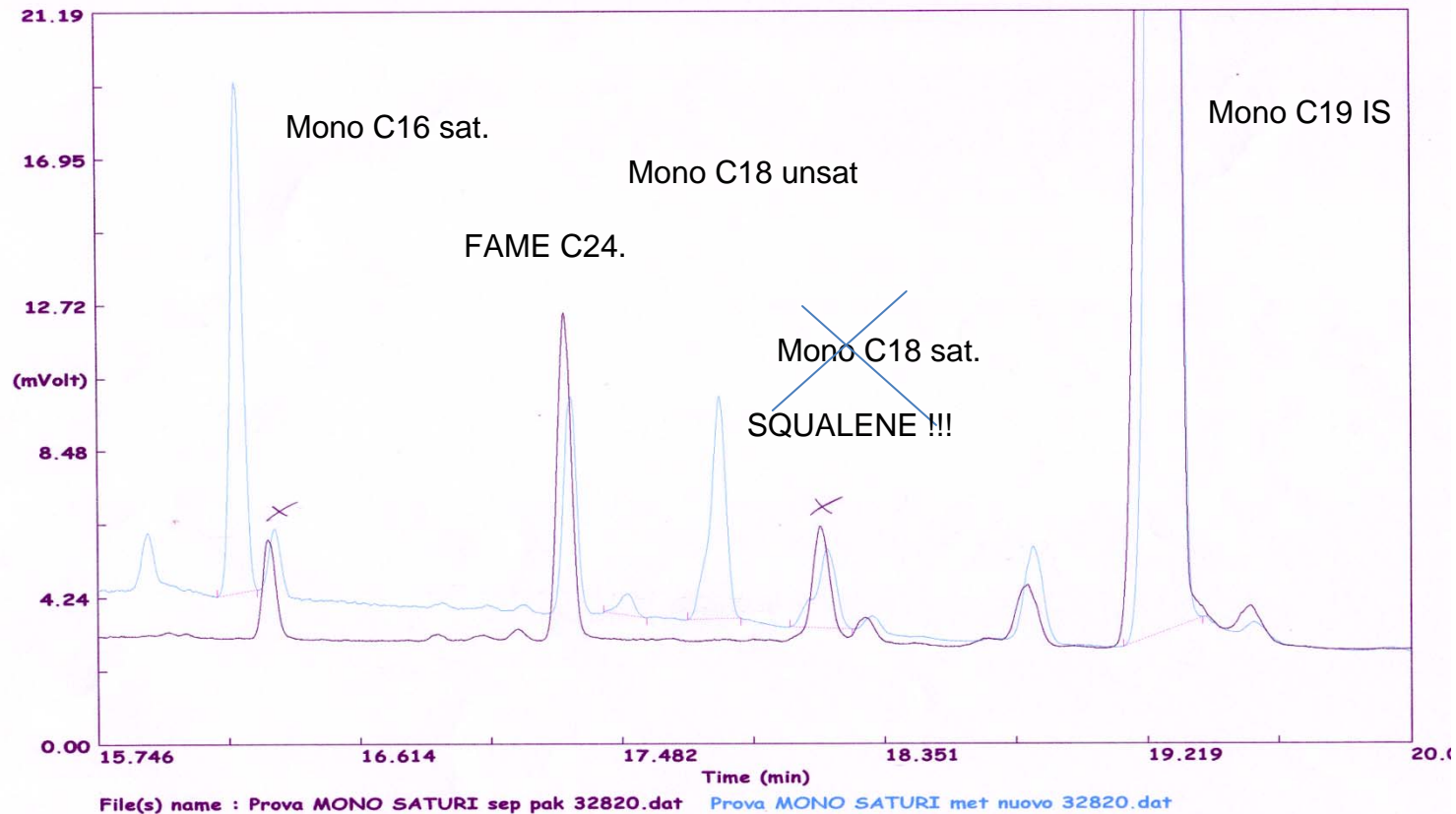
*Nota: ulteriori problemi emersi nel corso della riunione del giorno successivo*





**Conclusione: OK per Glicerilmonopalmitato !**

## Il problema del Mono C18 sat



Olio Vegetale	% Acido Palmitico	% Acido Stearico
Colza	2.5-7.0	0.8-3.0
Soia	8.0-13.5	2.0-5.4
Palma	39.3-47.5	3.5-6.0
Girasole	5.0-7.6	2.7-6.5

