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AN APPARATUS FOR THE DETECTION AND QUANTITATION OF VOLATILE HUMAN EFFLUENTS

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SUMMARY

Methods for the collection and identification of trace amounts of human effluents are presented. A variety of organic structures are included among the effluents: alcohols; ketones; ethers; esters; unsaturated, branched, cyclic and aromatic hydrocarbons; sulfhydryl, cyano and heterocyclic compounds. Over 135 effluents were identified in 16 man tests; three times this number was observed. Samples were trapped by a cryogenic process in the first eight tests; in the others, porous polymer collection was used. Five compounds found in the effluvia of most test subjects were quantitated. Their respective rates of emission are presented.

INTRODUCTION

Humans emit large numbers of chemicals in the form of waste products produced by normal body functions. The means of exuding these chemicals may be oral (breath and saliva), skin (sweat and sebum), dermal cells, urine, feces or flatus. Much of the earlier work to establish the nature and amount of human effluent was performed in connection with national space programs and submarine development. The Naval Research Laboratory has been active in determining trace contaminant composition in enclosed environmental atmospheres since the mid-1930s. Subsequent studies led to attempts to classify contaminants in submarine atmospheres: those from their crew; their activities, such as smoking and cooking; from operating machinery, including diesel engines, compressors and refrigerator systems; from off-gassing from batteries, etc.[1]. Combined gas chromatography–mass spectrometry (GC–MS) was used to analyze samples collected and desorbed from charcoal. The complexity of this effort is illustrated by the fact that more than 5000 contaminants were found in nuclear submarine atmospheres.

A related type of study concerned with the contaminants produced by man in a space cabin simulator was conducted at Brooks Air Force Base, Texas[2].

Experiments were designed to delineate those compounds produced specifically by man. Cryogenically concentrated samples were analyzed by GC, IR spectroscopy and MS. Ninety-seven compounds were identified and measured in samples taken daily for 21 days from a simulated space cabin in which four men were stationed. In the two related studies, the effluents coming from the men could not be isolated from those coming from the submarine or spacecraft.

Total vapor effluents (from the breath and skin) of humans have been studied experimentally by two other organizations. In the first work[3], a stainless steel–glass cabin was used. Air samples were trapped cryogenically and analyzed by gas–liquid chromatography. About 23 components were separated on the chromatograph but were not identified. The investigators concluded that this effort had only limited success because the "background" contamination was too great. In one case, GC peaks observed by the electron capture detector were traced to solvents with which the subject had worked several days previously. The chamber design and material of construction were such that the surfaces may have been coated with airborne hydrocarbon and grease films that served as vapor adsorbers. The temperature and the airflow pattern were not controllable. Hence, the vapor components that had accumulated at surfaces during construction and in the previous experiments were carried over into the following experiments. This study illustrated the complexity of the problem of detecting humans by their naturally emitted vapors.

The second work[4] was directed towards reducing the environmental background to a minimum and to eliminating the trace contaminants from the sample acquisition system. The objective was to detect human effluents at levels of 1 μg/h. Effluent collection lasted for 1 h, during which 2000–4000 l of air were sampled. The subject lay semi-naked on a stretcher-like frame inside a glass tube as compressed breathing-quality air from a cylinder was swept through at 1 p.s.i. positive pressure. Typical experimental conditions were: air flow, 1 l/sec; temperature in the test cell with the subject, 31°; and relative humidity at the exit from the cell, 40–60%. Three traps were used in series to collect and provide a preliminary separation of effluents. The first traps were glass spirals, coated internally with thin films of high-boiling esters such as Apiezon L and diethylene glycol adipate. The second trap, an ice-bath at 1–2°, was used to condense water and materials of similar boiling points. The third trap was liquid nitrogen at −196° and removed the remainder of the effluents. Compounds were eluted by a stream of cryogenically purified helium and concentrated in a stainless-steel capillary in a −196° bath. The bath was removed and the capillary heated electrically to provide rapid injection of the sample into a gas chromatograph: the temperature was programmed to rise at 6°/min from 45° to 205° on a 10-ft. SE-30–Chromosorb W column. After the few background peaks had been eliminated, the chromatograms showed the presence of a minimum of 24 and up to 44 substances in the C_5 and higher molecular size range. One important finding was the presence of substances heavier than the C_{12} range. Again, attempts were not made to identify the effluent.

