



MDHS 54

Methods for the
Determination of
Hazardous Substances

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Protocol for assessing the performance of a pumped sampler for gases and vapours

Health and Safety Executive: Occupational Medicine and Hygiene Laboratory

INTRODUCTION

1 It is important to know the reliability and accuracy of the methods which they are used to measure the concentration levels of airborne pollutants 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 to the are carefully validated. Protocols exist for the validation of techniques based on analysing samples taken by means of an air pump and sorbent trap or filter; for example NIOSH¹ and Chapman *et al.*². Some modifications to the NIOSH Protocol have been proposed^{3,4}. These latter papers have been concerned mainly with defining more clearly the use of terms such as 'accuracy' and 'precision'

2 More recently, an evaluation protocol for diffusive samplers has been proposed⁵, in which emphasis is placed on the determination of the accuracy of the standard atmosphere used to calibrate the samplers and on field testing the samplers in a variety of occupational environments. This diffusive sampler protocol is more demanding than the NIOSH pumped sampler protocol¹, particularly in its insistence on field trials, and it is considered appropriate to apply a similar validation protocol to pumped methods which use a sorbent trap. A further protocol for pump-and-filter methods for collecting dusts is in preparation.

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 para 14 and twenty paired comparisons in para 28. These numbers take into account the workload involved and the statistical value of the sample size and seem reasonable on the basis of practical test experience. Other numbers may be more appropriate in individual circumstances.

4 As in the diffusive sampler protocol⁵, no attempt has been made to define acceptance criteria. An experimental protocol is recommended, and examples are given of suitable statistical treatments which enable estimates to be made of the accuracy of the method. The acceptability of a method is dependent not only on its accuracy, but on convenience, immediacy of result, the range of applicability of the method 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

Definitions

5 A pumped sampler is a device which is capable of taking samples of gas or vapour pollutants from the atmosphere at a rate controlled by an air sampling pump.

6 In this protocol, the term 'accuracy' is used to describe the variability of a test result relative to the true value of that determination. Accuracy has two components; precision and bias. Precision is a measure of the variability of a set of replicate test results and is usually expressed as a standard deviation (absolute number) or coefficient of variation (CV,% relative to the mean of those values). Alternatively, if the test results have all been obtained by the same worker at the same time, precision may be expressed as repeatability according to the ISO definition⁶. Bias is the difference between the mean of the replicate test results and the true value of the determination. Measured values of the precision and mean of a set of test results are only estimates of the population values.

Sampling capacity and efficiency

7 Gases and vapours, when present as airborne pollutants, may be collected in bubblers or impingers containing a liquid adsorbent medium. Normally, a liquid adsorbent medium will not be 100% efficient at collecting an airborne pollutant, although it may be close to 100% efficient if the medium reacts with the pollutant to give a product of very low vapour pressure. The sampling efficiency may vary with the design of the bubbler/impinger, the volume of sampled air, the flow rate, the volume of adsorbent medium, the pollutant concentration and the air temperature. Thus, before conducting the laboratory experiments beginning in para 11, the sampling efficiency (SE) should be determined by sampling from a standard atmosphere at approximately 2 x exposure limit (EL) and at a flow rate appropriate for 10 min sampling for periods ranging between 10 min and 8 h. This may be done by sampling with two sampling units in series. The time at which sampling efficiency falls below an acceptable level, say 95%, should be determined.

8 Gases and vapours may be collected by pulling air through an adsorbent packed in a tube. With this type of sampling device, the sampling efficiency should be 100%, up to a point where 'breakthrough' of the pollutant through the tube occurs. This point is conveniently defined by a measurement of the volume of air that can be sampled before breakthrough occurs. The breakthrough volume (BV) may vary with the sampling flow rate, the weight (or bed length) of adsorbent medium, the pollutant concentration and the air temperature and humidity. Thus, before conducting the laboratory experiments beginning para 11, the breakthrough volume should be determined by sampling from a standard atmosphere at approximately 2 x EL and the maximum recommended sampling flow rate and determining the time at which the effluent concentration is 5% of the applied test concentration. This may be done by monitoring the effluent air with a flame ionisation or other suitable detector.

