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Petroleum products — Density versus temperature relationships of current fuels, biofuels and biofuel components

Produits pétroliers — Densité contre température relations des carburants actuels, les biocarburants et leur composants

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by ISO/TC 28, *Petroleum and related products, fuels and lubricants from natural or synthetic sources*.

Introduction

The density of hydrocarbon fuels at a standard condition of temperature and pressure is used to define the quantity (standard volume) of the product during trade and fiscal transactions. To ensure standardization in the calculation of standard volume and density from actual conditions the thermal and pressure expansion factors are calculated through the application of standardized methods and algorithms.

In the advent of new fuel compositions like HVO ("Hydrogenated Vegetable Oil") as well as blends with bio products like ethanol and FAME ("Fatty Acid Methyl Esters") in the markets, the question was raised whether the density/temperature relationships, which have been applied for more than 60 years to transform the density or volume of a petroleum product, are a temperature measured at transport time or a "reduced" density or volume value at a standard temperature (15°C and in some areas 60 °F).

In order to identify potential differences for these new products, the German petroleum standardization committee (DIN-FAM) started as early as 2003 to make extensive density/temperature measurements starting with FAME. Examination of additional products followed, and other associations like AFNOR and the Energy Institute (EI) also shared their results of similar investigations.

This document also recommends procedural steps to obtain data which will determine the thermal expansion of new or alternative fuels and blends hence allowing a comparison to accepted and standardized correction factors (e.g. Petroleum Measurement Tables - ISO 91, IP 200 and API MPMS chapters 11.1, 11.2.4 and 11.5).

This document collates the executed measurements, modelling procedures and results in order to keep measured data available for later reference, including some recommendations for further work and a list of possibly unresolved questions.

For a number of reasons the work has been restricted to fuels, bio fuel components, and their blends and to some burner fuels and components. The majority of these examined products followed European Fuel Specifications such as EN 228, EN 590, EN 14214, EN 15376, and the reference temperature was kept at 15 °C. The work only covers the thermal expansion of the products at a standard condition of pressure and has not been extended to compressibility.

This document also recommends procedural steps to obtain data which allows a decision to be made on whether any completely new fuel composition can or cannot use the published internationally accepted API Petroleum Measurement Tables ("PMT") which are also the basis of several international and national petroleum measurement standards.

In addition, this document contains an extensive list of publications which can yield further in-depth information about this complex and interesting petroleum measurement topic.

Petroleum products — Density versus temperature relationships of current fuels, biofuels and biofuel components

1 Scope

This document lists and describes recent density measurements at different temperatures for biofuel components and biofuel blends such as gasoline E5, E10, E85 and biodiesel B100, B7, as well as domestic heating oils and paraffinic diesel fuels.

It can be used to calculate <alpha15>, the thermal expansion coefficient from a given temperature to 15 °C. This document can also serve to compare several aspects of density/temperature modelling and to check for compliance with and limitations in relation to existing calibration requirements. It can help in the determination of specific necessities for the grouping of fuels into common product family classes, also suggesting ways to treat fuels or components with an unusual behaviour. In addition, this document proposes possible steps for an internationally harmonized handling of new components coming into the market.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

4 Summary

Several extensive sample sets comprising artificial blends as well as market fuels were analysed with respect to their temperature-dependent densities. The purpose of these analyses was to find out if the density, as well as the volume, at a certain temperature can be predicted using the constants, group constants and regression models of the internationally used API Petroleum Measurement Tables (PMT) published in 1960 and revised in 1980[13].

The examined products were:

— diesel fuels (B0, B5, B7) according to the European standard fuel specification EN 590[28], supplemented by some additional blends with FAME;

— fatty acid methyl esters (biodiesel) of different compositions and origins which are in the market today[31];

— petrol (E0, E5, E10) according to the European standard fuel specification EN 228[27], supplemented by some additional blends with ethanol up to E100;

— domestic heating fuels according to DIN 51603-1[29], also as low sulfur grade;

— several samples of paraffinic diesel fuels (GTL, XTL) for which an European standard fuel specification is established as EN 15940[30].