In recent years, several efforts have been directed to determining volatile constituents from human breath, blood and urine. Horning and Horning[5] studied the GC profiles of endogenous constituents in urinary steroids, serum and urinary sugars and alcohol. Zlotkis and Liebich[6], using GC and MS, identified 41 volatile components in urine in the presence of possibly 300 others. Pauling *et al.*[7] have been studying

the components of both urine and breath by GC and by MS and have recently reported the identity of 25 chemical components of urine.

The purpose of this work was to identify all components coming off from man. To achieve this aim, a metabolic chamber was constructed which could safely house a man for 4-h periods. A system for purifying room air and suitable collection systems relatively free of contaminants were developed. A gas chromatograph–mass spectrometer, interfaced without a molecular separator, which could detect 0.1 μg of most types of compounds, was used to separate and identify the effluents.

METHODS, MATERIALS AND EQUIPMENT

The man chamber

Description. The chamber is an airtight cylinder with an internal volume of 34.3 ft.^{3} (971 l) (Fig. 1). It is made of type 316 stainless steel, glass and Viton (used for sealing mating surfaces). A unique "bumping" process was used to contour the cylinder wall and minimize the need for welded joints. All welded joints were heli-arc

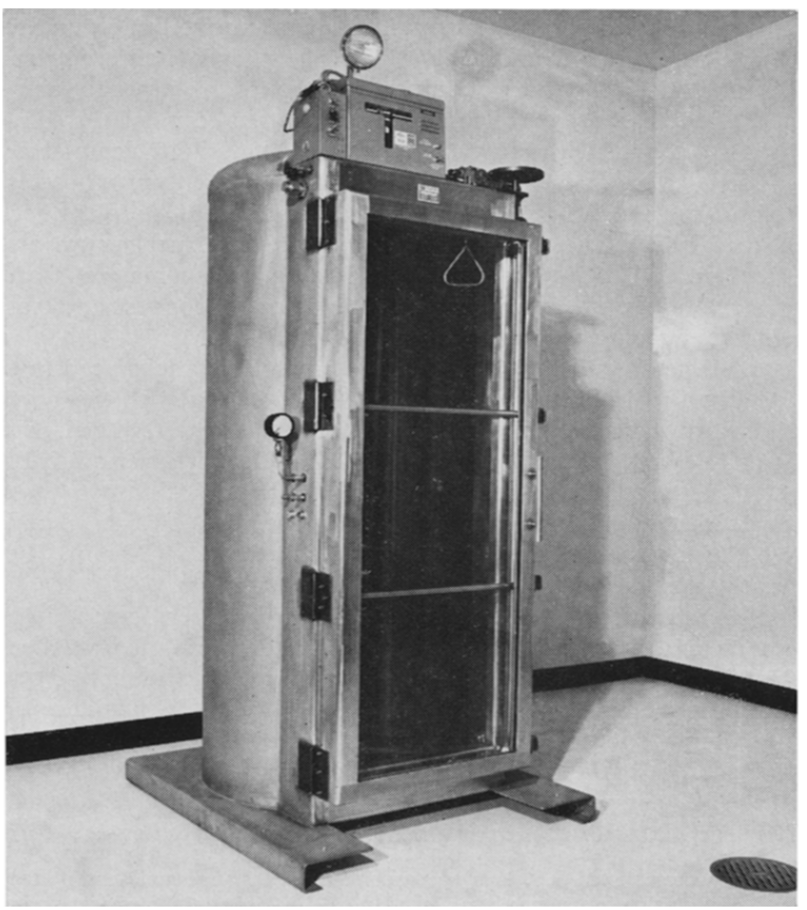

Fig. 1. One-man metabolic chamber.

welded internally and externally. The chamber is 41 × 36 in. at the base and 84 in. high. The total weight is 860 lb. The interior surfaces of the chamber were belt-ground before assembly to present a smooth surface for cleaning. The interior of the chamber is equipped with a removable, stainless-steel seat attached to the wall (the subject can either sit or stand), a light and a circulating fan. The outside of the chamber is equipped with an air inlet, an outlet, three sample probe fittings, four instrumentation fittings and two electrical connectors.

The chamber door is designed for easy ingress and rapid egress. The door provides an opening of 21 × 61 in. with an 8-in. step-over threshold. The door is equipped with a clear-view, 20 × 60-in. glass window to allow an unobstructed view of the subject under test. The door design was selected to permit maximum seal contact without requiring additional protrusions or grooves that would be difficult to clean.

