CONSELHO REGIONAL DE QUÍMICA - IV REGIÃO (SP)

Minicursos 2009

Soluções em química analítica para biodiesel e bioetanol

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Apoio

Araçatuba, 12 de setembro de 2009

Observação: A versão original desta apresentação, com slides coloridos, no formato PDF, está disponível na seção downloads do site do CRQ-IV (www.crq4.org.br)

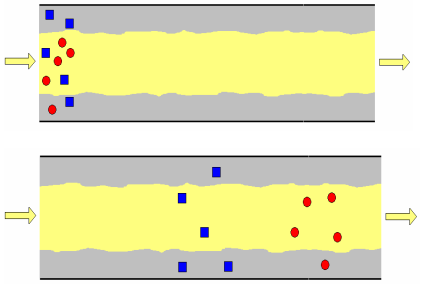
Soluções em Química Analítica para Biodiesel e Bioetanol

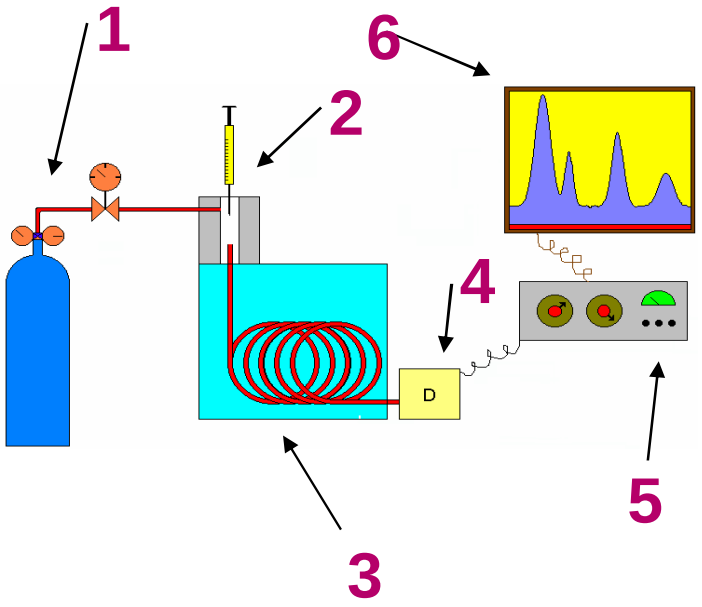
AGENDA

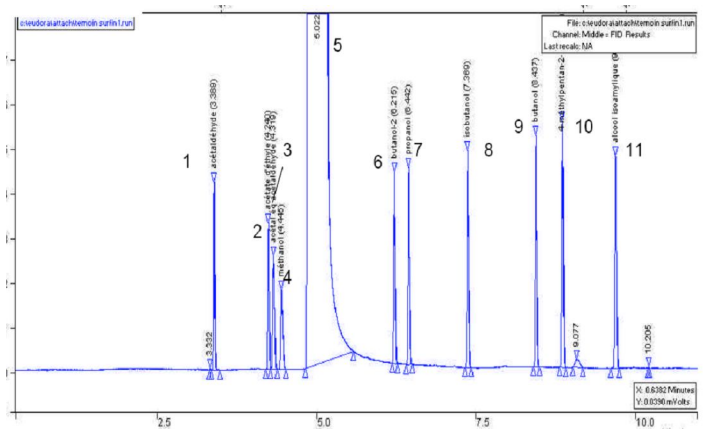
- EQUIPAMENTOS ANALÍTICOS E ALGUNS CONCEITOS
- PANORAMA DE BIOCOMBUSTÍVEIS NO BRASIL E NO MUNDO
- MÉTODOS ANALÍTICOS PARA BIODIESEL
- NOVAS TECNOLOGIAS PERKINELMER
- MÉTODOS ANALÍTICOS PARA BIOETANOL
- MÉTODOS ANALÍTICOS PARA BIOCOMBUSTÍVEIS

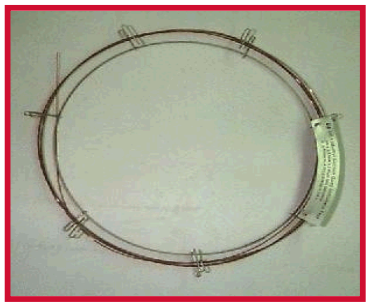
EQUIPAMENTOS ANALÍTICOS E ALGUNS CONCEITOS

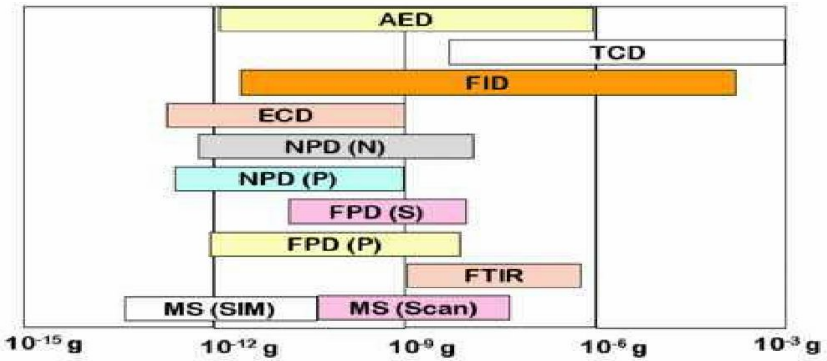
CONCEITO – CROMATOGRAFIA EM FASE GASOSA

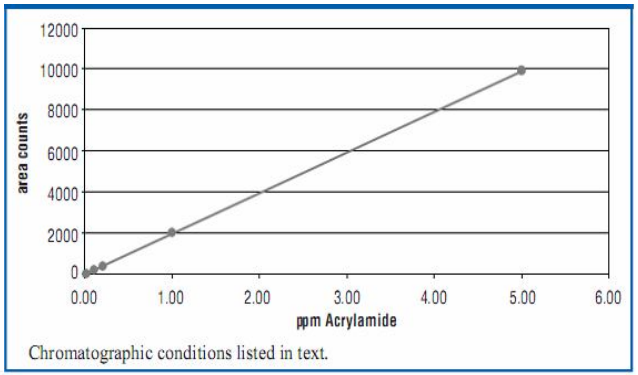












FAMÍLIA CLARUS / TURBOMATRIX

Clarus 500 GC

Turbomatrix ATD

Turbomatrix HS e HS TRAP

Clarus 600 GC

Clarus 600 MS

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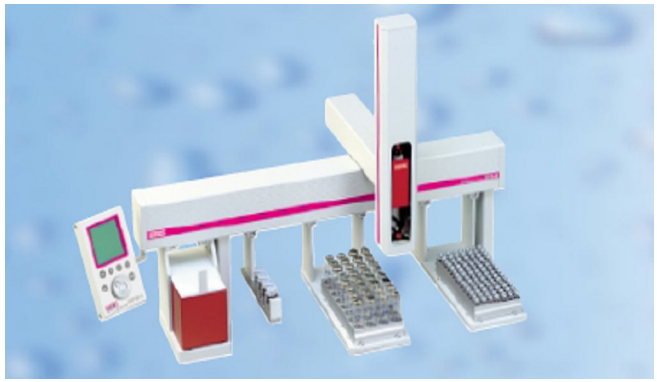
Clarus 400 GC

Pirolisador

Purge & Trap HT3

PerkinElmer-Arnel Refinery Gas Analyzer

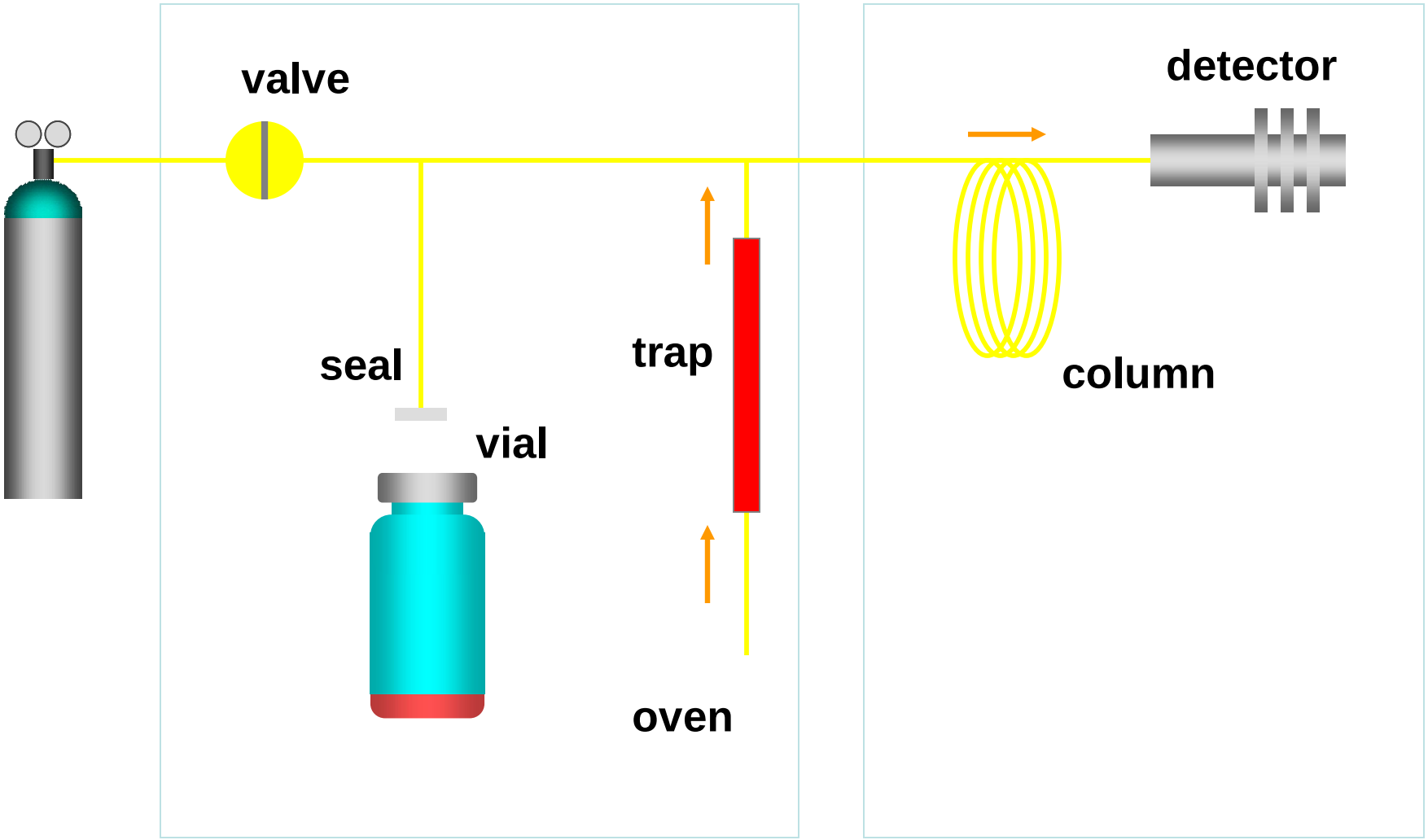


Gerstel MPS2

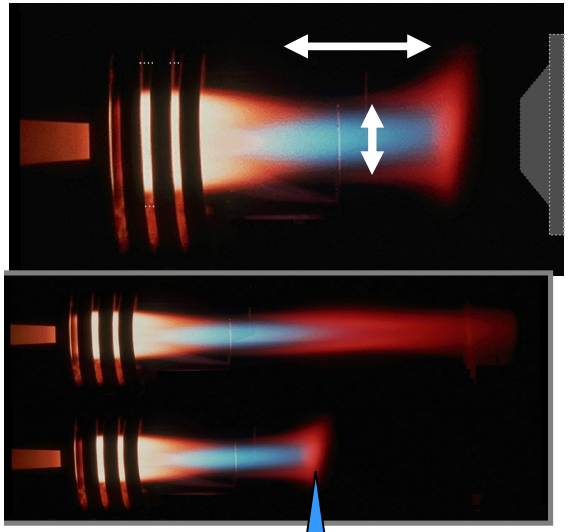
TurboMatrix HEADSPACE (HS) e HEADSPACE TRAP

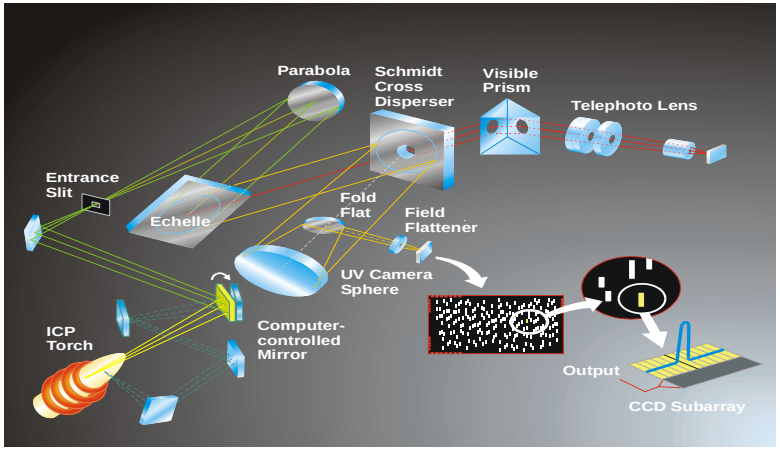
TurboMatrix HS

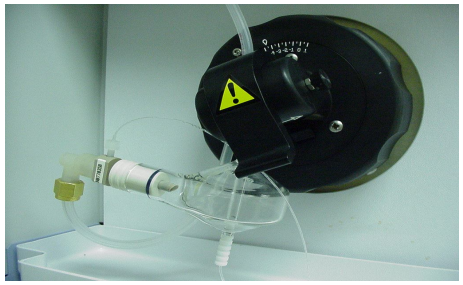
TurboMatrix HS Trap

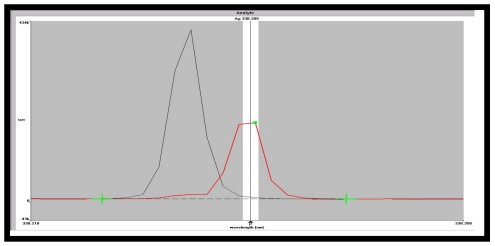

valve
detector
seal
trap
vial
column
oven
Headspace Sampler
Gas Chromatograph

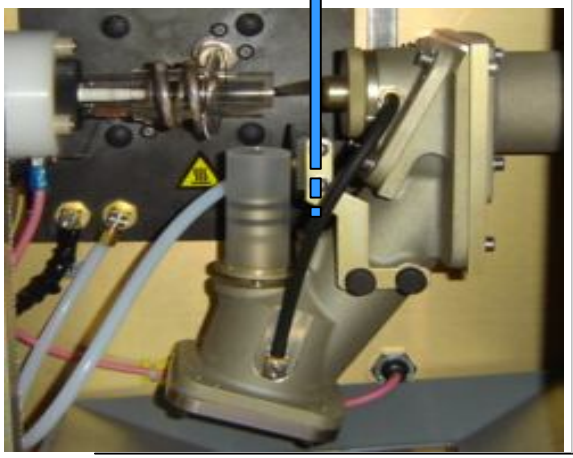
•CONCEITOS ICP OPTIMA 7300 DV E 7000 DV

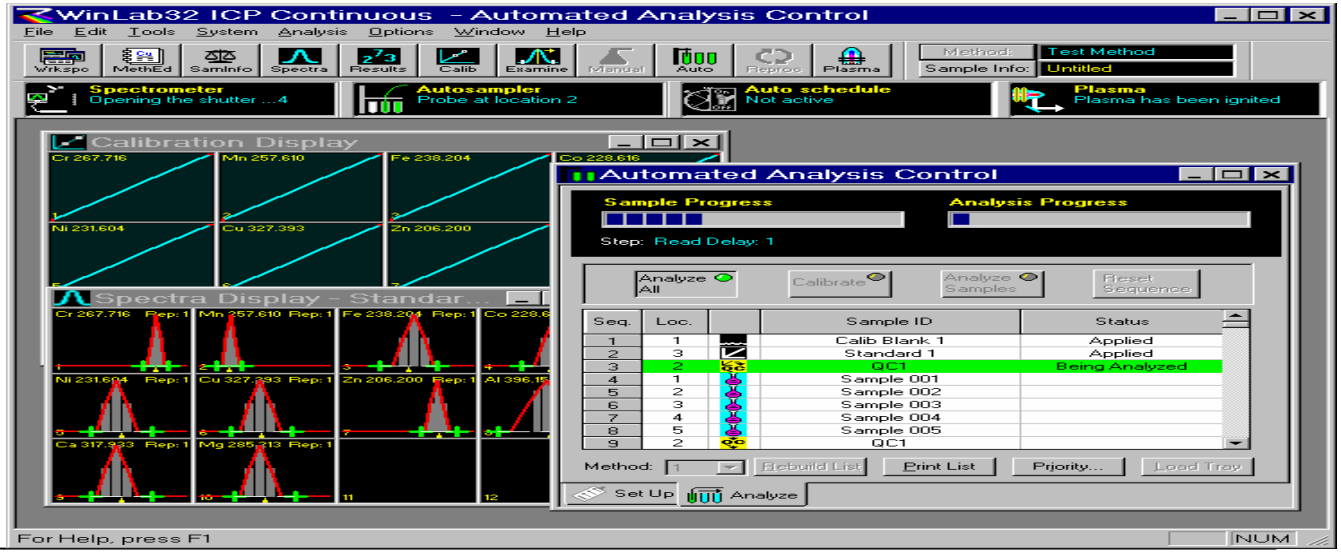




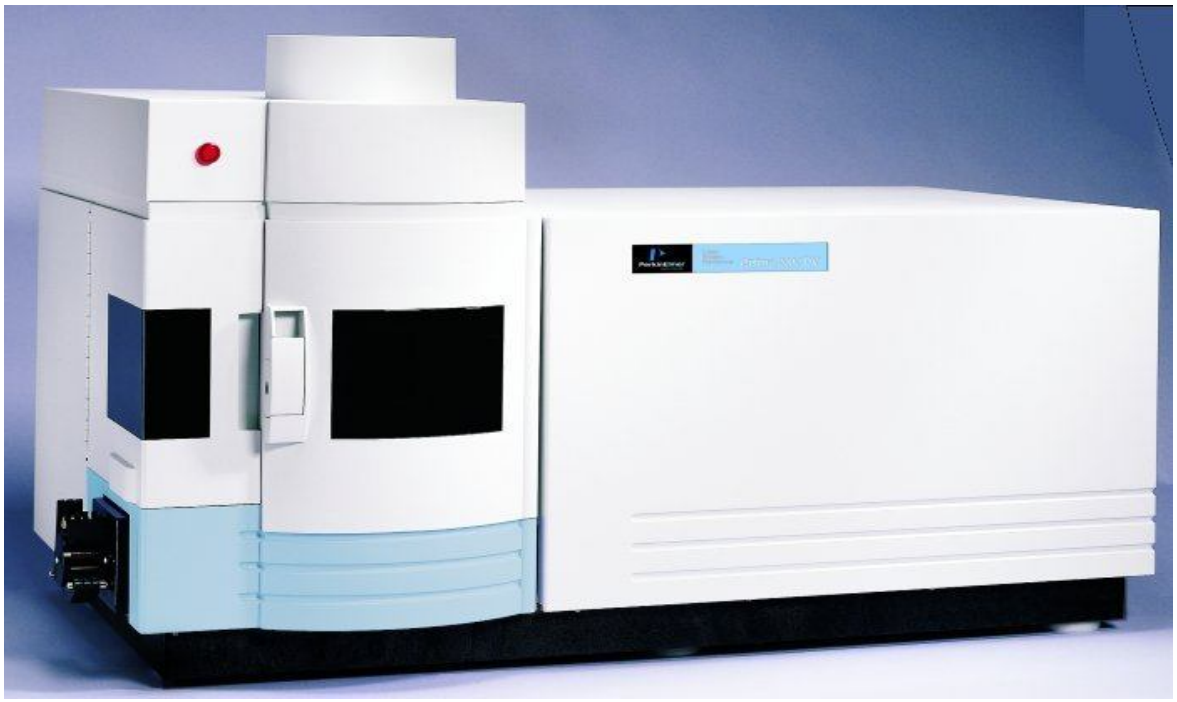








PerkinElmer Optima 7X00



Optima 7000 Series

OPTIMA 7000 DV

OPTIMA 7100 DV

OPTIMA 7200 DV

OPTIMA 7300 DV

OPTIMA 7300 V

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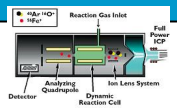
Soluções em Quím. Analítica para Biodiesel e Bioetanol

Features/Performance

DRC Technology Systems



Lowest BEC, Highest S/B — ELAN DRC II

Robust HF resistant sample intro DRC system — ELAN DRC-e

Conventional ICP-MS system

Robust basic system — ELAN 9000

ICP-MS

Simultaneous Systems

Dual view, dual detector — Optima 7300DV

Vertical torch/Radial View, dual detector — Optima 7300V

Dual view, single detector + extended λ — Optima 7200DV

Optima 7100DV — Dual view, single detector

Hybrid system

Optima 7000DV — Lower Cost system

ICP-OES

High-end Flame/ Furnace

AAnalyst 800 — Flame + THGA Zeeman

AAnalyst 700 — Flame + HGA Furnace

AAnalyst 600 — Dedicated THGA Zeeman Furnace (no flame)

Entry-level Flame (Furnace)

AAnalyst 400 — Flame (opt. HGA Furnace)

AAnalyst 200 — Flame (opt. HGA Furnace)

FIMS — Dedicated Hg CVAA)

AA

Price

PANORAMA DE BIOCOMBUSTÍVEIS NO BRASIL E NO MUNDO

Table 3-1: Typology of Liquid Biofuel

Fuel	Feedstock	Regions where currently produced	Greenhouse Gas (GHG) reduction impacts vs. petroleum fuel	Costs	Biofuel yield per hectare of land	Land Types
Ethanol	Grains (wheat, maize)	US, Europe, China	Low-moderate	Moderate	Moderate	Croplands
Ethanol	Sugar cane	Brazil, India, Thailand	High	Low	High	Croplands
Ethanol	Biomass (cellulose)	None	High	High	High	Croplands, Marginal lands
Biodiesel (FAME*)	Oil seeds (rape, soy)	US, Europe	Moderate	Moderate	Low	Croplands
Biodiesel (FAME)	Palm Oil	Southeast Asia	Moderate	Low-moderate	Moderate	Coastal lands
Biodiesel (BTL**)	Biomass	None	High	High	High	Croplands, marginal lands

Source: IEA
*Fatty Acid Methyl Ester
**Biomass-to-liquids

Table 3-3: Worldwide - Top Biofuel Producing Countries (in Million Liter), 2005

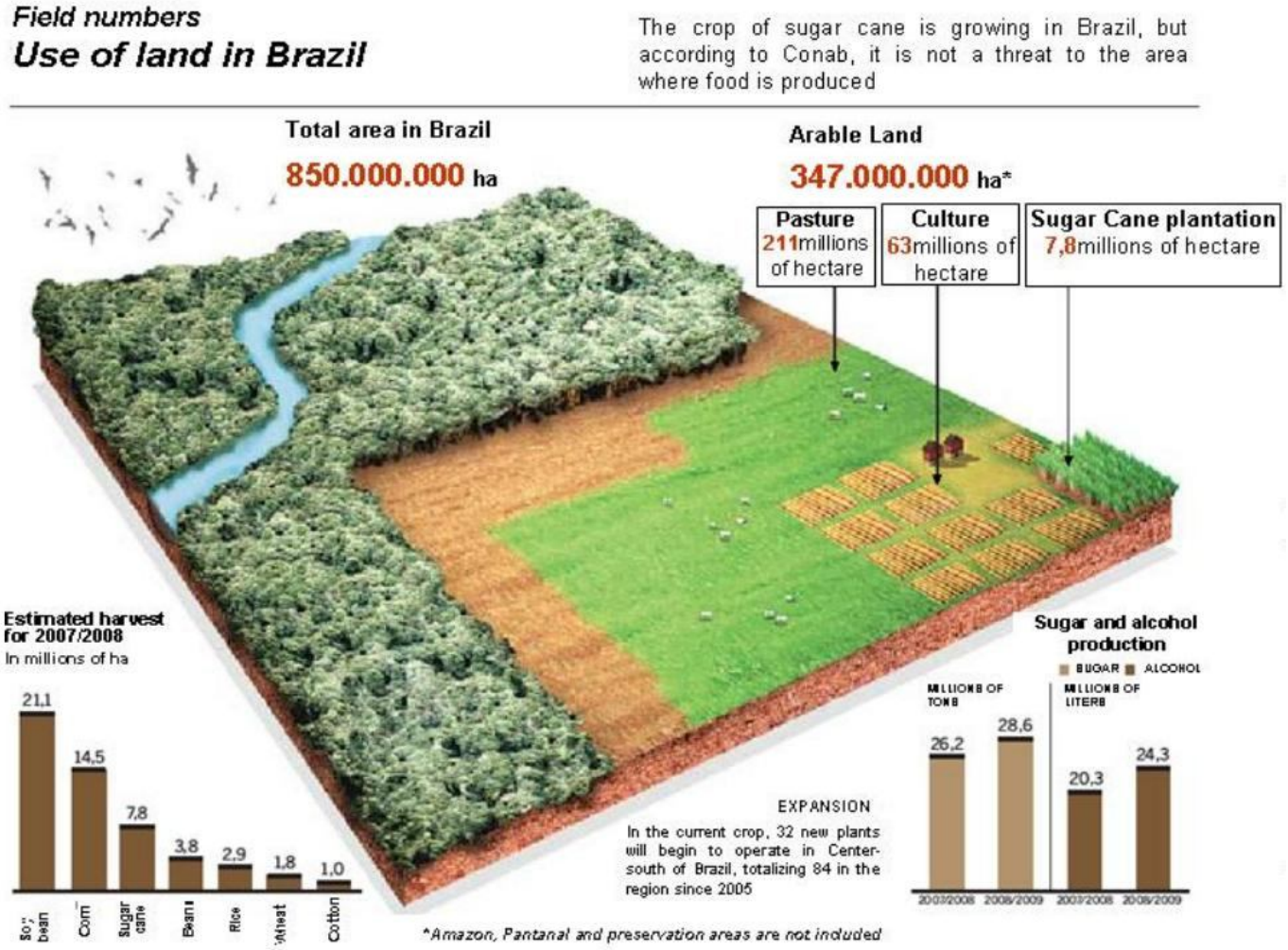
	Ethanol	Biodiesel
United States	16,214	284
Brazil	16,067	70
China	3,800	-
India	1,700	-
France	910	557
Russia	750	-
South Africa	390	-
Spain	376	84
Germany	350	1921
Thailand	300	-
United Kingdom	290	74
Ukraine	245	-
Canada	230	-
Poland	220	-
Indonesia	170	-
Saudi Arabia	170	-
Argentina	165	-
Italy	150	227
Australia	125	57
Japan	113	-
Czech Republic	-	136
Denmark	-	80
Poland	-	80
Sweden	-	7
Other Countries	2,139	463
World	44,874	4125

