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JRP-Coordinator	
Name, title, organisation	Dr. Martin Thedens, Physikalisch-Technische Bundesanstalt
Tel:	+49 531 592 37 30
Email:	martin.thedens@ptb.de
JRP website address	http://www.ptb.de/emrp/PartEmission.html
Other JRP-Partners	
Short name, country	JRP-Partner 1 PTB, Germany JRP-Partner 2 BAM, Germany JRP-Partner 3 DFM, Denmark JRP-Partner 4 EJPD, Switzerland JRP-Partner 5 IJS, Slovenia JRP-Partner 6 JRC, EC JRP-Partner 7 LNE, France JRP-Partner 8 MIKES, Finland JRP-Partner 9 NPL, United Kingdom JRP-Partner 10 VSL, The Netherlands
REG-Researcher (associated Home Organisation)	
Researcher name, title	Dr. Thomas Tuch, Germany — Start date: 01.09.2011
(Home organisation Short name, country)	IfT, Germany — Duration: 33

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1 Executive Summary

Introduction

Improvement in the quality of life for European citizens cannot be achieved by measuring ambient air alone. Also important is the identification, quantification and finally the regulation of the emission sources. In this context, the task of reducing vehicle emissions should be approached as part of an overall strategy. The EURO 5 and 6 and the EURO VI standards are two of the measures designed to reduce the actual emissions of air pollutants such as particulate pollutants (PM) as well as ozone precursors such as nitrogen oxides (NO_X) and hydrocarbons. Accurate measurements ensure that emissions can be monitored, their effects better understood and appropriate regulation developed. The project built expertise in the measurement of three main constituents of exhaust emissions where measurement infrastructure was lacking: Soot particles, Platinum Group Elements (PGE) and Mercury.

The Problem

1. The vehicle emissions regulation (ECE R83, R49) defines the requirements for measurement instruments. This new requirement is applicable for type approval according EURO 5b for diesel vehicles (starting September 2011 for new types) and later for direct injection gasoline vehicles when passing to EURO 6. So even today there is a definition for the calibration procedure of the equipment. However, those procedures allow a high degree of freedom for the calibration laboratories which can result in different calibrations and hence test results whilst there is a lack of a standard to establish traceability for the number concentration and full uncertainty evaluation in accordance with the GUM. *This is the basic prerequisite for introducing a new metric in regulation.* In order to fulfil these prerequisites internationally harmonised measurement standards for number concentration are required for establishing a calibration infrastructure. Furthermore harmonised measurement protocols would replace, or at least amend national initiatives within Europe and enable comparability of measurement results. The enforceability of the related European Regulations cannot be assured before this work has been finished.

2. To comply with the European Standard and Directive 94/12/EEC and further 70/220/EEC (amended a number of times, the latest one being the EC regulation No. 595/2009) on ambient air quality, all new cars should be fitted with a catalytic converter to reduce hazardous emissions of CO, HC and NO_X to below the legislated level. In recent years evidence was provided that these converters consist of an 'indirect' source of pollution with Pt, Pd and Rh (often referred to as Platinum Group Elements, PGE), which are their main components. Recent studies on their toxicity, bioavailability, and concentrations in biologically relevant media indicate that exposures to these metals pose an environmental risk and may cause serious health problems.

3. European Directives require a rigorous metrological infrastructure to enable measurements to be accurate and traceable in order to allow the introduction of target values for mercury in emissions (such as exhaust emissions) and in ambient air. Such an infrastructure is still not available. Air quality legislation is now normal across Europe for similar toxic elements. In other countries the same applies. E.g. on March 15, 2005, US EPA issued the Clean Air Mercury Rule to permanently cap and reduce mercury emissions from coal-fired power plants. However, due to measurement issues related to the non-existence of the proper metrological infrastructure for mercury measurements, the American Court cancelled the Clean Air Mercury Rule on February 8th, 2008.

The Solution

1. This project has established a sound metrological basis for particle emissions in exhaust gases of diesel vehicles in Europe. This includes the establishment of a particle number concentration standard for soot particles providing calibration services for end users and industry, in particular for the calibration of measuring instruments for the type approval of Euro 5 and Euro 6 diesel vehicles. Furthermore a validation of novel instrument types measuring the soot particle concentrations in exhaust gases from diesel vehicles was developed, being capable of being used for the regulatory periodic emission control of vehicles.

2. The release of PGE into the environment is damaging in terms of public health, ecological and economic interests. Now, in order to accurately and reliably assess the risks reliable, accurate and comparable data on the release rates of PGE from automotive catalysers are known. The outcome of this JRP is to assess the PGE content not only in terms of PGE mass per total emitted mass, but also in terms of PGE mass emitted per driven distance. To produce a reference procedure fulfilling the requirements of a primary method of measurement can only be performed by combining all validated single steps and setting up a complete uncertainty budget. The solution from this project is, that Certified Reference Materials (CRM) are available. Additionally comparisons with a similar analytical procedure were performed using the same artefact. The

whole analytical procedure was validated by combining all validated single steps and setting up a complete uncertainty budget.

3. A global metrological framework for the determination of mercury in various environmental compartments was developed. In addition, mercury vapour calibration procedures were determined, by using very high concentration mercury vapour sources, which are suited for the accurate calibration of the low mass concentration levels found in exhaust emissions and in ambient air. So the project has also produced SI traceable mercury vapour sources, at much lower concentration levels than had previously been achieved.

Impact

The ability to accurately measure the three pollutant groups not only enables effective type approval of new engines and periodic testing of engines in use, but also supports introduction of better and more accurate instrumentation for testing procedures and the development of more efficient engines. The scientific knowledge developed in the project has been transferred to industrial users, the scientific community and analytical labs via a variety of 43 technical meetings, conferences and workshops as well as 23 papers in peer reviewed journals. Visits and interactions with key stakeholders such as Chevron in San Ramon, USA Linde Electronic and Specialty Gases, US EPA (USA) and Tekran (Canada) for Mercury measurements and Volkswagen AG, Johnson Matthey, Umicore for PGE have increased their awareness of project research and findings. As a result the outputs of the research are already being used, examples include;

- New and improved calibration facilities for particle number are now available at partner NMIs enabling SI traceability between vehicles undergoing periodic engine exhaust testing for Euro 6c soot emissions and condensation particle counters calibrated by NMI.
- Five instrumentation manufacturers (BOSCH, MAHA, AVL, MatterAerosol/Testo, Pegasor) involved with the periodic or type testing of soot emissions from engines benefited from participation in the round robin exercises, gaining first-hand experience of improved measurement methods and instrument calibrations. Knowledge gained from this interaction has enabled one manufacturer to further develop instrumentation enabling on-road testing of vehicle emissions to demonstrate compliance with the Euro 6c emission regulations.
- Several recommendations were provided to manufacturer members of the European Garage Equipment Association, on the device used for regulatory periodic emission control which has potential to enable more regular checks of new devices for motor type approval tests by implementation of calibration routines and modification of inlet sampling systems.
- Regulation bodies (TÜV and DEKRA) have incorporated project outcomes for implementation in national directives leading to more reliable measurement of soot emissions from diesel vehicles during periodic emission control.
- Project results have been shared with the membership of six normative standard working groups leading to contributions to new draft standards and revisions to existing standards. ISO/DIS 27891 on Condensation Particle Counters calibrations used in vehicle exhaust particle testing now explicitly includes the role of NMIs in calibrating both CPCs and aerosol electrometers for monitoring soot emissions resulting from the project.
- A new collaboration with the Commissariat à l'Energie Atomique (CEA) research centre of Grenoble (France) was established towards the end of the project for the analysis of PGE in automotive catalysts leading to Isotopically enriched certified reference material solutions for Pt and Pd and for Rh will enable analytical laboratories to apply the analytical procedures for Pd, Pt & Rh developed within this project.
- Project methods and results were highlighted during a Special Session on 'providing underpinning traceability for mercury vapour measurement' at the International Conference on Mercury as a Global Pollutant Edinburgh 2013. The Global Mercury Observing System (GMOS) has adopted project approaches. A further EMRP project is continuing research on traceability for mercury measurements (Metra project) and an EMPIR Support for Impact project is working with the relevant standards bodies (CEN, ISO) and the members of the UN Particle Measurement Programme to widen the adoption of the project's outputs (Autopart project).

2 Project context, rationale and objectives

Context

Numerous epidemiological studies show the effect of increased ambient pollution. Therefore air quality measurement networks have been installed and a European Directive requires the monitoring of air pollution. However improvement in the quality of life for European citizens cannot be achieved by observing ambient air alone, it is also important to be able to identify, to quantify and finally to regulate the emission of distinct sources relevant for air quality. For this reason it is essential to establish a metrological basis for the measurement of certain critical pollutants.

The Sixth Community Environment Action Programme adopted by Decision No 1600/2002/EC of the European Parliament and of the Council of July 22nd, 2002 establishes the need to reduce pollution to levels which minimise harmful effects on human health, paying particular attention to vulnerable members of the population and to the environment as a whole. European Community legislation has established appropriate standards for ambient air quality for the protection of human health and susceptible individuals in particular, as well as for national emission ceilings. Following its communication of May 4th, 2001, which established the 'Clean Air For Europe (CAFE) programme', the Commission adopted another communication on September 21st, 2005 entitled 'Thematic strategy for air pollution'. One of the conclusions of this thematic strategy is that further reductions in emissions from the transport sector (air, maritime and land transport), from households and from the energy, agricultural and industrial sectors are needed to achieve EU air quality objectives. This project aims to provide the underpinning metrology infrastructure and research to better understand, measure and therefore control a key source of pollution - automotive exhaust emissions. It addresses the three main constituents of exhaust emissions where measurement infrastructure is lacking: Soot particles, Platinum Group Elements (PGE) and Mercury.

Automotive vehicles are a major source of environmental pollution in particular the primary atmospheric contaminants, such as CO, NO_X, SO_X and hydrocarbons as well as soot particles as a result of incomplete fuel combustion. Petrol combustion also causes pollution with a number of metallic elements, such as mercury (Hg), which is naturally occurring in fossil fuels while PGE can be present from catalytic converters, and sub-micron soot particles are present in exhausts from the combustion of diesel fuel. In order to assess the risks from these additional pollutants and introduce appropriate regulation, practical and traceable measurements are required.

Objectives

The project scientific and technical objectives were focused the development of methods and standards to enable traceable measurements of three key pollutant groups:

- To develop methods and standards for the traceable characterisation of particle emissions from motor-vehicle exhaust for (soot) particle sizes down to 20 nm.
- To develop methods and standards for traceable measurements of platinum-group elements (PGE) in motor-vehicle exhaust emissions.
- To develop methods and measurement standards for traceable measurements of mercury in the vapour phase.

3 Research results

Objective 1: To develop methods and standards for the traceable characterisation of particle emissions from motor-vehicle exhaust for (soot) particle sizes down to 20 nm.

Automotive combustion particle metrics

The vehicle emissions regulations UN-ECE R49 and R83 define the requirements for particle number measurement instruments. The entire measuring system consists of a volatile particle remover (VPR) and a specific condensation particle counter (CPC). The regulations require particle number concentration measurements in exhaust emissions to be made at certified particle mobility diameters between 23 nm and 100 nm and at certified number concentrations between 10^1 cm^{-3} and 10^4 cm^{-3}. Due to the lack of a particle number standard for engine exhaust measurements differently calibrated instruments produce varying test results. Yet, comparable test results are a basic prerequisite for the newly regulated metric.

The aim was to establish a particle number standard for soot particles between several hundred and ten thousand particles per cubic centimetre. The goal was to provide calibration services for the end users and industry, in particular for the calibration of measurement instruments for type approval of Euro 5b, Euro 6 and Euro VI vehicles.

Particle size standards:

This work was realised collaboratively by METAS, PTB, JRC-IET, IfT and DFM. This work was led by METAS. Several bottled reference materials were sent around to all partners. All partners analysed reference materials for the calibration of the differential mobility analyser (DMA). A DMA is an essential part of the calibration setup for engine exhaust-CPC.

The particle diameter and particle number size distribution of monodisperse and nominally spherical gold, silver and polystyrene latex particles in the size range 20 nm to 200 nm were analysed and certified by Atomic Force Microscopy (AFM), Scanning Mobility Particle Sizing (SMPS) and Transmission Scanning Electron Microscopy (TSEM). For reference, gold nanoparticles below 100 nm were used. Systematic deviations between the three sizing methods AFM, SMPS and TSEM were observed (see Figure 1).

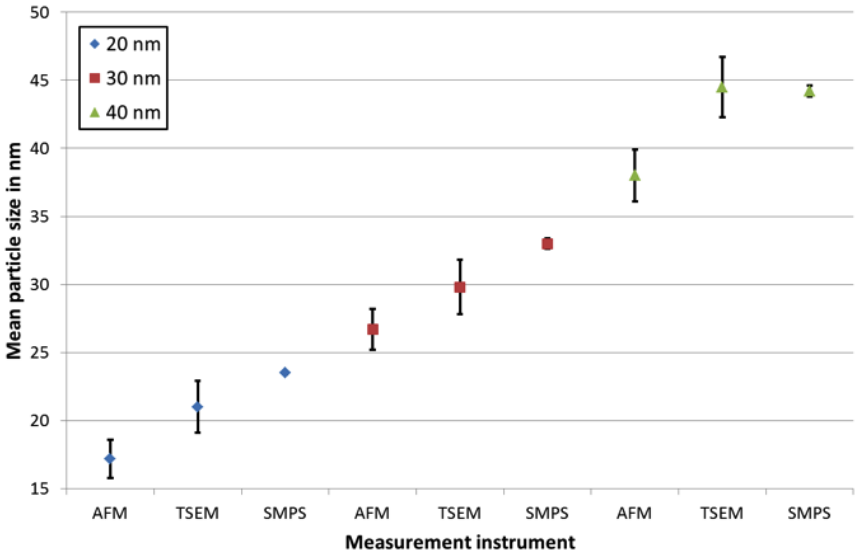

Figure 1: Differences are plotted for the particle sizing techniques AFM, TSEM and SMPS for reference gold nanoparticles of nominal 20 nm, 30 nm and 40 nm diameters.

