Getting a handle on HAPs

The Clean Air Act depends on our ability to measure hazardous air pollutants – but this is no simple task, as Jim McKinley explains.

It is widely accepted that "what you cannot measure, you cannot control." For controlling the more that 170 compounds plus 17 compound categories identified in the 1990 Clean Air Act as hazardous air pollutants (HAPs), there are two challenges. The first is to develop reliable methods for sampling and detecting the various HAPs in industrial atmospheres. The second is to provide reliable calibration standards for testing those analytical methods and actually quantifying the measurements. Effectively, without a calibration standards there can be no effective measurement, which in turn means no control of the HAP.

Validating an analytical method requires testing the method on known samples that simulate actual samples for which the method is designed. For air analysis, gas standards are required and should include variable relative humidity. If controls are to be enforced, the composition of the calibration standard should be traceable to accepted national standards.

Historically, calibration gas standards have become equated with static gas mixtures, and more specifically, with high-pressure gas mixtures. But less than a third of the compounds identified in the original HAPs list published by the Environmental Protection Agency (EPA) are available as static gas mixtures at any concentration. Some of the remaining two thirds of the compounds are simply not 'gas analysis' candidates. Examples include asbestos, phosphorous, heavy metal salts and other compounds that are basically dust inhalation hazards as opposed to vapor hazards. Among the remaining HAPs presenting vapor hazards, many of the compounds have very low vapor pressure and are highly reactive, so they are not really candidates for high-pressure static mixtures. As a result there has been limited progress in the HAPs program.

To circumvent this technical barricade, calibration gas standards for that latter group of compounds must be generated in-situ, using dynamic gas blending techniques.

The three key elements required for a dynamic gas blending system are: 1) a source of known base mixture; 2) a dilution apparatus; and 3) and an effective delivery method.

The big challenge is element 1 - obtaining a known base mixture containing the HAP compound. Dynamic dilution requires two flows: a base flow containing the HAP compound, and a dilution flow to form the required mixture concentration. In the case of HAPs the base flow must be generated from a compound with vapor pressure that is far less that atmospheric pressure. The key resources for creating that mixture are permeation tubes, diffusion tubes, and dynamic headspace vapor dilution. Each of these techniques creates a base concentration flow by mixing the HAP vapor with a small dilution flow.

In permeation tubes a small quantity of the pure HAP compound is sealed inside a length of plastic (usually Teflon®) tubing. The HAP vapor permeates through the tubing wall (membrane)

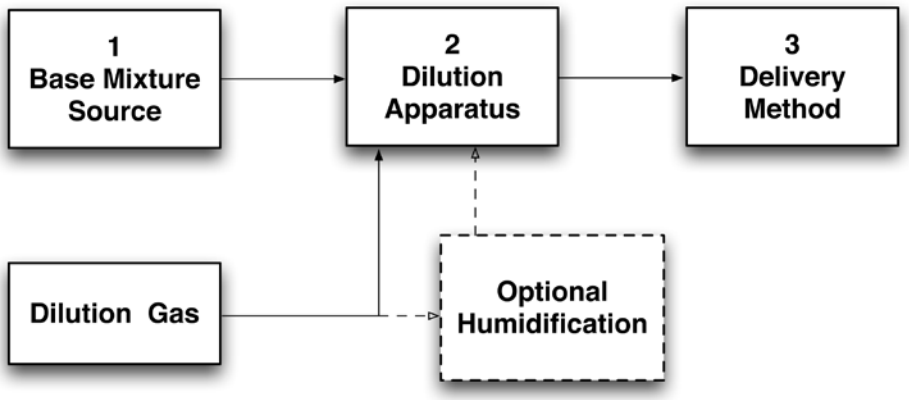

Figure 1: *HAPs handle*

The logical choice for element 3, the delivery method, is the analytical sample acquisition system, or as large a portion of that system as practical. The dilution apparatus (element 2) is conceptually simple, but requires extreme care in design and choice of components. Surfaces contacting low concentrations of the HAP compounds should be minimal, clean, and as inert to the HAP compound as possible. Several stand-alone dilution systems are commercially available, plus gas standards-generating instruments usually have dilution apparatus built into the basic instrument.

and mixes with a small flow of clean carrier gas flowing over the outside of the tube to form the base flow.

