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Applied Occupational and Environmental Hygiene

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uaoh20

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Version of record first published: 30 Nov 2010

To cite this article: Martin Harper (2001): Performance Evaluation of On-Site Colorimetric Air Sampling Techniques, Applied Occupational and Environmental Hygiene, 16:12, 1092-1096

To link to this article: http://dx.doi.org/10.1080/10473220127407

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Applied Occupational and Environmental Hygiene
Volume 16(12): 1092–1096, 2001
1047-322X/01 $12.00 + .00

Analytical Instrument Performance Criteria

Performance Evaluation of On-Site Colorimetric Air Sampling Techniques

Kevin E. Ashley, Ph.D., Column Editor

Reported by Martin Harper

One of the oldest and simplest methods for analysis of chemicals is through the development of color as used, for example, in determining the end point of titrations. Chemicals that change color in response to the presence of another chemical species lend themselves to rapid and simple field analyses, of which the most basic method is the use of litmus paper. Gradual changes in color with concentration can be compared to standards simply by eye, or by means of an instrumental color comparator, spectrophotometer, or densitometer. This equipment is uncomplicated, relatively cheap, and portable, and the costs of field measurements using these techniques compare favorably with those that involve sampling followed by laboratory analysis. Since access to a sophisticated laboratory is not required, these devices have great promise for use in remote locations. The main advantage of on-site analysis, however, is the potential for rapid assessment and response to problem situations in the workplace.

In air sampling, colorimetric and similar devices can be designed for short-term, near real-time monitoring or for longer term time-integrated measurements. Their mode of sampling can be further classified as either "active" (pumped) or "passive" (diffusive). Depending on the type of sampling, the type of reaction, and the type of measurement, the theory of operation leads to linear or semilinear relationships between the measurement (length or depth of stain, absorbance, or reflectance) and the concentration of the species being measured. However, little credence is given to theoretical relationships without adequate confirmation from performance testing, and rightly so, as there are many possible interferences that may be encountered during sampling and analysis. This article covers the available standards for performance evaluation of these types of equipment. A useful guide to the types of accessible equipment has already been published.[1]

Detector tubes are generally active, near real-time, length-of-stain samplers, although both active and passive time-integrated versions exist. They are normally used for screening measurements and rarely for regulatory compliance purposes, since few regulations require near real-time measurements and because large numbers of samples would be needed to encompass a long-term sampling period with statistically adequate coverage. The performance of these tubes may be evaluated in accordance with standards that have been published by the American National Standards Institute (ANSI) (U.S.) and European Standards Committee (CEN) (Europe). In the United States, this work is undertaken by third-party certifier, the Safety Equipment Institute (SEI), while in Europe, the manufacturer often performs the tests.

Diffusive samplers are normally long-term, time-integrated, passive samplers, although some are available with sufficient sensitivity to be used for shorter periods. They possess a wide variety of analytical conclusions, including versions that simply change color at a specific alarm dose. Samplers that are used to demonstrate compliance with regulations or other exposure standards should provide results within a specific accuracy range. These ranges are specified in standards issued by the U.S. (National Institute for Occupational Safety and Health; NIOSH) and Europe (CEN). Several protocols for evaluating the performance of these samplers have been published (NIOSH, CEN, American Society for Testing and Materials (ASTM), ANSI, International Organization for Standardization (ISO)), but there is currently no single agency undertaking the actual work of validation.

Mechanical instruments that use colorimetric methods are also available. In general, these are not small enough to be worn as personal dosimeters for entire work shifts, although some are handheld. They are typically used for leak detection or in fixed-point alarm monitoring. There is little performance characterization activity outside of that undertaken by the manufacturers themselves; however, the Environmental Protection Agency's (EPA) Environmental Technology Verification (ETV) Program could be useful in this area.

Detector Tubes

The operation of short-term detector tubes is relatively simple. The ends of the tubes are broken, using a device supplied by the manufacturer, to ensure an opening wide enough to allow unrestricted flow through the tube. For near real-time monitoring (often called "grab" sampling), the tube is fitted in the appropriate leak-tight orifice of a manually operated bellows or piston-type pump. One advantage of such pumps is that they may be considered safe for use in flammable atmospheres. Also, they are not affected by, nor are they sources of, radio frequency interference. If powered pumps are available, then intrinsic safety and radio frequency interference may be serious considerations. Air is pulled through the detector tubes by applying the appropriate number of strokes to the bellows or piston. Typically, each stroke is about 100 ml, and the number of strokes required may be as little as one or as many as one hundred. In many cases, the sensitivity of the tube can be enhanced by increasing the number of strokes. Some pumps are equipped with a counter that records the actual number of strokes. This is very useful, as it is surprisingly easy to lose track of as few as ten strokes when distracted. Care must be exercised to ensure the completion of each sampled stroke; adequate time must be allowed for the vacuum to reach equilibrium with atmospheric pressure.

