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TECHNIQUES FOR THE GENERATION AND MONITORING OF VAPORS

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TECHNIQUES FOR THE GENERATION AND MONITORING OF VAPORS*

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ABSTRACT

Controlled test atmospheres can be produced using a variety of techniques. Gases are usually generated by using flow dilution methods while vapors are produced by using solvent injection and vaporization, saturation, permeation and diffusion techniques. The resulting gas mixtures can be monitored and measured using flame ionization, photoionization, electrochemical and infrared analytical systems.

An ideal system for the production of controlled test atmospheres would not only be able to generate controlled test atmospheres, but also monitor all pertinent environmental parameters, such as temperature, humidity, and air flow.

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INTRODUCTION

The preparation and measurement of test atmospheres have concerned those involved with animal exposure experimentation for a long time. Test gas and vapor mixtures must be produced continuously and dynamically to prevent a build-up of unwanted contaminants in the exposure chamber. We will discuss the general techniques of gas and vapor mixture production.[1] We will also discuss several common methods that can be used to monitor the concentration of the test atmospheres. In addition, we will describe an ideal system for the production of controlled test atmospheres.

GAS AND VAPOR MIXTURE GENERATION TECHNIQUES

FLOW DILUTION

The most common method of producing dynamic gas mixtures is the dilution of gases with one another after measuring their flow rates. Gases can be metered as pure components or be previously diluted to facilitate production of low concentrations.

A basic element of a flow dilution system is the variable-area flowmeter (rotometer) which measures the flow of air and contaminant gas. Flowmeters should always be calibrated against a primary or intermediate gas standard at the pressure and temperature conditions of use. Electronic-mass flowmeters (i.e., Kurz, Tylan and Brooks) and controllers, though normally insensitive to pressure and temperature variations, should be calibrated with the gas of interest.

Figure 1 shows a typical flow dilution system in which contaminant gas is continuously blended with air. The range of variable-area flowmeters extends from 5 mL/min to an excess of 300 L/min. Flows as low as 0.1 mL/min can be obtained if electronic-flow devices are used.

Double-flow dilution techniques have been used to obtain low gas concentrations; however, such techniques are not recommended because the resulting pressure changes interfere with the validity of flowmeter readings.

SOLVENT INJECTION

Vapors can be added to a moving airstream by the solvent injection method shown in Figure 2. In this technique, contaminant liquid is placed in a gas-tight syringe and pumped (i.e. Sage Model 355) through a stainless-steel needle surrounded by a heated block. As the liquid encounters the hot needle walls, it evaporates, and the vapors enter the system countercurrent to the moving airstream. If the vaporization rate is too irregular, the vapor-air mixture is passed through a large mixing chamber to dampen vapor pulsations. A cartridge of activated carbon can also be used to reduce concentration irregularities.

SATURATION

High concentrations of air-vapor mixtures can be prepared by the saturation method shown in Figure 3. In this method, air is passed over a boiling, refluxing liquid, and the saturation concentration is determined from the refluxing temperature. The air-vapor mixture is generally diluted to produce the desired concentration.

Although the saturation method appears straightforward, it can yield false concentration information. This is because (1) the solvent vapor volume must be known and added to the air being saturated, (2) the saturation temperature must be known to within 0.5°C, and (3) the air must reside in the flask long enough to come in contact and mix with vaporized solvent. For these reasons, we suggest that a dynamic system using the saturation method be checked by an alternate chemical technique.

PERMEATION TUBES

A dynamic system using a permeation tube (Figure 4) can produce contaminant concentrations in the low ppm range. Commercial examples include Metronics, Analytical Instrument Development Company, and Dynacal. Gas is compressed to the point of liquefaction and sealed inside a type of polymeric container. Contaminant gas in the permeation tube dissolves in and permeates through the tube walls at a constant rate, mixing with the passing, diluent gas. The permeation rate, determined gravimetrically, is highly dependent upon temperature. A difference of 1°C can cause a rate change of 10%. It is imperative, therefore, that proper temperature control is maintained.