Analytical recovery

9 Before conducting the laboratory experiments beginning in para 11, the analytical recovery should be determined independently of the sampling efficiency by spiking the adsorbent medium with a range of weights of analyte in order to determine the point at which the desorption efficiency (DE) falls below 75%. A method of spiking charcoal tubes is given in MDHS 33⁷ and a method of spiking porous polymer tubes in MDHS 22⁸.

Sources of sampling error

10 A major source of sampling error is in the estimation of the sample volume drawn by the air sampling pump. Therefore, before conducting the laboratory experiments beginning in para 11, pump errors should be determined in the laboratory by setting up representative sampling pumps, and allowing them to run for 8 hours while monitoring the flow rate. Errors of $\pm 5\%$ (CV, precision) in the constancy of the pump flow rate and of $\pm 10\%$ (bias against absolute displacement meter) in the total estimated air volume, are considered reasonable.

LABORATORY EXPERIMENTS

Test apparatus

11 The apparatus used for the laboratory validation of test samplers should consist of:

- (a) an exposure chamber constructed of inert materials such as glass or PTFE, and of sufficient capacity to accommodate simultaneously at least six test samplers and six samplers of an independent method (para 13).
- (b) a system for generating, pre-mixing and delivering a known concentration of a test pollutant-in-air to the exposure chamber.
- (c) provisions for measuring, controlling and varying, systematically, the concentration, temperature and humidity of the test atmosphere (it is not normally necessary to vary air pressure).

12 The system for generating and delivering the test atmosphere should be based on the use of, for example, a ram-driven syringe⁹, a permeation tube¹⁰, a diffusion cell¹¹, or a certified gas mixture ($\pm 2\%$). The 'true' concentration of the pollutant vapour in the test atmosphere should be calculated, for example, from the syringe injection rate or the rate of loss of vapour from the permeation tube and the volumetric flow of diluent air. This flow should be determined with an appropriate calibrated test meter. The atmosphere should be at known temperature, pressure and relative humidity. The air flow through the chamber should exceed the total rate at which air is extracted or absorbed by the test or independent samplers.

Independent sampling method

13 An independent method should be used to verify the concentration of the generated standard atmosphere in the exposure chamber. This method may be a different pumped adsorbent tube or pumped absorbent bubbler method, or, if the pollutant is a vapour, might be a diffusive sampler method. This method should have been validated over ranges of pollutant concentration, sampling time, etc similar to those described in this protocol, or, if a diffusive method, should have been validated against the diffusive sampler protocol⁵. Alternatively, the generated atmosphere can be checked with an independently calibrated on-line instrument, such as a flame-ionisation detector, an infra-red analyser or mass spectrometer. The 'true' concentration can be considered as verified if the mean concentration indicated by the independent method (corrected for any known bias) is within $\pm 10\%$ of the calculated value. This check is done in each investigation described in para 15.

14 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 this criterion is intended only for checking the standard atmosphere and should not be taken to imply any overall performance criteria for the test or independent samplers.

15 The investigation of the effects of exposure variables on sampler performance should consist of sets of experiments, in each of which six test samplers and six samplers using the independent method are allowed to withdraw vapour from the exposure chamber each for a known period of time and at a known concentration. Typical personal sampling pumps (para 9) should be used. Conditions should be chosen such that the SE is at least 0.95 (95%) and the analytical recovery (DE) is at least 0.75 (see paras 6 to 8).

For each exposure, the normalised test result (NTR) is given by:

$$\text{NTR} = \frac{\text{observed mass collected by test method (mg)}}{\text{'true' concentration (mg/m)} \times \text{sample vol (m}^3\text{)} \times \text{DE} \times \text{SE}}$$

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

16 This set of experiments is designed to determine the normalised test result (NTR) and also the random

error of this determination under a variety of sampling conditions typical of the intended use of the sampler (para 25). The recommended procedure for determining the NTR and its relationship with sampling volume and exposure concentration is to conduct a series of experiments in the exposure chamber according to the 2-factor design shown in Table 1.

