Density-Temperature Relationships for Ethanol and FAME

Recent Measurement Results for Biofuels and Biofuel Blends

Respectfully submitted by
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Developments in Petroleum Product Production ..

- In the „old days“, petroleum products were simple → „straight run processes“
- with more chemical engineering and processes → more product variability
- appearance of new sources like bio components → even more variability

→ considerable changes to composition and petroleum characteristics over the years

.. unleaded / reformulated gasoline;
.. advent of „oxygenates“, FAME, other bio-components;
.. Fuel components from pyrolysis, algae, tallow, yellow grease, Fischer – Tropsch, …

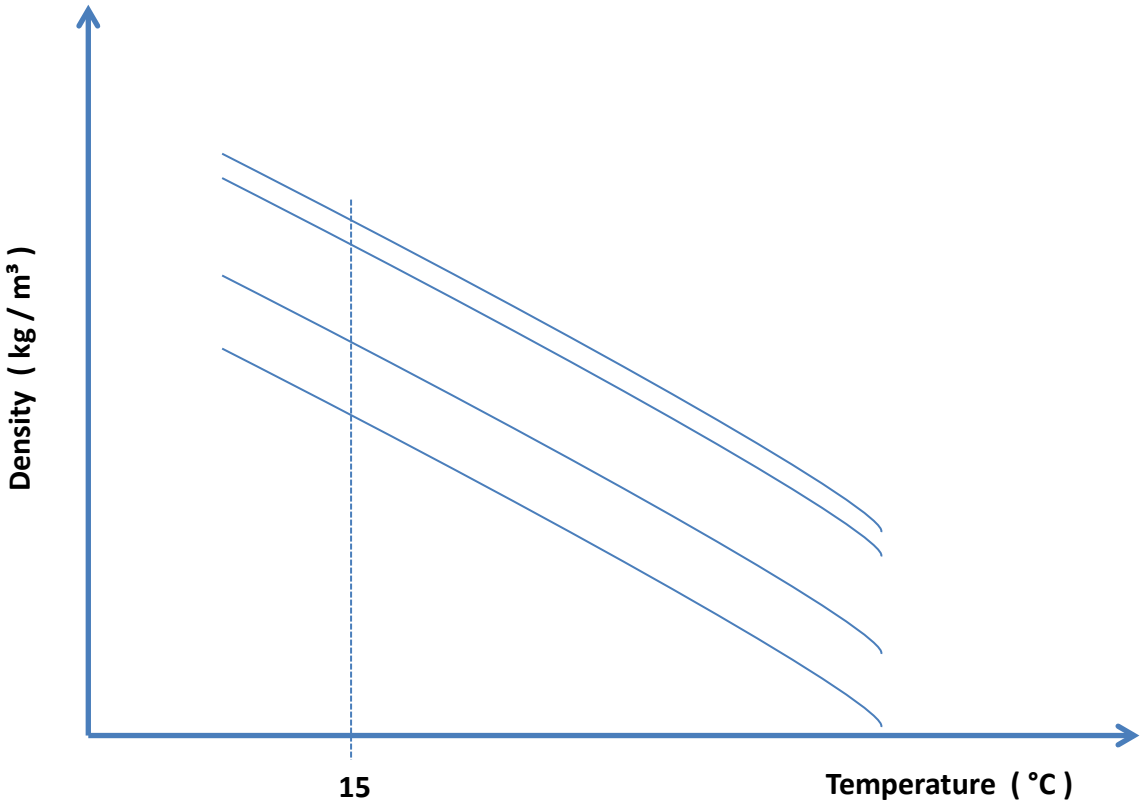
.. other fuel matrix changes like sulfur, aromatics, water content, many more

- Checks and updates for density behaviour of petroleum liquids in recent years have been published from API, EI, ASTM and others [see bibliography]
- The process of increased product variability is ongoing with advent of „new generation“ biofuels and possibly more complex biofuel components…

Measurement of Density for Petroleum related Products - Synopsis

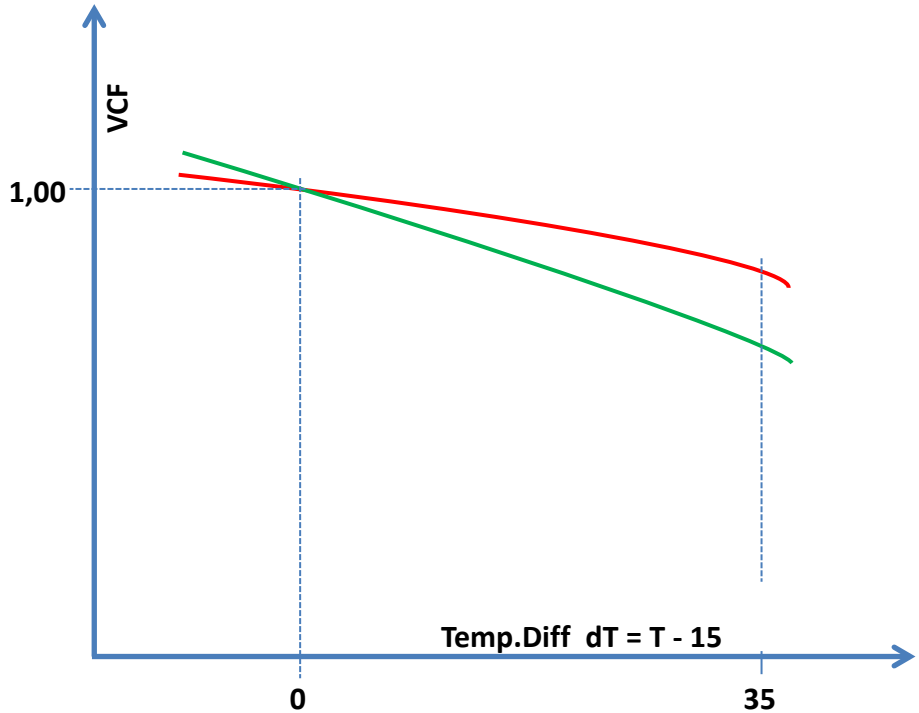
Definition:	Density = Mass / Volume $\rho = m / V$	***simpler: use also "D"***
Common Units:	kg / m³	*also: g/cm³ or g/mL*
Reference Temperatures:	**15°C (59 F)**, 60 F (15,556°C)	*older: 20 °C, …*
Common Test Methods:	**Volume Meters** **Hydrometer** **U-Tube Quartz Oscillator** **Density Bottle, other**	→ *e.g.* ***in transport*** → EN ISO 3675 → **EN ISO 12185** → (DIN 51757, other)
Density Properties:	**depends on temperature & pressure** **prefer measurement at ref.temperature** vary with product composition	→ linear & nonlinear → "product families"
Applications:	**density measurement (preferably)** **product trade, transport, tax, …** **CALIBRATION of volume meters**	→ **at ref. temperature** → ***at any temperature*** → **Gov. Chemist, …**