The main intention of this study was to find out if individually calculated thermal expansion coefficients α_{15} and their corresponding densities (or volumes) at 15 °C are close enough to the values predicted by the published PMT values, taking into consideration the precision requirements of the EC Measuring Instruments Directive. This directive is of particular importance e.g. for the calibration of volume metering equipment.

The executed studies indicate that although some small biases were found in most cases, the predictions described in the PMT may still be used, except for a smaller number of cases being:

— MD/diesel blends with more than about 50 %(*V/V*) of coconut methyl ester (CME);

— automotive E85 fuels with more than about 40 %(*V/V*) ethanol content;

— some new products like paraffinic diesel fuel.

Since it not possible to extrapolate such findings to any other kind of new product types, a recommendation is given to investigate such temperature versus density/volume behaviour when new fuel specifications are under development.

In any case it is strongly recommended to decide before any such investigation if the resulting model should be just good enough to fulfil the requirement or if best possible precision is wanted. This decision can have some influence about the choice of the best suited regression model.

As a long term perspective, a full revision of the PMT models and constants should be considered especially if it is expected that there will be much more variation in fuel composition as compared to the last, say 50 years.

5 Background and motivation

It is common knowledge that the density of a product in its liquid phase depends mainly on product composition; temperature, due to extra- and intermolecular motion.

In addition, pressure can also affect density, but this effect was not investigated here because the changes caused by pressure are orders of magnitude smaller than those from temperature changes.

For trading and transport, the density-temperature function of a product is a very important product property for the determination of the product amount because the temperature of a liquid fuel can be as high as 50 °C, whereas, e.g. for tax reasons, almost all regulatory requirements demand that product densities are reported at a standard temperature of 15 °C (or, like in the US, also at 60 °F) as a prediction using these density-temperature procedures.

The internationally accepted procedures for the determination and application of density and volume transformation from one temperature to another or to a standard temperature have been developed and standardized by the API and ASTM and are commonly referred to as the Petroleum Measurement Tables (PMT). These tables have been adopted by ISO (ISO 91) and by OIML by referring to ISO 91[14].

The tables and the procedures within them have been have been applied successfully and with satisfactory precision for more than 60 to 70 years and provide a standardized and accepted basis for trade[1][2][3][4].

NOTE 1 This report refers to the three latest version of the API tables, published in 1960, 1980 and 2000. The version from 2000 is a computer adoption of the 1980 version, including pressure correction.

It is evident that this success is mainly based on the existence of comparatively small compositional changes across a specific product family. The advent of biofuels and biofuel components like FAME (Fatty Acid Methyl Esters) in the market raised the question of whether the PMT tables could still be applied with acceptable precision for the predicted density at reference temperature. This question

led to several series of FAME density measurements at different institutions in Germany, the UK and France, and probably also in many other countries.

Later this campaign was extended to ethanol, petrol blends (E0, E5, E10, … E85, E100) and to several other products like Hydrogenated Vegetable Oil (HVO), paraffinic Diesel fuels (GTL, XTL).

NOTE 2 Most of the mentioned calculations and procedures and their background are documented at least in part in the available standards, publications and regulatory documents, so a large portion of the described detail is supposed to be common knowledge for the experts working with petroleum measurement regularly. It is the intention of this document to describe everything to such a degree of detail that also people new to this field of expertise have a chance to follow and understand all of the contained reasoning.

Although the latest version of the PMT and ISO 91 are recommended, older versions are sometimes still employed as defined in local regulation, practice or commercial agreements.

These facts might be able to explain some differences which could not be explained otherwise.

6 Basic analytical considerations

6.1 Intentions of this document

In order to fully comprehend the discussions and arguments presented in this document, the following clauses set out the relevant definitions, procedures, facts, calculations and consequences.

It is not the intention of this document to copy already existing content from other existing publications or standards, but it was found essential to compile all relevant facts in one place. For further information, see the Bibliography.

