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THE USE OF DIFFUSIVE SAMPLERS FOR MONITORING OF AMBIENT AIR

Position paper on their environmental potential and the need for further research
(Technical Report)

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The use of diffusive samplers for monitoring of ambient air (Technical Report)

ABSTRACT

Diffusive monitors have been used for workplace air monitoring for many years, and in many cases have been found to be valid and cost-effective alternatives to conventional pumped or 'active' samplers. The state of the art of diffusive sampling is reviewed briefly, with particular reference to workplace air monitoring, and the potential for using similar or adapted devices for measuring concentrations of environmental pollutants examined. In particular; can samplers be used to measure concentration levels some three orders of magnitude lower than in the workplace; are blanks and sensitivity adequate? Is the sampling rate affected by concentration? What is the effect of ambient air movement? Are there sufficient validation data? Can diffusive samplers measure particulates? These questions are addressed generally and by reference to specific applications. Some conclusions are reached and recommendations made for future research.

DIFFUSIVE SAMPLING

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 (Berlin, et al, 1987). It should be noted that in the US, the adjective "passive" is preferred in describing these samplers and should be regarded as synonymous with "diffusive".

This type of diffusive sampler should not be confused with the annular or aerosol denuders, which not only rely on diffusion to collect the gas or vapours but also upon the air in question being simultaneously drawn through the annular inlet into the sampler. Aerosol particles have diffusion coefficients too low to be collected on the annular inlet and are trapped on a backup filter.

Diffusive sampling in the occupational environment dates back at least to the 1930s when qualitative devices were described, but the first serious attempt to apply science to quantitative diffusive sampling was in 1973 when Palmes described a tube-form sampler for sulfur dioxide (Palmes and Gunnison, 1973). Since then, a wide variety of samplers have been described, some relying on diffusion through an air-gap, some relying on permeation through a membrane, and some using both techniques, for the rate-controlling process in sampling (Jost, 1960, Tompkins et al, 1977, Bamberger et al, 1978). Many of these devices are commercially available.

The theoretical basis for diffusive sampling is now well established. Diffusion and permeation processes can both be described in derivations of Fick's first law of diffusion, which result in expressions relating the mass uptake by the sampler to the concentration gradient, the time of exposure, and the sampler area exposed to the pollutant atmosphere (Moore, 1987). Expressions have also been derived for the application of Fick's law to diffusive sampling in the "real" world, ie, taking into account nonsteady-state sampling, the effects of fluctuating concentrations, sorbent saturation, wind velocity and turbulence at the sampler surface, temperature, pressure, and so on (Bartley et al, 1983, Pozzoli and Cottica, 1987). Except for sorbent saturation, which may lead to reduced (although sometimes predictable) uptake rates, these modifications to the basic Fick's law expression do not lead to significant errors for well-designed samplers. Such samplers may be regarded as truly integrating devices with accuracies similar to those of active samplers.

A variety of diffusive samplers have been described (Squirrell, 1987). Diffusive equivalents to the more familiar pumped methods exist for nearly all types; the main exception being the direct collection of gas samples, where the nearest equivalent is an evacuated canister. Thus, the diffusive equivalent of an impinger is a liquid-filled badge such as the Pro-Tek™ inorganic monitor or the SKC badge; the diffusive equivalent of the charcoal tube is the charcoal badge such as the 3M OVM or the MSA VaporGard™ organic; and the diffusive equivalent of the thermal desorption method is the Perkin-Elmer tube or the SKC thermal desorption badge. There are also diffusive devices based on reagent impregnated solid supports, and these feature quite strongly in environmental applications.

PREVIOUS REVIEWS

A good general introduction to the use of diffusive samplers as an alternative approach to (workplace) personal monitoring is given in Saunders (1981).

The theoretical basis of diffusive samplers is described in greater detail in Fowler (1982), which covers Fick's first law, the effect of environmental factors (temperature and pressure), sampler response time, effect of air face velocity and the relative advantages of devices based on diffusion and permeation.

A more extended review by Rose and Perkins (1982) covers similar ground to Fowler, but also includes a contemporary account of practical applications. It is one of the earliest papers that stresses the importance of field validation, which is usually interpreted as a comparison of the diffusive method side-by-side to a conventional (pumped) method.

