

Using Thermogravimetry for Weight Loss Monitoring of Permeation Tubes Used for Generation of Trace Concentration Gas Standards

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Permeation tubes are convenient analyte sources for generating standard gas mixtures (containing, in particular, volatile organic compounds) used in the calibration of analytical instruments. For small permeation rates, corresponding to trace levels of analytes, the calibration of permeation tubes is time-consuming. The use of thermogravimetry as a means to measure rapidly the weight loss at constant temperature was investigated. An attempt to apply this technique to calibrating a permeation tube filled with benzene is described. In the 20 ng/min range of permeation rate, day-to-day variations of <5% were observed. The continuous weight loss monitoring of permeation tubes by thermogravimetry allows their rapid characterization.

Analysis of volatile organic compounds (VOC) at trace concentrations, for example in the monitoring of outdoor and indoor air quality, poses calibration problems. The preparation of trace concentration gas standards can be carried out using static or dynamic methods, the latter including the use of permeation tubes.¹ The key advantage of permeation tubes is the range of compounds for which the method can be used.^{2–8} Permeation tubes may be purchased from manufacturers or made and calibrated by the final users. Recent papers mention permeation tubes as a convenient calibration means for solid-phase microextraction analysis of VOC in air.^{5–8} The traceability of the emission rate of the analyte is linked to mass, time, and temperature standards through weight loss measurements, elapsed time, and

operating temperature, respectively. A wide range of permeation rates can be achieved by varying the type of permeation tube material as well as the length and thickness of the tubes, with typical rates ranging from 5 to 50 000 ng/min. For low-rate permeation tubes, a long time interval between weighings is required to reach a reasonable precision using a bench microbalance. For example, using a microbalance of 1 µg resolution, at least one week is needed to obtain a reading error of 1% for a tube with a permeation rate of 20 ng/min. Under these conditions, a weight loss repeatability test, taking into account all sources of variance, may necessitate at least one month.

Permeation is a temperature-sensitive process. The permeation rate changes by about 1% for 0.1 °C temperature variation. Permeation tubes are used in constant temperature chambers regulated to ±0.1 °C maintained typically at 30–50 °C under constant gas flow. Therefore, discontinuous weighing at the microgram level at ambient temperature requires a stabilization period, which introduces additional errors.

Continuous high-precision monitoring of weight loss under controlled temperature and gas flow can be in principle achieved using thermogravimetry (TG). An attempt to use such a technique for calibrating a permeation tube filled with benzene is described here.

EXPERIMENTAL SECTION

Permeation Tube. It was made from a piece of Teflon tubing (3.2-mm o.d., 1.5-mm i.d., 20-mm length) stoppered by two brass plugs. After setting the plugs, the remaining volume length was 11 mm. One plug was machined using a small drilled extension to allow the suspension of the permeation tube during measurements. Before sealing, the tube was partially filled with analytical-grade benzene. The initial weight of the permeation tube after filling with benzene was ~0.6 g.

Safety Note. Precaution during handling of benzene is necessary, because this substance is classified as a carcinogen.

Weight Loss Monitoring. For discontinuous weighting, an analytical microbalance (Mettler, M3) of 1-µg readability and a capacity of 3050 mg was used. Before weighting, the microbalance was allowed to stabilize for 1 h. The permeation tube was then

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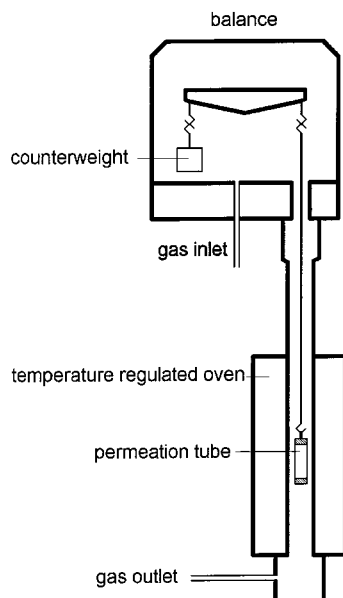


Figure 1. Scheme of the thermobalance used for the weight loss monitoring of permeation tubes.

suspended in the oven of the microbalance, and readings for temperature equilibration were taken after about one-half hour. Under these conditions, repeatability was about $\pm 2 \mu\text{g}$.

Continuous weight loss was monitored using a thermobalance (Setaram, TG 92–12). This apparatus has a digital resolution of $0.2 \mu\text{g}$, a $1\text{-}\mu\text{g}$ detection limit, and a maximum load of 20 g. The chamber housing the balance and the connected oven constitute a gastight system, allowing weight loss monitoring under vacuum or under a controlled circulating atmosphere (Figure 1). The oven temperature was regulated to $\pm 0.2^\circ\text{C}$. The permeation tube was suspended from the beam using a platinum wire in such a way as to position the tube in the temperature-regulated part of the oven. Measurements were carried out in isothermal conditions at 31.0°C under a nitrogen flow of $\sim 0.5 \text{ L/h}$. Calibration of the gas flow was not necessary, because knowledge of the exact composition of the evolved gas was not the concern of this exploratory study. The nitrogen gas exhausting from the oven and containing traces of benzene was sent to a vented hood. After preliminary trials, not reported here, two series of experiments were performed during two consecutive weeks. For each series of experiments, the permeation tube was left in position under the constant conditions given above. As a result of software limitation, data acquisition was restarted manually every 24 h. For each acquisition, 50 points were sampled. The permeation tube was weighted using the bench microbalance before and after each series of TG weight loss monitoring.