6.2 Physical property density

The physical property density is defined as the ratio of mass over volume as shown in Formulae (1) and (2). It is important to note that the density depends to a large extent on the product temperature such that with increasing temperature density decreases (volume increase e.g. due to more molecular motion) while mass remains constant. As this document only deals with (liquid) fuels, phase transitions to the gaseous or solid state are not discussed. Such transitions can become a problem at extreme product temperatures.

NOTE 1 While density is normally represented by the Greek letter ρ, this document uses a capital D for density for easier and more clear writing. Further information is often added as an index or given in brackets. This means that e.g. $D15$ and $D(15)$ will mean the same thing:

$$\rho_t = m / V_t \,(1)\, \rho_t = m^* V_t \tag{1}$$

$$D(t) = m / V(t) \tag{2}$$

where

ρ, D is the sample density; usually in g/ml or kg/m^3;

m is the sample mass (NOT the weight); usually in g or kg;

V is the sample volume; usually in ml or m^3;

t is the sample's temperature; usually in °C.

The numerator of the density definition is mass and not, as sometimes wrongly stated, weight, which is the property when gravity acts on the mass of a product. Therefore, constructs like density in air or density in vacuum simply do not exist. For cases where weight is required, a correction for the air buoyancy mass can be applied.

NOTE 2 There are several incarnations of a reported density value, depending on the fact if this value was obtained by direct measurement at the required temperature; or if it was predicted from measurement at a different temperature using PMT procedures for appropriate conversion to standard temperature. In cases where this can become relevant, corresponding mention is made in this document.

NOTE 3 There are several test methods, all using different physical principles for the determination of the density of petroleum products/fuels (see experimental section). Only the quartz oscillator test method has been used in this report as prescribed in ISO 12185. This is currently the most used density test method for liquid fuels.

6.3 Density for (defined) product blends/mixtures

For many product blends density follows a linear regime, i.e. the density/volume of the blend has a linear relationship with the volumes and densities of the components when measured at the same temperature.

However exceptions to this rule are known from literature and recent work which show that for blends of some components the relationship can be far from linear. Examples include:

— temperature of mixture changes during blending;

— molecular and compositional structures of blend components are significantly different;

— other physical effects occur such as modified molecular solvent cages e.g. for alcohols (OH bonding).

6.4 The volume correction factor (VCF)

The definition for the volume correction factor (VCF) is given in Formulae (3) and (4). The VCF is simply the ratio of density at the temperature t of interest over density at standard temperature (normally 15 °C). It is therefore the basic proportionality function for the calculation (prediction) of density (or volume) at standard temperature from a density (or volume) measured at another temperature t or vice versa. Elaborate models like the PMT and several others have been developed for construction of this VCF function for single products as well as for commonly used product families. The following sections of this document will give more detail about these models and their modelling strategies. But first we should have a look at the basic definitions.

$$\mathrm{VCF}(t,\mathrm{ref}\cdot t) = D(t) / D(\mathrm{ref}\cdot t) \tag{3}$$

$$\mathrm{VCF}(t,\mathrm{ref}\cdot t) = V(\mathrm{ref}\cdot t) / V(t) \tag{4}$$

where

VCF being volume/volume or density/density ratios (dimensionless);

D, V being density and volume as explained in Formula (1);

$ref{\cdot}t$ being the sample's reference temperature; usually 15 °C;

t being the sample's temperature; usually in °C.

It is evident that the VCF has the value 1,000 0 at the reference temperature (usually 15 °C). Also, individual VCF(t) functions for different products will by default always intersect at the reference temperature. It is also important to note that each single VCF function has been derived for a specific sample of a product family for limited temperature or density ranges which should not be extrapolated.