17 The full design shown in Table 1 entails nine separate experiments, each as described in para 15, and will permit a statistical analysis of the results to examine any differences among the NTR values for the different combinations of conditions. For each exposure concentration/sampling time combination, the sampling flow rate specified in the method should be used. (For some methods, the flow rate is the same for long and short-term samples; for others the sampling flow rate may be varied to keep the total sample volume approximately constant).

18 A stepwise experimental approach may be used in the determination of the NTR. This would entail conducting a smaller number of experiments consisting of the four treatment combinations covering the extremes of the test factors as indicated by asterisks in Table 1. If a statistical analysis of the data from this abbreviated experiment showed that there were no significant differences among the mean NTR values for each of the four combinations of conditions, then the NTR could be assumed not to vary with exposure conditions and there would be no need to continue with the full design. An example of the use of the abbreviated analysis including a suitable statistical protocol is given in Appendix 1.

Effect of storage

19 It is recommended that the effects of a period of storage of the sampler after exposure to the pollutant should be investigated. If the factorial design described above is used, then it would be possible to use two extra samplers for each of the four treatment combinations represented by asterisks in Table 1 and to store these extra samples at normal laboratory temperature for at least two weeks, the remaining samples being analysed immediately. Any difference between stored and unstored sample results should be noted. If stored sample results fall rapidly in comparison with results from unstored samples, it may be desirable to conduct several experiments for different storage times and quote the time at which stored samples give results which are within a certain percentage, say 20%, of unstored sample results.

20 Storage over extended periods may not be relevant for devices which give an immediate measurement on site and are then discarded. However, sampling devices which use chemical reagents should be tested for pre-exposure stability.

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

21 A further set of experiments should be conducted as described in para 15 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 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 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 para 15, and would enable a statistical analysis of the variances and of the differences (if any) between the NTR values 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 NTR value of a particular pollutant by a particular type of sampler.

22 The concentration of atmospheric pollutant, if expressed as mg m^{-3} , changes with temperature and pressure. Thus, if a 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 or if a correction to 25°C, 760mm Hg is desired.

Determination of the effect of potential interferences on sampler performance

23 A further set of experiments should be conducted as described in para 14 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 samplers and are likely to be interferences. In the case of samplers using nonspecific sorbents, interferences are likely to be of consequence only if present in much higher concentrations than the analyte of interest.

Determination of NTR

24 An estimate of the bias of the method, i.e. the difference between the mean of replicate observed results and the true concentration may be obtained from the mean normalised test result (NTR). In most cases, after having taken account of sampling efficiency and analytical recovery, the NTR will be constant (although subject to random error) over a range of sampling conditions. If so, a mean value over this range should be calculated and reported. This value should be close to 1.0 for the method to be of practical value. If a significant bias is found, a check should be made to see if it varies with analyte level.

25 The random error in the NTR should be expressed either as a coefficient of variation or as a repeatability (for the latter, see the ISO recommendations, Ref 6). Examples of suitable statistical analyses are given in Appendix 1.

26 The random error in the observed NTR is a multicomponent error, i.e. it contains variance components due to pump error, analytical error and errors associated with the determination of desorption efficiency. A check should be made to see if the random error varies with analyte level.

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 (e.g. accuracy) of both test and independent sampling methods might differ from that determined in laboratory experiments under controlled conditions. It is thus desirable to include field comparisons of the test sampling method with the independent method of 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 'test' 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. For both sampling methods, the results of measurements should be expressed in either milligrams per cubic metre (mg m^{-3}) or parts per million (ppm) and should be corrected for desorption efficiency and sampling efficiency.

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 $n \geq 20$ 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 relationships between the two sampling methods by a linear regression analysis of the results. Such an analysis would provide a measure of the degree of association between the two methods over the range of conditions covered by the field tests (i.e. the correlation coefficient) together with 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

$$\begin{array}{l} \text{or} \quad y = a + bx \quad \text{----- } 2 \\ \quad \log y = a + b \cdot \log x \quad \text{----- } 2a \end{array}$$

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

Note A logarithmic (as in Equation 2a) 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), i.e. 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 2 or 2a 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 12), 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 (paras 13 and 25) or from the field comparison (para 34).