The review by Harper and Purnell (1987) includes references to more recent work on response time, principally from Bartley and colleagues from NIOSH, reflecting a heightened interest in this aspect. The ability of diffusive samplers to respond accurately to transient changes in concentration was being questioned. However, most mathematical derivations conclude that errors are likely to be small in the real sampling situation, provided the total sampling time is sufficiently large relative to the response time. This sampling time is dependent on sampler geometry; for tube-type samplers it is about 10 - 30 mins, for badge-type samplers, a few minutes. Harper and Purnell (1987) also examines sampling efficiency on a theoretical basis, linking it to the measurement of adsorption isotherms.

The best general introduction to diffusive sampling, however, is the Proceedings of the Diffusive Sampling Symposium held in Luxembourg in 1986 (Berlin et al, 1987). This covers all the aspects noted above - theoretical basis, effects of environmental factors, practical applications - and is particularly strong on validation and quality control. It is a little 'light' on the effect of transients. It concentrates on workplace applications, but there are a significant number of ambient air applications (which will be seen in later cited articles), reflecting a growing interest in this area.

ENVIRONMENTAL MONITORING POTENTIAL

A number of problems have to be faced and solved before diffusive samplers can be used in environmental applications - and by 'environmental' is meant any non-industrial application - as a means of determining air quality.

Can samplers be used to measure concentration levels some three orders of magnitude lower than in the workplace; are blanks and sensitivity adequate?

The most obvious difference between workplace air and environmental air is that the pollutants of interest are present at widely differing concentration levels. In addition, the important pollutants are different, although there is some overlap. In general terms, exposure limits or their equivalents are some 30 times lower for environmental pollutants, and the concentrations of major pollutants are typically two to three orders of magnitude lower.

In conventional environmental monitoring technology, therefore, it is common to sample many litres or even cubic metres of air in order to have sufficient sensitivity. Such volumes can only be sampled in reasonable periods by means of a sampling pump. On the other hand, diffusive samplers operate at an equivalent of a few millilitres a minute. The latter are only practical, therefore, if blanks can be made extremely low by meticulous attention to cleanliness; by having much increased sensitivity in the analytical stage (relative to the blank!), or by sampling for very long times. The last option can be a very useful one, for whilst sampling with an electrically driven pump is impractical for more than a day or so without a dedicated power supply, diffusive samplers can be exposed indefinitely, at least in principle. The trade-off is of course lack of time-resolution in the integrated result.

Is the sampling rate affected by concentration?

The sampling rate of a diffusive sampler is usually expressed in units of ng/(ppm.min) (Note A). If the concentration component of this expression (ppm) is replaced by mg/m³, the expression becomes ng/((mg/m³).min) or cm³/min - as if it were a real flow of air through the sampling device. An air concentration can therefore be deduced from a measured mass uptake (which is usually the analytical result) if the time of exposure is known.

It is important, therefore, that the sampling rate is constant, i.e. does not change with pollutant concentration or time of exposure.

The fundamental equation describing diffusion is Fick's first law. From this it can be deduced that the sampling rate of a diffusive sampler is directly proportional to the diffusion coefficient of the particular pollutant in air, the concentration and the time of exposure, provided the concentration gradient is maintained. It is also proportional to the cross-sectional area of the diffusion path and inversely proportional to its length.

The diffusion coefficient, so far as can be ascertained from the literature, is not expected to be concentration-dependent, at least at concentrations below 1000 ppm. However, the concentration gradient can be reduced if the sorbent begins to reach saturation.

For a pumped sampler, sampling efficiency will be reduced or 'breakthrough' will occur if the sorbent becomes saturated. A similar phenomenon occurs with diffusive samplers, and may occur earlier than full saturation (depending on the shape of the adsorption isotherm) if a significant vapour pressure exists at the sorbent surface relative to the ambient concentration of pollutant. For most sorbents used in environmental monitoring (commonly a reagent-coated screen or a strong surface adsorbent, such as charcoal), this is not a problem. However, for organic vapours sampled on thermal desorption tubes, it is sometimes difficult to have sorbents which are both strong enough to provide negligible back-diffusion and weak enough to be convenient for thermal desorption. Even so, for environmental monitoring concentrations, diffusive sampling rates remain fairly constant even when non-ideal sorbents are used, as can be shown from a computerised model developed by Van den Hoed (1987).

