Division 3

Chemical Physics and Explosion Protection

Metrology for gaseous and liquid energy carriers

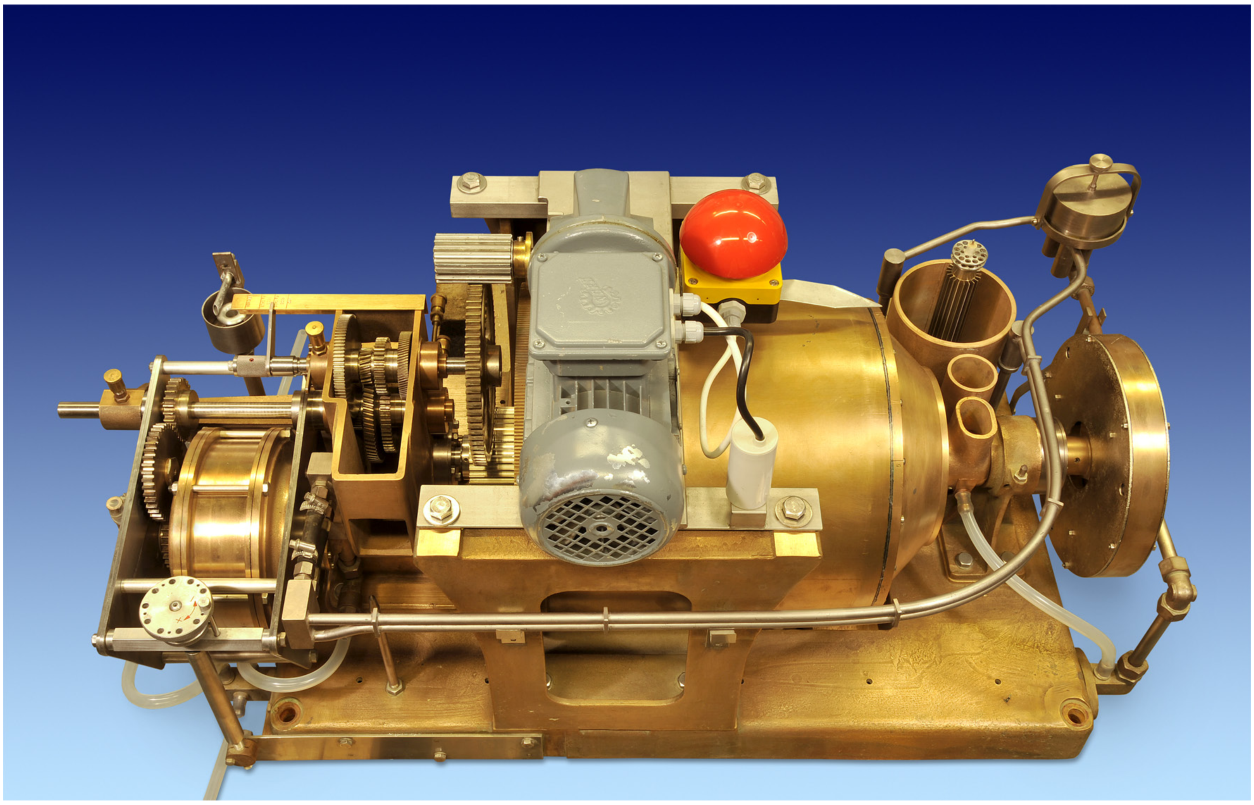
In the course of the current efforts to increasingly utilize regenerative energy, a series of new metrological issues arises. PTB has, in particular, dealt with the thermophysical measurands relevant for legal metrology. Thereby, the most important aspect is the change of thermophysical properties caused by the addition of renewable energy carriers. Measurement procedures and standards must be adapted to the new challenges in order to assess the reliability of technical components, prediction models and bills.

Gaseous energy carriers
Calorimeters for non-conventional fuel gases

When non-conventional fuel gases are added to natural gas, the thermophysical and the calorific properties of the resulting natural gas mixture change without the existing metrological infrastructure of the natural gas grid being prepared for these changes.