35 Alternatively, an approximate estimate of the linear functional relationship may be obtained, by the method of Bartlett^{12,14}. 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, i.e.

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

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

36 In some cases, the measurement errors, referred to in para 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 12 and 14.

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 (e.g. 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

* For the calculation of 95% confidence limits, see Ref 12

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 test 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.

Exceptions to the general protocol

42 It may not be possible or practicable to prepare standard atmospheres, e.g. for some aerosols or potent carcinogens. In such cases, it may be permissible to assume that the sampling efficiency is 100%. Laboratory experiments may then be restricted to determining the analytical recovery from spiked samples (para 8). More emphasis than usual should then be placed on the field trials.

43 There may be no acceptable independent method available for the determination of the test analyte. In this case, standard atmospheres must be checked with a meter or calibrated instrument. Field trials should be conducted using spiked samplers instead of the samplers of the independent method. The difference between spiked and unspiked samples (relative to spike size) could then be used as an estimate of the field NTR. In descending order of preference, the technique should consist of;

- (a) spike in same phase as sample, *on site*
- (b) spike in same phase as sample, *in lab*
- (c) add dissolved or suspended spike, *on site*
- (d) add dissolved or suspended spike, *in lab*

A method of undertaking technique (a) is given in Ref 17 (MDHS 5).

44 In some cases, the test method may be arbitrary. If so, bias has no relevance, and the evaluation protocol should be designed to test precision only.

NOTE

This protocol has been prepared by an editorial task force (part of HSE Committee of Analytical Requirements) consisting of Dr R H Brown (chairman), Dr A Critchlow, Mr R P Harvey, Dr T L Ogden, Dr K J Saunders and Dr K T Walkin.

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Table 1 Experimental data :
observed values of NTR

Concentration	Exposure time		
	30 min	120 min	480 min
0.2 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 para 18

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

Concentration	Air Temperature			
	5°C		30°	
	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

16 Acton, F.S., Analysis of Straight Line Data. Wiley: New York, 1959.

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APPENDIX 1 ANALYSIS OF EXPERIMENTAL DATA

The normalised test result (NTR) of the test method is expected to be constant over a wide range of sampling conditions, assuming that adequate correction has been made for desorption efficiency (DE) and sampling efficiency (SE). It would normally be necessary only to confirm this by conducting the limited tests suggested in para 18, an example of which is given below. Only if significant variation of the NTR with exposure conditions were found would it be necessary to conduct the full experiment (para 17).

Example

The data (individual NTR values) in Table A1 were obtained from an abbreviated two-factor experiment on a tube-type thermally desorbable sampler. The pollutant used was a gas having an exposure limit of 5 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 is shown in Table A2.

In this example, the overall mean, NTR, of the data in Table A1 indicates that there is no residual bias in the determination of exposure concentration by this test method. Thus

overall mean, NTR	= 1.0147
variance of NTR (se^2)	= 0.00413
standard deviation of NTR (se)	= 0.0643
coefficient of variation (CV)	= 6.3%
standard error of NTR ($se/\sqrt{5n}$)	= 0.0088
95% confidence limits for NTR	= $NTR \pm 0.0088$
	= $t_{(n-1)}$
	= 0.9966 and
	1.0328 where
	$t_{(n-1)} = 2.06$

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

* For the calculation of 95% confidence limits, see Ref 12

described in the main text. The data used in the examples are the results of field comparisons of heat-desorbable tube-type samplers used in either the pumped (test) or diffusive (independent) mode. The samplers were each measuring a pollutant with an exposure limit of 5 ppm.

Personal sampling exercise

Paired measurements of the exposure of 24 workers were made using the sampling methods referred to above. The sampling time was 8 hours.

The results are presented in Table A3. The two sets of results (test and independent) do not differ significantly (at the 5% level) by the paired t-test ($t = 1.14$).