DIFFUSION TUBES

Vapors can diffuse through tubes at uniform rates if their temperatures and concentration gradients remain unchanged and if tube geometry remains fixed. Figure 5 illustrates a dynamic system using a diffusion tube. The solvent is contained in a reservoir beneath the diffusion tube. Air passes in and out of a controlled-temperature oven and carries away the vapors which diffuse up through the tube. The diffusion rate, like the permeation rate, is highly dependent upon temperature. The rate is also influenced by the tube's cross-sectional area, its length, and its diffusion coefficient. The diffusion concentration should not only be calculated but also checked by a proper analytical method. As in the permeation devices, the diffusion technique is most useful in the low (<10ppm) concentration range.

GAS DETECTION AND MONITORING TECHNIQUES

Gas and vapor dynamic generation methods can be easily monitored by a number of commercially available analyzers. Although a number of specific monitors exist, only general techniques, which respond to a wide variety of potential test contaminants, will be discussed.

HYDROCARBON ANALYZERS

Hydrocarbon analyzers generally employ the flame ionization (FID) method of detection. Commercial sources include Beckman Instruments, Bendix and Gow-Mac. The sample is first mixed with hydrogen and burned in air; ions and electrons formed in the flame enter a gap between two electrodes and decrease the gap resistance, permitting a current to flow in the external circuit.

The magnitude of the signal is in direct proportion to the number of carbon atoms in the flame. The small current is amplified and converted to a millivolt signal on a meter or recorder.

This analyzer measures total hydrocarbons in a range of 0.1-2000 ppm methane with a response time of about one second. The FID method is insensitive to water vapor and shows diminished response to molecules which contain no hydrogen atoms (i.e., carbon tetrachloride). Although FID systems are relatively sensitive, they show no specificity unless used in concert with a gas chromatograph.

PHOTOIONIZATION DETECTORS

The process of photoionization occurs when an organic molecule is ionized with ultraviolet light via the reaction:

$$R + h\nu = R^{+} + e^{-}$$

where R^{+} is the ionized species and $h\nu$ is a photon which has an energy equal to or greater than the ionization potential of the molecule.

The sensor consists of a sealed, UV light source that emits photons which are energetic enough to ionize many trace species (particularly organics) but do not ionize the major components of air such as oxygen, nitrogen, carbon dioxide, or water. A chamber adjacent to the ultraviolet source contains a pair of electrodes. When a positive potential is applied to one electrode, the created field drives any ions formed by absorption of the UV light to the collector electrode where the current (proportional to concentration) is measured.

The instrument is similar in response to the flame ionization detector but the photoionization detector requires no gases to produce a flame source. This process is nondestructive, and relatively nonspecific. A partial list of species is shown in Table 1 (note that three source lamps are available to fit specific detection needs).[2]

ELECTROCHEMICAL ANALYZERS

Electrochemical analyzers use a sealed module contacting the sample stream through a semipermeable membrane. The gas to be analyzed diffuses through the membrane into the module where it reacts with the electrolyte film on the surface of the sensing electrode. The electrochemical oxidation of the gas releases electrons that cause a current flow from the sensing electrode to the counter electrode. The current is proportional to the concentration. Response specificity is determined by the semipermeable membrane, the electrolyte, the electrode materials, and the retarding potential. This potential is used to retard oxidation of those sample components that are less readily oxidized than the gas of interest.

Electrochemical analyzers are typically single-gas detectors and are used for carbon monoxide, hydrogen sulfide, sulfur dioxide, oxides of nitrogen, ammonia and chlorine. Typical concentration ranges vary from 0.1 to 1000 ppm. Commercial sources include Theta Sensor, Interscan and Energetics Science.

INFRARED ANALYZERS

Infrared analyzers offer a fast, relatively simple, nondestructive, functional-group specific method of gas and vapor detection. This method involves passing infrared radiation through a cell containing the sample and measuring the attenuation of the incident radiation. The light absorbed is proportional, to some degree, to the gas concentration in the cell.

The advent of the microprocessor has had a profound change on the traditional single-beam, single-component analysis. For example, the Foxboro

MIRAN, Model 80 can monitor for 10 compounds simultaneously. The Miran 801 offers multiple-station sampling, signal-averaging capability as well as interference and compensation for water vapor.

The sensitivity of the infrared method varies widely; all organic molecules are absorbed to some degree and detection limits of 0.1 ppm are not uncommon. In addition, oxygen and nitrogen are inactive infrared absorbers but water vapor and carbon dioxide can be significant interference problems in certain infrared regions.

