Market Specification and Methods for Ethanol Analysis

Workshop - Measurement and Standards for Biofuels: Enabling a Transition from Petroleum as a Vehicular Energy Source

INMETRO

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José Felix Silva Junior
jfsagro@uol.com.br

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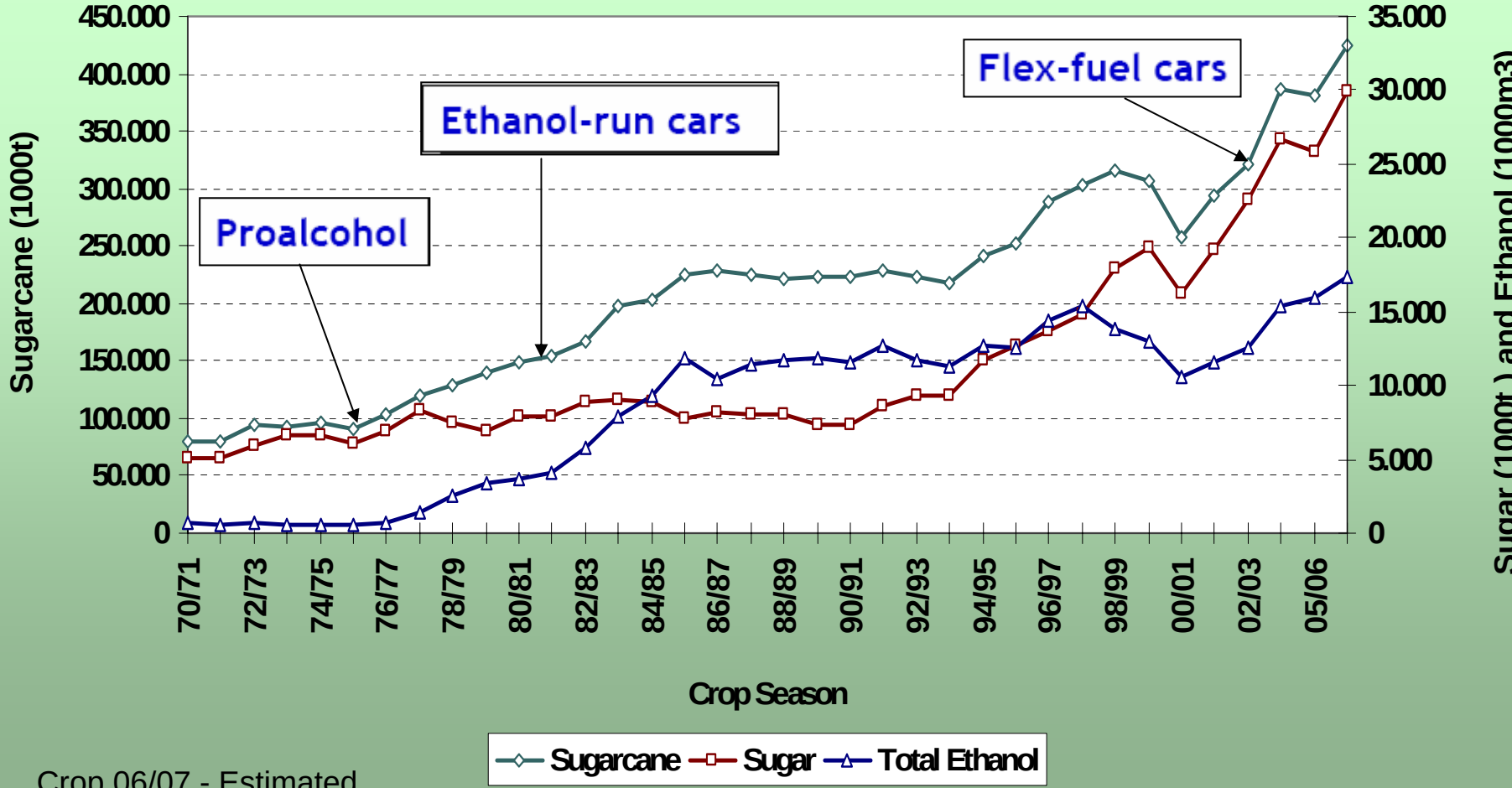
What I will try to show!!!!

