ARPA SICILIA
Agenzia Regionale per la Protezione dell'Ambiente

Sistema Nazionale per la Protezione dell'Ambiente

MTT2025

Monitoring Technology Tableau
Tecniche di misura per la qualità dell'aria

Palermo, 29-30 Ottobre 2025

PERMEATION TUBE APPLICATIONS

FINE METROLOGY

WHAT ARE PERMEATION TUBES

- Small containers made of **inert material**
- Filled with a pure compound in **liquid/gas or solid/gas equilibrium**
- Inserted into a **carrier gas flow** with controlled flow rate
- At constant temperature, they release the gas through a **permeable membrane**
- Provide a **stable, continuous, and reproducible emission** over time
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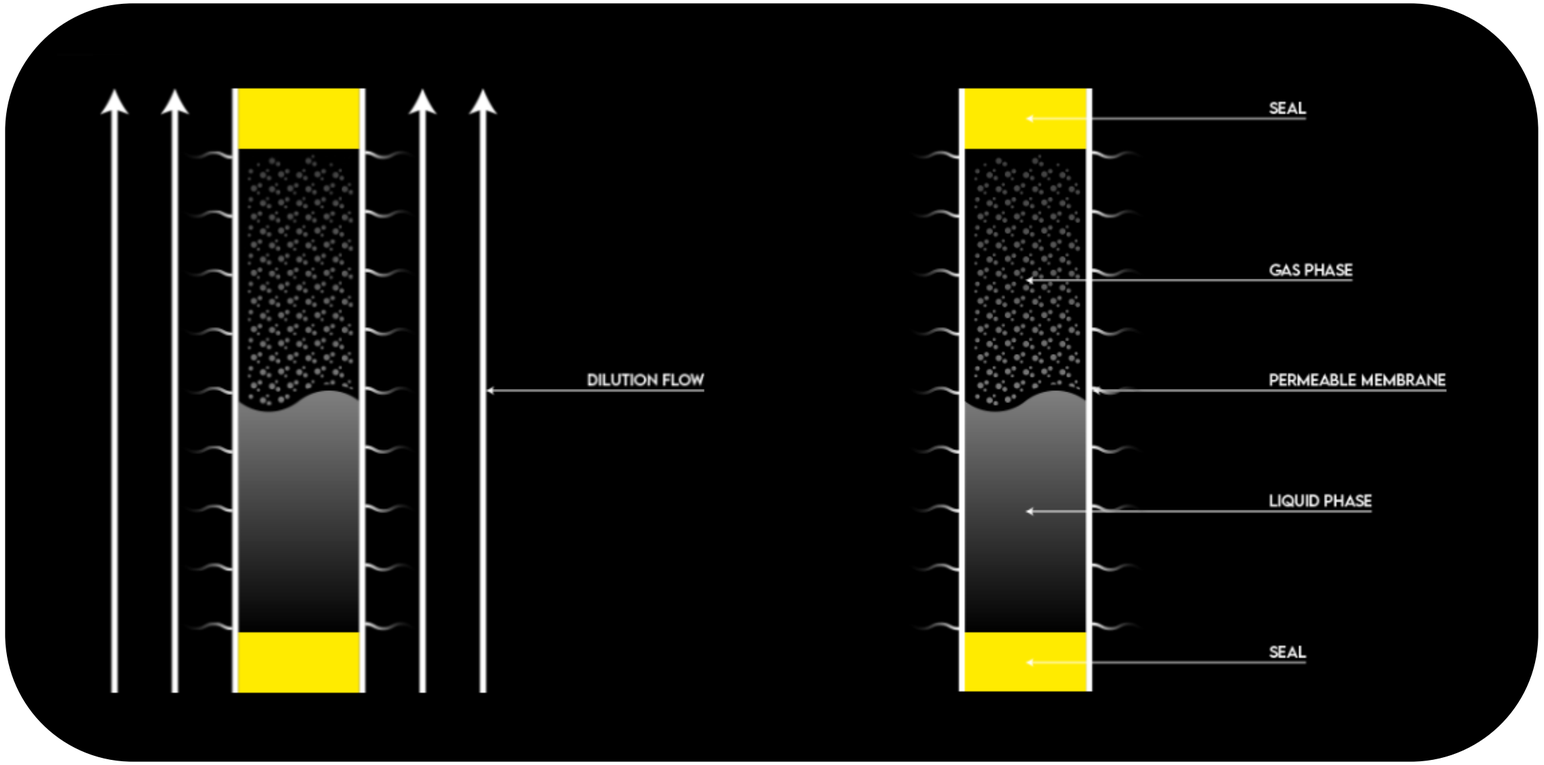
- A **safe and traceable alternative** to standard gas cylinders