For these reasons, Department 3.3 has performed investigations on the suitability of two commercial calorimeters for the determination of the calorific value of non-conventional fuel gases within the scope of a joint European project. Further participants were the French LNE, which used an absolutely measuring reference gas calorimeter, and the Romanian INM-BRML. Figure 1 shows the metrological components of the commercial Foster-Cambridge calorimeter used at PTB in the dismounted state.

For each calorimeter used by the metrology institutes, a calibration strategy of its own was developed. Whereas the reference calorimeter of the LNE could be calibrated by means of electric energy, binary and ternary calibration gas mixtures – composed of methane, carbon dioxide and hydrogen sulphide – were used for the commercial calorimeters. The calorimeter of the INM-BRML was calibrated in accordance with DIN 51899, using one calibration gas and one quality control gas. The calorimeters of PTB were calibrated in accordance with ISO 6143, using four calibration gases. For validation, six binary or ternary biogas-resembling mixtures as well as a 10-component gas similar to coalbed gas were used. Figure 2 shows the relative deviations of the measured calorific values from calorific values calculated according to DIN EN ISO 6976 and their uncertainties.



Cover picture:
Fuel samples, collected from all regions of Germany for the measurement of density and viscosity

Figure 1: Metrological components of the Foster-Cambridge calorimeter in the dismounted state. .

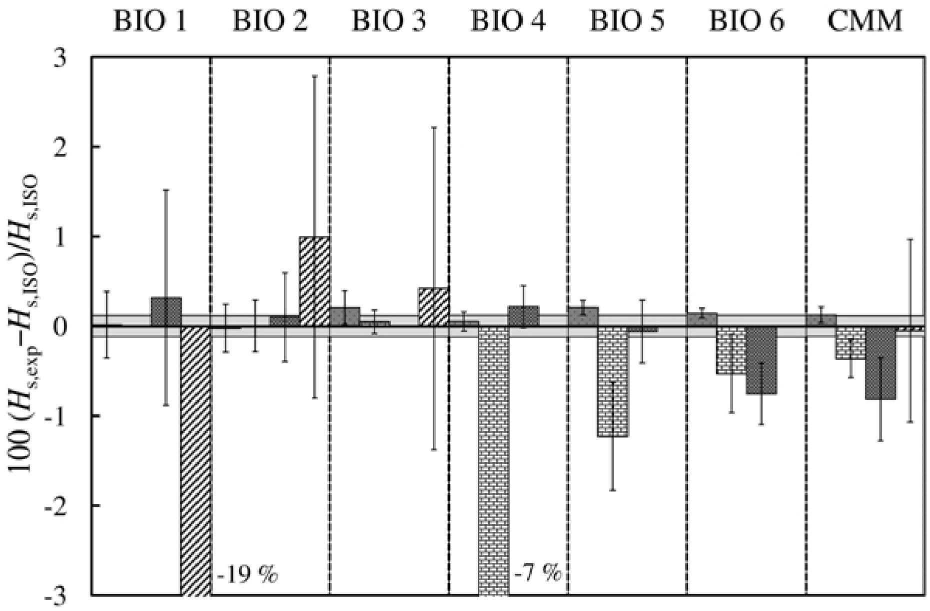


Figure 2: Relative deviations of the experimentally determined calorific values Hs,exp from values calculated according to DIN EN ISO 6976 and their uncertainties (k = 2). LNE reference calorimeter; PTB Foster-Cambridge calorimeter; PTB Union Instruments CWD 2005 CT; INM-BRML Union Instruments CWD 2000; uncertainty of the DIN EN ISO 6976 values.

The results show that the uncertainties specified by the manufacturers of the devices are valid only in a limited measurement range; however, with an adapted calibration strategy, they can also be clearly undercut.

Gas-quality reconstruction procedure for distribution grids

The increasing diversification of the fuel gases causes larger quality variations for the consumers. To correctly detect these variations, the mathematical procedure of the so-called "*gas-quality reconstruction*" can be used for distribution grids instead of using numerous measuring instruments. In the case of these procedures, the migration of a "gas portion" through the gas grid is reconstructed for a defined grid area from the measured supplied and discharged quantities, the gas quantities measured at the feeding points, and from the known topology of the gas grid, using the relevant flow equations. For many years, the use of such reconstruction systems (cf. Figure 3) in the transport grid has been common practice. These systems must, however, be adapted to the individual case of application.