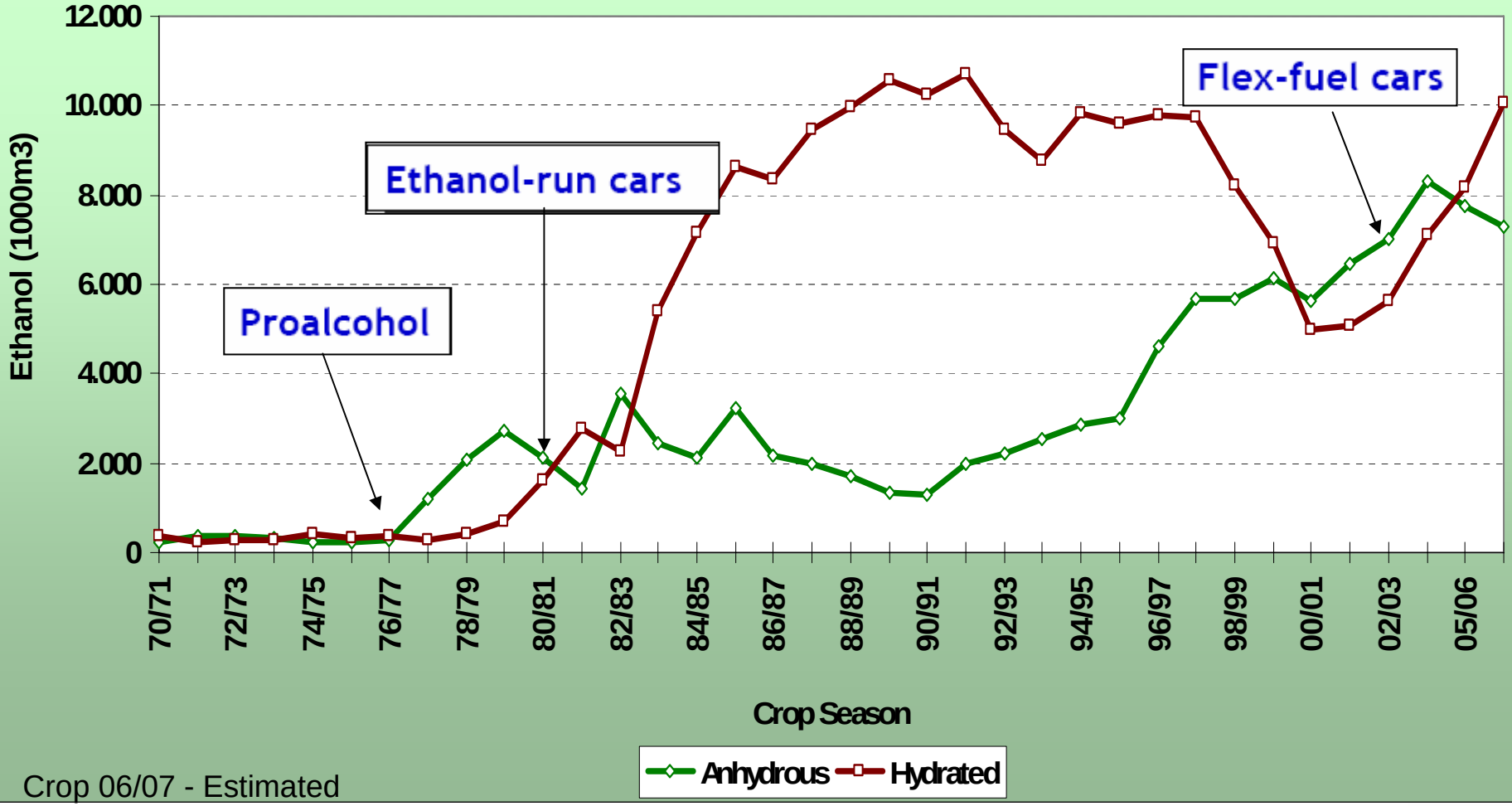
- Information and scenario of Brazilian Production
- Brazilian and other specifications
- Specification and methods comments
- Revision of Brazilian Standards
- Proficiency test
- Suggestion