The glass window is made of three strength-tempered sheets laminated to form one 0.750 × 20 × 60-in. assembly. The glass is mounted in a 0.125-in. Viton U-channel seal and held in compression by 64 bolts. In addition, two tension bars offset bending movements when latching and opening the door. The door seal is made of 1.0-in. O.D. × 0.375-in. I.D. Viton cord.

The door hardware and latching mechanism are designed to facilitate positive closing against the seal and easy egress from the chamber. The door latches are lever-action, eccentric, self-locking hasps capable of compressing the door seal when properly adjusted. The latches are retained by a release mechanism that employs the cam-and-pawl principle. When the pawl is withdrawn from the cam, it allows the cam-shaft to turn, releasing the door latches. The pawl is operated by applying approximately 75 lb in. to either of two pull-rings (delta-rings) located inside and outside the chamber. The materials selected to fabricate the door hardware and release mechanism are mild steels; stainless steel proved to be susceptible to seizing. These materials are treated with an anticorrosive finish. The chamber passed a rigid air-lock test and was free of impurities, excluding water in concentrations above 50 ng/l.

Proof and leak tests. The chamber was completely assembled and placed in a horizontal position. The interior was filled with water to a level even with the door seal. A calibrated gage was attached to the sample fitting above the water level. Air was introduced into the chamber to sustain a pressure of 4.5 p.s.i.g. for a period of 10 min. After completion of the test, inspection showed no damage.

Following the proof test, the internal pressure was reduced to 3.0 p.s.i.g. and the air inlet valve closed. The internal pressure decreased to 2.6 p.s.i.g. in 30 min. The leakage rate was adequate to satisfy operating criteria for a man-test.

Operation of chamber. Prior to and after a man-test, the chamber, located in a relatively isolated and clean area, was flushed with purified air for 4–5 h, then washed with methanol and with water. A pair of cotton shorts was placed on the seat of the chamber. The chamber door was closed and the chamber heated from the outside with six 250-W IR heat lamps. Simultaneously, laboratory air, passed only through silica gel, was directed into the chamber at a rate of 10–15 l/min for at least 1 day. On the day of the man-test, the heating lamps were removed and the chamber was flushed with charcoal-purified air for 3 h prior to starting time. A nude subject* entered the

* The subjects in these tests were enlisted U.S. Army personnel. These tests are governed by the principles, policies and rules for medical volunteers as established in AR 70-25, and the Declaration of Helsinki.

chamber and put on the shorts. The occupied chamber was flushed with silica gel and charcoal-purified air for approximately 1 h prior to sample collection. The rate of air flow, 25 l/min, maintained the carbon dioxide content at a level of less than 1.8% for over 4 h and permitted a constant level of humidity of about 80%. The sampling rate was 1 l/min for about 3.5 h for cryogenic collection, and 2 l/min for 25 min for porous polymer collection. Chamber temperature, relative humidity and carbon dioxide content were monitored continuously through the probe and instrument openings.

Procedure for preparing clean air systems

Preparation of purified air for chamber ventilation. Ordinary laboratory air was too contaminated for use in chamber ventilation. A number of procedures were tested to find the most suitable and economical method for supplying clean air to the man chamber. Commercial "zero air", having less than 2 ppm of hydrocarbons expressed as methane, was unsatisfactory. When ordinary room air was passed through a column of a high-grade activated carbon at −75°, even at a flow-rate of 50 l/min, a nearly contaminant-free air was obtained and found to be satisfactory for chamber air.

Another method tested for preparation of clean air was by pyrolysis of the contaminants in laboratory air. The air was passed through a drying column containing silica gel and through a bed of 0.5% palladium on 1/16-in. high surface-extruded alumina pellets at a temperature of 325°. GC data showed that this method did not remove a great number of contaminants. The procedure was discarded.

