Dynamic generation of trace gas standard mixtures of both SVOCs and oxygen-sensitive SVOCs at ppm(v/v) to sub-ppb(v/v) concentrations using Tracer Cert® diffusion tubes

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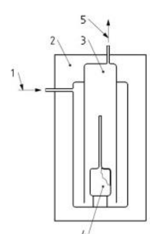
The design of diffusion tubes shown in ISO 6145-8-2005 “Gas Analysis – Preparation of calibration gas mixtures using dynamic volumetric methods – Part 8: Diffusion methods” is very clearly not at all easy to use with volatile liquids but it is impossible to use for viscous or solid SVOCs, as can be seen in the illustrations from the ISO standard which are shown below.

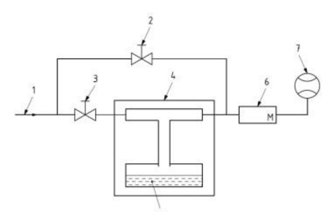
On the other hand, the wide range of sizes of the uniquely identifiable, laser-engraved, refillable and re-useable Tracer Cert® diffusion tubes (see photographs below and Journal of Environmental Monitoring, 2009, 11, 1543-4) are easy to fill with even viscous or solid SVOCs.

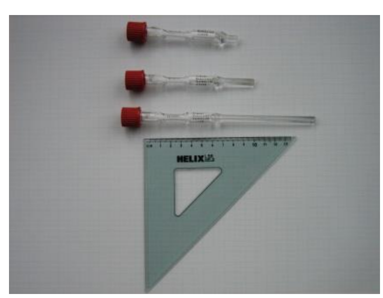
We have used these diffusion tubes with a couple of SVOCs, as illustrative example: siloxane D5 (with chemical name decamethylcyclopentasiloxane) and an oxygen-sensitive SVOC, which is commercially very important: the phenolic antioxidant, BHT (3,5-di-t-butyl-4-hydroxytoluene).

A standardised method of storing and handling oxygen-sensitive SVOCs in nitrogen was used and oxygen-free nitrogen was used as the carrier gas in the experiments using such substances.

Air was used as the carrier gas for the experiments in which SVOCs insensitive to oxygen were used.







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A rough guide to choosing a suitable size of diffusion tube by estimating emission rates at a chosen temperature for the compound of interest

As a guide, if we have suitable data on vapour pressures at different temperatures and have or can estimate the diffusion coefficient versus temperature, we can use the following equation to estimate approximately the emission rate of the vapour:

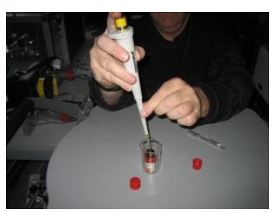
$$S = \{[DMPA]/[RTL]\} \times \ln[P/(P-p)]$$

Where
S is the rate of diffusion of the vapour out of the capillary in g s^{-1}
D is the diffusion coefficient in cm^2 s^{-1}
P is the pressure in atmospheres at the open end of the diffusion tube
A is the cross-sectional area of capillary bore in cm^2
R is the molar gas constant in ml atmos mol^{-1} K^{-1}
T is the temperature of the diffusion tube in Kelvins
L is the diffusion length of the precision bore capillary
p is the vapour pressure of the compound at T Kelvin in atmospheres

We used this for benzene at 313K in a 2cm long tube of 0.2mm bore and it gave an estimate one third higher than observed experimentally, so it is only a rough but useful guide. Most vapour pressure and diffusion coefficient are of limited reliability except for a limited number of substances.
When deciding on a suitable Tracer Cert® diffusion tube, the capillary bore length and the bore diameter are the key dimensions.
Having calibrated a tube gravimetrically a given size of tube, the equation above suggests doubling the capillary length halves the emission rate, whereas doubling the bore diameter quadruples the emission rate.
The vapour diffuses out of the capillary into a carrier gas flow, so the concentration of trace vapour is dependent upon the rate of diffusion out the chosen tube at T Kelvin and the carrier gas flow rate. The higher the flow rate the lower the concentration (flow rates can vary from 100ml/min to many litres/min.