Brazilian Production of Sugarcane, Sugar and Ethanol



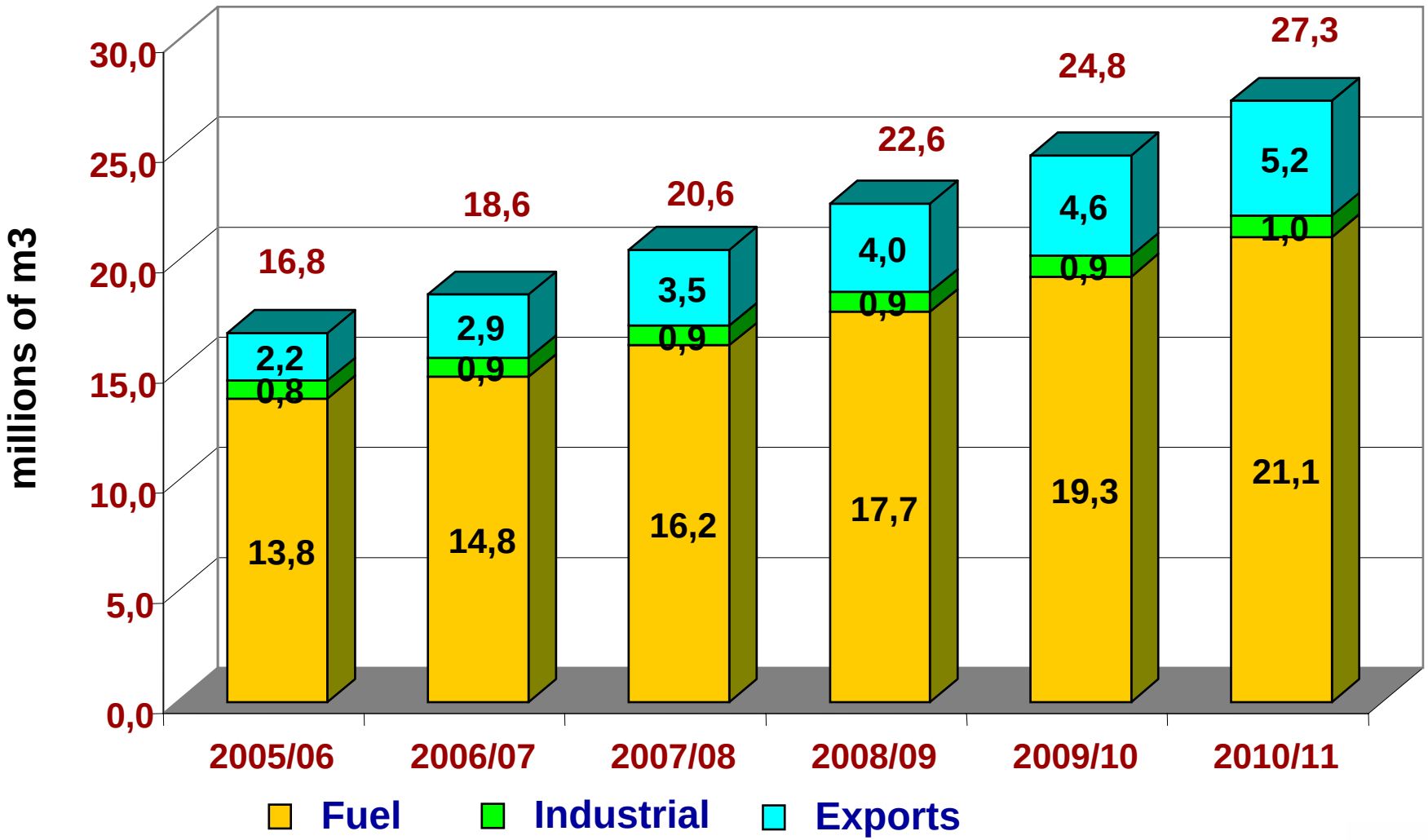
Crop 06/07 - Estimated

Brazilian Production of Anhydrous and Hydrated Ethanol



Crop 06/07 - Estimated

Copersucar's Scenario for Ethanol Demand

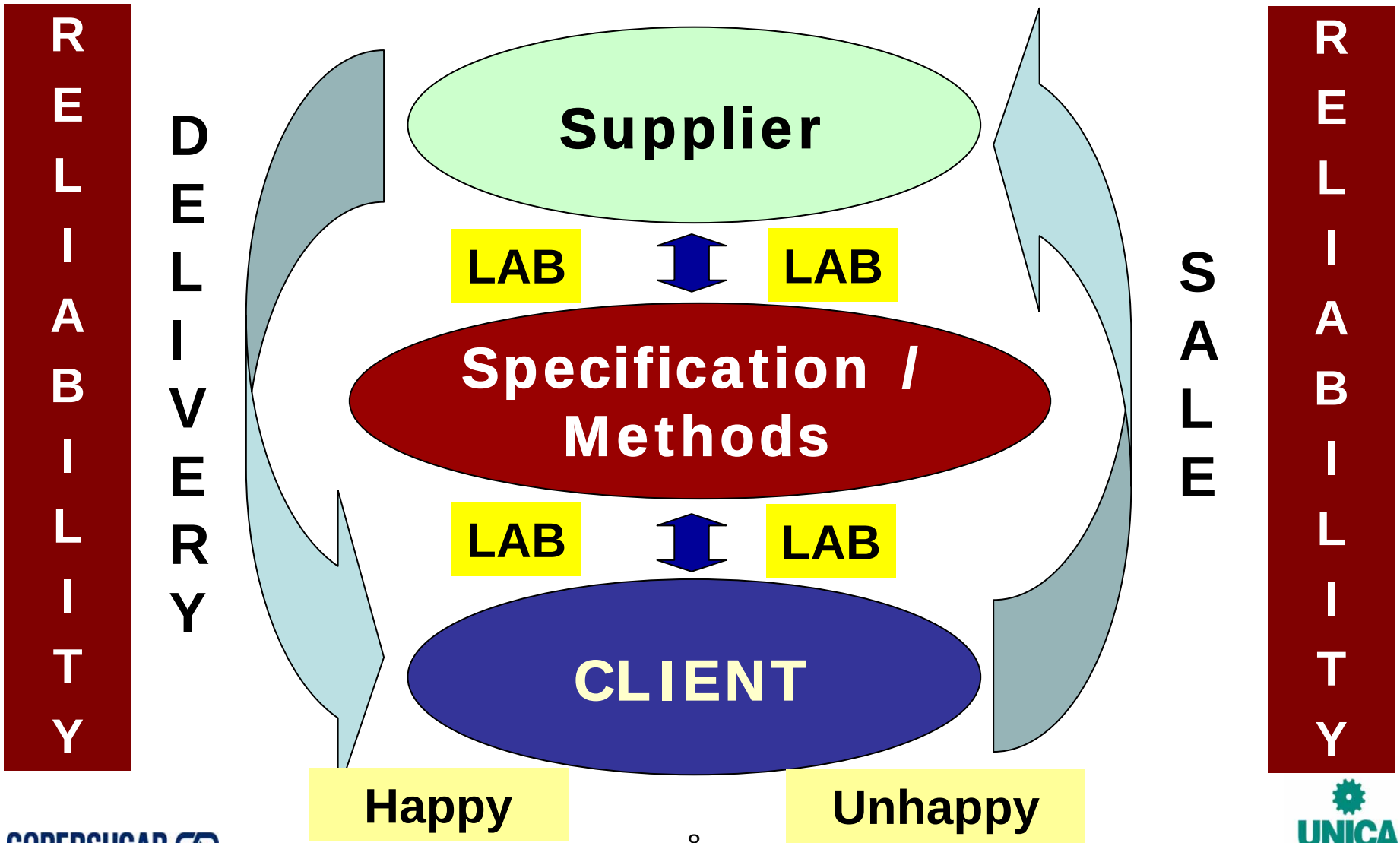


Ethanol Specification

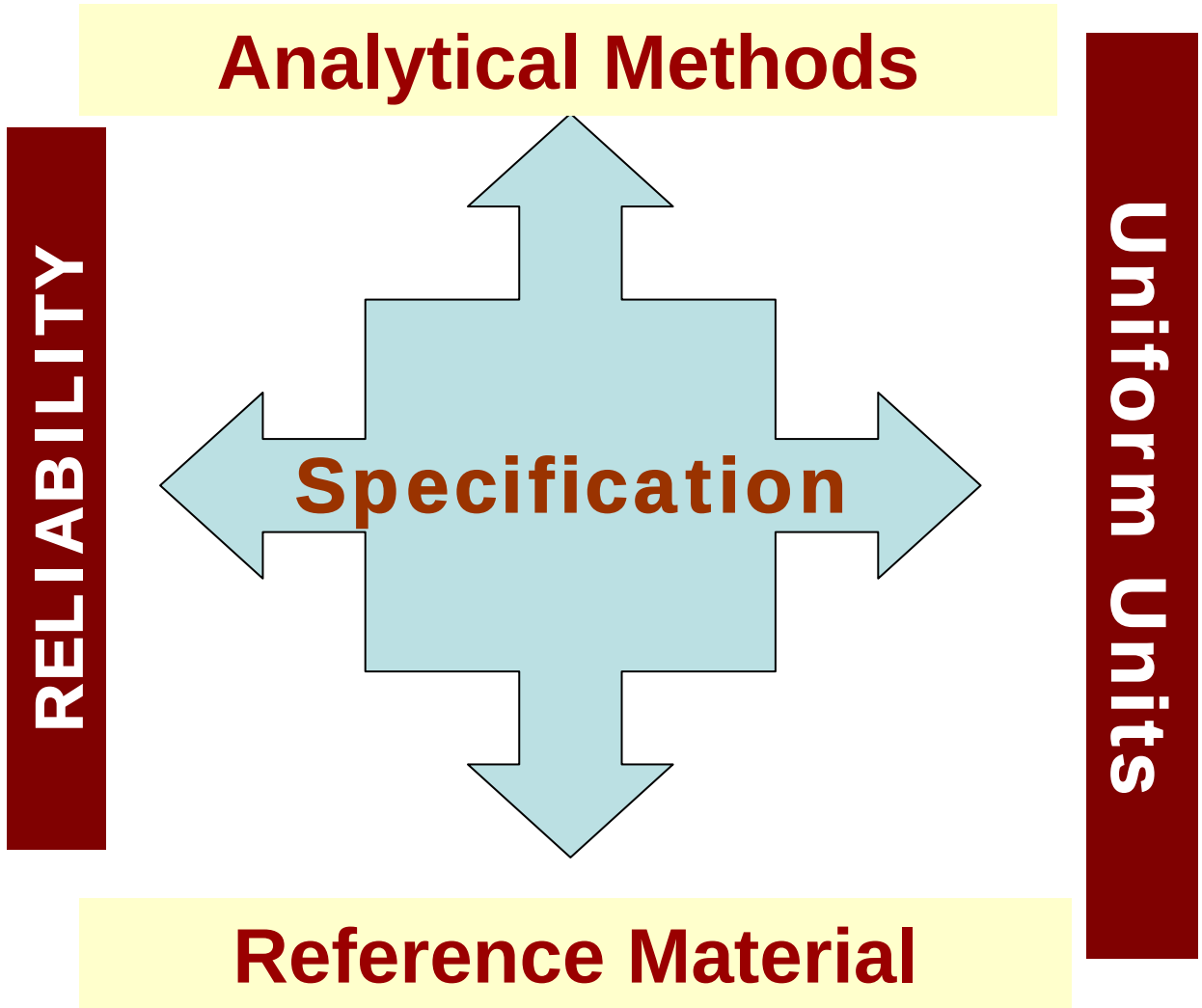
The definition and implementation of a specification and quality system is a complex task that has to involve technicians from all the supplier-user chain.

It is necessary to know the needs of the client (buyer/user), but at the same time offer an economically viable product.

Relationship – Client - Supplier



Specification - Laboratory



Quality Assurance

Process Control at the factory

Factory Lab

Quality Control at the Factory Tanks

Factory Lab

Supervisory Co. Lab

Transportation – trucks, railway cars

Supervisory Co. Lab

Quality Control at the Port Tanks

Supervisory Co. Lab

Quality Control at the Ship in the origin Port

Supervisory Co. Lab

Quality Control at the Ship in the destiny Port

Who is responsible by the specification?

Brasil

- **Internal Market**
  - **Fuel ethanol (anhydrous and hydrated) – ANP**
  - **Industrial hydrated Ethanol – Clients**

Other countries

- **External Market**
  - **Fuel Ethanol – ASTM, NYBOT, Europa(?), Japão(?), China(?), etc.**
  - **Industrial hydrated Ethanol – Clients**

Types of Anhydrous Ethanol

- **Denatured Anhydrous Ethanol**

  Ethanol which has been rendered toxic or otherwise undrinkable, and in some cases dyed.

- **Undenatured Anhydrous Ethanol**

  Pure ethanol without any chemical additive.

- **Ethanol from oil or gas**
- **Ethanol from biomass - fermentation**

