



MDHS 27

Methods for the
Determination of
Hazardous Substances

February 1994, revised

Protocol for assessing the performance of a diffusive sampler

INTRODUCTION

1 It is important to know the reliability and accuracy of the methods which are used to measure the concentration levels of airborne pollutant vapours to which people may be exposed in the course of their work. To this end, it is necessary to ensure that the measuring techniques available are carefully validated. Protocols exist for the validation of techniques based on analysing samples taken by means of an air pump and sorbent trap, for example NIOSH,¹ Chapman et al,² and HSE.³

2 More recently, general recommendations on method evaluation, including diffusive sampling methods, have been published by NIOSH.⁴ With pumped methods, the accuracy of the pump can be treated separately, while with diffusive methods there is no pump and the uptake rate (equivalent to a pump flow rate) can be a function of adsorbent capacity, ambient air velocity, and other factors. Moreover, since diffusive sampling techniques are relatively new, it is considered expedient (as in Refs 4 and 5) to place emphasis on field trials as well as laboratory trials. In field trials, the diffusive sampler is exposed in parallel with an established sampling technique in the practical situation.

3 This protocol makes some recommendations about the number of samples, exposure times and exposure concentrations that should be used, for example replicates of six in paragraph 12 and 20 paired comparisons in paragraph 28. These numbers take into account the workload involved and the statistical value of the sample size and seem reasonable on the basis of preliminary test experience. Other numbers may be more appropriate in individual circumstances.

4 Unlike previous protocols, we have not attempted to define acceptance criteria. We have sought only to define the experiments that might be done and the results that should be quoted. The acceptability of a method is dependent not only on its accuracy, but on convenience, immediacy of result, its range of applicability, the availability of alternative procedures and the particular occupational hygiene circumstances. However, the hygienist must have basic information on the accuracy and reliability of a sampling device in order to make a proper judgement about its application: the tests recommended here are intended to provide such information.

PRINCIPLES

Definition

5 A diffusive sampler is a device which is capable of taking samples of gas or vapour pollutants from the atmosphere at a rate controlled by a physical process such as diffusion through a static air layer or permeation through a membrane, but which does not involve the active movement of the air through the sampler.

Uptake rate units

6 A mass uptake rate for a diffusive sampler may be defined as:

$$\text{uptake rate} = \frac{\text{mass uptake}}{\text{pollutant concentration} \times \text{exposure time}} \quad (1)$$

When a sample is analysed, the quantity determined is usually in mass units, for example ng. Pollutant concentration is measured conveniently in ppm (v/v) and exposure time in minutes. Thus convenient units are ng (ppm)⁻¹ (min)⁻¹. These units are roughly equivalent dimensionally to ml (min)⁻¹, where the volume term refers to the volume of air from which the mass of pollutant has been extracted by the sampler. These latter units are useful for making comparisons with the sampling rate of pumped devices, but should not be taken to imply that there is any net movement of air during diffusive sampling.

Factors affecting uptake rate

7 Ideally the uptake rate of a diffusive sampler is a constant, since it should depend only on the geometry of the sampler and the individual pollutant vapour, which has a particular diffusion coefficient in air. In practice, the uptake rate may vary slightly with changes in pollutant concentration, exposure time, atmospheric temperature, pressure, humidity, turbulence, etc. Thus, in this protocol, the uptake rate is determined under a variety of conditions, both in laboratory and field trials, and any changes in the rate resulting from changed conditions noted.

LABORATORY EXPERIMENTS

Test apparatus

8 The apparatus used for laboratory validation of diffusive samplers should consist of:

- (a) an exposure chamber of sufficient capacity to accommodate simultaneously at least six diffusive samplers and six independent method samplers (paragraph 10);
- (b) a system for generating and delivering a known concentration of a test vapour-in-air to the exposure chamber;
- (c) provisions for measuring, controlling and varying, systematically, the rate of air flow through the chamber and the concentration, temperature and humidity of the test atmosphere (it is not normally necessary to vary air pressure).

9 The system for generating and delivering the test atmosphere should be based on the use of either the syringe injection,⁶ the permeation tube,⁷ or equivalent technique. The 'true' concentration of the pollutant vapour in the test atmosphere should be calculated from the syringe injection rate or the rate of loss of vapour from the permeation tube (whichever is used) and the volumetric flow of diluent air. This flow should be determined with an appropriate calibrated test meter. The atmosphere should be at typical and known temperature, pressure and relative humidity, and the air flow rate should be above the minimum required by the geometry of the diffusive samplers, except in experiments where these parameters are varied.

Independent sampling method

10 An independent method should be used to verify the concentration of the generated standard atmosphere in the exposure chamber. This method will often be a pumped adsorbent tube or pumped absorbent bubbler method. This method should have been validated over ranges of pollutant concentration, sampling time, etc similar to those described in this protocol for diffusive samplers. The 'true' concentration can be considered as verified if the mean concentration indicated by the independent method (corrected for any known bias) is within ±10% of the calculated value. This check is done in each investigation described in paragraph 12.

