TDTS 2

Prediction of uptake rates for diffusive tubes

Introduction

Diffusive (passive) monitoring provides a cost-effective and 'wearer-friendly' approach to monitoring atmospheric concentrations of volatile organic air pollutants. The standard sorbent tube-type diffusive monitor, reported by Brown and co-workers in 1981[1], overcame the air-speed restrictions of early badge-type diffusive samples, and is now widely used for both workplace and ambient air measurements.

Diffusive monitoring can only be used for quantitative measurements, however, if an uptake rate constant (U) is known for the particular analyte-sorbent combination in use. Uptake rates have already been determined for many compounds on standard tubes[2] (see also Markes' Application Note TDTS 1), and international protocols[3–5] now also exist for validating new methods. However, the experimental procedures demanded by such official validation protocols can be time-consuming and expensive to carry out.

To overcome this limitation, several researchers have investigated techniques for accurately predicting uptake rates.

Prediction of uptake rates

The ideal uptake rate (U_{ideal}) of an analyte on a diffusive tube is independent of the sorbent and can be calculated using the appropriate diffusion coefficient. U_{ideal} may be used for quantitative measurements in some cases, particularly for strongly retained analytes. However, the actual or effective uptake rate (U_{eff}) that applies in practice will differ considerably from U_{ideal} for more volatile, less well-retained components. There is therefore a need for a simple method of calculating U_{eff}.

Coutant *et al.*[6] and Posner and Moore[7] proposed simple linear-isotherm models for thin-bed samplers, but for tube-type (thick-bed) diffusive samplers, this model cannot be applied.

Work carried out by van den Hoed *et al.*[8,9], on the application of Freundlich isotherms to the prediction of diffusive tube sampler behaviour, led to the development of a FORTRAN computer program for predicting U_{eff} from U_{ideal} using an iterative process. Further work by Kristensson and Nordstrand[10,11] facilitated translation of the original program into PC-compatible software and simplified several operational aspects. Using the PC program,[12] U_{ideal} is calculated and combined with isotherm data to derive U_{eff}. This work has advanced the cause of accurate prediction of U_{eff}, but the method still requires Freundlich isotherms to be determined for the sorbent–sorbate combination concerned. The determination of Freundlich isotherms requires the generation of standard atmospheres at a range of concentrations. These atmospheres are then sampled to determine the breakthrough volume at each concentration. This relatively complex procedure limits the usefulness of the approach.

Recent work sponsored by the European Commission Measurement and Testing Program (MPT, formerly known as BCR[13]), has shown that, under certain conditions, U_{eff} for the standard tube can be predicted to ±10% from the specific retention volume (V_g) alone. Broadly speaking, these conditions are:

- Total atmospheric concentration less than 10 ppm
- Exposure time between 2 and 8 hours
- When the specific retention volume (V_g) falls within the range 100–10,000 L/g.

The following empirical relationship between U_{eff} and V_g was derived from sampling intercomparisons with analytes of wide-ranging volatility and polarity on both Tenax™ and Chromosorb™ 106. It should be independent of sorbent type.

$$U_{eff} = (0.154 \log_{10} V_g + 0.4) U_{ideal} \qquad (1)$$

Determining V_g and U_{ideal}

The factors V_g and U_{ideal} must be obtained before Equation (1) can be used to calculate U_{eff}. The determination of V_g does require some limited experimental work, and the following stepwise procedure is recommended:

1. Inject 0.5 mg of analyte into a stoppered ~1 L glass flask fitted with a septum. Check that all the analyte has evaporated.
2. Buy or prepare a standard sample tube with the maximum 6 cm bed length of sorbent. Condition the tube carefully.
3. Connect the sample tube to the injection port of a GC. Use 530 mm, uncoated fused silica capillary tubing, or other appropriate narrow bore tubing, to connect the other end of the sample tube to a FID detector. Use ¼″ fittings with graphite ferrules to connect to the sample tube itself. [*N.B.* Metal ferrules damage the tube and result in leak test failures on UNITY™ and other thermal desorbers.]
4. Set a nitrogen carrier gas flow of 50 mL/min through the tube.

5. Inject a 0.1 mL sample of the vapour-phase standard onto the tube using a gas syringe. Adjust the GC oven temperature so that the analyte peak elutes on the FID between 1 and 20 min.
6. Repeat the experiment 4 or 5 times using different GC oven temperatures within a 30 or 40 °C range. The retention time of the peak will vary considerably with temperature. Try to ensure that at each of the GC temperatures selected, the peak elutes in the range 1–20 min. [Note: Use the time from injection to peak crest as the retention time. This may have to be measured manually, depending on the type of integrator available. Strictly speaking, the mass median or 'centre of gravity' of a peak is the more rigorous measure of retention time, but the difference can be usually ignored.]
7. Inject a sample of methane to measure the delay time of the system, and subtract this from the analyte retention times determined in step 6.
8. Use the flow of nitrogen carrier gas and corrected retention times to calculate the analyte retention volumes at different sorbent temperatures.
9. Plot a graph of $\log_{10}$ of the retention volume *vs.* the reciprocal of the temperature (in K). This should be a straight-line plot that can be readily extrapolated to ambient temperatures. Use this to obtain V_g.
10. Check your technique, if possible, with a compound that has a known literature value.

This procedure should take no longer than half a day per analyte.

The ideal uptake rate (U_{ideal}) is calculated using the PC program described above[12]. The program calculates U_{ideal} using a procedure related to atomic volumes[14]. The information required by the software includes the chemical formula of the analyte of interest and whether or not the substance is aromatic. Once these details have been entered U_{ideal} will be predicted.

Calculation of the effective uptake rate U_{eff}

Once V_g and U_{ideal} have been determined as described above, U_{eff} can be calculated using Equation (1). For example:

- A U_{ideal} of 2.6 ng/ppm/min and a V_g of 1000 L/g would give a U_{eff} of 2.24
- A U_{ideal} of 3.3 ng/ppm/min and a V_g of 250 L/g would give a U_{eff} of 2.54.

Summary

Provided a relatively strong sorbent–sorbate combination is selected with V_g >100 L/g, this method applies to all routine industrial hygiene and ambient air monitoring applications, *i.e.* to all atmospheres with analyte concentrations below ~10 ppm.

The U_{eff} values predicted using Equation (1) are reported[12] to be accurate within 10%. This is well within international standards for method performance criteria[15]. A simple, parallel-pumped and diffusive monitoring exercise may be used to confirm U_{eff} if required.

By facilitating accurate prediction of U_{eff} for tube-type diffusive samplers in almost every practical monitoring situation, this procedure allows the cost and labour-saving benefits of diffusive monitoring to be realised for an even wider range of air pollution applications.

Trademarks

UNITY™ is a trademark of Markes International Ltd, UK.

Tenax® is a registered trademark of Buchem B.V., The Netherlands.

Chromosorb® is a registered trademark of Manville Corporation, USA.

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