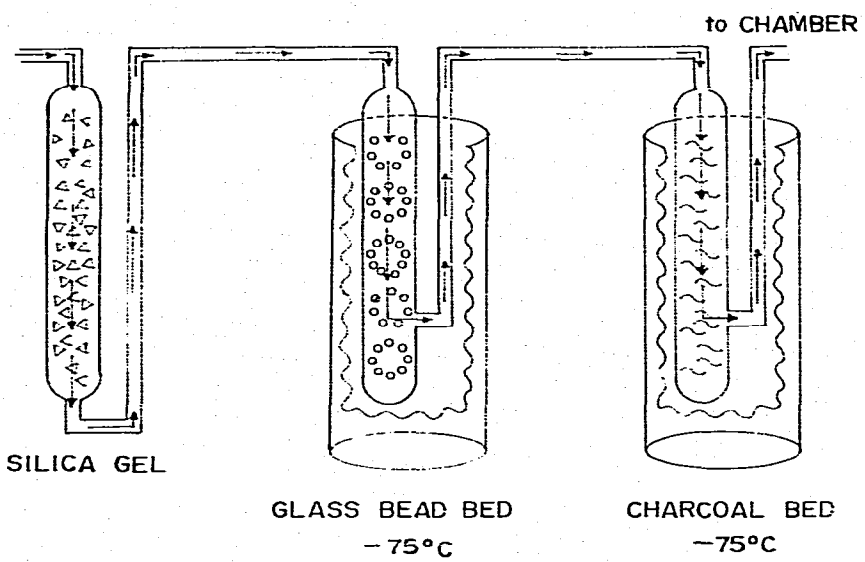

Fig. 2. Air purification system for man chamber.

Fig. 2 shows the various components of the cryogenic clean-air system that was finally adopted. The system removes water, hydrocarbons and other contaminants from ordinary room air. The first system tested consisted of five components: (1) a pump, (2) a cylinder containing silica gel to remove water, (3) a large cylinder of glass beads which was immersed in a bath of isopropanol and dry-ice at −75° and (4) a

container of 16-mesh activated charcoal immersed in a −75° bath. Containers for the silica gel, glass beads and activated charcoal were made of glass and designed so that air could flow through their contents. The cryogenic baths were large stainless-steel Dewar flasks. The system has proved to be satisfactory for 6–8 h.

To prepare the air purification system for operation, the glass-bead trap and the charcoal bed are filled with helium or dry nitrogen and the outlet is stoppered. Each cylinder is placed in the isopropanol–dry-ice bath at −75°. Next, the two cylinders are connected, and the silica gel bed is connected to the inlet tube of the glass bead trap. Room air is pumped through the system at approximately 20 l/min for several minutes. Then the outlet from the charcoal bed is connected to the inlet of the chamber. The air flow-rate is monitored at the outlet of the chamber.

Following each run, the system is reconditioned. The silica gel is removed and reactivated in an oven at 120 . The glass-bead component is heated with relatively dry air flowing through it. The charcoal bed is reactivated by heating it to above 100 and simultaneously evacuating it to 200 μm Hg.

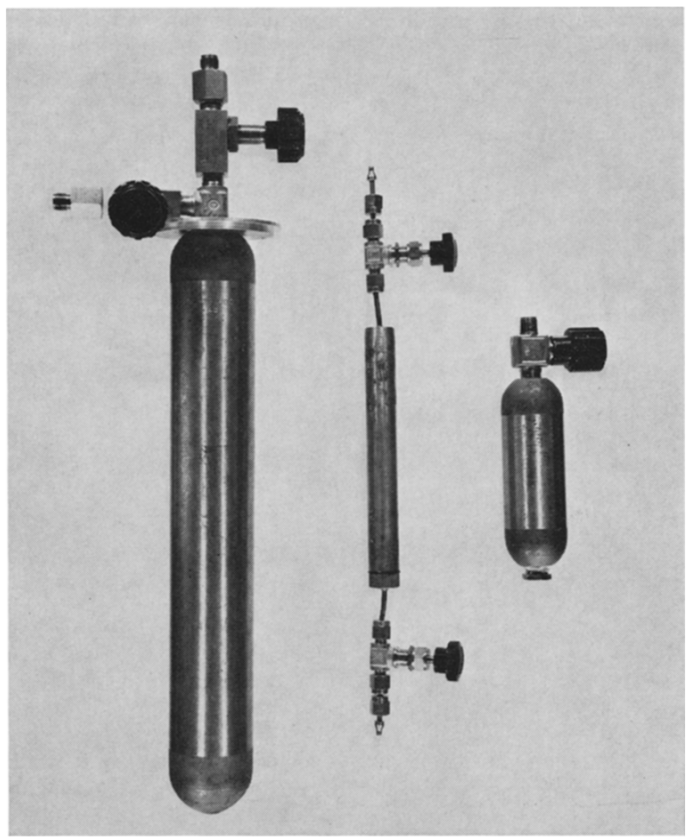

Fig. 3. Left and right: 500-ml and 75-ml stainless steel bottles. Center: porous polymer collector.

