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From Generation of Combustion Aerosols to Reference Materials

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Abstract
Using various measuring techniques for aerosols in the field of the legal control of emissions or immissions the traceability of the measurements has a mayor priority. Therefore a method is demanded, that allows to calibrate or adjust instruments for aerosol measurements.
In the field of combustion aerosols a solution seems to be found: The continuous, controlled and reproducible production of a real combustion aerosol with a generator enables the quantification of its characteristics. All other artificial aerosols doesn't cover the complex matrix and the reactive constituents. As soon as the characteristics and their uncertainties are determined, the standard combustion aerosol (SCA) can be named "reference material" and can be certified. Because it is not possible to establish the traceability chain for all conceivable characteristics, a selection of measurands must be made. Due to the fact, that the production of the combustion aerosol is well defined, its assumed that the other quantities are reproducible.
The Swiss Federal Office of Metrology (OFMET) in Wabern is preparing the instrumentation for the certification of standard combustion aerosols (SCA). The traceability chain will be established first for the number of particles, the equivalent mobility diameters, the equivalent aerodynamic diameters and the main gaseous components as CO, CO_2, NO_x, O_2, H_2O, and O_2.
Then certified standard combustion aerosols make possible to compare aerosol measurements and to introduce legal regulations for exhaust emissions.

1 Introduction

During all measurements - whether at a research laboratory, in trade or fulfilling a legal order - following questions must be asked periodically:

- Is the measurand sufficiently defined?
- Is the measuring method suitable for the measurand to be determined?
- Does another laboratory measure the same for identical samples?
- Does the instrument indicate everyday the same?
- How to validate the measurements?
- What are the uncertainties of the measurement?

One task of legal metrology is to determine the measurands for the judgment of air quality and exhaust emissions. In this area the above questions are of central importance, because the measurements have important consequences for concerned persons and institutions. Therefore procedures for all measurands need to be determined, that firstly guarantee the traceability of the result to national or international standards and second allow to control the measuring systems periodically.

2 Chains of Traceability

2.1 Definitions

First some metrological terms shall be explained [1]:

A (measurement) Standard is defined according to VIM [2] as follows: A standard is the material measure, measuring instrument, reference material or measuring system intended to define, realize, conserve of reproduce a unit of one or more values of a quantity to serve as a reference [3].

A reference Material is defined according to VIM as follows: A reference material is a material or a substance one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials [4].

In the field of analytical chemistry a standard often consists in a reference material. The measurands, that means the measured quantities, of certified reference materials - e.g. from NIST [5] or BAM [6] - were determined by different measuring methods in order to minimize the uncertainty of measurement.

Traceability means according to VIM: Traceability is the property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties [7].

Primary standards (national or international) constitute always the starting points of the measurements. In order to give the opportunity to use working standards, these working standards must be traceable to primary standards. Only a complete chain of traceability guarantees a reliable and comparable measurement, whose error and uncertainty are known.

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1) In this section the terms defined in VIM are underlined.
2) International vocabulary of basic and general terms in metrology (VIM). BIPM/IEC/OIML/IUPAC/IUPAP. Second edition (1993).
3) German: Ein Normal ist die Massverkörperung, Messgerät, Referenzmaterial oder Messeinrichtung zum Zweck, eine Einheit oder einen oder mehrere Grössenwerte festzulegen, zu verkörpern, zu bewahren oder zu reproduzieren.
4) German: Referenzmaterial bezeichnet Material oder Substanz von ausreichender Homogenität, von dem bzw. von der ein oder mehrere Merkmalswerte so genau festgelegt sind, dass sie zur Kalibrierung von Messgeräten, zur Beurteilung von Messverfahren oder zur Zuweisung von Stoffwerten verwendet werden können.
5) National Institute of Standards and Technology
6) Bundesanstalt für Materialforschung und -prüfung (Federal Institute for Materials Research and Testing), Germany
7) German: Die Rückverfolgbarkeit bezeichnet die Eigenschaft eines Messergebnisses oder des Wertes eines Normales, durch eine ununterbrochene Kette von Vergleichsmessungen mit angegebenen Messunsicherheiten auf geeignete Normale, im allgemeinen internationale oder nationale Normale, bezogen zu sein.