At constant temperature the permeating HAP vapor forms a very low, but extremely stable flow that is proportional to the partial pressure difference between the vapor pressure of HAP inside the tube and the near zero vapor pressure of the HAP outside the tube. The permeate flow is not affected by changes in pressure around the permeation tube and only rarely by choice of carrier gas. To measure the permeation rate the tube is held at its operating temperature

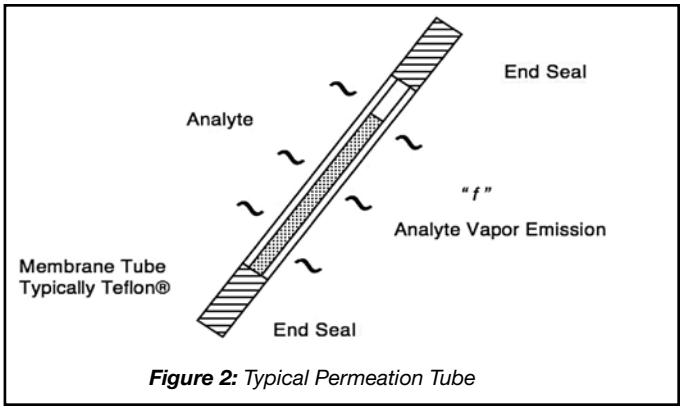

Figure 2: *Typical Permeation Tube*

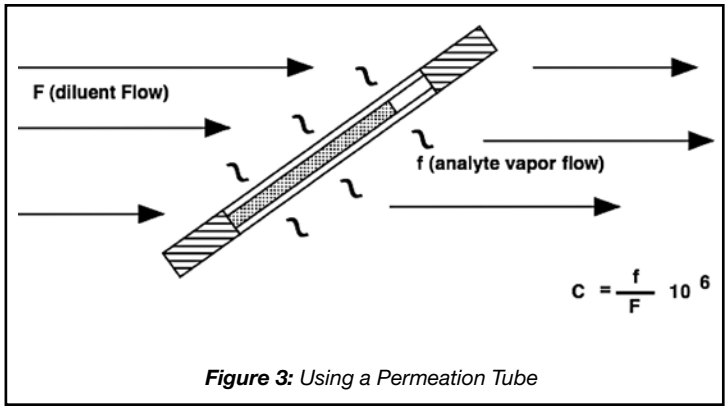

Figure 3: *Using a Permeation Tube*

and weighed periodically to measure the rate of weight loss. If the temperature, time and weight measurements are traceable to US National Institute of Standards and Technology (NIST) standards, then the permeation flow rate is traceable to NIST through those physical standards. The permeation tube method is the most stable, easy to use, and least subject to random error of the available vapor generation methods.

The diffusion tube method is similar is similar to the permeation method, but the HAP vapor flow is controlled by the partial pressure difference across a capillary tube rather than a membrane. Diffusion tubes work best for medium to high boiling point compounds, and are not recommended for those with a low boiling point such as acetaldehyde and acrolein. Innovative designs make it possible to use diffusion tubes with subliming solids like naphthalene and phenol. A major advantage of the diffusion tube is that at any given temperature a much higher vapor flow is possible, so higher base concentrations are possible. In cases where the HAP compound is temperature-sensitive, the diffusion tube method can produce mixtures at lower operating temperature than permeation tubes.