Similar deviations have been reported in the literature [1, 2] and could not be resolved during the project. The consortium therefore released the following recommendation on how to calibrate a Differential Mobility Analyser (DMA):

1. “The certified size standards shall consist of monodisperse spherical particles normally in a suspension with a certification as a reference material according to ISO Guide 30:1992 [3]. The material for the particles shall allow perfect spheres.
2. The certified size standards shall have particle diameters above 80 nm and the standard deviation of size distribution shall be below 5 % of the diameter.
3. The DMA shall be adjusted with at least one certified size standard. The initial calibration of particle sizing is performed according to the relevant equations of ISO 15900 [4]. The adjustment of the DMA particle selection is done by changing the high voltage or the sheath air flow. The aerosol flow shall be kept constant during adjustment and subsequent measurement.
4. The particle mobility diameter for particles below 80 nm is calculated using the equations from ISO 15900 [4] and is assumed to be correct by convention.”

Temperature Resistant Aerosol

This work was conducted by METAS, MIKES, JRC-IET and PTB. The partners tested the thermal heating resistance of different calibration aerosols. All partners worked closely together and shared results regularly.

The temperature stability of combustion particle calibration aerosols (silver and graphite) has been studied up to 400 °C.

- The combustion aerosol was generated using a miniCAST (combustion aerosol standard). The miniCAST can be operated either in a fuel-lean or fuel-rich combustion mode; the latter presumably producing less thermally stable particles due to the increased volatile organic compounds (VOC) fraction. By using a PALAS thermodenuder, thermal stability of up to 400 °C, could be reached even for the more critical fuel-rich combustion mode. This was demonstrated by the use of the “golden” VPR from JRC as a second VPR, which was downstream from the PALAS thermodenuder. The change in diameter upon passing the “golden” VPR (mostly due to evaporation of the remaining volatile or semi-volatile compounds) is shown in Table 1. These results show that the use of a thermodenuder yields good thermal stability for 30 nm and 50 nm particles, and this is still sufficient thermal stability for 100 nm. The maximal particle number concentration is in the order of 10^4 cm^{-3}.

- Silver aerosols were generated using a nucleation oven at temperatures up to 1250 °C with and without a sintering oven operated at 400 °C downstream from the nucleation oven. During sintering the nucleated silver particles shrink by 1 nm to 17 nm in the size range 15 nm to 50 nm. By using a setup with two sintering ovens, the thermal stability of the sintered silver particles was demonstrated. The achievable maximum silver particle size is limited to 50 nm.

- An aerosol of graphite particles was generated using the PALAS spark generator DNP 3000. Particles in this generator are produced in a spark discharge between two graphite electrodes. By varying the spark frequency and the diluting air and nitrogen flows, particle sizes in the range between 20 nm and 100 nm are generated. Particle number concentrations up to 10^7 cm^{-3} are achievable. The thermal stability of the particles was demonstrated up to 400 °C. Observed particle diameter changes are below 1 %.

Table 1: Change in diameter due to the evaporation of the remaining volatile compounds in a second VPR after thermal treatment of miniCAST combustion particles.

Particle diameter [nm]	Concentration upstream VPR [cm^{-3}]	Change in diameter [%]
30	≤ 6’000	-1.3 ± 0.5
50	≤ 10’000	-1.4 ± 0.7
100	≤ 20’000	-3.4 ± 0.3

For all three calibration aerosols thermal stability was demonstrated up to 400 °C. Thermal treatment proved to be necessary in the cases of combustion and silver aerosols. The calibration aerosol with homogeneously nucleated silver particles was limited by the achievable maximum particle size. The combustion and graphite aerosols proved to be thermally stable for the full range of particle diameters.

"Soot-like"-Aerosol

JRC-IET, METAS, PTB and DFM collaborated closely on this work. JRC-IET hosted two measurement campaigns in Ispra, and METAS and PTB supported JRC with measuring instruments.

"Soot-like" behaviour was subsequently studied by determining the size dependent counting efficiency of an UN-ECE compatible test CPC with a nominal "cut-off" at 23 nm using a combustion aerosol, a graphite aerosol and "real soot". The "real soot" was generated either with a Daimler V6 HD Engine, a DAF Paccar engine or a moped engine at the JRC site. The "real soot" was probed either in the CVS (constant volume sampler) tunnel or directly in the exhaust pipe. The particle number concentrations of size selected aerosols with particle sizes of 23 nm and 41 nm were simultaneously measured with the test CPC and a faraday cup electrometer (FCAE TSI 3068B) and/or a calibrated standard CPC (TSI 3772). In order to reproduce the same conditions occurring during real working operation, the tested aerosol was thermally treated with a PMP pre-conditioning unit (diluters and evaporation tube). Two measurement campaigns were performed (May and December 2013). The first exploratory measurement campaign indicated that the CPC counting efficiency at 23 nm, obtained with real soot, depends on engine operating conditions (speed and torque). The second campaign aimed to improve the quality of the data collected in the first campaign, so the measurements were performed according to the ISO/DIS 27891 procedure and two types of thermal treatments were employed: PMP and catalytic stripper (CS). The addition of CS allowed the oxidation and removal of the most volatile compounds of the tested aerosol that may be responsible for part of the variation of the counting efficiency. At 23 nm, the resulting counting efficiencies as a function of the combustion aerosol and the thermal treatment were as follows:

- 42.5 % - 51.8 % for HD real soot thermally treated with PMP
- 44.2 % - 48.4 % for HD real soot thermally treated with CS
- 33.3 % - 46.7 % for miniCast aerosol thermally treated with PMP
- 33.9 % - 47.8 % for miniCast aerosol thermally treated with CS
- 43.8 % for moped aerosol thermally treated with PMP
- 39.5 % for moped aerosol thermally treated with CS

The results demonstrate that the counting efficiency at 23 nm, of the tested PMP compliant CPC, is clearly material dependent, and more importantly it confirmed that the counting efficiency depends on the different types of real soot. The real soot generated with the same engine showed variability in the counting efficiency of about 10 % due to the operating conditions of the HD engine. The use of the CS reduced the variability to 4 % for the real soot generated with the HD engine. The variability of the counting efficiency obtained with the miniCAST aerosol was about 13 % and did not depend on the thermal treatment method. The quality of the data was ensured by additional tests performed at different aerosol concentrations. These tests demonstrated that particle number concentrations have a minor effect on the CPC counting efficiency.

Atomic force microscopy (AFM) was used to investigate the morphologic equivalence of aerosols produced with different aerosol generators. AFM images revealed that a generator can itself produce morphologically equivalent particles independent of the size setting, yet there are significant morphological differences between aerosols from the two laboratory aerosol generators. It was concluded that "soot-likeness" is not the best criterion for a calibration aerosol considering the intrinsic variability of "real soot" and tested aerosols. Better criteria are monodispersity, single charge, tuneable size, sufficient number concentration, controlled morphology (spherical) and thermal stability of the particles. A heterogeneously nucleated silver aerosol [5] is the most promising primary calibration aerosol for condensation particle counters according to ISO/DIS 27891. [6] While this aerosol material, and its generation procedure, would result in the definition of a primary aerosol standard, it is important to have an easy-to-use secondary aerosol standard for use in industrial laboratories. It was successfully demonstrated that particles sizes well above 100 nm can be generated with this method.

National particle number standards

This work was undertaken by DFM, METAS, JRC-IE, MIKES, NPL and PTB. NPL organised the two comparisons in close collaboration with the host.

ISO/DIS 27891 [5] allows traceability for CPCs either via a certified Faraday Cup Aerosol Electrometer or a certified CPC. In both cases the ability of NMIs to certify these instruments is crucial. Some limited traceable calibration services of particle number concentrations have been available. To validate the extended and newly developed NMI capabilities for calibration services, two distinct comparisons were conducted.

- A first comparison, to demonstrate comparability of charge concentration measurements by Faraday Cup Aerosol Electrometers (FCAE), took place at the Tampere University of Technology. It made use of the university's unique facility to produce singly charged particles over a wide size range. In order to have a worldwide impact, participants from the US (APSL) and Japan (AIST) were invited to the comparison. For singly charged particles in the size range 20 nm to 100 nm and number concentrations above 5000 cm^{-3} participants agreed within 3 %. Larger deviations were observed at lower particle sizes and concentrations. In Figure 2 the results for a soot aerosol (acetylene burner) with a particle size of 30 nm are depicted. Due to impaction in the internal sampling line of the FCAE, the JRC result is not concordant with the reference value (weighted mean of all participants except JRC).

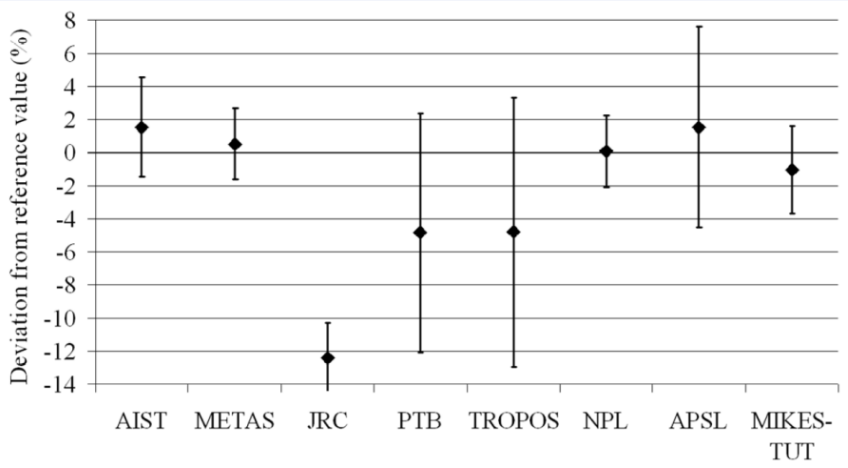

Figure 2: Comparison results for 30 nm soot particles and a charge concentration of 10 fC cm^{-3}. The charge concentration corresponds to a particle number concentration of 3800 singly charged particles per cm^3. The reference value is the weighted mean of participants except JRC**.**

- The second comparison, to demonstrate comparability of the number concentration measurements by CPCs of NMIs and TROPOS (REG(IfT)), was conducted in Leipzig. Again APSL and AIST participated in the comparison. Aerosol sources were silver, sintered silver and soot. The size range was between 6 nm and 100 nm and number concentrations varied between 100 cm^{-3} to 25'000 cm^{-3}. The results show discrepancies between instruments with a relatively high (23 nm) 50% cut-off size of the CPC, even at aerosol particle sizes well above the cut-off size. Apart from this, the results showed that for the full concentration range, and sizes between 23 nm and 100 nm, agreement to ±10 % between reference laboratories is currently achieved. In Figure 3 the results for soot at 41 nm are depicted.

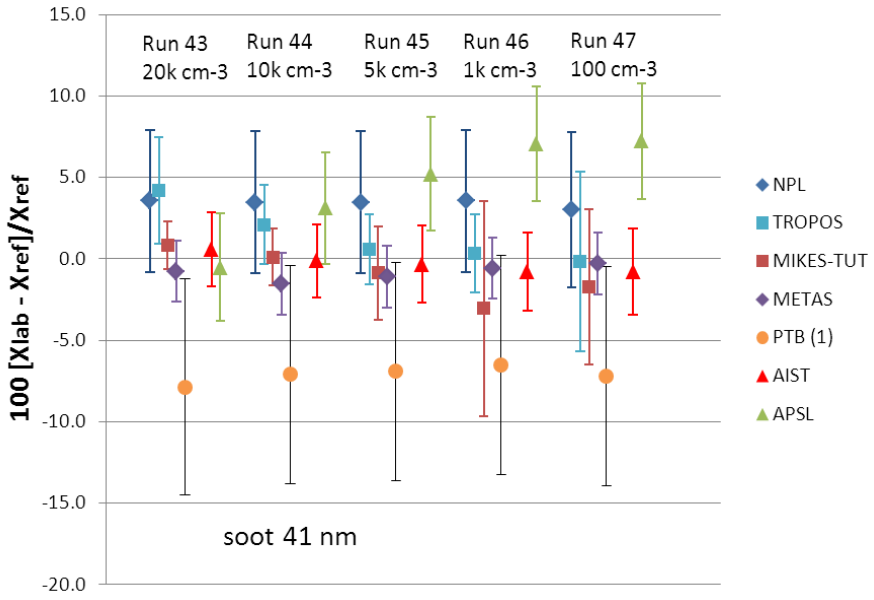

Figure 3: Comparison results for 41 nm soot particles in the particle number concentration range 100 cm^{-3} to $2*10^3$ cm^{-3} are shown**.** The reference value is the weighted mean of all participants.

Calibration services

NPL and EJPD already deliver particle number concentration calibration services. These services were extended to size ranges < 40 nm after the successful validation by *National particle number standards.* PTB plans to offer corresponding services in the near future.

Round robin test

NPL together with REG(IFT) organised the round robin test in parallel to the comparison. Two undisclosed instrument manufacturer participated.

Manufacturers had the opportunity to compare their capabilities with NMIs in a round robin test, which was done in parallel with the NMI comparison in Leipzig. The results were discussed at a dedicated workshop with the manufacturers. NPL led this activity.

In summary, the project improved and built up the anticipated infrastructure in Europe to ensure future comparable particle number concentration measurements in type evaluations of EURO 5b, EURO 6 and EURO VI vehicles.

[1] “Traceable size determination of nanoparticles, a comparison among European metrology institutes”, F. Meli et al, Meas. Sci. Technol. 23: 125005 (2012).