11 If the criterion for checking the standard atmosphere is not met, a fresh standard atmosphere should be set up or the independent method changed. Note that the criterion is intended only for checking the standard atmosphere and should not be taken to imply any overall performance criteria for diffusive samplers.

12 The investigation of the effects of exposure variables on sampler performance should consist of sets of experiments, in each of which six diffusive samplers and six samplers using the independent method are exposed within the exposure chamber or are allowed to withdraw vapour from the exposure chamber each for a

known period and at a known concentration. The uptake rate, U, is then given by:

$$U = \frac{\text{observed mass uptake of diffusive sampler (ng)}}{\text{'true' concentration (ppm) x exposure time (min)}} \quad (2)$$

Determination of the effect of external air movement on sampler performance

13 A set of experiments is conducted as described in paragraph 12 with different velocities of airflow through the exposure chamber, covering the range of velocities likely to be encountered in the practical use of the diffusive sampler. The mean uptake rate of the diffusive samplers is calculated for each experiment and is plotted against a suitable function of air movement. From experience, a suitable function is the linear air velocity past the face of the samplers calculated as if laminar flow were maintained. For most diffusive sampler geometries, the orientation of the samplers with respect to the direction of air flow is not likely to be critical, and the relationship between air velocity and uptake rate is likely to be of the form shown in Figure 1. The air velocity equivalent to an uptake rate of 95% of the standard uptake rate should be calculated. This velocity is the minimum referred to in paragraph 9.

14 It is necessary to determine this minimum velocity for one pollutant only for a given diffusive sampler. Alternatively, manufacturer's data may be used.

Determination of the effect of exposure concentration and time on sampler performance

15 The uptake rate of the diffusive samplers may be a constant for any combination of exposure time and concentration (within certain limits) or it may be a quantity which varies as a function of concentration and time, as illustrated in Figures A2 and A3. The recommended procedure for determining the uptake rate, U, and its relationship with exposure time and concentration is to conduct a series of experiments in the exposure chamber according to the 2-factor design shown in Table 1.

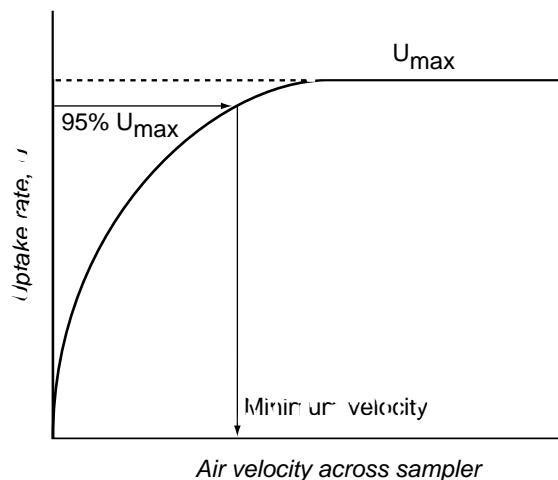


Figure 1 Typical relationship between air velocity and uptake rate for diffusive samplers

16 The full design shown in Table 1 entails nine separate experiments, each as described in paragraph 12, and will permit a statistical analysis of the results to determine whether there are any differences among the mean uptake rates for the different combinations of conditions, and hence will permit the determination of U and its standard error (see paragraph 25).

17 A stepwise experimental approach may be used in the determination of U. This would entail conducting a smaller number of experiments, indicated by the four exposure combinations marked with an asterisk in Table 1. If the statistical analysis of the uptake rate data from this abbreviated experiment showed that there were no significant differences among the mean values for each of the four combinations of conditions, then U could be taken to be constant and there would be no need to continue with the full design. Examples of the use of the abbreviated and full analyses are given in Appendix 1.

Exposures to zero concentration

18 It is recommended that the effects of a period of at least four hours' exposure to clean air following a period of exposure to a given pollutant should be examined. If the factorial design above were used, it would be possible to use, say, two extra samplers in each of the three cells representing 30 minutes' exposure to the test atmosphere (two cells in the abbreviated form) and to leave these extra samplers exposed to clean air for a further four hours, by removing the pollutant source but leaving the environmental conditions in the exposure chamber otherwise unchanged.

Effect of storage

19 It is recommended that the effects of a period of storage after exposure to a pollutant vapour should be investigated. If the factorial design described above is used, it would be possible to use two extra samplers in each of the three (or two) cells representing 480 minutes' exposure and to store these extra samplers at normal laboratory temperature for up to two weeks, the remaining samples being analysed immediately. Any difference between stored and unstored sampler results should be noted. If stored sampler results fall rapidly in comparison with results from unstored samplers, it may be more convenient to quote the time at which stored samplers give results which are within a certain percentage, say 20%, of unstored sampler results.

20 Storage over extended periods may not be relevant for certain types of read-out devices. However, it may be relevant to test pre-exposure stability for devices utilising chemical reagents.

Determination of the effects of temperature, pressure and humidity on sampler performance

21 A further set of experiments should be conducted as described in paragraph 12 in which atmospheric temperature and humidity (and pressure, if desired) are varied, one at a time, to include conditions likely to be encountered in the practical use of the diffusive sampler.