Note that as the number of required strokes increases, it becomes less possible to refer to the sample as instantaneous. A considerable amount of time is required to complete 100 strokes. Long-term detector tubes may be active or passive. Active samplers use a small personal sampling pump to pull air through the tube at a defined flow rate. The tube is typically calibrated in terms of exposure dose (exposure × time) to allow a time-weighted average concentration to be calculated from the time of sampling. Long-term diffusive-type tubes are placed in a special holder after the sampling end has been opened. These are also calibrated in terms of exposure dose.

Many color reactions are used in the large number of available detector tubes,(2) but there are three general classes that are widely used: reduction (e.g., of chromate or iodine pentoxide), pH indicator color change, and reaction with dyes such as *o*-tolidine or tetraphenylbenzidine. These reactions are generally not specific to a single chemical, and cross-sensitivity is often an issue that must be considered. Sometimes the same reaction might be involved for two similar chemicals, with only the tube calibration being different. The reacting chemicals are coated on granular, generally inert substrates such as silica gel, alumina, ground glass, pumice, or resin. Precleanse layers may be added to remove water vapor or other interfering chemicals (such as hydrogen chloride in the determination of hydrogen cyanide), or there may be layers designed to react to form a secondary analyte that undergoes the color reaction (e.g., liberation of halogens from halogenated hydrocarbons). The reactivity of these chemical systems may preclude a long shelf life for the product, although this can be improved by refrigerated storage.

In the general case where the sampling period is relatively short, and the flow rate is relatively high, complete equilibrium is not reached between the reactant in the gas or vapor phase and that on the solid substrate, and the length of the color reaction, generally called the "length-of-stain" (L), is determined by the kinetic rate of reaction and is proportional to the logarithm of the concentration of the airborne species for a given air volume.(3) If the reaction rate at which equilibrium can be achieved is sufficiently fast, then the length-of-stain is directly proportional to the concentration. For long-term detector tubes, equilibrium is achieved, but combination of the governing equation with Ficks' Law (see below) results in a more complex, nonlinear relationship.

In all cases, the length-of-stain is compared to a calibration marked on the outside of the tube, with extrapolation to values between those marked. This is generally done by eye. The type of color change may be very obvious (e.g., white to dark blue) or less so (e.g., white to pale salmon-pink). In addition, although tubes are designed to provide sharp and level reaction fronts where possible, boundaries may be diffuse and irregular, making accurate determination difficult. Reading the concentration value is probably the single largest source of error associated with these devices, and the accuracy of determination may not reach the requirements of Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) compliance monitoring. Recently, electronic devices for the reading of tubes that may reduce the subjective component of variation have been introduced. The American Industrial Hygiene Association has published a useful manual on detector tubes.(4)

At the same time that NIOSH was engaged in the Standards Completion Program for air sampling methods development, it was also involved in a program to evaluate detector tubes, and many were found to have accuracies in the ±25 to ±35 percent range. A formal certification program was implemented(5,6) with testing at the NIOSH office in Morgantown, West Virginia, but this was terminated after about 10 years due to lack of funding. In 1986, the SEI began a voluntary program for third-party certification,(7) based on the NIOSH program, that is still in place today. The SEI is a private, nonprofit organization established in 1981 to administer nongovernmental, third-party certification programs to test and certify a broad range of safety and protective products. SEI's certification program is accredited by the ANSI in accordance with ANSI Standard Z34.1-1993, "Third Party Certification Programs for Products, Processes, and Services." The program not only includes product testing every three years, but also requires an annual (initially every six months) quality assurance audit of the manufacturer to ensure compliance with SEI's quality assurance requirements.

EN 1231 is the European Standard that governs the requirements and test methods for short-term detector tubes.(8) ANSI 102 is the U.S. equivalent(9) used by the SEI. In many ways, these documents are similar; however, they differ in several important respects. The ANSI Standard assumes that the detector tubes are designed for a specific concentration, which is referred to as the "test standard," and which is defined in the Standard as the current American Conference of Governmental Industrial Hygienists' Threshold Limit Value (ACGIH® TLV®), although, for example, the tube for benzene is certified at the much higher OSHA PEL. The concentration range for testing purposes is 0.5 to 5 times this value.