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

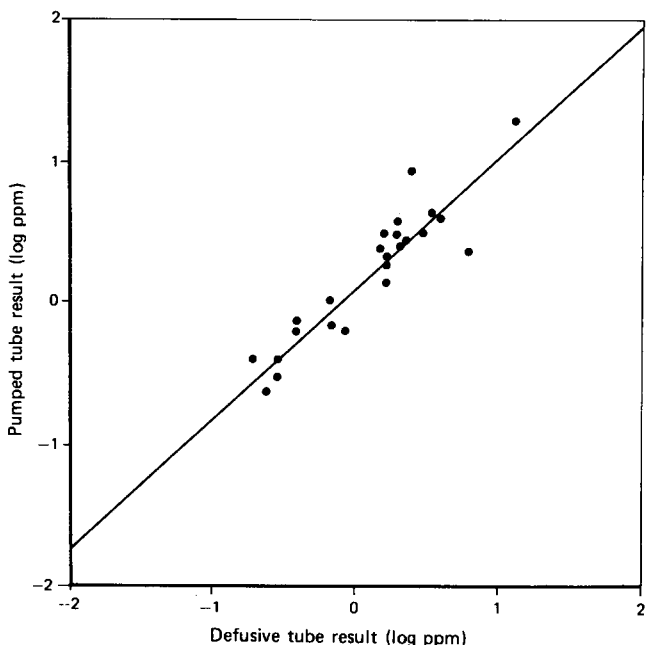
$$\log y = a + b \log x$$

where x and y were the concentrations measured by the independent and test samplers respectively. The analysis was done on a logarithmic transformation of the data because this has been found generally to stabilise the standard deviation of measurements made at different concentrations of a pollutant, which otherwise tends to vary proportionally with concentration. One of the basis 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)	= 0.338
intercept (a)	= 0.0901
standard error of a	= 0.0392
slope (b)	= 0.9076
standard error of b	= 0.0809
correlation coefficient (r)	= 0.923

The fit of the regression equation of the data is indicated in Fig A1.



In the absence of bias, 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 are estimates of these parameters). In the present example, the 95% confidence limits for a and b are

intercept, a	= 0.0901 ± 0.0811
slope, b	= 0.9076 ± 0.1675

Thus, the 95% limits on the intercept do not embrace zero (although the 99% limits do), indicating the possibility of a small systematic difference between the results given by the two methods (there was no evidence of statistically significant systematic difference in the t-test). The slope limits, however, include unity.

*For the calculation of 95% confidence limits, see Ref 12

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 seven 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 fourteen samplers in each group were then taped together to form a block. The sampling time for each group was 8 hr.

The results from the three groups of paired samplers are given in Table A4. Since the samplers are arranged in pairs, it is possible to arrange the data as in Table A5, excluding unmatched pairs. A paired sample t-test on this data does not reveal any systematic difference between the results given by the two types of sampler ($t = 0.93$).

This type of analysis, however, does not use all the data available and an alternative is to examine the data sets from each group separately, as in Table A6. In all three groups, the statistical analysis indicated that there was no significant difference in the data set variances (F -test) and subsequently (t -test) that there was no significant difference between the data set means (at the 5% level). In groups 1 and 3, several of the pumped tube results are outliers (zero results being recorded). In groups 2 and 3, there are large differences between the method means. However, these differences are of opposite sign and are not statistically significant in view of the coefficients of variation of both methods (see next para).

The coefficient of variation for the pumped charcoal tube method was higher, at each test location, than that for the diffusive sampler (20.3 and 16.1% respectively). It would be reasonable to report these figures as estimates of the field variability for the two

techniques, for the range of loadings covered by the exercise. The field variability may be expressed either as a coefficient of variation, as here, or as a repeatability. It is suggested that the higher field variability of the pumped method might have been due

to pump (volume) errors. The field variability of both methods is greater than their laboratory variabilities (para 25 and Appendix 1), since the atmosphere sampled in the field will be less homogeneous than the laboratory standard atmosphere.