ELECTRONICS AND MICROCHIPS

Cleanrooms and Semiconductors – Contaminant Control

In the **microelectronics** and **semiconductor manufacturing** sectors, controlling **air purity** is essential to ensure the integrity of production processes.
Permeation tubes enable the **generation of highly stable and traceable reference gas mixtures**, used for the **calibration and verification** of monitoring systems in **cleanrooms**.

- Air purity is essential in the production of **microchips and wafers**
- Controlled generation of **HCl, HF, HBr, organic acids** to simulate contaminants
- **Calibration and verification** of sensors and analyzers in **cleanrooms**
- **Traceable and reproducible concentrations** down to a few ppb
- Used in **automated systems** for continuous **monitoring and calibration**

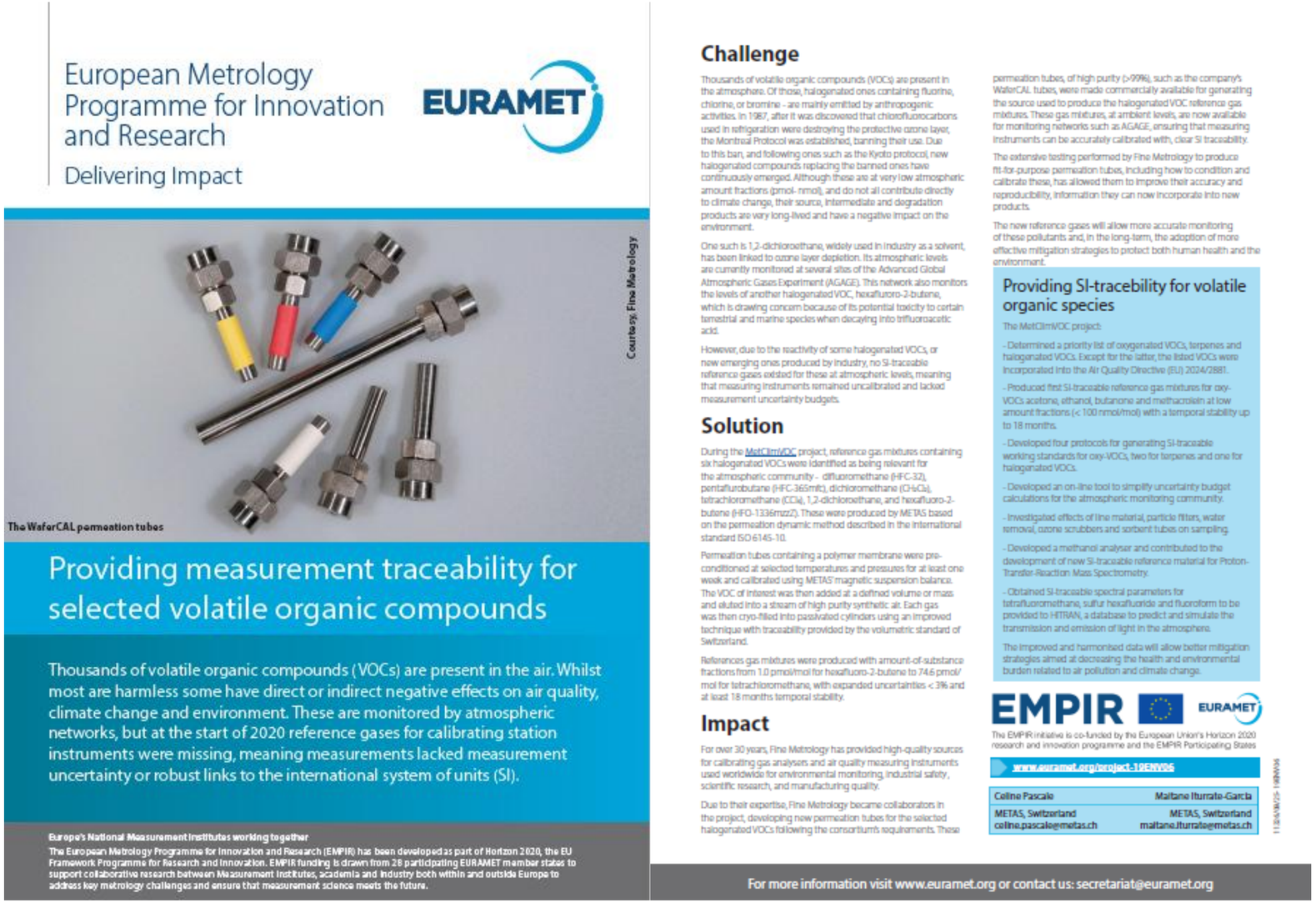
ENVIRONMENT AND AIR QUALITY

VOC – Volatile Organic Compounds (indoor/outdoor)

Volatile organic compounds (VOCs) include a wide range of substances with **high volatility and reactivity**, involved in **photochemical pollution** and **tropospheric ozone formation**.
The **controlled generation of reference mixtures** using **permeation tubes** is essential to ensure **accuracy and traceability** in air quality measurements, both **indoor** and **outdoor**.

- **Controlled generation** of pure **VOCs** or complex mixtures
- **Calibration** of **analyzers and sensors** *(GC-FID, PTR-MS, automated systems)*
- **Stable and reproducible emission** over the long term
- **Traceable concentrations** down to a few ppb
- Used in **monitoring networks** and **environmental laboratories**

ENVIRONMENT AND AIR QUALITY



European Metrology Programme for Innovation and Research

Delivering Impact

EURAMET

Courtesy: Fine Metrology

The WaferCAL permeation tubes

Providing measurement traceability for selected volatile organic compounds

Thousands of volatile organic compounds (VOCs) are present in the air. Whilst most are harmless some have direct or indirect negative effects on air quality, climate change and environment. These are monitored by atmospheric networks, but at the start of 2020 reference gases for calibrating station instruments were missing, meaning measurements lacked measurement uncertainty or robust links to the international system of units (SI).

Europe's National Measurement Institutes working together