[2] "Size characterization of airborne SiO2 nanoparticles with on-line and off-line measurement techniques: an interlaboratory comparison study", C. Motzkus et al, J Nanopart Res 15:1919 (2013).

[3] ISO Guide 30, Terms and definitions used in connection with reference materials (1992).

[4] ISO 15900, Determination of particle size distribution - Differential electrical mobility analysis for aerosol particles (2009).

[5] “Seeded growth of monodisperse and spherical silver nanoparticles”, S. Zihlmann, F. Lüönd, J.K. Spiegel, Journal of Aerosol Science, Volume 75, 81-93 (2014).

[6] ISO/DIS 27891, Aerosol particle number concentration - Calibration of condensation particle counters (draft version 12, 2013)

Methods for periodic emissions testing

Evaluation and characterisation of novel measuring instruments for periodic emissions control

JRC-IET, PTB, METAS and MIKES shared information regularly and organised different campaigns to complete this work.

At the first stage, consistent requirements were specified for novel measuring instruments (prototypes) and any conflicts with European legislative requirements were determined. An investigation of national requirements showed that Directive 72/306 EEC is implemented in the respective national requirements for measuring instruments for road traffic in the European member states. The opacimeter calibration requirements specified in the European regulation as well as in the national requirements for opacimeters can be classified into two categories: a) checks against smoke or gas having an opacity measured with a reference opacimeter, and b) the use of optical density filters representative of a gas of known opacity. Both methods mentioned here only consider the effects of the dynamics of free acceleration in a narrow way. But the effective (physical and electrical) response time and the dampening are absolutely decisive for the result (see ISO 11614).The second option (optical density filters) is not applicable to the calibration of the novel instrumentation. On the other hand, the low sensitivity of currently applicable opacimeters imposes limitations with respect to the lowest emission levels while the novel instrumentation can be checked. Furthermore, an accepted reference instrument for the novel instruments does not exist, as is the case for the reference opacimeter defined in Germany.

Alternative metrics to be employed for the calibration of the novel instrumentation include gravimetrically determined particulate matter (PM) and “non-volatile” particle number (PN), both of which are regulated in the UNECE Regulations No. 83 and No. 49. The gravimetrically determined mass of particulate matter however, is not a well-defined metric. The definition is rather based on the sampling and measurement procedure employed and, of course, on the emission source, all of which are difficult to reproduce for calibration purposes. Gravimetric calibration causes two problems: The standard gravimetric method is designed for longer sampling times and larger smoke volumes (steady state or accumulated probe), and the uncertainty for gravimetric measurements increases at lower concentrations. Condensation Particle Counters (CPCs), used to measure the particle number, have the advantage of being very sensitive and even being capable of detecting single particles. Their use as a reference instrument has the additional advantage of providing a link to the automotive particle emission metrics work. It is important though to investigate whether, and to what extent, the correlations between PN, opacity and the properties measured by the novel instrumentation depend on the calibration material and the underlying size distribution. It is also important to consider that (owing to the long service life of the vehicles) future periodic inspection procedures should ideally be applicable to both conventional high-emitting diesel vehicles and the latest DPF-equipped vehicles. The particle number emissions from conventional diesels (in the order of 10^8 cm^{-3}) may be more than three orders of magnitude higher than DPF-equipped diesels. It is not clear whether it would be feasible for a single candidate instrument to cover this wide concentration range. Yet, if the purpose of a periodic inspection check is to identify malfunctions of the emission control devices, and particularly cracks in the DPFs, different procedures may be appropriate for non-DPF- and DPF-equipped diesel vehicles.

Conclusively, two reference metrics have been identified, namely: particle number and opacity. The device under test needs to be assessed through comparison to particle number- and/or opacity-based instrumentation. Checks should be performed over a wide range of number concentrations (10^5 to 10^8 cm^{-3}) and light extinction coefficients (0.01 m^{-1} to 3.00 m^{-1}) using a range of size distributions (polydisperse aerosols) typical for light-duty diesel exhaust (geometric mean diameter of 50 nm to 100 nm and a geometric standard deviation of 1.6 to 1.9). Calibration aerosols should consist of soot-like material (e.g. graphite or soot from flame combustion).

The performance characteristics to be investigated include measurement accuracy, sensitivity and dynamic response. All of these need to be assessed for the complete measurement system, including all necessary sample conditioning devices. Special attention needs to be given to investigating the potential effect of the sample pressure and temperature on the instrument response.

In March 2012 a call of interest was started, which was sent to approx. fifty European manufacturers of automotive emission testing instruments and their associations. At first there were eight confirmations and finally five manufacturers (Pegasor, MAHA, AVL, BOSCH, Matter Engineering, now TESTO) and one

university (Czech Technical University, Prague) provided a prototype of their newly developed instruments. The candidate instruments were assessed via comparative measurements of particle number concentration, particle mass concentration and opacity. Different detection principles are covered by the candidate instruments. Three instruments determine particle mass as well as light extinction coefficients by traversing the particles through a laser beam and measuring the scattered light at different angles. These instruments were developed for the measurement of exhaust emissions and were more sensitive, by a factor of 100, than the established opacimeters. Two other instruments detected the particle mass, number and surface concentration by charging the particles, and subsequently collecting them and measuring the total current carried by the particles. This measuring principle is known as diffusion charging. These two instruments were equipped with a dilution unit. Another instrument follows the new approach of using a set of commercial smoke detectors (Ionisation Chambers) to determine the particle mass and number from the total particle length. (see also Vojtisek-Lom, M. et. al: Total Diesel Exhaust Particulate Length Measurements Using a Modified Household Smoke Alarm Ionization Chamber, J. Air & Waste Manage. Assoc. 61:126–134)

Candidate instruments with the different operating principles (e.g. light scattering, diffusion charging and ionization chamber) were evaluated in three different laboratories (Germany (PTB), Switzerland (METAS) and Finland (MIKES)). The displayed concentrations of the candidate instruments (opacity, particle mass, surface or number concentration) were compared with metrologically traceable instruments owned by the NMIs. Thereby different types of combustion aerosol were used: a combustion aerosol with a high soot concentration and larger particle sizes from the HiMass-CAST soot generator (L. Jing, Zollikofen, Switzerland) at PTB, a CAST-soot generator (L. Jing, Zollikofen, Switzerland) with lower concentrations of small particle sizes at METAS, and a laboratory generated diesel soot aerosol at MIKES. Details on the soot aerosols are summarised in Table 2. In particular, the tested parameters were the sensitivity of the instruments (signal to noise level, linearity for different combustion particle concentrations and an ability to measure particles below 100 nm), the response times of the instruments and the treatment of volatile particles.

Table 2: Specification of the aerosols used at the different NMIs.

NMI	Campaign date	Aerosol type	Generator	Size		Number concentration	Mass concentration	Opacity
				GMD[a]	MWSD[b]			
PTB	Jan/Feb 2013	CAST	High mass CAST [c]	50 – 240 nm	1.6 – 2.2	$1.16 \cdot 10^7$ – $1.1 \cdot 10^8$ cm^{-3}	3000 – 380000 µg m^{-3}	0.01 – 2.98 m^{-1}
METAS	June 2013	CAST	Prototype CAST [d]	23 – 200 nm	1.4 – 1.7	$4 \cdot 10^4$ – $1.5 \cdot 10^6$ cm^{-3}	5 – 2800 µg m^{-3}	Not measured
MIKES	Sep 2013	diesel soot	diesel soot generator [e]	30 – 150 nm	1.7 – 2.2	$6 \cdot 10^3$ – $1 \cdot 10^6$ cm^{-3}	[f]156 – 721 µg m^{-3}	Not measured

[a] Geometric mean diameter (GMD) of the size distribution
[b] mean width of size distribution (MWSD)
[c] modified HiMass-CAST
[d] homebuilt at METAS
[e] homebuilt at MIKES
[f] Gravimetric measurements only at these mass concentrations

In the laboratory tests, the instrument that delivered the best measurement results for particle sizes and concentrations relevant for modern diesel exhaust emissions was a diffusion size classifier. It was the only instrument capable of measuring sub 100 nm diesel particles reliably at particle concentrations down to 10^4 cm^{-3} at MIKES. Moreover, it was the instrument that was the closest to the requirements for nanoparticle instruments defined in SR 941.242 (METAS). Additionally, it is the only instrument which is able to evaporate volatile compounds such as tetracontane, as an evaporation unit is integrated into the instrument. It is recommended that all instruments should integrate an evaporation system in future.

The light scattering instruments were able to measure diesel particles larger than 100 nm by detecting their particle mass concentration at MIKES. This shows that the prototypes of light scattering instruments reach their limits at small particle sizes and low concentrations.

The ionization chamber, although not a commercial instrument was able to measure diesel particles in the whole studied particle size range from 30 nm to 150 nm. Overall, even considering that the conversion of the particle length as the measurand is based on an assumption of a given particle size and particle size distribution, the IC is an instrument with the potential to become a cheap alternative to a diffusion charger instrument.

The measurement principles of electrical charging and sensing as well as of the ionization chamber can be considered as suitable for measuring sub 100 nm particles from modern diesel vehicle exhausts. One of the diffusion charging instruments showed the best performance. It reliably measured particles below 100 nm, thus giving representative particle mass and number concentrations for modern diesel emissions.

Finally, a complementary instrument should be considered, in addition to the established opacimeter, for measuring the low emissions from modern diesel vehicles.

Applicability of novel measuring instruments for periodic emissions control in field tests

Mainly JRC-IET and PTB collaborated together to fulfil the requirements of this work. The next two work steps of the investigations involved field measurements for practical tests with suitable instruments under the required conditions at JRC-IE and practical usability tests at DEKRA (Stuttgart, Germany). Two vehicles were tested at JRC: a Fiat 500L (Test Vehicle 1) and a Peugeot 508 (Test Vehicle 2), both diesel vehicles were equipped with a Diesel Particulate Filter and were compliant to the emission standard Euro 5.

The vehicles were tested in the VELA1 facility of JRC for 4 test cycles:

- *New European Driving Cycle (NEDC)*
- *Worldwide harmonized Light vehicles Test Cycle (WLTC)*
- *Repeated accelerations*
- *Steady states*

The six prototype periodic emission control instruments, validated during these tests, were connected in parallel to the tailpipe by means of a multi-probe connector. In addition, a Particulate Matter Programme (PMP) compliant particle counter APC (AVL) was also connected in parallel to the prototype instruments. The measurements were then compared to the reference value provided by the PMP system connected at the Constant Volume Sampler (CVS). Another PMP compliant reference instrument (NanoMet-C from Matter Aerosol) was installed at the tailpipe of the vehicles inside the test cell in parallel to the periodic emission control instruments. Both reference instruments are fully compliant with the PMP measurement programme requirements as described in the regulation UNECE-R83. Figure 4 (see below) reports the particle emissions measured by a PMP compliant system sampling at the tailpipe and the emission standard Euro 5b of $6 \cdot 10^{11}$ #/km (black dashed line). The devices under tests were compared to the reference concentration provided by the AVL Particle Counter.

The PMP compliant particle counters (sampling at the CVS and at the tailpipe) are reported in green and black respectively. These instruments track each other very well with an average deviation of 20 % and a maximum deviation of 50 %, giving us an indication of the acceptable variability between CVS and tailpipe measurements with PMP compliant particle counters. Overall, the responses of the DC2 instrument, based on the diffusion charging technique, resulted in a response closer to the reference instrument when compared to the other devices. DC2 is also the instrument that better captured the small variability of the emissions deriving from the different test cycles. The average relative difference between the DC2 instrument and the reference instrument over all the tests was 15 % (DC2 overestimated the reference value by 15 %). It was the instrument that showed the lowest deviation from the reference across the whole measurement campaign.

The average relative difference between the DC1 instrument and the reference instrument through all the tests was 81 % (DC1 underestimated the reference value by 81 %).

The IC instrument overestimated the reference concentrations by a factor of 19.14 and the results were not capable of following the small variability of the results. The light scattering instrument L1 overestimated the reference concentration by almost 3 orders of magnitude. L1 suffered from being too close to the detection limit, and showed a large variability spanning both above and below the Euro 5b particulate mass emission standard. As anticipated, the other two light scattering devices under test L2 and L3 were not able to detect the emissions of the Euro 5 diesel vehicles with DPF due to the extremely low concentrations of soot. The reason for this is that the light scattering instruments were designed to cover a wide range of emissions in order to capture possible failures of the DPFs, and they were not specifically designed to measure particle number concentration as the reference instrument.

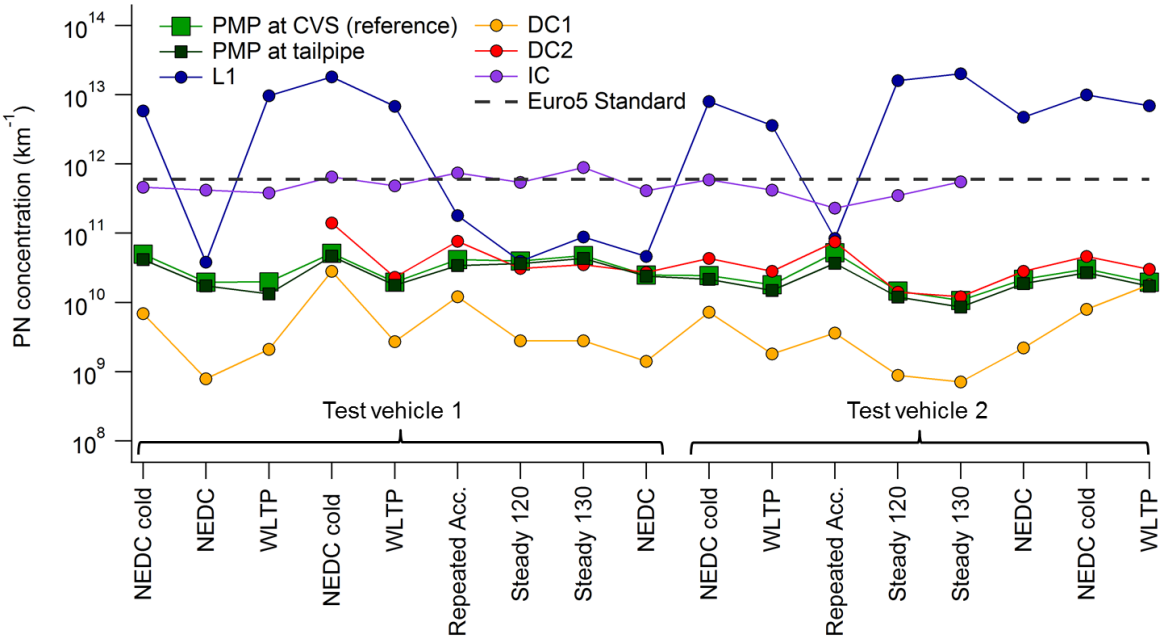

Figure 4: Comparison of the distance specific PN emissions measured by the reference instrument (AVL Partcile Counter PMP compliant at CVS), a PMP compliant particle counter at the tailpipe (Nanomet-C, Matter Aerosol) and the devices under test (L1, DC1, DC2 and IC) for both tested diesel vehicles.