Source: Worldwatch

Renewable Energy in Brazil

- In 2007: 42% of primary energy came from renewable resources
  - 13% was Hydropower
  - 29% was Biomass
    - 13% Sugarcane
    - 13% Wood and related
    - 3% different other sources
- 50% of transportion fuel comes from Ethanol
- about 2% of arable land is used for production of bioethanol from sugarcane

Landusage in Brazil



Bioethanol

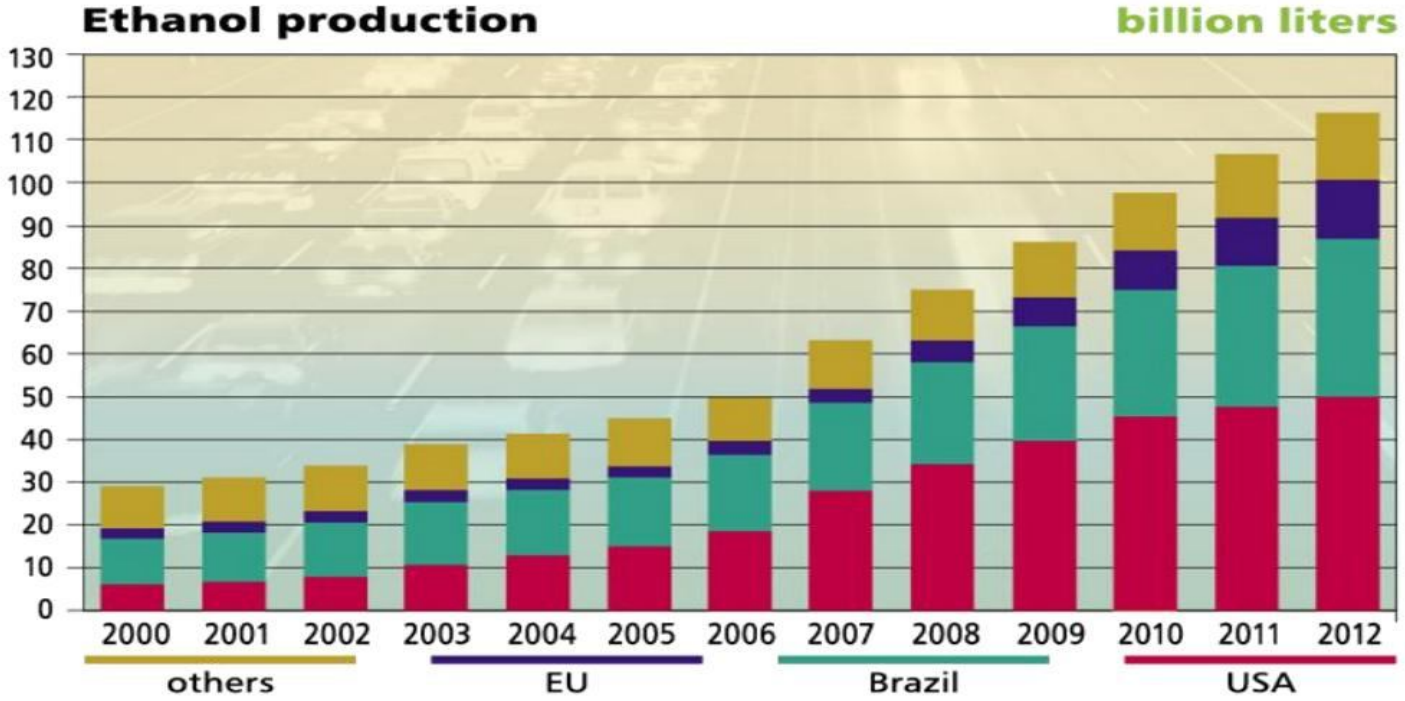
Global Availability

WORLD MAP OF SUGARCANE PRODUCTION

100 countries could supply BioFuels to 200 nations,
while currently 20 oil producers provide fossil fuels to 280 nations.

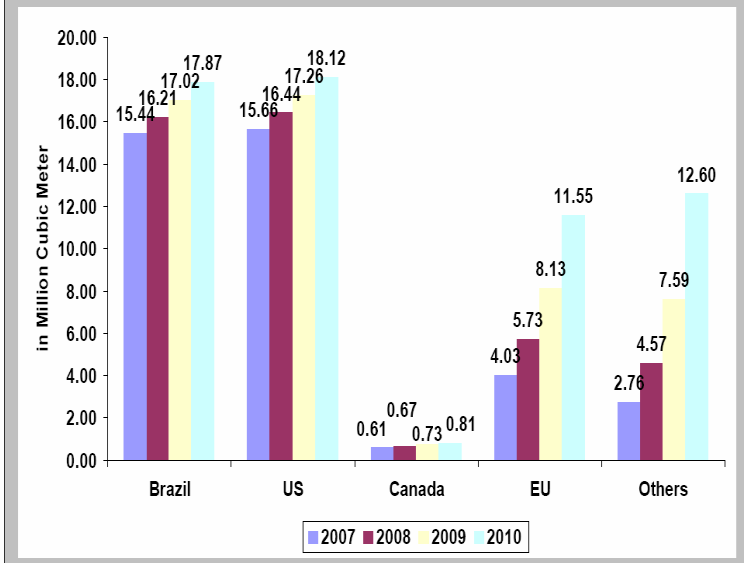
– Source: British Sugar, Prepared by UNICA

Global Production of Ethanol



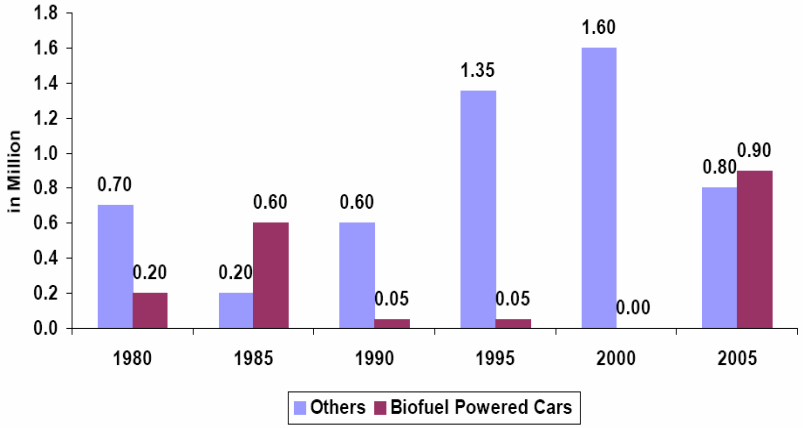
Note: *Projections for 2008/2012 based on announced production capacities and targets in main producing countries.*
Sources: *Fapri, Acti, FO Licht, Unica and Toepfer*
Data compiled *by Unica and Ícone*

Figure 3-8: Worldwide - Forecast of Ethanol Demand (in Million Cubic Meter), 2007-2010



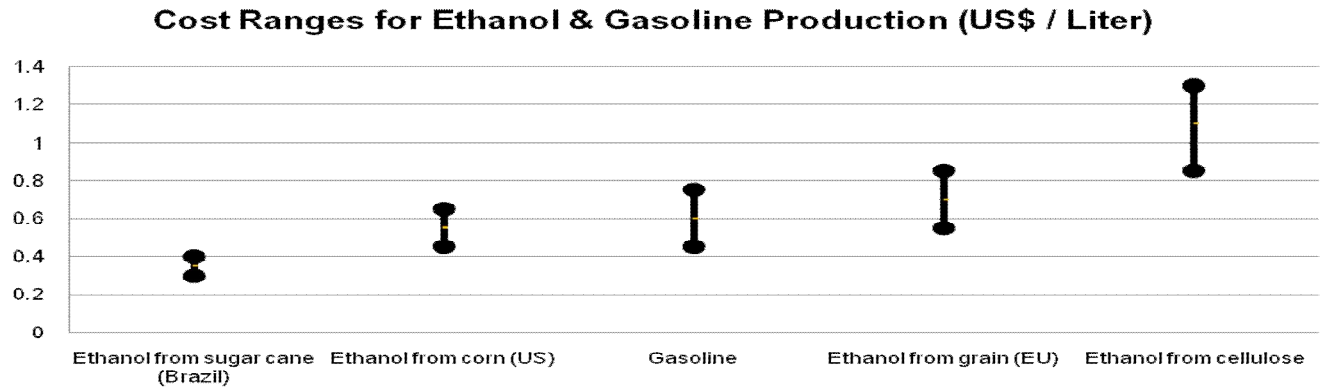
Source: F.O. Litch, RNCOS

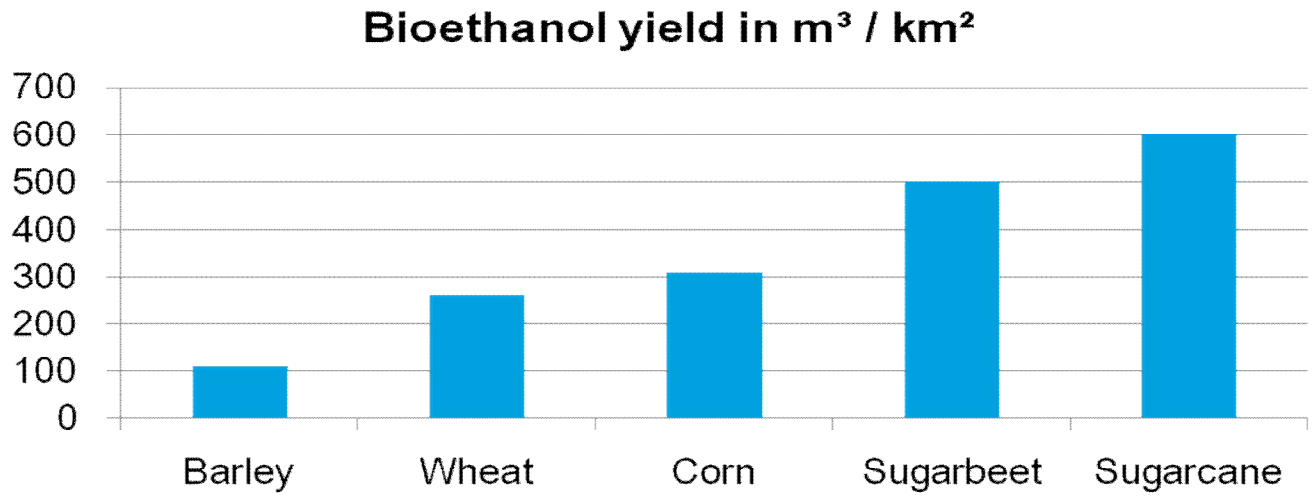
Figure 4-1: Brazil - Production of Vehicles (in Million), 1980, 1985, 1990, 1995, 2000 & 2005



Source: Brazilian Association of Car Manufactures

Different feedstocks for Bioethanol...





The global targets for Biodiesel are…

United States:
0.5% today
1% in 2009
2% in 2012
>15% in 2022

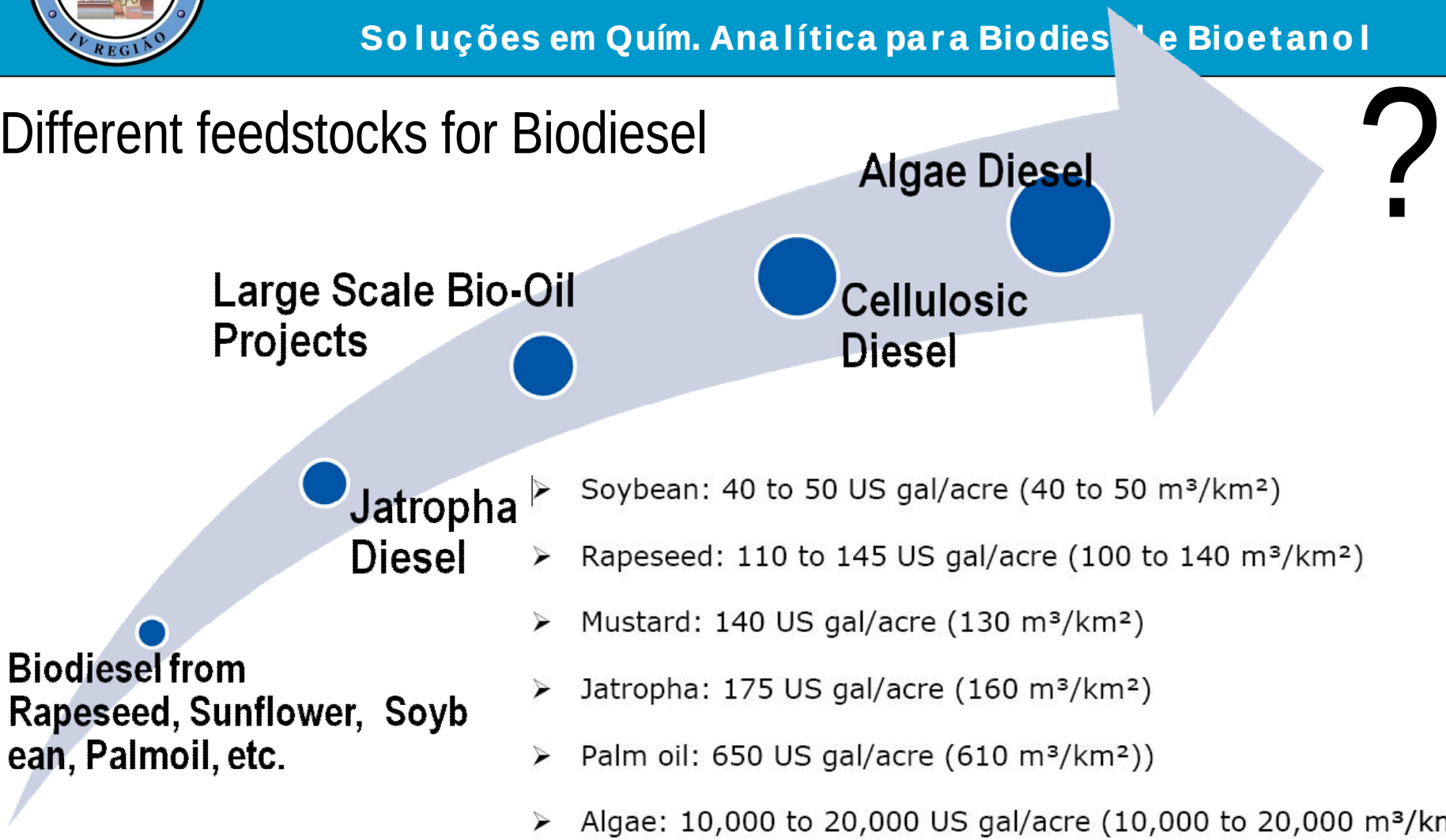
European Union:
2 - 3% today
5,75% in 2010/2015*
10% in 2020*

China:
0.3% to 0.5% today
~ 2% in 2010
~ 10% in 2020

India:
5% today
20% in 2012

Brazil:
3% in 2009
5% in 2013

Different feedstocks for Biodiesel



- Soybean: 40 to 50 US gal/acre (40 to 50 m³/km²)
- Rapeseed: 110 to 145 US gal/acre (100 to 140 m³/km²)
- Mustard: 140 US gal/acre (130 m³/km²)
- Jatropha: 175 US gal/acre (160 m³/km²)
- Palm oil: 650 US gal/acre (610 m³/km²))
- Algae: 10,000 to 20,000 US gal/acre (10,000 to 20,000 m³/km²)

Current Global Biofuel Facilities …

	Biodiesel	Bioethanol
Production sites		
North America	165	200
South America	60	340
European Union	120	70
India	15	25
China	35	50
Rest of World	60	40
Total	455	545
Blenders	170 +	
Regulator/TestLab	650 +	
Total	~ 2000*	

*Universities and Agricultural-R&D facilities are not included; this would add another 300-500

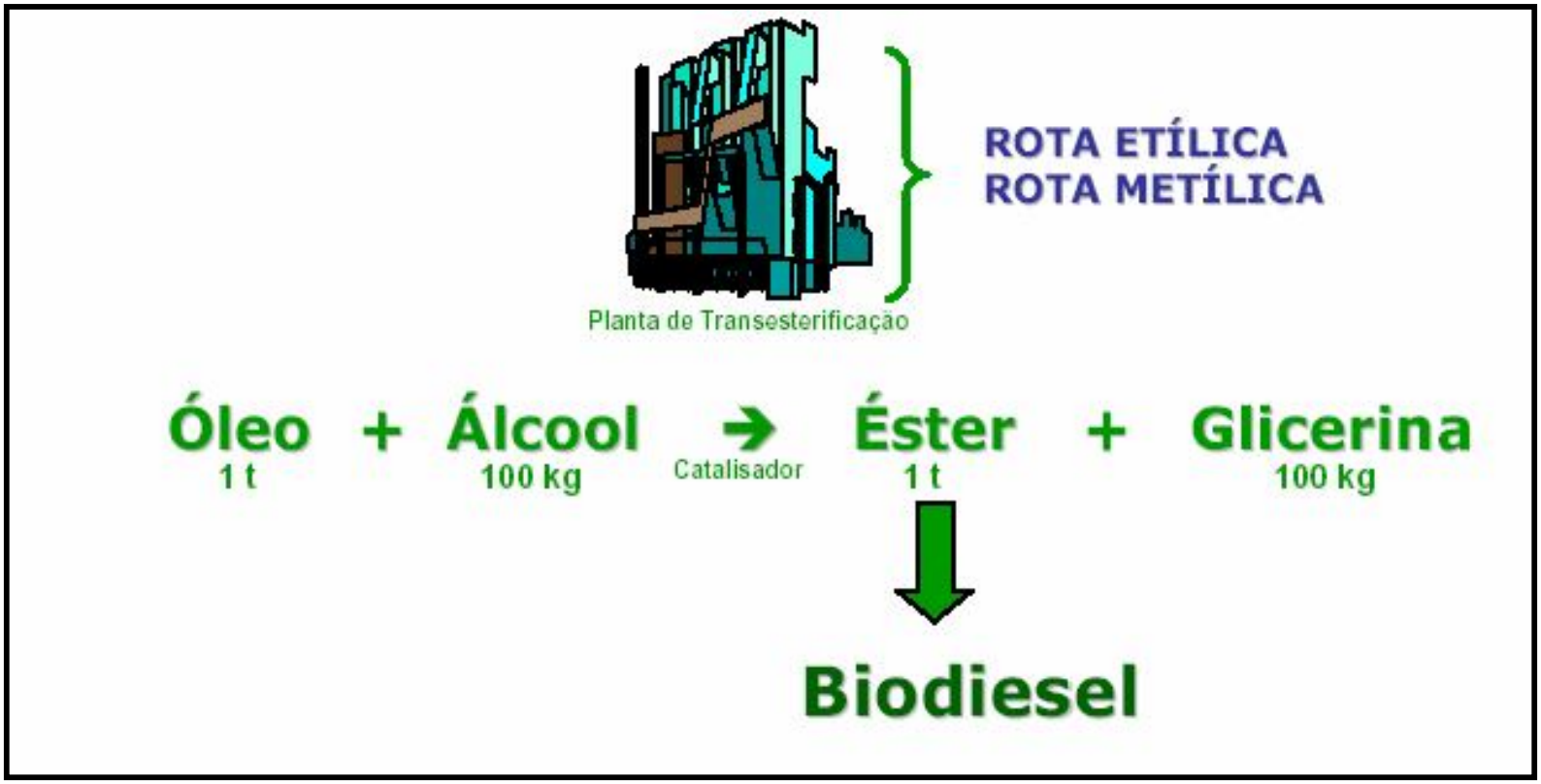
Top Global Biofuels Producers

Prodcers Biodiesel	
Bunge	http://www.bunge.com/
Neste oil	http://www.nesteoil.com/
Cargill	http://www.cargill.com/products/industrial/ps_ethanol.htm
Novaol	http://www.novaol.it/
Diester	
Green Hunter	http://www.greenhunterenergy.com/
Natural Fuel	http://www.naturalfuel.com.au/
Renewable Energy Group	http://www.renewable-energy-group.com/
Abengoa	http://www.abengoa.es/sites/abengoa/en/index.html
Prodcers Bioethanol	
VeraSun	http://www.verasun.com/
Archer Daniels Midland (ADM)	http://www.admworld.com/
Cargill	http://www.cargill.com/products/industrial/ps_ethanol.htm
Pacific Etahnol	http://www.pacificethanol.net/
Monsanto (?)	http://www.monsanto.com/
BlueFire (Cellulosic)	http://bluefireethanol.com/
Grupo Coimex	http://www.grupocoimex.com.br/ingles/index.htm
Construction companies	
Lurgi	http://www.lurgi.com/website/index.php?id=19
BDI	http://www.biodiesel-intl.com/default.aspx?LNG=EN
Praj	http://www.praj.net/fuelethanolplants.htm

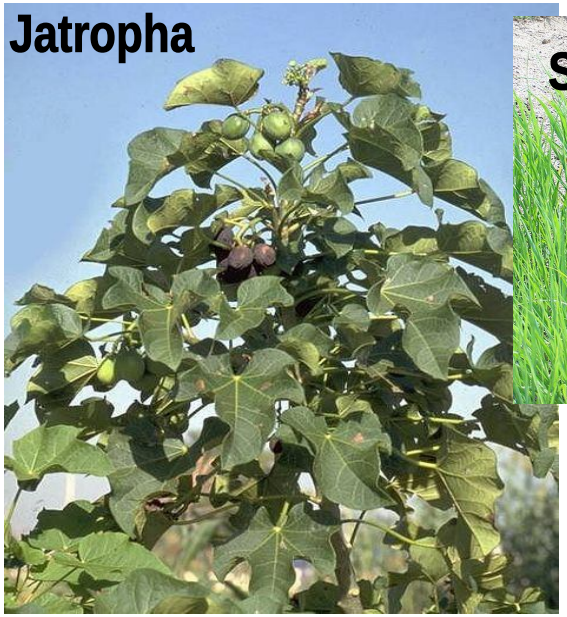
First Generation Biofuels

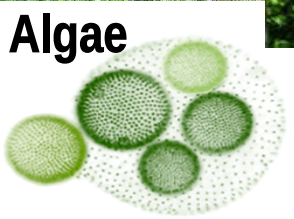
- Biodiesel
- Ethanol

BIODIESEL: ÉSTER PRODUZIDO NA REAÇÃO DE TRANSESTERIFICAÇÃO



What are Next Generation Biofuels?