What is the effect of ambient air movement?

Diffusive sampling rates can also be affected by air movement external to the sampler. Most studies have examined the effect of low air velocities. For the concentration gradient to be maintained as the driving force for diffusion, external air movement has to be sufficient to reduce the 'boundary layer' (Schlichting, 1955) effectively to zero. Another way of looking at this is to imagine that at low air velocities, a static layer of air external to the sampler will cause 'starvation' or an extension of the diffusive path and hence a flattening of the concentration gradient. Experiments on samplers exposed to air velocities typical of the workplace suggest that the 'face velocity' effect is small provided a minimum of about 0.1 m/s linear air velocity is maintained (Harper and Purnell, 1987). This is unlikely to be a problem in measuring ambient air

Note A: in this text, ppm refers to a volume fraction (ϕ) = 10⁻⁶.

element (Palmes and Gunnison, 1973). The device commonly termed the 'Palmes tube', was a later development (Palmes et al, 1986) and consisted of a simple acrylic tube, about 8 cm by 1 cm i.d., with one closed end. Sampled gases enter the tube at the open end, migrate down the tube by molecular diffusion and are collected at the closed end by an (efficient) adsorbing medium, in this case triethanolamine (TEA; 2,2',2''-nitrilotriethanol) coated on stainless steel grids. NO₂ is trapped as nitrate ion and is measured spectrophotometrically after reduction to nitrite and reaction with sulphanilamide and naphthylethylenediamine.

The Palmes tube was developed initially for workplace monitoring of NO₂, but its use was extended to indoor air monitoring by Atkins et al (1978). The authors acknowledged its limitations in sensitivity and dependence on wind speed.

The minimum level of detection has been reported to be about 300 ppb.hr (Appling et al, 1979; Boleij et al, 1986) (Note B). Blanks are of the order of 100 ppb.hr, mainly the result of exposure of the coated screens during manufacture (Colls 1986). Measurement of ambient air levels of a few ppb therefore requires exposure of the sampler for a week or more unless sensitivity can be improved. Miller (1988) reports lowering the detection limit to 30 ppb.hr (blank 7 ppb.hr) by replacing the acrylic tube with stainless steel and changing to ion chromatographic analysis. Miller also found reversible adsorption of NO₂ on the walls of the perspex sampler and storage problems with the stainless steel sampler.

Gair (1990) found a similar detection limit and blank by preparing tubes in situ with ultra clean reagents. An increase in blank level of about 34 ppb.hr for each week of storage was noted and was ascribed to permeation of NO₂ through the walls of the tubing. Contamination did not increase in tubes stored in the freezer.

Hisham and Grosjean (1990) found that peroxyacetyl nitrate (PAN) was a positive interferent for NO₂ using TEA coated (pumped) cartridges and HPLC-UV detection. However, Gair et al. (1990) found only a <6% positive interference which they considered non-significant.

Atkins et al (1978) report good agreement between Palmes tubes and a chemiluminescent method in measuring NO₂ in houses, but present only limited data. A larger study (Appling 1979) reached a similar conclusion, as did studies by Hoen et al (1984). Boleij et al.(1986) included some 50 comparisons of Palmes tube results with a chemiluminescent monitor, measuring NO₂ levels in homes. The overall correlation coefficient was 0.93. Biases (relative to the monitor) of up to 30% (some positive, some negative) were observed in particular locations, but as the CV of each method was estimated at about 10%, these differences are probably not significant.

A detailed comparison between diffusion tubes and chemiluminescent monitors used for ambient air monitoring has also been published (Atkins et al, 1986). It covered the low ppb range (2-35 ugN/m³) and compared weekly diffusion tube measurements with means of hourly concentrations measured by the monitors. The authors concluded that there were no significant differences between the two methods. Other workers have reported similar results (Hangartner and Burri, 1987; Gair et al, 1990).