Brazilian Specification for Fuel Ethanol Resolução ANP Nº 36, December 6, 2005

Characteristics	Unity	Anhydrous	Hydrated
Aspect	Visual	clear	clear
Color (4)	Visual	Sudan Red	colorless to yellowish
Total Acidity (as acetic acid) , max	mg/L	30	30
Electrical conductivity, max	µS/m	500	500
Specific weight 20º C	kg/m3	791.5 max.	807.6 to 811.0 (5)
Alcoholic Strength	% w/w	99.3 min.	92.6 to 93.8 (5)
pH			6.0 a 8.0
Residue after evaporation, max. (5)	mg/100mL		5
Hydrocarbons content (5) (7)	%vol.	3.0	3.0
Ethanol content, min. (6)	%vol.	99.3	92.6
Chloride, max. (5)	mg/kg		1
Sulphate, max	mg/kg		4
Iron, max.	mg/kg		5
Sodium, max.	mg/kg		2
Copper, max. (8)	mg/kg	0.07	

(4) - Color additive - 15 mL/m3 - Sudan Red (Orange)
(5) – Limits for the distribution and import of ethanol. Not required for the producers.
(6) – Required for ethanol not produced by fermentation process.
(7) – Allowed 3.0% vol. of hydrocarbons in the anhydrous ethanol imported for the producers.
(8) – Measured only when contamination is suspected.
(9) – Measured only when contamination is suspected or the distillery has equipment with copper.

Methods – ANP Specification

Methods	Title
NBR 5992	Density and Alcoholic strength
NBR 8644	Evaporation Residue
NBR 9866	Alcalinity and Total Acidity
NBR 10422	Sodium - Flame Photometry
NBR 10547	Electrical conductivity
NBR 10891	pH
NBR 10893	Copper - AAS
NBR 10894	Sulfate - Ion Chromatography
NBR 10895	Chloride - potentiometric
NBR 11331	Iron - AAS
NBR 12120	Sulfate - volumetry
NBR 13993	Hydrocarbons
ASTM D512	Chloride Ion in Water
ASTM D1125	Electrical Conductivity and Resistivity of Water
ASTM D1613	Acidity in Volatile Solvents
ASTM D4052	Density and Relative Density by Digital Density Meter
ASTM D5501	Ethanol Content of Denatured Fuel Ethanol by GC

