Dynamic generation of trace gas standards of oxygen-sensitive VVOCs at below zero temperatures using Tracer Cert® diffusion tubes

presented at PEFTEC 2015, Antwerp

John M. Thompson[1 & 2], David C. Howse[1 & 2] and Daniel J. Blenkhorn[2]

1. Tracer Measurement Systems Ltd., Institute of Research and Development, Birmingham Research Park, Birmingham B15 2SQ, UK

2. Molecular Physics Group, School of Physics and Astronomy, University of Birmingham, Birmingham B15 2TT, UK

E-mail: tracerms@btinternet.com

Website: http://tracerms.co.uk

For info about diffusion tubes contact: info@tracerms.co.uk

VOCs: Vapour or gas?

- Volatile Organic Compounds can form vapours
- They only form gases at temperatures above their critical temperatures

Difference between vapours & gases

- Trace vapours are below their critical temperatures under normal conditions
- They have clusters of molecules in the vapour phase
- They can also condense to liquids or even freeze.

What are VVOCs?

- VVOCs or Very Volatile Organic Compounds have a confusing definitions:
- WHO: b.p. <0 to 50-100°C
- ISO 16000-6 (2011) only defines VOCs, so we might use the converse of that as all VOCs of bp <69°C or having <6 carbon atoms per molecule.
- ESVOC CG in Europe don’t have a definition
- Salthammer in Indoor Air (2014) 1-14 reviewed VVOCs in detail in indoor environments but is not conclusive about their definition

What are oxygen-sensitive VVOCs?

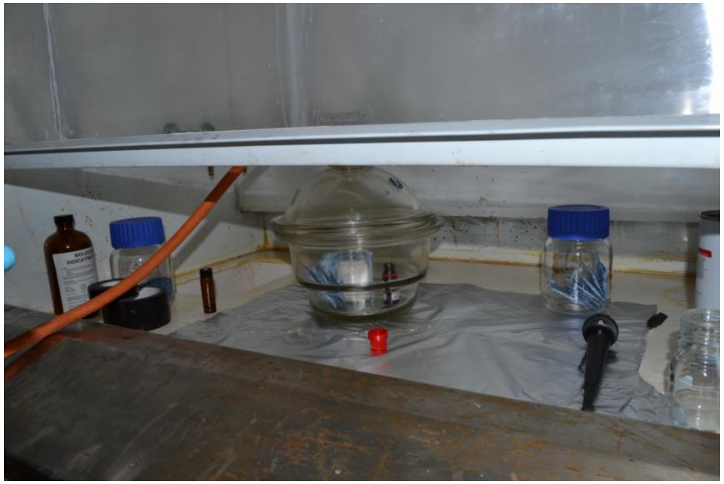
- VVOCs which react with oxygen or with ozone, hydrogen peroxide or free radicals derived from these such as hydroxyl or superoxide radicals
- These initiate degradative reactions, as well as oligomerisation or polymerisation
- So oxygen and sources of oxygen need removing or excluding to ensure stability

Handling VVOCs

- Best stored in a refrigerator or freezer
- Cool all devices, containers or other equipment used in handling or transferring
- Be especially careful with VVOCs which are oxygen-sensitive

Handling oxygen-sensitive VVOCs

Handle, manipulate or transfer in a nitrogen atmosphere preferably, or, if that is not practical or possible, flush air out of containers as in the photographs below



Why use trace vapour standards?

- Uses of standards:
- Calibration of analyses for Quality Control
- Analytical Method Development
- Method Validation
- Process Development
- Types of standards: static and dynamic

Why use dynamic generation methods of trace vapour standards?

- Disadvantages of static standards
- Permeation tubes
- Diffusion tubes
- Other dynamic methods

Dynamic generation of trace vapour standards of oxygen-sensitive VVOCs: what are the problems?