„The Density – Temperature Space“



→ increasing temperature → decreasing Density → “molecular motion”
→ similar product compositions → similar D(T) behavior → allows “product families”
→ Common Ref. Temperature → 15 °C (ISO, EU) → 60 F (other)

„The VCF – Temperature Space“



VCF : “Volume Correction Factor”

VCF = D(T) / D(15)

→ Normalize D(T) such that Density at T_{ref} is equal to 1,0000

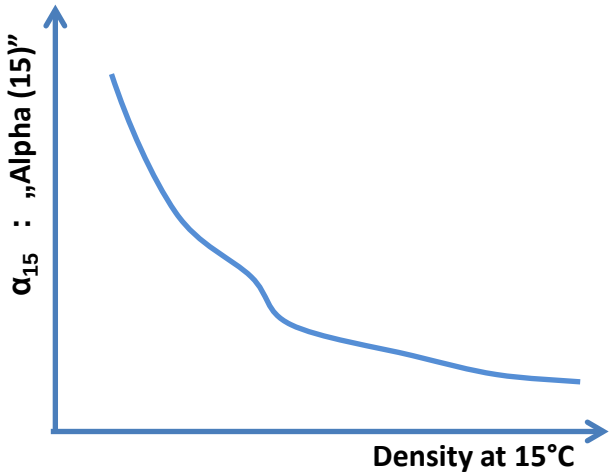
→ Differences in D(T) behavior easy to see at higher dT …

International agreement on VCF – Modeling:

For Fuels, Naphtha, Jet, Burner fuels, …
→ API MPMS Chapter 11 (“Group B”)

$$VCF = \exp\left(- \alpha_{15} * dT * \left(1 + 0{,}8 * \alpha_{15} * dT \right) \right)$$

„The alpha15 – Density15 Space“ („Group B“ family only..)



→ Regression on D(T) gives α_{15} and **D(15)**

For Fuels, Naphtha, Jet, Burner fuels, …
→ API MPMS Chapter 11 (“Group B”)

$$VCF = \exp(-\alpha_{15} * dT * (1 + 0{,}8 * \alpha_{15} * dT))$$

→ Regression over product family members :

specific constants for product family:

$$(K_0, K_1) = \text{regression}(\alpha_{15}, D(15))$$

$$\alpha_{15} = K_0 / D(15)^2 + K_1 / D(15)$$

Blue Curve:

→ Empirical D(T) behavior for common Petroleum Products

→ established and re-approved by Metrology, API, ASTM and other scientific bodies by regression over many representative product family members

→ Contants are tabled and internationally used as Petroleum Measurement Tables (“PMT”)

Some commonly used Modeling Functions for VCF

I. Definition: $VCF = D(T) / D(15°C)$ *dimensionless ratio and conversion function*

II. Current Model for Fuels, Burner Fuels, ("Group B") :
API Petroleum Measurement Tables for Fuels **"MPMS Chapter 11"**

$$VCF = \exp(-\alpha_{ref} * dT * (1 + 0{,}8 * \alpha_{ref} * dT))$$

with $dT = T - T_{ref}$;
T_{ref} = **15°C, or 60 F,** *or …*

III. "Linear" Group B Model (II) simplified by Taylor Series expansion :

$$VCF = 1 - \alpha_{ref} * dT - 0{,}3 * (\alpha_{ref} * dT)^2$$ *(simplification step 1)*

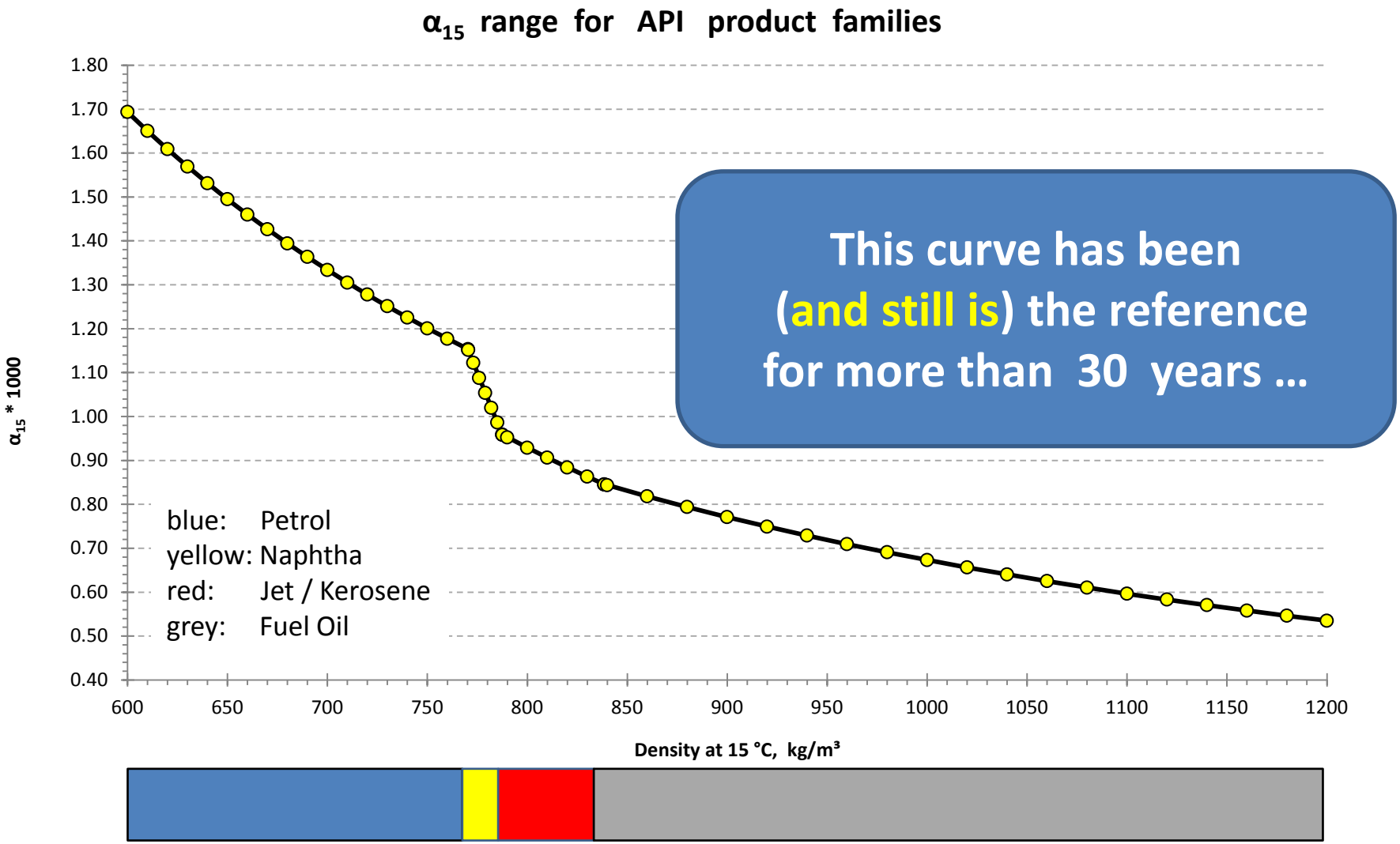
$$VCF = 1 - \alpha_{ref} * dT$$ *(simplification step 2)*
*(**no curvature anymore..**)*