The last piece of this work involved the evaluation of the user handling experience of the instruments under test at DEKRA in Stuttgart, Germany. The measurements were performed as in usual periodic emission tests with three different vehicles. The sampling was realised simultaneously for all instruments using an extension tube behind the exhaust pipe of the vehicles on which the single sampling tubes of the instruments were clamped on. It is assumed that a sufficient sampling was guaranteed by the small ratio between the sampling volume and the exhaust volume. Probably problems which could occur through an insufficient dynamic pressure during the sampling can be excluded, because the only instrument which works according this principle showed the best results when compared with the reference.

After a warm up, the accelerator pedal was fully depressed 5 times. This procedure was repeated 3 times leading to 3 mean values for the peak absorption coefficient and the biggest difference between the single values measured by the highly sensitive reference opacimeter (AVL 439). Here, the measuring mode of the opacimeter was changed between mode 1 (Peak value, mode A, without filter) and mode 2 (ECE R24, EEC 72/306) which is commonly used in usual periodic emission tests. Note that measuring mode 2 leads to significantly lower absorption coefficients, compared to mode 1, in the response of the reference opacimeter, because of the different ranges for the calculation of the mean value.

The first test vehicle was a low emitting Audi A4 (compliant to the emission standard Euro 5). During the three test cycles the reference opacimeter displayed a very low absorption coefficient from 0.003 m^{-1} to 0.001 m^{-1} for mode 2. The light scattering instruments as well as the diffusion charger had no response for the three acceleration cycles. The second test vehicle was a VW Passat with a cracked DPF. It had a comparatively high particle concentration in the exhaust. During this test the three light scattering instruments showed different responses: L1 displayed a relatively low adsorption coefficient between 0.25 m^{-1} and 0.3 m^{-1}. The indicated values of instrument L2 (0.65 m^{-1}up to 0.85 m^{-1}) matched the reference values well. The displayed absorption coefficients of L3 were relatively low and showed a higher variability than the other light scattering instruments, ranging from 0.22 $m^{-1}$to 0.47 m^{-1}. The particle number concentration measured by DC1 was more than one order of magnitude higher than that measured by the IC. This was because there was no particle number reference during this test, and there was no information about the actual particle number concentration in the exhaust. A VW Multivan, Euro 4, with an upgraded DPF was the third test vehicle. During this test the reference opacimeter showed absorption coefficients in mode 2 of 0.37 m^{-1}. In this particle concentration range the instruments under test showed a similar response to the opacimeter and also the values measured by the different instruments under test are more consistent to each other, when compared to the tests performed with the two previous vehicles (see Figure 5).

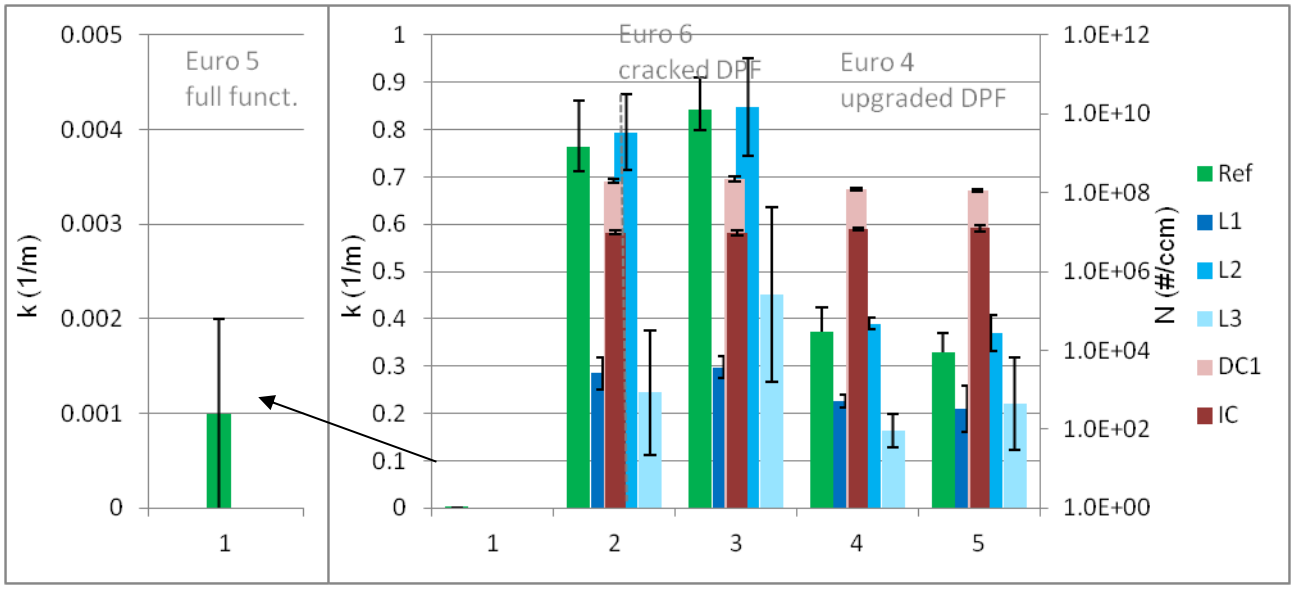

Figure 5: Mean response of the reference instrument (opacimeter, AVL 439. DEKRA) for mode 2 and the measuring instruments under test for two representative acceleration cycles (L-Light scattering instruments, DC-Diffusion Charger, IC- Ionisation Chamber) to the emitted particle concentration (primary vertical axis: absorption coefficient in m^{-1}, secondary vertical axis: particle number concentration in particle/cm^3).

The results with the low emitting Euro 5 vehicle (equipped with a fully functional DPF system) showed that the emitted particle concentration was below the detection limit of the instruments. The difference between the results of the Diffusion Charger (DC1) and the Ionisation Chamber (IC) for the test vehicle 1 could be explained by the presence of the volatile particle remover (VPR) in the DC1 that removed most of the volatile particles. Despite the presence of the VPR, the particle emissions of the other two test vehicles measured by the DC1 was more than one order of magnitude higher than the value measured by the IC. Due to the missing particle number reference, there was no information about the actual particle number concentration in the exhaust, so we cannot state which instrument shows a realistic response. The results showed that instruments working with the light scattering principle were able to detect malfunctions of the after treatment system for a Euro 6 vehicle and were also able to measure the particle concentrations of the Euro 4 vehicle. In order to determine the long term stability and operational reliability of the instruments, the 2013 results were compared with the results of the measurements which were performed one year later (2014). IC and DC2 were not available during the measurement campaign of 2014 so there is no direct comparison with the measurement campaign of 2013. The correlation of the light scattering instruments and the diffusion charge instrument DC1 with the

reference instrument was calculated from data collected in 2013 and in 2014. The large changes observed from 2013 to 2014 in the linear correlations of some of the light scattering devices suggest that it would be better to perform the re-calibration of the light scattering instruments more frequently than once a year. Additional measurements performed at shorter time intervals are needed in order to determine the exact maximum period of time after which the light scattering instruments should be re-calibrated. The long term stability of the diffusion charge instrument DC1 was assessed against the reference opacimeter, showing an improvement of the performance of the diffusion charge instrument in 2014 compared to 2013 (probably also due to the replacement of the internal sensor). The correlation improved remarkably especially for absorption coefficient values smaller than 0.5 m^{-1}, above which the instrument reached saturation. The instruments based on diffusion charging have recently received a great boost in their development due to the EC programme aimed at measuring particulate number emissions with on-board measurement systems. Additional checks on their long term stability should be performed in the near future to assess the performance of the more advance prototype diffusion charging instruments and possibly of CPC based instruments.

Objective 2: To develop methods and standards for traceable measurements of platinum-group elements (PGE) in motor-vehicle exhaust emissions.

Primary measurement of PGE

To comply with the European Standard and Directive 94/12/EEC and 70/220/EEC (amended a number of times, the latest one being the EC regulation No. 595/2009) on ambient air quality, all new cars are required to be fitted with a catalytic converter to reduce hazardous emissions of CO, HC and NOX to below the legislated level. In recent years, evidence was provided that these converters are an 'indirect' source of pollution with Pt, Pd and Rh (often referred to as Platinum Group Elements, PGE), which are their main components. Recent studies on their toxicity, bioavailability, and concentrations in biologically relevant media indicate that exposures to these metals pose an environmental risk and may cause serious health problems, for several reasons:

(i) the emitted PGE may be easily mobilised and solubilised by various compounds commonly present in the environment, thereby enhancing their bioavailability.

(ii) PGE may be transformed into more toxic species upon uptake by organisms. For instance, the presence of chloride in lung fluids may lead to the formation of halogenated PGE complexes that have a greater potential to induce cellular damage.

These considerations highlight the need to monitor the auto-vehicles' emission of PGE in the environment. Nevertheless, their determination in auto-vehicles' emissions and environmental matrices poses a big challenge because of:

• their very low levels (~ 10-12 ng/kg), which makes their determination (at ultra-trace levels) an analytical challenge.

• there is no analytical procedure available for quantifying PGE, which delivers metrologically valid, and traceable results.

The research focused on the development and application of metrologically valid procedures for the quantification of Pd, Pt and Rh in automotive exhaust emissions and a screening procedure for Ru, Os and Ir. The presentation of the research results in this subsection is organised according to the major steps outlined in part 2 "Project context, rationale and objectives".

Selection, preparation and characterisation of suitable calibration materials and calibrated spikes for IDMS (BAM, PTB)

BAM prepared the primary assay for Pd and Pt as well as the Pd and Pt spikes. The calibration of the spikes was jointly carried out by BAM and PTB. The Rh primary assay was produced by PTB. All primary assays and spikes were used later in the project for the quantification of Rh, Pd and Pt.

Before the project started, no calibrated spikes for Pd and Pt and no primary standard for Rh were available. Therefore, suitable enriched isotopes, ^{194}Pt and ^{106}Pd, for preparing the Pd and Pt single spikes were selected

and purchased. Additionally, pure Pd, Rh and Pt with sufficient purity (< 99.9 %) were selected and purchased. The pure Pd and Pt, with natural-like isotopic composition, were used as so-called back-spikes in order to characterise the Pd and Pt spikes by reverse IDMS. The pure Rh was used as the base material for the Rh primary standard.

Pd & Pt spike: The enriched isotopes, ^{194}Pt and ^{106}Pd, were dissolved in aqua regia and diluted to give a mass fraction of ≈ 20 mg/kg for ^{194}Pt and for ^{106}Pd in the corresponding final solution. The final spike solutions were then added to quartz ampoules, so that each contained 7 mL of spike solution. The quartz ampoules, < 100 ampoules for Pd and Pt each, were flame-sealed after filling. Three ampoules, each for Pd and Pt, were used to prepare blends with the Pd and Pt back-spikes for reverse IDMS. The isotope ratios in these blends were determined by MC-ICPMS. The obtained isotope amount fractions for the Pd and Pt spike and the mass fractions of ^{194}Pt and ^{106}Pd in the spikes are listed in the Tables 3 and 4:

Table 3: Isotope amount fractions in the Pd and Pt single spikes with associated uncertainties given in brackets

$n(^{102}Pd)/n(Pd)$	$n(^{104}Pd)/n(Pd)$	$n(^{105}Pd)/n(Pd)$	$n(^{106}Pd)/n(Pd)$	$n(^{108}Pd)/n(Pd)$	$n(^{110}Pd)/n(Pd)$
0.00007798 (93)	0.0012287(78)	0.007408(21)	0.985429(31)	0.004717(18)	0.0011393(85)

$n(^{190}Pt)/n(Pt)$	$n(^{192}Pt)/n(Pt)$	$n(^{194}Pt)/n(Pt)$	$n(^{195}Pt)/n(Pt)$	$n(^{196}Pt)/n(Pt)$	$n(^{198}Pt)/n(Pt)$
0.00000108(51)	0.0003125(19)	0.91430(36)	0.06755(30)	0.015990(63)	0.001848(13)

Table 4: ^{106}Pd and ^{194}Pt mass fractions in the Pd and Pt single spikes with associated uncertainties given in brackets

	Mass fraction in mg/kg *	
	^{106}Pd	^{194}Pt
Pd spike	20.2347 (53)	n/a
Pt spike	n/a	18.1851 (51)

* IUPAC values for the natural isotopic composition are set as constant, as they cancel in double IDMS

The Pd and Pt spikes are currently in the certification process and will be made available as certified isotope reference materials ERM-AE140 and AE141. More details can be obtained from the draft certification report (see Section 6).