Specifications for Anhydrous Ethanol

Characteristics	Unit		ASTM	NYBOT	Sweden	Europe	ANP
Density (20ºC)	kg/m³	máx.			792,0		791,5
Alc. Strength a 20°C	INPM, %m/m	mín.					99,3**
Alc. Strength a 20°C	GL, %v/v	mín.	92,1*	98*	99,7*	98,7*	99,6**
Water (KF)	%v/v	máx.	1,0	0,8	0,3	0,3	
Total Acidity	mg/L (%m/m)	máx.	56 (0,007)	70	56 (0,007)	56 (0,007)	30
Electrical Conduc.	uS/m	máx.	-		500		500
pHe	-		6,5 a 9,0	6,5 - 9,0	6,5 - 9,0	6,5 - 9,0	
Copper	mg/kg	máx.	0,1	0,1	0,1	0,1	0,07
Chloride	mg/kg (mg/L)	máx.	40 (32)	40	10	25	
Solvent-washed gum	mg/100 mL	máx.	5,0	5,0	5,0		
Aspect	-		Límp.	Límp.	Límp.	Límp.	Límp.
Color	-						LA
Methanol	%v/v	máx.	0,5	0,5	0,5	1	
C3-C5	%v/v	máx.			2,0 m/m	2,0 m/m	
Denaturant	%v/v		1,96 a 4,76				
Sulfur	mg/kg	máx.			50	10	
Phosphorus	mg/L	máx.				0,5	
Non-volatil Mat.	mg/L	máx.				100	

* GC ** Densimetry

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Methods for Anhydrous Ethanol

Characteristics	Unit	ASTM	NYBOT	Sweden	Europe	ANP
Density (20ºC)	kg/m³			D 4052 / ISO 12185		NBR 5992 / D4052
Alc. Strength a 20°C	INPM, %m/m					D4052
Alc. Strength a 20°C	GL, %v/v	D5501	D5501	D4052	EC2870	D4052
Water (KF)	%v/v	E203	E203	E 1064 / ISO 12937	prEN 15489	
Total Acidity	mg/L (%m/m)	D1613-06	D1613-06	D1613-06	prEN 15491	NBR 9866 / D1613
Electrical Conduc.	uS/m	-		D2624 / ISO 6297		NBR 10547
pHe	-	D6423	D6423	D6423	prEN 15490	
Copper	mg/kg	D1688A	D1688A	D1688A	prEN 15488	NBR 10893
Chloride	mg/kg (mg/L)	D512-04	D512-04	D4929B	prEN 15484 / prEN 15492	
Solvent-washed gum	mg/100 mL	D381	D381	D381 / ISO 6246		
Aspect	-	Visual	Visual	Visual	Visual	Visual
Color	-	Visual	Visual	Visual	Visual	Visual
Methanol	%v/v	D5501	D5501	D5501	EC2870 / EN13132 / EN1601	
C3-C5	%v/v	D5501	D5501	D5501		
Denaturant	%v/v					
Sulfur	mg/kg			D 5453	prEN 15485	
Phosphorus	mg/L				prEN 15487	
Non-volatil Mat.	mg/L				EC2870	

More Specification (1)

No.	Attribute	Specification limits	Units	Test method
1*	Water	max. 6.5	%	DIN 51777
2*	Ethanol	min. 93.5	%	GC
3*	Methanol	max. 50	mg/kg	GC
4*	Higher alcohols (Total)	max. 600	mg/kg	GC
5*	Higher alcohols (Fraction C3-C4)	max. 200	mg/kg	GC
6*	Aldehydes (acetaldehyde)	max. 100	mg/kg	GC
7*	Other organic compounds	max. 300	mg/kg	GC
8*	Colour	max. 25	APHA	DIN ISO 6271
9*	Inorganic impurities (sulphate, nitrate, chloride)	max. 1	mg/kg	IC
10*	Total sulphur	max. 2	mg/kg	ASTM D3120

More Specification (2)

PROPERTIES	SPECIFICATION / UNITS	TEST METHOD
Alcohol Strength	minimum 99.4% weight	ASTM D5501
- Ethanol	minimum 98.4 %wt	
- Methanol	Maximum 0.6 % wt	
water content	0.6% weight max	ASTM D1744
Higher alcohols	max 200g/hl (= max 0.25% weight)	ASTM D5501
Acidity as acetic acid	max 100 ppm	ASTM D1613
Chlorure	max 10 ppm	IMPCA-002
Esters	max 50 g/hl (= max 0.06% weight)	CEE.L.130
Aldehydes	max 50 g/hl (= max 0.06% weight)	CEE.L.130
Sulfur	max 10 ppm (= max 0.001 % weight)	ASTM D-3961
Cyclohexane	max 20 ppm (= max 0.002 % weight)	ASTM D3054
Benzene	max 10 ppm (= max 0.001 % weight)	ASTM D4534
Iron	Max 1 ppm	
pHe	< 7.5	
Suspended matters	Free	
Non volatiles	Max 50 ppm	

UNDENATURATED BIO ETHANOL

Characteristics	Method		Value
Alcohol content	ASTM-D-3505	% v/v	min 99.70
Ethanol content	ASTM-D-5501	% v/v	min 99.00
Methanol content	ASTM-D-5441	% v/v	max 0.50
Water content	ASTM-E-1064	% v/v	max 0.30
Density at 20 deg C	ASTM-D-3505 or ASTM-D-4052	g/mL	max 0.792
Acidity, as acetic acid	ASTM-D-1613	mg/L	max 56
Sulphur content	ASTM-D-5453	mg/kg	max 5
Appearance	ASTM-D-2090 or ASTM-D-4176		clear and bright, without particles
pH	ASTM-D-6423		6.5 - 8.0
Basic nitrogen	UOP 269	ppm	max 1
Chlorides	ASTM D512 (NM269)	ppm	max 2

Specification for Anhydrous Ethanol

➢Comments

- **Units in volume and mass – for ethanol is a big difference, around ±26% from volume to mass and vice-versa.**

  Expressions in %, mg/L, mg/100mL, hectolitres, ppm(?).
- **Many methods for the same parameters.**
- **Methods developed for other matrix is used for ethanol. Who tested them?**

Specification for Anhydrous Ethanol

➢Comments (cont.)