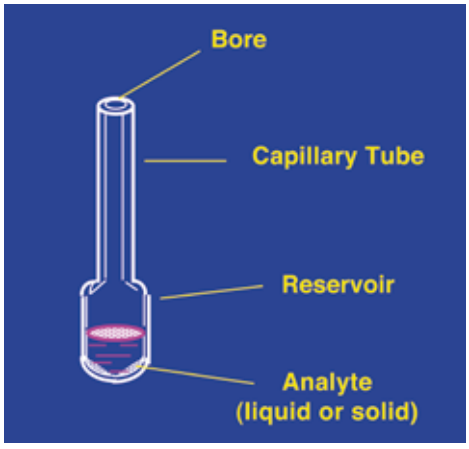

Figure 4: *Basic Diffusion Tube*

There are two main drawbacks with diffusion tubes. First, the flow through the capillary tube depends on the carrier used and is pressure dependent, so the technician must measure emission rate (HAP flow) at actual operating conditions. Also, since the capillary tube is an open channel, pressure transients affect the instantaneous flow. The second drawback is that capillary tube contamination can result in significant changes in the output flow. To achieve traceability through the same path as the permeation tube method, additional measurement and operating pressure control is required. In some respects the diffusion tube method is more fundamental than the permeation method, because flow across a capillary depends solely on measurable physical characteristics. But measuring and controlling the emission is simpler for permeation tubes.

In the dynamic headspace method, passing a small flow of carrier gas directly over the HAP compound (held at constant, known

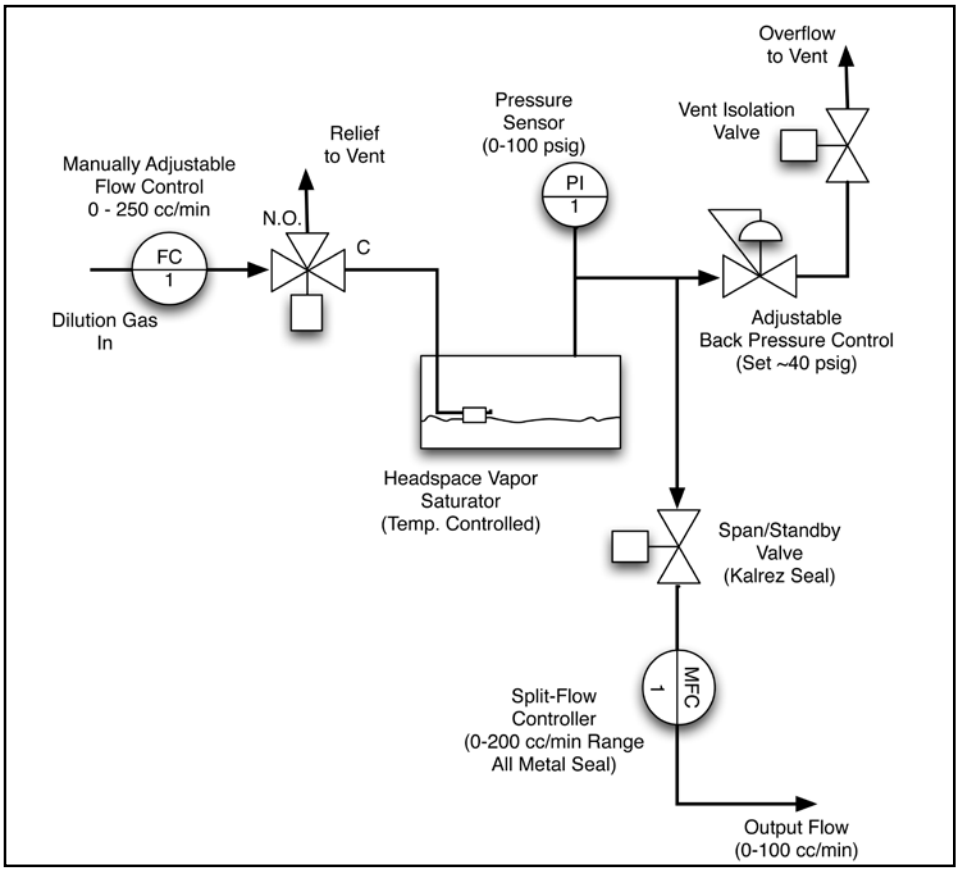

Figure 5: *Dynamic Headspace Flow*

HAPs Calibration Gases: 0 = available X= unavailable

Chemical Abstracts Service (CAS)