IV. More "precise": **DIN 51757 – "Y – Table"** *(both **α** and **k** in regression)*

$$VCF = \exp(-\alpha_{ref} * dT * (1 + k * \alpha_{ref} * dT))$$ *(e.g. for petrochemicals)*

V. Other Group B models ??
.. like cubic / quadratic regression *(less helpful for larger dT …)*
.. calculate mean α_{15} independent from D(T) *(mechanical volume meters ??)*

API – PMT empirical reference curve (Group B – products)



Contstants for Calulation of α_{15} according to API PMT

API PMT „Group B“ Conditions ..

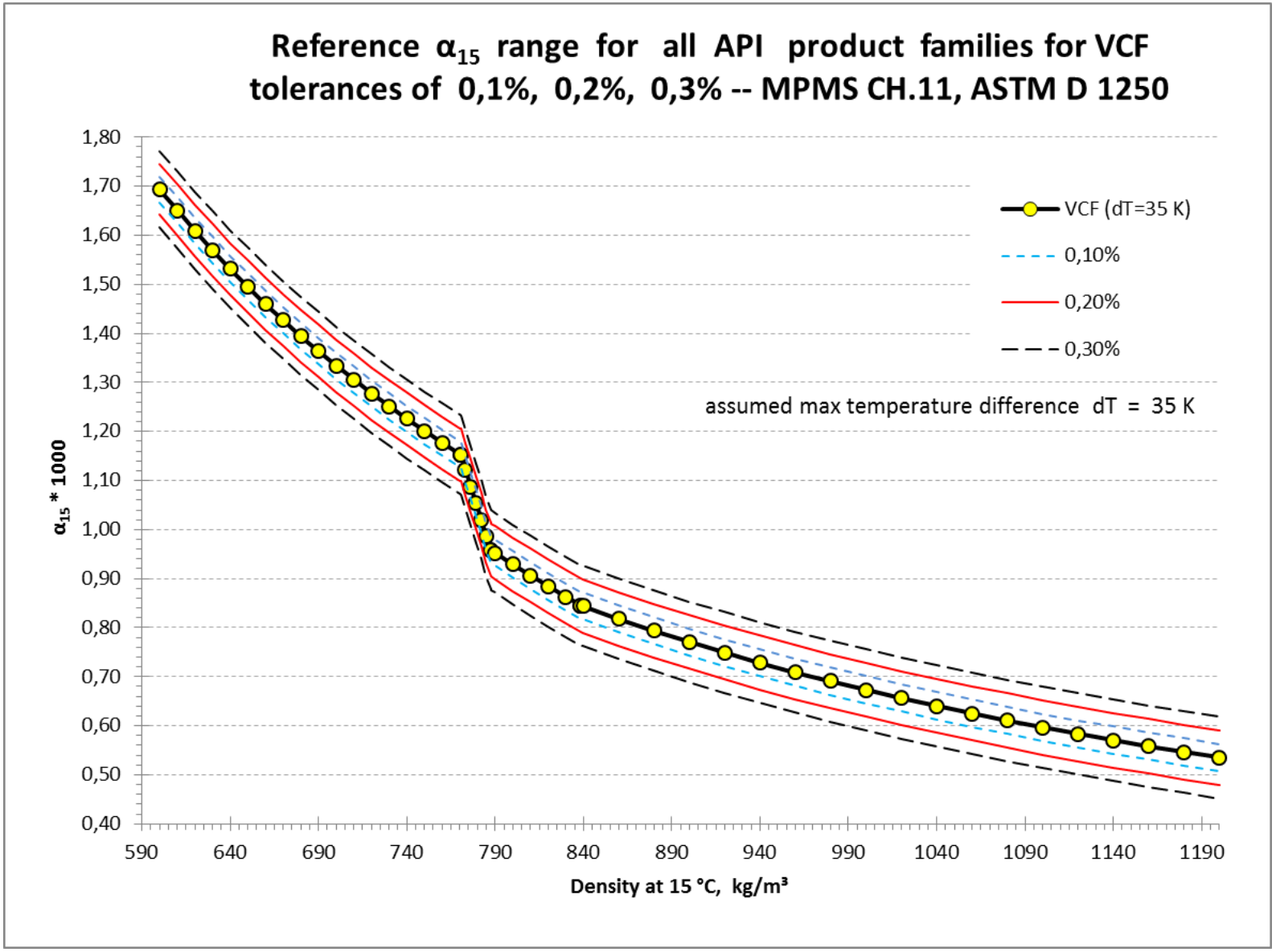
		Petrol		Naphtha		Jet/Kero		Fuel Oil
Group const.	K0	346,42280	A	-0,00336	K0	594,54180	K0	186,96960
Group const.	K1	0,43880	B	2680,32060	K1	0,00000	K1	0,48620
Dens 15-ref	lo	600,0	lo	770,5	lo	787,6	lo	838,6
Dens 15-ref	hi	770,4	hi	787,5	hi	838,5	Hi	1200,0