2.2 Requirements for Certified Reference Materials

The requirements for reference material are determined in the ISO Guides 30 to 35 [8]. The following principal points summarize the requirements:

- The field of application of the reference material must be determined. It can only be used for fields, for which it is characterized.
- The matrix of the reference material must be determined: Pure substances or real life sample.
- The reference material is characterized with its measured numerical values for one or more measurands.
- The uncertainty of the measurement must be known. The measurement procedure determines the selectivity and the accuracy of the measurement.
- The results of the measurement must be traceable to national or international standards.
- The reference material must be sufficiently homogeneous. Using the recommended amount of substance the measurand must be within the specified tolerances in spite of inhomogeneities. The inhomogeneities shall be taken into account in the calculation of uncertainties.
- The reference material is only stable during a certain time. Therefore the conditions for transport, storage and use must be declared. Consequently for example following indication are necessary: Expiration date, ambient temperature, humidity, protective atmosphere. The expiration date indicates the duration, within the uncertainties are guaranteed.
- A certificate specifies all mentioned points above.

3 Artificial Aerosols as Reference Materials?

3.1 Common Artificial Aerosols

There are a lot of industrial realizations for the generation of particles, dusts or powders. Even in the range of nanoparticles different generators for aerosols are available:

- Generators of graphite aerosols produce agglomerates of dry graphite particles.
- Atomizer for oils or paraffin etc. produces droplets.
- Atomizer for suspensions with polystyrene latex spheres (PSL) allows the production of monodisperse aerosols with known diameter.
- Nebulizer for powders produces a mainly dry and inorganic aerosol.
- The aerosol from an atomizer for suspension with salts is often dried and used as an inorganic aerosol.

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[8] ISO Guide 30, 1992: Terms and definitions used in connection with reference materials
ISO Guide 31, 1981, Contents of certificates of reference materials
ISO Guide 32, 1997, Calibration in analytical chemistry an use of certified reference materials
ISO Guide 33, 1989, Uses of certified reference materials
ISO Guide 34, 1996, Quality system guidelines for the production of reference materials
ISO Guide 35, 1989, Certification of reference materials - General an statistical principles

- Moreover diesel particulate matter (solid matter)[9] is available for the measurement of PAH (*polycyclic aromatic hydrocarbons*). In this reference material only the content of PAH is certified.

All known generators for aerosols are suitable for calibrating or for testing of specific measurands. Examples are the measurement of particle diameter (with PSL spheres giving an equivalent diameter), the number of particles (number of PSL spheres) or mass of particles comprising specific substances (carbon, liquid).

3.2 Real Combustion Aerosol

The knowledge of the chemical and physical composition of a combustion aerosol from engines - particularly diesel engines - is an important field of science [10]. The combustion aerosol always consists of following main components:

- Agglomerates with solid carbon nuclei (the pictures with the branched off agglomerates are well known),
- Gaseous inorganic substances (H_2O, CO_2, CO, NO, NO_2, etc.),
- Gaseous and liquid organic substances (unburned or half burned fuel and oil),
- Ashes,
- Sulfates.

The composition of combustion aerosols depends on the construction and the operation condition of the engine. This makes the variety of the structure of the agglomerates extremely complex and the number of liquid or gaseous substances enormous. Moreover the structure and the composition continuously evolve in time and space due to chemical reactions among the combustion products, condensation, and coagulation of particles. These processes start in the engine, continue in the exhaust system and slow finally down while the exhaust gas is diluted with ambient air. Therefore the measurement results depend considerably on the sampling conditions.

Summarized combustion aerosols are:

1. Complex mixture (complex matrix) of particles and substances, that
2. Undergo rapid change (dynamic systems: short lifetime).

3.3 Limits of Artificial Aerosols

All artificial aerosols have their limitations in order to test instruments for combustion aerosols. The instruments are manly sensitive to specific characteristics of combustion products. As an example the mobility diameter does not correspond to a geometric diameter, both do not correspond to an aerodynamic diameter. The sensitivity of an instrument to a specific type of diameter cannot be tested correctly with spheres. Likewise diverse instruments that measure surfaces of particles can

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9) Standard Reference Material (SRM), No 1650

10) David B. Kittelson, et al. (1999), Review of diesel particulate matter sampling methods, Final report, University of Minnesota, http://www.me.umn.edu/centers/cdr/Proj_EPA.html

only be compared with a real combustion aerosol. The same is true for the measurement of adsorbates, gases and liquids.
Consequentially the merit of aerosol generators for the calibration of measuring instruments is determined by their degree of approximation to the real aerosol.

4 Combustion Aerosol as Reference Material

4.1 Short Lifetime and Complex Matrix

The combination of the properties short lifetime and complexity is new in the field of quantitative measurements. Elaborate experience is available up to now with either property alone:

- The handling of reference material with a short life time is known from other fields in metrology. As an example ozone is so reactive, that it must be produced for each calibration straightaway. Its production is kept under well defined conditions. Since only a few substances participated in the production process. The generation takes place in a clean surroundings and the comparisons can be made in a gas mixture of only two constituents (nitrogen and ozone).
- The handling with complex but stable reference materials is known for example with soot. The "United States National Institute of Standards and Technology" (NIST) offers soot from diesel engines with a defined quality as a reference material for PAH. But the amount of PAH is only certified for six main substances, all other substances are present in an unknown amount.