- Food vs. Fuel
- Marginal Lands
- More Efficient
- Reduce the cost to produce and distribute

MÉTODOS ANALÍTICOS PARA BIODIESEL


BIOFUEL DEVELOPMENT
ecoanalytix
PerkinElmer
REGULATORY STANDARDS
Biodiesel:
ASTM D6751, EN14214, ANP42/2004
Bioethanol:
ASTM D4806, EN15376, ANP36/2005
JATROPHA
SUGAR CANE
CELLULOSE
CORN
ALGAE
TRACE METALS
METHANOL & ESTER PROFILE
GLYCERIN
GLYCERIN & METHANOL
FAME
FERMENTATION SUGARS
OXIDATION STABILITY
BIO-CONTENT
LIMS
HS GC
HS GC Dual Oven
LC
LSC
ICP-OES
GC
IR
DSC
LABWORKS
greenLIMS

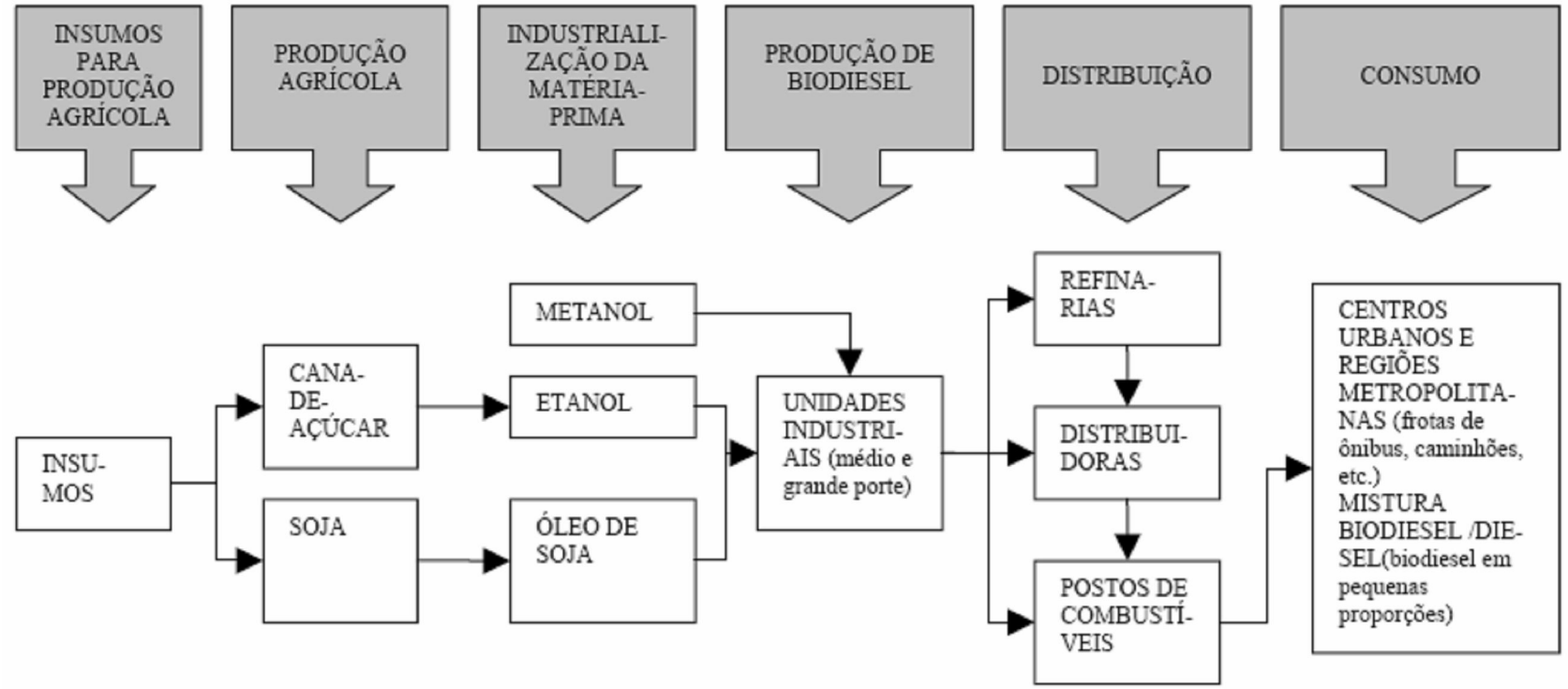
Tabela I: Especificação do Biodiesel

CARACTERÍSTICA	UNIDADE	LIMITE	MÉTODO		
			ABNT NBR	ASTM D	EN/ISO
Aspecto	-	LII (1)	-	-	-
Massa específica a 20°C	kg/m³	850-900	7148, 14065	1298, 4052	EN ISO 3675 - EN ISO 12185
Viscosidade Cinemática a 40°C	mm²/s	3,0-6,0	10441	445	EN ISO 3104
Água , máx. (2)	mg/kg	500	-	6304	EN ISO 12937
Contaminação Total, máx.	mg/kg	24	-	-	EN 12662
Ponto de fulgor, mín.	°C	100,0	14598	93	-
Teor de éster, mín	% massa	96,5	-	-	EN ISO 3679 EN 14103 (3)
Resíduo de carbono (4)	% massa	0,050	-	4530	EN ISO 10370
Cinzas sulfatadas, máx.	% massa	0,020	6294	874	ISO 3987
Enxofre total, máx.	mg/kg	50	- -	5453	- EN ISO 20846 EN ISO 20884
Sódio + Potássio, máx.	mg/kg	5	- -	- -	EN 14108 EN 14109
Cálcio + Magnésio, máx.	mg/kg	5	-	-	EN 14538
Fósforo, máx.	mg/kg	10	-	4951	EN 14107
Corrosividade ao cobre, 3h a 50 °C, máx.	-	1	14359	130	EN ISO 2160
Número de Cetano (5)	-	Anotar	-	613 6890	EN ISO 5165
Ponto de entupimento de filtro a frio, máx.	°C	Anotar	14747	6371	EN 116
Índice de acidez, máx.	mg KOH/g	0,50	14448 -	664 -	- EN 14104 (6)
Glicerol livre, máx.	% massa	0,02	15341 - -	6584 (3) (6) -	- EN 14105 (3) (6) EN 14106 (3) (6)
Glicerol total, máx.	% massa	0,25	15344 -	6584 (3) (6) -	- EN 14105 (3) (6)
Mono, di, triacilglicerol (5)	% massa	Anotar	15342 15344	6584 (3) (6)	- - EN 14105 (3) (6)
Metanol ou Etanol, máx.	% massa	0,20	15343	-	EN 14110 (6)
Estabilidade à oxidação a 110°C, mín.(2)	h	6	-	-	EN 14112 (6)

Biodiesel

Property	European Union EN	United States ASTM	Brazil ANP	Technology Used	PKI Capability
Oxidation stability	EN 14112	EN 14112	EN 14112	DSC	✓
Iodine Number	EN 14111		EN ISO 14111	GC	✓
FAME Composition	EN 14103		ABNT NBR 15342	GC	✓
Content of linolenic acid methyl ester	EN 14103			GC	✓
FAME Blend	EN 14078	ASTM D7371		IR	✓
Content of polyunsaturated methy esters	EN 14103			GC	✓
Methanol content	EN 14110		ABNT NBR 15343	HS-GC	✓
Content of Monoglycerine	EN 14105		ABNT NBR 15342	GC	✓
Content of Diglycerine	EN 14105		ABNT NBR 15342	GC	✓
Content of Triglycerine	EN 14105		ABNT NBR 15344	GC	✓
Free glycerine	EN 14105; EN 14106	ASTM D6584	ABNT NBR 15341	GC	✓
Total glycerine	EN 14105	ASTM D6584	ABNT NBR 15344	GC	✓
Na and K	EN 14108; EN 14109	UOP 391	EN 14108; EN 14109	ICP	✓
Ca and Mg	EN 14538	UOP 389	EN 14538	ICP	✓
Phosphorus content	EN 14107	ASTM D4951	EN ISO or ASTM	ICP	✓
Sulfur Content	EN ISO 20846, EN ISO 20884	ASTM D5453	EN ISO or ASTM	ICP	✓

CADEIA DE PRODUÇÃO

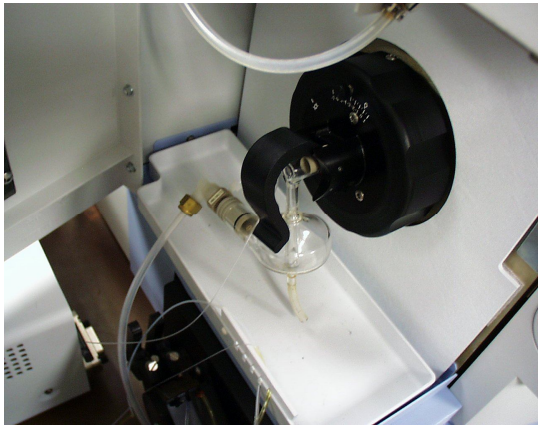


Objectives

- To develop a method for the simultaneous, high through put and accurate analysis of trace metal impurities in biodiesel samples by using ICP-OES (EN 14538, EN 14107)
- Perform analysis at the levels specified in ASTM D 6751 and EN 14214
- Apply the developed method for the quality control of biodiesel samples obtained from different feed stocks.

Metal impurity	Effects
Phosphorus	Can damage the catalytic convertor system
Calcium & Magnesium	Contribute to injector clogging, fuel pump, piston and engine wear, engine deposits
Sodium & Potassium	Contribute to injector clogging, fuel pump, piston and engine wear, engine deposits Can cause soap formation May get collected in exhaust Adverse effects on particulate trap technologies
All metals	Will affect oxidational stability of biofuels

ANÁLISE DE METAIS POR ICP-OES



Parameter	
Plasma gas flow	18 L/min
Auxiliary gas flow	1.6 L/min
Nebulizer gas flow	0.5 L/min
RF power	1450 watts
Viewing height	15 mm
Plasma view	Radial
Read delay	90 seconds
Read parameters	Min 0.5 and max 2.0 s
Pump rate	1.0 mL/min
Processing	Peak area
Spray Chamber	Baffled cyclonic
Nebulizer	Low flow GemCone
Injector Alumina	1.2 mm i.d.
Sample tubing	Solvent flex (0.76 mm)
Drain tubing	Solvent flex (1.14 mm)
Quartz torch	3-slot
Sample capillary	Teflon® (1 mm)

- Two biodiesel samples based on different feed stocks were analysed
- Palm oil and Jetropha based
- Samples were diluted 1:10 with high purity kerosene
- Internal standard was mixed with the diluent
- Blank was prepared with PerkinElmer blank oil and diluted with diluent containing Internal standard
- Samples were prepared in duplicate
- QC sample was prepared from Spex Certiprep ICP oil standard
- One sample from each feedstock was spiked with QC sample prior to analysis

U.S. and EU specifications for elemental content in biodiesel (mg/kg)

Metal	ASTM D6751	EN 14214
Phosphorus	10	10
Calcium	5 (combined)	5 (combined)
Magnesium		
Sodium	5 (combined)	5 (combined)
Potassium		

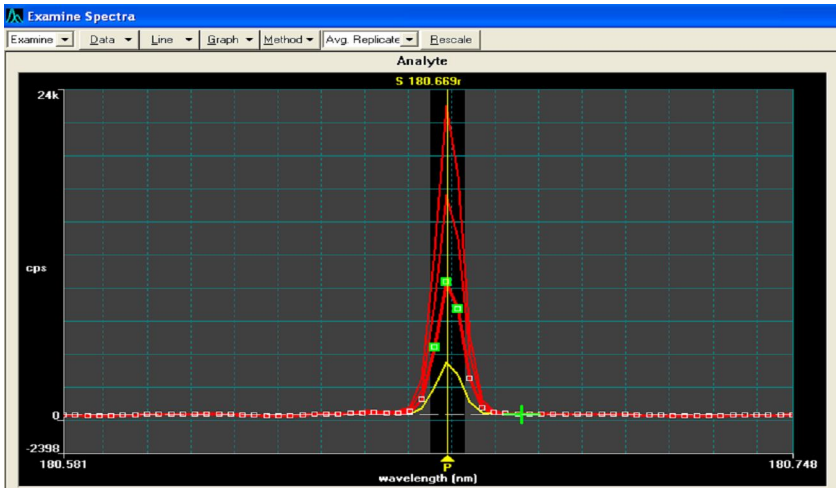
Estimated Detection Limits

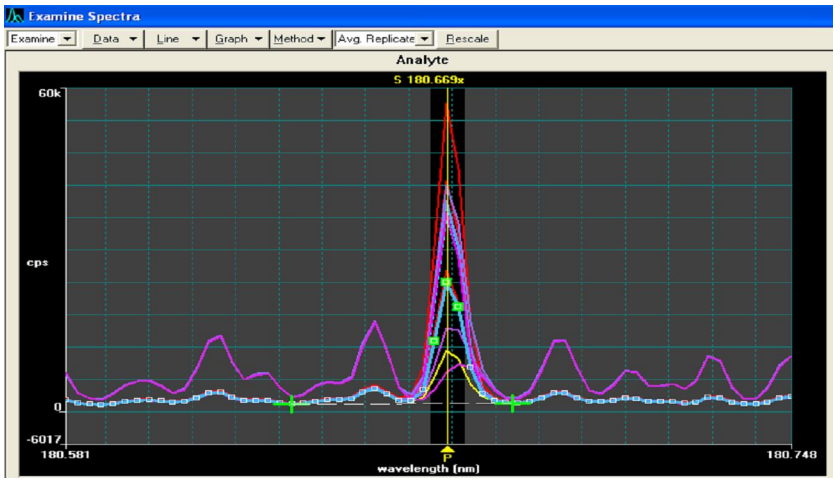
Element	Wavelength (nm)	Instrument DL (mg/kg)	Biodiesel DL (mg/kg)
Phosphorus	213.620	0.04	0.4
Sodium	588.993	0.02	0.2
Potassium	766.485	0.08	0.8
Calcium	422.673	0.004	0.04
Magnesium	285.213	0.002	0.02

S por ICP-OES

Sample ID	Mean (mg/kg)	SD (mg/kg)	% RSD	%RPD
NIST 2723 I	11.32	0.102	0.89	
NIST 2723 II	10.93	0.066	0.61	
Mean of Duplicates	11.13			3.5
NISTCertified Value	11.0 +/- 1.1			

Emissão do enxofre em 180.669 nm



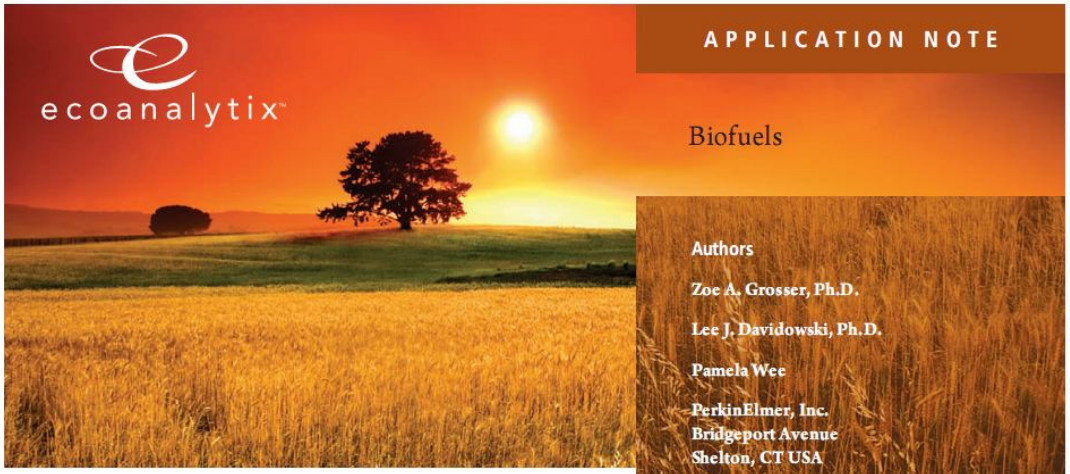


APLICACOES PERKINELMER

FIELD APPLICATION REPORT

ICP OPTICAL EMISSION

Sulphur and Phosphorus Analysis in Vegetable Oil and Beef Tallow for Biodiesel Production Using the Optima Inductively Coupled Plasma-Optical Emission Spectrometer



APPLICATION NOTE

Biofuels

Authors

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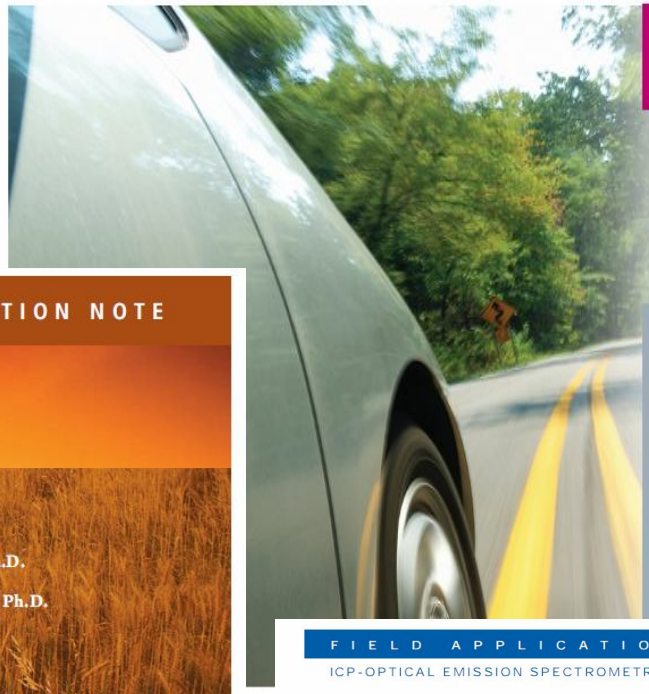

APPLICATION NOTE

ICP-Optical Emission Spectroscopy

Author

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FIELD APPLICATION REPORT

ICP-OPTICAL EMISSION SPECTROMETRY

Phosphorus, Calcium and Magnesium Analysis of Soybean Oil-Feedstock for Biodiesel Production Using the Optima Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES)

Outras informações

- OS EQUIPAMENTOS AA200 E AA400 TAMBÉM PODEM SER UTILIZADOS PARA ANÁLISE DOS METAIS

GLICERINA LIVRE	• Subproduto do processo de transesterificação cujo teor depende da separação dos ésteres/glicerina.
	• Acarreta depósitos no injetor, entupimento do filtro, forma
GLICERINA TOTAL	• Soma de glicerina livre e mono-, di- e triglicerídeos.
	• Depende do processo.
	• Formação de coque no injetor, entupimento do filtro, formação de sedimento.
MONO E DI GLICERÍDEOS	• Oriundos do processo, são produtos intermediários do processo que não terminaram de reagir .
	• Provocam depósitos nos injetores e nos anéis do cilindro.
	• Os monoglicerídeos apresentam alto ponto de fusão e baixa solubilidade o que implica em cristalização.
TRIGLIGERÍDEOS	• Produtos que não foram transestereficados.
	• Aumentam a viscosidade do biodiesel.
	• Provocam depósitos nos cilindros e nas válvulas.
ÁLCOOL METANOL OU ETANOL	• Utilizado em excesso no processo, podendo influenciar o ponto de fulgor.
	• Corrosão em peças de alumínio e zinco.
	• Reduz número de cetano e lubricidade do biodiesel.

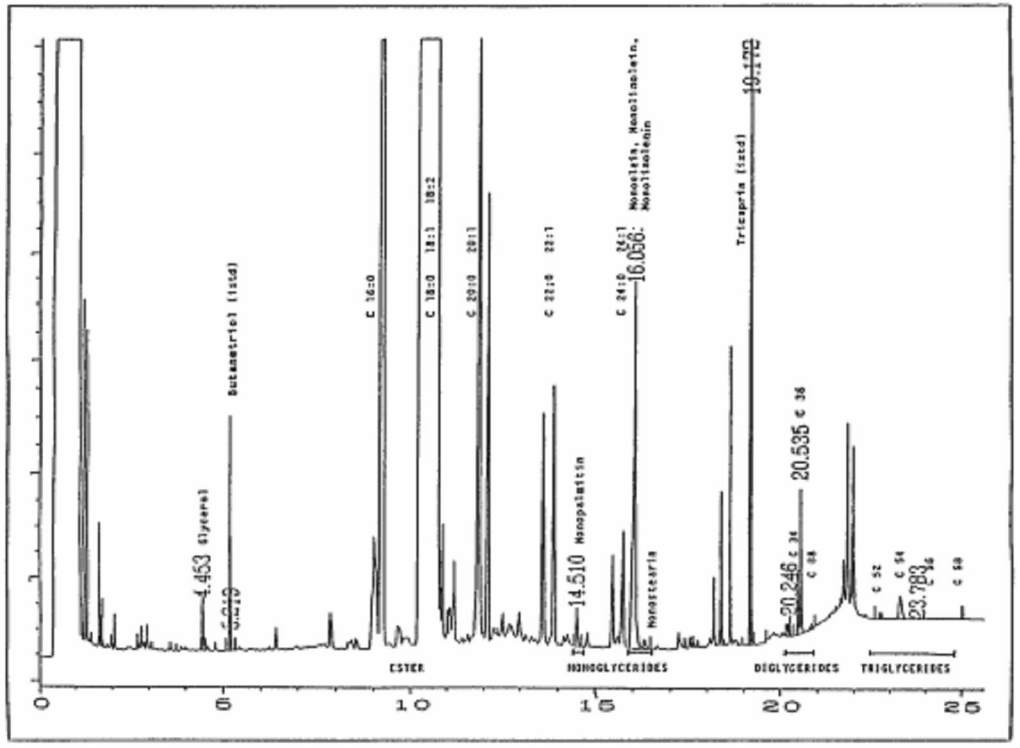
Configuração recomendada para ASTM D-6584

- Clarus® 500 GC with Liquid Autosampler and Programmable Pneumatic Control (PPC)
- TotalChrom® control and data-handling software
- Programmable On-Column (POC) inlet
- Flame Ionization Detector (FID)
- 5-µL syringe with 0.47-mm OD needle

Inside the oven:

- Column: Elite 5 HT, 15 or 30 meter, 0.10-µm film thickness, 0.32-mm ID
- High-Temperature Guard Column, 0.53-mm diameter
- Low-volume union or hourglass column connector

- Oven Ramp:
  - Initial: 50 oC, hold 1.0 minutes
  - 15 deg/min to 180 oC, hold 0.0 minutes
  - 7 deg/min to 230 oC, hold 0.0 minutes
  - 30 deg/min to 380 oC, hold 10.0 minutes
- Programmable On-Column Inlet:
  - Initial: 50 oC
  - Oven-tracking mode to 380 oC
- FID Detector:
  - 380 oC, 45 mL/min Hydrogen and 450 mL/min Air
- Carrier Gas Flow:
  - 3.0 mL/min Helium



➢ **Weigh 100 mg +/- 0.1 mg of biodiesel into a 10 mL septa vial**

Internal Standard Addition (ISTD)

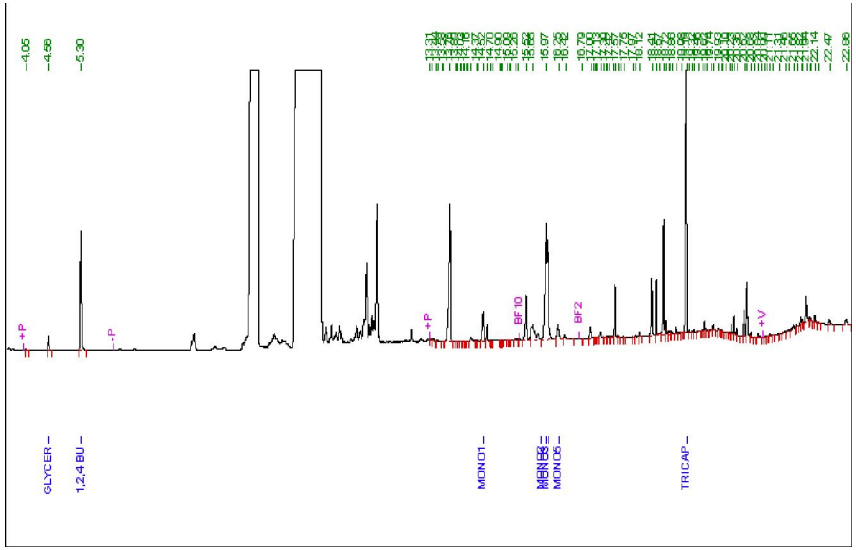
➢ **Add 100 µL of 1,4 Butantriol & Tricaprin by syringe to the vial**

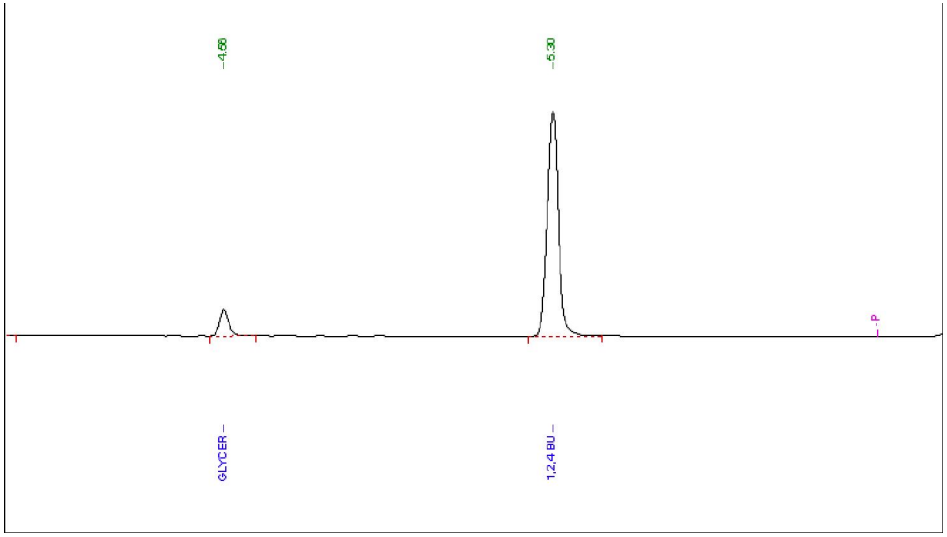
➢ **Add 100 µL of MSTFA (derivitizing solution)**