Rh primary assay: The development of a digestion procedure to prepare a primary solution of Rh with an element content of 1 g/L and an uncertainty of ≤ 0.001 g/L was key within this work. The rhodium primary assay was prepared according to the following experimental procedure:

Rhodium foil (thickness 0.025 mm, 99.8 %, Alfa Aesar GmbH, Germany, lot MM48317) was cut into pieces of approximately 100 mg each. The pieces were cleaned using an ultrasonic bath for 1 minute in acetone (SupraSolv®, Merck KGaA, Germany), in nitric acid ($n(HNO_3)/m$ = 0.15 mol/kg), in water (σ < 0.066 µS/cm, Milli-Q Element A10, EMD Millipore Corporation, USA) and again in acetone. After drying in a clean environment at room temperature, one piece was weighed directly into each of four thoroughly pre-cleaned and blank-checked 35 mL quartz vessels (MLS GmbH, Germany). To each vessel 15 mL hydrochloric acid (w(HCl) = 0.32 g/g, ultrapur, Merck KGaA, Germany) and 3 mL hydrogen peroxide ($w(H_2O_2)$ = 0.31 g/g, ultrapur, Merck KGaA, Germany) were added. After attaching PTFE-caps featuring pressure release holes, the vessels were placed in a microwave-autoclave (turboWAVE, MLS GmbH, Germany). At room temperature a base pressure of 50 bar was applied to the autoclave using argon (5.0, Linde, Germany). The samples were heated (microwave-assisted) within 15 min to 260 °C (≤ 105 bar). After holding this temperature for another 50 min the samples were allowed to cool down to 35 °C within 30 min. Then the remaining pressure was

released at a rate of 5 bar/min. The vessels were placed on a hot-plate. The rhodium solution was evaporated to near dryness within 6 h by applying a hot-plate surface temperature of 130 °C. 1 mL sub-boiled nitric acid (prepared from $w(HNO_3)$ = 0.65 g/g, EMSURE® ISO using a Cetac OmniPure, Teledyne Technologies Inc., USA) was added. After evaporation to near dryness the residues were re-dissolved in sub-boiled nitric acid ($w(HNO_3)$ = 0.025 g/g) and homogenisation was achieved by placing the vessels in an ultrasonic bath heated to 70 °C for about 4 hours. Finally, the solutions were transferred into a thoroughly pre-cleaned and blank-checked 500 mL PFA bottle (AHF Analysentechnik, Germany). The air buoyancy-corrected mass m_0 of the PFA bottle was determined beforehand. A suitable amount of nitric acid ($w(HNO_3)$ = 0.025 g/g) was added, which resulted in approximately 500 g of a solution with a rhodium mass fraction of $w(Rh) \approx 1.5$ g/kg. Several of these stock solutions were prepared and diluted gravimetrically to yield an according number of 500 g-aliquots of the desired 1 g/kg solution.

Note: The first calibrated Pd and Pt spikes and the first primary assay for Rh will be made available through this project, which will enable SI-traceable results for Rh, Pd and Pt measurements.

Development of a separation procedure, which is capable of isolating the analyte elements (PGE) from the sample matrix and from interfering elements, with sufficiently high recoveries of PGEs (BAM, LNE)

LNE developed the separation procedure described in case a, and BAM developed the two stage separation procedure described in case b. Exchange of the findings between both institutes significantly accelerated the work.

Analyte-matrix separation is a key requirement for applying IDMS as primary method of measurement. This is of special importance when quantifying pg amounts of Pd and Pt in complex samples such as automotive exhaust emissions. The key requirements for analyte-matrix separations are separation from matrix and interfering elements, sufficiently high analyte recovery (> 50 %) and sufficiently low blanks (here < 100 pg). Considering this, two parallel strategies have been followed within this project: a) a separation procedure with nearly complete analyte recovery at the expense of complete separation from interfering elements and b) complete separation from the matrix and interfering elements at the expense of complete analyte recovery. Case a) is intended for combination with collision cell ICPMS, where some interferences can be removed and the remaining interferences have to be corrected mathematically. Case b) is intended for combination with sector field ICPMS without the need for additional corrections, thus the achievable measurement uncertainty should be slightly better.

Case a) Separation using the cationic resin

In HCl media PGE form negatively charged chloro-complexes that are not retained on cationic resin. Glass columns are packed with about 6 g of resin which is cleaned by passing 100 ml of 6M HCl through the column and it is then equilibrated with 0.6M HCl. PGE, Pd, Pt and Rh, are collected in the first fraction, 2 ml of HCl 0.6 M, where interfering metals are eluted later during the addition of HCl 0.6 M. The recovery for Rh, Pd and Pt was complete (≈ 100 %). Limits of quantification, LOQ, obtained with synthetic solutions are the following: 0.002 ng/ml (Pd), 0.001 ng/ml (Pt), and 0.0005 ng/ml (Rh).

Case b) Two stage separation procedure

Several resins were tested for their suitability (see requirements above) regarding the separation of Pd and Pt from the sample matrix and interfering elements. An additional requirement was the elution of Pd and Pt in separate fractions to enable separate mass spectrometric measurements, which improve the precision of isotope ratio determination.

The Cl resin was developed as an extraction chromatographic resin for Cl and I when loading the resin with silver. Therefore, it also shows selectivity for PGE, gold and silver. Several tests with different eluents showed Pd recoveries below 15 % and Pt recoveries between 60 % and 75 %. Due to the low Pd recoveries the resin was unsuitable for this work.

Several tests with a “Ni resin” containing diacetyl dioxime groups, which should also retain PGE, resulted in recoveries of less than 45 % for Pd and less than 28 % for Pt in the best case. Pd and Pt coelute in the same fraction and more than 15 % of the Pd and 45 % of the Pt elute together with the matrix. These results make the “Ni resin” unsuitable for this work.

The anion exchange resin AG 1-X8 showed recoveries for Pd and Pt << 50 % due to the strong retention behaviour of the resin, which also causes relatively high blank levels (0.1 ng level). Additionally, some interferences such as Mo, W, Hg partially coelute with Pd and Pt. One way to increase the recovery was to digest the resin after loading the sample. However, removing the resin from the column and transferring it into the digestion vessel was tricky as the material was sticky. High blank levels (75 pg Pd, 135 pg Pt, 600 pg Cd, 80 pg Ru, 8 ng Hg) and the difficult handling made the AG 1-X8 resin unsuitable for the IDMS analysis of Pd and Pt in the pg range.

Pd and Pt were not retained at the cation resin AG 50W-X12 as they were present in the form of negatively charged chloro-complexes. All elements, which do form negatively charged chloro-complexes or which were weakly bound in dilute HCl such as Ge, Ru, W and Ir and partially Rb and Hg coeluted with Pd and Pt in the first fraction (sample loading). The recoveries for Pd and Pt were between 95 % to 100 % and the blanks were below 10 pg for Pd and Pt. As Pd and Pt coeluted with some interferences this resin alone did not fulfil the requirements described above.

DGA, which is a weak anionic resin, also retains Pd and Pt when loaded in 3 mol/L HCl. The resin showed recoveries of approximately 75 % for Pd and Pt when coeluting in one fraction. Unfortunately, also Cd, Ga, Mo, Y, Zn and Ge coeluted and blanks were relatively high for Pd (≈ 300 pg) and Pt (≈ 50 pg). With extra washing steps and extra elution steps the blanks could be reduced and Pd and Pt could be eluted in separate fractions. However, the coelution of interfering elements could only be reduced, but not removed. Therefore the DGA resin alone did not completely fulfil the requirements for the separation.

As none of the tested resin materials completely fulfilled the requirements described above, it was decided to develop a two stage separation procedure consisting of the DGA resin which nearly fulfilled the requirements and the AG 50W-X12 resin, which offers a complementary mechanism for retaining the dissolved elements. After several optimisation experiments the requirements could be fulfilled:

- Pd and Pd were obtained in separate elution fractions.
- The overall recovery for the complete separation was always > 50 % for Pd and > 70 % for Pt.
- Most interfering elements could be removed by the separation or even reduced by a factor of at least 20. Additional tests of the formation rates of the interfering species showed insignificant contributions to the Pd and Pt signals. Combining formation rates and the maximum element masses after separation resulted in a bias on the isotope ratio of 106Pd/105Pd and 195Pt/194Pt of << 3 ‰, which is the precision of the isotope ratio determination for both.
- Blank levels for the two stage separation procedure were below 100 pg for Pd and Pt (see procedure blanks).

Finally, the developed separation procedures are suitable. The developed two-stage separation procedure enabled the complete removal of interfering elements for ID-ICPMS analysis of Pd and Pt for the first time. More details can be obtained from the manuscript submitted to JAAS (see Section 6).

Limits of detection in the pg range have to be obtained for PGEs. This means a very sensitive IDMS procedure has to be developed with specific attention being paid to isotope ratio precision at low concentration levels and to blank issues. (BAM)

The following work was carried out by BAM:

a) Isotope ratio precision

Isotope ratio precision is an important parameter for IDMS based quantification. Especially, the repeatability of the isotope ratio determination in the spiked sample blends, which is a large contribution to the overall measurement uncertainty in IDMS. To meet the target uncertainty (k = 2) of 1 % for Pd and Pt quantification the repeatability for the isotope ratio determination should be better than 0.5 % for Pd and Pt mass fraction in the low ng/g level.

Consequently, a procedure for the determination of Pd and Pt isotope ratio determination was developed using a sector-field ICP-MS, which is best suited for this work. The procedure was developed in the normal mass resolution mode. High resolution capabilities were not an option, because most of the interferences cannot be separated and in parallel the sensitivity drops to a few percent compared to the normal resolution. Therefore, all interferences have to be separated prior to ICPMS measurements by chemical means (see analyte-matrix separation). Optimisation of the isotope ratio determinations on $^{195}Pt/^{194}Pt$ and $^{105}Pd/^{106}Pd$ were carried out with the sector field ICP-MS Element 2. Measurements were run on standard solutions containing 1 ng/g Pd or Pt respectively.

The repeatability within one measurement which consists of 4000 scans is expressed as a standard deviation (also called “in run precision”). It was < 0.2 % for $^{195}Pt/^{194}Pt$ and < 0.3 % for $^{105}Pd/^{106}Pd$. The repeatability of more than 12 subsequent measurements (also called “long-term precision”) was < 0.2 % for $^{195}Pt/^{194}Pt$ and < 0.3 % for $^{105}Pd/^{106}Pd$, also expressed as a standard deviation. For standard measurements no drift effects could be observed. For real sample measurements typical drift effects during one sequence were less than - 0.5 % for Pd and -0.2 % for Pt isotope ratios, which were corrected for.

Alternatively, another method for determining Pd and Pt isotope ratios has been developed by using collision and reaction cell ICPMS. The main feature here is that some interferences (ArCu & ArZn interferences on Rh & Pd) can be eliminated or at least dramatically reduced, while others may not (e.g. WO interference on Pt). Additionally, the sensitivity of Pt can be increased significantly by a factor of 5. The repeatability on the determination of Pd and Pt isotope ratios was typically 0.2 % to 0.3 %, expressed as a standard deviation. The biggest advantage with this method is that less efficient separation procedures, such as the cationic resin separation using the AG 50W X8, can be used, because some interferences which are not removed by the resin can be removed by the collision cell.

b) Reagent blank levels

The analysis of reagent blanks is very important, because up to several mL of H_2O, H_2O_2, HCl and HNO_3 are used throughout the analytical procedure for digestion and analyte separation. Elevated blank levels in these reagents would determine the detection limits (LoD) of the analytical procedure. In order to check these blank levels several batches of ultrapure H_2O and H_2O_2 and of the acids HCl and HNO_3, each purified by double subboiling distillation, were analysed as follows. Approximately 25 g to 50 g of each reagent was evaporated to dryness under a clean air fume hood and was redissolved in a small amount (a few mL) of dilute (2 %) nitric acid. These solutions were analysed by sector field ICPMS. Using the results of the ICPMS analysis the blank levels in the original, undiluted acid could be calculated. The average blank levels presented as mass fractions are given in Table 5. With these values the contributions of the acids to the total procedure blank is less than 3 pg Pd and 1 pg Pt.

Table 5: Pd and Pt blank levels in the used reagents

Reagent	Mass fraction in pg/g	
	Palladium	Platinum
H_2O	0.06	0.02
H_2O_2	0.2	0.04
HCl	0.3	0.1
HNO_3	0.3	0.1

c) Procedure blank levels

The quantification and subtraction of procedure blanks is of utmost importance for accurate and reliable Pd and Pt analysis in the low ng and pg range. Before performing procedure blanks, blank digestions in the digestion vessels were carried out. The resulting blank solutions were evaporated to dryness, redissolved in 2 % HCl and analysed by ICPMS. The detected blanks were (9 ± 3) pg Pd and (2 ± 1) pg Pt in the HPA quartz vessels (n = 9) and (11 ± 6) pg Pd and (2 ± 2) pg Pt in the microwave TFM vessels (n = 38), given with the corresponding standard deviation.

With sufficiently low reagent and labware blanks (see above) total procedure blanks can be carried out. For each sample preparation and measurement sequence several independent procedure blanks have been prepared and spiked. The first procedure blanks (≈ 160 pg Pd, ≈ 22 pg Pt) were already nearly sufficient for the work. However, further optimisation, especially of the separation procedure, improved the blank levels to average levels of (55 ± 13) pg Pd and (3 ± 4) pg Pt, with the corresponding standard deviation (n=18). As the procedure blanks are more constant within each sample preparation series (n=3; s ≤ 4 pg Pd; s ≤ 2 pg Pt), than between the series, the LODs, defined as three times the standard deviation of the procedure blank, were calculated for each sample preparation series separately. The maximum value of these individual LODs, which are LOD_{Pd} = 12 pg and LOD_{Pt} = 7 pg, were taken as the LOD for the analytical procedure. These procedure blanks and the resulting LODs, which were significantly lower than those reported for similar analytical procedures, are sufficient for determining Pd and Pt masses in the ng to pg range.