- **Methods for denatured ethanol is asked for undenatured one – unnecessary.**
- **Tables for density or specific weight are different – IUPAC, OIML, in air, in vacuum.**
- **There are no method comparison to know the differences. (as far as I know).**
- **Uncertainty are not know.**
- **Repeatability and reproducibility are not know for all methods.**

Ethanol Measurements

Simple Measurements

- **Alcoholic Strength - Glass Densimeter or Electronic Digital Densimeter**
- **Acidity - Titration**
- **pH – potentiometer/specific electrode for hydrated and anhydrous ethanol**
- **Conductivity – conductivimeter/cell constant equal to 0.1cm^{-1}**
- **Aspect – Visual**
- **Color - Visual**

Complex Measurements

- **Metals**
  - **Copper - Atomic Absorption / Graphite Furnace**

- **Anions**
  - **Sulfate and Chloride**
    - **Titration - Dimethylsulfonazo**
    - **Titration - Specific electrode**
    - **Ion Chromatography**

Complex Measurements

- **Gas Chromatography**
  - **Ethanol content**
  - **Methanol**
  - **C3-C4**
  - **Higher alcohols**

- **Sulfur**
  - **Sulfate**
  - **Sulfur**

Complex Measurements

- **Nitrogen (?)**
- **Phosphorus (?)**
- **Water – Karl Fischer**
- **Solvent-washed Gum (?)**
- **Non-volatil Material**

Ethanol Measurement

- **Simple Measurement**
  - **It can be performed in almost any laboratory without special equipment and special trained technicians**
  - **Low cost to implement and maintain**
  - **Easy calibration**
- **Complex Measurement**
  - **It can be performed in well-equipped laboratory with special equipment and trained technicians**
  - **High cost to implement and maintain**
  - **Special calibration**
  - **Equipment used only to measure the quality of the ethanol, without any other use for the process**

Water Content in Different Mixture Anhydrous Ethanol and Gasoline

		Anhydrous 99,0 %w/w
		Water = 1,0 % w/w
Gasoline	Ethanol	Weight of water in the mixture
% v/v	%v/v	g
97,0	3,0	0,024
90,0	10,0	0,079
78,0	22,0	0,174
75,0	25,0	0,198
15,0	85,0	0,674

Anhydrous Ethanol - pH

pH measurement

- **pH is measured to relate it with corrosion.**
- **Corrosion due to ethanol is insignificant.**
- **“Steel underground storage tanks have been tested and found to be compatible with ethanol and methanol fuel blends”.**

  Compatibility of Steel with Oxygenated Fuels. Wayne B. Geyer. Steel Tank Institute. 16th Annual ILTA Conference, JUNE 10-11, 1996.

Anhydrous Ethanol - pH

pH measurement.

There is almost no corrosion in tanks and pipes.

Worst case scenario - pitting, for a fuel blend of 85% methanol and 15% water - the corrosion rate corresponded to a 150-year life upon a 10 gage (0.134”) steel tank.

There is no evidence of corrosion or other problem in tanks and cars with a mixture 75/25 with anhydrous ethanol with different pH.

Anhydrous Ethanol - pH

- **ACTIVE STANDARD: D6423-99(2004) Standard Test Method for Determination of pHe of Ethanol, Denatured Fuel Ethanol, and Fuel Ethanol (Ed75-Ed85)**
- **Specific electrode produced by one company**
- **A pHe value for alcohol solutions is not directly comparable to pH values of water solutions.**
- **The value of pHe will depend somewhat on the fuel blend, the stirring rate, and the time the electrode is in the fuel.**
- **Results will be inconsistent if the operational conditions are not maintained.**

Anhydrous Ethanol – Organic Compounds

It is not necessary to measure the content of other organic components in ethanol by gas chromatography.

"The presence of aldehydes, esters and other alcohols in hydrated ethanol, with content 4, 13 and 20 times higher than the emission standard, did not caused any significant difference in the content of the same components in the exhaust gas."

Influence on the car emission of the content of aldehyde, ester, higher alcohols and gasoline in fuel hydrated ethanol. Laerte Graner e Maurício C. Carmona. Volkswagen Emission Laboratory.

What we are doing in Brazil

Revision of the Brazilian Standards – ABNT/CEET

Standards in Public Consultation

- **ABNT NBR 9866 - Álcool etílico - Determinação da acidez total - Método colorimétrico**
- **ABNT NBR 10547 - Álcool etílico - Determinação da condutividade elétrica**
- **ABNT NBR 10891 - Álcool etílico hidratado - Determinação do pH - Método potenciométrico**

Revision of the Brazilian Standards – ABNT/CEET

- **Standards to be revised**
  - **NBR 5992 – Determinação da massa específica e do teor alcoólico do álcool etílico e suas misturas com água**
  - **NBR 10422 – Álcool Etílico – Determinação do teor de sódio por fotometria de chama**
  - **NBR 10895 – Álcool Etílico – Determinação do íon cloreto por técnica potenciométrica**

Revision of the Brazilian Standards – ABNT/CEET

- **Standards to be revised**
  - **NBR 12120 – Álcool Etílico – Determinação do teor de sulfato por volumetria**
  - **NBR 11331 – Álcool Etílico – Determinação do teor de ferro por espectrofotometria de absorção atômica**
  - **NBR 10893 – Álcool Etílico – Determinação do teor de cobre por espectrofotometria de absorção atômica**

Revision of the Brazilian Standards – ABNT/CEET

- **New Standards**
  - **Álcool Etílico - Determinação da massa específica por densimetria eletrônica (ASTM D4052)**
  - **Teor de etanol por cromatografia gasosa (ASTM D5501)**
  - **Água, Karl Fischer (ASTM E1064/203)**
  - **pHe em álcool anidro (ASTM D6423)**
  - **Goma Atual Lavada (ASTM D381/ISO 6246)**
  - **Metanol e C3-C5 (ASTM D5501)**

Proficiency Program
Sugarcane Technology Center (CTC)