EPA/Monsanto badge

It has already been noted that a diffusive sampler has a relatively low sampling rate and for environmental applications it may be necessary to expose the sampler for several days to collect sufficient material for accurate analysis. An alternative is to increase the surface area of the collection medium and to reduce the diffusive path length, both of which cause a corresponding increase in sampling rate. The geometry of the sampler changes from a tube to a badge. An increase in sensitivity of typically 100 is achieved by increasing the cross-sectional diameter by a factor of 3 and decreasing the path length by a factor of 10. Increasing the sampling rate still further is counter-productive, because boundary layer effects begin to predominate.

One such badge was described by Mulik et al (1989). Their 'high efficiency passive sampling device' (PSD) consisted of a series of diffusion barriers placed on either side of a cavity for

Note B: in this text, ppb refers to a volume fraction (ϕ) = 10⁻⁹.

concentrations, but may cause difficulties in indoor air. The solution in indoor air is to switch from a badge design to a tube design, where the effect is less pronounced, or to ensure artificial enhancement of air movement, by suspending the sampler on a thin thread, for example. In outdoor air, however, air velocities far in excess of those encountered in workplaces may occur, and these too can cause problems if air penetrates the draft shield (if any) and disturbs the static air layer within the sampler. This calls for careful design of the diffusive sampler.

A novel, alternative, solution to the problem of external mass-transfer resistance at low air velocities (Persoff and Hodgson, 1985) is to expose a series of tubes of differing air-gap and extrapolate to infinite length.

Are there sufficient validation data?

Not only must chemical analysis give the right answer, but it must be seen to give the right answer. This means method validation, intercomparisons, quality control, accreditation and Reference Materials.

All are in their infancy, and arguably environmental monitoring a little behind workplace monitoring in these matters.

Procedures for method validation are now in place for workplace air monitoring, for example MDHS 27 in the UK (HSE, 1987; Brown, et al, 1984) and prEN 838 from CEN/TC 137. Both include field validation as well as laboratory tests, although the CEN document regards laboratory tests as a sufficient minimum requirement. Intercomparisons are common, although mostly on an ad-hoc basis: the Community Bureau of Reference has completed some half-a-dozen intercomparisons and has produced the first Certified Reference Material applicable to diffusive sampling (Vandendriessche et al., 1991). The author knows of no formal validation protocol for environmental applications of diffusive sampling, although the principles of MDHS 27 and prEN 838 will apply.

As a result, published validations of environmental applications are currently rare, and fragmentary and unstandardised where they exist.

Can diffusive samplers measure particulates?

A limitation of diffusive sampling, which may in some circumstances be an advantage is that only gases and vapours are sampled. The diffusion coefficients of particulate material in air are some four orders of magnitude smaller than those for gases, and are not sampled to a significant extent, unless a specially designed (electrostatic) sampler is used (Brown, 1993). Many ambient pollutants will be wholly in the gaseous phase, but a significant number may be particulate, a mixed-phase aerosol, or vapour adsorbed onto particulate matter. These in general are not suitable for diffusive sampling, unless information is required on the vapour phase only, or separately for vapour and particulate phases. Dust can also be a problem if it collects on or in the sampler and analyte continues to diffuse to the sorbent after the sampler is formally sealed.

Particular problems may be ammonia, where part of the ambient aerosol may be particulate ammonium salts; some acid gases with low vapour pressures; formaldehyde which may be adsorbed onto non-specific particulates.

SPECIFIC APPLICATIONS

Nitrogen oxides

The Palmes tube

Palmes' original development of a diffusive sampler was for SO₂ (see below) and took the form of a squat cylinder with a tube insert as diffusion barrier and a liquid sorbent as the collection

containment of the collection element, in this case reagent-coated glass fibre filter paper. TEA was used as the reagent for NO_2 . As expected, sampling rates were high, enabling measurements of ambient air quality over relatively short time periods.

An examination of the effect of temperature and humidity on badge performance (Moschandreas et al, 1990) revealed that badges were unaffected by humidity or temperatures up to 40°C . However, NO_2 levels were severely underestimated at extremes of temperature (-20 or $+50^\circ\text{C}$), the former possibly because triethanolamine freezes at $+20^\circ\text{C}$.