registry number	Name	Cyl. Gas	Perm. Tube	Diff. Tube	Head Space
75070	Acetaldehyde	X	X	0	0
60355	Acetamide	0	X	X	X
75058	Acetonitrile	X	X	X	X
107028	Acrolein	X	X	0	0
107131	Acrylonitrile	X	X	X	X
107051	Allyl Chloride	X	X	X	X
62533	Aniline	X	X	X	X
71432	Benzene	X	X	X	X
100447	Benzyl chloride	X	X	X	X
92524	Biphenyl	0	X	X	X
117817	Bis (2-ethylhexyl) phthalate (DEHP)	0	X	X	X
542881	Bis (chloromethyl) ether	0	X	X	X
75252	Bromoform	X	X	X	X
106990	1,3-Butadiene	X	X	X	X
75150	Carbon disulfide	X	X	0	0
56235	Carbon tetrachloride	X	X	X	X
463581	Carbonyl sulfide	X	X	0	0
120809	Catechol	0	X	X	X
7782505	Chlorine	X	X	0	0
108907	Chlorobenzene	X	X	X	X
67663	Chloroform	X	X	X	X
107302	Chloromethyl methyl ether	0	X	X	X
126998	Chloroprene	X	X	X	X
95487	o-Cresol	0	X	X	X
108394	m-Cresol	0	X	X	X
106445	p-Cresol	0	X	X	X
98828	Cumene	X	X	X	X
111444	Dichloroethyl ether (Bis (2-chloroethyl) ether)	0	X	X	X
68122	Dimethyl formamide	0	X	X	X
57147	1,1-Dimethyl hydrazine (UDMH)	0	X	X	X
131113	Dimethyl phthalate	0	X	X	X
77781	Dimethyl sulfate	0	X	X	X
123911	1,4-Dioxane (1,4-Diethylenoxide)	X	X	X	X
106898	Epichlorohydrin (l-Chloro-2,3-epoxypropane)	X	X	X	X
140885	Ethyl acrylate	X	X	X	X
100414	Ethyl benzene	X	X	X	X
51796	Ethyl carbamate (Urethane)	0	X	X	X
75003	Ethyl chloride (Chloroethane)	X	X	X	X
106934	Ethylene dibromide (Dibromoethane)	X	X	X	X
107062	Ethylene dichloride (1,2-Dichloroethane)	X	X	X	X
107211	Ethylene glycol	0	X	X	X
75218	Ethylene oxide	X	X	X	X
75343	Ethylidene dichloride (1,1-Dichloroethane)	X	X	X	X
50000	Formaldehyde	X	X	X	X
76448	Heptachlor	0	X	X	X
118741	Hexachlorobenzene	0	X	X	X