The European Metrology Programme for Innovation and Research (EMPIR) has been developed as part of Horizon 2020, the EU Framework Programme for Research and Innovation. EMPIR funding is drawn from 28 participating EURAMET member states to support collaborative research between measurement institutes, academia and industry both within and outside Europe to address key metrology challenges and ensure that measurement science meets the future.

Challenge

Thousands of volatile organic compounds (VOCs) are present in the atmosphere. Of those, halogenated ones containing fluorine, chlorine, or bromine - are mainly emitted by anthropogenic activities. In 1987, after it was discovered that chlorofluorocarbons used in refrigeration were destroying the protective ozone layer, the Montreal Protocol was established, banning their use. Due to this ban, and following ones such as the Kyoto protocol, new halogenated compounds replacing the banned ones have continuously emerged. Although these are at very low atmospheric amount fractions (pmol- nmol), and do not all contribute directly to climate change, their source, intermediate and degradation products are very long-lived and have a negative impact on the environment.

One such is 1,2-dichloroethane, widely used in industry as a solvent, has been linked to ozone layer depletion. Its atmospheric levels are currently monitored at several sites of the Advanced Global Atmospheric Gases Experiment (AGAGE). This network also monitors the levels of another halogenated VOC, hexafluoro-2-butene, which is drawing concern because of its potential toxicity to certain terrestrial and marine species when decaying into trifluoroacetic acid.

However, due to the reactivity of some halogenated VOCs, or new emerging ones produced by industry, no SI-traceable reference gases existed for these at atmospheric levels, meaning that measuring instruments remained uncalibrated and lacked measurement uncertainty budgets.

Solution

During the MetClimVOC project, reference gas mixtures containing six halogenated VOCs were identified as being relevant for the atmospheric community - difluoromethane (HFC-32), pentafluorobutane (HFC-365mfc), dichloromethane (CH_2Cl_2), tetrachloromethane (CCl_4), 1,2-dichloroethane, and hexafluoro-2-butene (HFO-1336mzzZ). These were produced by METAS based on the permeation dynamic method described in the international standard ISO 6145-10.