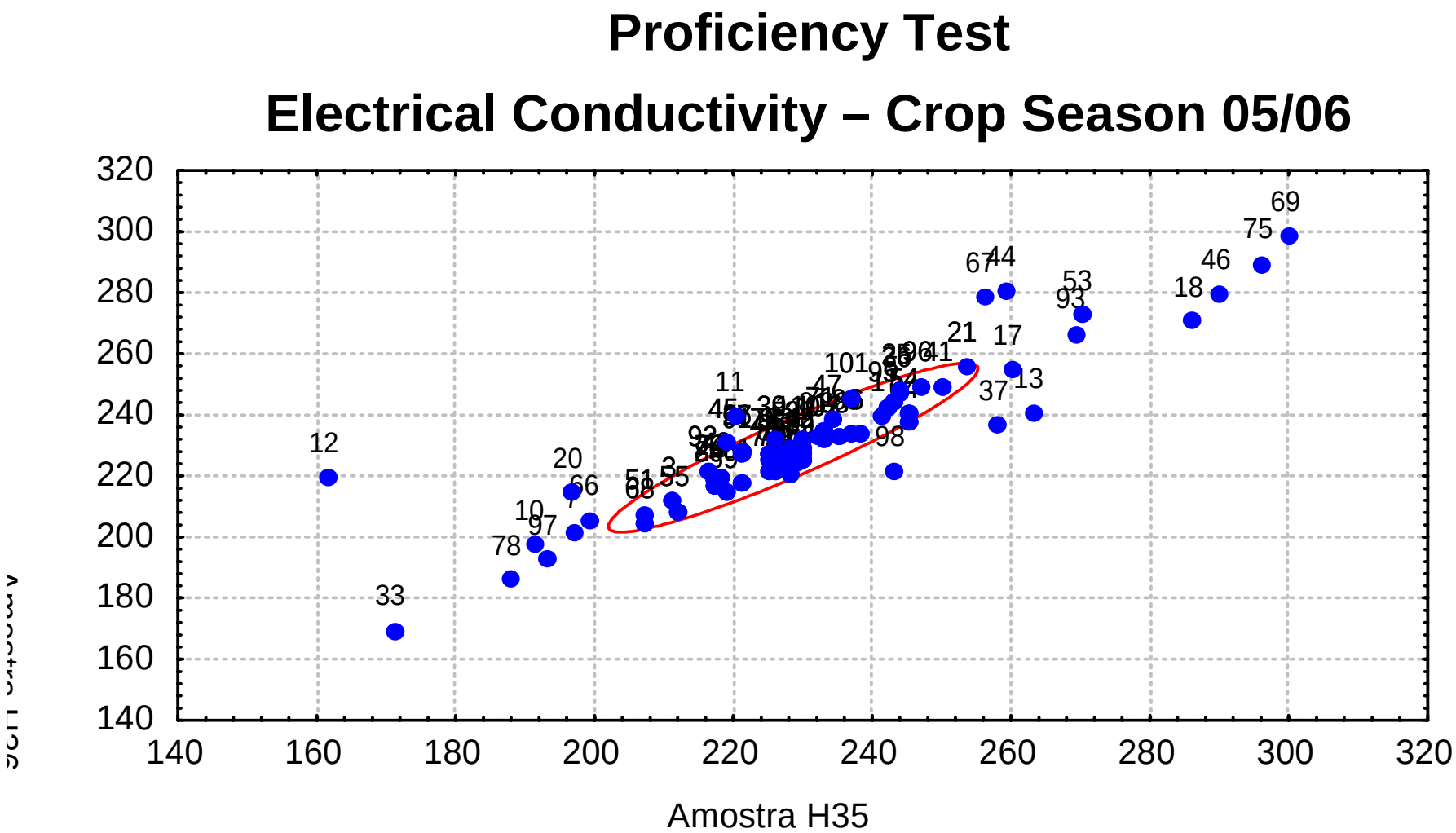
Reproducibility values for ethanol analyses

Characteristics	Unit	Anhydrous	Hydrated
Alcoholic Strength	% m/m	0.2	0.2
Acetic Acidity	mg/L	4.5	4.5
Electrical Conductivity	μS/m	15	15
pH	-	-	0.3

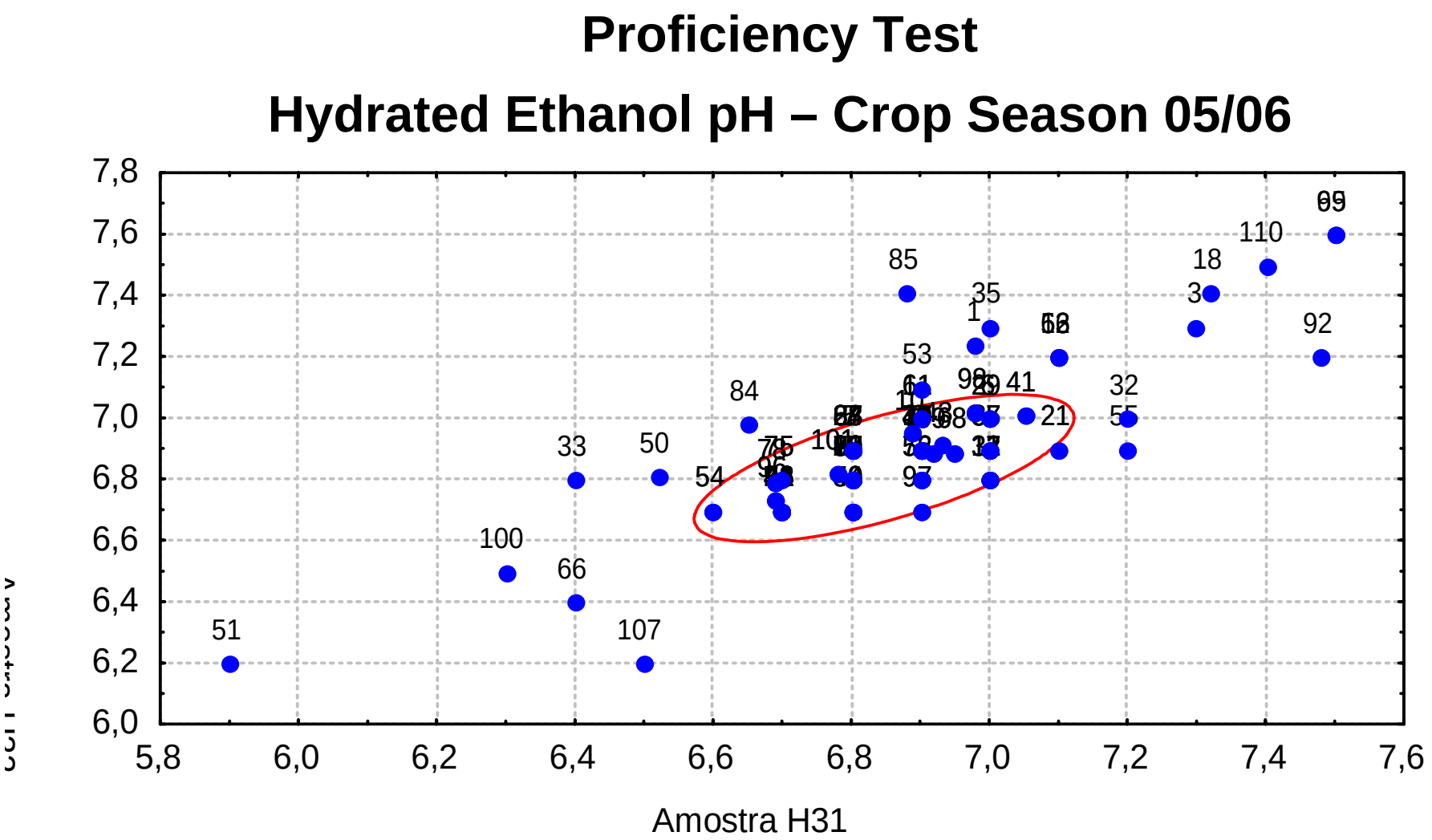
The values were defined from interlaboratory programs with sugar and ethanol mills coordinated by Copersucar from 1992 to 2000 and from the literature.