Filling a Tracer Cert® diffusion tube

The photographs show the filling the tube with a liquid using a 100µl pipette tip. Up to 400-500µ can be added. More can be added with a larger reservoir up to 5ml



Weighing a Tracer Cert® diffusion tube

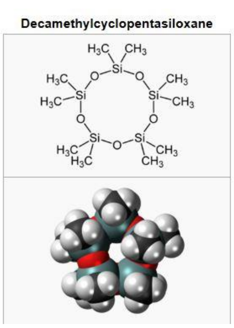
Diffusion tube calibration is readily done gravimetrically with a calibrated digital Electronic balance reading to 0.1mg, as in the photograph on the right. Some National Standards Laboratories using the Tracer Cert® diffusion tubes measure the weight continuously to 10µg.

Handling oxygen-sensitive SVOCs

<u>What are SVOCs?</u>

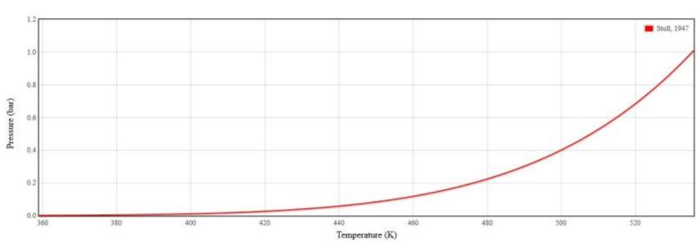
SVOCs or Semi-Volatile Organic Compounds have higher boiling points than VOCs and, although many are liquid, others are solid at room temperature. Various definitions of SVOC exist The definitions are sometimes different depending on whether the environment being monitored Is outdoors or indoors for air quality. It is often the boiling point range that is chosen and for SVOCs, the WHO has designated the boiling point range from 240°C to about 400°C.
Other definitions are found in the various EU states as well as being under consideration under REACH. There are further definitions based on gas chromatographic retention time (AgBB and EMICODE both in Germany or on vapour pressure at 25°C (EU Solvent Emissions Directive).
One of our illustrative examples, siloxane D5, is probably best classified as an SVOC even though its b.p. is only 210°C. The other example used, BHT, is solid at room temperature and its m.p. is 265°C so WHO would regard it as an SVOC.

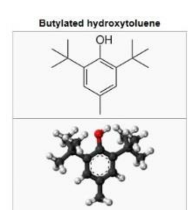
Properties of Siloxane D5 useful in planning calibration experiments in Tracer Cert® diffusion tubes



The molecular weight is 370.77, the melting point is -47°C (226K) and the boiling point is 210°C (483K). The vapour pressure at 25°C is about 20Pa. Little is published about the vapour pressure versus temperature curve, so the Clausius-Clapeyron equation could be used to estimate the vapour pressure at different temperatures or you could plot the 3 known points (m.p., b.p. and v.p. at 25°C on a plot of log p vs 1/T and interpolate v.p. at the desired temperature that would give a useful, crude estimate. The diffusion coefficient could be estimated from that of another compound with a known diffusion coefficient using Graham's Law.

Properties of BHT useful in planning calibration experiments in Tracer Cert® diffusion tubes

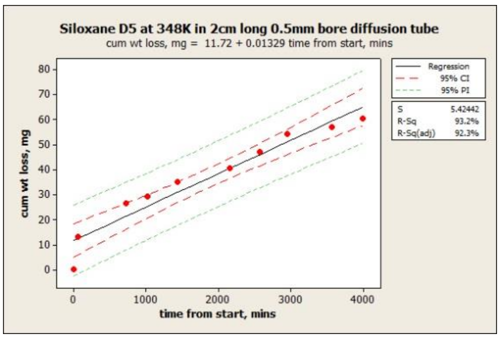




The vapour pressure temperature curve shown above is from the US NIST Webbook. From the interactive on-line version, we can find any vapour pressure in the displayed range of temperatures, e.g., at 373.136K (100°C) which we used in our experiment, we find the vapour pressure is 0.293mbar.
The molecular weight is 220.36, the melting point is 70°C (343K) and the boiling point is 265°C (538K). We can estimate the diffusion coefficient using Graham's Law, as above.

Results for Siloxane D5

This SVOC was thermostatted at 75°C in a Tracer Cert® diffusion tube with air as the carrier gas at 100ml/min. The diffusion tube chosen for the calibration experiment had a precision bore tube section of length 2 cm and bore diameter 0.5 mm.



Results for BHT

This Oxygen-sensitive SVOC was thermostatted at 100degC in a Tracer Cert® diffusion tube with nitrogen as the carrier gas at 100ml/min. The diffusion tube chosen for this calibration experiment had a precision bore tube section of length 2 cm and bore diameter 1 mm.