Calibration Calculation Steps and Method

The permeation tube emits bromoform at a known rate. This was determined from the shipping certificate and verified by repeated weighing of the permeation tube.

Permeation tube rate = **343 ng min^{-1}**

The flow rate of nitrogen through the permeation oven was maintained by a Porter valve attached to the regulator on the cylinder. This was verified by digital flow meter.

Permeation flow rate = **100 ml min^{-1}**

The concentration of bromoform is determined by the division of tube rate by flow rate.

Concentration in the flow is 343 ng min^{-1} / 100 ml min^{-1} = **3.43 ng ml^{-1}**

The permeation flow was passed through a fixed sampling loop before being flushed to a halocarbon trap. The amount of bromoform on introduced onto the adsorbent trap could be varied (in multiples of 1x, 2x 3x etc.) by adding repeated loops flushed to the trap.

The amount of bromoform in each loop was calculated:

Loop volume = **100 μl** = **0.1 ml**

Mass of bromoform in the loop is the concentration of flow multiplied by the loop volume

Mass of bromoform: 3.43 ng ml^{-1} * 0.1 ml = **0.343 ng**

Number of moles of bromoform in 1 loop was calculated as the mass of bromoform divided by the Molar mass (**252.73 g mol^{-1}**). The mass of bromoform on the loop was first divided by 1 x 10^9 to convert ng to g.

Number of moles: (0.343 ng / 1 x 10^9) / 252.73 g mol^{-1} = **1.36 x 10^{-12} mol**

The number of molecules of bromoform in 1 loop was calculated by multiplying the number of moles by Avogadro's Constant (6.023 x 10^{23}).

Number of molecules = 1.36 x 10^{-12} mol * 6.023 x 10^{23} **= 8.17 x 10^{11} molecules**

The total number of molecules in an air sample is calculated from the air number density for air (**2.5 x 10^{25} molecules m^{-3}**) and the sample volume (**1.5 l**). The air number density is divided by 1000 to convert m^3 to litres. This is then multiplied by the sample volume

Total number of molecules: (2.5 x 10^{25} molecules m^{-3} / 1000) * 1.5 l = **3.76 x 10^{22} molecules**

The mixing ratio of bromoform equivalent to a single loop is therefore:

$(8.17 \times 10^{11}$ molecules / 3.76×10^{22} molecules$) * 1 \times 10^{12} =$ **21.76 ppt**

Two and three loop injections are, of course, 2 or 3 times this amount.

Regression analysis of the relationship between mixing ratio and peak area yields a calibration equation for the conversion of measured peak areas to mixing ratios

Regression equation: peak area = 237.03*Mixing ratio – 196.86

Therefore, the measured bromoform mixing ratio is given by:

Measured mixing ratio = (peak area + 196.86) / 237.03