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AMBIENT AIR CONTAMINATION--CHARACTERIZATION AND DETECTION TECHNIQUES

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Until recently, work on indoor contamination has focused primarily on: 1) the criteria air pollutants [oxides of S, N and C, particulates and ozone]; 2) uniquely indoor contaminants [e.g., radon, formaldehyde, tobacco smoke and asbestos]; and 3) the work place pollutants for which American Conference of Governmental Industrial Hygienists (ACGIH) sets guidelines [e.g., organic solvents, metal fumes and wood dust).

Currently, concern centers on outgassing of synthetic construction and maintenance materials such as adhesives, sealants, insulation, wall coverings, cleaners, and electronic equipment inside of new, well-insulated, energy-conserving buildings. The effects of outgassing of synthetic materials in a closed system on human health and productivity is relevant to Space Station.

Indoor contaminants may cause acute reactions (e.g., poisoning by combustion products) or, more often, chronic problems develop due to low-level, long-term exposure. Southwest Research Institute (SwRI) has assisted many industrial clients in determining the source of contamination of the latter type that cause decreased worker productivity.

Chemical characterization of indoor contaminants can be divided into methods which are designed to target compounds, and those which provide for a broad range search. Typical of the former are the National Institute of Occupational Safety and Health methods that often involve either the use of solid adsorbants, or liquid impingers for sampling followed by analysis for target compounds by GC, or colorimetric detection. In cases where an

organic contaminant is suspected but unknown, broader range techniques are required. Samples may be taken by pulling ambient air through adsorbants, e.g., Tenax® and Carbosieve®, which can be desorbed thermally onto GC columns for subsequent GC/MS analysis. A further refinement is to cryogenically focus the trapped organics then to volatilize them as a discrete plug onto a fused-silica capillary GC column, thus obtaining the advantages of increased resolution and overall superior chromatography.[1]

Another approach to organic sampling is the use of polyurethane foam (PUF) plugs which are relatively inert and allow for the collection of large sample volumes (e.g., 285 L/min for 4 hours). PUF samples have been used to sample for trace concentrations of relatively high molecular weight organics, e.g., PCBs, dioxins and pesticides.[2,3]

At SwRI we are characterizing the organics generated from indoor materials at ambient conditions and upon combustion. These experiments are conducted in a closed system (bell jar) with evolved organic compounds being collected on Tenax®, PUF plugs and/or liquid impingers. In one such study organic emissions from a very small electrical fire were characterized. A 5-cm^2 postion of circuit board was placed in the test vessel and a resistor (100 ohm) was overloaded causing it to flare and scorch approximately 1 cm^2 of the circuit board. The duration of the "fire" was approximately 10 seconds. The volume of the test vessel (2.8 L) was then collected on Tenax® and analyzed by GC/MS to reveal a variety of organics (Table 1) including halogenated and aromatic hydrocarbons. Analysis of system blanks also showed that the 5-cm^2 portion of circuit board emitted detectable levels of trichloroethylene and trichlorotrifluoroethane at ambient conditions.

An additional example is provided by the organic emissions from an insulation material that causes dramatic biological effects when combusted.[4] Although a wide variety of organics were characterized (Table 2), the chemical responsible for its unusual biological activity has not yet been identified.

Departing from the discussion of airborne contaminant characterization, I want to mention briefly the detection of critical levels of specific compounds or compound classes with coated quartz oscillators. Sensors of this type may be used to protect equipment as well as people.

Piezoelectric quartz crystals have been used for many years as precision frequency-determining elements in electronic oscillators. When properly cut and prepared, such crystals can maintain the frequency of an oscillator stable within a few parts per million over a nominal temperature range; with close temperature control, frequency stability on the order of parts per billion can be achieved.

The resonant frequency of a piezoelectric quartz crystal is determined by the particular mechanical mode in which the crystal operates and by certain critical dimensions characteristic of the mode. Additionally, as with any mechanical vibrating system, mass added to the surface of the crystal produces a loading effect that lowers resonant frequency. The absolute change in frequency is linearly related to added mass over a substantial range.

At Southwest Research Institute, this basic principle has been applied to measurement of the quantity of odorant in natural gas.[5] The technique employed is to apply a thin coating to the surfaces of a quartz frequency-

control crystal. The materials in the coating were designed to react with tertiary butyl mercaptan (TBM), a commonly used odorant for natural gas. The crystal was connected in an electronic oscillator circuit, oscillation frequency of which was monitored by a precision electronic counter. Odorant-containing natural gas was flowed through a sample chamber surrounding the crystal (see Figure 1), and oscillator frequency changed in inverse proportion to the mass added to the crystal by reaction of the odorant with the crystal coating. By using known concentrations of odorant, it was possible to calibrate the frequency change in terms of odorant concentration.