4.2 New Ways with the Standard Combustion Aerosol

Due to the combination of the short life time and the complexity of the combustion aerosols a new way for the production of reference materials has to be chosen.

In a joint project between several Swiss institutes [11] a Standard Combustion Aerosol Generator was conceived and has recently been constructed at the Swiss Federal Office of Metrology (OFMET). A prototype of this generator has already been presented by Jing [12] [13] [14]. In recent investigations we have proved, that the main measurands of this Standard Combustion Aerosol (SCA) are reproducible. Then for the first time a precisely adjustable real combustion aerosol is available.

The SCA is a material with a certain number of known quantities and with an additional large number of unknown, but reproducible quantities. It cannot been considered as an ordinary reference material, because all its quantities are fixed

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11) OFMET: Swiss Federal Office of Metrology, ETH: Eidgenössische Technische Hochschule (Swiss Federal Institute of Technology), SUVA: Schweizerische Unfallversicherungsanstalt, BUWAL: Bundesamt für Umwelt,Wald und Landschaft (Swiss Agency for Environment, Forests and Landscape)

12) Lianpeng Jing (1998), Generation of Combustion Soot Particles for Calibration Purposes, Proceedings to Second International ETH-Workshop, 7. August 1998

13) Lianpeng Jing (1999), Russgenaerator für Kalibration von Russmessgeräten, Vortrag am EAM vom 27. Mai 1999

14) Lianpeng Jing (1999), Improved Generation of Combustion Soot Particles for Calibration Purposes, Proceedings to Third International ETH-Workshop, 9/10. August 1999

during its controlled generation by few tuning parameters. These tuning parameters are to be determined. The gaseous constituents in the source will come first, then the geometry of the generator and also the temperatures in and around the generator will follow.

The main quantities of SCA, e.g. number of particles, the equivalent mobility diameter or the gaseous components, will be measured and if possible certified. When the SCA is used for testing quantities, that are not certified, these may be linked to the tuning parameters or the certified quantities.

4.3 Requirements for Standard Combustion Aerosol

One condition for the application of SCS as a reference material is the proof of the postulate, that starting from the controlled production (fixed tuning parameters) and the reproducibility of the main quantities it can be assumed, that all other quantities are reproducible too. In this case the requirements for the SCA are as follows:

- The values for selected measurands (e.g. number or equivalent diameter of particles) can be adjusted by the tuning parameters.
- All main quantities of SCA are reproducible.
- All certified measurands are traceable to national or international standards.
- The SCA is comparable to (diluted) combustion aerosols from engines.
- The sensitivity to ambient conditions and construction is known and quantified.
- All other unknown quantities are reproducible with a high probability.

5 Confirmation of Standard Combustion Aerosol as Reference Material

5.1 Tasks

In the next steps OFMET will verify, if the SCA fulfills the above requirements:

1. Investigations on the main characteristics (e.g. number of particles, based on condensation particle counter and electrometer; equivalent mobility and aerodynamic diameter, based on PSL spheres; main gas components CO, CO_2, O_2, H_2O, NO, NO_2, HC (as a signal from NDIR = *nondispersive Infrared measuring method* or FID = *flame ionization detector*), and O_2, all based on gravimetric produced gas mixtures).
2. Determination of the tuning parameters, that are necessary and sufficient in order to describe the SCA unambiguously.
3. Establishment of the traceability chain for the tunable parameters, the main quantities and other quantities of interest.
4. Examination of the sensitivity of other quantities (e.g. photoemission, adsorbates) on the quantities. The more quantities were checked (according to this aspect) the higher the probability, that all other and not yet measured quantities are reproducible as well.

5.2 Further Investigations and Applications

The OFMET evaluates to build up the traceability chains also for the following measurands of combustion aerosols:

- Mass of constituents of particles (PM = *particulate matter*, EC = *elementary carbon*, SOF = *soluble organic fraction*, PAH)
- Photoemission (NanoMet™ [15]): the basis must be defined first.
- Volatile organic compounds: Selection of trace substances from adsorbates or gaseous constituents.

As soon as a generator for SCA is ready to use as a reference material, following applications can be realized:

- International comparisons between laboratories for particulate matter (research, test plants etc.
- International regulations for the particulate emissions can be established
- Investigations on the behavior of particles and exhaust gas during dilution and in the atmosphere.
- Investigation of the influence on cell cultures, organs and organisms to assess the risk of particulate exhaust aerosols.

15) NanoMet™, nanoparticle measurement technique by Matter Engineering