Within the scope of a third-party project funded by the DVGW, PTB is developing procedures for the determination of gas qualities in regional distribution grids. In addition to the fact that the topological structure is more complex – compared to the transport grids – these grids are characterized by the fact that in many places, the discharge flows are not measured continuously, but must be replaced by

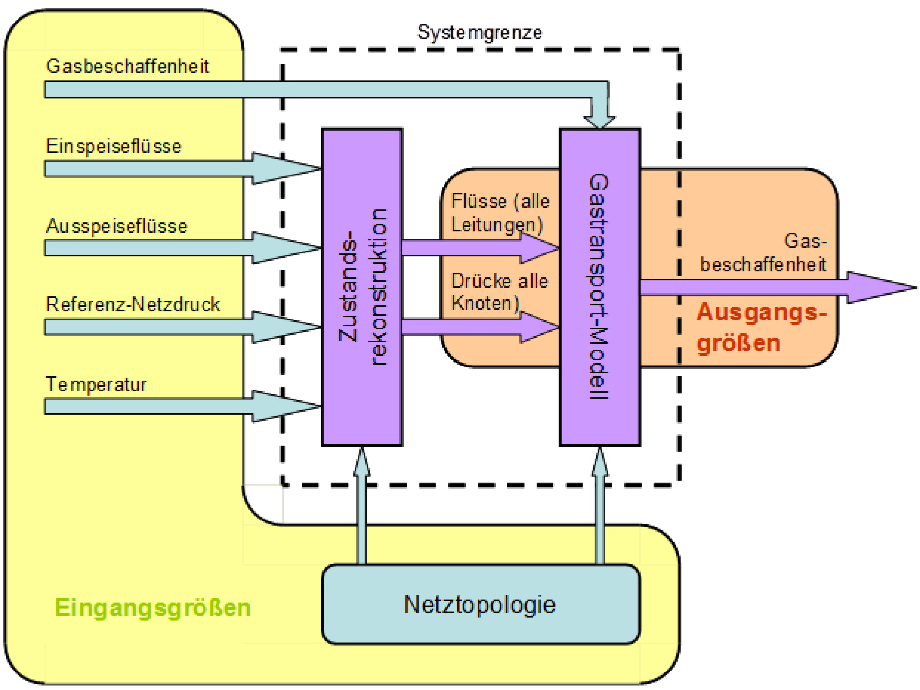


Figure 3: Schematic representation of the interaction between the input and the output quantities of a gas-quality reconstruction procedure.

Figure 4: Photo of the reference GC system for the certification of gas mixtures.

so-called standard load profiles. By using a Monte Carlo simulation it has, for the first time, been possible to determine a spatially resolved measurement uncertainty for such grids. This facilitates the decision to use superior measuring instruments in places where the uncertainty of the measuring instruments has a particularly large influence on the uncertainty of the result, whereas the measuring instruments may even be superfluous at places where the influence on the uncertainty of the result is low.

Certification of calibration and verification gases for biogas measuring instruments

Since the creation of the legal basis for the feeding of biogas into natural gas grids in 2006, 127 feeding facilities have meanwhile been put into operation nationwide (as of November 2013).

Thereby, the measurement technology for billing the energy "biogas" is, as required in commercial transactions, subject to verification law. In addition to the quantity, the calorific value is to be determined with approved measuring instruments.

Since the end of 2010, also special devices for biogas that is capable of being fed in, can be approved at PTB. Since then, a large share of the new calibration and test gas mixtures which are required for these process gas chromatographs (PGCs) has been certified at PTB.

In addition to hydrogen, also oxygen is contained in the natural gas matrix. This converts these mixtures into so-called "oxyfuels" which require special safety measures in their production.