Permeation tubes containing a polymer membrane were pre-conditioned at selected temperatures and pressures for at least one week and calibrated using METAS' magnetic suspension balance. The VOC of interest was then added at a defined volume or mass and eluted into a stream of high purity synthetic air. Each gas was then cryo-filled into passivated cylinders using an improved technique with traceability provided by the volumetric standard of Switzerland.

References gas mixtures were produced with amount-of-substance fractions from 1.0 pmol/mol for hexafluoro-2-butene to 74.6 pmol/mol for tetrachloromethane, with expanded uncertainties < 3% and at least 18 months temporal stability.

Impact

For over 30 years, Fine Metrology has provided high-quality sources for calibrating gas analysers and air quality measuring instruments used worldwide for environmental monitoring, industrial safety, scientific research, and manufacturing quality.

Due to their expertise, Fine Metrology became collaborators in the project, developing new permeation tubes for the selected halogenated VOCs following the consortium's requirements. These permeation tubes, of high purity (>99%), such as the company's WaferCAL tubes, were made commercially available for generating the source used to produce the halogenated VOC reference gas mixtures. These gas mixtures, at ambient levels, are now available for monitoring networks such as AGAGE, ensuring that measuring instruments can be accurately calibrated with, clear SI traceability.

The extensive testing performed by Fine Metrology to produce fit-for-purpose permeation tubes, including how to condition and calibrate these, has allowed them to improve their accuracy and reproducibility, information they can now incorporate into new products.

The new reference gases will allow more accurate monitoring of these pollutants and, in the long-term, the adoption of more effective mitigation strategies to protect both human health and the environment.

Providing SI-tracebility for volatile organic species

The MetClimVOC project:

- Determined a priority list of oxygenated VOCs, terpenes and halogenated VOCs. Except for the latter, the listed VOCs were incorporated into the Air Quality Directive (EU) 2024/2881.
- Produced first SI-traceable reference gas mixtures for oxy-VOCs acetone, ethanol, butanone and methacrolein at low amount fractions (< 100 nmol/mol) with a temporal stability up to 18 months.
- Developed four protocols for generating SI-traceable working standards for oxy-VOCs, two for terpenes and one for halogenated VOCs.
- Developed an on-line tool to simplify uncertainty budget calculations for the atmospheric monitoring community.
- Investigated effects of line material, particle filters, water removal, ozone scrubbers and sorbent tubes on sampling.
- Developed a methanol analyser and contributed to the development of new SI-traceable reference material for Proton-Transfer-Reaction Mass Spectrometry.
- Obtained SI-traceable spectral parameters for tetrafluoromethane, sulfur hexafluoride and fluoroform to be provided to HITRAN, a database to predict and simulate the transmission and emission of light in the atmosphere.

The improved and harmonised data will allow better mitigation strategies aimed at decreasing the health and environmental burden related to air pollution and climate change.

EMPIR EURAMET

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

www.euramet.org/project-19ENV06

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EURAMET EMPIR 19ENV06 MetClimVOC

The European project **MetClimVOC (19ENV06)**, coordinated by **EURAMET**, addressed the **lack of traceable reference standards for the measurement of volatile organic compounds (VOCs)** in ambient air.
The objective was the **development of primary reference sources and metrological standards** for selected VOCs — including **hydrocarbons, terpenes, and halogenated VOCs** — in order to improve the **comparability and reliability** of measurements at the European level.

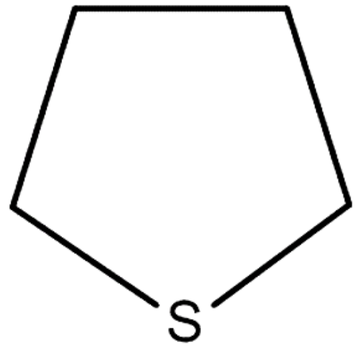
- **Development of new reference sources** for VOCs at atmospheric concentration levels
- **Dynamic generation method** compliant with **ISO 6145-10**
- **Interlaboratory testing and validation** with **NPL**, **METAS**, **VSL**, and other National Metrology Institutes
- **Emission stability within ±1 % over 18 months**, even for reactive organic compounds
- **Supply and validation of permeation tubes** for halogenated and oxygenated VOCs