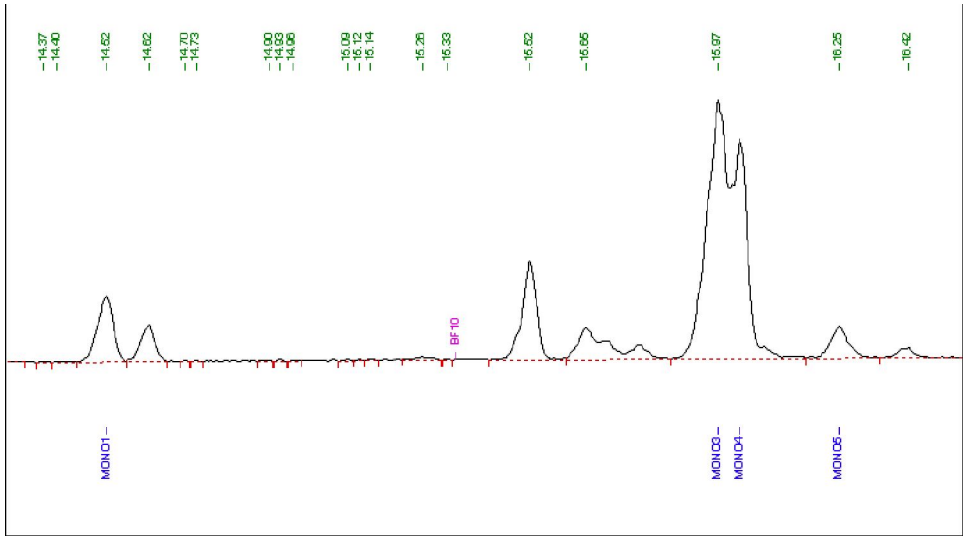
➢ **Shake solution and allow to react to for 15-20 minutes**

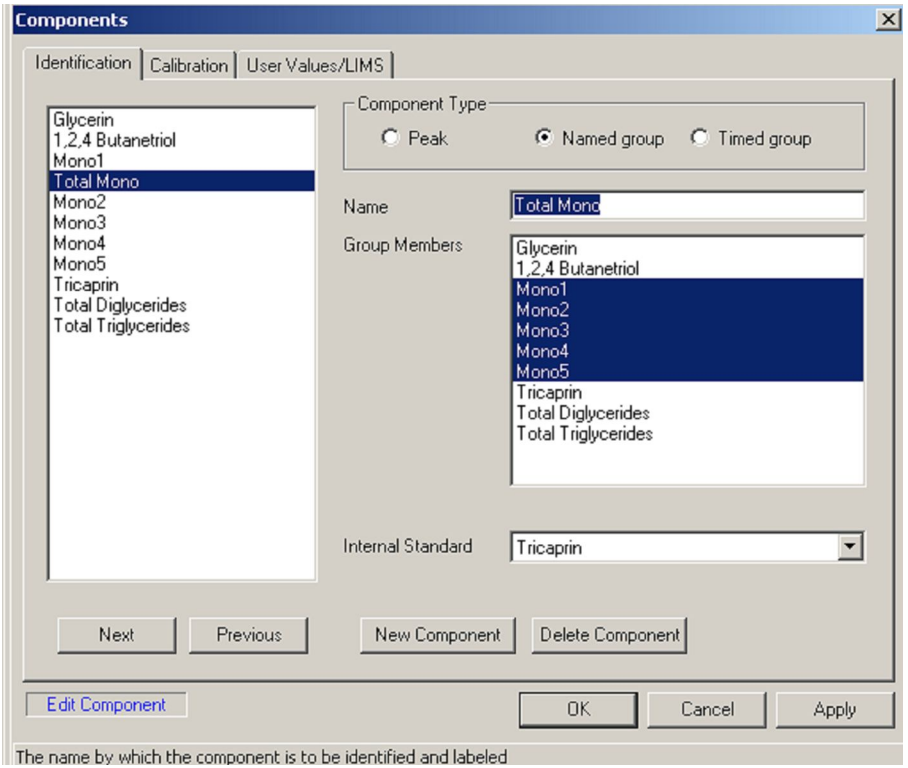
Dilute with 8 mL of Heptane and shake to mix

This solution is now ready for analyses!

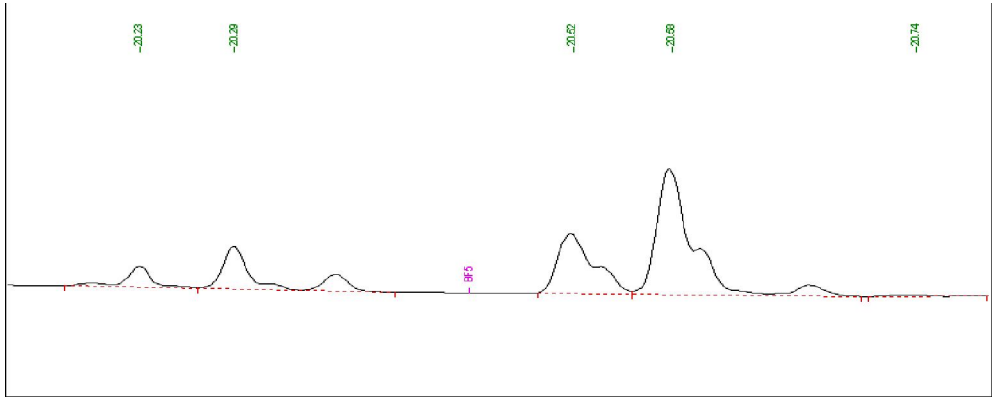

4.05
4.56
5.30
+P
P
+P
BF10
BF2
+V
GLYCER
1,2,4 BU
MONO1
MONO3
TRICAP

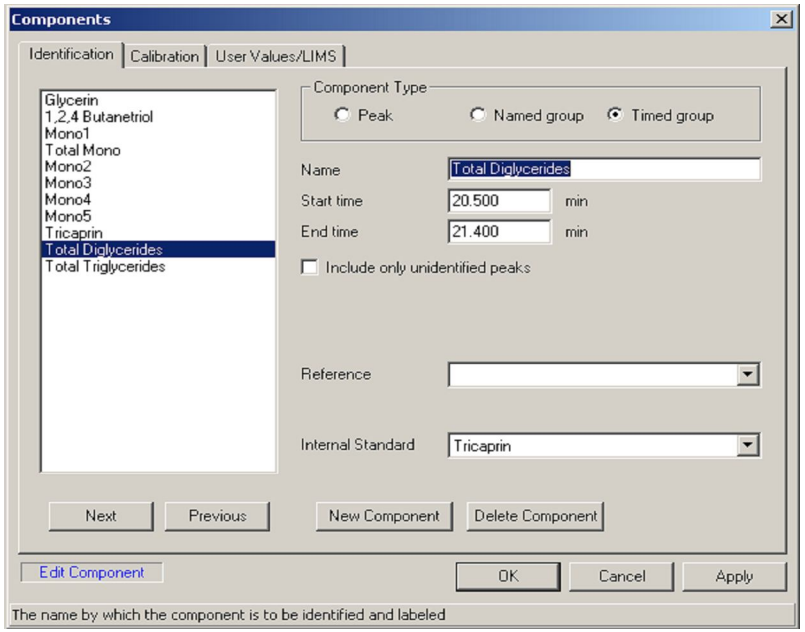

4.56
5.30
P
GLYCER
1,2,4 BU


14.37
14.40
14.62
14.62
14.70
14.73
14.90
14.93
14.96
15.09
15.12
15.14
15.26
15.33
15.62
15.66
15.97
16.25
16.42
BF10
MON01
MON03
MON04
MON05

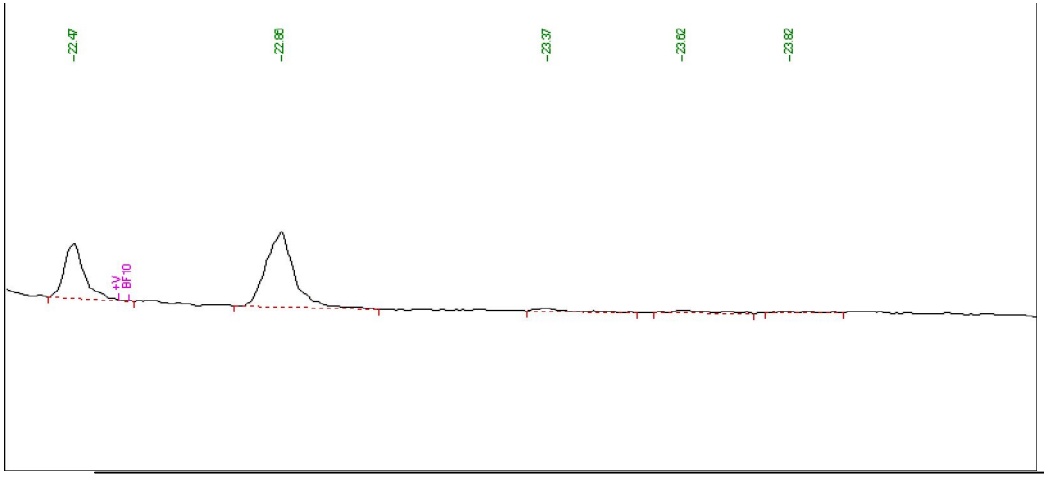

Components
Identification
Calibration
User Values/LIMS
Glycerin
1,2,4 Butanetriol
Mono1
Total Mono
Mono2
Mono3
Mono4
Mono5
Tricaprin
Total Diglycerides
Total Triglycerides
Component Type
Peak
Named group
Timed group
Name
Total Mono
Group Members
Glycerin
1,2,4 Butanetriol
Mono1
Mono2
Mono3
Mono4
Mono5
Tricaprin
Total Diglycerides
Total Triglycerides
Internal Standard
Tricaprin
Next
Previous
New Component
Delete Component
Edit Component
OK
Cancel
Apply
The name by which the component is to be identified and labeled

Diglicerídeos





Triglicerídeos



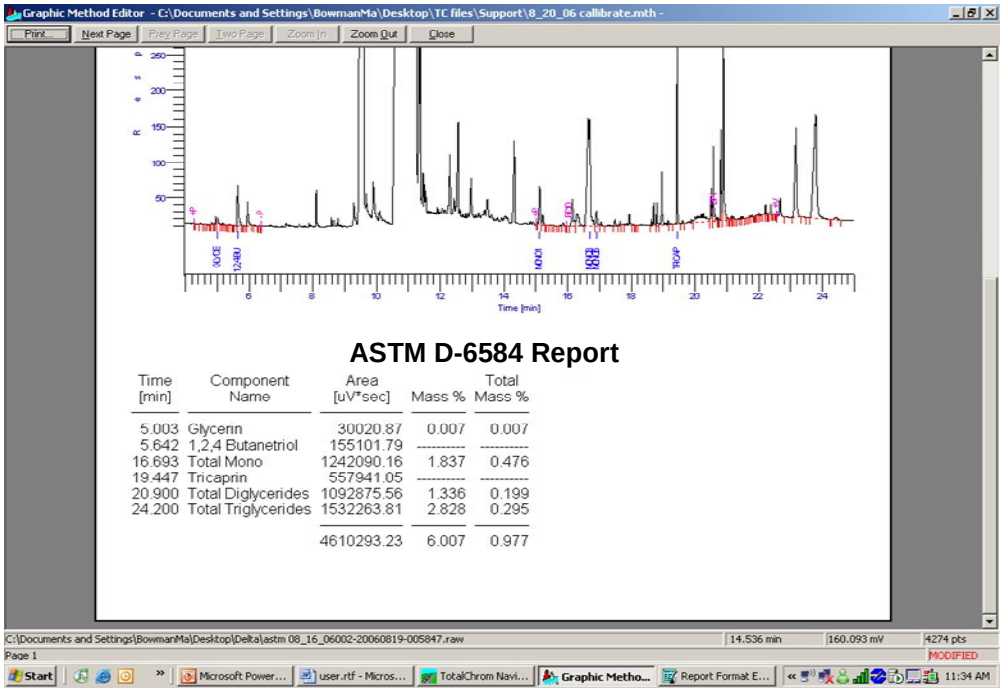
The Mono-, Di- and Tri- glycerides have a portion of the molecule due to glycerin structure. This is the bound glycerin. Only the glycerin portion of the glycerides are to be included in the total glycerin in the biodiesel. This requires each of the calculated glycerides to be multiplied by a factor relating to the glycerin portion prior to summing all the results.

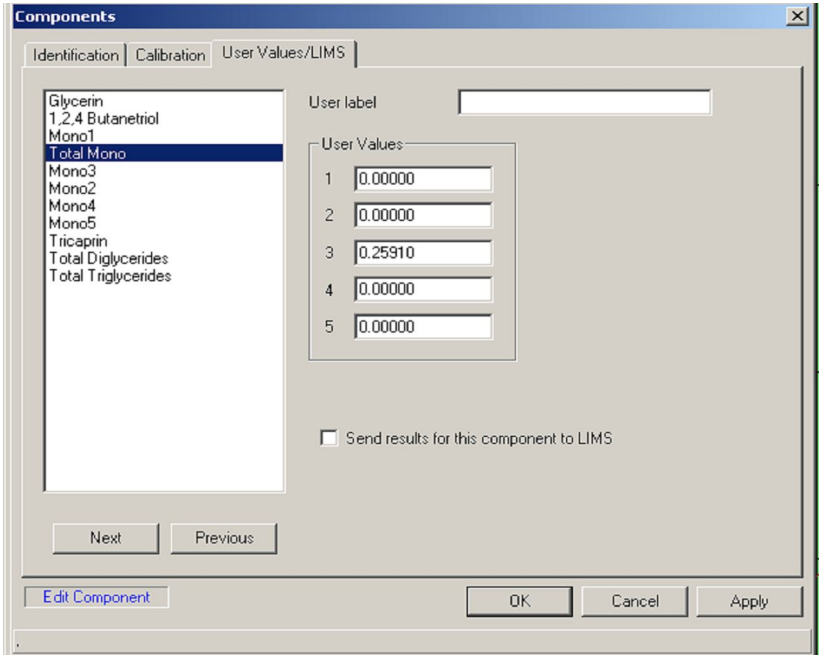
Example, per the ASTM D-6584:

Glycerin	**0.015 * 1.0000 = 0.015**
Total Monoglycerides	**0.016 * 0.2591 = 0.004**
Total Diglycerides	**0.194 * 0.1488 = 0.029**
Total Triglycerides	**0.032 * 0.1044 = 0.003**

Total Glycerin = 0.051 % mass

Make sure your data-handling package can do this without exporting to some other second party software





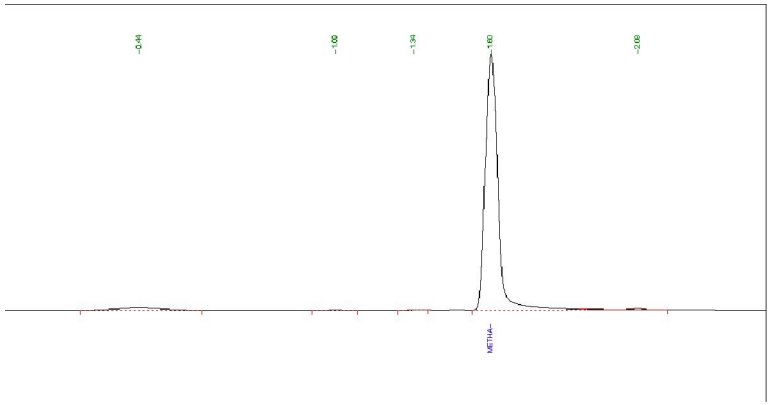
Mét. EN14110 - Metanol

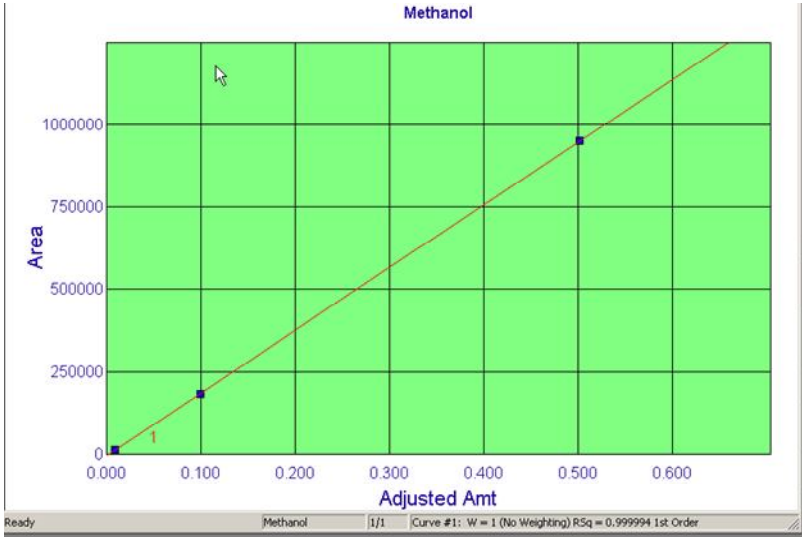
- **Methanol is used in the reaction process with a catalyst to create the fatty acid methyl ester, glycerin is formed as a by product**
- **Residual methanol and glycerin are removed by washing with water 4 to 6 times or more**
- **Methanol can be tested by:**
  - **Flashpoint**
    - **Quantification is Highly subjective and slow**
  - **Infrared Spectroscopy**
    - **Below 1% methanol is difficult to quantitate**
  - **Gas Chromatography**
    - **EN 14110 – Headspace GC**
    - **ASTM methods yet to be created**

Europe utilizes a HS-GC technique for determination of residual MeOH, this is a simple technique. No ASTM method exists yet. Most users follow EN 14110 or modify EN 14110.

- **5 g of biodiesel is added to a 20 mL HS vial, with 5 µL of 2-propanol (ISTD),or ESTD procedure is also accepted**
- **The vial is heated and equilibrated, by the HS instrument, at 80 ºC for 45 min**
- **Manual headspace injection is allowed but automated HS injection is recommended in the EN 14110 method**

Any of several columns can be used, none are compatible in the same GC oven as the glycerin column due to the high temperature of the glycerin analysis, therefore a second GC is required.





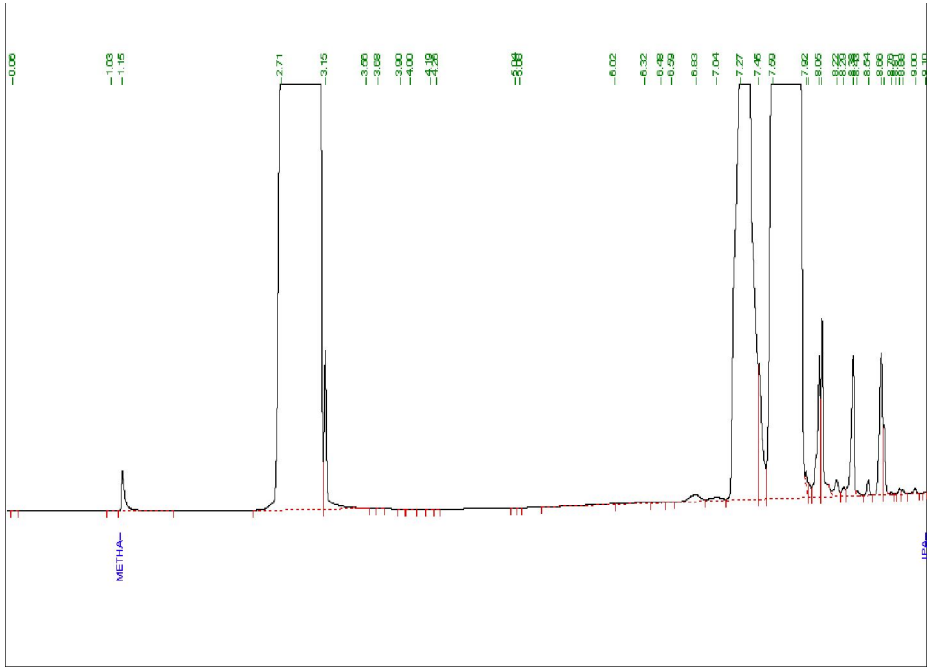
METANOL – INJEÇÃO DIRETA

- Simplest and least expensive method, but not recommended
- Utilizes same GC and column as glycerin analysis
- Biodiesel sample is diluted with heptane or injected neat
- Internal Standard can be used
- Not as accurate and slower than headspace
- Methanol is unretained and therefore co-elutes with any very minor unretained artifacts (biggest reason for not recommended)
- Probably not acceptable once ASTM method is created

Instrument Conditions:

- POC inlet: 50 ºC initial, hold for 2 minutes, ramp to 380 ºC
- FID: 380 ºC
- Oven: 50 ºC initial, hold for 2 minutes, ramp to 380 ºC

Method takes approximately 9 minutes



Minicursos CRQ-IV - 2009

Soluções em Quím. Analítica para Biodiesel e Bioetanol

Biodiesel Glycerin & Methanol Analyzer

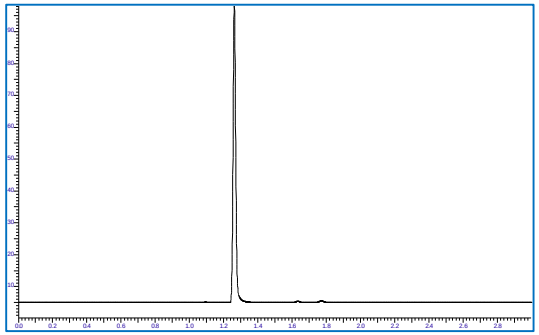
ASTM D6584, EN 14105, EN 14110

Automated headspace sampler optimizes productivity and simplifies sample preparation

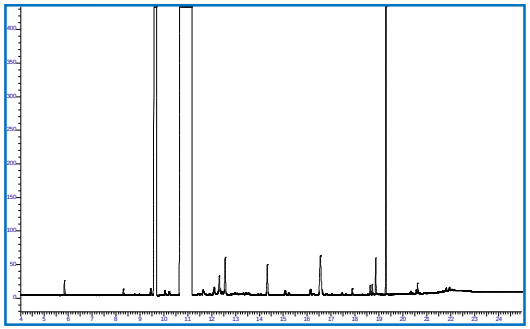
Two Solutions in One: Dual oven to complete both GC analyses on a single instrument; no need to modify hardware setup or swap columns

Rapid Ramp-up - complete package with instrument, software, SOPs, consumables, application-specific installation and qualification procedures

Clarus® 500 GC
ırboMatrix™ Headspace



0.1% methanol in a biodiesel matrix



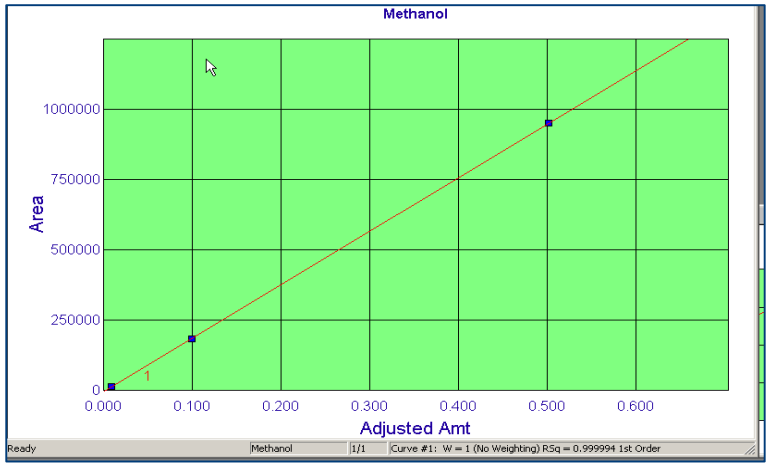
Analysis of a biodiesel sample for free and total glycerin.

