



## ENV52 HIGHGAS

Dynamic methods for trace concentrations and dissemination to the field

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RÉFÉRENCES

Clés de la COMPÉTITIVITÉ et d'un MONDE PLUS SÛR

#### **Context**



- Results of international comparisons on greenhouse gases
  - Dynamic generation methods do not have the necessary accuracy to meet the uncertainty requirements for global monitoring
- Need of significant research to lead to a new generation of methods for providing these dynamic standards
- Key challenges for developing a new generation of dynamic devices to provide high accuracy reference standards
  - Lower concentrations and uncertainties
  - Capability to provide stable measurements in long-term to be used in field monitoring
  - Accurate methods for the quantification of target components in the diluent gas
  - Detailed investigation of the materials used for constructing the device in order to minimise adsorption of the reference standard
  - Accessible cost.



#### **Objectives and participants**



- Objectives
  - Development of novel dynamic generation methods and devices
    - Dissemination of the traceability to field measurements at monitoring stations
    - Validation of the gravimetric reference standards prepared in the framework of this JRP
- Which type of dynamic devices ?
  - Based on dynamic dilution of static gas mixtures at a higher concentration
  - Based on the permeation or diffusion method
- Participants
  - LNE, NPL, VSL, METAS, CMI, FMI, TUBITAK, EMPA



#### **Development of dynamic generation devices**



- Development of novel dynamic generation methods and devices for
  - On-site preparation of reference standards with uncertainties that meet WMO targets
    - CO between 50 and 500 nmol/mol; target uncertainty of 2 nmol/mol



- N₂O between 50 and 500 nmol/mol; target uncertainty of 0.1 nmol/mol
- A selection of strategically important F-gases (including SF<sub>6</sub>)
  - ◆ HFCs, perfluorocarbons (PFCs), SF<sub>6</sub> (Kyoto Protocol) and chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs)
  - Concentrations in the range of 100 to 1000 nmol/mol



With a target uncertainty of 3%



#### High accuracy dynamic reference standards for CO and N<sub>2</sub>O



- First step: development of new high accuracy dynamic reference standards for atmospheric CO and N<sub>2</sub>O
  - Development of different dynamic systems from static reference standards
    - One at LNE for generating dynamic reference standards of CO and N<sub>2</sub>O
    - One at TUBITAK for generating reference standards of CO
    - One at FMI for generating reference standards of N<sub>2</sub>O
  - Requirements on the development
    - Use different kind of flowmeters
      - Laminar flow meters
      - Complementary Metal Oxide Semiconductor (CMOS) mass flow controllers
      - Sonic nozzles



### High accuracy dynamic reference standards for CO and N<sub>2</sub>O



- First step: development of new high accuracy dynamic reference standards for atmospheric CO and N<sub>2</sub>O
  - Requirements on the development
    - Use of static reference standards
      - At about 5 μmol/mol of the target component
    - Use of dilution gases
      - Synthetic air
      - Whole air
    - Generation of several concentrations
      - Range : 50-500 nmol/mol
      - At least five concentrations



#### High accuracy dynamic reference standards for CO and N<sub>2</sub>O



- Second step: validation of new high accuracy dynamic reference standards for atmospheric CO and N<sub>2</sub>O
  - Validation of these new dilution devices with comparison made to inhouse static reference standards
  - Organization of an inter-laboratory comparison to validate the dynamic mixtures against the gravimetric reference standards
    - CO : NPL, LNE, TUBITAK
    - $\bullet$  N<sub>2</sub>O : FMI, VSL
  - Organization of a comparison of the dynamic reference standards of CO (LNE and TUBITAK) and  $N_2O$  (LNE and FMI), generated with these facilities to existing NOAA and AGAGE scales (standards supplied by EMPA)





#### **High accuracy dynamic reference standards for F-gases (1)**

- First step: Development of new high accuracy dynamic reference standards for F-gases at sub nmol/mol concentrations
  - Purity of the used F-gases
    - ◆ Development of a method for the purification of F-gases (including SF<sub>6</sub>) in synthetic air and the determination of the level of F-gas contained
    - Ensure a F-gas concentration of less than 0.5 pmol/mol
  - Development of a novel high accuracy dynamic device based on dilution using CMOS technology or sonic nozzles (METAS and CMI) to generate dynamic reference standards of SF<sub>6</sub> at concentrations close to 100 pmol/mol as a step towards the WMO target of 20 pmol/mol
  - For the other F-gases, generation of dynamic reference standard at 1 µmol/mol using either a permeation or a diffusion device (METAS)
  - Use of the dynamic device based on dilution developed before in conjunction with the permeation or diffusion device to generate reference standards of F-gases (including SF<sub>6</sub>) at concentrations close to 100 pmol/mol with a target standard uncertainty of 3%



#### **High accuracy dynamic reference standards for F-gases (2)**



- Second step: Field dissemination and comparison to global scales for F-gases
  - Aim
    - Evaluate the concordance between international scales and an independent European scale
    - Improve world-wide traceability of F-gases (especially for emerging requirements for new components where current calibration scales do not exist)
  - Comparison of the SF<sub>6</sub> reference standards (dynamic device based on dilution) and the reference standards of other F-gas components (permeation or diffusion device) to existing calibration scales (NOAA and SIO for AGAGE measurements)
    - Form basis of an independent European scale
    - Provide an essential link for SI traceability to the globally accepted NOAA and SIO scales



#### **High accuracy dynamic reference standards for F-gases (3)**



- Second step: Field dissemination and comparison to global scales for F-gases
  - Development of a novel portable device for disseminating reference standards of F-gases to field measurements (suitable for monitoring station usage)
    - Set up of this novel portable device via dynamic dilution of high concentration gas at pmol/mol levels (METAS, EMPA)
    - Validation of this device at pmol/mol levels by comparison to at least one reference standard used in the field and generated at EMPA
    - Use of this dilutor device by EMPA as an on-site or travelling calibration unit and test it in the field (at least one monitoring site) by comparison with traditionally filled air standards from global background sites





# Thank you for your attention

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Any questions?

