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GRAVIMETRIC CALIBRATION OF STANDARD GASES

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ABSTRACT

Permeation rates of specific gases (e.g. SO_2, NO_2) in the range of 10^{-9} g min^{-1} were directly measured using a high performance microbalance. The gases were trapped in small permeation tubes with total weights of about 2.5 g. By controlling the microbalance's temperature the measurements were done at set temperatures between 25°C and 60°C to obtain a reference graph (permeation rate vs. temperature) for each gas. The microbalance was connected to a metered flow of a clean-air device. With adjustable flow rates up to 50 l min^{-1} the permeating gas could be diluted down to volume mixing ratios in the 10^{-9} and even the 10^{-12} range.

INTRODUCTION

For the measurement of gaseous pollutants which typically occur in the atmosphere at levels of 10^{-6} to 10^{-12} volume mixing ratio, the calibration of the detection systems reveals a fundamental problem. Gaseous mixtures of precisely known concentrations can be obtained either from static mixtures in gas cylinders or from dynamic gas dilution systems (ref.3). In each case a source of a standard gas is necessary. So-called permeation tubes are commonly used as such gas sources.

The permeation tube used in this study consists of a gas tight stainless-steel cylinder containing the gas under investigation in its purest form. The cylinder is capped with a PTFE plug through which minute amounts of gas are escaping. The permeation rate of such tubes can best be determined gravimetrically as the mass loss per unit time (in our case: 10-1000 ng min^{-1}). The use of a conventional analytical balance would result in long weighing periods of several days or even weeks. Under these circumstances uncontrolled deviations in the permeation rate may occur and the required precision is not guaranteed. However using a thermostated microbalance the measurements can be performed precisely within a couple of hours due to its high load to precision ratio (LPR) (ref.1, ref.8).

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THE MICRO WEIGHING SYSTEM

For our investigations a Sartorius microbalance model 4102 was used. Because this balance can be loaded with a total mass of only up to 2.5 g on each side, conventional permeation tubes cannot be weighed. Only by the design of a miniature tube with a total mass of less than 2.5 g it has been possible to carry out the weighings in the nanogram region. (See Fig 1). The offered LPR of the Sartorius microbalance is 10^{-7}. This would in principle be sufficient to evaluate permeation rates of 10-1000 ng min^{-1} within a few hours. However, running a micro weighing system usually generates some disturbances which can seriously affect the sensitivity of microbalance readings. The following effects must be eliminated in order to maintain a sensitivity of ± 100 ng.

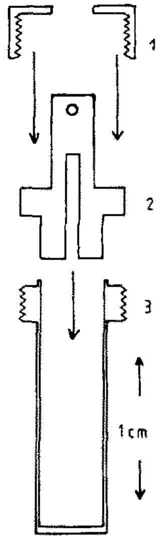

Fig. 1. Scheme of the permeation tube: 1 = steel nut, 2 = PTFE cap, 3 = steel cylinder.

Vibrational effects

To avoid building vibrations the microbalance base is erected in the basement of the institute's building. According to the "heavy table - weak spring" method (ref.4) a spring supported table was constructed in the basement which always remains in the state of stable equilibrium (ref.6). This construction has a low pass filter characteristic and a natural frequency of 4.4 Hz, while the microbalance has a natural frequency of 1 Hz and a high pass filter characteristic. Only in a small frequency band (0.7-7 Hz) vibrational disturbances can be transmitted and affect the readings. Zero readings of the microbalance show constancy within ± 100 ng over a period of several hours.

Temperature fluctuations

Microbalances usually undergo severe drift problems due to temperature fluctuations. Therefore the whole micro weighing system is established in a thermostated enclosure (see Fig. 4). Temperature inside the enclosure is thermostated to ± 0.3 K.

For the purpose of gravimetric calibration of standard gases thermostatic operation of the balance in the mentioned enclosure is not sufficient, since the permeation rates reveal a very strong temperature dependence (7-80 ng min^{-1} K^{-1}, see Fig. 3). Therefore a pair of identical furnaces encloses both hangdown tubes. A transistorized temperature control circuit was developed (ref.6) to supply continuous dc power to the oven windings. Accuracy of the temperature control was better than ± 0.05 K.

PRINCIPLE OF PERMEATION

Polymer plastics are permeable to some gases. The temperature dependent permeation mechanism is initiated by the difference in partial pressure of the gas inside and outside of the permeation tube. Brubaker et al. (ref.3) describe the mechanism as three subsequent steps: solution of the gas in the membrane material at the high pressure side, diffusion through the plastic membrane and re-evaporation at the low pressure side.

The pure gas is cryogenically trapped in the tube. After capping the tube with a

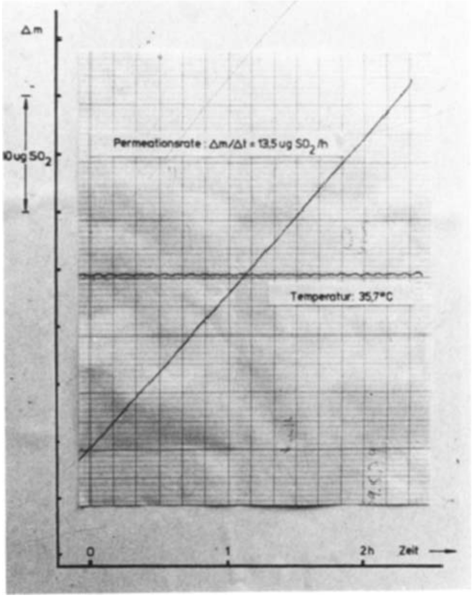

Fig. 2. Recording of a permeation tube's mass loss.