The preferred approach, especially if it were believed that there might be interaction effects between these variables, would be to start by conducting a 2³ factorial experiment in which three factors - humidity, temperature and pollutant loading - each at two levels, were combined as shown in Table 2. This design would require eight experiments, each as described in paragraph 12, and would enable a statistical analysis of the variances and of the differences (if any) between the mean uptake rates for the different combinations of conditions. A modification of this design involving fewer tests would be used, of course, if one of the variables were known to have no effect on the uptake rate of a particular pollutant by a particular type of diffusive sampler.

22 The concentration of atmospheric pollutant, if expressed as mg m⁻³, changes with temperature and pressure. Thus, if a conventional pumped sample is taken, for which the measured parameters are weight of pollutant recovered and air sample volume, the ambient temperature and pressure will also have to be known if a conversion to ppm (v/v) is required. Conversely, if a diffusive sampler is calibrated in uptake rate units of ng ppm⁻¹ min⁻¹, the pollutant concentration is given directly in ppm and ambient temperature and pressure will need to be known only if it is desired to convert to mg m⁻³.

23 There may be some effect of temperature and humidity on the capacity of the adsorbent used and consequently on the sampling rate of a diffusive sampler (or the breakthrough volume of a pumped sampler).

Determination of the effect of potential interferents on sampler performance

24 A further set of experiments should be conducted as described in paragraph 12, except that the samplers are exposed simultaneously to the pollutant of interest and any co-pollutants that are likely to be encountered in the practical use of the diffusive samplers and are likely to be interferents. In the case of diffusive samplers using non-specific adsorbents, interferents are likely to be of consequence only if present in much higher concentrations than the analyte of interest.

Determination of standard uptake rate

25 The standard uptake rate is defined here as a quantity which is determined under standard conditions and is used to convert the results of mass uptake obtained during subsequent practical use of the sampler into concentrations by the use of:

$$\frac{\text{concentration (ppm)} = \text{observed mass uptake of diffusive samplers (ng)}}{\text{standard uptake rate} \times \text{exposure time (min)}} \quad (3)$$

The standard uptake rate has units of ng ppm⁻¹ min⁻¹ and may apply over a range of environmental conditions, as indicated by the experiments outlined above. Standard conditions will normally be conditions typical of the workplace environment, ie 20°C, 101 kPa and 50% relative humidity.

26 The random error in the uptake rate should be expressed either as a coefficient of variation or as a repeatability (for the latter, see the ISO recommendations, Ref 8). Examples of suitable statistical analyses are given in Appendix 1.

FIELD EXPERIMENTS

27 In the practical situations in which air sampling devices have to be used, there can be considerable random and systematic variability of the concentrations of airborne pollutants during sampling periods. Under such conditions, the performance (eg accuracy) of both diffusive and pumped sampling methods might differ from those determined in laboratory experiments under controlled conditions. It is thus essential to include field comparisons of the diffusive sampling method with the independent method as part of the test programme.

Paired comparisons - personal sampling

28 For a given airborne pollutant, a minimum of 20 personal comparative time-averaged concentration measurements should be made using in each case a diffusive sampler and an independent sampler worn simultaneously, as close together as possible, on one lapel of a person at work. These measurements should be made to cover as wide a range of field conditions as possible and should be made for an exposure (averaging) time of 8 hours or a full working shift, whichever is the lesser.

29 The results of the paired measurements can be examined in two ways. The first approach is to apply a statistical test to the set of differences between results for the n≥20 pairs, to decide whether the two sampling methods differ significantly overall. The test applied may be either the paired t-test, which assumes that the underlying distribution of the population of differences is normal, or a non-parametric test such as the Wilcoxon matched-pairs signed-ranks test, which makes no assumption about the form of the underlying population distribution. Use of the latter would be preferred where there was clear evidence of a non-normal distribution or where there was any doubt as to the form of the distribution.

30 The other approach which may supplement the first by giving a little more information, is to examine the relationship between the two sampling methods by a linear regression analysis of the results.^{9,10} Such an analysis would provide a measure of the degree of association between the two methods (ie the correlation coefficient) on the assumption that a linear relationship exists between them, over the range of conditions covered by the field tests. It would also provide estimates of the confidence intervals for the constant terms and the regression coefficient in that analysis which would serve to indicate whether or not the two methods differed significantly.

31 The linear relation determined by the regression analysis might take the form

$$y = a + bx \quad (4)$$

or
$$\log y = a + b \cdot \log x \quad (4a)$$

where y and x are the pollutant concentrations measured by the test and independent methods respectively.

Note: A logarithmic (as in Equation 4a) or other transform may be necessary, to stabilise any concentration dependence of the method variances.

32 A worked example showing the analysis of the results of a field experiment by the foregoing methods is given in Appendix 2. The statistics which should be given in any report of an assessment of this kind are listed in that example. The test method is considered acceptable if the estimated line of best fit is not significantly different from y = x (or its transform), ie if the 95% confidence limits* in a and b embrace, respectively, 0 and 1.

33 An important problem in assessing the field performance of one method of pollutant-in-air sampling against another is that both methods are certain to be subject to random measuring error. Thus both x and y in Equation 4 or 4a are really measured with error, while the use of simple regression analysis assumes that one parameter, x, is measured without error. The analysis therefore gives only a crude approximation to the true functional relationship between the two methods.