A further example of a badge-type diffusive sampler for NO_2 is that developed by Krochmal and Górski (1991). This is similar to the EPA/Monsanto badge in that it uses a TEA-impregnated glass fibre disc as the collection element, although a number of alternative substrates were tested. The authors report on humidity and temperature effects. The method forms the basis of a Polish Standard (PN/Z-04092/08; Wydawnictwo Normalizacyjne "Alfa", Warsaw, 1989)

Nitrogen monoxide

In principle the Palmes tube can also be used to monitor NO if oxidised to NO_2 . Indeed, an early paper by Palmes (1977) refers to a NO_x sampler which monitors both NO and NO_2 . Sampled NO (together with any NO_2) diffuses down the tube, through the TEA-coated screen where it meets an oxidising layer and diffuses back as NO_2 . NO is measured by difference between tubes with and without oxidising layer. In the Palmes version, the oxidising layer is a chromic acid coated screen which has to be inserted immediately before sampling and removed immediately afterwards. The same principle is used in a badge design by Ferber et al (1976) (which incidentally predates the EPA/Monsanto badge). A prototype based on the Palmes tube which appears to have a stable oxidising element has been described by Eickeler (private communication).

A further device that can be used for both NO and NO_x is marketed by Ogawa. The Ogawa Passive System was originally built for NO/ NO_2 , but a version for ozone (q.v.) is also available. The technology was developed by Hirano in Yokohama, Japan, but has not been published. It is a dual-faced sampler in which NO_2 is determined on one side and NO_x on the other; NO is determined by difference. TEA is used to collect NO_2 and a proprietary reagent for NO_x . A joint study by US-EPA, the Harvard School of Public Health and ManTech Environmental Technology (Mulik, et al., 1991) demonstrated good agreement between Ogawa PSDs and weekly real-time averages from instrumental methods. For NO/ NO_2 , only precision data was available; CVs of about 20% were found for weekly measurements in the range 2-10 ppb, but these included variance components due to the siting of the replicates in three co-located positions (sampling shelters).

Sulfur dioxide

As noted above, the use of a diffusive device for measuring SO_2 predates the use for NO_x . Palmes' original SO_2 sampler was not however a Palmes tube as it later became, but a squat cylinder with a tube insert as diffusion barrier and a liquid sorbent as the collection element (Palmes and Gunnison, 1973). The sorbent was mercury(II) chloride solution. Palmes also developed similar samplers containing concentrated H_2SO_4 or silica gel for diffusive monitoring of water vapour. The colorimetric determination of SO_2 by complexing with mercury(II) chloride is commonly known as the West/Gaeke procedure, and it is not surprising that West himself developed a sampler for SO_2 (and other analytes). Reiszner and West (1973), in the same year as Palmes, described a similar device using a liquid collection element, but incorporating a silicone membrane as a permeation barrier rather than an air gap as purely diffusive barrier.

Killick (1976) evaluated the West badge for ambient SO_2 measurement in laboratory tests, sampling over 1 - 19 days. He found generally good agreement with a continuous conductometric instrument - in 75% of tests, the ratio of badge to instrument was between 0.80 and 1.17. More recent papers, however, have returned to the Palmes tube for monitoring ambient air. Triethanolamine forms a complex with SO_2 as well as with NO_2 and the product may be analysed by the para-rosaniline method. Preliminary results (Hangartner and Burri, 1987) suggest a high correlation with a fluorescence monitor under field conditions, but the response was only 50% of the expected value. More recently (Hangartner, Burri and Monn, 1989) problems were reported with storage recovery and the effect of relative humidity.

Orr (1987) modified the West badge to incorporate a porous (diffusion-limited) membrane rather than a silicone one and a potassium carbonate / glycerol impregnated filter rather than an absorption solution. The modified badge had a higher collection rate but also greater dependence on air velocity.

Also to gain higher sensitivity, Scheeren et al (unpublished) used a short circular badge to a design by Willems (1990) and investigated both TEA and potassium carbonate as collection media.

Hallberg and Rudling (1989) have designed a liquid medium sorbent badge, in which the diffusion is controlled by a number of small channels. The sampler was designed to be versatile; sodium carbonate/ hydrogen carbonate buffer was used as the absorbing medium for SO₂, and dilute sulfuric acid was used as the absorbing medium for ammonia (see below).