For the traceable certification of these mixtures, PTB uses its reference GC system which is composed of 2 laboratory gas chromatographs with TCD and FID detectors as well as a micro-gas chromatograph with 4 channels. Figure 4 shows a photo of the system.

The system is calibrated in a multiple measurement cycle. The evaluation is performed according to the multiple-point calibration in accordance with DIN EN ISO 6143 and DIN 51899.

The volume-related calorific mixture values at reference temperature and the reference pressure for the combustion are calculated from the quantitative analysis and the calorific values of the pure components according to DIN EN ISO 6976. Up to now, the measurement uncertainty of the calorific value from the PTB analysis calculated in this way has been 0.12 %, this value being limited by the uncertainty of the calorific value of pure methane from the standard. As to the quality of the above analysis, reducing the uncertainty contribution of the calorific value of methane by half – which has already been realized by new PTB investigations carried out by means of a reference calorimeter – also leads to a reduction of the uncertainty of the mixture's calorific value to half the value.

Metrological infrastructure for hydrogen-enriched natural gas

To make use of the temporal or local oversupply of power generated by wind energy and solar plants, it makes sense to use this excess power to electrolytically generate hydrogen ("Power to gas"), to mix it with natural gas and to utilize it via the existing natural gas infrastructure. Due to the large transport and storage capacity of the natural gas grid, it is, thus, also possible to establish a seasonal balance between energy generation and energy consumption (see Figure 5).

At present, the German natural gas industry is aiming at a maximum concentration of hydrogen in natural gas of 10 % because up to this value, most of the natural gas installations and facilities should operate reliably and safely without major problems, except for the pressure tanks for automobiles powered by natural gas, for which a limit value of 2 % has been laid down in the respective standard.

Presently (November 2013), only a few pilot plants for hydrogen production with a power of $P_{el} = 2$ MW and a hydrogen production of $V_n(H_2) = 360\ m^3/h$ exist in Germany. It is planned to construct facilities with a power of 100 MW by 2020.

By adding hydrogen to natural gas, its thermophysical and calorific properties change, in particular its specific energy content. PTB has started several projects to create a metrological infrastructure, composed of adapted measuring instruments and suitable calibration gases, to determine the volume, the mass, the calorific value and the composition of the hydrogen-enriched natural gas.

Liquefied natural gas (LNG)

Within the scope of a secure and reliable energy supply, liquefied natural gas is – due to its volume, which is 600 times smaller in the liquid state, and due to the better storage capacity associated with this – regarded as a strategically important alternative and, in the case of transport distances longer than 2000 km, as an economical alternative to the gas supply via pipelines across the borders. Furthermore, LNG can be transported to consumers who have no access to the gas supply grid. As fuel in inland water transportation, LNG could minimize sulphur and nitrogen oxide emissions because in principle, only water and carbon dioxide are produced during the combustion process.

The EMRP project "Metrology for LNG" which was concluded this year comprised the most diverse metrological challenges induced by LNG – from a determination of the energy content of LNG in commercial transactions which was twice as good – to the realization of traceable flowrate and density measurements, and to the use of the results in directives and ISO standards. These tasks have been tackled by a community of European research and industry partners (TUV NEL (Great Britain), INRIM (Italy), VSL (The Netherlands), PTB, E.ON Ruhrgas (Germany), Enagas (Spain), Elengy (France), Ruhr University Bochum) under the guidance of the VSL.