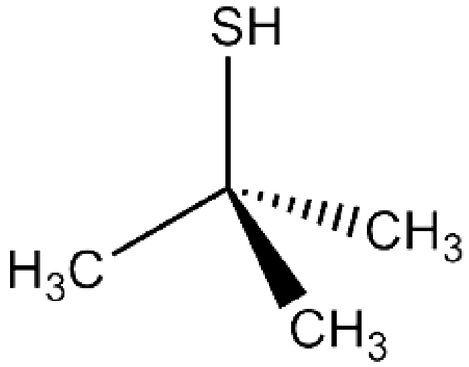
ENVIRONMENT AND AIR QUALITY

Odorant Analysis – Tetrahydrothiophene (THT) and tert-Butylmercaptan (TBM)

In the **energy** and **gas distribution** sectors, **odorization** is a mandatory **safety measure** to make potential leaks of **natural gas** or **LPG**, normally odorless, detectable.
The most commonly used odorants are **THT (Tetrahydrothiophene)** and **TBM (tert- Butylmercaptan)**, selected for their **low olfactory threshold, chemical stability,** and **compatibility** with gas distribution network materials.

- **Controlled generation** of THT and TBM at known and traceable concentrations
- **Calibration** of **gas leak detectors** and **industrial safety sensors**
- **Periodic verification** of odorization systems in **methane and LPG networks**
- Applications in **mobile laboratories, distribution plants,** and **calibration centers**
- Odorization regulated by **Law No. 1083/1971, UNI 9463, UNI 7133**
- **Stable and reproducible emission** over time using **permeation tubes**



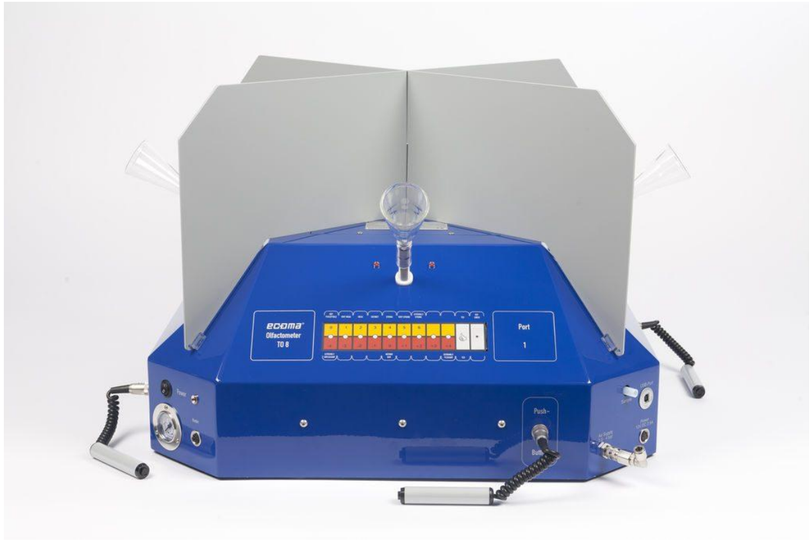


ENVIRONMENT AND AIR QUALITY

Odour Monitoring

Odour monitoring plays a crucial role in **air quality control** and in the **assessment of the environmental impact** of industrial plants, landfills, and wastewater treatment facilities.
Permeation tubes allow the **generation of reference gas mixtures** containing odorous compounds at extremely low concentrations, ensuring **traceable calibrations** and **reproducible measurements**.