Ammonia

Diffusive sampling of NH₃, too, has its source in workplace air monitoring applications. Mazur (1978) described a rectangular badge, based on the organic vapour badge marketed by Abcor Inc. The charcoal cloth collection element was replaced with an acid-impregnated glass fibre pad and the diffusion screen by a charcoal impregnated glass fibre pad pre-treated with alcoholic KOH. Kring et al (1982) described a badge-type sampler with a multicavity diffusion path and absorber solution, which was analysed chemically with specific reagents contained in plastic blisters. Versions were available for NH₃, NO₂ and SO₂. For NH₃, the absorbing solution was boric acid and sodium potassium tartrate, and the colour development based on a modified Nessler's reagent.

A parallel development was described by Benedict, Reiszner and West (1983). This used the same sampler as for SO₂ (Reiszner and West, 1973) and also incorporated boric acid as the collection solution and the Nessler reaction. Analysis by ion-selective electrode was offered as an alternative.

More recently, the ideas incorporated in workplace monitors have been extended to develop samplers for environmental monitoring. Willems (private communication) has described an extension of the Benedict sampler. As with the EPA/Monsanto badge for NO₂, the modification maximises the sampling rate by having a design of large surface area and short diffusion path, and relies on an impregnated filter for adsorption. Tartaric acid was found to be the best coating. Face velocity effects are considered not significant but were tested only between 1 - 3 m/s. Excellent correlation between monitors and an impinger reference method was found in field trials; a small bias (about 10%) was noted, but not explained. Concentrations of (particulate) ammonium salts in the Netherlands were not thought sufficient to explain the higher impinger results.

Frenzel has also used the Palmes tube principle successfully for NH₃. In an unpublished paper (Frenzel, Grimm and Druetzmacher), he uses standard laboratory glass vials (4.3 cm x 1.72 cm diameter) the bottom of which have been treated with phosphoric acid. Ammonia (as ammonium phosphate) is dissolved in 50µl water and determined by flow injection analysis. The detection limit was 1.2 µg/m³ for a sampling time of 24 hours. The sampling rate was close to theoretical, and (high) wind speed effects were eliminated by covering the end of the sampler with microporous PTFE tape. Contamination from laboratory air and water was a problem. Field trials against impinger sampling were encouraging, but were complicated by the difficulty of eliminating particulate matter in the impingers by pre-filters.

Organic gases (Volatile Organic Compounds or VOCs)

The EPA/Monsanto badge (see nitrogen oxides) had been developed initially for ambient air monitoring of chlorinated hydrocarbons, and was evaluated extensively in laboratory and field trials. It is described in Wooten et al., 1983, but more accessible references are Wooten et al., 1984 or Lewis et al., 1985. In its original form, it used a thermally desorbable solid sorbent cartridge in place of the glass fibre filters in the cavity between the diffusion screens. Porapak R was used for a variety of chlorinated hydrocarbons, but the sampler can easily be used or modified for a wider

range of organic volatiles, including aliphatic and aromatic hydrocarbons (Coutant, 1985; Coutant, 1986). In Wooten et al., 1984 and Lewis et al., 1985, Tenax is preferred to Porapak because the latter gave poor recoveries of low levels of some chlorinated hydrocarbons.

The EPA/Monsanto badge has been evaluated alongside passivated canisters in an ambient air field study (Varns, et al., 1990). In this study, the 'passive' sampling devices agreed with respective canister data in assessing the targeted volatiles (benzene, toluene, chlorobenzene and dichlorobenzene) at four sampling sites.

The Perkin-Elmer tube sampler (Brown, Charlton and Saunders, 1981) on the other hand, was developed for workplace air monitoring. It too uses a thermally desorbable sorbent, but the diffusion path is simply an air gap at one end of the tube between the sorbent and a draft screen. Initially validated for benzene, it has been used subsequently for a wide range of organic volatiles, particularly hydrocarbons (HSE, 1989: MDHS 66). It has been adapted for ambient air monitoring by Choo-Yin and Layton-Matthews (1987). In this modification, a wide-bore adaptor is added to the end of the tube; during sampling, the sorbent is tipped into the adaptor, where it presents a larger surface area to the sampled atmosphere and after sampling it is tipped back again for desorption.