AN IDEAL CONTAMINANT GENERATION AND MEASUREMENT SYSTEM

A high quality, exposure-test system must not only produce and measure the contaminant concentration but also control the temperature, humidity and air flow parameters. Such a system can be constructed using four, commercially available, components: a temperature-humidity indicator, a dual flow-temperature-humidity control system, a series of mass-flow controllers for the contaminant gas and an infrared analyzer to monitor the concentration (see Figure 6).

The flow temperature-humidity control system and temperature-humidity indicator are linked electronically to process the air stream. Direct-reading potentiometers, mounted on the control module, are used to select parameters. The control module shows actual flows, while the indicator displays temperature and humidity.

Basically, the system consists of three separate controlling mechanisms, sensors, and various safety features. Air and water are supplied to the control module; the air then passes through a humidification vessel in which water is maintained at a constant level. The desired humidity is achieved by activating the heater in the water reservoir. The air stream is then split and passes through flow controllers where the airflows are established. These controllers maintain and display the flow at standard conditions, regardless of temperature and pressure variations in the flow system. The humidified air is then heated to the proper level just before it leaves the control module. Sensors placed in the airstream outside the control module measure the actual temperature and humidity.

Once the system parameters are set, the variation in indicated airflow is ±1% full scale. The temperature variation, after the initial overshoot stabilizes, is ±0.1°C, with an accuracy of 0.2°C. The humidity typically varies ±0.5% and is accurate to within 2%, if the indicator is properly calibrated. System conditions are upset slightly when cool water enters the reservoir during the refilling process. However, the heaters react quickly to compensate for such excursions, and conditions return to normal in less than a minute.

After the air flows exit the control system, one flow goes directly to the control animals. The contaminants of interest are added to the other flow. This can be done using mass-flow controllers, diffusion or permeation devices, or some type of solvent-injection technique.

The resulting gas mixture then passes into a Miran Model 80 infrared gas analyzer. All the contaminants are measured periodically using the programmed averaging and wavelength-cycling process. Background concentrations of carbon dioxide and carbon monoxide are monitored as well as any other suspected interferences. The test gas mixture then proceeds to the animal species in the exposure test chambers.

SUMMARY

Controlled test atmospheres can be produced using a variety of techniques. High concentrations of gases can be generated using flow dilution methods. High concentration of vapors can be produced using solvent injection or saturation techniques. Low concentrations of gases or vapors (<10 ppm) can be generated using permeation or diffusion tubes.

The resulting concentrations of gas mixtures can be monitored and measured using flame ionization or photoionization techniques. If greater specificity is desired, then electrochemical and infrared analytical systems can be used.

REFERENCES

1. G. O. Nelson, Controlled Test Atmospheres-Principles and Techniques (Ann Arbor Science Publishers, Inc., Michigan 1971).
2. HNU Systems, Inc., Newton Upper Falls, MA, Bulletin PI-101/375, 1975.

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TABLE 1. Solvent vapor response to photoionization detection techniques.

	Photoionization response[a]		
Class species	9.5 eV 1 amp	10.2 eV 1 amp	11.7 eV 1 amp
paraffins and unsaturated hydrocarbons			
methane	NR	NR	NR
ethylene	NR	L	H
acetylene	NR	NR	H
1-butene	H	H	H
hexane	NR	L	H
chlorinated hydrocarbons			
methyl chloride	NR	NR	H
carbon tetrachloride	NR	NR	H
chloroform	NR	NR	H
dichloroethane	NR	NR	[illegible]
vinylidene chloride	L	H	H
vinyl chloride	L	H	H
trichloroethylene	H	H	H
heterocyclics & aromatics			
phenol	H	H	H
pryidine	H	H	H
benzene	H	H	H
toluene	H	H	H
xylene	H	H	H
styrene	H	H	H
aniline	H	H	H

TABLE 1. (cont.)