34 A more complex statistical analysis may be used (Ref 9), which assumes that both variables, x and y, are measured with error. For this analysis it is necessary to know the ratio of the error variances of the two methods. Estimates of this ratio may be obtained from the laboratory experiments (paragraphs 13 and 25) or from the field comparison (paragraph 40).

35 Alternatively, an approximate estimate of the linear functional relationship may be obtained, by the method of Bartlett.¹¹ This method assumes that the paired data may be divided into three non-overlapping groups in at least one (x or y) direction. The linear regression line is then drawn through the overall mean of the results (x,y) and has a slope defined by the means of the upper and lower groups, ie:

$$b = (y_3 - y_1)/(x_3 - x_1)$$

For poorly correlated data, the Bartlett method tends to underestimate the true slope.

36 In some cases, the measurement errors, referred to in paragraph 33, may be so large as to obscure the true functional relationship between the two sampling methods, unless further data are collected and more refined statistical analysis techniques are used. Some additional techniques are described in Refs 13 and 14.

* For the calculation of 95% confidence limits, see Ref 9.

Table 1 Experimental data: observed values of uptake rate, U

Concentration	Exposure time		
	30 min	120 min	480 min
0.1 EL	data* (six values)	data (six values)	data* (six values)
1.0 EL	data (six values)	data (six values)	data (six values)
2.0 EL	data* (six values)	data (six values)	data* (six values)

Notes: EL = Exposure limit for pollutant

* = Abbreviated experiment; see paragraph 17

Table 2 2³ factorial design for the study of the effect of environmental factors on U

Concentration	Air temperature			
	5°C		30°C	
	Relative Humidity		Relative Humidity	
	20%	90%	20%	90%
0.5 EL	data	data	data	data
2.0 EL	data	data	data	data

Notes: EL = Exposure limit for pollutant

data = six values

Multiple comparisons - static sampling

37 It is considered necessary to include personal sampling comparisons in the field experiments, to be sure of covering all of the environmental variables (eg conditions due to the wearer's movements) which might affect the performance of the sampling device. However, these comparisons suffer from a lack of control of variables which could make it difficult in some cases to detect differences between sampling methods and to define the relationship between them.

38 Somewhat better control of variables such as the nominal concentration level of the pollutant being assessed, the range of levels covered and the number of measurements made at each level, can be achieved by undertaking a series of static, multiple sampling tests at different sampling locations. In addition, this series of tests enables a more precise estimate to be made of the sampling variation of each (test and independent) sampling method separately under field conditions.

39 The protocol is thus to set up, at each of at least three separate locations selected to cover as wide a range of pollutant levels as possible, an array of at least six diffusive and six independent samplers. The actual number of samplers is the same at each location. In each case, the distance between the samplers in the array is as small as possible. The exposure or averaging time for all samplers in each test array should be 8 hours or a full shift, if less.

40 The mean, standard deviation and coefficient of variation can be determined for each sampling method at each test location and the differences between the sampler results, if any, can be determined by the statistical techniques already described.

41 A worked example for multiple comparison sampling is given in Appendix 2.

NOTE

This protocol has been prepared by an editorial task force (part of HSE's Committee of Analytical Requirements, Working Group 5) consisting of Dr R H Brown (chairman), Mr J Charlton, Mr R P Harvey, Mr A L Jones, Dr C J Purnell and Dr K J Saunders.

A European Standard, which is partly based on this MDHS, is under preparation. For further information, see the draft prEN 838 entitled *Workplace atmospheres - requirements and test methods for diffusive samplers for the determination of gases and vapours*. This draft is obtainable from Sales Administration (drafts), BSI, Linford Wood, Milton Keynes MK14 6LE, Fax 0809 320856, as BSI document 92/56577.

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APPENDIX 1: ANALYSIS OF EXPERIMENTAL DATA TO DETERMINE CALIBRATION FACTORS

In the main text it is stated that the uptake rate of a diffusive sampler may be either a constant or may vary in some way. To illustrate these two types of behaviour and to demonstrate the statistical analysis of data obtained from the two-factor experiment in Table 1, two practical examples are considered below.

Example 1

The data (individual U-values) in Table A1 were obtained from an abbreviated two-factor experiment on a tube-type diffusive sampler. The pollutant used was a solvent having an exposure limit of 100 ppm. An analysis of variance showed that there were no statistically significant differences among the means of the four cells in Table A1, ie that there was no effect of concentration or exposure time, or of a concentration x exposure time interaction, on the uptake rate. The analysis of variance with non-significant interaction effects excluded is shown in Table A2.

In this example, the overall mean, \bar{U} , of the data in Table A1 was taken as the standard uptake rate or calibration factor, and data from Table A2 were used in the calculation of the error variance. Thus:

standard uptake rate, \bar{U}	= 2.1269
variance of U (s_e^2)	= 0.01468
standard deviation of U (s_e)	= 0.1212
coefficient of variation (CV)	= 5.7%
standard error of U (s_e / \sqrt{n})	= 0.0303
95% confidence limits* for U	$\cong U \pm 2.13(0.0303)$ $\cong 2.0624$ and 2.1914

The relationship between the mean uptake rate (cell means) and pollutant loading (concentration x exposure time) is shown in Figure A1.