The European Standard, on the other hand, recognizes that a useful tube may not meet this exact range, or may operate completely outside of the TLV range. The concentration range for testing is, therefore, defined as that which is claimed by the manufacturer, and the levels are the minimum, maximum, and 20 percent of the maximum value. Another significant difference is that the European Standard requires testing at multiple temperature and humidity levels (approximately 70°F and 50% humidity; 50°F and 20% humidity; and 85°F and 80% humidity), while the ANSI Standard uses only one combination (70°F and 50% humidity). Detector tubes may be affected by temperature and humidity,(10,11) and the ANSI Standard has been criticized for only testing under a single set of environmental conditions.(12)

The final difference is in the calculation of accuracy. The ANSI Standard does not explicitly detail a testing protocol; however, the SEI uses the Military Standard 414(13) to determine quality, following the example of the NIOSH program. Twenty tubes are tested at each concentration level; the mean and standard deviation are used to determine a "Quality Index," which is used to ascertain the probability of "defective units" within a larger lot size (1,301–3,200 units). Approximately 13 percent of this lot are allowed to be above or below the specification limit. The European Standard uses 10 tubes for each test, and calculates an accuracy based on a combination of bias and precision (twice the standard deviation), in a manner similar to NIOSH, for method validation. The accuracy requirement of the ANSI Standard is given as better than 25 percent at one to five times the limit value range, and better than 35 percent at the 0.5 value. The accuracy requirements for monitoring methods in Europe are governed by EN 482,(14) which also uses a multitiered approach. However, because of differences in the method of calculation, the requirements are not strictly comparable.

The European Standard has the advantage of being a more thorough evaluation of environmental factors than the ANSI Standard. However, it is unlikely that tubes are tested to the European Standard on a regular basis, the argument being that consistent quality, demonstrated through ISO 9000 audits, is sufficient. Perhaps the most comprehensive performance evaluation is a combination of the two systems: preliminary evaluation to the European Standard, with ongoing certification through the SEI, or similar, program. It is interesting to note that both Matheson/Kitagawa (Newark, CA) and Gastec (St. Petersburg, FL) have detector tubes that are certified for each of the 21 chemicals listed on SEI's October 2000 Certified Product List, while Draeger (two) and MSA (Pittsburgh, PA) (one) use this system to a much lesser extent. This may reflect a difference in geographic market focus. Other standards are in use in other parts of the world, e.g., Japan.(15) A single, harmonized performance evaluation standard through the ISO is strongly recommended.

Interchangeability

The ANSI Standard includes a statement that advises against the interchange of pumps and tubes from different manufacturers. This declaration is based on historic data from NIOSH,(16) which shows wide variations in readings for certain combinations, particularly when piston pumps and bellows-type pumps are interchanged. The authors of the chapter on detector tubes in the ACGIH Air Sampling Instruments Handbook(1) strongly endorse this recommendation. However, several manufacturers have demonstrated compatibility between their and other manufacturers' equipment in the 30 years since NIOSH published its data, some of which is third-party data.(17,18) The two largest manufacturers have taken out joint advertisements stating their opposition to any interchange of components. Manufacturers advocating interchangeability can use the European Standard, which makes no statement regarding interchangeability, to evaluate a mixed system. The performance of the system, at least in theory, could be certified on an ongoing basis using the ANSI Standard. No manufacturers appear to have taken advantage of this option.

Diffusive Samplers

Diffusive samplers made their first significant impact on industrial hygiene exposure monitoring in the early 1970s.(19) In accordance with Ficks' Law, they operate by diffusion of the contaminant molecules across a defined quiescent air gap to the sorbent. The sorbent can be a thin, flat bed that slowly changes color with exposure, or a long, narrow tube (similar to a detector tube), along which a color change progresses. The thin bed samplers can be compared to a color chart or read electronically in a portable spectrophotometer, while the detector-tube type is normally calibrated for the length-of-stain by markings on the side of the tube. In the former case, the uptake of chemical is proportional to the product of concentration and time, while in the latter case, the continually increasing diffusion path makes the calibration inherently nonlinear. If the former type of sampler is analyzed by absorption, the calibration is generally linear. However, if the analysis involves reflectance, then the calibration is nonlinear. Either the linear portion of the calibration must be used or a correction must be applied to the nonlinear portion of the calibration.