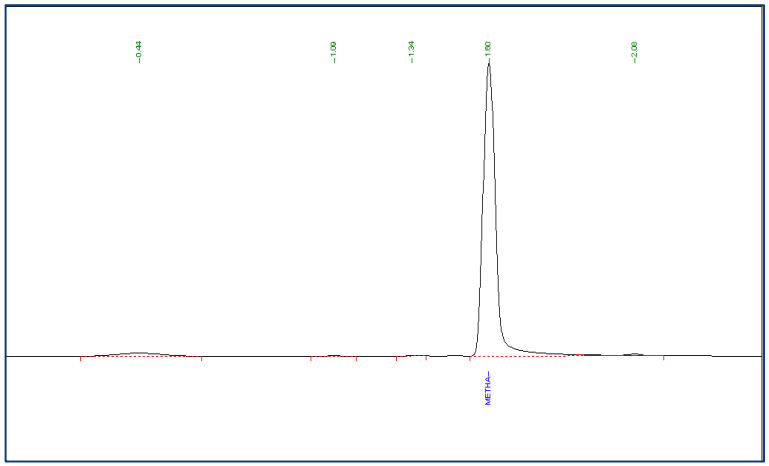
ASTM D6584/EN14105 Report

Time [min]	Component Name	Area [uV*sec]	Total Mass %
4.442	Glycerin	7405.23	0.014
5.159	1,2,4 Butanetriol (ISTD)	144966.27	----------
15.53	Total Monoglycerides	515808.44	0.142
18.95	Tricaprin (ISTD)	515249.64	----------
20.31	Total Diglycerides	82765.76	0.011
22.44	Total Triglycerides	116084.59	0.004
	Total Glycerides		0.171

The EcoAnalytix™ Biodiesel Glycerin & Methanol Analyzer

- All of the benefits from the Clarus 500 GC plus the very best from TurboMatrix HS
- 12-sample overlapping heating oven for high throughput
- Pressure balanced injection
- Very reliable and repeatable sampling





Biodiesel FAME Determination by GC

EN 14103

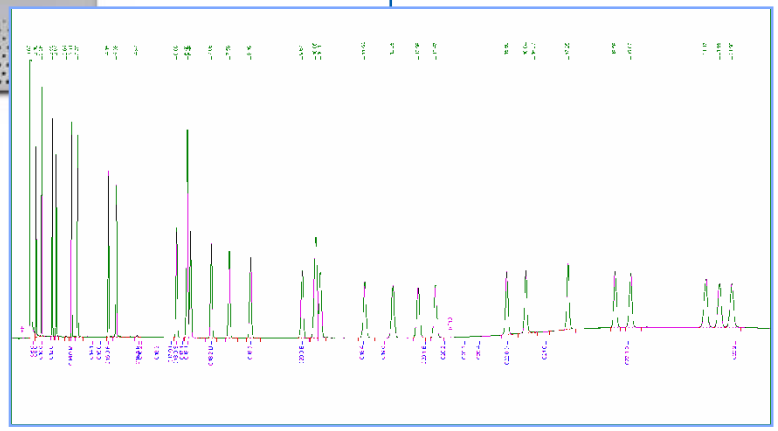
Profiling the source of feedstock, looking for unwanted by-products

Calculation of different parameters from FAME profile, like iodine number, degree of transesterification, etc.

Rapid Ramp-up of sampling and analysis with consumables package

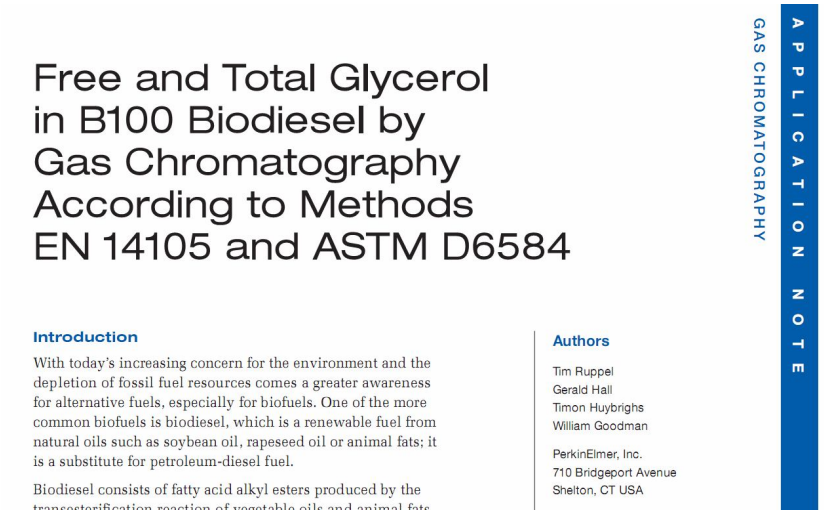
Clarus® 500 GC

Intuitive touch-screen interface allows quick set up and operation



GC chromatogram FAME standard C14:0 to C24:1

APLICATIVOS PERKINELMER



GAS CHROMATOGRAPHY

APPLICATION NOTE

Free and Total Glycerol in B100 Biodiesel by Gas Chromatography According to Methods EN 14105 and ASTM D6584

Introduction

With today's increasing concern for the environment and the depletion of fossil fuel resources comes a greater awareness for alternative fuels, especially for biofuels. One of the more common biofuels is biodiesel, which is a renewable fuel from natural oils such as soybean oil, rapeseed oil or animal fats; it is a substitute for petroleum-diesel fuel.

Biodiesel consists of fatty acid alkyl esters produced by the

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Gerald Hall
Timon Huybrighs
William Goodman

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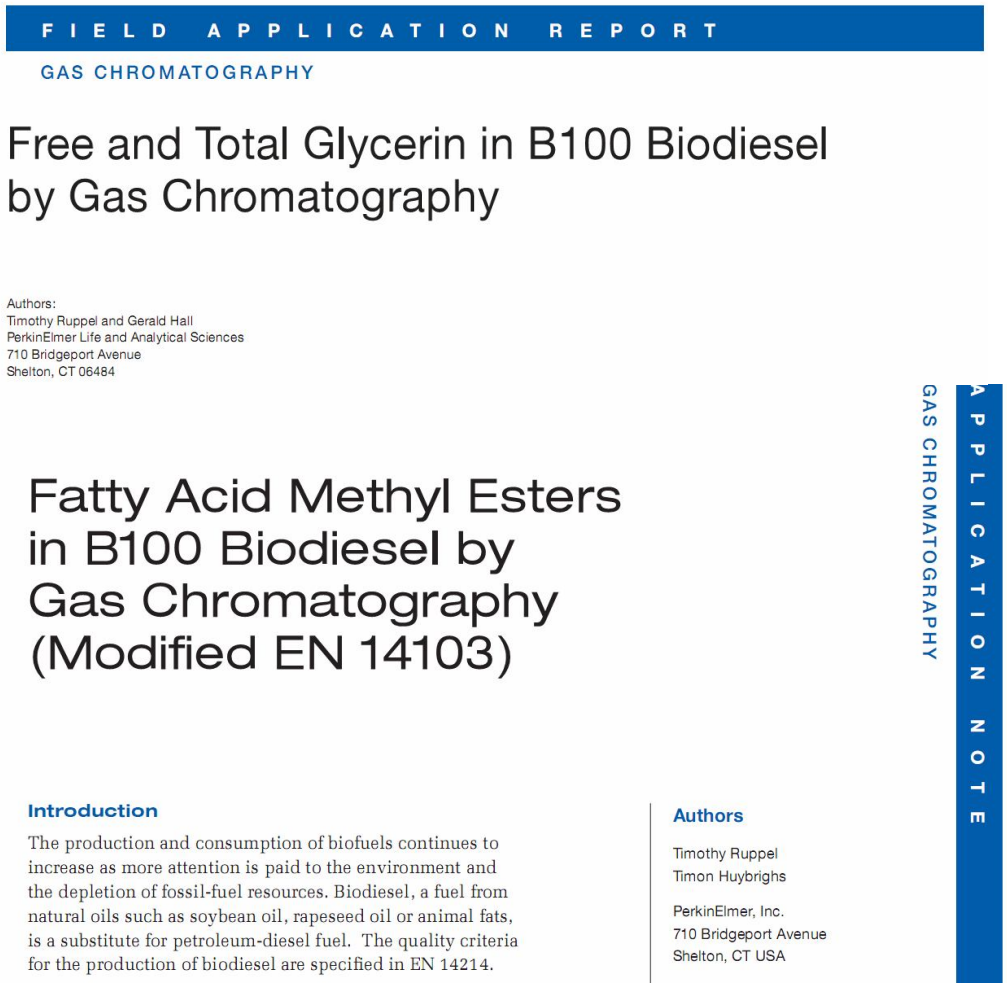

FIELD APPLICATION REPORT

GAS CHROMATOGRAPHY

Free and Total Glycerin in B100 Biodiesel by Gas Chromatography

Authors:
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PerkinElmer Life and Analytical Sciences
710 Bridgeport Avenue
Shelton, CT 06484

GAS CHROMATOGRAPHY

APPLICATION NOTE

Fatty Acid Methyl Esters in B100 Biodiesel by Gas Chromatography (Modified EN 14103)

Introduction

The production and consumption of biofuels continues to increase as more attention is paid to the environment and the depletion of fossil-fuel resources. Biodiesel, a fuel from natural oils such as soybean oil, rapeseed oil or animal fats, is a substitute for petroleum-diesel fuel. The quality criteria for the production of biodiesel are specified in EN 14214.

Authors

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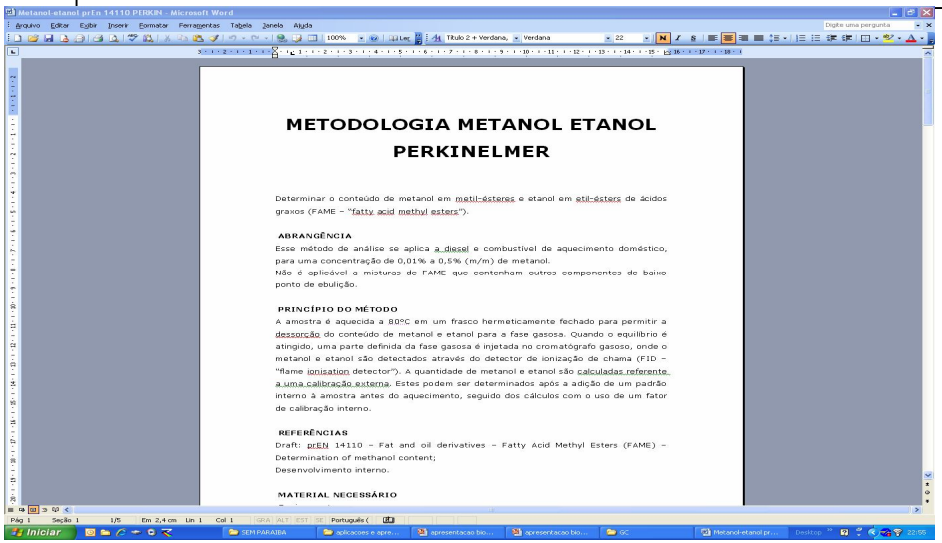
Minicursos CRQ-IV - 2009

Soluções em Quím. Analítica para Biodiesel e Bioetanol

APLICATIVOS PERKINELMER BRASIL



METODOLOGIA METANOL ETANOL
PERKINELMER

Determinar o conteúdo de metanol em metil-ésteres e etanol em etil-ésters de ácidos graxos (FAME – "fatty acid methyl esters").

ABRANGÊNCIA

Esse método de análise se aplica a diesel e combustível de aquecimento doméstico, para uma concentração de 0,01% a 0,5% (m/m) de metanol.
Não é aplicável a misturas de FAME que contenham outros componentes de baixo ponto de ebulição.

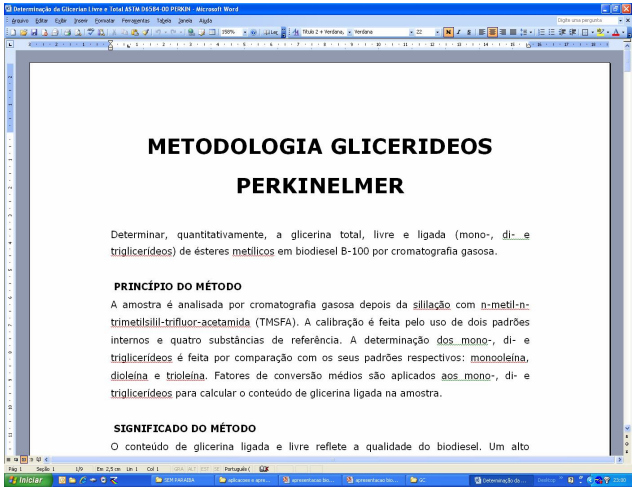
PRINCÍPIO DO MÉTODO

A amostra é aquecida a 80ºC em um frasco hermeticamente fechado para permitir a dessorção do conteúdo de metanol e etanol para a fase gasosa. Quando o equilíbrio é atingido, uma parte definida da fase gasosa é injetada no cromatógrafo gasoso, onde o metanol e etanol são detectados através do detector de ionização de chama (FID – "flame ionisation detector"). A quantidade de metanol e etanol são calculadas referente a uma calibração externa. Estes podem ser determinados após a adição de um padrão interno à amostra antes do aquecimento, seguido dos cálculos com o uso de um fator de calibração interno.

REFERÊNCIAS

Draft: prEN 14110 – Fat and oil derivatives – Fatty Acid Methyl Esters (FAME) – Determination of methanol content;
Desenvolvimento interno.

MATERIAL NECESSÁRIO



METODOLOGIA GLICERIDEOS
PERKINELMER

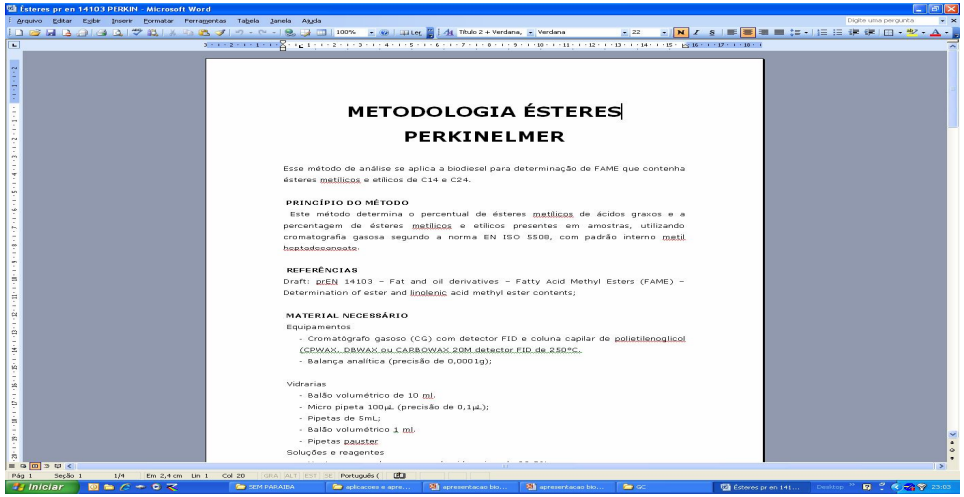
Determinar, quantitativamente, a glicerina total, livre e ligada (mono-, di- e triglicerídeos) de ésteres metílicos em biodiesel B-100 por cromatografia gasosa.

PRINCÍPIO DO MÉTODO

A amostra é analisada por cromatografia gasosa depois da sililação com n-metil-n-trimetilsilil-trifluor-acetamida (TMSFA). A calibração é feita pelo uso de dois padrões internos e quatro substâncias de referência. A determinação dos mono-, di- e triglicerídeos é feita por comparação com os seus padrões respectivos: monooleína, dioleína e trioleína. Fatores de conversão médios são aplicados aos mono-, di- e triglicerídeos para calcular o conteúdo de glicerina ligada na amostra.

SIGNIFICADO DO MÉTODO

O conteúdo de glicerina ligada e livre reflete a qualidade do biodiesel. Um alto



METODOLOGIA ÉSTERES
PERKINELMER

Esse método de análise se aplica a biodiesel para determinação de FAME que contenha ésteres metílicos e etílicos de C14 e C24.

PRINCÍPIO DO MÉTODO

Este método determina o percentual de ésteres metílicos de ácidos graxos e a percentagem de ésteres metílicos e etílicos presentes em amostras, utilizando cromatografia gasosa segundo a norma EN ISO 5508, com padrão interno metil heptadecanoato.

REFERÊNCIAS

Draft: prEN 14103 – Fat and oil derivatives – Fatty Acid Methyl Esters (FAME) – Determination of ester and linolenic acid methyl ester contents;

MATERIAL NECESSÁRIO

Equipamentos
- Cromatógrafo gasoso (CG) com detector FID e coluna capilar de polietilenoglicol (CPWAX, DBWAX ou CARBOWAX 20M detector FID de 250°C.
- Balança analítica (precisão de 0,0001g);

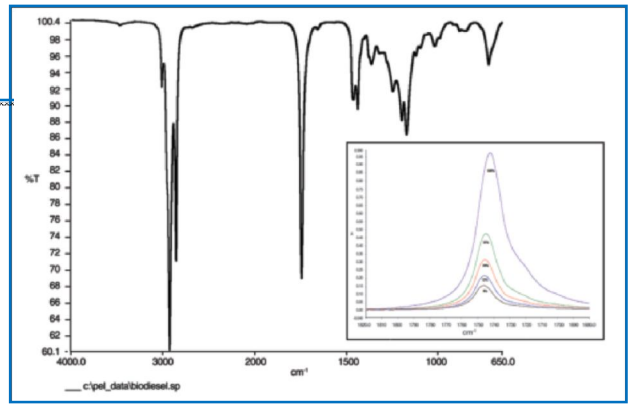
Vidrarias
- Balão volumétrico de 10 ml.
- Micro pipeta 100µL (precisão de 0,1µL);
- Pipetas de 5mL;
- Balão volumétrico 1 ml.
- Pipetas pauster

Soluções e reagentes

Biodiesel IR FAME Analyzer

ASTM D7371, EN 14078

Wide range of accessories for many different sample types



Typical Spectrum for B5 Blend

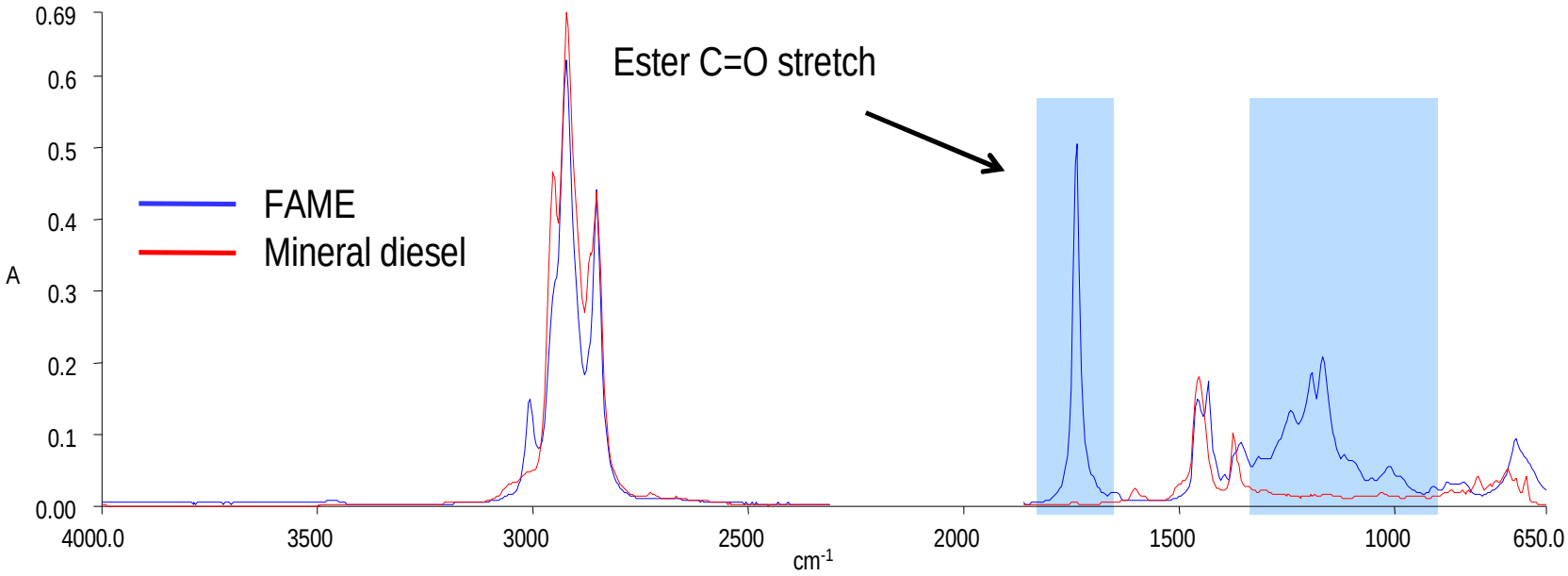
Spectrum 100 FTIR

Rapid Ramp-up

SOPs, consumables package with starter calibration model

Identification and quality of incoming feed stocks; monitoring of conversion process to determine progress of reactions & yield

Biodiesel blend analysis by FTIR



- **EN 14078**
  - **European standard**
  - **Transmission (0.5 mm)**
  - **Linear correlation against carbonyl band**

➢ **ASTM D 7371**

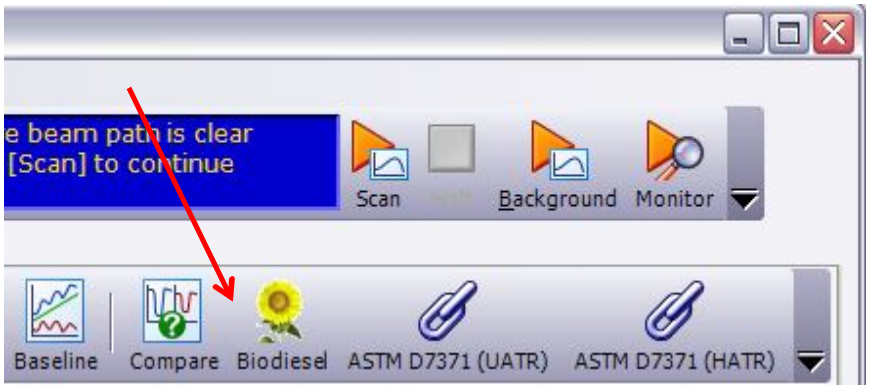
- **American standard**
- **ATR sampling**
- **Chemometric calibration (PLS) using two spectral regions (shaded)**

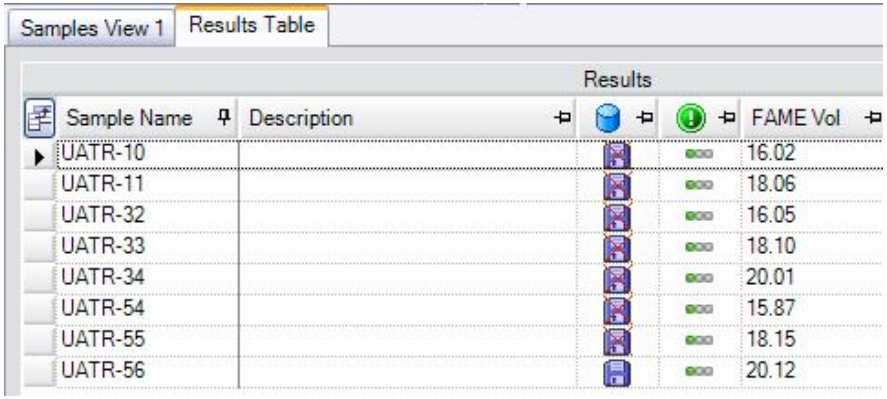
Why use ATR?