- Current so-called “permeation ovens” do not have low enough operating temperatures.
- Normally, their lowest operating temperatures are about 40°C although some can be adapted to operated at 30 to 35°
- They are usually only able to supply air as the carrier gas and adaptions are needed to use nitrogen or other oxygen-free sources
- Needs special precautions in high ambient temperatures, especially for field calibration

Dynamic generation of trace vapour standards of oxygen-sensitive VVOCs: solutions to the problems

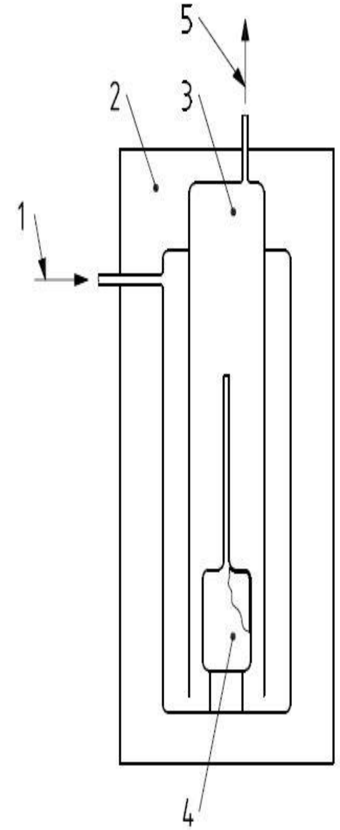
- It is obvious that nitrogen is an economical and practical carrier gas.
- Achieving suitable low temperatures by rather old-fashioned practical methods in the lab is possible using crushed ice, salt-ice cooling mixtures, slush baths (J. Chem & Eng Data, 1965, p124) or dry-ice baths
- We are developing a range of sub-ambient thermostats using Peltier devices for use either in the laboratory or in the field which will become available next year.

Flawed design of diffusion tubes in ISO 6145-8 and the improved design of Tracer Cert® diffusion tubes

ISO 6145-8-2005 “Gas Analysis – Preparation of calibration gas mixtures using dynamic volumetric methods - Part 8: Diffusion methods

- This tube design has to be filled from the top, through the capillary tube
- It is very difficult to do
- Only suitable for liquids
- No use for solids
- Capillary may not drain of viscous liquids at all
- Cannot be properly cleaned and decontaminated