Cleaning collection bottles before sample collection. Before stainless-steel bottles (Fig. 3) are suitable for use in the cryogenic system for collection of air samples, they must be relatively free of trace contaminants as determined by GC analysis. After cleaning, each bottle is tested for background contaminants on the same gas chromatograph used in the analysis of the effluents collected from a man-test.

In preliminary cleanings, the bottles are first washed thoroughly with 15% nitric acid, rinsed with water, and dried at temperatures above 100 . They are filled with methylene chloride and allowed to stand for several hours. After removal of the methylene chloride, the bottles are washed with methanol and then with water. The metal parts of the dismounted valves are cleaned in a similar manner. The assembled bottles are heated to about 190 in an oven especially designed for cleaning bottles (Fig. 4). The bottles are then evacuated to <1 μm Hg for 24 h, then filled with helium. The contents are then analyzed for contaminants. The absence of peaks on the chromatogram or the presence of a very few low peaks indicates that contamination has been reduced to nearly zero.

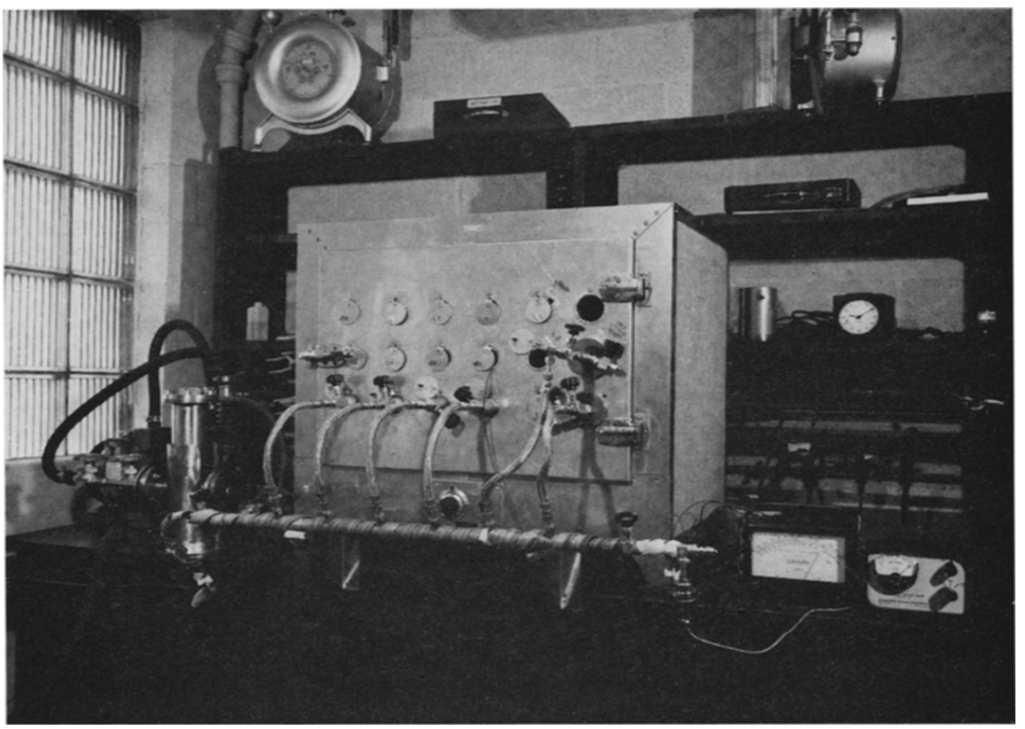

Fig. 4. Manifold for cleaning stainless-steel bottles.

Chromatograms from bottles cleaned by the above procedure contained only a few small peaks.

Cleaning porous polymer samplers before sample collection. The stainless-steel cylinders (Fig. 3) are heated to 200 while flushing with helium at approximately 100 ml/min for 24 h. After the temperature is reduced to 140 , the cylinders are flushed

with helium at 60–100 ml/min and this is continued for a further 1–2 days. The cleanliness of the sampler is determined by the transfer of a simple to a gas chromatograph. Note that the transfer of a sample is in the direction opposite to that of the helium flow: in other words, one passes helium or an inert gas into the end opposite from that used in the cleaning of the sampler to get an effluent sample into the gas chromatograph.