Class species	Photoionization response[a] 9.5 eV 1 amp	10.2 eV 1 amp	11.7 eV 1 amp
heterocyclics & aromatics (cont.)			
chlorobenzene	H	H	H
nitrobenzene	NR	L	H
nitrogen compounds			
formamide	NR	H	H
ammonia	NR	L	H
hydrazine	H	H	H
methyl amine	H	H	H
acetonitrile	NR	NR	NR
acrylonitrile	NR	NR	H
sulfur compounds			
sulfur dioxide	NR	NR	NR
hydrogen sulfide	NR	H	H
carbonyl sulfide	NR	NR	H
carbon disulfide	H	H	H
methyl mercaptan	H	H	H
dimethyl sulfide	H	H	H
dimethyl disulfide	H	H	H
aldehydes, ketones, alcohols, acids, esters			
formaldehyde	NR	NR	H
acetaldehyde	NR	H	H
propionaldehyde	L	H	H

TABLE 1. (cont.)

	Photoionization response[a]		
Class species	9.5 eV 1 amp	10.2 eV 1 amp	11.7 eV 1 amp
aldehydes, ketones, alcohols, acids, esters (cont.)			
acrolein	L	H	H
crotonaldehyde	L	H	H
acetone	L	H	H
methanol	NR	NR	H
ethanol	NR	L	H
formic acid	NR	NR	H
acetic acid	NR	L	H
methyl methacrylate	L	H	H
others			
ethylene dibroide	R	H	H
ethylene oxide	R	L	H
tetraethyl lead	H	H	H
phosphine	R	H	H
arsine	R	H	H
iodine	H	H	H

[a] NR-no response; L-low response; H-high response.

FIGURE CAPTIONS

Fig. 1. Typical flow dilution using rotometers.

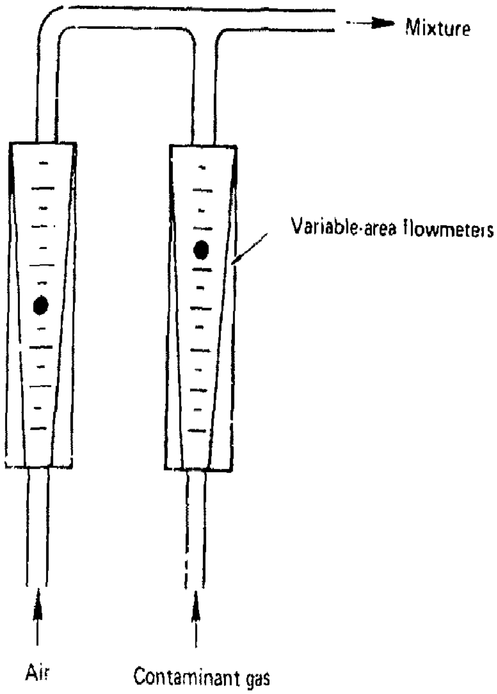
Fig. 2. Solvent injection method to produce vapors in a moving air stream.

Fig. 3. Air saturation method for producing high concentrations of vapors in air.

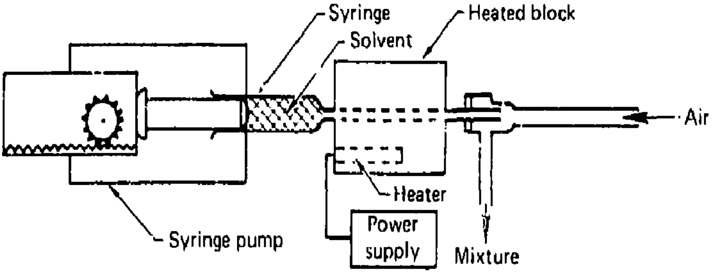
Fig. 4. Gas blending system using a permeation tube.

Fig. 5. Vapor blending system using a diffusion tube.

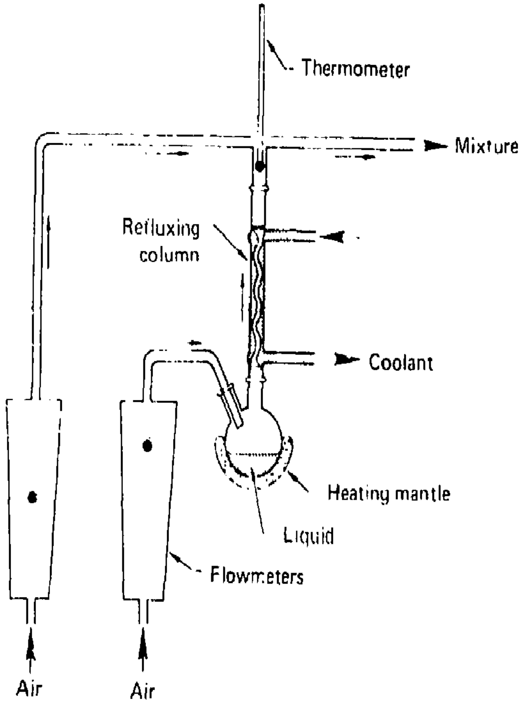
Fig. 6. Schematic of the fully automated system for producing gas or vapor mixtures at a known flow, humidity, concentration, and temperature.