Fonte: Norme NGD

Grasso Animale	% Acido Palmitico	% Acido Stearico
Sego bovino	25.0-29.0	20.0-28.0
Strutto	20.0-27.0	11.0-18.0
Cavallo	26.0-32.0	3.5-6.5
Pollo	22.0-25.0	5.5-7.5
Tacchino	22.0-25.5	6.5-10.5

## La questione monogliceridi

Richiesta SHELL: Mono Saturi 200 mg/kg max

Non si può pensare di arrivare con metodo attuale

Proposta FISCHER:

Accoppiare det. Mono tot. secondo EN 14105 con acidi grassi saturi EN 14103

$$\text{Mono Saturi} = (\text{Mono totali} \times \% \text{ AG saturi}) / 100$$



## Monogliceridi saturi, conclusioni

- Con 14105 modificato è possibile dosare Mono C16, ma non Mono C18
- Esiste una interferenza da Squalene, non eliminabile nelle condizioni di prova
- E' possibile usare il Mono C16 come marker, in analogia con EN 15579 (PUFA) ?
- In alternativa bisogna pensare ad una separazione preliminare, previa acetilazione degli –OH liberi (problema di separazione GC)

## Petroxy

- Numero EN per Petroxy: prEN 16091
- Impatto EHN: risolto con warning nel testo (?)

*"The presence of ignition improvers may lead to lower oxidation stability results by this test method. In practice it has been observed that the addition of EHN can reduce the measured oxidation stability values"*

Parametri di precisione (X in minuti):

$$r = 0,0228 X + 0,4966$$

$$R = 0,0863 X + 1,3772$$

Conclusioni per prEN 16091:

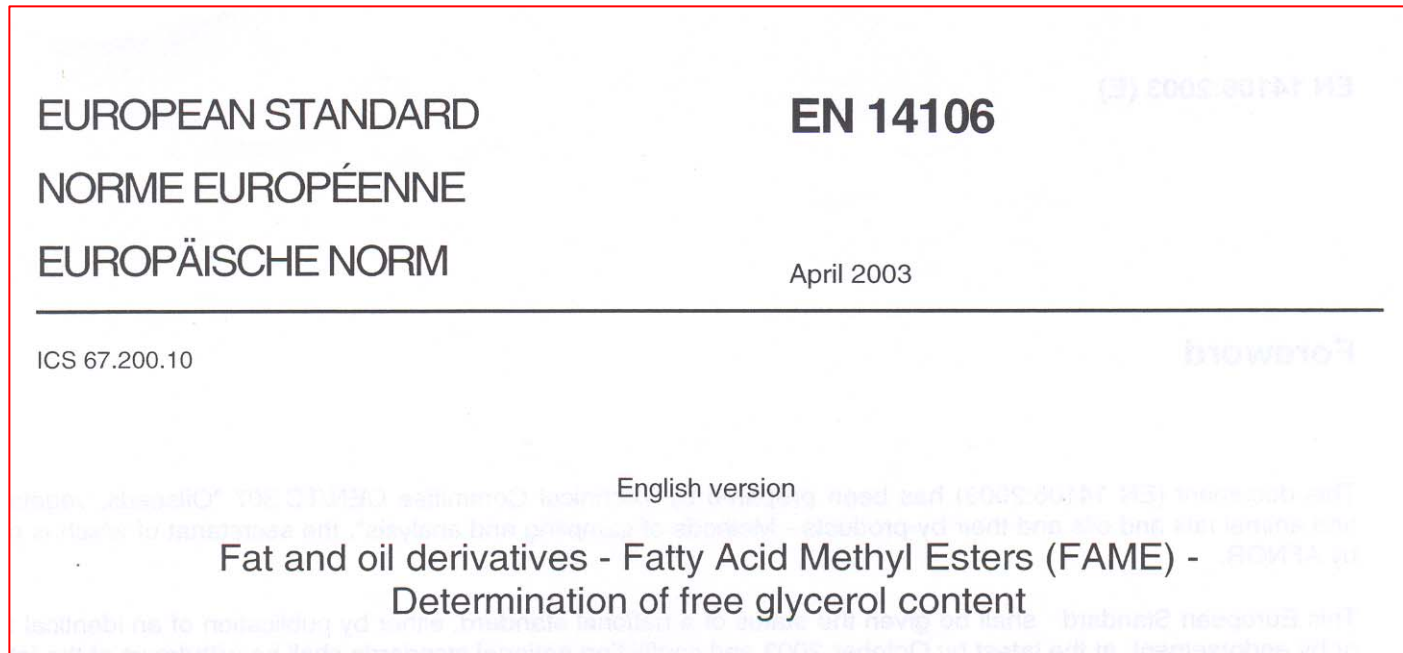
- più preciso di EN 15751
- meno preciso per valori superiori alle 40h IP Rancimat