Validation of the whole analytical procedure by combining all of the validated single steps and by setting up a complete uncertainty budget. (BAM, LNE)

This work was jointly carried out by BAM and LNE: BAM applied procedure B (Table 6) and LNE applied procedure A (Table 6).

After the development and validation of each single step of the analytical procedure all parts were combined and the complete analytical procedure was validated. For the validation, complete uncertainty budgets were set up and calculated. In parallel, validation with matrix reference materials was performed on both described procedures: a) cationic resin separation with reaction cell ICPMS, b) two-stage separation with sector field ICPMS.

Unfortunately, no suitable matrix reference material for PGEs in automotive exhaust emissions was available. Therefore, reference materials with certified PGE mass fractions and, as far as possible, a similar matrix were selected. Additionally, synthetic samples were prepared based on screening of automotive exhaust emissions and these were used for the validation of procedure b). The results obtained during validation are listed in Table 6.

Table 6: Determined Pd and Pt mass fractions in reference samples and certified reference materials with their associated expanded uncertainty compared with the reference values

Sample	Matrix	Procedure	Pd mass fraction in $ng \cdot g^{-1}$		Pt mass fraction in $ng \cdot g^{-1}$	
			weighed	measured	weighed	measured
Synthetic	Filter + Int.	B	9.486 (6)	9.57 (10)	n/a	n/a
Synthetic	Filter + Int.	B	n/a	n/a	10.504 (6)	10.45 (34)

CRM	Matrix	Procedure	Pd mass fraction in $ng \cdot g^{-1}$		Pt mass fraction in $ng \cdot g^{-1}$	
			certified	measured	certified	measured
BCR-723	Road dust	A	6.1 (1.9)	5.69 (55)	81.3 (2.5)	82 (6)

BCR-723	Road dust	B	6.1 (1.9)	6.5 (2.2)	81.3 (2.5)	88.5 (4.3)
IAEA-450	Algae	A	n/a	n/a	74 (2)	73.5 (1.6)
IAEA-450	Algae	B	n/a	n/a	74 (2)	74.2 (1.1)

The determined Pd and Pt mass fractions obtained with both analytical procedures agree very well with the reference values and they are within the stated uncertainty. Only in the case of Pt in BCR-723 was a value, slightly higher than the certified value, obtained with procedure b, which, however, agrees very well with the IDMS mean value obtained from the GeoReM database for BCR-723. The inhomogeneity of BCR-723, which results from the spread of data listed in GeoReM and which is also published in Sutherland's review on BCR-723, makes this material unsuitable for validation IDMS as primary method of measurement for Pd and Pt amounts in the low ng and pg range.

The significantly larger uncertainties for the mean value of the synthetic sample are due to a relatively large variation in the filter blanks and in the case of BCR-723 it is due to the spread between independent sample measurements. For IAEA-450, which is quite a homogenous sample as shown in CCQM-K75,[6] the relative expanded measurement uncertainty (k = 2) for the mean value is 1.5 % and thus only slightly larger than those of the single independent measurements. In summary, it can be noted that the determined Pt mass fractions of the synthetic samples and the certified reference material IAEA-450 agree very well with the reference values within the associated uncertainties (Table 6).

The relative expanded measurement uncertainties (k = 2) for the Pd and Pt mass fraction determined in one sample aliquot are typically ≤ 1 % for total analyte masses of 1 ng to 5 ng. The significantly larger uncertainties for the mean value of the synthetic sample are due to relatively large variations in the filter blanks and in the case of BCR-723 they are due to the spread between independent sample measurements.

For ideal, homogenous samples the relative expanded measurement uncertainties (k = 2) for the Pd and Pt mass fractions are typically ≤ 1 % for total analyte masses around 1 ng. More details on both procedures and their validation can be obtained from the draft manuscripts listed in Section 6.

Calibration technique for Rh and Rh quantification in automotive exhaust emissions (PTB, LNE)

PTB developed the calibration technique in section a), which was then successfully applied to the Rh quantification in section b) by LNE.

a) Calibration technique for rhodium

To establish a reference procedure for the quantification of Rh, accounting for its unfortunate property of being monoisotopic, a standard addition procedure combined with the use of an internal standard was developed. Completely gravimetric sample preparation is crucial (including even an air buoyancy correction) as well as the unsurpassed measurement performance, regarding the sensitivity and precision of a multi-collector ICP mass spectrometer. After dissolving the sample, the resulting sample solution should be divided into 5 aliquots of the mass m_x. To all aliquots a suitable amount (mass m_y) of an indium solution has to be added. To all but one aliquot suitable amounts (mass m_z) of a rhodium standard solution (with a Rh mass fraction w_z) have to be added in a way that the intensity ratios $R_i = I(^{103}Rh)/I(^{115}In)$ determined in the i-th solution fall to within the approximate range of $0.5 \leq R_i \leq 2$ in order to get the most precise and accurate measurement results. The solutions can be diluted to yield signal intensities that are best suited to the linear range of the detector used. The solutions should be measured five times in the order of increasing intensities yielding n = 25 data points. The data evaluation has to be done using the following equations:

$$x_i = \frac{m_{z,i}}{m_{x,i}}$$

$$y_i = R_i \cdot \frac{m_{y,i}}{m_{x,i}} = \frac{I_i\left(^{103}\mathrm{Rh}\right)}{I_i\left(^{115}\mathrm{In}\right)} \cdot \frac{m_{y,i}}{m_{x,i}}$$

Perform an ordinary least squares algorithm to calculate the best fit linear line

$$y = a_1 \cdot x + a_0$$

The slope a1 and the y-intercept at 0, yield the mass fraction of Rh in the dissolved sample

$$w(\mathrm{Rh}) = \frac{a_0}{a_1} \cdot w_z$$

Its associated relative expanded uncertainty can be calculated from the following equations:

$$\left(\frac{u(w(\mathrm{Rh}))}{w(\mathrm{Rh})}\right)^2 = \left(\frac{u(w_z)}{w_z}\right)^2 + \frac{S^2}{a_0^2} \cdot \left[\frac{1}{n} + \frac{\left(\frac{w(\mathrm{Rh})}{w_z} + \bar{x}\right)^2}{\sum_{i=1}^{n}(x_i - \bar{x})^2}\right]$$

$$S^2 = \frac{\sum_{i=1}^{n}\left[y_i - (a_1 \cdot x_i + a_0)\right]^2}{n-1}$$

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$

Measurements performed according to this protocol result in relative expanded uncertainties which are associated with the mass fraction of rhodium well below 2 %, provided that the measurements were done using an MC-ICP-MS. Details on this were published in ACQUAL (see “Section 6).

b) Rhodium analysis on real sample BCR 723

In order to demonstrate the applicability of the developed calibration technique Rhodium analysis was carried out in BCR-723, which has previously been used as reference material in the case of Pd and Pt analysis. The developed standard addition technique has been applied in combination with single collector ICPMS. The matrix separation was carried out using the cationic exchange procedure. Around 0.2 g of the CRM (8 replicates) was digested in a microwave oven with quartz reactors to minimise contamination.

The Rh mass fraction obtained as a mean value (n = 8) was 14.1 ± 1.1 ng/g with its associated expanded uncertainty (k=2). This result overlaps with the certified value of 12.8 ± 1.3 ng/g within the confidence interval. The application of single collector ICPMS with the standard addition technique together with the cationic exchange results in expanded uncertainties of around 8 % for Rh amounts in the low ng range.

Screening analysis of Ru, Ir and Os in automotive exhaust emissions (PTB)

For the screening analysis, a one-point calibration procedure was found to be suitable and it was used in all experiments in combination with a sector field ICPMS. Traceable Ru, Ir and Os calibration standards have been selected and purchased with uncertainties better than 2 %.

Digestion experiments were carried out in parallel to those for Rh, Pd and Pt to check for the recovery of the above mentioned PGEs from the filters used in exhaust emission measurements, but also to determine blank levels as well as the limits of detection/quantification. Recovery was found to be complete within expanded measurement uncertainties, which were below 20 %, relative. The blank levels were below the limit of detection of approximately 10 pg/g in the case of Ru and Ir, and 20 pg/g in the case of Os.

Six filters, which were used during the first, second and third phase of the EPA Federal Test Procedure to collect automotive exhaust emissions were leached; Pt was between 0.7 ng/g and 1.1 ng/g and Pd was between 37.7 ng/g and 52.0 ng/g. Screening for the other PGEs (Ru, Os, Ir and Rh) resulted only for Pd, Ru and Os in mass fractions higher than the background level.

Sampling of the automotive exhaust emissions (JRC, BAM, LNE, PTB)

This work was carried out by JRC-IE using the required test benches. The sampling was carried out following discussion between all of the partners who were involved in this work. The sampling strategy and filter material was continuously optimised based on discussions between the partners. A second set of filters was obtained in a cooperation between Volkswagen and PTB.

Several filter materials were tested for their suitability (blank, digestion) for Pd and Pt measurements in exhaust emissions using the above described IDMS procedure. Texture filters made from quartz fibre and those made from borosilicate microfibers reinforced with woven glass cloth and bonded with PTFE and quartz showed very high Pd and Pt blank values in the ng range, which made them unsuitable for PGE analysis. Polycarbonate and Teflon filters showed low Pd and Pt blanks, however, these filters have a very smooth surface, from which soot particles can easily fall off. Therefore, these filters also were assessed as being unsuitable. Cellulose and cellulose-esther filters hold the collected particles stronger than teflon and polycarbonate filters due to the textile type structure. Additionally, they offer the lowest Pd and Pt blank values of all tested filter materials, which were (21 ± 3) pg Pd and (39 ± 8) pg Pt for cellulose filters and (35 ± 2) pg Pd and (10 ± 4) pg Pt for cellulose-esther filters, given with their expanded uncertainties (k = 2). These results mean that cellulose and cellulose-esther filters were well-suited for Pd and Pt quantification in exhaust particles.

In total, more than 60 filter samples with automotive exhaust emissions were collected from Gasoline Port Fuel Injection vehicles, a Diesel vehicle equipped with a Diesel Particulate Filter (DPF), and a Heavy Duty Diesel engine equipped with an Oxidation Catalyst and a DPF. The different engines/vehicles were tested under different test cycles (e.g. the World Harmonised Transient test Cycle, WHTC; New European Driving Cycle, NEDC; Common Artemis Driving Cycle, CADC). Samples were collected from both the Constant Volume Sampler (CVS) and a Partial Flow Dilution System (PFDS).

For 41 of the collected filter samples, Pd and Pt data were obtained by applying the described analytical procedures. Discussion of these results in combination with the applied sampling procedures and the engines/vehicles which were used is still ongoing (see Section 6).

Progress beyond the state of the art

- The first calibrated Pd and Pt spikes and the first primary assay for Rh will be made available through this project. This will enable SI-traceable results for Rh, Pd and Pt measurements.
- A two stage matrix separation procedure has been developed, which separates the matrix and all interfering elements from the Pd and Pt.

- Primary methods of measurements have been developed for the quantification of Rh, Pd and Pt in automotive exhaust emissions, allowing expanded measurement uncertainties at the 1 % level for Pd and Pt.
- A screening procedure was developed for obtaining SI-traceable results for amounts of Ru, Os, and Ir in automotive exhaust emissions collected on filters.
- SI-tracable results for Pd and Pt have been obtained for more than 40 automotive exhaust emission samples.

Objective 3: To develop methods and measurement standards for traceable measurements of mercury in the vapour phase.

Traceability for mercury vapour measurement

Mercury in its many chemical forms is highly toxic to human, animal and environmental health. Its ability to accumulate in terrestrial and aquatic biosystems makes it a particularly insidious threat to environmental sustainability. Its long lifetimes and ability to be transported in air over long distances mean that it is ubiquitous to all environmental compartments and is a pollutant of global concern. The increase in the presence of mercury in the environment has been due to human activity over the last one hundred years, and whilst legislation is in place to limit human releases, the assessment of the ongoing effect of mercury on humans and the environment is critically dependent on accurate measurements to assess concentrations and trends. This challenge is complicated by the various chemical forms of mercury and its presence in a number of different matrices. Despite this, the measurement infrastructure to provide traceable measurements of forms of mercury that are currently regulated and to underpin advanced analytical techniques to support the next generation of environmental mercury measurement is absent in Europe, and globally.

The measurement of mercury in emissions is complicated by the fact that mercury is reactive, difficult to store and to handle, and extremely challenging to measure in a comparable way. The development of measurement methodology and primary standards for mercury in the vapour phase has been urgently required by natural gas and gasoline producing and transporting companies, coal-fired power plants, and by regulators, as at the moment e.g. it is not possible to prescribe mercury levels in European directives.

The main objective was to assess the characteristics of suitable materials for the sampling of low level mercury concentrations. A materials study was carried out to select the best candidate materials to be tested with respect to their suitability for the sampling of mercury in ambient air and exhaust emissions. During visits to the Mercury 2011 conference (Halifax, Canada), Linde Electronics and Specialty Gases (USA), NIST (USA), US EPA (USA) and Tekran (Canada) it became clear that glass could be used in conjunction with Teflon tubes, e.g. FEP-type and PFA-type. In most cases a preference was found for the Teflon PFA-type tubes.

Several types of Teflon tubes were tested by VSL, whereas glass was tested by JSI. Both JSI and VSL used a Tekran 2537B CV AFS instrument for mercury measurements. In this instrument's manual it is advised to use an FEP type of Teflon because it has smoother walls and is less porous than PTFE types of Teflon. Furthermore ¼ inch (6.35 mm) OD Teflon lines are advised with a recommended wall thickness of 0.030 inch (0.76 mm). In addition to the Tekran 2537B monitor, JSI also used a Brooks Rand CV AFS detector Model I.

FEP and PFA types of Teflon and Pyrex glass proved to be suitable materials as no effects were found due to the absorption or permeation under standard test conditions.

Non-passivated glass also proved to be a suitable material as no effects were found due to adsorption or permeation under standard test conditions.