- ATR effectively allows a very short pathlength (a few µm)
- No need for sample dilution
- Sample introduction is much easier (no syringes needed)
- Cleaning is very quick and requires minimal solvent
- Diamond ATR maximises the advantages:
  - Extremely durable
  - Excellent reproducibility
  - Extremely easy cleaning

FAME measurement procedure

1. Place one drop of the sample on the ATR crystal
2. Press the Go button to measure the spectrum
3. Clean the crystal
4. Click the Biodiesel button in the Spectrum Express software





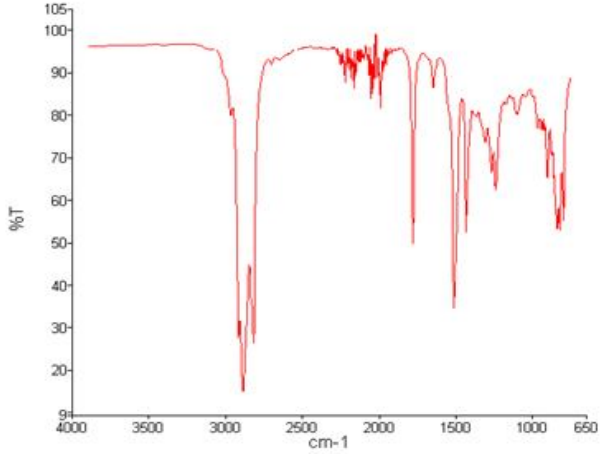
Reporting

- Reports can be automatically printed or saved (.rtf format)
- A running record of analysis results can be saved to a .csv file that can be opened in Excel

PerkinElmer Spectrum Express Version 1.03.00
28/07/2008 18:52

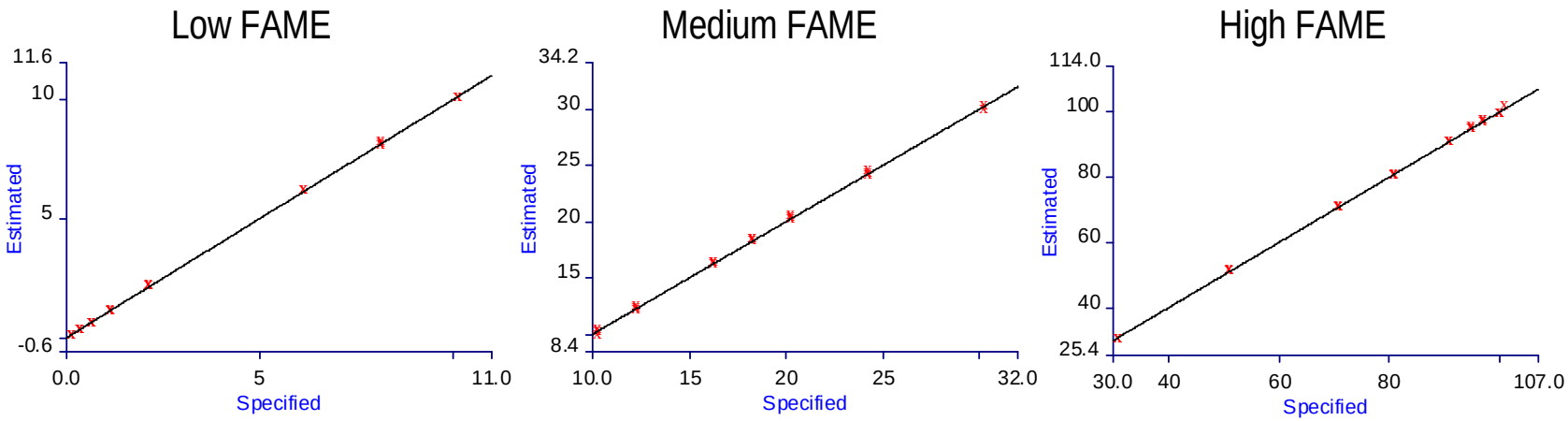
FAME Analysis by ASTM 7371-07 Report

Analyst	Administrator
Date/Time	28 July 2008 18:52
Software Product	PerkinElmer Spectrum Express Version 1.03.00
Report File	C:\pel_data\Biodiesel\ASTM 7371\Reports\2008_7_28\UATR-1_FAME_ASTM_7371(1).rtf
Sample Description	UFAME
Low Concentration (0 - 10%) Quant Method	C:\IQuant\PLS1\Methods\BDUATRA.MD
Low Concentration Component	BioQuest
Medium Concentration (10 - 30%) Quant Method	C:\IQuant\PLS1\Methods\BDUATRB.MD
Medium Concentration Component	BioQuest
High Concentration (30 - 100%) Quant Method	C:\IQuant\PLS1\Methods\BDUATRC.MD
High Concentration Component	BioQuest
Pathength	1



Sample	RMS Value	Peak to Peak Value	Total M-Distance	Residual Ratio	FAME Value
UATR-1	0.0021852	0.0082682	0.85742	1.635	-0.26318

"Starter" calibrations for ASTM D 7371



- Calibration models developed according to ASTM D 7371 methodology, using soy-based biodiesel
- Separate PLS models for 0–10%, 10–30%, 30–100% FAME
- Start using the analyzer immediately

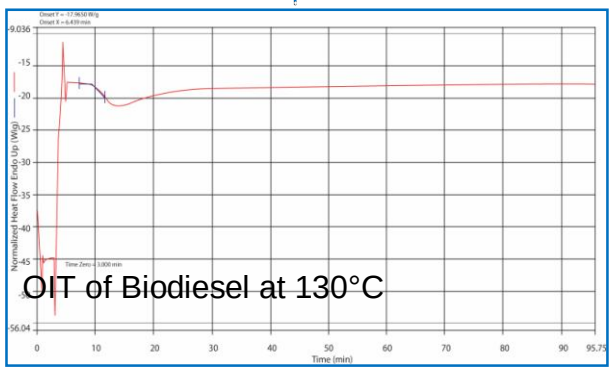
Biodiesel Oxidation Stability Testing by DSC

ASTM D6186

Unique Fast Scan DSC technology for unmatched sensitivity and superior signal resolution so you don't miss transitions

DSC 8000/8500

Quickly screen for oxidation stability in less than 10 minutes



OIT of Biodiesel at 130°C

Sample	1	2	3	4
Oxidation onset temperature (degrees Celsius)	155	167	155	134

Table 1. OT summary

SOURCE: PERKINELMER

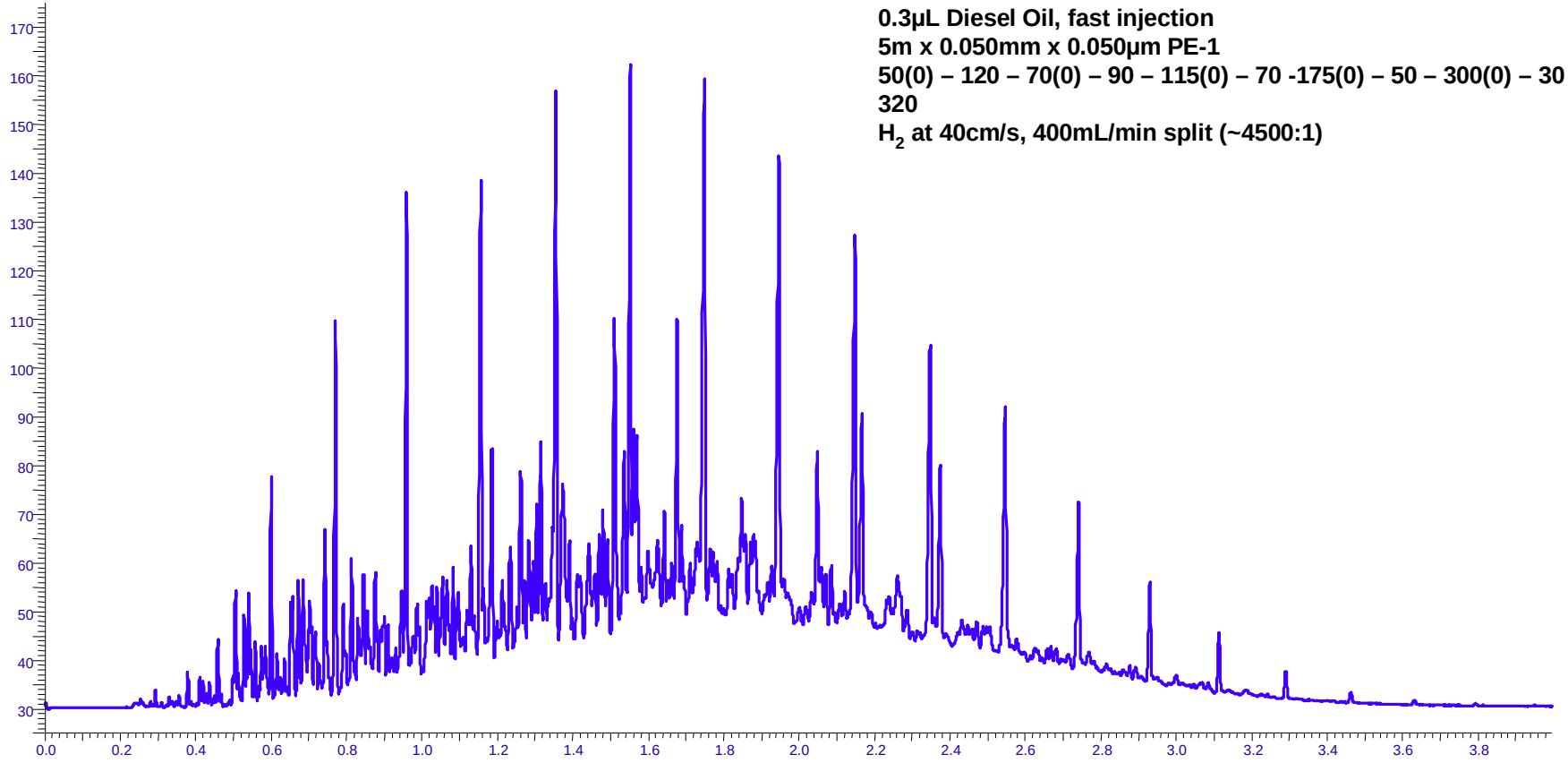
Low-mass furnaces for quick response time and high throughput; Power compensation design for true isothermal measurements

NOVAS TECNOLOGIAS PERKINELMER

High Speed Gas Chromatography

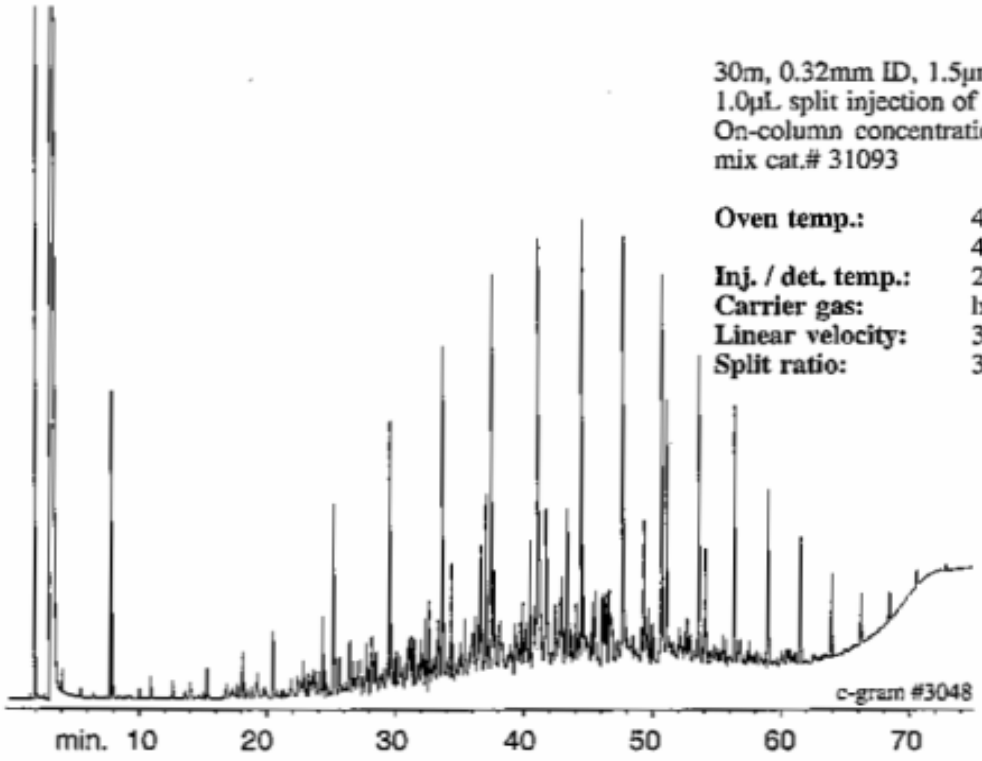
- O que significa "High Speed GC"?
  - Colunas Curtas (~2 a 5 m)
  - Colunas capilares de diâmetro interno muito pequeno (~0,05 m)
  - colunas de filme estreitos
  - programas de temperatura rápidos
  - possibilidade de uso de hidrogênio como gás de arraste
  - fluxos de gás de arraste maiores

Diesel Oil on the Clarus 600 with High Power Heater

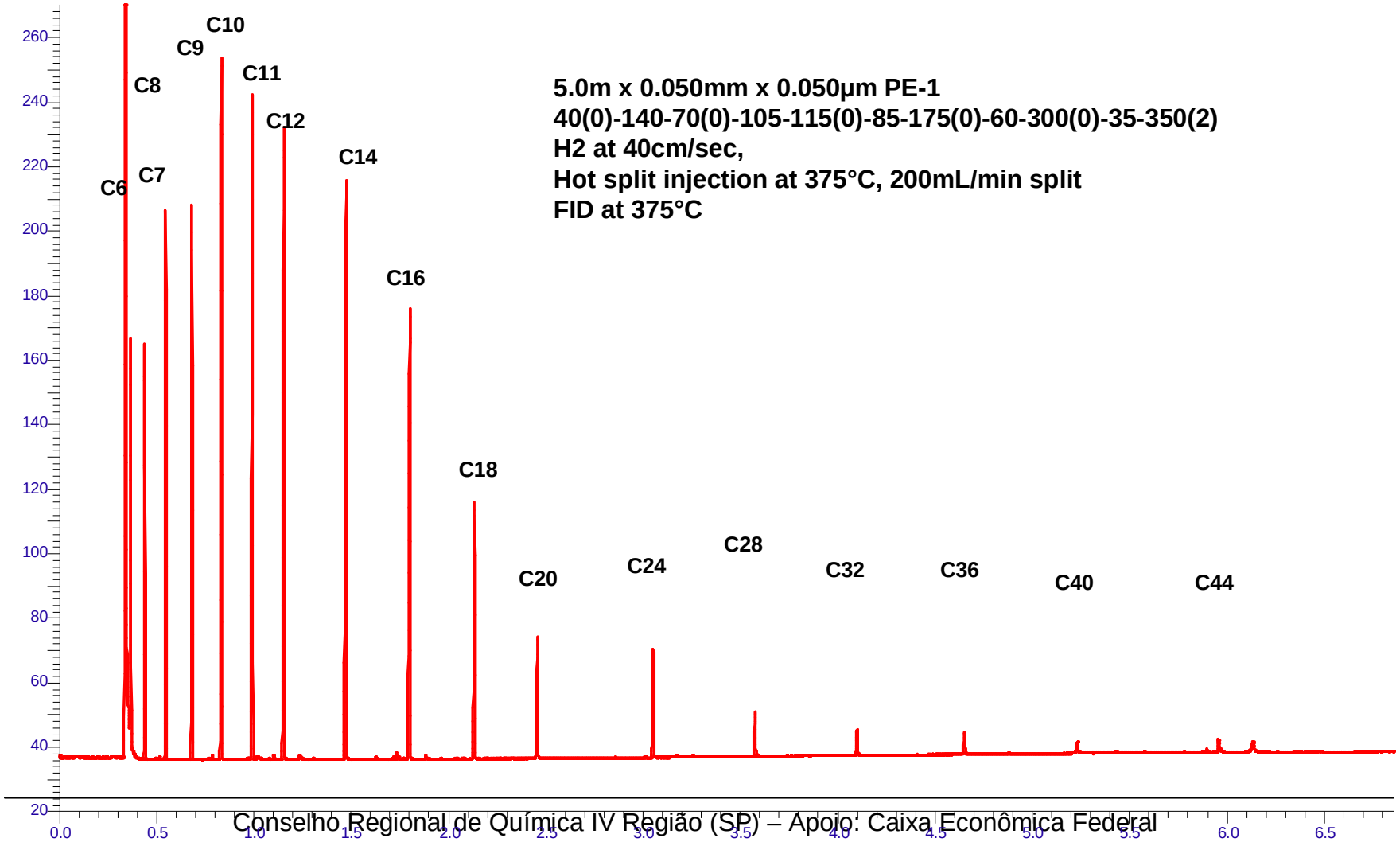


From the Restek Catalog

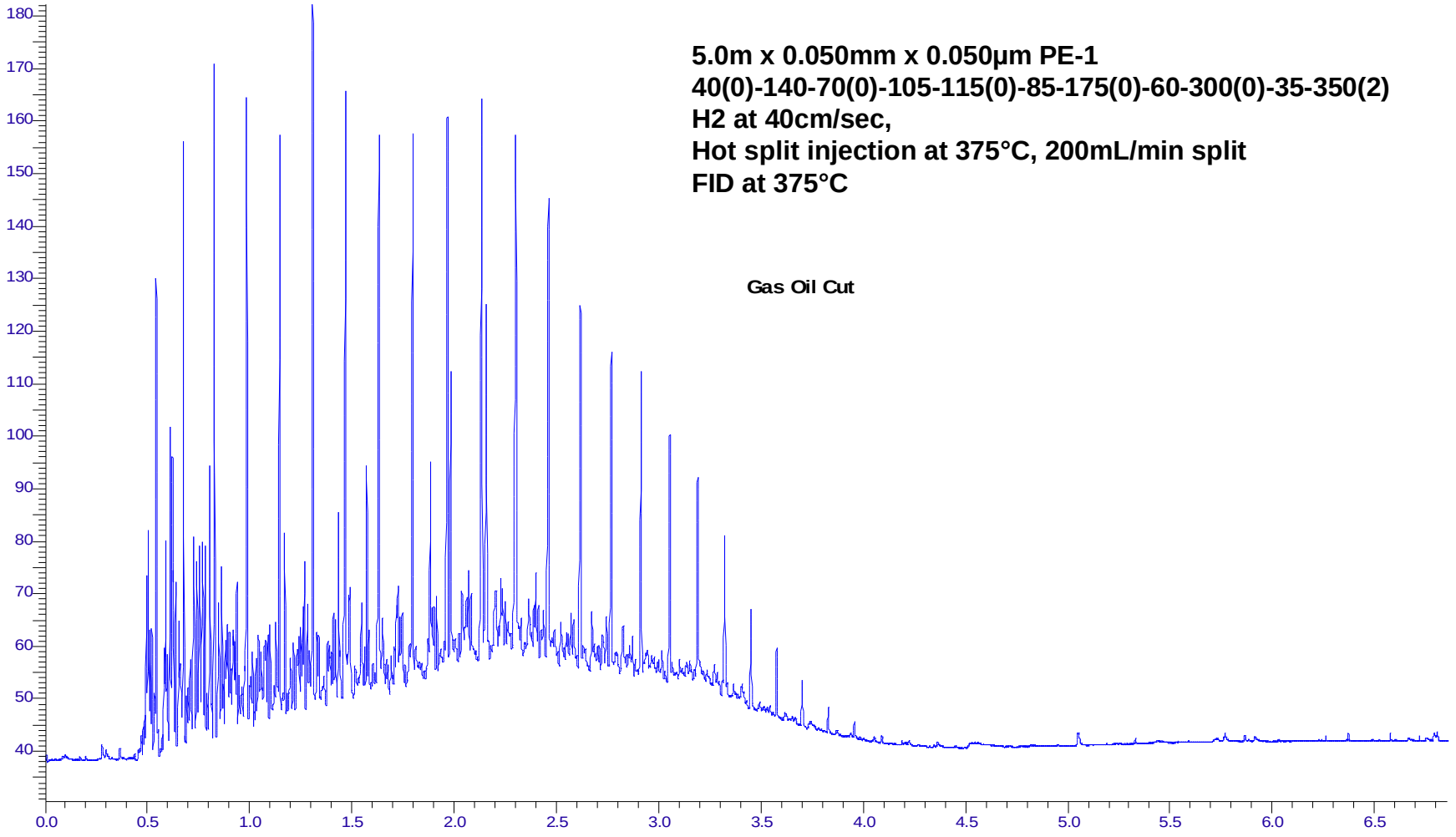
Diesel
Rtx®-1
(split injection)



$C_6 – C_{44}$ ASTM D2887 Calibration Standard



Gas Oil Cut

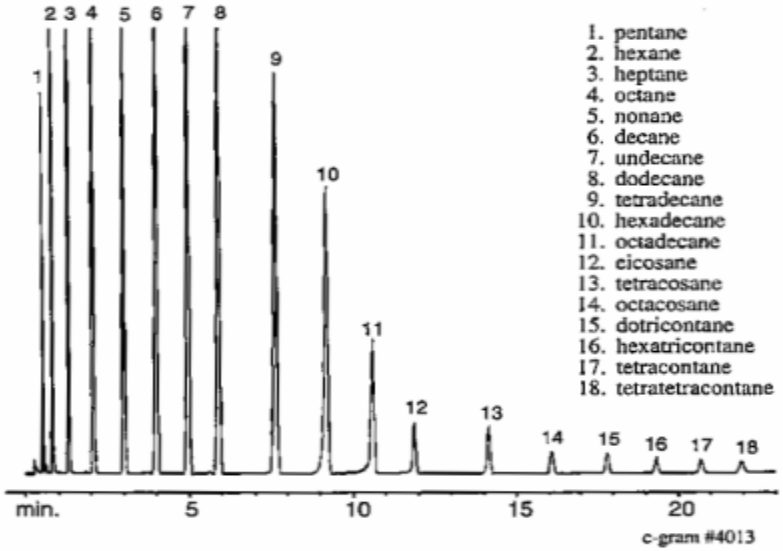

5.0m x 0.050mm x 0.050µm PE-1
40(0)-140-70(0)-105-115(0)-85-175(0)-60-300(0)-35-350(2)
H2 at 40cm/sec,
Hot split injection at 375°C, 200mL/min split
FID at 375°C
Gas Oil Cut
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5

From the Restek Catalog

Sim Dist
ASTM D-2887 C5 to C44 Standard
Rtx®-2887
(direct injection)

10m, 0.53mm ID, 2.65µm Rtx-2887 (cat.# 10199)
1.0µL direct injection of a 0.1 to 0.01 wt % hydrocarbon standard in carbon disulfide.

Oven temp.:	35°C to 360°C @ 15°C/min. (hold 5 min.)
Inj. & det. temp.:	360°C
Carrier gas:	nitrogen
Linear velocity:	112cm/sec. (15mL/min.)

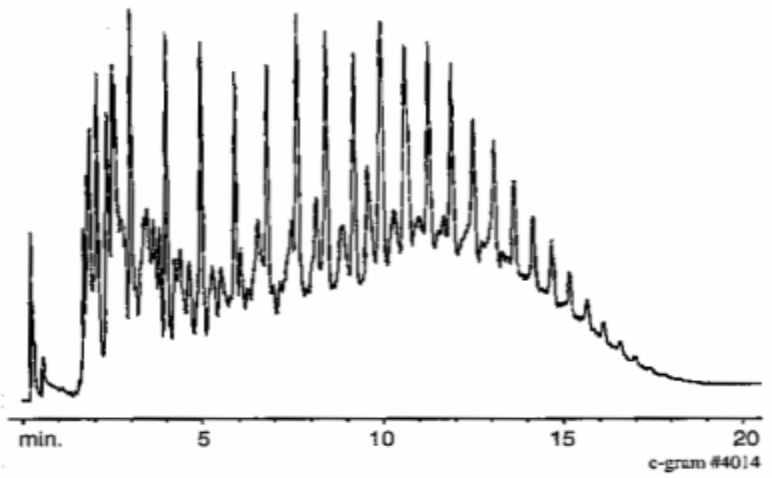


1. pentane
2. hexane
3. heptane
4. octane
5. nonane
6. decane
7. undecane
8. dodecane
9. tetradecane
10. hexadecane
11. octadecane
12. eicosane
13. tetracosane
14. octacosane
15. dotricontane
16. hexatricontane
17. tetracontane
18. tetratetracontane

Sim Dist
ASTM D-2887 Reference Gas Oil #1
Rtx®-2887
(direct injection)

10m, 0.53mm ID, 2.65µm Rtx-2887 (cat.# 10199)
1.0µL direct injection of a 0.1 to 0.01 wt % hydrocarbon standard in carbon disulfide.

Oven temp.:	35°C to 360°C @ 15°C/min. (hold 5 min.)
Inj. & det. temp.:	360°C
Carrier gas:	nitrogen
Linear velocity:	112cm/sec. (15mL/min.)



