Final Publishable JRP Summary for ENV02 PartEmission
Emerging requirements for measuring pollutants from automotive exhaust emissions

Overview

Vehicle emissions can damage human health and the environment. 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.

Need for the project

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.

Scientific and technical objectives

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

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
2. Development of methods and standards for periodic emissions testing of particle emissions from motor-vehicle exhaust for (soot) particle sizes down to 20 nm.
3. To develop methods and standards for traceable measurements of platinum-group elements (PGE) in motor-vehicle exhaust emissions.

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European Metrology Research Programme
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4. To develop methods and measurement standards for traceable measurements of mercury in the vapour phase.

Results

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

This objective required the development of a standardised surrogate soot aerosol suitable for use in the calibration of condensation particle counting instruments routinely used for new engine type testing and the periodic testing of diesel engine exhaust emissions to enable demonstration of compliance with Euro 5 and Euro 6 regulations. The soot aerosol is also needed to test and demonstrate the performance of novel instrumentation intended for the same purpose. .

a). 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 was used in the project for evaluation of novel instruments and to underpin the calibration facilities developed within the project.

b). 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, and sizes between 23 nm and 100 nm, 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.

c). There are concerns that current European opacimeter based exhaust measurement instruments used for routine engine testing are unable to accurately detect exhaust emissions from Euro 5 /Euro 6 compliant diesel engines and may not be able to detect defective particle filters. To overcome this, 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.

2. *Development of methods and standards for periodic emissions testing of particle emissions from motor-vehicle exhaust for (soot) particle sizes down to 20 nm.*

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.

3. *Development of methods and standards for traceable measurements of platinum-group elements (PGE) in motor-vehicle exhaust emissions.*

Automobile catalysts use platinum group elements (PGE), (platimum (Pt), palladium (Pd), rhodium(Rh), ruthenium (Ru), iridium (Ir) and Osmium(Os)), to reduce NOx, carbon monoxide and hydrocarbons in vehicle exhausts. Reduction processes take place at high temperatures (900 °C) creating the potential for toxic and

allergenic responses to PGE released by abrasion or volatilization into the environment and subsequently the food chain. The accurate measurement and calibration of instruments used for environmental monitoring for PGE releases is crucial in terms of public health, ecological and economic interests and requires the improvement/introduction of an SI traceable metrological framework. This objective supported the development of analytical reference procedures for the quantification of Pt, Pd and Rh and a screening procedure for Ru, Ir and Os present in exhaust emissions.

This project has produced the first SI-traceable measurement methods with associated uncertainties allowing future data comparability. Additionally, the sensitivity of the developed procedures will enable detailed investigations on the effect of operating conditions and exhaust after treatment technologies on vehicular PGE emissions, as well as the suitability of established sampling procedures. Validated reference procedures and methods were derived enabling the quantification of PGE in exhaust gases for:

a). Pt and Pd using a two-stage separation procedure, isotope dilution mass spectrometry (IDMS) and a combination of cation and anion exchange chemistry. This enables the separation of Pt from Pd and the matrix. Increased method precision was achieved using inductively coupled plasma mass spectrometry (ICPMS).

b). Rh based on the standard addition technique. A Rh standardised solution has been produced and is now available for use by NMI.

c). Ir, Os and Ru (secondary PGEs) collected on filters during the first, second and third phase of the EPA Federal Test Procedure without pre-analytical sample treatment was performed using high-resolution mode ICPMS at PTB. Results showed that ng quantities of Pt and Pd, background levels of Ir and Rh, and slightly elevated background levels (low pg range) of Ru and Os were present.

The fully validated methods were applied to filters containing PGE collected in accordance with European legislation (UNECE Regulations 49 and 83) from the diluted exhaust from a heavy-duty diesel engine vehicle and from a direct injection petrol car. Although the low emission rates achieved for the PGEs correspond well with published, but non-traceable values, the general variability of emission rates between the individual experiments make it difficult to draw detailed conclusions on the difference between the tested catalyser/engine combinations.

4 *Development of methods and measurement standards for traceable measurements of mercury in the vapour phase.*

The use of enormous quantities of fossil fuel hydrocarbons containing traces of mercury as fuels has introduced mercury pollution into the atmosphere. European Directives require the introduction of a metrological infrastructure to enable accurate and SI traceable mercury measurements to facilitate the introduction of target values for mercury in ambient air and waste emissions. Further efforts are still required to provide the necessary underpinning metrology for accurate environmental/atmospheric? Mercury measurements. The project:

a). 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 ina calibration exercise for mercury measurement systems leading to the derivation of a set of calibration procedure recommendations.

b). 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.

c). 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.

Further efforts are still required to provide the necessary underpinning metrology for accurate measurements of mercury in gaseous, liquid, and solid samples.

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 (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).

List of publications

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