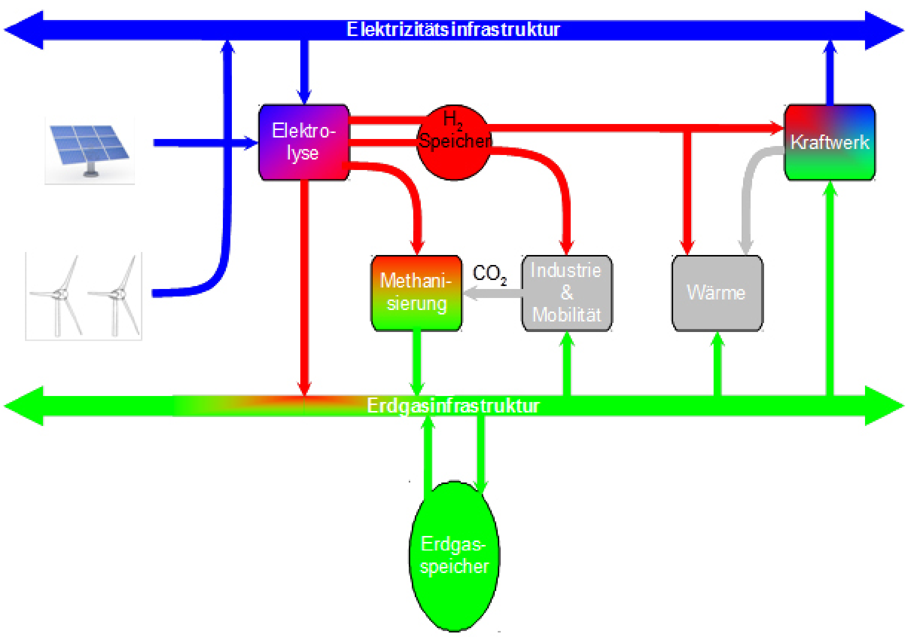


Figure 5: Interaction of the power and gas infrastructure by "Power to gas."

Figure 6: Measuring instrument for measuring the density of liquid fuels and their temperature dependence.

PTB guaranteed the calibration of sinkers (Working Group 3.23 "Thermal State Behaviour and Density") for the density measuring facility of the Ruhr University Bochum and thus ensured the traceability of the LNG density measurements to the SI. Working Group 3.31 "Caloric Quantities" furnished calculations of enthalpies of formation and calorific values of LNG, including the associated uncertainties over a large range of thermodynamic conditions.

Liquid Energy Carriers

The addition of agro-technically generated fuels ("biofuels") to fossil fuels not only requires that modifications be made to engines and injection systems, but – for purposes under verification law, fiscal law and quota law – also a new measurement of the transport properties and of the energy content of the new mixed fuels.

In trade, liquid fuels are measured in volume units. Tax burdens and specifications of the quota law are also related to a volume unit. To create a comparison quantity which is independent of the measurement temperature, all data related to the volume are converted to a reference temperature of 15 °C. Therefore, the density-temperature relation must be known for all fuels.

For this reason, PTB has set up measuring facilities for the precise measurement of the density of fuels and their temperature dependence. The density can be measured in a temperature range from -25 °C to +50 °C with an uncertainty of 0.02 kg/m^3, using an electronic density measuring device which has been modified especially for this purpose.

This apparatus was used to perform measurements on a large number of fuels and fuel mixtures. For this purpose, mixtures of fossil fuels with biofuels were prepared in the complete mixture range from 0 % of bio components to 100 % of bio components. To determine the deviations of the density caused by the addition of biofuels in relation to the scattering of fuels obtainable on the market, 145 samples from 18 German refineries were collected in addition and also measured. Thereby, both gasoline-ethanol fuels and diesel-biodiesel fuels as well as heating-oil biodiesel fuels were taken into account in summer and winter quality.

The results show that the scattering of the measurement data for samples of different origin is approximately as large as the change in density and thermal expansion coefficient if bio components are added up to 30 %. A change of the verification instructions for the conversion of the measured volumes to a target temperature of 15 °C, the so-called volume conversion, is, therefore, not required for additions of up to 30 %.

International harmonization

In 2013, a joint metrology project, which was aimed at developing reference measurement procedures for the chemical and physical characterization of biofuels of the first generation and to harmonize them on the European scale, was successfully concluded. Among the 13 European partners, PTB was repre-

Figure 7: Commercially available fuel samples collected from 18 different German refineries.