SWAFER

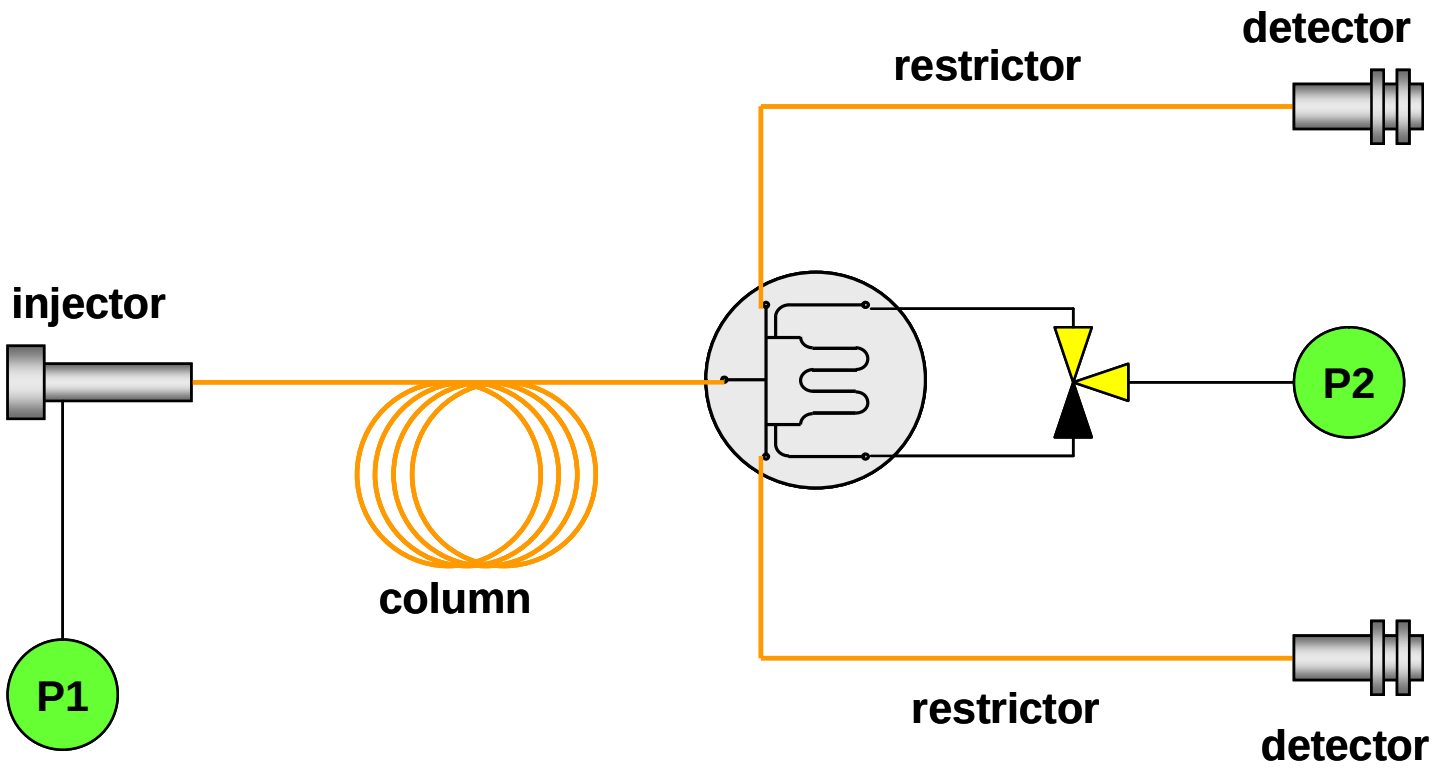
- SWAFER
  - EXISTEM DOIS SWAFER :
  - D-SWAFER E O S-SWAFER
  - D-SWAFER
    - PODE-SE FAZER BACKFLUSH DE MAIS PESADOS E TAMBÉM DO SOLVENTE QUE FOI INJETADO
    - PODE-SE FAZER SPLIT DE UMA COLUNA PARA 2 DETECTORES , OU 2 COLUNAS PARA UM INJETOR
    - PODE-SE FAZER DESVIO DE SUBSTÂNCIAS QUE : NÃO SEPARAM EM UMA COLUNA E “JOGAR” ESSAS SUBSTÂNCIAS EM OUTRA COLUNA, COMO UM SISTEMA GCXGC.
    - PERMITE DEIXAR INSTALADOS HEADSPACE E INJETOR LÍQUIDO, OU COM ATD
    - S-SWAFER , APLICAÇÕES MAIS RESTRITAS

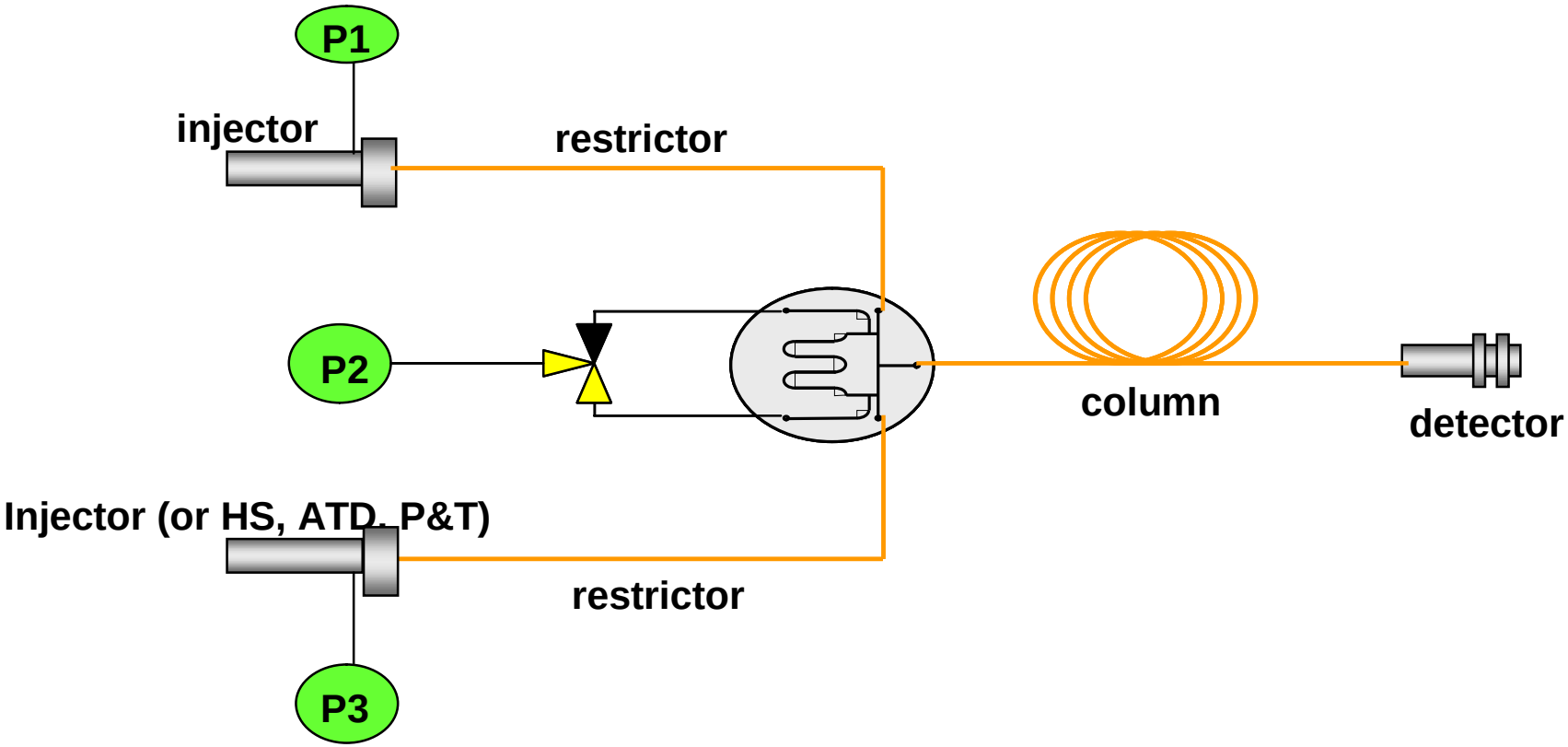
Figure 1. The switching and splitting wafers

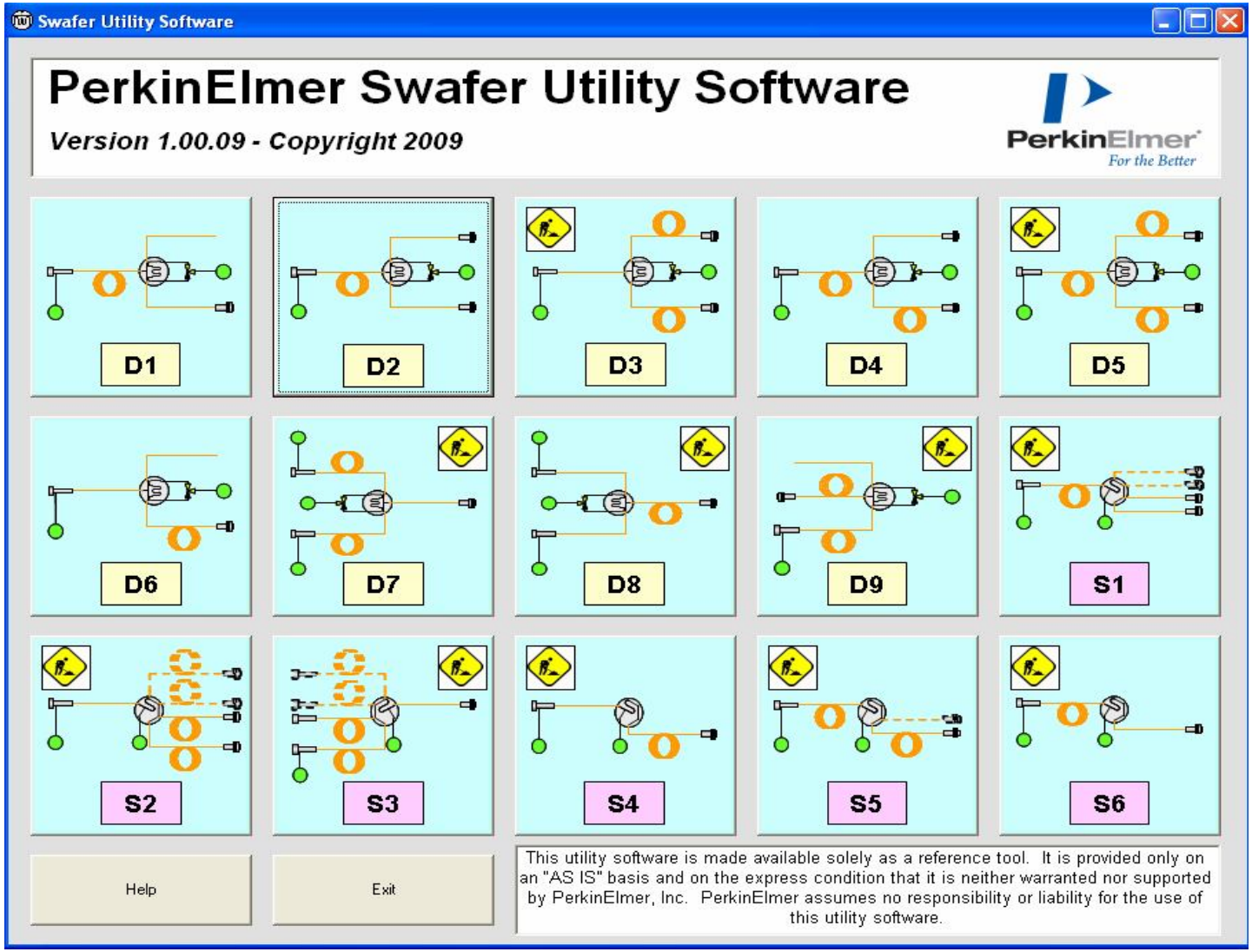
Figure 2. Installing the wafer in the holder

Figure 3. Wafer mounted in the threaded holder

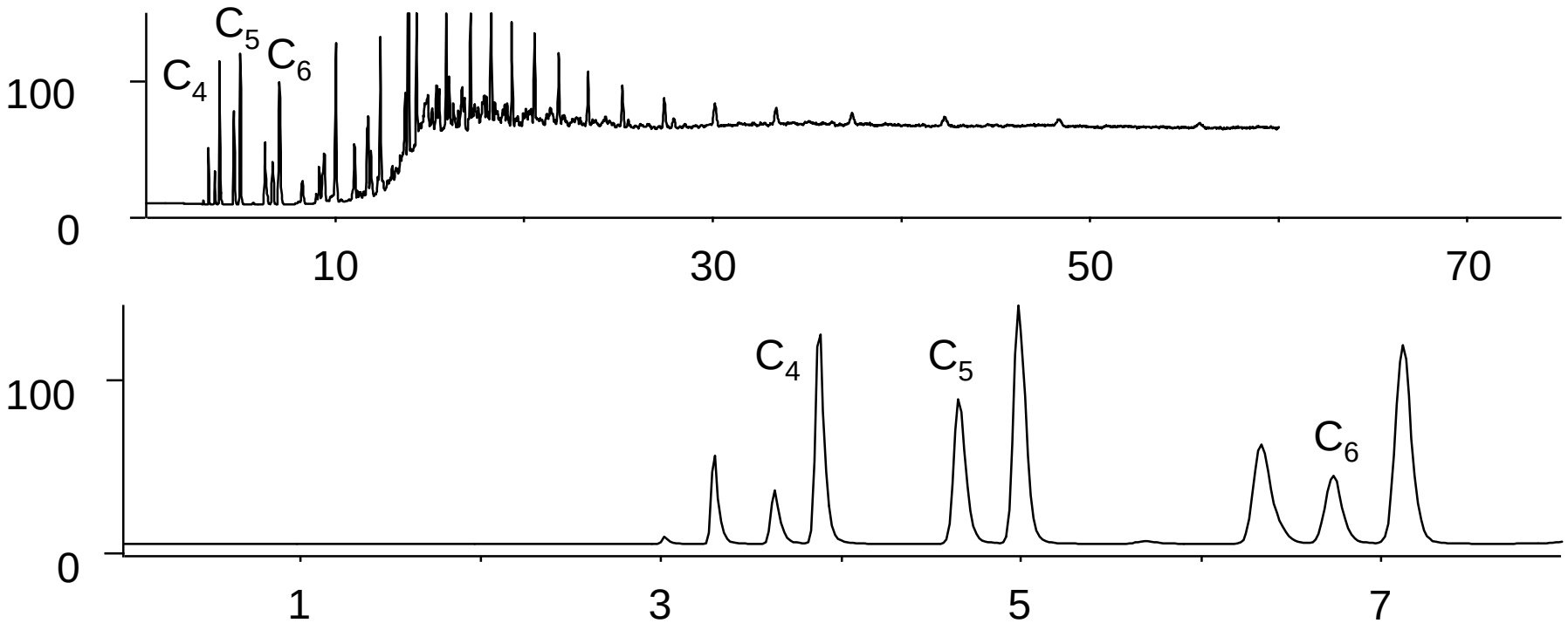
Figure 4. The holder containing the wafer mounted on the GC oven wall and external connections being made.


detector
restrictor
injector
P2
column
P1
restrictor
detector


P1
injector
restrictor
P2
column
detector
Injector (or HS, ATD, P&T)
restrictor
P3

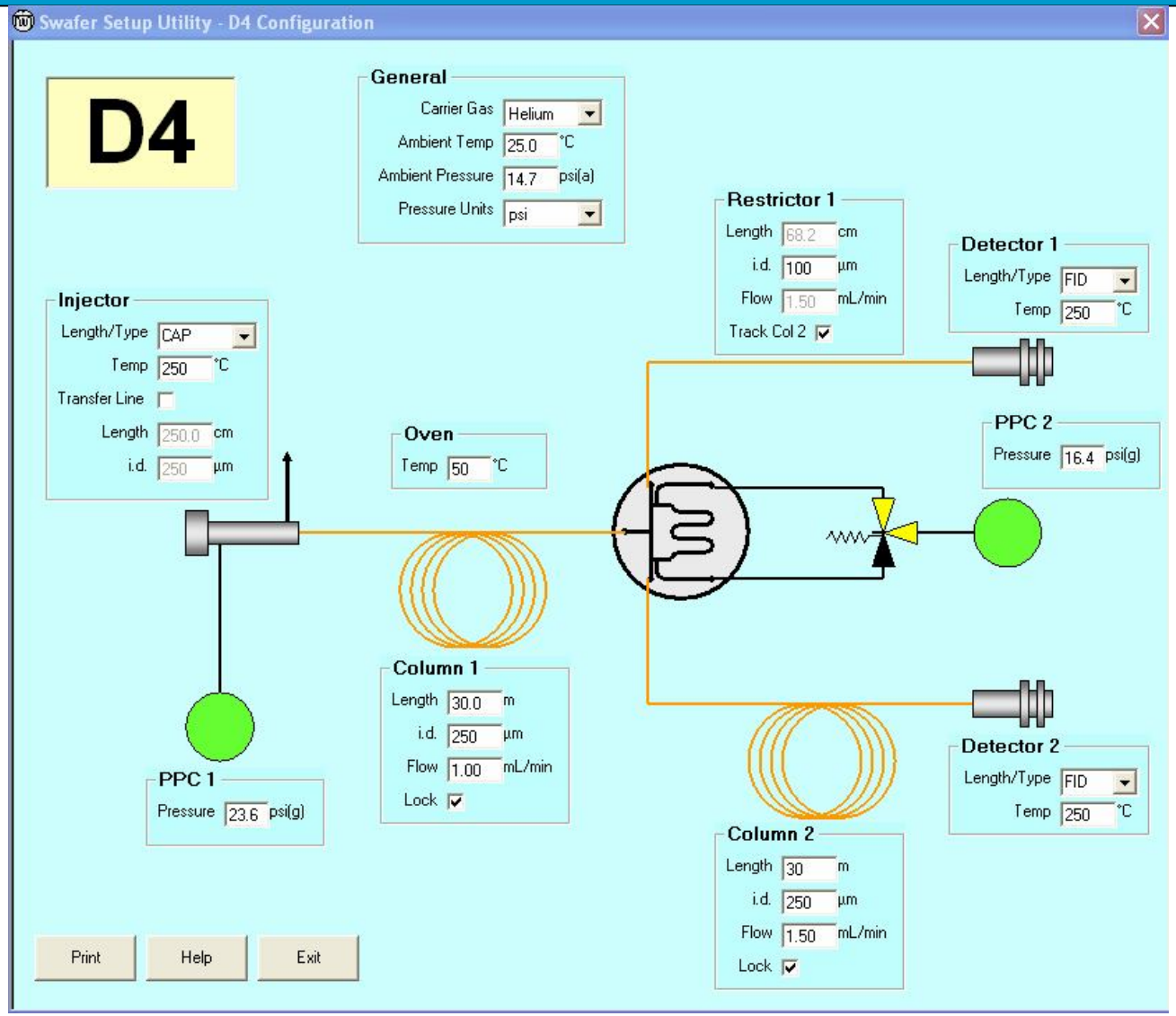

Swafer Utility Software
PerkinElmer Swafer Utility Software
Version 1.00.09 - Copyright 2009
PerkinElmer
For the Better
D1
D2
D3
D4
D5
D6
D7
D8
D9
S1
S2
S3
S4
S5
S6
Help
Exit
This utility software is made available solely as a reference tool. It is provided only on an "AS IS" basis and on the express condition that it is neither warranted nor supported by PerkinElmer, Inc. PerkinElmer assumes no responsibility or liability for the use of this utility software.

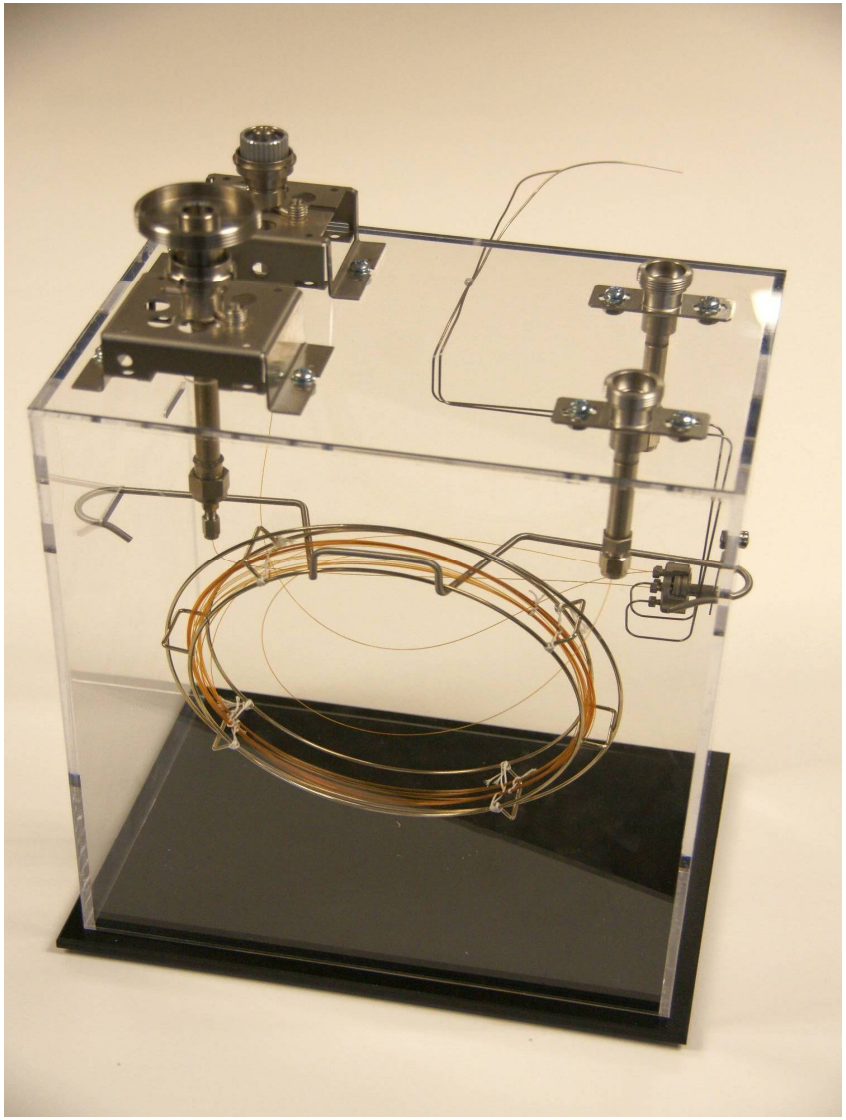
Makes backflushing easy – get rid of unwanted components



Significantly reduces runtime

Less wear on column; therefore, they last longer … reduces costs


Swafer Setup Utility - D4 Configuration
D4
General
Carrier Gas Helium
Ambient Temp 25.0 °C
Ambient Pressure 14.7 psi(a)
Pressure Units psi
Restrictor 1
Length 68.2 cm
i.d. 100 µm
Flow 1.50 mL/min
Track Col 2
Detector 1
Length/Type FID
Temp 250 °C
Injector
Length/Type CAP
Temp 250 °C
Transfer Line
Length 250.0 cm
i.d. 250 µm
Oven
Temp 50 °C
PPC 2
Pressure 16.4 psi(g)
Column 1
Length 30.0 m
i.d. 250 µm
Flow 1.00 mL/min
Lock
PPC 1
Pressure 23.6 psi(g)
Detector 2
Length/Type FID
Temp 250 °C
Column 2
Length 30 m
i.d. 250 µm
Flow 1.50 mL/min
Lock
Print
Help
Exit



MÉTODOS ANALÍTICOS PARA BIOETANOL

Bioethanol

Property	European Union	United States	Brazil	Technology	PKI Capability
	pr EN 15376	ASTM D4806			
Ethanol: %vol	Calculated	ASTM D5501	ASTM D5501	GC	✓
Ethanol + C3-C5 sat alcohols: %vol	DIN 51627-3	ASTM D4052		GC	✓
C3-C5 sat alcohols: %vol	DIN 51627-3	Calculated		GC	✓
Methanol content: %vol	DIN 51627-3	ASTM D5501		GC	✓
Denaturant: %vol *	*Set by country*			GC	✓
Hydrocarbons: %vol *			NBR 13993	GC	✓
Copper: mg/kg**	EN 15488	ASTM D1688	NBR 10893	ICP	✓
Sodium: mg/kg**				ICP	✓
Iron: mg/kg**				ICP	✓
Phosphorous: mg/l**	EN 15487			ICP	✓
Sulfur: mg/kg**	EN 15485/EN 15486	ASTM D2622/5453	NBR 9867	ICP	✓
Fermantation process***				LC	✓
^{14}C- Content in Biofuels****				LSC	✓

* not specified yet, can be measured by GC

** Intended to be measured by ICP-OES

*** not specified yet, can be measured by LC

**** not specified yet, can be measured by LSC

Bioethanol Alcohol Determination by GC

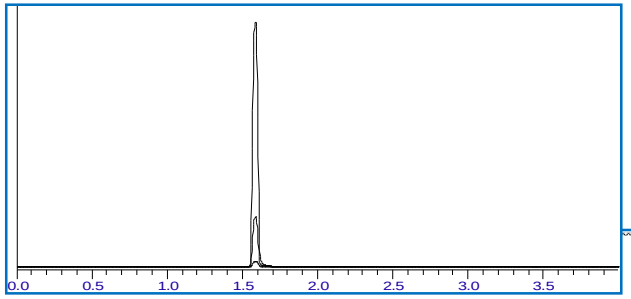
ASTM D5501, DIN 51627-3

Fastest heat-up and cool-down conventional GC oven optimizes productivity

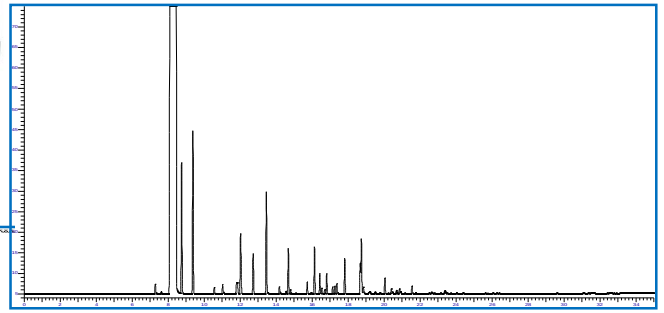
Rapid Ramp-up - consumables package with calibration standards provided

Clarus® 600 GC

For determination of methanol, ethanol, other alcohols ranging from C1 to C5 (extending to C10) and other denaturants (hydrocarbons and aldehydes)



Overlay of Calibration standards



Typical Chromatogram of Bioethanol

Ethanol for Fuel - ASTM D5501

- Clarus 500/600 GC with Liquid Autosampler and programmable pressure control (PPC)
- TotalChrom control and data handling software
- Capillary Injector
- Flame Ionization Detector (FID)
  - Ethanol 93-97%
  - Methanol 0.1-0.6%
  - Higher boiling components 3-6% total