Each country / economic region can have a different set of products and possibly diverging product family ranges

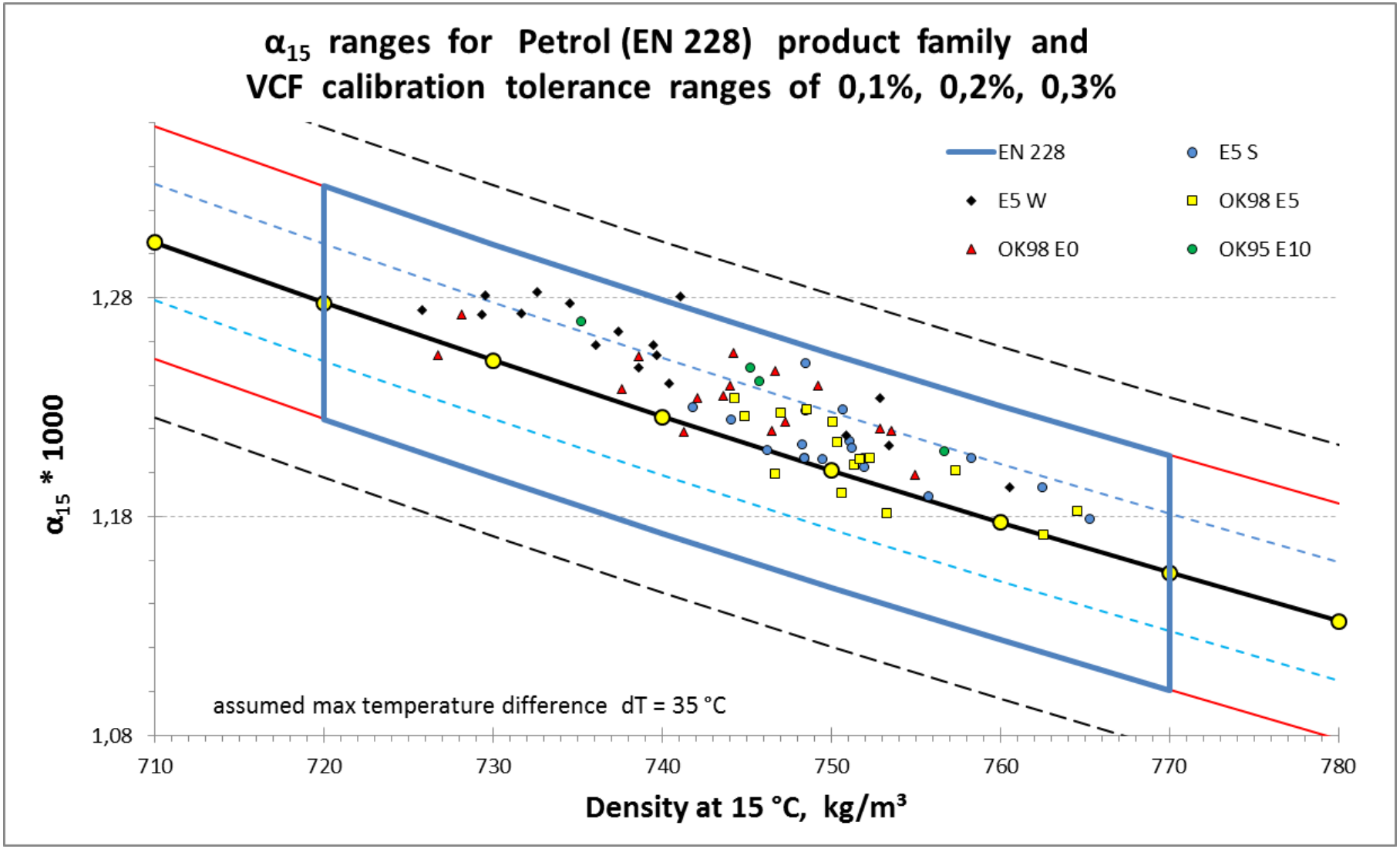
European Fuel Specifications ..

	EN228	Petrol	EN 590	Diesel	EN 14214	FAME
Group const.						
Group const.						
Dens 15-ref	lo	720,0	lo	820,0	lo	860,0
Dens 15-ref	hi	775,0	hi	845,0	hi	900,0

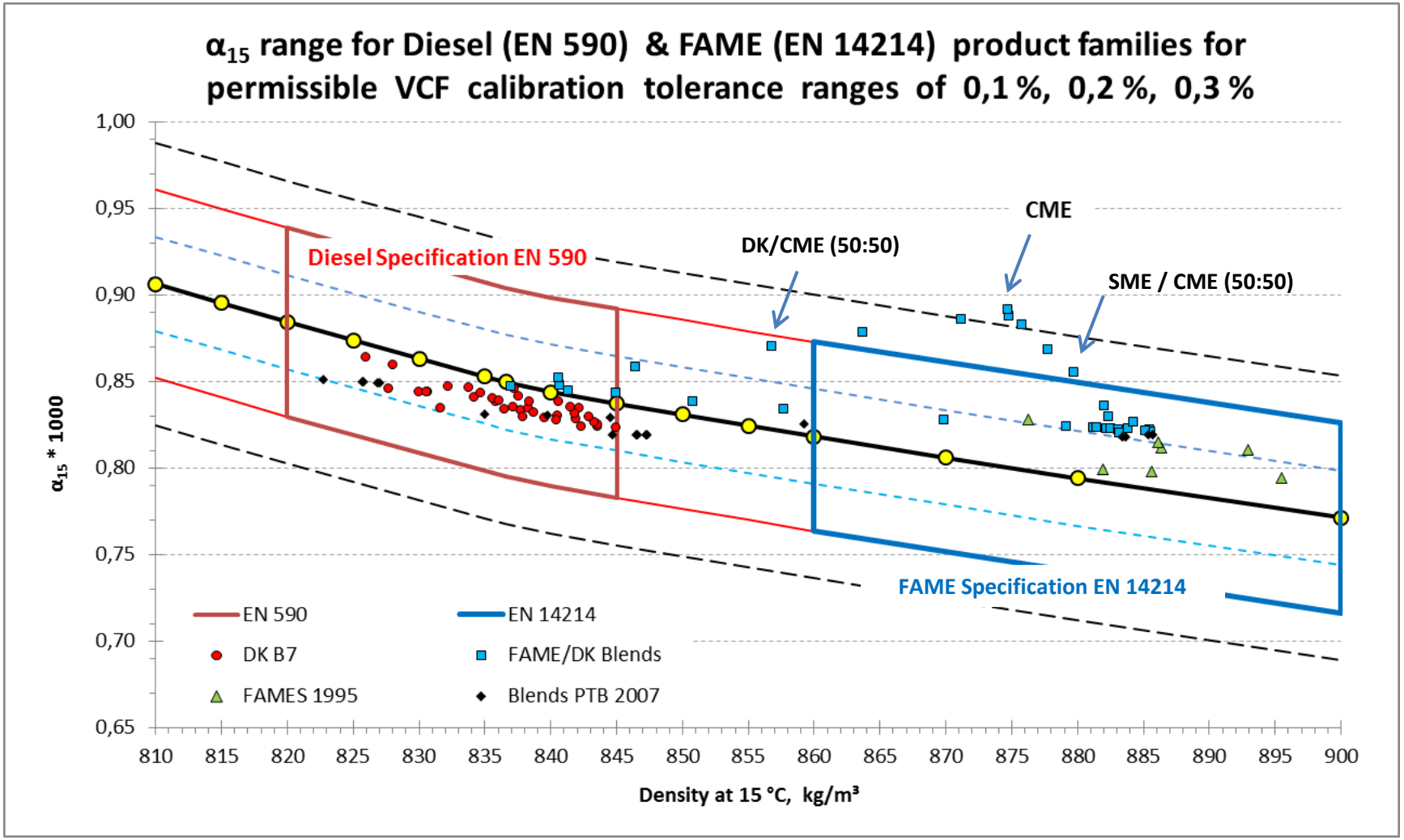
API – PMT empirical Reference Curve – added Calibration Tolerances