JSI conducted further studies that included the testing of the non-passivated and passivated glass material under increased temperature conditions, in the presence of water vapour, and other gases (CO_2, NO_x, …) that

are found in automotive exhaust. It was proved that elemental Hg does not interfere with water vapour and other gasses, showing quantitative recovery using FER and FPA types of Teflon and Pyrex glass tubing.

VSL assessed the current stability of state-of-the-art static mercury vapour in gas standards and produced SI traceable mercury vapour sources, at much lower concentration levels i.e. better than the 5 % threshold which has previously been achieved.

Current measurement and calibration capabilities for mercury vapour in air are maintained at levels of 0.2 µg Hg m^{-3} - 40 µg Hg m^{-3}. In this work, a mercury vapour generator was developed to establish metrological traceability to the international system of units (SI) for mercury vapour measurement results ≤15 ng Hg m^{-3}, i.e. closer to realistic ambient air concentrations (1 – 2 ng Hg m^{-3}).

In order to realise SI traceability, based upon gravimetry, at the low mercury vapour content levels found in the atmosphere, we developed a mercury vapour generator based upon an improved diffusion method. Key innovations included a modified type of diffusion cell, a new measurement method to weigh the loss in (mercury) mass of the diffusion cells during use (ca. 6 – 8 µg mass difference between interval weighings), and a new housing for the diffusion cells to maximise flow characteristics and to minimise temperature variations and adsorption effects.

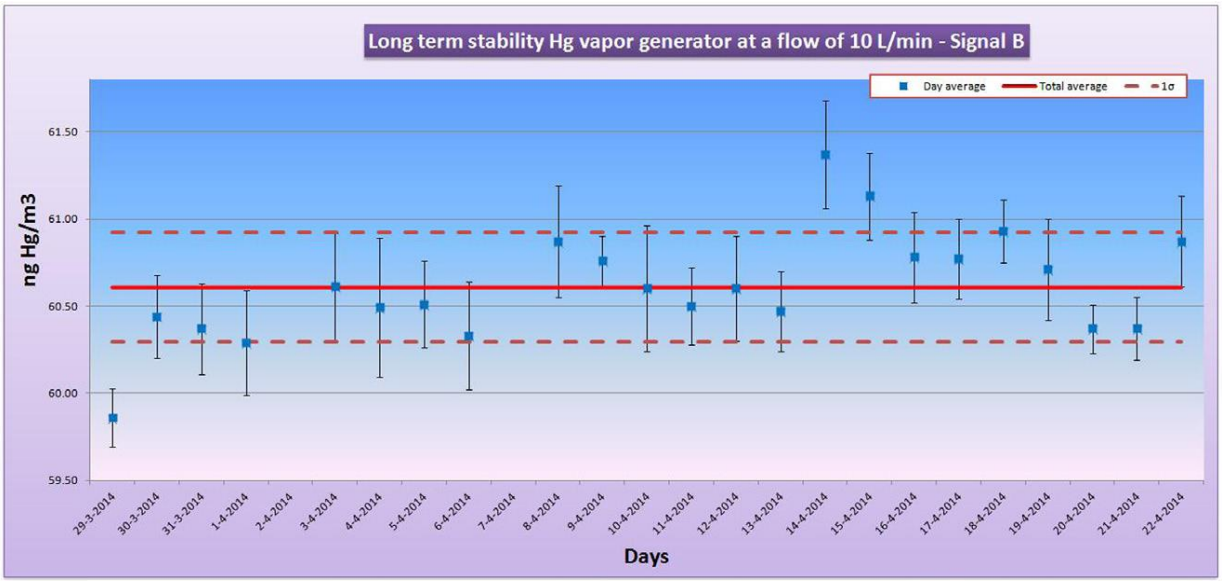

Figure 6: Long term stability of pressure controlled diffusion by a mercury vapour generator (Ent et al. 2014).

Innovations that were developed include a modified type of diffusion cell, a new measurement method to weigh the loss in (mercury) mass of these diffusion cells during use (ca. 6–8 µg mass difference between successive weighings), and a new housing for the diffusion cells to maximise flow characteristics and to minimise temperature variations and adsorption effects.

The newly developed mercury vapour generator system was tested by using diffusion cells generating 0.8 ng Hg min^{-1} and 16 ng Hg min^{-1}. The results also show that the filter system, to produce mercury free air, is working properly. Furthermore, and most importantly, the system is producing a flow with a stable mercury vapour content.

Some additional improvements are still required to allow the developed mercury vapour generator to produce SI traceable mercury vapour concentrations, based upon gravimetry, at much lower concentration levels and with reduced measurement uncertainties. The challenges to be met are especially related to developing more robust diffusion cells and better mass measurement conditions. This additional work is being undertaken in

the ENV51 MeTra project.

The developed mercury vapour generator will contribute to more reliable measurements of mercury vapour at ambient and background air levels, and also to better safety standards and cost reductions in industrial processes, such as the liquefied natural gas field, where aluminium main cryogenic heat exchangers are used - these are particularly prone to corrosion caused by mercury.

The newly developed mercury vapour generator has been proven to give a very stable mercury vapour output and it has the potential, after the introduction of some modifications, to produce SI traceable measurement results (based upon gravimetry) at much lower concentration levels and measurement uncertainties than have been achieved previously. It will contribute to more reliable measurements of mercury vapour at ambient and background air levels.

The work was published in:

Hugo Ent, Inge van Andel' Maurice Heemskerk, Peter van Otterloo, Wijnand Bavius, Annarita Baldan, Milena Horvat, Richard J C Brown and Christophe R Quétel, *A gravimetric approach to providing SI traceability for concentration measurement results of mercury vapour at ambient air levels*, Meas. Sci. Technol. 25 (2014) 115801 (11pp) doi:10.1088/0957-0233/25/11/115801

JRC-IRMM provided SI traceability for mercury vapour measurements by using state-of-the-art ID-ICP-MS technology (Quetel et al, 2015, 2015).

The work was published in:

Christophe R.Queťel, Mariavittoria Zampella, Richard J.C.Brown, Hugo Ent, Milena Horvat, Eduardo Paredes, and Murat Tunc, International System of Units Traceable Results of Hg Mass Concentration at Saturation in Air from a Newly Developed Measurement Procedure, Anal. Chem. 2014, 86, 7819−7827.

C. R. QUÉTEL, M. ZAMPELLA; R. J. C. BROWN (2015) Temperature dependence of Hg vapour mass concentration at saturation in air: New SI traceable results between 15 and 30°C, Trends in Analytical Chemistry, doi: 10.1016/j.trac.2015.12.010

The data most commonly used at present to calibrate measurements of mercury vapour concentrations in air come from a relationship known as the "Dumarey equation". It fits a relationship to a set of experimental results that was obtained nearly 30 years ago. The way these results relate to the international system of units (SI) is not known. This has caused difficulties for the specification and enforcement of limit values for mercury concentrations in air and in emissions to air as part of national or international legislation. Furthermore, there is a significant discrepancy (around 7 % at room temperature) between the Dumarey data and data calculated from mercury vapour pressure measurements in the presence of only liquid mercury. As an attempt to solve some of these problems, a new measurement procedure is described for SI traceable gaseous Hg concentrations at saturation in millilitre samples of air. The aim was to propose a scheme as immune as possible to analytical biases. It was based on isotope dilution (ID) in the liquid phase with the 202Hg enriched certified reference material ERM-AE640 and measurements of the mercury isotope ratios in ID blends, subsequent to a cold vapour generation step, by inductively coupled plasma mass spectrometry.

The process involved a combination of interconnected valves and syringes operated by computer controlled pumps. This ensured continuity under closed circuit conditions from the air sampling stage onward. Quantitative trapping of the gaseous mercury in the liquid phase was achieved with 11.5 μM KMnO4 in 2 % HNO3. Mass concentrations, at saturation, derived from five measurements under room temperature conditions, were significantly higher (5.8 % on average) than data calculated from the Dumarey equation, but they were in agreement (−1.2 % lower on average) with data based on mercury vapour pressure measurement results. Relative expanded combined uncertainties were estimated following a model based approach. They ranged from 2.2 % to 2.8 % (k = 2). The volume of air samples was traceable to the kilogram (via weighing the water used for the calibration of the sampling syringe). Procedural blanks represented on average less than 0.1 % of the mass of Hg present in 7.4 cm^3 of air, and correcting for these blanks was not an important source of uncertainty.

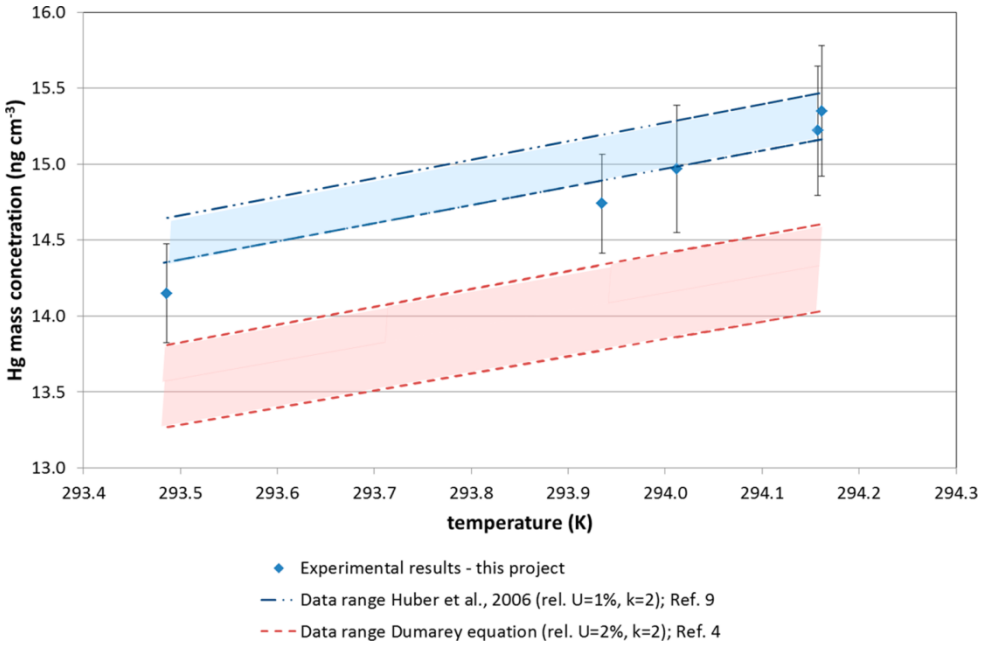

Figure 7: Hg mass concentration results (in ng cm^{-3}) obtained under room temperature conditions in this project. They correspond to five replicates produced on a separate day, over 2 weeks. Vertical bars are expanded combined uncertainty estimations (k = 2). For comparison purposes, data corresponding to the Dumarey equation (red shading) from results of mercury vapour pressure measurements in the presence of only liquid mercury from Huber's work (blue shading) have also been reported (Quetel et al., 2014).

More efforts and developments are necessary to enable measurements with this new procedure under temperature conditions which are different from the ambient. Modifications include the transfer of the experimental setup to a thermo- regulated chamber. This will be reported in a subsequent paper. The first objective was to investigate the possibility of fitting a new mathematical expression describing the evolution of this Hg concentration as a function of the temperature conditions at atmospheric pressure. If the trends described above are confirmed, this could reopen the door to the discussion on the possibility of predicting the mass concentration of gaseous mercury at saturation in air on the basis of mercury vapour pressure correlation data.

NPL and JSI demonstrated accurate and traceable mercury measurements in exhaust emission and in ambient air. The work was divided into methods related to car exhaust measurements and ambient air measurements and this part was intended for the development and testing of a method to measure Hg in exhaust gas. Mercury in gasoline has very complicated chemistry, which has been proven in many different articles/reports. It can transform into other oxidation states, form complexes, precipitate, etc. Therefore the first challenge is to measure total Hg gasoline accurately. The work implemented so far has also proven that it is important to determine total gaseous Hg in exhaust, however even more important is to perform speciation, where elemental and oxidized mercury needs to be determined.

In the framework of this project, total Hg in gasoline and diesel was determined by well-established methods that have been validated some years ago (*Liang, Horvat et al., 1996, 2003*). The analyses of several gasoline samples, obtained in Slovenia, showed that Hg concentrations vary from 0.2 ng/L to 1.2 ng/L, which is very low compared to those reported some years ago. Nevertheless, the experimental set up was established to determine total Hg and its species in exhaust gas.

For the speciation of mercury in exhaust gas the Ontario Hydro Method (ASTM D6784-02) was chosen, while for total Hg the US EPA 324 method was used. Mercury collected in the above procedures was detected using a cold vapour atomic fluorescence detector, calibrated by gaseous mercury obtained from saturated gas chambers kept at room temperatures. Most effort was spent on the validation of the sampling procedures.

The Ontario hydro method (ASTM D6784-02) was chosen by the EPA for measuring Hg(0), Hg(II), Hg(P) and total Hg from stationary coal-fired plants. A sample was withdrawn from the exhaust gas stream at a constant rate (isokinetically) through a probe and an external filter, maintained above 120 °C (± 15 °C), and followed by eight impingers in an ice bath. A set of eight impingers consists of three KCl solution impingers, one HNO_3/H_2O_2 solution impinger, three $KMnO_4/H_2SO_4$ solution impingers, and at the end of the sequence a silica gel desiccant (200 g - 300 g). Exhaust gas passes through KCl first, then H_2O_2, and finally $KMnO_4$ solutions. The oxidised mercury is trapped in the KCl solution, and the elemental mercury is trapped in the $KMnO_4$ solution. The mercury trapped in the H_2O_2 solution is considered elemental mercury and is added to the mercury portion from $KMnO_4$ in the final calculation. The filter and rinses of the nozzle and probe are used to measure the concentration of particle-bound mercury. The QSEM sorbent method (EPA method 324: Determination of Vapour Phase Flue Gas Mercury Emissions from Stationary Sources – Dry Sorbent Trap), validated by the US EPA, was designed for semi-continuous sampling of vapour phase mercury emissions and represents the sum of elemental and oxidised forms of mercury in combustion flue gases using dry sorbent traps. Known volumes of flue gas, with a nominal flow rate of 0.2 L min^{-1} - 0.6 L min^{-1} are extracted from a duct through a single or paired dry carbon traps (containing a specially treated form of activated carbon). Sorbent trap tubes are mounted and inserted in probes into the gas stream. The temperature is maintained between 93 °C and 191 °C. Large sorbent tubes can be used to go to a maximum temperature limit of 218 °C.