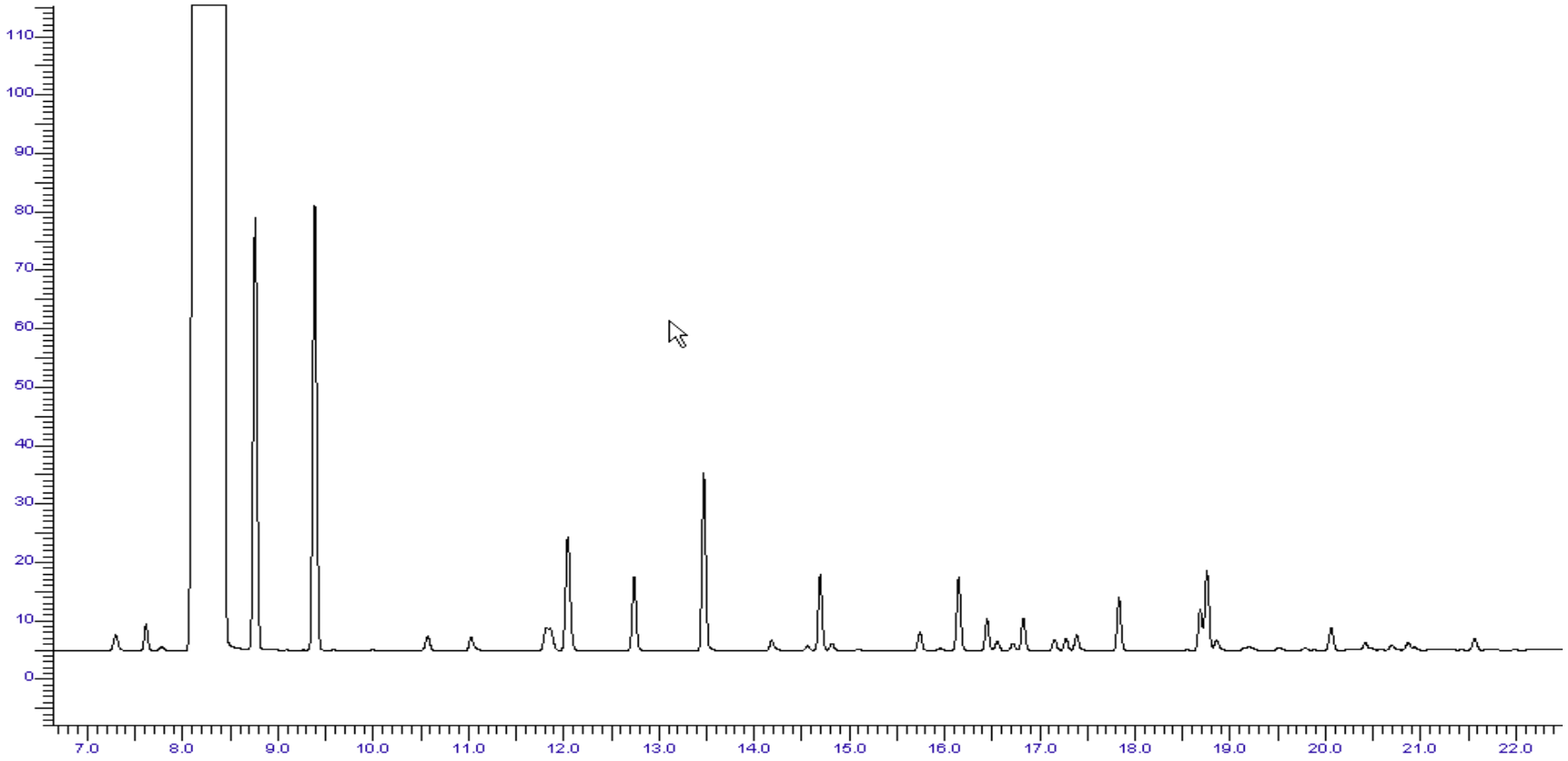
Inside the oven:

Column- Elite 1, 100-150 meter, 0.5 um film thickness, 0.25 mm ID

- Any column allowed that can give separation
- Long columns = long analysis time
- Some people use 30m BAC1 type column for 10 min analysis

- Ethanol can be blended into gasoline E10 - E85
  - Pure ethanol at Indy 500

Ethanol fuel by GC/FID; 100m x 250u x 0.5u RTx1-PONA



Ethanol fuel contaminant compounds

	Sys1
methanol	7.28
acetaldehyde	7.28
acetal (1,1-diethoxy ethane)	7.28
ethanol 0.5min wide	8.06
acetone	8.80
isopropyl alcohol	9.16
ethyl formate	9.53
t-butyl alcohol	9.91
n-propyl alcohol	11.12
2-butanol	13.02
ethyl acetate	13.51
isobutanol (2-methyl-1-propanol)	14.19
1-butanol	15.71
isoamyl alcohol (3-methyl-1-butanol)	18.70
n-amyl alcohol (1-pentanol)	19.93
active amyl alcohol (sec-butanol)(2-methyl-1-butanol)	
System 1: 100m x 250u x 0.5u RTx1 PONA	No resolution acetaldehyde/methanol
25cm/sec H2 @ 40degC	Poor resolution high conc ethanol/acetone/ipoh/ethyl formate
40(12)20deg/min250(10) =35min	marginal resolution high conc ethanol/t butanol
0.5ul inj split 40ml/min	capable of 10ppm, maybe down to 2ppm

Bioethanol Fermentation Determination by LC

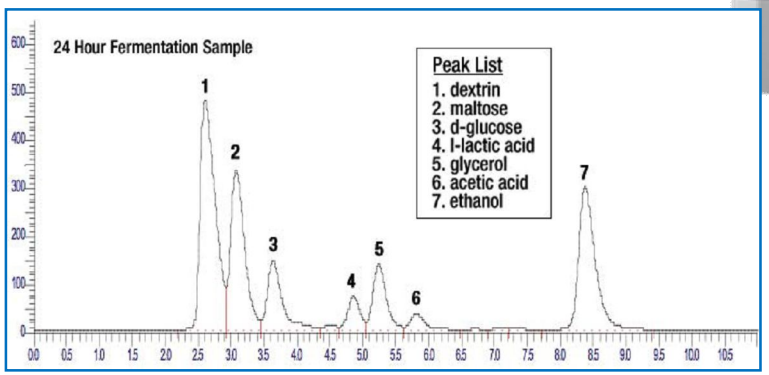
Fermentation Broth Analysis

Flexar HPLC
Refractive Index Detector

Excellent reporting capabilities with TotalChrom

Fastest method for determining ethanol produced and monitoring of fermentation broth – now only 10 minutes

Determines wanted and unwanted by-products during fermentation process



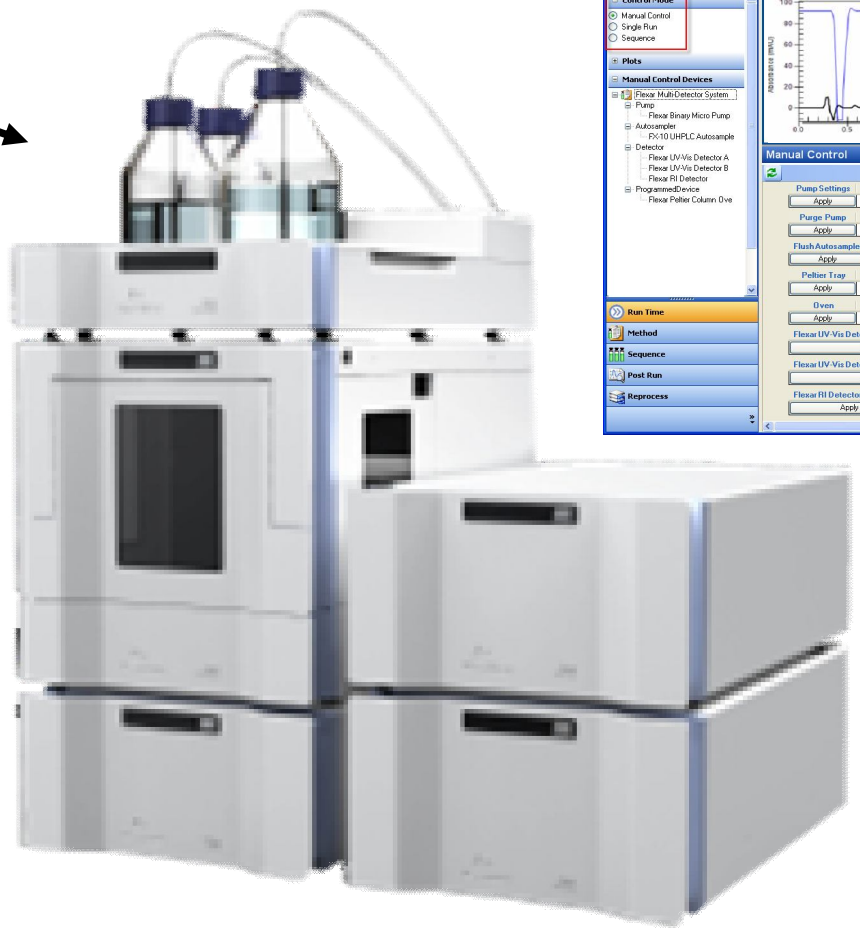
Typical HPLC chromatogram and report

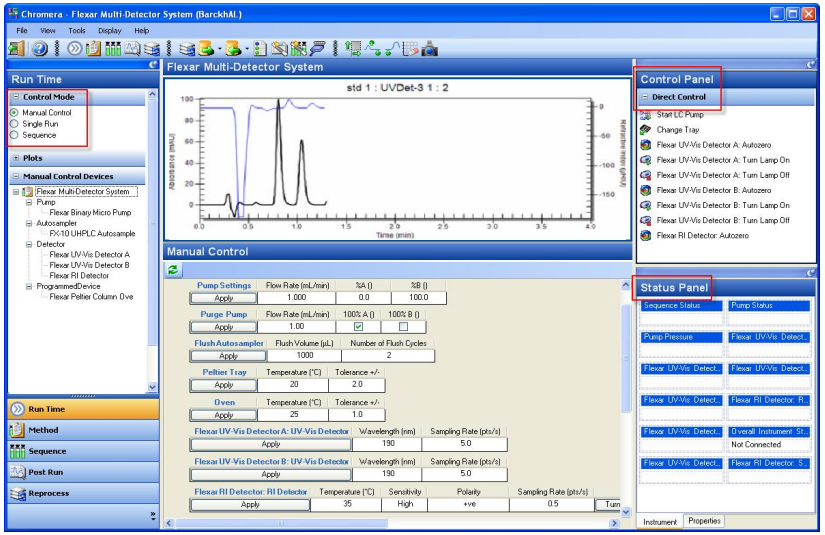
SISTEMA FLEXAR

Solvent Degasser and Mobile Phase Bottles

FlexarAutosampler

Flexar Isocratic Pump





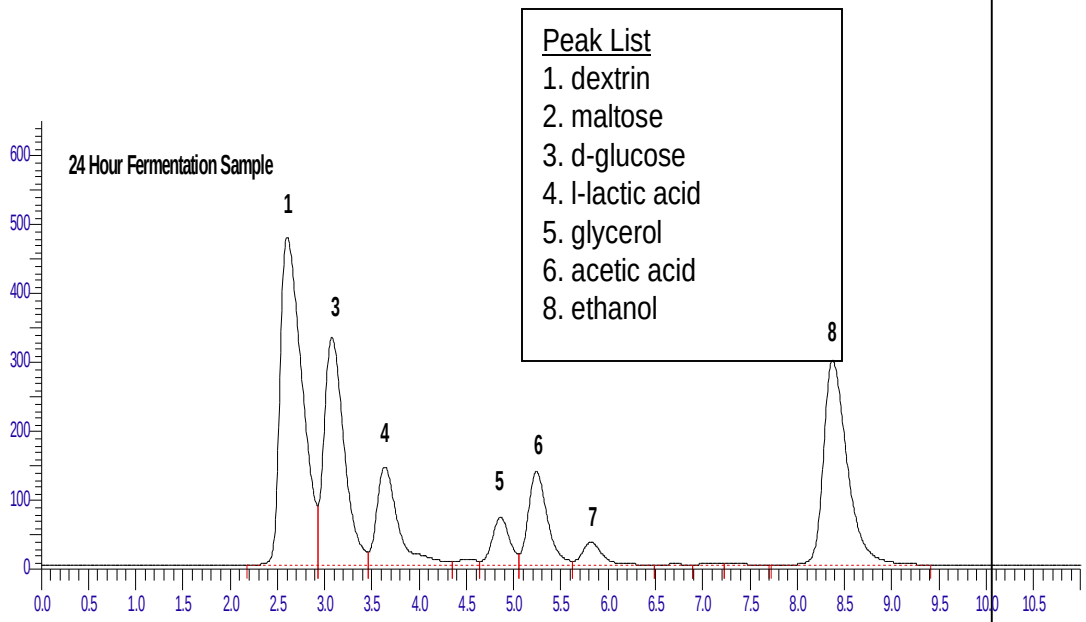
Series 200 RI detector

Flexar Column Oven

Fermentation Analysis using Aminex Column

- Fast easy assay for eight Fermentation analytes
  - dextrin
  - maltotriose
  - maltose
  - d-glucose
  - l-lactic acid
  - glycerol
  - acetic acid
  - ethanol

- Column: BIO-RAD Aminex
- Mobile Phase: 0.001M H2SO4
- Flow rate: 0.8 mL/min



ANÁLISE DE METAIS EM ETANOL POR ICP

Table 1 – Calibration Standard Concentrations, mg/L

	Std 1	Std 2	Std 3	Std 4
Copper	0.05	0.10	0.20	0.40
Phosphorus	0.10	0.50	1.0	1.5
Sulfur	1.0	5.0	10	20

All analyses were performed on a PerkinElmer Optima 7300DV atomic emission spectrometer utilizing the axial plasma view for best sensitivity. The system was operated in high resolution mode to achieve complete separation between closely spaced wavelengths of copper and phosphorus.

Sample introduction system comprised a PFA microspray concentric nebulizer equipped with a 100 uL/min self-aspirating capillary (ESI, Omaha, NE), a quartz cyclonic spray chamber, 1.2 mm i.d. ceramic injector and 3-slot quartz torch (PerkinElmer, Shelton, CT).

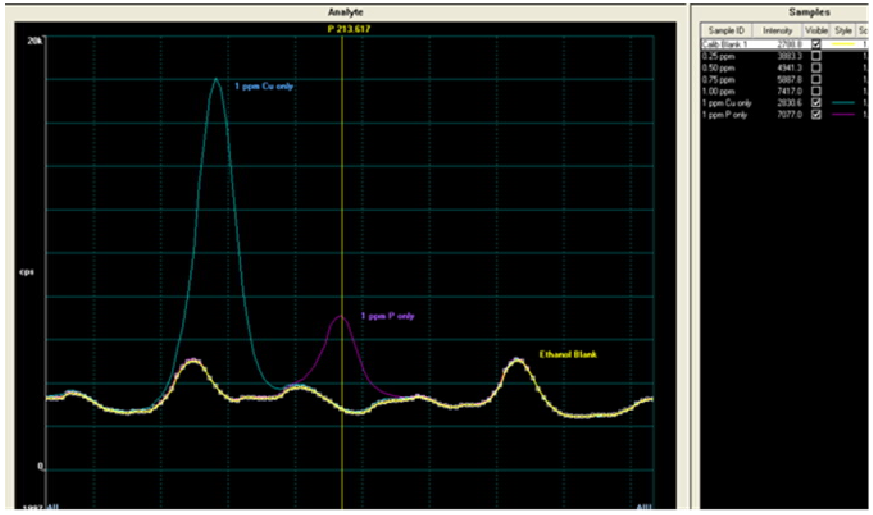


Table 2. System Operating Parameters

Plasma Gas Flow	20 L/min
Auxiliary Flow	0.5 L/min
Nebulizer Gas Flow	0.60 L/min
RF Power	1500 Watts
View	Axial
Resolution	High

MÉTODOS ANALÍTICOS PARA BIOCOMBUSTÍVEIS

ANÁLISE DE METAIS EM GASOLINA POR ICP

FIELD APPLICATION REPORT

ICP-Optical Emission Spectroscopy

Author
Daniel H. Jones
PerkinElmer, Inc.
710 Bridgeport Avenue
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A Novel Analysis of Highly Volatile Solvents using the PerkinElmer Optima 7300 DV with a Total Consumption Sample Introduction System

Introduction

The analysis of volatile solvents for trace metal contamination is important for a variety of reasons. Inorganic contaminants can damage the refinery process and certain catalysts can be poisoned making the chemistry of the process inefficient. These contaminants may also be harmful to the products the solvents are used in. They may cause premature breakdown or wear of mechanical equipment. Perhaps most importantly, these contaminants may be discharged into the environment causing harmful effects to ecosystems.

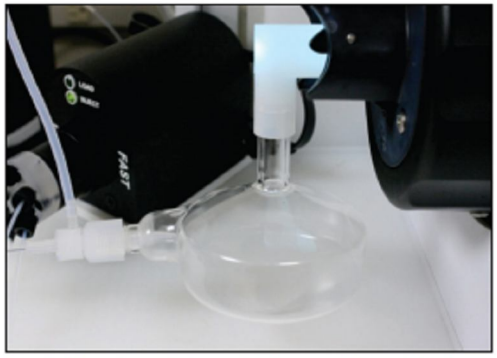


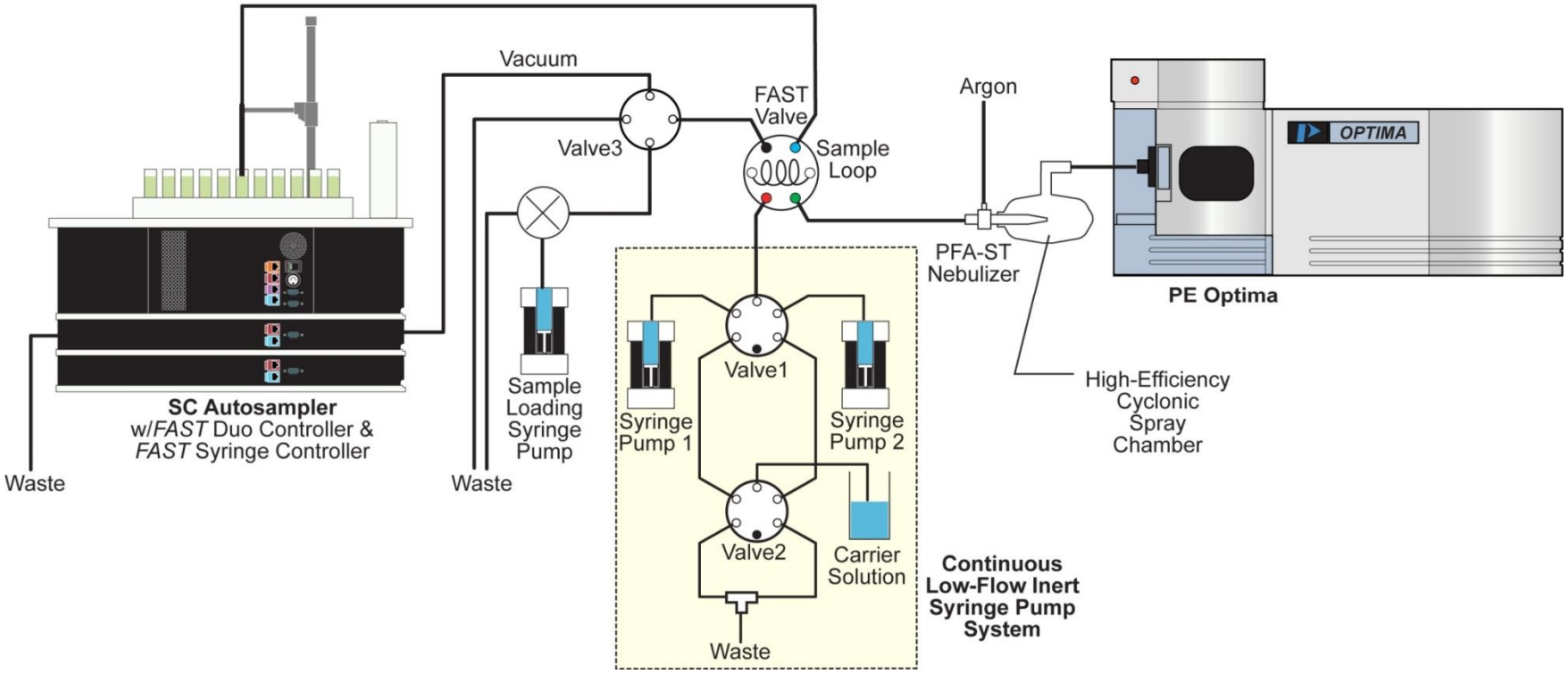
Figure 1. A large volume cyclonic spray chamber was used. Due to the "total consumption" nature of the system, no drain was required.

Table 2. Samples were spiked by weight with 160 ppb organo-metallic multi-element standard. Samples were then analyzed against a calibration curve made in heptane.

	Butane (1:5)		Naptha		Gasoline		Hexane		Hexadecane (1:5)	
Analyte	Conc. ppb	Spike % Recovery	Conc. ppb	Spike % Recovery	Conc. ppb	Spike % Recovery	Conc. ppb	Spike % Recovery	Conc. ppb	Spike % Recovery
Al 308.215	<50	102	<10	97	<10	95	<10	103	<50	96
Ca 317.933	<5	103	1	100	1	89	4	99	30	99
Cd 228.802	<5	104	<1	98	<1	91	<1	102	<5	98
Cr 267.716	<5	105	1	100	<1	99	1	102	5	101
Cu 327.393	<5	103	2	99	8	97	1	103	10	101
Fe 238.204	<5	103	1	99	11	94	<1	101	5	99
Mg 285.213	<5	102	2	98	<1	99	2	102	10	97
Mn 257.610	<5	104	1	99	<1	98	1	102	5	100
Mo 202.031	<15	102	<3	99	<3	84	2	101	10	97
Pb 220.353	<75	102	<1	94	11	91	16	86	15	94
Ti 334.940	<5	104	<1	100	<1	91	<1	104	<5	102
V 290.880	<5	105	<1	100	<1	88	<1	103	5	101
Zn 206.200	<5	102	23	101	29	92	<1	98	<5	97

Sample Introduction System

Petrochemical/Organic Solvents High Efficiency Introduction System



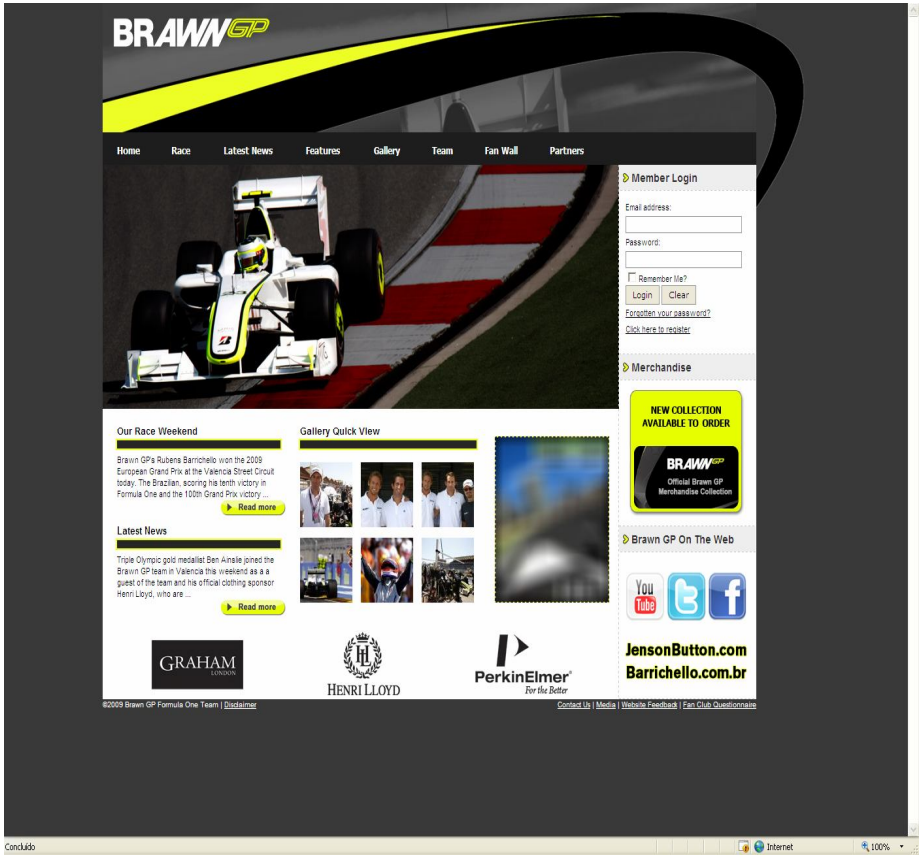
Alguns CLIENTES

From methanol to ethanol

For many years, 100 percent methanol was used in the high-performance race car engines. In 2006, the IndyCar Series introduced a blend of 90 percent methanol and 10 percent ethanol as a transition fuel before full incorporation of ethanol. The IndyCar Series' conversion to the renewable fuel was introduced by the late Paul Dana, a driver who was killed in 2006 during a practice session, and was supported by the Ethanol Promotion and Information Council (EPIC), a non-profit alliance of ethanol industry leaders.

The use of the Clarus GC for fuel analysis

PerkinElmer tests use its Clarus® chromatography (GC) controlled by a PerkinElmer TotalChrom® chromatography data system for collecting, processing and reporting data. The Clarus GC separates the fuel to identify additives that may give one car a competitive advantage over others. The testing takes approximately 5 minutes and can detect impurities down to concentrations of 0.10 percent.



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