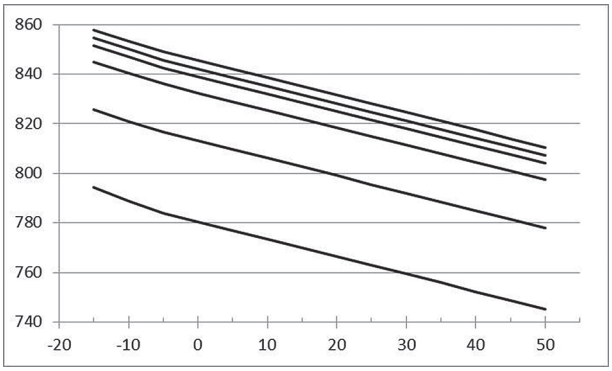
The form of the VCF function can range from nonlinear/exponential, linear, and even constant (like for some products with little variation in composition and density/temperature range). The models used for petroleum metering should reflect such different functional behaviours.

For products of similar/comparable density, temperature and composition, the PMT allow some grouping into product families. Here, a hopefully large and representative number of product family

members is investigated. This investigation results in a set of constants K_0, K_1, K_2, from which the thermal expansion coefficient α_{ref} can be calculated with inclusion of the density at reference temperature (see modelling section for more detail).

6.5 Graphical representations of the density/temperature behaviour

Figure 1 shows a commonly used and typical graphical representation of the $D(t)$ behaviour for a selection of six gas oils.

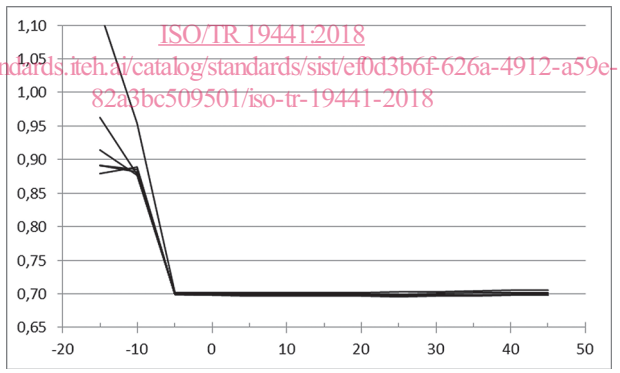


Key

X temperature in °C

Y density change in kg/m³ per °C

Figure 1 — Density/temperature function



Key

X temperature in °C

Y density in kg/m³

Figure 2 — K_0E/temperature function

The graphs display a number of issues to remember.

— Densities for members of one product family can stretch over a large range.

— The slopes for members of a product family are often very similar (but not necessarily identical (depending on the required prediction quality).