More recently, improvements in sorbents and blank levels have enabled the Perkin-Elmer tube to be used for ambient air measurements without modification. According to Saunders (private communication), ppb levels of benzene can be monitored accurately in 14-day exposures using Chromosorb 106.

The same tube, with Tenax as sorbent, has been used for the determination of VOCs in indoor air (Brown, Crump and Gardiner, 1992). With this sorbent, the more volatile fraction is less efficiently sampled because of back diffusion over the long sampling times. However, good agreement was found between intermittent pumped sampling and continuous diffusive sampling over 31 days for toluene, xylene and total VOC. Agreement for decane was less good. These authors observed that the same sampling rates were obtained for tubes with and without the diffusion cap, and did not use the latter in later experiments in case of misuse by inexperienced operators. However, problems can be encountered at very high face velocities if a draught shield is not used.

A similar Chrompack tube has been used to monitor ppb levels of volatile organic compounds (VOCs) in indoor air (De Bortoli, 1987). This study looked particularly at the changing uptake of benzene on Tenax tubes. As noted by Brown and Walkin (1981) uptake decreases initially but stabilises after about 24 hours (this effect is much less with Chromosorb 106).

A problem, however, with thermal desorption methods is that some adsorbents give rise to artefacts (particularly benzaldehyde) on reaction of the polymeric sorbent with NO_x and ozone. The levels are very low and are insignificant for workplace air but may be serious in environmental applications.

The 3M charcoal-based badge sampler has also been used for ambient as well as indoor air monitoring (Coutant and Scott, 1982). These authors looked at 3M and two other commercial badges, but found that generally high blanks and poor sensitivity limited their usefulness for ambient air monitoring. A later study (De Bortoli, Mølhav and Ullrich, 1987) included an interlaboratory comparison of monitor results taken from a standard vapour atmosphere of nine common solvents (total VOC $5\text{mg}/\text{m}^3$). With the exception of some polar compounds (for which desorption efficiency might have been a problem), agreement between badge results and reference pumped tubes was good, although reproducibility was poor (about 13% on average). The statistical analysis suggested that the interlaboratory variance was some 2 - 2.5 times the intralaboratory variance. Encouraging results were also found by Cohen et al. (1990), Shields and Weschler, (1987) and Wolkoff et al (1991) using 3M badges for monitoring VOCs.

Formaldehyde

One of the most rapid and sensitive methods of determining formaldehyde is HPLC of the 2,4-dinitrophenylhydrazone of formaldehyde. This method has been used in workplace air monitoring as a pumped filter method and can give a sensitivity of about $1\text{ ug}/\text{m}^3$ (1 ppb) for a 50

litre sample (Levin, et al., 1985). These authors also developed a diffusive version (Levin, et al., 1988) and demonstrated that it could be used to monitor down to 5 ppb in an 8-hour sample. An almost identical diffusive sampler has been developed by Grosjean and Williams (1992).

The EPA/Monsanto badge has also been modified for the measurement of formaldehyde (Mulik et al., 1989), and forms the basis of EPA Indoor Air Method IP-6C (EPA, 1990). However, EPA do not currently advocate its use because of blank problems (R. Lewis, private communication). Ishii and Aoki (1988) have described a diffusion sampler based on DNPH which uses an absorption solution of tetramethylene sulfone-water-DNPH. The authors claim a lower detection limit of 2ppb for 24 hours sampling.

Artifact problems may arise when using DNPH-based samplers in atmospheres containing relatively high ozone levels (Arnts and Tejada, 1989), although this has been disputed by Levin (unpublished). Grosjean and Williams (1992) found that spiked filters mounted in diffusive samplers and exposed to 120ppb ozone for 24 hours lost approx 56% of the hydrazone, but admitted that this exposure to ozone was unrepresentative of most outdoor situations.

Stability of the hydrazone may be a problem with adsorption tubes (Oehme, private communication), although an extensive study undertaken on behalf of the BCR (Levin, 1992) suggests both impregnated filters and solutions are stable for many months.