registry number	Name	Cyl. Gas	Perm. Tube	Diff. Tube	Head Space
87683	Hexachlorobutadiene	0	X	X	X
822060	Hexamethylene-1,6-diisocyanate	0	X	X	X
110543	Hexane	X	X	X	X
302012	Hydrazine	0	X	X	X
7647010	Hydrochloric acid (hydrogen chloride)	X	X	0	0
7664393	Hydrogen fluoride (Hydrofluoric acid)	X	X	0	0
7783064	Hydrogen sulfide	X	X	0	0
108316	Maleic anhydride	0	X	X	X
67561	Methanol	X	X	X	X
74839	Methyl bromide (Bromomethane)	X	X	X	X
74873	Methyl chloride (Chloromethane)	X	X	X	X
71556	Methyl chloroform (1,1,1-Trichloroethane)	X	X	X	X
78933	Methyl ethyl ketone (2-Butanone)	X	X	X	X
60344	Methyl hydrazine (MMH)	0	X	X	X
74884	Methyl Iodide (iodomethane)	X	X	X	X
108101	Methyl isobutyl ketone (Hexone)	X	X	X	X
624839	Methyl isocyanate	0	X	X	X
80626	Methyl methacrylate	X	X	X	X
1634044	Methyl tert butyl ether (MTBE)	X	X	X	X
75092	Methylene chloride (Dicholoromethane)	X	X	X	X
91203	Naphthalene	0	X	X	X
79469	2-Nitropropane	X	X	X	X
108952	Phenol	0	X	X	X
75445	Phosgene	X	X	0	0
7803512	Phosphine	X	X	0	0
123386	Propionaldehye	X	X	X	X
78875	Propylene dichloride (1,2-Dichloropropane)	X	X	X	X
75569	Propylene oxide	X	X	X	X
100425	Styrene	X	X	X	X
96093	Styrene oxide	0	X	X	X
79345	1,1,2,2-Tetrachloroethane	X	X	X	X
127184	Tetrachloroethylene (Perchloroethylene)	X	X	X	X
108883	Toluene	X	X	X	X
584849	2,4-Toluene diisocyanate	0	X	X	X
95534	o-Toluidine	0	X	X	X
120821	1,2,4-Trichlorobenzene	X	X	X	X
79005	1,1,2-Trichloroethane	X	X	X	X
79016	Trichloroethylene	X	X	X	X
121448	Triethylamine	0	X	X	X
108054	Vinyl acetate	X	X	X	X
75014	Vinyl chloride	X	X	0	0
75354	Vinylidene chloride (1,1-Dichloroethylene)	X	X	0	0
95476	o-Xylene	X	X	X	X
108383	m-Xylene	X	X	X	X
106423	p-Xylene	X	X	X	X

temperature) to saturate the carrier flow with the HAP vapor forms the base mixture. This initial mixture, however, is not stable. The slightest increase in pressure or decrease in temperature leads to condensation and significant errors, so in practice the carrier is saturated at elevated pressure. Reducing the total pressure immediately after saturation stabilizes the base mixture. This method is most useful for compounds with very low vapor pressure and for making relatively 'high concentration' mixtures.

The headspace method is, in principle, a fundamental method that can generate known concentrations if the vapor pressure characteristics of the HAP compound are well known. The method can always produce a percent-of-saturation value for the HAP.

The methods described above provide a range of options for working with many of the 'impossible' HAP compounds. Permeation tubes are commercially available as 'certified' sources for 88 of the listed HAP compounds. Of those compounds, 32 are not readily available as cylinder mixtures. Many of the other HAP compounds are candidates for permeation tubes, but have not yet been studied.

Diffusion tubes are also available commercially, but are not widely available with certified emission characteristics like permeation tubes. Typically permeation and diffusion tubes can be used interchangeably in the same gas blending apparatus.

Headspace systems are not yet widely available as standard instruments, but will likely become more popular as the need for gas standards of low vapor pressure compounds grows. SGR

Jim McKinley

Jim McKinley founded Houston, TX-based Kin-Tek Laboratories, Inc. in 1970 and continues serving as president and technical director. He has contributed significantly to the development of techniques and equipment for gas analyzer calibration, extending the number of compounds available in permeation tubes from less than 30 to over 500. Other achievements include developing a method for certifying gas-fed permeation tubes which operate from only the vapor phase of the analyte and extending standard ranges from the low ppm only in both directions - down to sub-pptr and up over one percent. McKinley has also adapted the method from gas-only applications to the addition of trace VOCs to water. Contact Jim at **JmcKinley@kin-tek.com** or visit **www.kin-tek.com**