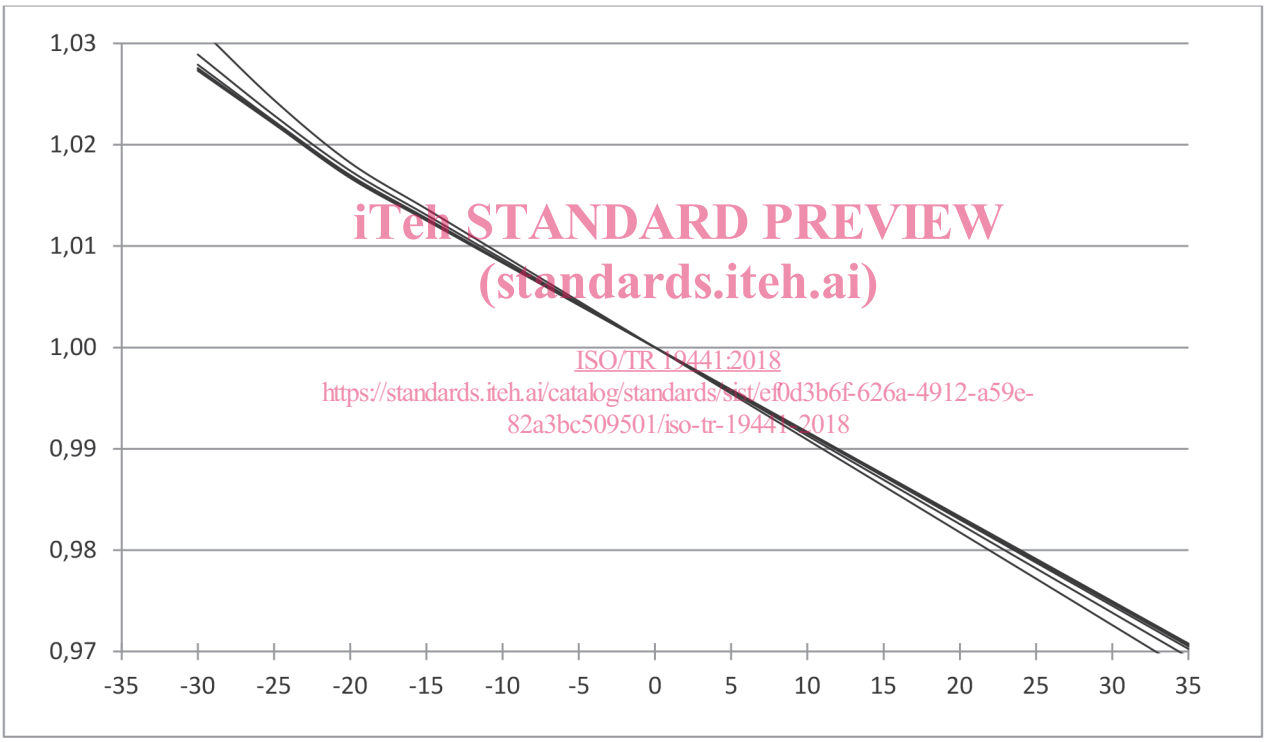
— From a superficial viewpoint, the $D(t)$ curves seem to be (almost) linear. However, this can be quite different for other product families. Therefore, a nonlinear (exponential) modelling approach has been (and still is) used traditionally in the international PMT community.

Figure 2 indicates that the temperature range for the $D(t)$ modelling can also be quite important. The displayed case for six gas oils suggests that irregular behaviour can occur at lower temperatures where there is a good chance of crystal formation or even solidification. A model has to consider these phase transition effects when a reliable and most precise prediction is wanted (same is true for extreme high temperatures (bubbles, evaporation, boiling).

Current experience from field transport experts suggest that for the petrol, diesel and biofuels investigated in this document, a temperature range of about −5 °C to about 50 °C is usually sufficient.

Figure 3 displays the VCF(t) plot for the same six gas oils. At $X = 0$ (i.e. at standard temperature of 15 °C) all curves intersect in the same point (at y = 1,00) by definition, and potential differences between product family members become more visible the farther the temperature is away from the standard temperature.

NOTE The VCF(t) curve shown in Figure 3 is simply constructed by division of each $D(t)$ value by the sample's reference $D(15)$ value. These curves do not represent the results from the PMT procedures, for which the use of a specific PMT regression model is assumed. Nevertheless, the plot shows nicely the similarities and differences between similar samples of one gasoil family.



Key

X (t−15) in °C

Y VCF(t,15)

Figure 3 — *VCF*(t,15) plot for the same six gasoil samples

7 Applicable VCF models

7.1 General

Several models have been developed over the years for petroleum measurement of diverse petroleum products. For an in-depth sight and some important history, see the Bibliography. Since the focus of

this document is on fuels, bio fuels and their components (i.e. Tables B of the petroleum measurement tables), the list of useful and common models is reduced to the following:

— exponential model — the mainly used model in the PMT for fuels of group B;

— linear models — a simplified model derived from the exponential model;

— constant value model — promoted by some government chemist associations.

Other sometimes proposed models like third order parabolic regression do not, at least in Europe, play any important role in the trading of conventional and bio-based fuels and their components.