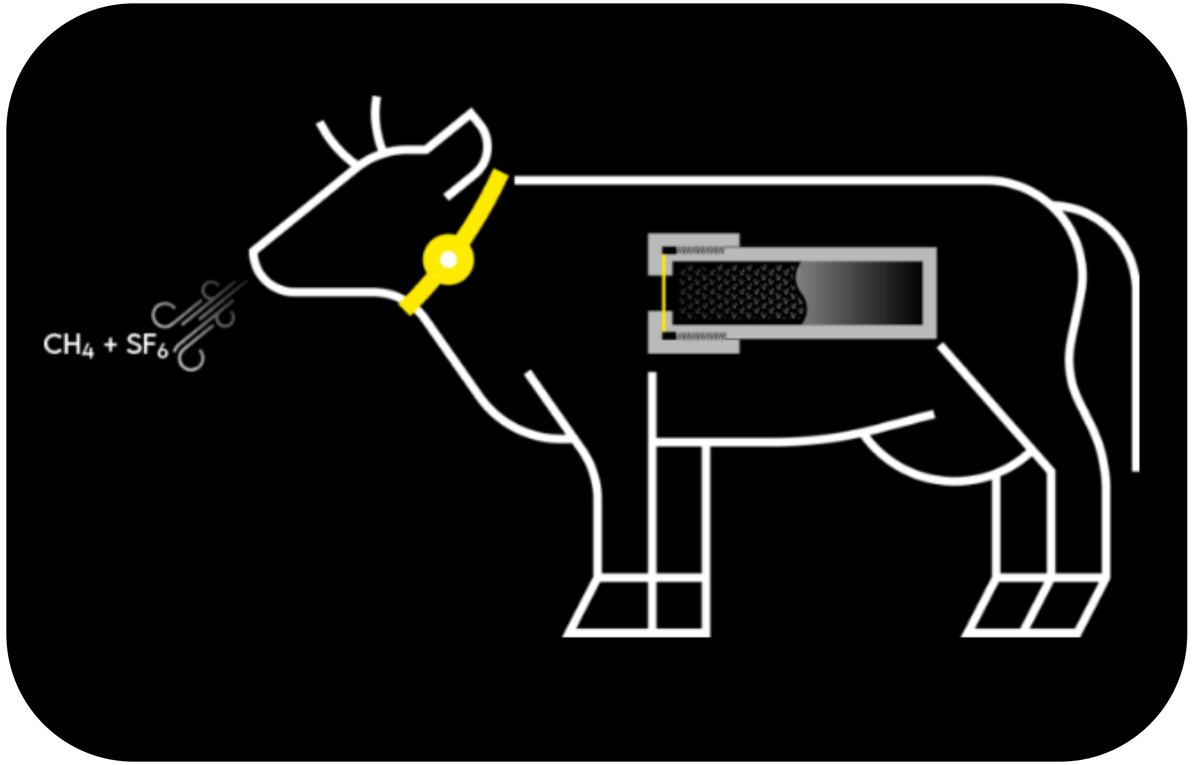
- **Controlled generation** of odorous compounds (acetaldehyde, sulfides, mercaptans)
- **Calibration** of **electronic noses**, **olfactometers**, and **environmental sensors**
- **Simulation of real emission conditions** in industrial plants
- Applications in **environmental monitoring networks**, **ARPA laboratories**, and **waste treatment plants**
- Standards and regulations: **EN 13725, UNI 16000, UNI/TS 11537**
- **Traceable and repeatable concentrations** down to a few ppb



AGRI-FOOD AND LIVESTOCK SECTOR

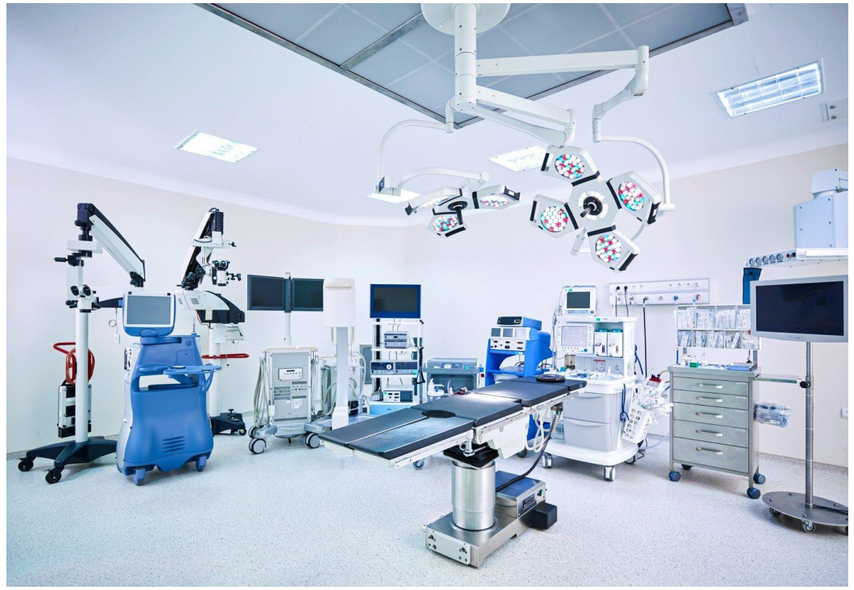
Measurement of Enteric Emissions in Ruminants