*For the calculation of 95% confidence limits, see Ref 9.

Example 2

The data in Table A3 were obtained from a full two-factor experiment as shown in Table 1 involving a tube-type diffusive sampler. The pollutant used was a gas having an exposure limit of 50 ppm. An analysis of variance on logarithmic transformations (necessary to improve the homogeneity of the cell variances) of these data showed that there were statistically significant differences among cell means, ie that both exposure time and concentration affected the uptake rate of the sampler. The analysis of variance is shown in Table A4. Since there was no significant concentration x time interaction, the error and interaction sum of squares in Table A4 were pooled to give a revised estimate of 0.01941 for the error variance, σ_e^2 .

The estimates of the variance components due to concentration, exposure time and error are respectively:

<i>Variances</i>	<i>Standard deviations</i>
$s_c^2 = 0.0555$	$s_c = 0.2356$
$s_t^2 = 0.0532$	$s_t = 0.2307$
$s_\epsilon^2 = 0.0194$	$s_\epsilon = 0.1393$

The last of these components, the random sampling analytical error, s_ϵ , is of the most interest here. The limits of the 95% confidence interval, determined using the χ^2 distribution, are 0.1736 and 0.1164. The value of $s_\epsilon = 0.1393$, which is on the logarithmic (to base e) scale, corresponds to a coefficient of variation (or relative standard deviation) of about 15% on the natural scale.

The relationship between mean uptake rate (cell means) and pollutant loading is shown in Figure A2 and the relationship between mean mass uptake and pollutant loading in Figure A3. It is clear, in this example, that since the uptake rate varies with loading, the calibration curve in Figure A3, rather than a fixed value of the uptake rate, would have to be used to convert a mass uptake to a concentration during the practical use of the sampler for the pollutant in question.

The estimated coefficient of variation of mass uptake, m , due to sampling/analytical error would be the same as that for uptake rate found by the analysis described above, ie 15%. Thus the standard error of the mean uptake, \bar{m} , at each point on Figure A3 is:

$$0.15 \bar{m} / \sqrt{6},$$

or

$$0.0612 \bar{m}$$

Assuming that m for each combination of concentration and time is normally distributed, estimates of the 95% confidence limits* for each \bar{m} can be obtained from:

$$\bar{m} \pm 2.57(0.0612) \bar{m}$$

or

$$\bar{m}(1 \pm 0.1124)$$

As an alternative to the use of the actual graph (such as Figure A3) for converting observed mass uptake to a concentration, it may be possible to find a mathematical expression to relate mass uptake and loading. In this example such an expression might take the form

$$\ln m = a + \ln Ct$$

or

$$C = \frac{\exp(\ln m - a)}{b t}$$

where m is the observed mass, a and b are constants, t is the exposure time and C the concentration to be determined.

* For the calculation of 95% confidence limits, see ref 9.

APPENDIX 2: ANALYSIS OF DATA FROM FIELD EXPERIMENTS

The examples below demonstrate the kinds of statistical analysis which may be useful in the examination of data obtained in the field experiments described in the main text. The data used in the examples are the results of field comparisons of heat-desorbable tube-type diffusive samplers and pumped charcoal tube samplers each measuring a pollutant with an exposure limit of 100 ppm.

Personal sampling exercise

Paired measurements of the exposure of 41 workers were made using the sampling methods referred to above. The sampling time varied between 1 and 2 hours.

The results are presented in Table A5. The two sets of results (diffusive and independent) do not differ significantly (at the 5% level) by the paired t-test ($t = 0.77$) on log-transformed data.

The relationship between the two sampling methods was also examined by means of a linear regression analysis, the fitted equation being of the form

$$\log y = a + b \cdot \log x$$

where x and y were concentrations measured by the pumped and diffusive samplers respectively. The analysis was done on a logarithmic transformation of the data because this has been found generally to stabilise the standard of deviation of measurements made at different concentrations of a pollutant, which otherwise tends to vary proportionally with concentration. One of the basic assumptions of the regression model used is that this standard deviation, or rather the error variance, is constant.

The results of the regression of y upon x were as follows:

residual variance(s^2)	= 0.00581
intercept(a)	= 0.100
standard error of a	= 0.064
slope(b)	= 0.934
standard error of b	= 0.040
correlation coefficient (r)	= 0.967

The fit of the regression equation to the data is indicated in Figure A4.

It can be inferred from these results that there was a high degree of association (correlation) between the two sampling methods when measuring this pollutant, and that there was no systematic difference between the two methods. For perfect agreement between the two methods, the true values of the intercept and slope parameters should be respectively 0 and 1 (note that a and b are estimates of these parameters). In the present example, the 95% confidence limits* for a and b respectively are

$$\text{intercept, } a = 0.100 \pm 0.128$$

$$\text{slope, } b = 0.934 \pm 0.080$$

* For the calculation of 95% confidence limits, see Ref 9.