α_{15} constants for ~ 70 representative EN 228 Market Petrol Fuels



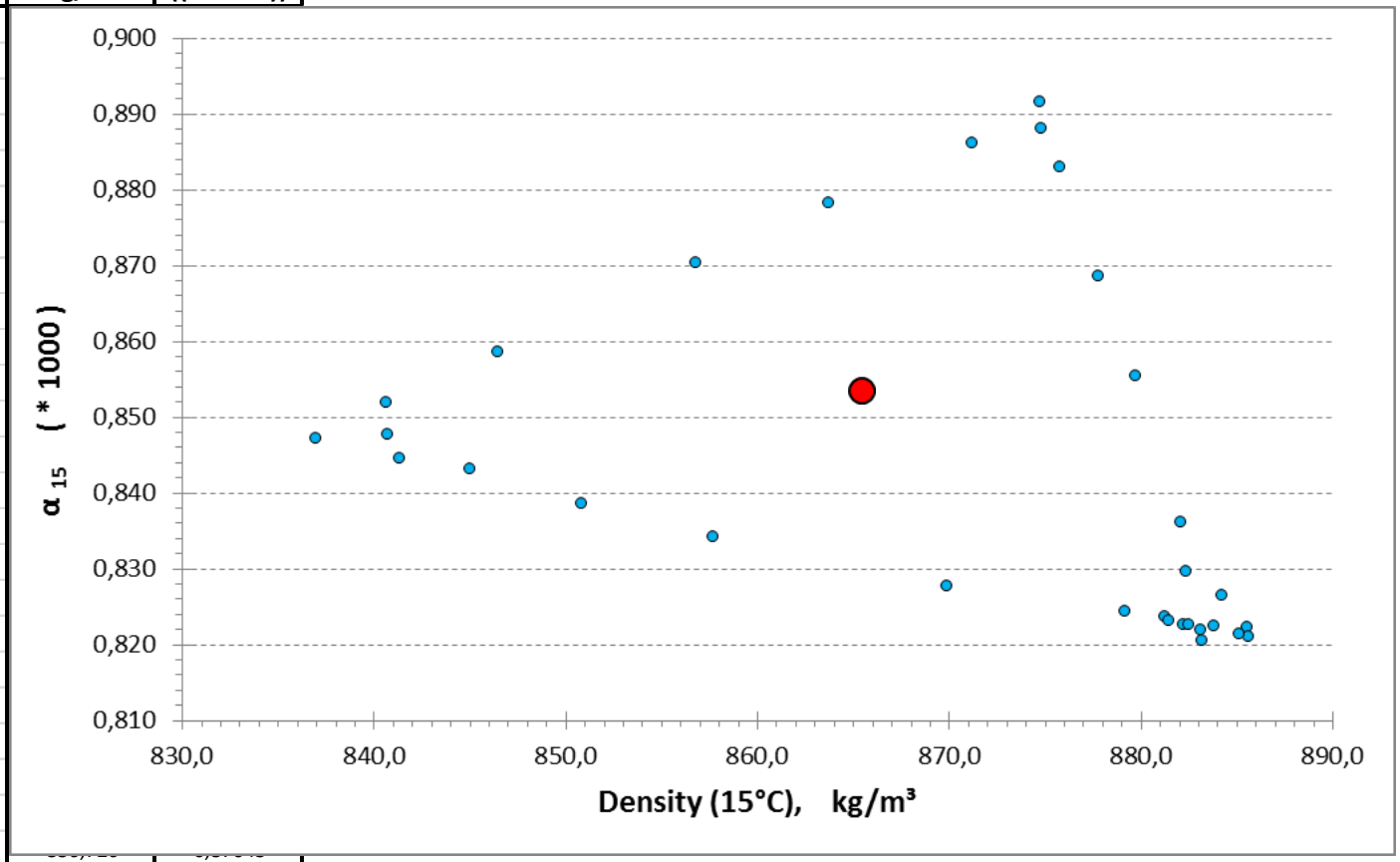
α_{15} Region for EN 590 Diesel Fuels & EN 14214 FAME



"FAME 1995" = Methyl esters from Rapeseed, HO Sunflower, Linseed, Cooking Oil, Sunflower, Soybean
"Blends PTB 2007" = DK/FAME/HEL B7, B10, B20, B50, B100