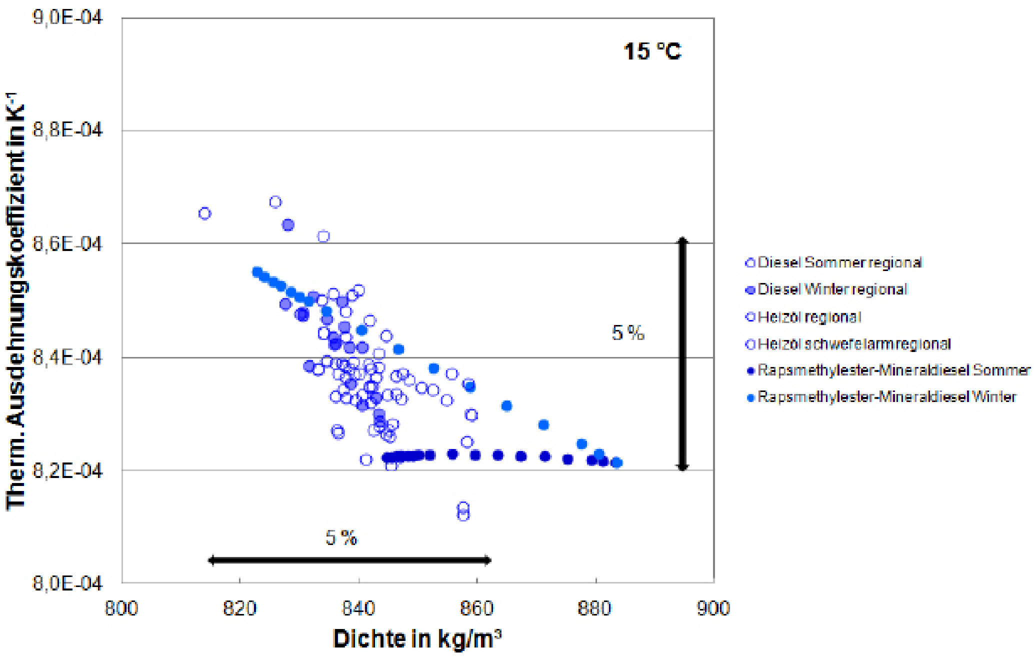


Figure 8: Scattering of the value couples density – thermal expansion coefficient for samples of different origin, compared with the change in density and the change in the thermal expansion coefficient caused by the addition of biodiesel.

sented by Division 3 with four working groups. The focal points lay on the determination of the origin of biofuels, the harmonized quality assessment, and the quantitative determination of physical parameters.

One focal point was the harmonization of the calorific value measurement, which is presently still determined with three methods (Washburn corrections with regard to standard conditions, DIN 51900 and ISO 1928). For the first time, the strengths and differences of these methods were highlighted on the basis of uncertainty calculations.

Under the guidance of PTB, the density-temperature behaviour of the diesel-biodiesel mixtures was also determined within the scope of this project. In addition, the investigations aimed at harmonizing different measurement methods at the three European partners.

In addition, international harmonization is advanced by a trilateral cooperation of PTB and the natio-

Figure 9: Bomb calorimeter for the measurement of the calorific value of liquid fuels.

nal metrology institutes from France and Brazil with the objective of harmonizing measurement procedures and carrying out comparison measurements in particular for alternative fuels.

Headlines: News from the Division

Fundamentals of Metrology

Fundamental improvement of the standard addition procedure
(O. Rienitz, FB 3.1, olaf.rienitz@ptb.de)

Universal standard for the calibration of Raman microscopes developed
(S. Zakel, R. Stosch, FB 3.1, rainer.stosch@ptb.de)

New approach to the quantitative determination of metal proteins in clinical samples within the scope of the EMRP project HLT05
(C. Swart, FB 3.1, claudia.swart@ptb.de)

European spectroscopy infrastructure for the measurement of molecular spectral data
(J. Brunzendorf, O. Werhahn, V. Ebert, FB 3.2, volker.ebert@ptb.de)

New 1.6 GPa pressure-measuring multipliers
(W. Sabuga, FB 3.3, wladimir.sabuga@ptb.de)

Metrology for the Economy

Metrology for electrochemical energy storage systems: Determination of the state of charge and the state of health of lithium-ion batteries
(P. Spitzer, FB 3.1, petra.spitzer@ptb.de)

Metrology for Society

Successful use of the new SEALDH-II laser hygrometer in the AIRTOSS-ICE flight campaign
(B. Buchholz, V. Ebert, FB 3.2, volker.ebert@ptb.de)