7.2 Exponential model (for a single sample)

Used and published in the PMT, it represents clearly the most often applied and internationally accepted VCF model. The definition is given in Formula (5). The two constants α_{15} and K describe the slope and curvature of the VCF function. For all fuel related products of mineral oil group B, a fixed valued of K = 0,8 has emerged over the years and is still used in the PMT. The development of group family constants for α_{15} is explained in the next clause.

$$\mathrm{VCF} = \exp\left(-\alpha_{15} * dt * \left(1 - K * \alpha_{15} * dt\right)\right) \tag{5}$$

where

α_{15} is the thermal expansion coefficient at reference temperature (normally 15 °C, but some countries also use 60F as ref. temperature, in which case α is given as α_{60F});

K is a constant describing the curvature. Normally this value is always fixed at K = 0,8;

dt is the difference between measured and reference temperature (normally 15 °C).

The α_{15} is calculated and used for only the specific sample for which at minimum 10 densities at different temperatures have been measured. This temperature range should include the temperatures of interest used during transport, but some care should be taken at extreme temperatures to avoid solidification or bubbling in the sample. These measured data pairs $D(t)$ and t are then submitted to a regression procedure specified in API MPMS Chapter 11.1. Annex A contains a script using the public domain statistical scripting language R, which may be used for the determination of α_{15}.

IMPORTANT — It should be noticed that the 60 °F reference temperature equals to 15,666 67 °C (i.e. 15 °C = 59 °F and not 60 °F), and that in the PMT, given α_{15} values are in reality values for 15,666 67 °C. It is an obvious international agreement to ignore this difference for "α" because the slopes at 15 °C and 15,666 67 °C should be quite similar. To avoid any doubts, this TR will give D(15), D(60 °F), α_{15} and $\alpha_{60\ °F}$ wherever possible. The difference between D(15 °C) and D(6 °F) can amount to more than 0,5 kg/m³. This should be considered when precision issues are discussed.

NOTE DIN 51757[17] has a section for pure petrochemical products (demonstrated Y-Table), for which also different values for K have been developed which to minimize the residuals between measured and predicted values. More information, including some example data, about this Y-table is given in Annex B.

7.3 The linear VCF model

The linear VCF model can best be described as a derivative/simplification of the exponential model via a Taylor series as described in Formula (6) – simplification 1) and Formula (7) – simplification 2). It may be used when curvature of the VCF function is minimal and when differences between linear and exponential model are tolerably small.

$$\mathrm{VCF} = 1 - \alpha_{\mathrm{ref}} * dt - 0{,}3 * \alpha_{\mathrm{ref}}^2 * dt \tag{6}$$

$$\mathrm{VCF} = 1 - \alpha_{\mathrm{ref}} * dt \tag{7}$$

Introducing the densities from the VCF definition then leads to:

$$D(t) = D(15) * (1 - \alpha_{15} * dt) \tag{8a}$$

$$\text{or } V(15) = V(t) * (1 - \alpha_{15} * dt) \tag{8b}$$

where

VCF is the volume correction factor for temperature t;

$D(t)$ is the density at temperature t;

$D(15)$ is the density at the reference temperature (15 °C);

α_{ref} is the thermal expansion factor at reference temperature (15 °C);

dt is the temperature difference (t – 15) in °C.

The linear model produces a straight line, forfeiting the chance to detect and incorporate any nonlinear behaviour of the VCF-function. One well-noticed advantage is that the needed regression for the detection of α_{15} from minimal 10 density/temperature pairs can be done with any regular regression function like those provided by Excel or other off the shelf statistical software.

As will be shown in the experimental section, this linear model can be applied to FAME, where the thermal expansion coefficients do not vary so very much over the FAMES' density ranges, but it is strongly recommended to check the residuals and compare them with those from the exponential models before decisions to use the linear model are made.

It is important to notice that, just like for the exponential model, the regression result α_{15} is in principle only valid for the examined sample. There is not much procedural documentation about how to arrive at a (possibly $D(15)$ independent) "α_{15}" group product family value like they can be found in the literature and published standards for petrol.