Results from a DIN – FAM Survey with ~ 30 FAMES & Blends

Sample No.	Type	Blend	D(15) kg/m³	alpha15 ((* 1000))
FAM.01	RME	B100 Gas.Station		
FAM.02	RME	B100 Gas.Station		
FAM.03	RME	B100 Gas.Station		
FAM.04	RME/PME	90 / 10		
FAM.05	SME (Soy)	B100		
FAM.06	RME/SME	75 / 25		
FAM.07	CME	B100		
FAM.08	RME/CME	90 / 10		
FAM.09	RME/CME	99,25 / 0,75		
FAM.10	RME / CME	99,995 / 0,005		
FAM.11	DK / RME	80 / 20		
FAM.12	DK / RME	70 / 30		
FAM.13	DK	B0		
FAM.14	PME	B100		
FAM.15	SME (soy)	B100		
FAM.16	CME	B100		
FAM.17	DK/PME	10 / 90		
FAM.18	DK/PME	30 / 70		
FAM.19	DK/PME	50 / 50		
FAM.20	DK/PME	70 / 30		
FAM.21	DK/PME	90 / 10		
FAM.22	DK/CME	10 / 90		
FAM.23	DK/CME	30 / 70		
FAM.24	DK/CME	50 / 50		
FAM.25	DM/CME	70 / 30	846,406	0,85876
FAM.26	DK / CME	10 / 90	840,587	0,85211
FAM.27	CME/SME	90 / 10	875,714	0,88310
FAM.28	CME/SME	70 / 30	877,712	0,86871
FAM.29	CME/SME	50 / 50	879,695	0,85554
FAM.30	CME/SME	30 / 70	882,019	0,83618
FAM.31	CME/SME	10 / 90	884,203	0,82654



→ Diesel Fuels & FAMEs blend linearly ...

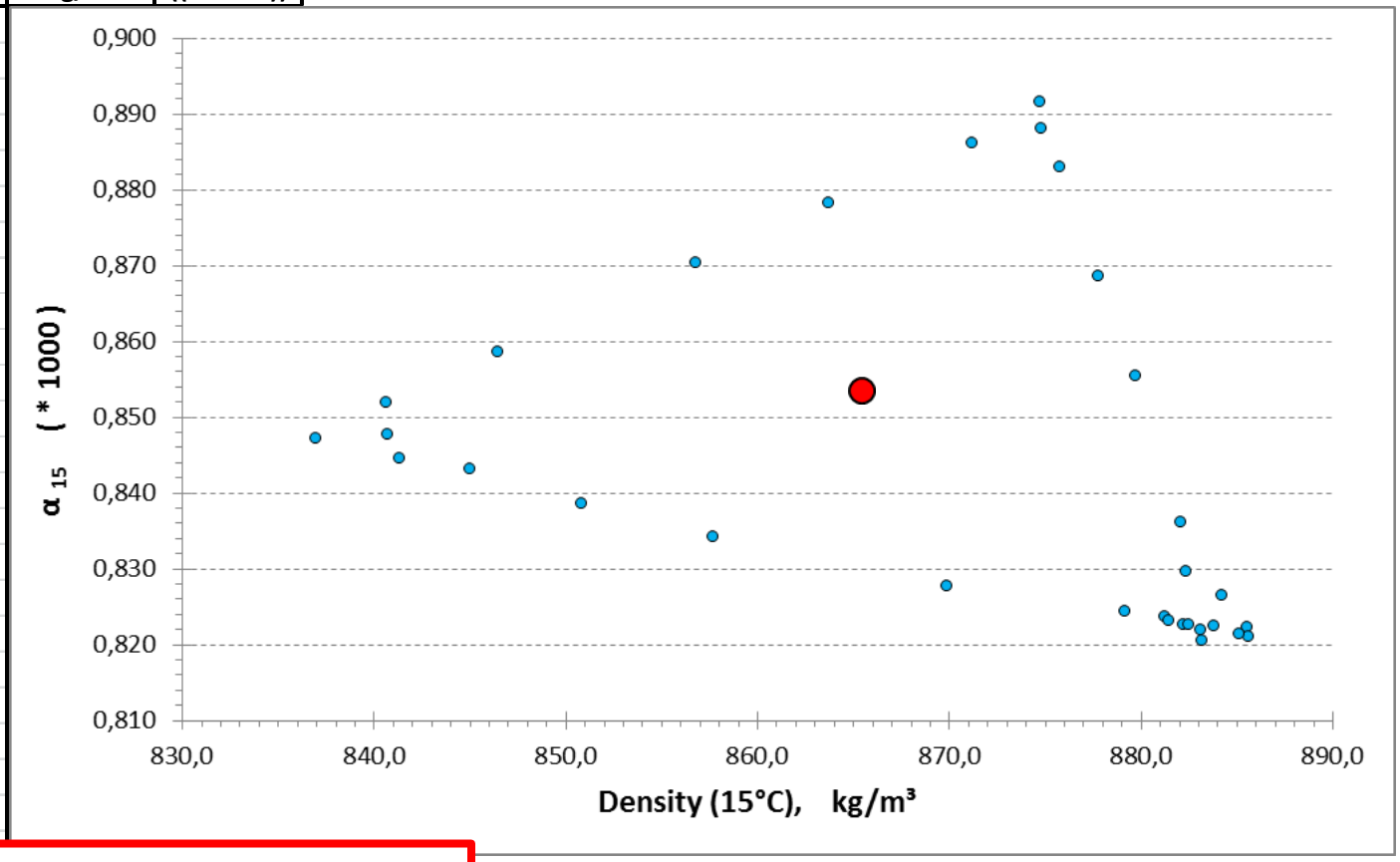
→ Mixtures can easily be (coarsely) predicted …

→ Not all fit well into the allowed calibration corridor

→ How to identify the "misbehaving" ones ???

Results from a DIN – FAM Survey with ~ 30 FAMES & Blends

Sample No.	Type	Blend	D(15) kg/m³	alpha15 ((* 1000))
FAM.01	RME	B100 Gas.Station		
FAM.02	RME	B100 Gas.Station		
FAM.03	RME	B100 Gas.Station		
FAM.04	RME/PME	90 / 10		
FAM.05	SME (Soy)	B100		
FAM.06	RME/SME	75 / 25		
FAM.07	CME	B100		
FAM.08	RME/CME	90 / 10		
FAM.09	RME/CME	99,25 / 0,75		
FAM.10	RME / CME	99,995 / 0,005		
FAM.11	DK / RME	80 / 20		
FAM.12	DK / RME	70 / 30		
FAM.13	DK	B0		
FAM.14	PME	B100		
FAM.15	SME (soy)	B100		
FAM.16	CME	B100		
FAM.17	DK/PME	10 / 90		
FAM.18	DK/PME	30 / 70		
FAM.19	DK/PME	50 / 50		
FAM.20	DK/PME	70 / 30		
FAM.21	DK/PME	90 / 10		
FAM.22	DK/CME	10 / 90		
FAM.23	DK/CME	30 / 70		