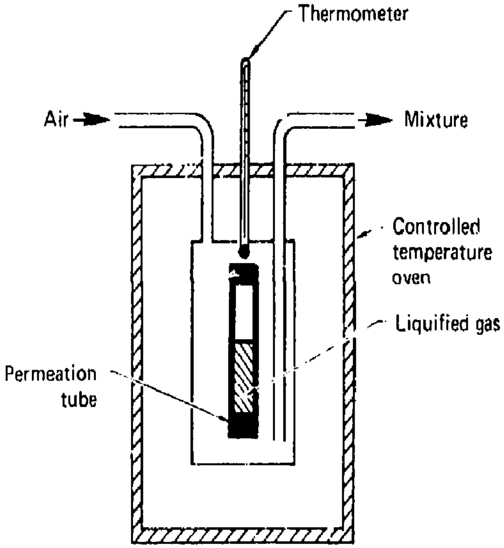
Nelson - FIG. 1


Syringe
Solvent
Heated block
Air
Heater
Power supply
Syringe pump
Mixture

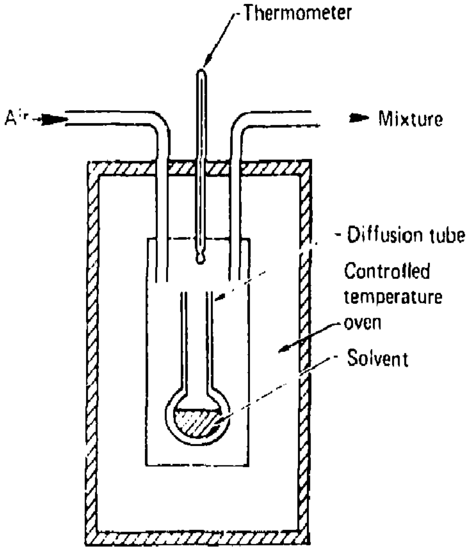
Nelson - FIG. 2


Thermometer
Mixture
Refluxing column
Coolant
Heating mantle
Liquid
Flowmeters
Air
Air

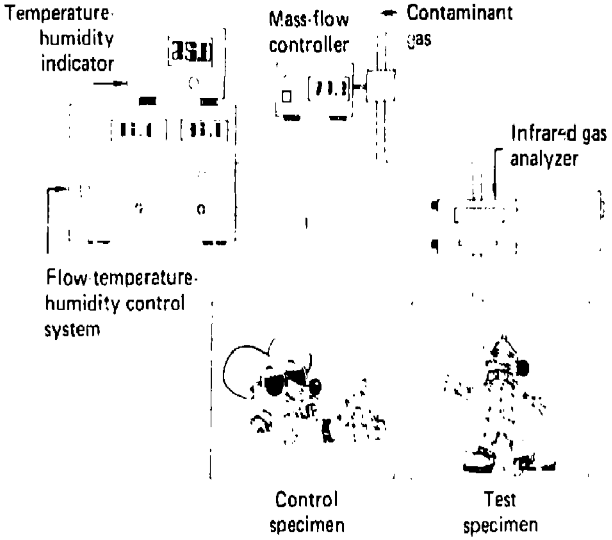
Nelson - FIG. 3


Thermometer
Air
Mixture
Controlled temperature oven
Liquified gas
Permeation tube

Nelson - FIG. 4


Thermometer
Air
Mixture
Diffusion tube
Controlled temperature oven
Solvent

Nelson - FIG. 5


Temperature-humidity indicator
Mass-flow controller
Contaminant gas
Infrared gas analyzer
Flow-temperature-humidity control system
Control specimen
Test specimen

Nelson - FIG. 6