RESULTS

The weight loss rates, expressed in nanograms per minute, as is common practice for permeation tubes, are reported in Table 1. The nine 24-h TG experiments, grouped in two series, A and B, were first examined separately (A1–A5 and B1–B4). Data for experiment A1 were lost because of a power failure. For each remaining experiment, the slope of the least-squares regression line, weight loss vs elapsed time, is given in column 2 along with its standard deviation. Elapsed time is given by the internal clock

Table 1. Weight Loss Rate of a Benzene-Filled Permeation Tube

series	weight loss rate (ng/min)	
	thermobalance	microbalance ^a
	mean squares ^b	range ^c
A1 ^d		
A2	22.40 ± 0.15	23.0
A3	21.92 ± 0.18	21.6
A4	21.58 ± 0.15	20.9
A5	26.40 ± 0.30	26.7
A1–5		22.6 ± 0.6
A2–5	22.44 ± 0.07	23.0
A2–4 ^e	21.69 ± 0.06	22.0
B1 ^f	17.76 ± 0.20	17.6
B2	21.51 ± 0.17	22.3
B3	20.07 ± 0.23	19.4
B4	20.28 ± 0.21	21.6
B1–4 ^f	20.88 ± 0.04	20.5
B2–4	20.93 ± 0.06	21.3
		22.7 ± 0.8

^a The indicated uncertainty is based on a repeatability of $\pm 2 \mu\text{g}$ on initial and final weights. ^b Slope of the least-squares regression line; indicated uncertainty corresponds to the standard deviation on the slope. ^c Slope calculated from the two extreme points of each series taking into account only the error arising from the limit of detection; the uncertainty is estimated to be in the range of 1–1.5 ng/min. ^d Not recorded because of a power failure. ^e A5 excluded because of a slope change of unknown origin. ^f Stabilization period excluded.

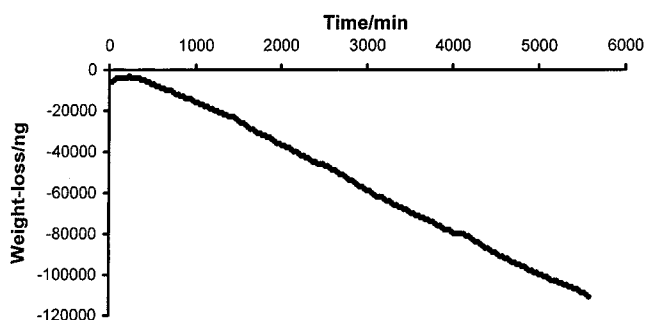


Figure 2. Thermogravimetric monitoring of a benzene permeation tube: Weight loss vs time plot for series B (see Table 1), corresponding to four consecutive 24-h acquisitions. The initial curvature is due to the slow stabilization of the permeation rate.

of the instrument computer. Therefore, uncertainties on time measurements are considered as negligible. Data for consecutive 24-h experiments were grouped within each series (A2–5, A2–4 and B1–4, B2–B4) and treated in the same way. The weight loss rates calculated taking into account only the first and last points in each data set are given in column 3. This is similar to a discontinuous weighing, but without the drawbacks linked to temperature changes. Results from microbalance weighings are given in column 4. Given uncertainties take into account weighing errors only; the relative error on time is assumed negligible for a period of 4 to 5 days. Permeation tubes necessitate a period of stabilization after their fabrication and when operating conditions are modified.^{3,7} This is apparent at the beginning of the curve in Figure 1 and explains the reason for which the result for B1 is significantly different from B2–B4, even when the initial part of the curve is deleted. After the stabilization period, a rather constant weight loss rate is observed in Figure 2, with small daily variations. Other experiments, except A5 for which an abnormally high weight loss rate is observed, gave consistent results.

The weight loss rates based on least-squares treatment have relatively small standard deviations. Nevertheless, small day-to-day variations were observed. They were attributed to the influence of external conditions such as temperature, gas flow, or atmospheric pressure changes. Specifications of the TG instrument indicate a drift of 10^{-6} per °C. With a mass of the permeation tube of about 0.6 g, a drift of about 0.5–1 μg is expected from 1 day to another. Errors in the same range are expected for the other weight measurements and lead to uncertainties indicated in columns 3 and 4 of Table 1. It should be noted that the use of a permeation tube of small volume minimizes buoyancy changes induced by temperature or pressure drifts. Under the current experimental conditions, the range of permeation rates from TG measurements is obtained with a precision better than 5%. Therefore, the weight loss rates reported in Table 1 can be considered to be in good agreement.

From data available from permeation tubes manufacturers, it appears that a permeation rate of about 20 ng/min is already in the lower range practically achievable. A better precision may be expected for larger permeation rates.

CONCLUSION

The use of a continuous weight loss monitoring apparatus, such as a TG instrument, for permeation tube calibration offers a

number of advantages: (i) the stabilization period is easily visualized, (ii) the permeation rates are easily evaluated within relatively short measurement periods (this may help in rapid screening of the tubes' quality), (iii) temperature and gas flow may be modified with minimal perturbations of the measurements conditions, and (iv) the gas flowing out of the oven may be directly transferred into gas analysis systems for on-line calibration. Utilization of the evolved gas as a trace concentration standard would require a precise flow control of the carrier gas. A dedicated instrument with better oven temperature regulation may help to reduce the short- and long-term mass measurement noise.

Quantitative uses of TG hyphenated with other identification methods,⁹ such as mass spectrometry, Fourier transform infrared spectrometry, or gas chromatography involve delicate calibration steps.¹⁰ Utilization of permeation tubes may be a convenient in situ calibration method.

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