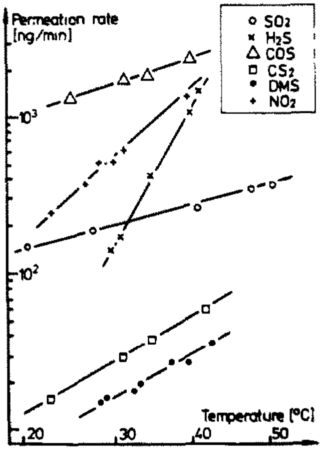

Fig. 3. Reference graphs of gases which have been investigated.

PTFE membrane it is warmed-up again and the gas inside the tube gets under high pressure. An equilibrium between gas and liquid phase in the tube is established and the membrane will be saturated with the gas. Each change in temperature will shift this equilibrium. Thus at a constant temperature the gas output is constant and its quantity depends only on the geometry of the membrane. The following equation (ref.1) gives the permeation rate under steady-state conditions:

$$Q = K\ P\ p\ \exp[-(E + H)/RT] \qquad (1)$$

where Q is the permeation rate (ng min^{-1}), K is a geometric constant (cm), P the permeability coefficient (ng min^{-1} cm^{-1} Pa^{-1}), p the partial pressure (Pa), E the activation energy (J mol^{-1}), H the heat of solution (J mol^{-1}), R the universal gas constant (J K^{-1} mol^{-1}), and T the temperature (K).

RESULTS

In order to avoid buoyancy effects, the weighings are carried out in a differential mode. The beam of the balance is loaded with a filled permeation tube (gas filling 200-300 mg) and an empty duplicate as counterweight. Thus, only the mass loss of the filled tube is recorded per unit of time. A typical record is shown in Fig. 2. For the standard gases SO_2, H_2S, COS, CS_2, $(CH_3)_2S$ (=DMS), NO_2, used in our research programs, the weighings were performed at set temperatures between 25°C and 60°C.

The results are usually plotted in a so-called reference graph. Fig. 3 shows such graphs for the different gases. It demonstrates fairly well the proposed exponential

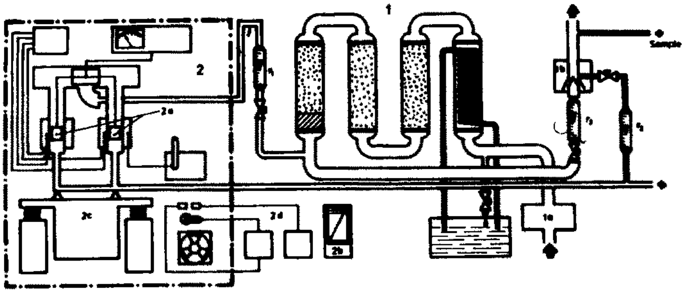

Fig. 4. Dynamic gas dilution system: 1 = Filter columns; 1a = Pump; 1b = Mixing device; 2 = Thermostated microbalance; 2a = Permeation tube and counter weight; 2b = Recorder; 2c = Spring supported weighing table; 2d = Temperature control.

relationship between permeation rate and temperature as given by equation (1). The different slopes of the curves are caused by different gas-specific permeability constants and thermodynamic properties.

Applications

In order to get standard gas mixtures the minute amounts of gas are diluted by a clean air stream. For that purpose the microbalance is connected with a clean air stream (see Fig. 4). By the aid of a pump outside air is pressed through several filter columns resulting in a dry air flow free of trace gases and particles. Then the air stream is split. A larger part enters the mixing device directly, while a smaller one flows through the microbalance. From the output line of the microbalance an aliquot is mixed into the main gas stream by the aid of a venturi jet. The volume mixing ratio is determined by the permeation rate of the tube and the flow rates of the gas streams. It can be calculated by the following equation:

$$m = \rho (M_a/M_g)\ r_2\ (Q/r_1)/(r_3 + r_2) \qquad (2)$$

where ρ is the density of air (ng l^{-1}), M_a/M_g the ratio of the molecular weights of air and the gas, and $r_{1...3}$ are the flow rates as indicated in Fig. 4 (l min^{-1}).

With the described ensemble of the permeation tube, the microbalance and the dilution system standard gas mixtures down to levels of 10^{-9} (ppb) and 10^{-12} (ppt) volume mixing ratio can be produced.

The accuracy of the standard gases is determined by the precision of the permeation and flow rate measurements. It typically equals ± 5%.

Our technique to prepare standard trace gases was compared with a static device of the Federal Environmental Agency of Germany which itself is assured by an international intercomparison test (ref.9). The results showed a good agreement (max. deviation 7%) (ref.1).

The presented system is applicable for all purposes where highly diluted standard gases are necessary, especially for calibration purposes of instruments which continuously monitor mixing ratios of gaseous atmospheric trace constituents even under background conditions. Furthermore, the sampling efficiency of so-called enrichment techniques can be tested under fairly realistic conditions (ref.7). Finally, the method can be used for laboratory investigations of chemical reactions of atmospheric trace gases where large amounts of gaseous reactants at very low mixing ratios are required (ref.2).

In summary, the application of a microbalance results in the very direct calibration of permeation tubes. The chosen experimental set-up provides a much more accurate, easier accessible and less time consuming technique for the preparation of trace gas standards than other conventional (volumetric and barometric) methods.

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