The former include zero and the latter include unity: hence the conclusion that the methods do not differ significantly. However, some caution should be exercised when drawing conclusions from this kind of analysis because the model assumes that x (a measurement made by the reference method) is without error, which is not likely to be true.

Static sampling exercise

Three groups of six samplers of each type were set up to sample the pollutant (the same pollutant as in the personal sampling exercise) at three different locations in a factory. In each group, the samplers were arranged in pairs consisting of a diffusive sampler taped to a pumped sampler so that the intakes of the two were no more than 2 cm apart. The twelve samplers in each group were then taped together to form a block. The sampling time for each group was 90 min.

Summary statistics for the three groups of measurements are given in Table A5. It had been intended originally to perform an analysis of variance on the full set of data, using a two-way model as in Appendix 1. However, this was not possible because the between-location variances were found to be inhomogeneous both using the raw data and after logarithmic transformation. It is thought that different aerodynamic conditions giving rise to differing temporal fluctuations in analyte concentrations around the samplers at the different test locations might have been the cause of this behaviour.

The coefficient of variation for the pumped charcoal tube method was higher, at each test location, than that for the diffusive sampler (11.4 and 8.1% respectively). It would be reasonable to report these figures as estimates of the measuring errors for the two techniques, for the range of loadings covered by the exercise. It is suggested that the higher variability of the pumped method might have been due to pump (volume) errors.

Column 10 of Table A6 indicates the results of comparisons of means for each location by the t-test. The application of a non-parametric test (Wilcoxon matched pairs test) led to the same conclusion, ie that the difference between the techniques at location 1 (highest pollutant loading) was statistically significant, but that the differences at the other locations were not. There was, then, some evidence of bias between the diffusive sampler results and the reference method at high pollutant loadings, which were not picked up in the personal sampling exercise. This bias appears to be confirmed by the application of linear regression analysis on the static sampling data. Thus:

residual variance(s^2) = 0.01248
intercept (a') = 0.3048
standard error of a' = 0.11469
95% confidence limits* on a' = 0.3048 ± 0.2431
slope (b') = 0.9115
standard error of b' = 0.03133
95% confidence limits* on b' = 0.9115 ± 0.0664
correlation coefficient (r) = 0.99

*For the calculation of 95% confidence limits, see Ref 9.

In this case, the 95% confidence limits on a' and b' do not contain 0 and 1 respectively. The fit of the regression equation to the data is shown in Figure A5.

Table A1 Experimental data - observed U values (ng ppm⁻¹ min⁻¹)

Concentration	Exposure time	
	30 min	480 min
0.2EL	2.04, 1.90, 2.30, 2.03	2.13, 2.18, 2.08, 1.88
2EL	2.27, 2.03, 2.21, 2.07	2.19, 2.18, 2.24, 2.30

Note: EL = exposure limit for pollutant

Table A2 Analysis of variance of data in Table A1

Source of variation	Sum of squares	Degrees of freedom	Mean square	F	Expected mean square
Between concentrations	0.0564	1	0.0564	3.84(ns)	$\sigma_\epsilon^2 + 8\sigma_c^2$
Between exposure times	0.0068	1	0.0068	0.46(ns)	$\sigma_\epsilon^2 + 8\sigma_t^2$
Error	0.1908	13	0.01468		σ_ϵ^2
Total	0.2540	15			

Note: (ns) = not significant at 5% level

Table A3 Observed U values from full two-factor experiment

Concentration	Exposure time		
	30 min	120 min	480 min
0.2EL	3.48, 2.72	2.40, 1.94	1.78, 1.42
	2.60, 2.96	2.10, 1.90	1.60, 1.34
	3.26, 2.26	2.05, 1.63	1.67, 1.30
1EL	2.40, 1.85	1.36, 1.38	1.09, 1.28
	1.60, 2.05	1.31, 1.53	1.11, 1.20
	1.69, 2.00	1.21, 1.69	1.39, 1.27
2EL	1.42, 1.25	1.49, 1.22	0.99, 1.28
	1.46, 1.70	1.40, 1.18	0.97, 1.20
	1.31, 1.92	1.38, 1.10	1.16, 1.05

Note: EL = exposure limit for pollutant

Table A4 Analysis of variance of logarithmic transformations of data in Table A3

Source of variation	Sum of squares	Degrees of freedom	Mean square	F	Expected mean square
Between concentrations	2.0376	2	1.0188	59.67*	$\sigma_\epsilon^2 + 18\sigma_c^2$
Between exposure times	1.9954	2	0.9777	57.26*	$\sigma_\epsilon^2 + 18\sigma_t^2$
Concentration x time	0.1828	4	0.0457	2.68(ns)	$\sigma_\epsilon^2 + 6\sigma_{ct}^2$
Error	0.7683	45	0.0171		σ_ϵ^2
Total	4.9440	53			

Notes: * = p<0.001
(ns) = not significant at 5% level

Table A5 Data from personal sampling field experiments
(units: ppm)