In the **agri-food and livestock** sector, **permeation tubes** are used in the **SF_6 tracer technique**, applied for the **accurate measurement of methane emissions** from ruminants.
This methodology allows for the determination of **individual emission rates** in a **precise and safe** way, contributing to the **assessment of environmental sustainability** and the **optimization of feed efficiency** in livestock farming.



- **Permeation tubes** filled with **SF_6** in liquid/gas equilibrium
- **Stable and controlled emission** at constant temperature (39 °C)
- **SF_6 tracer technique** for indirect measurement of **CH_4 emissions**
- **Continuous sampling** using **PVC canisters** connected to the animal
- **Calibration** of **collection and dilution systems** for emitted gases

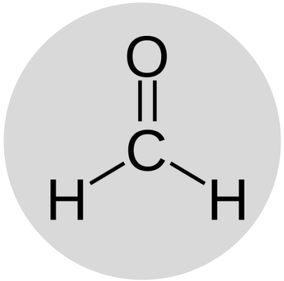
HEALTHCARE AND BIOMEDICAL SECTOR

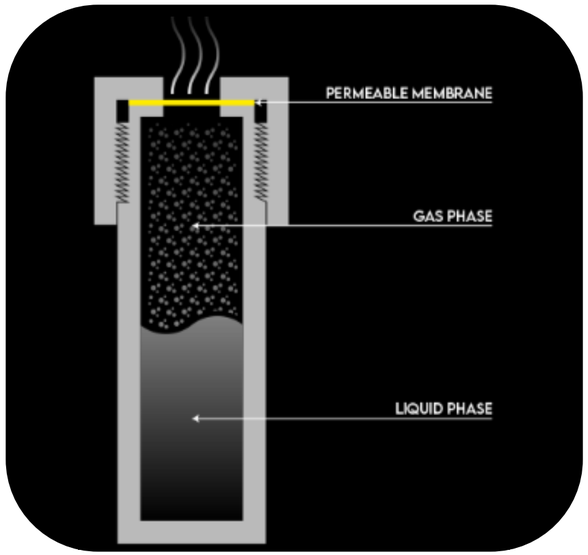


VOC Monitoring in Clinical and Hospital Environments

In the **biomedical and healthcare** sector, **permeation tubes** are used for the **generation of reference gases** to **calibrate diagnostic instruments and environmental monitoring systems**.
Their features of **stability, reproducibility, and safety** make them suitable for use in **sensitive environments** such as **hospitals, analytical laboratories, and operating rooms**, where measurement accuracy is essential to ensure both **data quality** and **personnel safety**.

- **Formaldehyde** in hospital environments and sterilization laboratories
- **Breath analysis** (VOC biomarkers: acetone, isoprene, NO, medical VOCs)
- **Ethanol analyzers** – calibration of portable and laboratory instruments
- **Operating room monitoring** – anesthetic and volatile compounds
- **Controlled generation** of traceable mixtures for diagnostic applications
- **Stable and reproducible concentrations** over time





HEALTHCARE AND BIOMEDICAL SECTOR

Breathalyzers – Calibration of Portable and Laboratory Instruments

In the **forensic and healthcare** sectors, **breathalyzers** require regular calibration to ensure the **accuracy and legal traceability** of ethanol measurements in exhaled air.
Ethanol permeation tubes enable the **dynamic and controlled generation** of reference gas mixtures, providing a **stable, safe, and flexible** alternative to traditional pressurized cylinders.

- **Controlled generation** of pure ethanol by permeation
- **Traceable and adjustable concentrations** in mg/L or ppm
- **Dynamic calibration** of IR or electrochemical breathalyzers and sensors
- **Stable and reproducible emission** over time
- **No pressurized cylinders** → improved safety and portability
- Applications in **metrological laboratories, law enforcement, and healthcare facilities**

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THANK YOU FOR YOUR KIND ATTENTION!

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