Approximately 5 parts per million of TBM is commonly used in natural gas as odorant. The instrument described could readily quantify this concentration of odorant with a precision of $\pm$0.5 part per million (Figure 2) and could detect changes in odorant concentration of less than 1 part per million absolute.

Quartz oscillators have a number of advantages for air monitoring including their small size, inherent sensitivity and potential for tailoring either coatings or the active quartz surface for high specificity.

Although the work I have briefly described characterizing organic air contaminants and detecting critical levels of target compounds in air is not related directly to cabin atmospheres the techniques involved become increasingly relevant to NASA as the duration of manned flights is extended and the volume and variety of on-board materials increase.

REFERENCES

1. Pellizzari, E. D. Development of Analytical Techniques for Measuring Ambient Atmospheric Carcinogenic Vapors. EPA Contract 68-02-1228, November 1975.

2. Lewis, R. G., A. R. Brown, M. D. Jackson. Anal. Chem., **49**:1668, 1977.

3. Lewis, R. G. and M. D. Jackson. Anal. Chem. **54**:592, 1982.

4. Kaplan, H. These proceedings.

5. Millar, J. D., H. S. Silvus, L. M. Adams, H. J. Schattenberg III and L. L. Altpeter. Development of a Portable Instrument to Determine Odorants in Gas Distribution Lines. Presented at the International Gas Research Conference, London England, June 1983.

TABLE 1. ORGANICS ARISING FROM FLARING A RESISTOR

Class	Compound	Amount, ng
Br-containing	bromomethane	26,000
	dibromomethane	3,400
	bromobenzene	2,500
	bromoethane	<1,000
Cl-containing	1,1,1-trichloroethane	170,000
	dichlorobenzene	78,000
	trichlorotrifluoroethane	53,000
	1,1-dichloroethane	22,000
	1,1-dichloroethylene	20,000
	dichlorotrifluoroethane	6,400
	chloroform	6,400
	vinyl chloride	<1,000
Aromatic Hydrocarbons	toluene	75,000
	C_2-benzenes	36,000
	benzene	22,000
Aliphatic Hydrocarbons		~80,000
Others	benzofuran	1,800
	benzoaldehyde	1,800
	phenol	<1,000
	acetone	5,200
	methylbutyne	5,200
	methylbutanol	5,100
	methylpentanone	<1,000
	2-furancarboxaldehyde	<1,000
	dimethylethylborane	1,000
	benzonitrile	1,000
	2-propenenitrile	<1,000

TABLE 2. COMPOUNDS GENERATED BY HEATING COMMERCIAL INSULATION

Chloromethylpropane
Dichlorobenzene

Benzene
Toluene
Xylenes

Pyridine
Methylpyridine

Methylpropeneitrile
Benzonitrile
Methylbenzonitriles
Dimethylbenzonitrile

Carbon Disulfide
Methylthiophene
Methylisothiocyanate

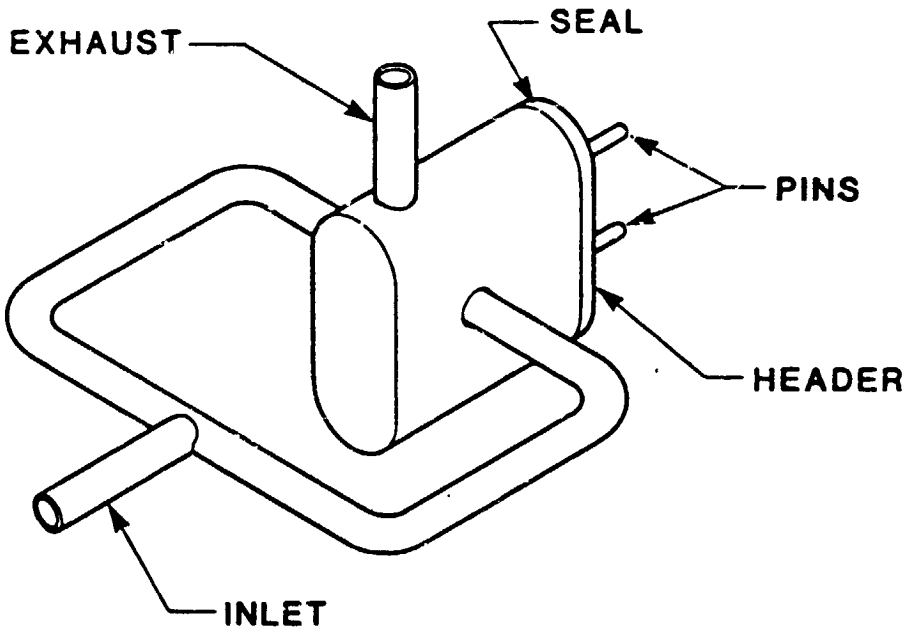

Figure 1. Experimental Arrangement for Evaluation of Quartz-Crystal Odorant Analyzer