The Flawed ISO design

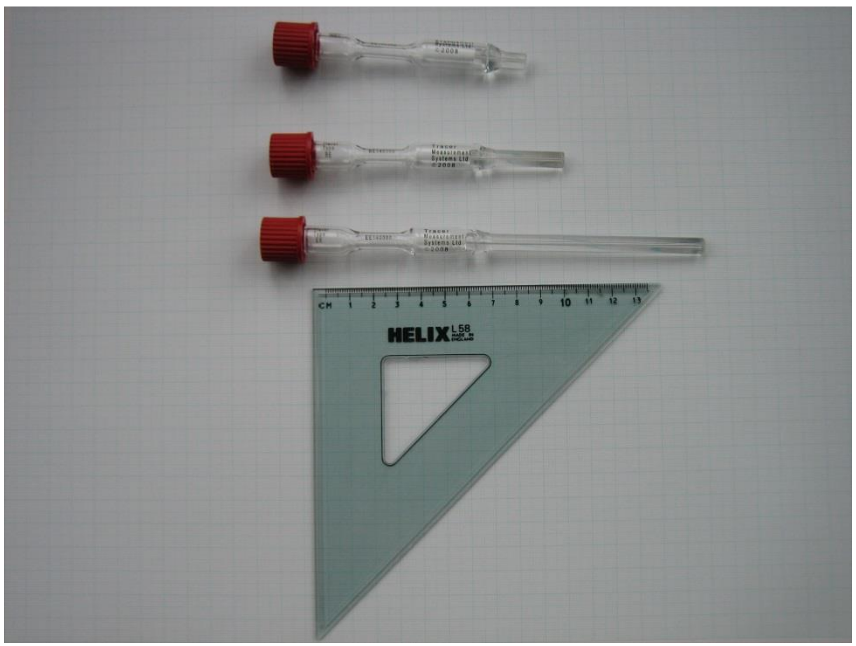


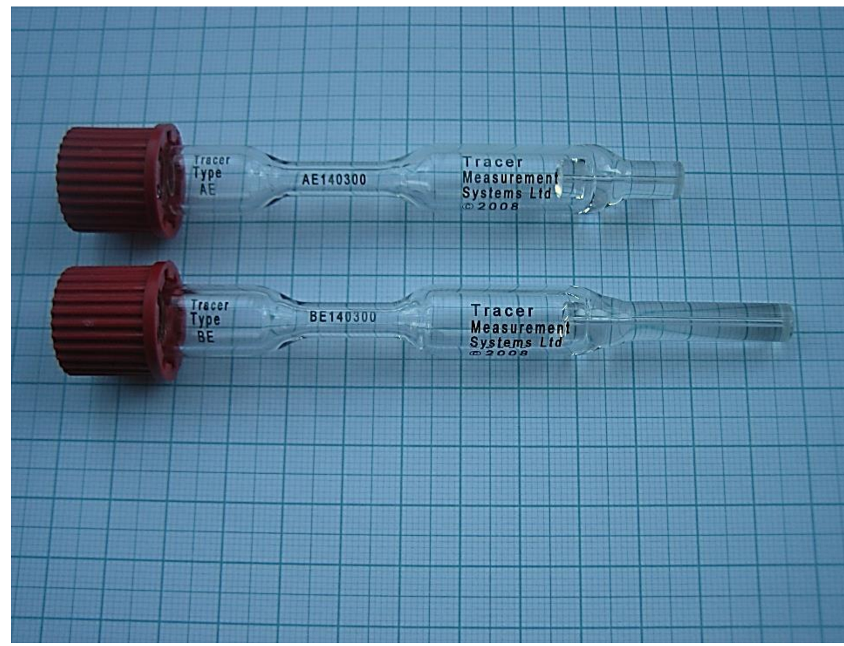
Tracer Cert® Diffusion Tubes:

A wide range of uniquely identifiable, laser-engraved, refillable & re-useable diffusion tubes for VVOCs, VOCs, SVOCs & inorganics suitable for both solids and liquids

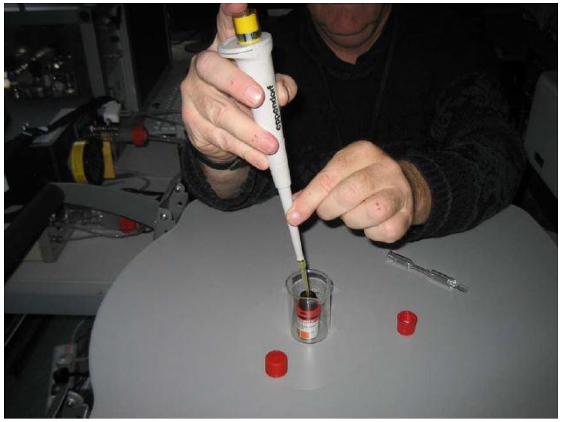
Precision bore capillary tube of 5 lengths & 9 bore diameters

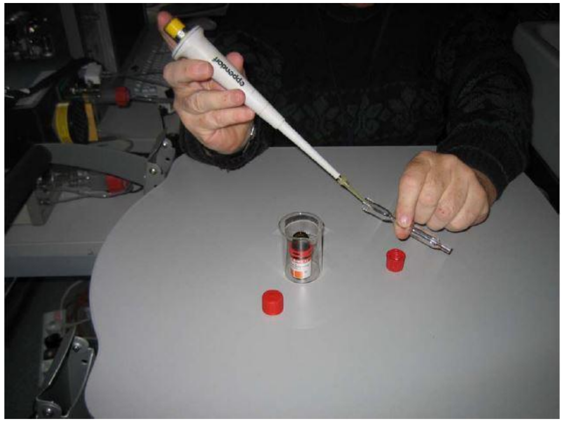
Laser-engraved unique I.D. code for each diffusion tube