<i>i</i>	<i>x(i)</i>	<i>y(i)</i>	<i>log x(i)</i>	<i>log y(i)</i>	<i>log x - log y</i>
1	7.4	8.8	0.869	0.944	-0.075
2	7.8	7.4	0.892	0.869	0.023
3	17	16	1.23	1.204	0.026
4	18	20	1.255	1.301	-0.046
5	19	27	1.279	1.431	-0.153
6	19	26	1.279	1.415	-0.136
7	19	21	1.279	1.322	-0.043
8	21	17	1.322	1.230	0.092
9	21	19	1.322	1.279	0.043
10	22	30	1.342	1.477	-0.135
11	24	23	1.38	1.362	0.018
12	26	19	1.415	1.279	0.136
13	28	30	1.447	1.477	-0.030
14	35	43	1.544	1.633	-0.089
15	39	23	1.591	1.362	0.229
16	42	38	1.623	1.58	0.043
17	47	36	1.672	1.556	0.116
18	60	55	1.778	1.740	0.038
19	72	74	1.857	1.869	-0.012
20	88	80	1.944	1.903	0.041
21	96	90	1.982	1.954	0.028
22	28	27	1.447	1.431	0.016
23	31	27	1.491	1.431	0.060
24	27	32	1.934	1.505	-0.074
25	31	38	1.491	1.580	-0.088
26	35	37	1.544	1.568	-0.024
27	36	40	1.556	1.602	-0.046
28	42	32	1.623	1.505	0.118
29	44	42	1.643	1.623	0.020
30	47	50	1.672	1.699	-0.027
31	60	66	1.778	1.820	-0.041
32	78	76	1.892	1.881	0.011
33	80	101	1.903	2.004	-0.101
34	85	85	1.929	1.929	0.000
35	87	80	1.940	1.903	0.036
36	90	88	1.954	1.944	0.010
37	92	83	1.964	1.919	0.045
38	95	80	1.978	1.903	0.075
39	105	90	2.021	1.954	0.067
40	102	92	2.009	1.964	0.045
41	99	105	1.996	2.021	-0.026

Notes: x = pumped tube
y = diffusive tube

Table A6 Results of static sampling: summary statistics

Test site	Pollutant concentration found by pumped charcoal tube method, ppm				Pollutant concentration found by diffusive sampler, ppm				<i>t</i> -value (2 tailed-test)
	<i>x</i>	<i>s</i>	<i>n</i>	<i>CV</i>	<i>x</i>	<i>s</i>	<i>n</i>	<i>CV</i>	
1	100.3	7.66	6	7.7%	91.32	4.35	6	4.8%	2.423(p<0.05)
2	34.22	5.41	6	15.8%	33.78	4.42	6	13.1%	0.152(ns)
3	13.05	1.40	6	10.7%	13.90	0.88	6	6.3%	1.263(ns)
Mean				11.4%				8.1%	

Notes: x = arithmetic mean
s = standard deviation
n = no of observations
CV = coefficient of variation
(ns) = not significant at 5% level

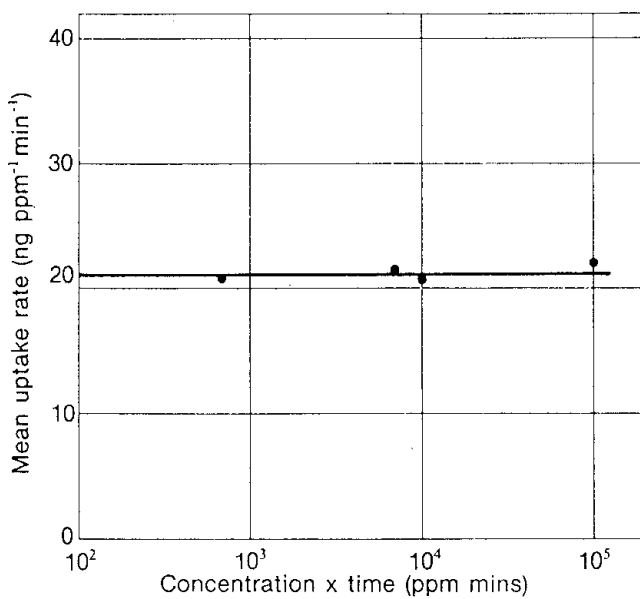


Fig A1
Relationship between uptake rate and pollution loading (first example)

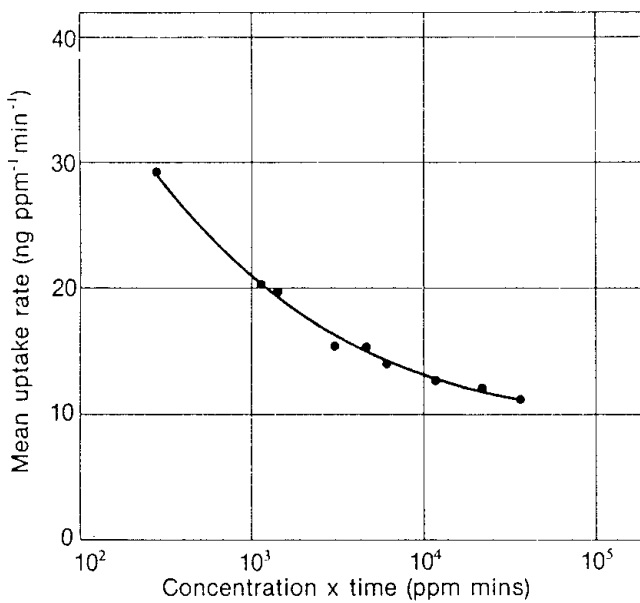


Fig A2
Relationship between uptake rate and pollutant loading (second example)