A variation of the Linear Model is also applied in the European FAME specification, EN 14214,[31] as specified in Formula (9). The slope of 0,723, and a mean density of $D(15)$ = 886,3 kg/m^3, averaged over seven different FAME samples has been developed in a research project lead by J. Rathbauer[9].

$$D(15\ °\mathrm{C}) = D(t) + 0{,}723 * (t - 15) \tag{9}$$

7.4 The constant value model for a specific product family

This model is best explained by Formula (10). It is mainly promoted by the metrology institutes, such as PTB (Physikalisch-Technische Bundesanstalt, German Metrology Institute), for the calibration of volume meters, taking into consideration the allowable prediction tolerance of max. ±0,2 % as specified in the EC machine directive.

Other than using a still density/sample dependent thermal expansion coefficient α_{15} like in the exponential and linear model, a mean slope k_{0E} is used obtained from the slopes of a number of samples from the product family under examination. Values for k_{0E} are generally prescribed in regulations for volume meter calibrations. For more details about this model see [10]. Figure 4 shows some k_{0E} values

suggested by the PTB (German government chemist) for commonly traded products. It should be noted that these averaged k_{0E} values do no longer depend on the sample's density.

$$\mathrm{VCF} = \frac{D(t)}{D(15)} = \frac{V(15)}{V(t)} = 1 - k_{0E} * (t - 15) \tag{10}$$

The maximum temperature difference of 35 °C and the precision requirement of maximum ±0,2 % then leads to a permissible tolerance band of $|\Delta k| \leq 5 * 10^{-5}$. Individual slopes k from which the mean k_{0E} is calculated have to fall inside the range ($k \pm \Delta k$), otherwise the average value model cannot use the prescribed k_{0E} for that particular product or sample.

This is also reflected by the fact that e.g. in Germany, the k_{0E} values have been updated in different editions of the volume meter calibration regulations (see e.g. Figure 4) along with several product composition changes over the years. It is also important to note that this mean k_{0E} is not influenced by the product reference density as will be shown is the case to the PMT exponential model.

Table 1 — k_{0E}-values for the constant value model as promoted by the PTB

Product group	Date of PTB publication	k_{0E} (1/K)	$\pm\Delta k$ (in 1/K) for Δt = 35 °C	Remarks
Group B,1	2004	$1{,}21 * 10^{-3}$	$5 * 10^{-5}$	For E0,E10, E80, E100
Group B,3 and B,4	2004	$0{,}84 * 10^{-3}$	$5 * 10^{-5}$	For Diesel, FAME (RME and SME) and Heating oil (HEL)
Group B,3 and B,4	2011	$0{,}84 * 10^{-3}$	$5 * 10^{-5}$	For Diesel, HEL, CME from B0 to B40
Group B,1 - petrol	2011	$1{,}27 * 10^{-3}$	$5 * 10^{-5}$	For E0 .. E40
Group B,1 - ethanol	2011	$1{,}14 * 10^{-3}$	$5 * 10^{-5}$	For E60 .. E100

Some additional aspects concerning the constant volume model should get some special attention:

— the major use is for the calibration of volume meters as prescribed by (e.g. national) regulators;

— use of a specific k_{0E} value can only cover a small variety of samples inside just one product family, and when there is too much variation in product composition or slopes of the $D(t)$ curves, the constant value model could no longer comply to the pre-set precision requirements;

— the constant value model is, of course, easy to use, but also using up most of the permissible measurement uncertainty, leaving little to no room for other measurement uncertainties like those coming from the determination of density and temperature. In the analytical community, this is sometimes seen as a contrast to the wish for best possible precision in the modelling of results.

NOTE Since this document does not intend to interfere with any regulated issues, the constant value model is not discussed any further here.

8 Developing the group constants K_0, K_1, K_2 for the PMT Group B products (see Table 1)

In the previous clauses we have described the development α_{15} and $D(15)$ for just one product. Much effort has been put into the measurement of these values for the different product families over the past decades to determine some sort of common model for a complete product family. ASTM and IP, for example, explain such measurements and additional regression work from several hundred product family members in their standards, and indeed, a useable and rather robust regression model for the