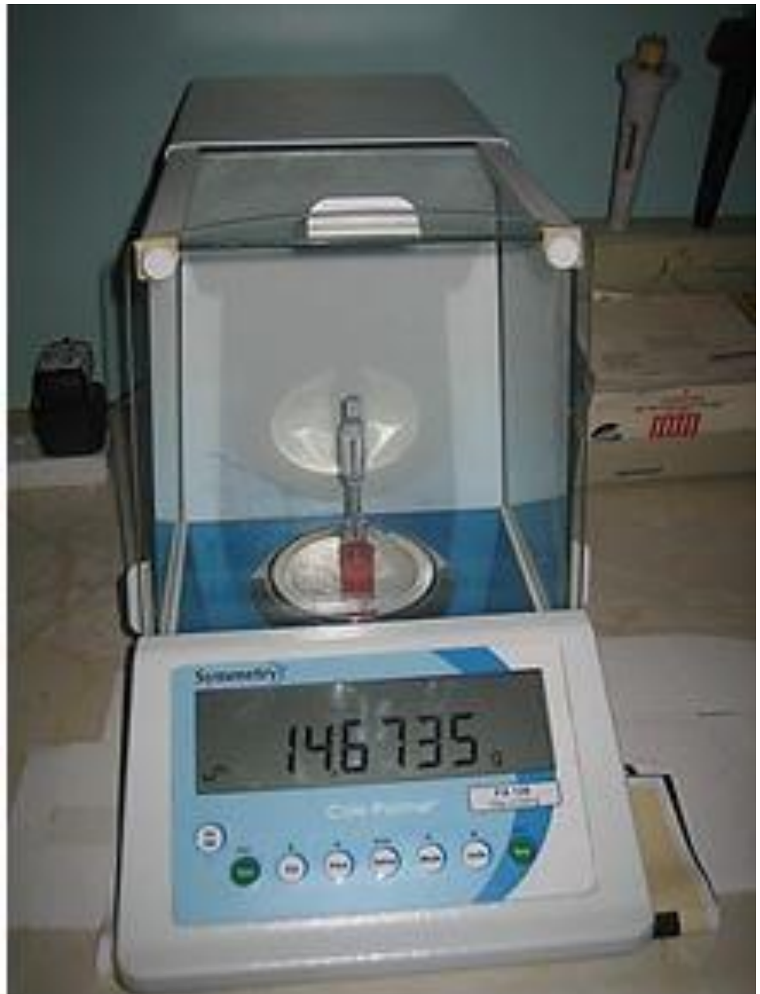


Tracer Cert® Diffusion Tubes: Easy to fill



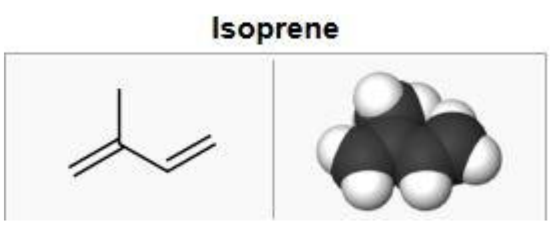


Tracer Cert® Diffusion Tubes: Easy to calibrate gravimetrically



Isoprene is an important example of an oxygen-sensitive VVOC. What is known about its vapour pressure and other useful properties?

Isoprene is important both commercially, in atmospheric chemistry and in plant, animal and clinical biochemistry.
It has a boiling point of only 34°C and only limited data is published by NIST about temperature variation of vapour pressure. There is a gap between 234.9K and 290K with no data. Other sources help, e.g., Cameo Chemicals:
v.p. at -6.7°C 194mbar, -12.2°C 147mbar, -17.8°C 111mbar
-23.3°C 82mbar, -28.9°C 59.5mbar
Critical temperature: 211.1°C (484.3K)



Pilot experiment at a sub-zero temperature to test the calibration of Tracer Cert® diffusion tubes with the Oxygen-sensitive VVOC, isoprene

A short pilot test in a prototype thermostat at -9°C (264K)

- **An aliquot of Isoprene was added to a diffusion tube which was weighed initially.**
- **3 weight loss measurements were made over a period of 40 minutes with a total weight loss of 7.5mg**
- **A sub-ambient thermostat is being developed to operate at a temperature of -21°C at which the vapour pressure will be much lower so we will get a lower rate of diffusion out of the tube**

ISOPRENE calibration at -9°C in 10ml/min N_2 carrier gas flow, a pilot sub-zero experiment