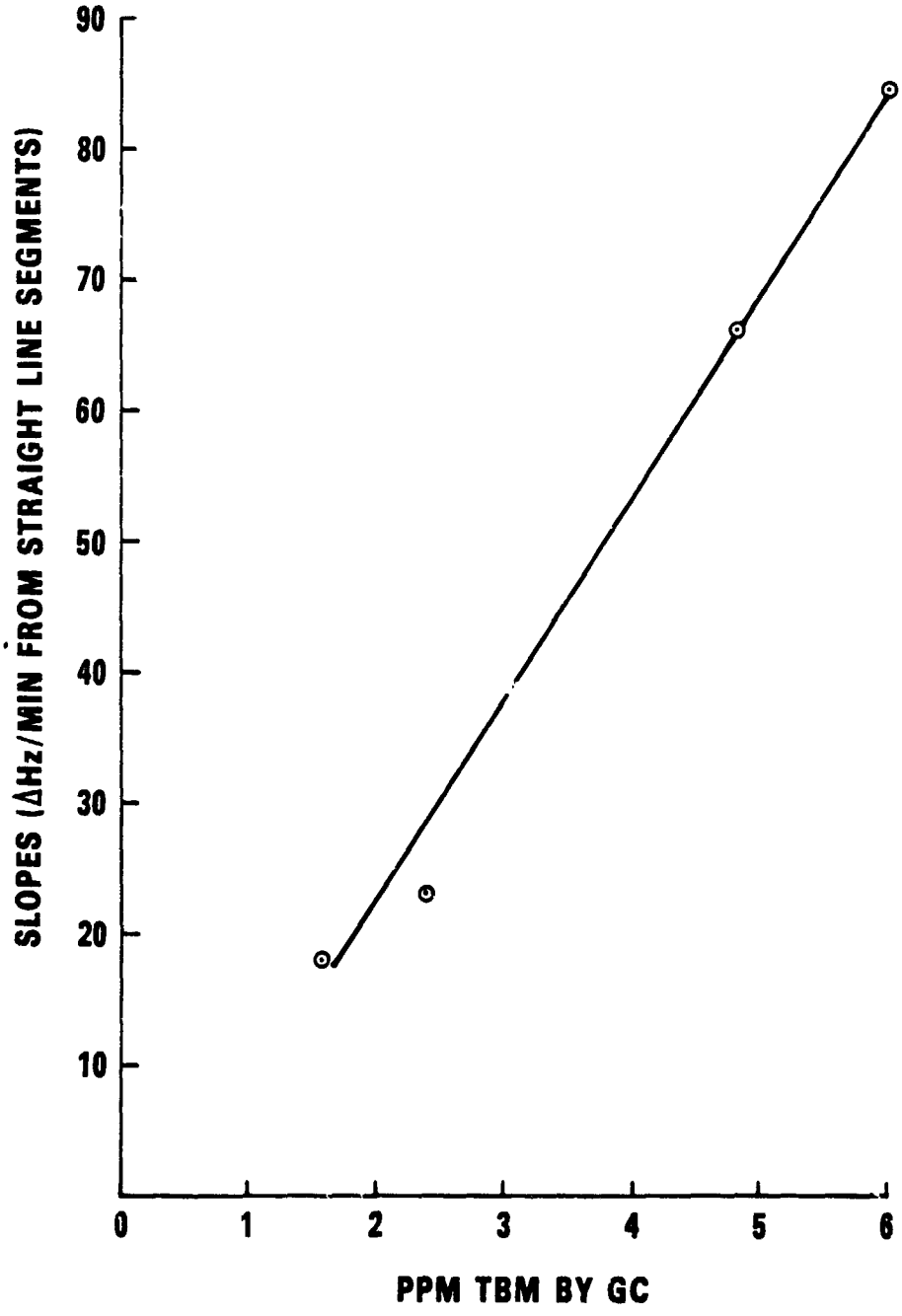

Figure 2. Response of Quartz-Crystal Sensor to Known Concentrations of Tertiary Butyl Mercaptan in Methane