As has been pointed out, many of the diffusive samplers that existed at the beginning of their history have now disappeared from the marketplace. This includes the colorimetric diffusive samplers evaluated by NIOSH(20) in its development of a diffusive sampler evaluation protocol (3M sulfur dioxide monitor, DuPont (Wilmington, DE) Pro-Tek sulfur dioxide and ammonia monitors, and MSA Vaporgard diffusion tubes for sulfur dioxide and ammonia) in the early 1980s. The NIOSH protocol was published in the proceedings of a European conference(21) and has only rarely been used by the majority of sampler manufacturers.(22) In its full version, the protocol required a very large number of tests, using over 200 samplers, and including tests of concentration, temperature, and humidity, as well as issues specific to diffusive samplers, such as ambient wind velocity, orientation to the wind, and reverse and diffusion over time. These factors are still included in more recent protocols. In the interim, various industry(23,24) or university research groups(25) have published validations of passive samplers, although not to a consistent, officially recognized protocol. (However, OSHA did accept the third-party validation of one personal formaldehyde sampler.)(25)

In an effort to gain greater acceptance for the technology, two recent standards have been published by voluntary consensus standards groups in the United States. The ASTM Standard D6246-98(26) is a Practice for the Evaluation of Diffusive Samplers and was supported in its development by NIOSH. It gives specific guidelines for the test protocol and conditions, as well as the method of calculation and requirements for accuracy. The ANSI Standard 104(27) is a guide for the same purpose and was initially supported by OSHA. It does not specify exact test procedures or conditions, and does not require specific limitations on accuracy, only that these be reported in a standard format. This standard references other, more specific standards, such as the ASTM Standard or the European EN 838,(28) which would be acceptable practice under the ANSI Standard. EN 838 is the European standard that governs the performance evaluation of diffusive samplers.

It should be noted that neither the ASTM nor the European Standard was written with the colorimetric type of sampler foremost in the minds of the authors, so issues specific to these types of samplers, such as interreader variation or variation in the time of reading after color development, are not explicitly addressed. Neither the ASTM nor the ANSI protocol has been universally adopted, and both have been only rarely used. It is also important to note that although standards dealing with workplace measurement have the force of law in all European Union countries, their application does not. Thus, again, we are faced with a confusing array of standards with limited use. Replacement of this situation with a single ISO standard, therefore, would also be welcomed. The ASTM standard has been published as an ISO Standard,(29) and it is recommended that this standard be used wherever possible.

Mechanical Colorimetric Samplers

The paper tape cassette monitors manufactured by Zellweger (Lincolnshire, IL) (MDA) and Scott/Bacharach (Exton, PA) (GMD) for isocyanates and other compounds are in this category. Air is drawn through a treated filter material that is wound on a cassette spool. The density of the color development is measured on successive spots to give both near real-time and time-weighted average data. Since these instruments typically are not used for compliance monitoring, there has not been the same call for comprehensive, third-party evaluation, and there is no standard specifically designed for such activity. However, the NIOSH protocols used for direct-reading instruments could be applied, and the EPA ETV Program, operated by Battelle Memorial Institute and other contractors for the EPA, might be suitable in cases where these instruments are used for fence-line or waste-stream measurements.

Conclusions

As with many other areas of industrial hygiene, the evaluation of colorimetric monitors is unevenly covered by a variety of standards from different sources. There is a need to reduce confusion and to harmonize coverage through the development of consensus international standards. However, without the force of law, there has been little incentive for manufacturers to use even those standards that are available. Since regulation in this arena is unlikely, it is up to the consumer to become educated and to require that existing or future performance standards be used. No manufacturer or vendor likes to admit that its products have not met a performance standard.

Unfortunately, the plethora of standards and lack of government recognition also make it less likely that manufacturers will use them. Therefore, regulatory agency recognition of harmonized standards is still needed. It is important to remember that, although some testing is better than none, a good performance evaluation should include all likely sources of potential environmental variation. It should also be kept in mind that independent, third-party evaluations are much more likely to be recognized by government agencies than manufacturers' in-house studies in which there is a perception of a potential for biased presentation of results.

Acknowledgments

The author would particularly like to express his thanks to the Safety Equipment Institute for providing information regarding its detector tube certification program, and to the manufacturers who provided materials.

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