Laser spectrometry for air quality monitoring
(A. Pogany, O. Werhahn, V. Ebert, FB 3.2, volker.ebert@ptb.de)

International comparison measurement of airborne hygrometers at the cloud simulation chamber AIDA of the KIT Karlsruhe (AquaVIT2)
(N. Böse, V. Ebert, FB 3.2, volker.ebert@ptb.de)

Metrology for laser-spectroscopic air quality monitoring in cleanrooms
(A. Rausch, O. Werhahn, V. Ebert, FB 3.2 volker.ebert@ptb.de

Determination of the trace humidity in methane, ethane and propane by means of a laser-optical hygrometer
(J. Nwaboh, V. Ebert, FB 3.2, volker.ebert@ptb.de)

In-situ residual gas quantification by means of diode laser absorption spectroscopy
(O. Witzel, A. Klein, V. Ebert, FB 3.2, volker.ebert@ptb.de)

Successful conclusion of the EMRP project ENG01 "Energy Gases"
(S. Pratzler, N. Böse, V. Ebert, FB 3.2, volker.ebert@ptb.de)

Development and use of a soot aerosol standard for particle and aerosol diagnostics
(A. Nowak, V. Ebert, FB 3.2, volker.ebert@ptb.de)

Establishment of an infrastructure for the traceability of condensation particle counters
(A. Nowak, V. Ebert, FB 3.2, volker.ebert@ptb.de)

Successful kick-off meeting for revision of the OIML R126 „Evidential Breath Analyzers" of 2012
(R. Klüß, V. Ebert, FB 3.2, volker.ebert@ptb.de)

Establishment of a measurement facility for measuring the density of seawater under pressure with an uncertainty of 0.02 kg/m³
(H. Schmidt und H. Wolf, FB 3.3, hannes.schmidt@ptb.de, henning.wolf@ptb.de)

13th BAM-PTB colloquium 2013 in Braunschweig
(T. Stolz, FB 3.4, thomas.stolz@ptb.de)

Safety-related characteristics of alcohol-air-mixtures – Explosion pressure, pressure increase with time, combustion velocity
(E. Brandes, FB 3.4, elisabeth.brandes@ptb.de)

Ignition temperatures of flammable liquids as a function of the enclosure
(E. Brandes, FB 3.4, elisabeth.brandes@ptb.de)

Introduction of the international "PTB Ex Proficiency Testing Scheme" for comparisons between Ex laboratories
(T. Krause, FB 3.5, tim.krause@ptb.de)

The Ex-Dienst® becomes Ex-Network e.V.
(U. Klausmeyer, FB 3.5, uwe.klausmeyer@ptb.de)

Investigation of safety-related ignition processes
(D. Markus, FB 3.5, detlev.markus@ptb.de)

Heino Bothe honoured with the IEC 1906 Award
(M. Beyer, FB 3.7, michael.beyer@ptb.de)

Investigation of the factors influencing the harmonic losses of (explosion-protected) permanent-magnet-excited synchronous motors
(C. Lehrmann, FB 3.7, christian.lehrmann@ptb.de)

Investigations of the time-dependent development of hot surfaces in friction contacts as a function of the construction materials
(L. Meyer, FB 3.7, lennart.meyer@ptb.de)

Investigations of the ignition capability of metallic friction contacts in explosive gas and vapour-air-mixtures
(L. Meyer, FB 3.7, lennart.meyer@ptb.de)

Safety-related conclusions regarding the ignition capability of ultrasound
(L. H. Simon, FB 3.7, lars.h.simon@ptb.de)

Determination of the electrostatic chargeability of insulating material without experimental charge test
(U. von Pidoll, FB 3.7, ulrich.v.pidoll@ptb.de)

Patent "Avoidance of electrostatic chargeability"
(U. von Pidoll, FB 3.7, ulrich.v.pidoll@ptb.de)

International Affairs

Prestigious award for scientists of PTB Braunschweig
(U. von Pidoll, FB 3.7, ulrich.v.pidoll@ptb.de)