For ***coarse*** preliminary checks & predictions :

→ we can use with sufficient precision a linear regression model for α_{15} using density values at only 10, 15, 25, 40 °C …

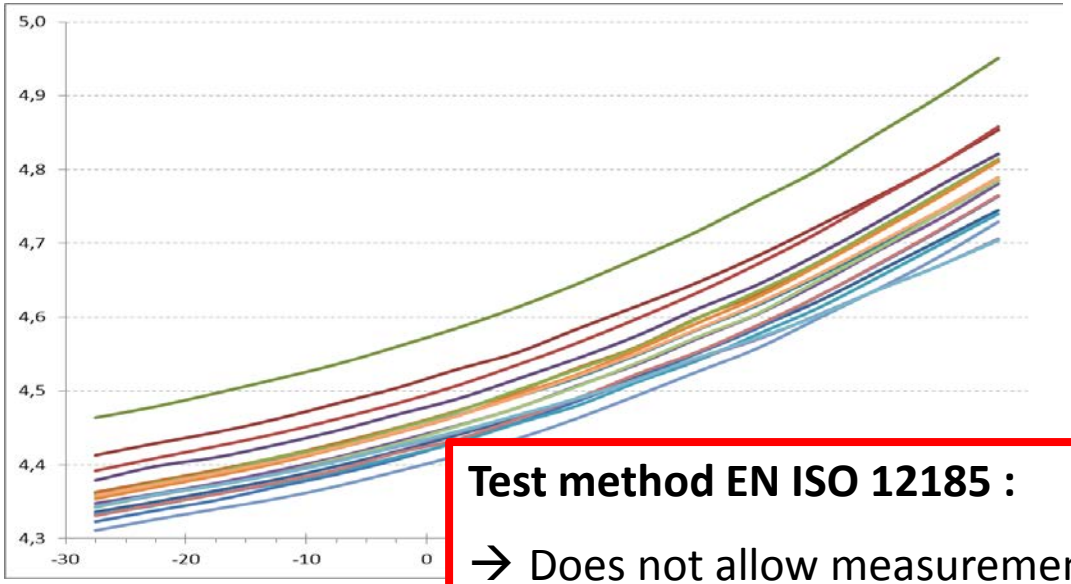
el Fuels & FAMEs blend linearly …

ures can easily be (coarsely) predicted …

all fit well into the allowed calibration corridor

to identify the "misbehaving" ones ???

D(T) Slopes per dT = 5K for gasolines and diesel fuels …



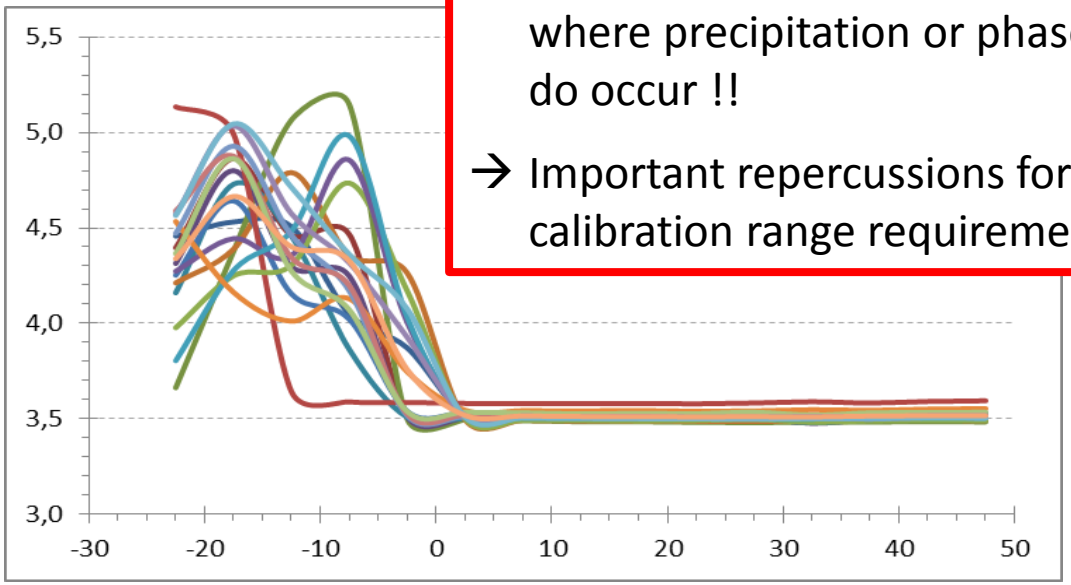
Samples: OK 95 (Summer)

→ Monotonic
→ clearly **not** linear
→ Calibration range T -30 .. + 50 °C

Test method EN ISO 12185 :

→ Does not allow measurement in ranges where precipitation or phase transitions do occur !!

→ Important repercussions for limitations on the calibration range requirements / compliance …



Fuel (Summer)