The program is based in ISO 5725 and ISO Guide 43-1:1997.

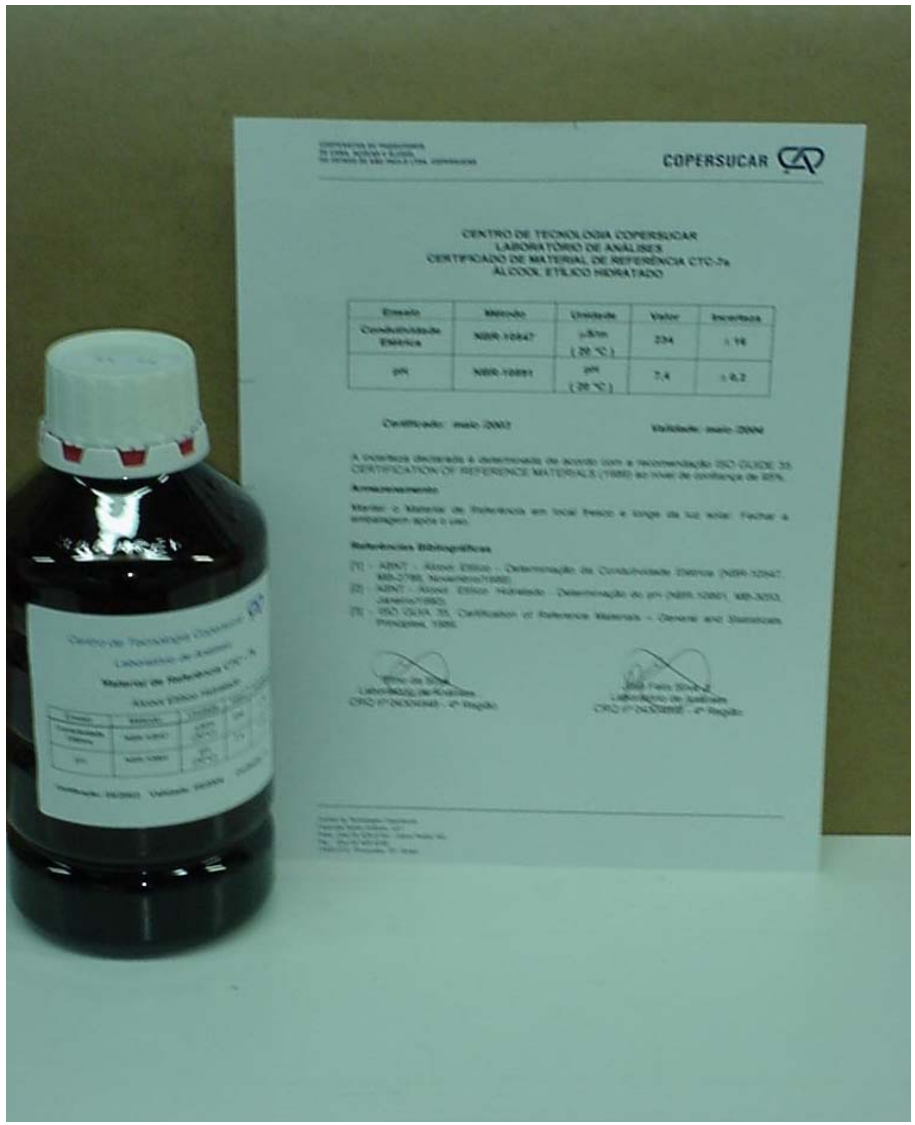
Proficiency Program (CTC) - Ethanol



Proficiency Program (CTC) - Ethanol



Reference Material (CTC) - Ethanol



What it is necessary?

Quality Program for Ethanol

- **Evaluate ethanol specifications and methods from other countries: ASTM, European, Japonese, etc.**
- **Define the desirable parameters and the acceptable limits.**
- **Try to know why each parameter is necessary for ethanol to be used as a fuel mixture.**

Quality Program for Ethanol

- **Encourage and sponsor studies and researches in new methods and in the production of certified reference material.**
- **Qualify laboratories to analyse ethanol with reliability**
- **Encourage the formation of a Brazilian or International Committee for Uniform Methods of Ethanol Analyses – ISO Standards (?)**

Thank you

José Felix Silva Junior
Copersucar
jfsilva@copersucar.com.br
jfsagro@uol.com.br