## Specifica per B30 – Parametri in discussione

Densità	Viscosità
CFPP	Curva Distillazione
Flash Point	Numero Cetano
Zolfo	StabOX
Aspetto	Acqua KF
Corrosione su rame	Ceneri
Metalli alcalini	Metalli alcalino-terrosi
Fosforo	



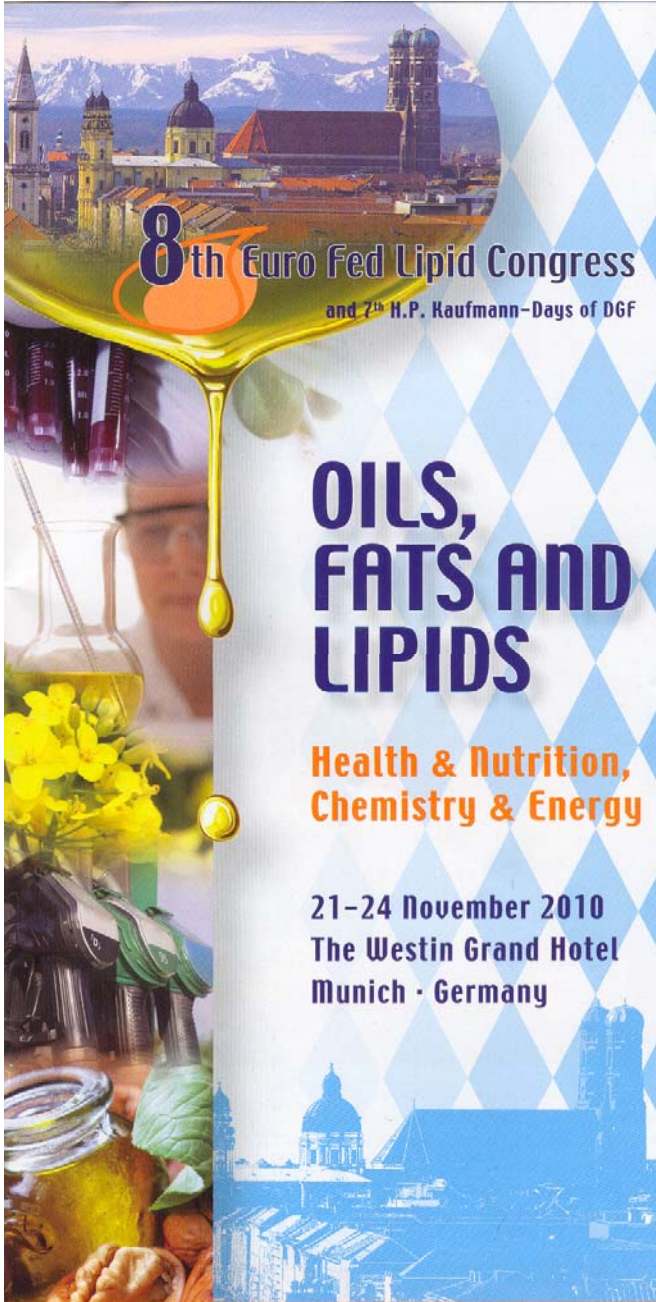
Una Vecchia Conoscenza  
**Revisione EN 14106:2003**



Laboratori che usano regolarmente EN 14106:2003

Laboratori disposti a nuovo RRT

[www.eurofedlipid.org](http://www.eurofedlipid.org)