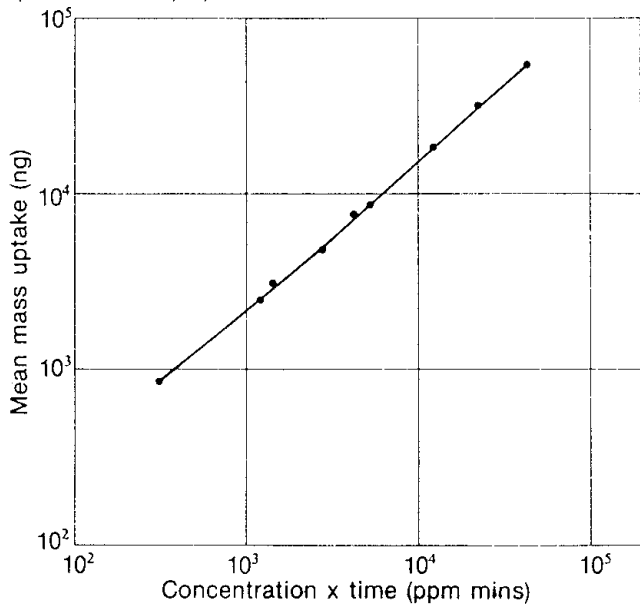


Fig A3
Relationship between mean mass uptake and pollutant loading (second example)

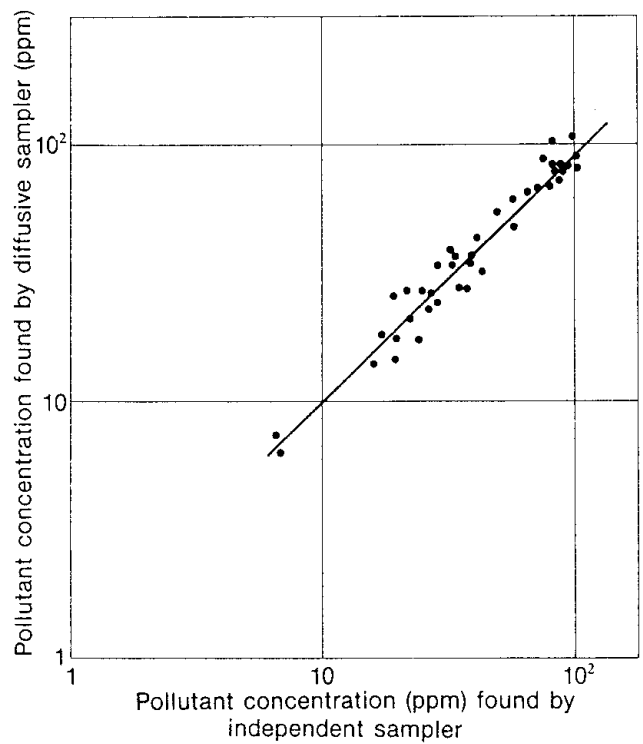


Fig A4
Relationship between diffusive and independent sampling methods - results of personal monitoring

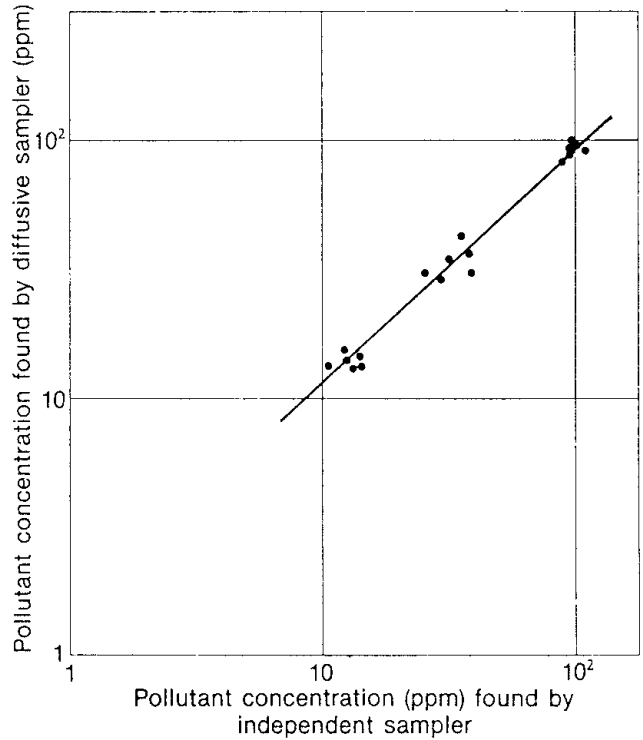


Fig A5
Relationship between diffusive and independent sampling methods - results of static tests

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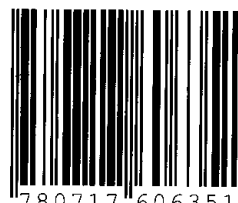
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