Both methods were validated at a laboratory scale with the help of a generator (using diesel fuel). A number of difficulties were observed during the validation procedures. Among the most persistent were:

(1) the low concentrations of Hg in diesel and gasoline, for which long sampling times were needed, resulted in a “poisoned” sampling system, low recoveries and irreproducible results.
(2) spiked (Hg(II) or Hg(0)) gasoline was used to validate the sampling procedure, however, concentrations of Hg in spiked gasoline were unstable. Consequently, the measurements of Hg species and/or total Hg in exhaust gas were irreproducible.

Measurements of total gaseous Hg in exhaust gas were also perfumed in car exhaust gas using gasoline as a fuel. Similar observations and analytical difficulties persisted during field tests.

In order to further develop and improve the sampling efficiency of the methodologies tested a new sampling design should be developed. However, this was outside the scope of the limited resources and time available in the project. However, very good experience and directions were set out for the continuation of this work in the future.

Mercury vapour adsorption tubes manufactured for pumped sampling and analysis have been evaluated for their performance as passive samplers. This has been done by exposing these tubes in a novel micro-exposure chamber. The uptake rates of these tubes have been found to be low (approximately 0.215 ml min^{-1}) as compared to bespoke passive samplers for mercury vapour (typically in excess of 50 ml min^{-1}). The measured uptake rates were shown to vary significantly between tubes and this was attributed to the variability in the air–sorbent interface and the proportion of the cross sectional area removed by the crimp in the quartz tubes, which is used to secure the sorbent material. As a result of this variability, the uptake rate of each tube must be determined using the micro-exposure chamber prior to deployment. Results have shown that the uptake rate determined in the micro-exposure chamber is invariant of concentration, and therefore these uptake rates may be determined at a high mercury vapour concentration for many tubes at once in less than one hour. The uptake rate of the adsorption tubes under these conditions may be determined with a precision of 5 %. Measurements made during a limited field trial in indoor and outdoor ambient air have shown that these tubes give results in acceptable agreement with more traditional pumped sampling methods, although longer sampling periods are required in order to reduce the uncertainty of the measurement, which is currently approximately 30 %.

Tests were also performed on how to accurately measure the mercury content in dichromate impinger solutions which are often used to collect mercury stack gases and/or ambient air at higher concentrations. Reduction with tin chloride has been used, followed by liberation of elemental mercury, using a pure argon stream and then detection using real time atomic fluorescence spectroscopy. The accuracy of the method has been benchmarked using seawater CRMs and is accurate to 5 % at low ppt levels. The procedure has been prepared as a NPL document for which NPL will apply for accreditation to ISO 17025. The method has been fully

validated and a paper describing a novel calibration procedure to accompany its use has been submitted to the journal Analytical Methods.

The observation of a physical matrix effect during the cold vapour generation–atomic fluorescence measurement of mercury in emissions samples has been reported. The effect is as a result of the different efficiencies of the liberation of reduced mercury from solution as the matrix of the solution under test varies. The result of this is that peak area to peak height ratios decease as the matrix concentration increases, passing through a minimum, before the ratio then increases as the matrix concentration further increases. In the test matrices examined – acidified potassium dichromate and sodium chloride solutions – the possible biases caused by differences between the calibration standard matrix and the test sample matrix were as large as 2.8 % (relative) representing peak area to peak height ratios for calibration standards and matrix samples of 45 and 43.75, respectively. For the system considered, there is a good correlation between the density of the matrix and the point of optimum liberation of dissolved mercury for both matrix types. Several methods employing matrix matching and mathematical correction to overcome the bias are presented and their relative merits are discussed; the most promising being the use of peak area, rather than peak height, for quantification.

Progress beyond the state of the art

- The measurements of the mass concentration of mercury vapour in air at saturation were the first of this type of measurement ever published in the literature. Previously only measurements relating to mercury vapour in vacuum had been made.

- The newly developed mercury vapour generator, based upon gravimetry, has been developed and provides SI traceable measurement results at much lower concentration levels and measurement uncertainties than have been achieved previously.

- SI traceability for mercury vapour measurements by using state-of-the-art ID-ICP-MS technology was developed.

- Sampling and measurement procedures for Hg measurements in ambient air and emission monitoring were developed with improved accuracy and reduced uncertainties of the measurement results.

Summary

Soot

- The criteria for a ‘soot’ surrogate aerosol standard were identified as monodispersity, single charge, tuneable size, sufficient number concentration, controlled morphology (spherical) and particle thermal stability. Heterogeneously nucleated silver was found to be the most promising candidate for a primary calibration aerosol standard and this was used in the project for the evaluation of novel instruments and to underpin the calibration facilities developed within the project.
- METAS, NPL and PTB have developed and demonstrated particle number concentration calibration capabilities for automotive particle emission instruments in the soot size range 20 nm to 500 nm for both condensation particle counters and aerosol electrometers. Two international comparisons for charge and particle number concentration were conducted with participants drawn from reference laboratories. Participant results agreed within 2.5 % for Faraday Cup Electrometers (EURAMET 1244) and CPC results showed that for the full concentration range, for sizes between 23 nm and 100 nm, there was an agreement of ±10 % (EURAMET 1282). A round robin test conducted in conjunction with the international EURAMET 1282 comparison and discussions with two instrument manufacturers enabled the validation of a calibration protocol developed within the project for soot and silver particles.
- It has been recommended to implement national requirements for gravimetric mass and particle number concentration as an alternative metric, however validated testing protocols and type approvals of the novel particle number instruments are required before this can be introduced.
- The applicability and performance of novel instruments (e.g. light scattering, diffusion charger and ionization chamber) for measuring soot particle concentrations in vehicle exhausts during regulatory

periodic emission testing were evaluated during the project. Whilst none of the instruments tested cover the entire soot particulate measurement range, instrumentation based on diffusion chargers or ionization chambers can be considered as suitable for measuring the sub 100 nm soot particles emanating from modern diesel vehicles (Euro 5 and Euro 6), and are also capable of detecting damaged diesel particle filters.

- Instrument testing for practical usability and the quantification of long term drift were also performed using exhausts from regular vehicle engines under standardised conditions. These indicated that the novel instruments based on light scattering were better at detecting both malfunctions of Euro 6 vehicle exhaust diesel particle filters and in measuring the low particle emission concentrations of Euro 4 vehicles. Diffusion charger and ion chamber based instruments did not perform as well in testing. A long term stability test showed that more frequent calibration checks will be required for these prototype instruments to guarantee repeatability and stability compared to current commercial instruments.

PGE

- The first calibrated Pd and Pt spikes and the first primary assay for Rh are made available through this project. This will enable SI-traceable results for Rh, Pd and Pt measurements.
- A two stage matrix separation procedure has been developed, which separates the matrix and all interfering elements from the Pd and Pt.
- Primary methods of measurements have been developed for the quantification of Rh, Pd and Pt in automotive exhaust emissions, allowing expanded measurement uncertainties at the 1 % level for Pd and Pt.
- A screening procedure was developed for obtaining SI-traceable results for amounts of Ru, Os, and Ir in automotive exhaust emissions collected on filters.
- SI-traceable results for Pd and Pt have been obtained for more than 40 automotive exhaust emission samples.

Mercury

- Developed a new SI traceable gaseous mercury generator and calibration operating procedure to try and overcome discrepancy problems with currently used methods. The method, based on isotope dilution, a computer controlled dispensing/sample preparation system and analysis using ICPMS to generate mercury vapour. Mass concentration measurements at saturation under room temperature conditions were found to be in agreement (−1.2 %) with mercury vapour pressure measurement results but significantly higher (5.8 %) than Dumarey equation calculated data. Uncertainties, estimated using a model based approach were between 2.2 % to 2.8 % at k = 2. The generator was used in a calibration exercise for mercury measurement systems leading to the derivation of a set of calibration procedure recommendations.
- Investigated factors affecting ambient air monitoring for mercury. Air sample vessel materials Teflon (FEP and PFA), Pyrex and non-passivated glass were all found to be suitable for storage purposes as no effects due to mercury adsorption or permeation were found under standard test conditions. Project research indicated that peak area rather than peak height would produce more reliable results for higher mercury-in-air concentration measurements of stack gases and/or ambient air using impinger solutions whilst lower mercury concentrations can be collected using extended collection times in absorption tubes traditionally used for pumped sampling.
- Investigated and attempted to validate measurements of mercury in vehicle exhausts. The use of extended sampling times due to the low levels of mercury present caused “poisoning” of the sampling system whilst unstable concentrations of mercury in petrol spiked with Hg(II) or Hg(0) led to problems in determining Hg species and/or total Hg in exhaust gases. Overall measurement procedures produced irreproducible results.

4 Actual and potential impact

The ability to accurately measure the three pollutant groups not only enables effective type approval of new engines and periodic testing of engines in use, but also supports introduction of better and more accurate instrumentation for testing procedures and the development of more efficient engines. The scientific knowledge developed in the project has been transferred to industrial users, the scientific community and analytical labs via a variety of 43 technical meetings, conferences and workshops as well as 23 papers in peer reviewed journals. Visits and interactions with key stakeholders such as Chevron in San Ramon, USA Linde Electronic and Specialty Gases, US EPA (USA) and Tekran (Canada) for Mercury measurements and Volkswagen AG, Johnson Matthey, Umicore for PGE have increased their awareness of project research and findings. As a result the outputs of the research are already being used, examples include;

- New and improved calibration facilities for particle number are now available at partner NMIs enabling SI traceability between vehicles undergoing periodic engine exhaust testing for Euro 6c soot emissions and condensation particle counters calibrated by NMI.
- Five instrumentation manufacturers (BOSCH, MAHA, AVL, MatterAerosol/Testo, Pegasor) involved with the periodic or type testing of soot emissions from engines benefited from participation in the round robin exercises, gaining first-hand experience of improved measurement methods and instrument calibrations. Knowledge gained from this interaction has enabled one manufacturer to further develop instrumentation enabling on-road testing of vehicle emissions to demonstrate compliance with the Euro 6c emission regulations.
- Several recommendations were provided to manufacturer members of the European Garage Equipment Association, on the device used for regulatory periodic emission control which has potential to enable more regular checks of new devices for motor type approval tests by implementation of calibration routines and modification of inlet sampling systems.
- Regulation bodies (TÜV and DEKRA) have incorporated project outcomes for implementation in national directives leading to more reliable measurement of soot emissions from diesel vehicles during periodic emission control.
- Project results have been shared with the membership of six normative standard working groups leading to contributions to new draft standards and revisions to existing standards. ISO/DIS 27891 on Condensation Particle Counters calibrations used in vehicle exhaust particle testing now explicitly includes the role of NMIs in calibrating both CPCs and aerosol electrometers for monitoring soot emissions resulting from the project.
- A new collaboration with the Commissariat à l'Energie Atomique (CEA) research centre of Grenoble (France) was established towards the end of the project for the analysis of PGE in automotive catalysts leading to Isotopically enriched certified reference material solutions for Pt and Pd and for Rh will enable analytical laboratories to apply the analytical procedures for Pd, Pt & Rh developed within this project.
- Project methods and results were highlighted during a Special Session on 'providing underpinning traceability for mercury vapour measurement' at the International Conference on Mercury as a Global Pollutant Edinburgh 2013. The Global Mercury Observing System (GMOS) has adopted project approaches. A further EMRP project is continuing research on traceability for mercury measurements (ENV51 Metra project) and an EMPIR Support for Impact Project is working with the relevant standards bodies (CEN, ISO) and the members of the UN Particle Measurement Programme to widen the adoption of the project's outputs (14SIP03 Autopart project).

5 Website address and contact details

A public website is available at: http://www.ptb.de/emrp/PartEmission.html

The contact person for general questions about the project is Martin Thedens, Dr. (martin.thedens@ptb.de).

PTB	Physikalisch-Technische Bundesanstalt	Germany	Bundesallee 100, D-38116 Braunschweig
BAM	Bundesanstalt fuer Materialforschung und -pruefung	Germany	Unter den Eichen 87, D-12205 Berlin
DFM	Dansk Fundamental Metrologi	Denmark	Matematiktorvet 307, DK-2800 Kongens Lyngby
EJPD	Eidgenoessisches Justiz- und Polizeidepartement	Switzerland	Lindenweg 50, CH-3003 Bern-Wabern
IJS	Institut Jozef Stefan	Slovenia	Jamova 39, 1000 Ljubljana
JRC	JRC -Joint Research Centre-European Commission	EC	Rue de la Loi, B-1049 Brussels
LNE	Laboratoire national de métrologie et d'essais	France	1, rue Gaston Boissier, FR-75724 Paris Cedex 15
MIKES	Mittatekniikan Keskus	Finland	Tekniikantie 1, P.O. Box 9, FI-02151 Espoo
NPL	NPL Management Limited	United Kingdom	Hampton Road, Teddington, Middlesex, TW11 0LW
VSL	VSL B.V.	Netherlands	Thijsseweg 11, P.O. Box 654, NL-2629 JA Delft

6 List of publications

Automotive combustion particle metrics and Methods for periodic emissions testing

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F. Lüönd Partikelmesstechnik: Die grosse Suche nach kleinen Partikeln. Gefahrstoffe Reinhaltung der Luft. 2014

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