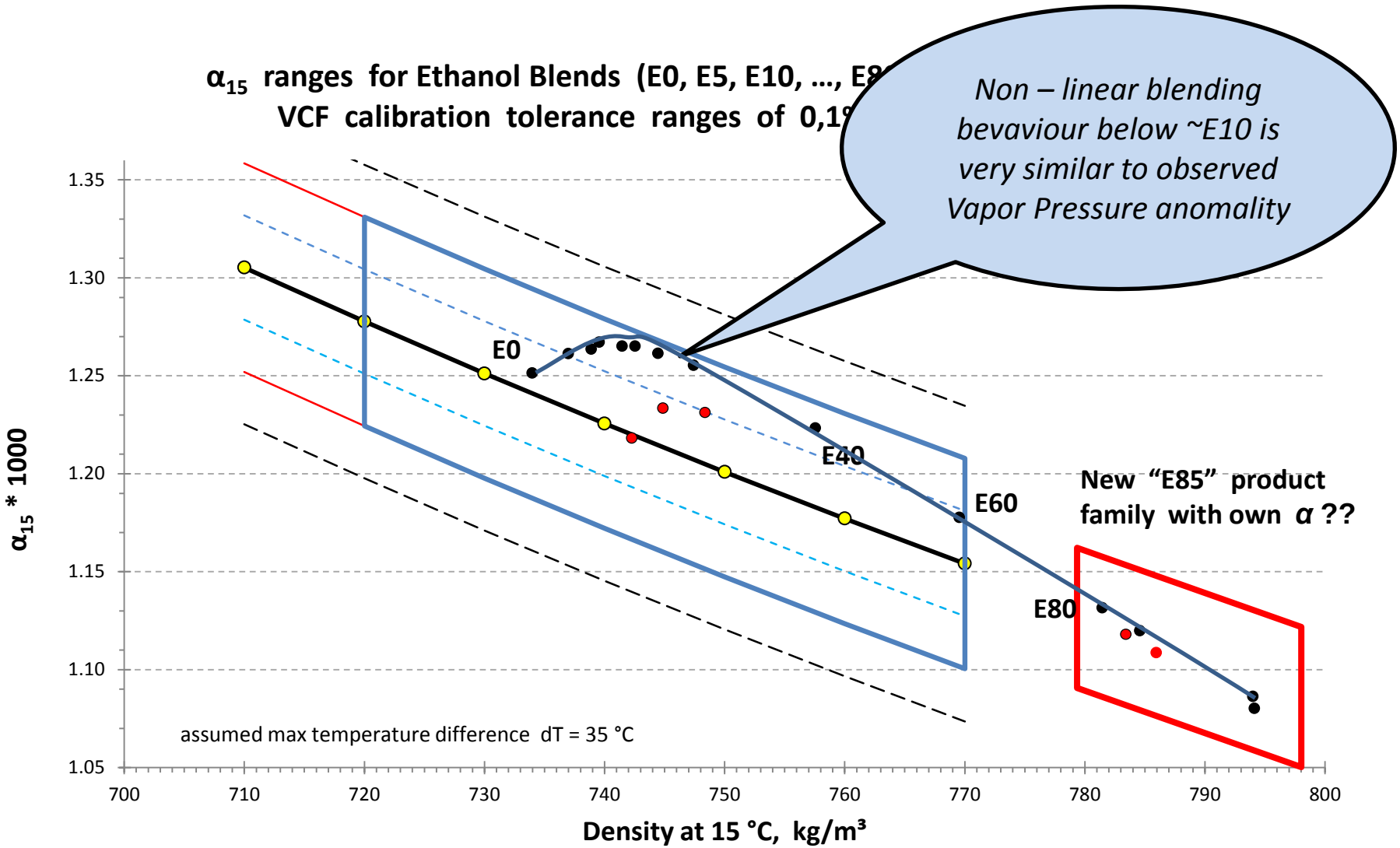
otonic
e ~~ 0°C
e ???

→ Measurement range (!!!)

?? Phase transitions ? Paraffins ??

→ Same behaviour also observed for other middle distillates

α_{15} constants for some Petrol / EtOH Blends



Issues, Conclusions, Proposals (I)

(1) For the regular currently marketed and standardized (european) fuels and fuel oils, there is until now no real need to update or change the PMT constants.

This may change dramatically with indroduction of additional variety brought into the system by new processes & components, no matter if these are "bio" or not ...

(2) As "misbehaving" components like "CME" or other completely new product types can enter the market, a closer watch and better communication on the needs to change density constants seems to be adviseable in order to minimize irritations and precariousness in the market. More aligned international cooperation could help here.

→ as a quick & preliminary check, a linear regression model using a set of min. 4 appropriate temperatures (here: 10, 15, 25, 40 °C) seems to be sufficient;

→ reference procedure should be API MPMS Ch. 11 – "Method C"

(3) More attention should also be paid to

→ compliance with specified measurement ranges and calibration requirements;
→ peculiar variations in product composition
→ the need to find better fitting product family definitions …
→ the need for working routines to check "unknown" products (e.g. API "Method C" ?)

Issues, Conclusions, Proposals (II)

As each single change of α_{15} constants

- to the Petroleum Measurement Tables,
- to existing bookkeeping software and metering hardware,
- to calculation routines and calibration procedures

will cost a lot of money and can produce considerable irritation in the market, we think it to be very important that changes to the PMT should only be done

- with best scrutiny and in international collaboration;
- with common efforts from all involved parties (government & industry,…);
- and when a real need has been demonstrated and verified for new products and streams ….

Also, more analytical attention needs to be paid to differences

- in product composition, product types, specifications and regulations in the markets of different (economical) regions…

→ **For new products, more attention must be paid to compositional issues (e.g. „E85“)**

→ **The plan is to provide more comprehensive data, modeling results and argument in a CEN Technical Report, anticipated for early 2013**

This is the end - (of my presentation)..

Thank you very much for listening !!
(you may applaud now ..)

to express your thanks also to my many valuable contributing colleagues, experts and technicians in German and European Standardisation …

Bibliography & suggested Reading …

- API Petroleum Measurement Tables (PMT) for Temperature conversion for Petroleum Products
- Erdöl und Kohle – Erdgas – Petrochemie 15, Nr 10, pages 738-739 (1960)
  Anderung der Dichte von Mineralölprodukten mit der Temperatur (Ergänzung zu DIN 51757)
- ASTM D 1250 – Standard guide for the use of "PMT" (still in use are the revsions from 1980, 2004, 2010, …)
- ISO 91-1, ISO 91-2 – Petroleum Measurement Tables (with references to API and ASTM)
- API MPMS chapter 11.1 and related chapters (also adjuncts to ASTM D 1250, IP 200/04)
  (see also www.quantityware.com/_data/Petroleum_ASTM_D1250-04_SP12.pdf)
- EN ISO 12185 – Density measurement of petroleum products using Qcillating U-tube
- EN ISO 3675 – Density measurement of petroleum products using Hydrometer
- Rathbauer, Bachler Int. Conference on Standardization and Analysis of Biodiesel, Nov. 6-7, 1995, Vienna
  Physical Properties of Vegetable Oil Methyl Esters
- Institute of Petroleum / API Work package "Volume Correction Fasctors by velocity of sound (December 2003)
- OIML publications D28.E04, G14(1987), G14 (2011), and more
- Several PTB papers to be found in the Internet
- Energy Institute Project HM 802/J901
  Volume Correction Factors for FAME and FAME / Mineral diesel Blends (2011-10)
- API MPMS Chapter 11.3.3 – Misc. Hydrocarbon Properties – Ethanol Density and Volume Correction Factors
- CEN Technical Report, including all recent data , ckinstants, discussions and findings for future reference
  (proposed for publication 1st Quarter 2013 …)