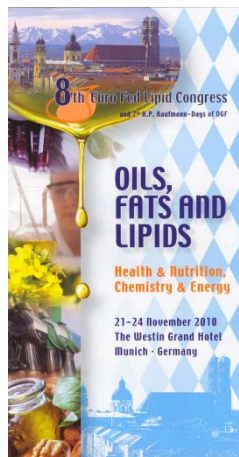


**8<sup>th</sup> Euro Fed Lipid Congress**  
and 7<sup>th</sup> H.P. Kaufmann-Days of DGF

**OILS,  
FATS AND  
LIPIDS**

**Health & Nutrition,  
Chemistry & Energy**

**21-24 November 2010**  
**The Westin Grand Hotel**  
**Munich · Germany**



Monday, 22 November 2010

Afternoon

**Oleochemistry, Biodiesel**

Hall Garmisch-Partenkirchen

Chair: Paolo Bondioli and Mark Rüsç gen. Klaas

- 15.40-16.20 **KEYNOTE LECTURE**  
**New Commercial Products from Bioglycerol: Routes of Chemical Ingenuity**  
 M. Pagliaro, Palermo/I, M. Rossi, C. Della Pina, Milan/I, R. Ciriminna, Palermo/I, H. Kimura, Kita-Kyusu-City/J
- 16.20-16.40 **Glycerol Acetals obtained by One-Pot Synthesis from Alkenes**  
 U. Kragl, L. Neubert, E. Paetzold, C. Fischer, U. Schuermann, T. Sadlowski, M. Beller, Rostock/D, U. Schoerken, P. Kempers, Düsseldorf/D
- 16.40-17.00 **Monoacylglycerols as Potential Antimicrobial Agents**  
 I. Doležalková, Zlín/CZ
- 17.00-17.20 **Oleochemical Uses of Oils and Biodiesel Derived Products**  
 Y. Raoul, Paris/F

Tuesday, 23 November 2010

Afternoon

**Oleochemistry, Biodiesel**

Hall Garmisch-Partenkirchen

Chair: Paolo Bondioli and Mark Rüsç gen. Klaas

- 15.40-16.00 **EUROPEAN YOUNG LIPID SCIENTIST AWARD 2010**  
**New Monomers and Polymers from Plant Oils via Thiol-ene Additions**  
 M.A.R. Meier, Potsdam/D
- 16.00-16.20 **Studies of Esters of Maleinized Fatty Compounds as Plasticizers**  
 U. Biermann, Oldenburg/D, A. Jungbauer, Emden/D, J.O. Metzger, Oldenburg/D
- 16.20-16.40 **Production Technology of Palm Oil-based Surfactants**  
 I. Adami, E. Caimi, A. Forcella, Milan/I
- 16.40-17.00 **Biofuels via Continuous Deoxygenation of Fatty Acids over Pd Supported Mesoporous Carbon Catalyst**  
 P. Mäki-Arvela, S. Lestari, H. Bernas, O. Simakova, D. Yu. Murzin, Turku/FIN
- 17.00-17.20 **Effective Functionalisation of Fatty Acids – On the Way to Biopolymers**  
 A.J. Vorholt, A. Behr, Dortmund/D

Wednesday, 24 November 2010

Morning

**Oleochemistry, Biodiesel**

Hall Garmisch-Partenkirchen

Chair: Paolo Bondioli and Mark Rüsç gen. Klaas

- 09.00-09.20 **Esterification of Acidic Oils over Amorphous Solid Catalysts**  
 N. Ravasio, F. Zaccheria, R. Psaro, Milan/I, S. Brini, Verbania/I
- 09.20-09.40 **Use of Ultrasound and Co-solvents to Optimise Microalgae Biodiesel Production via the *in-situ* Transesterification Process**  
 E.A. Ehimen, Z.F. Sun, C.G. Carrington, Dunedin/NZ
- 09.40-10.00 **Using Palm Oil for Biofuels in EU**  
 I. Lastikka, Espoo/FIN
- 10.00-10.20 **New Chemical Resources for the Production of Polyunsaturated Fatty Acids toward Healthy Applications**  
 A.C. Ngakegni-Limbili, M. Cerny, Z. Mouloungui, Toulouse/F, J.M. Ouamba, Brazaville/CG, B. Zebib Bachar, Toulouse/F
- 10.20-10.40 **Palm based Renewable Energy – The Way forward for Malaysia**  
 M.B. Wahid, Kajang, Selangor/MAL



*Paolo Bonducci*

Un caloroso ringraziamento  
per il lavoro di squadra a:

- Laura Della Bella
- Gabriele Rivolta



# Biodiesel - Evoluzione delle norme Europee

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**GRAZIE PER L'ATTENZIONE**