A Palmes-type tube has also been used for formaldehyde, for example as described by Geisling et al. (1982). These authors used a capped glass tube, 9.5cm x 2.4cm i.d., with a bisulphite-impregnated glass fibre filter as collection element. Such devices, however, are less sensitive than badges, because of the lower collection rate, and the authors quote a detection limit of 25 ppb for a 1-week sample.

Ozone

Hangartner and Burri (1987) and Hangartner (1990) used a Palmes-type tube about 5 cm by 1 cm i.d. with a dipyrildylethylene adsorption medium and MBTH analysis of the released aldehyde. The detection limit is claimed to be 3 $\mu\text{g}/\text{m}^3$ for a sampling time of 1 week and absorbance correlates well with an independent UV monitor method in field trials. The authors also looked at SO_2 , NO_2 and formaldehyde in Palmes-type samplers.

The ozone sampler developed by Ogawa has been noted above (see nitric oxide). The joint study (Mulik, et al., 1991) demonstrated good agreement between Ogawa PSDs and weekly real-time averages from instrumental methods. For ozone the agreement was, on average, within 10%, for measurements in the 10-50 ppb range. This work is being extended by EPA, Harvard and the developer, Hirano (Koutrakis, et al., unpublished). The sampler consists of a badge clip and a canister-shaped body containing two coated glass fibre filters. The principle component of the coating solution is nitrite ion, which is oxidised to nitrate by ozone. After sample collection and water extraction, the nitrate ion is determined by ion chromatography.

A colorimetric diffusive sampler has been developed for ozone (Grosjean and Hisham, 1992), which is based on a colorant (indigo carmine) which fades on reaction with ozone and can be estimated by reflectance colorimetry. Detection limits are 30ppb.day and 120ppb.day using a plastic grid and a PTFE filter respectively as diffusion barrier. Field tests have been conducted (Grosjean and Williams, 1992) and show little interference from NO_x , peroxyacetyl nitrate or formaldehyde.

RECOMMENDATIONS FOR RESEARCH

Development of validation protocol

An important need is to develop a standardised evaluation protocol for diffusive samplers along the lines of the CEN workplace monitoring standard (CEN prEN 838). Otherwise, validation will continue to be arbitrary and haphazard. A key feature would be field trials against established independent methods. A difficulty arises here, in that conventional methods that might be used as

the independent method may be more suitable for short-term or intermittent sampling. Comparisons with long-term TWA measurements from diffusive samplers may therefore be unmatched and misleading.

Alongside the evaluation protocol should be an agreed acceptance criterion similar to CEN prEN 482 - in terms of bias and precision or a combination of both.

Ambient air movement

As noted above, it is well established that diffusive sampling devices can experience starvation due to low face velocities. For most badge type samplers, the effect begins to get significant at velocities below typically 0.1 m/sec, although for tube type samplers, the critical velocity is about two orders of magnitude lower. In most outdoor situations, face velocities will be much greater than these values, but for some indoor air applications, it may be necessary to have a fan nearby to create the necessary air movement. A possible research area might be to design and build a sampler with integral fan, whilst still being small enough to be user friendly and cost effective. An alternative in some situations is to suspend the samplers on a fine thread (unspun silk is suitable) to maximise the effect of slight air movements.

Analytes studied

There appears to be a wide disparity in the research effort, development and usage of diffusive sampling for different analytes. Information on NO₂ far outweighs everything else put together. There is an obvious need, therefore, to investigate in fuller detail the less common applications.

On the other hand, there may be good reason why these other applications are less common. Is SO₂ more susceptible to irreversible adsorption on sampler bodies? Is NH₃ monitoring compounded by aerosols? Are Perkin-Elmer tubes impractical because of oxidation artefacts? More research is needed and more well-planned and well-executed field trials conducted to identify (and hopefully solve) any problem areas.

Detection limits

Attempts should also be made to push diffusive samplers to even lower detection limits. Improved analytical sensitivity coupled with the elimination of contamination (particularly in sampler manufacture) should enable the measurement of ppb levels of pollutants over sampling periods of a day or so. Only then will diffusive samplers have reached their potential as a cheap, cost-effective method for environmental monitoring.

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