Table A1 Experimental data :
observed values of NTR

Concentration	Exposure time					
	30 min	480 min				
0.2EL	1.044	0.940	0.988	1.056	1.070	0.968
	0.974	0.905	1.092	1.003	0.994	1.090
2.0 EL	0.949	1.086	1.090	1.070	0.926	1.041
	1.041	1.083	1.010	0.930	1.089	0.914

Note: EL = Exposure limit for pollutant

Table A2 Analysis of variance
of data in Table A1

Source of variation	Sum of squares	Degress of freedom	Mean square	F square	Expected mean square
Between concentrations	0.00045	1	0.00045	0.1	$\sigma_E^2 + 12\sigma_c$
Between times	0.00011	1	0.00011	0.02	$\sigma_E + 12\sigma_E^2$
Concentration x time interaction	0.0116	1	0.0116	2.8	$\sigma_E + 6\sigma_{ct}^2$
Error	0.0826	20	0.00413		σ_E^2
Total	0.0948	23			

Table A3 Data from personal
sampling field experiments

units ppm					
<i>l</i>	<i>Y(l)</i>	<i>log Y</i>	<i>X(l)</i>	<i>log X</i>	<i>Y-X</i>
1	1.4	0.146	1.7	0.23	-0.3
2	2.5	0.397	2.2	0.343	0.3
3	0.4	-0.397	0.2	-0.698	0.2
4	2.4	0.38	1.6	0.204	0.8
5	3.0	0.477	2.1	0.322	0.9
6	3.0	0.477	1.7	0.23	1.3
7	8.1	0.908	2.6	0.414	5.5
8	3.8	0.579	4.2	0.623	-0.4
9	4.0	0.602	3.6	0.556	0.4
10	2.0	0.301	1.7	0.230	0.3
11	1.0	0.0	0.7	-0.154	0.3
12	3.5	0.544	2.0	0.301	1.5
13	2.2	0.342	6.6	0.819	-4.4
14	0.6	-0.221	0.4	-0.397	0.2
15	1.8	0.255	1.7	0.23	0.1
16	0.7	-0.154	0.4	-0.397	0.3
17	3.0	0.477	3.0	0.477	0
18	0.3	-0.522	0.3	-0.522	0
19	0.4	-0.397	0.3	-0.522	0.1
20	18	1.255	14	1.146	4
21	0.7	-0.155	0.7	-0.155	0
22	2.8	0.447	2.3	0.362	0.5
23	0.2	-0.698	0.2	-0.698	0
24	0.6	-0.222	0.9	-0.046	-0.3

Y = Pumped molecular sieve tube

X = Diffusive molecular sieve tube

Table A4 Field comparisons :
7 x 7 multiple comparisons

Group No	Pumped tubes (ppm)		Diffusive tubes (ppm)	
1	2.1	2.0	2.2	2.3
	2.5	2.2	2.2	2.0
	<0.1	<0.1	1.9	1.9
	<0.1		2.0	
2	4.1	4.0	6.0	6.6
	6.8	5.4	6.5	6.0
	6.4	5.6	9.3	5.1
	1.8		6.4	
3	14	18	16	16
	18	21	14	11
	<0.1	<0.1	16	10
	<0.1		15	

Table A5 Data from static
sampling field experiments

units ppm			
<i>l</i>	<i>Y(l)</i>	<i>X(l)</i>	<i>Y-X</i>
1	2.1	2.2	-0.1
2	2.0	2.3	-0.3
3	2.5	2.2	0.3
4	2.2	1.9	0.3
5	4.1	6.1	-2.0
6	4.0	6.6	2.6
7	6.8	6.5	0.3
8	5.4	6.0	-0.6
9	6.4	9.3	-2.9
10	5.6	5.6	5.10.6
11	1.8	6.4	-4.6
12	14	16	-2
13	18	16	2
14	18	14	4
15	21	11	10*

* rejected on Dixon's outlier test

Y = Pumped molecular sieve tube

X = Diffusive molecular sieve tube

Table A6 Field comparisons
multiple comparisons :
Statistical analysis

Group No	Pumped tubes			Diffusive tubes			<i>F</i> _{found}	<i>t</i> _{found}	
	mean	SD	<i>n</i>	mean	SD	<i>n</i>			
1	2.20	0.22	4	2.08	0.15	7	2.15	0.96	NS
2	4.87	1.71	7	6.57	1.30	7	1.73	2.12	NS
3	17.75	2.87	4	14.0	2.52	7	1.29	2.21	NS

NS = Not significant at the 5% level

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* in preparation, revised

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