Trapping of volatile effluents emitted from a man in the chamber

The cryogenic trapping system consists of three 500-ml stainless-steel bottles (cylinders), each placed in a stainless-steel Dewar flask containing a refrigerant. The air to be collected and tested is passed through the three bottles connected in series. The refrigerant in the first Dewar flask is dry-ice and 20% methanol in water at $-10°$. The second flask contains dry-ice in isopropanol, giving a temperature of approximately $-75°$. The third Dewar flask contains liquid nitrogen. This latter trap has been modified to maintain a temperature of not lower than $-175°$ so that oxygen will not liquefy and obstruct the passage of air. Here a metal jacket is placed around the bottle, leaving approximately 3/8 in. between the bottle and jacket. Below the bottle and within the jacket is a small cup with perforations on the top. Nitrogen gas diffusing around the bottle serves as an insulator. The flow of nitrogen gas is regulated to yield a temperature of approximately $-175°$, as measured by a thermocouple inserted along the side of the trapping bottle. The air flow-rate during sample collection is 1 l/min.

A sampler containing approximately 5 g of either Porapak Q or Chromosorb

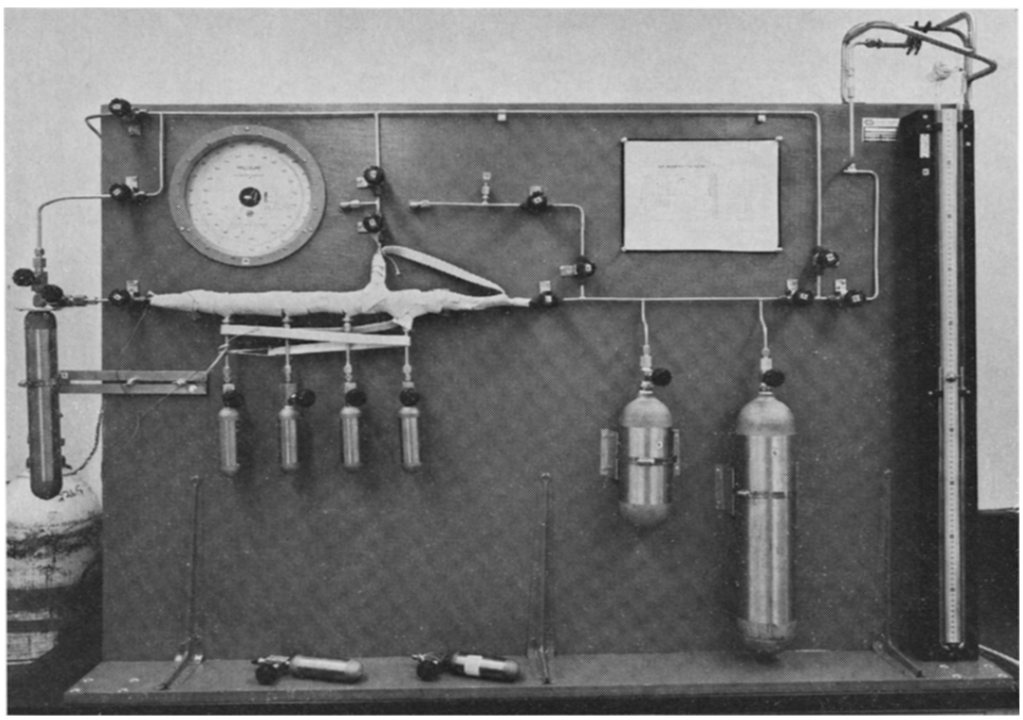

Fig. 5. Bottle splitting system.

102 is attached to a probe fitting on the chamber. A vacuum pump connected to the sample pulls air from the chamber at a rate of 2 l/min.

Sample splitting system

The collected samples in the 500-ml stainless-steel bottles are transferred to a high-vacuum-splitting system (Fig. 5), where the sample is divided into either three or four equal portions in 75-ml stainless-steel bottles. Each sample is tested on a separate gas chromatograph. This system was fabricated by Aerojet-General Corporation, Azusa, Calif., U.S.A. and shipped to this laboratory. The 75-ml stainless-steel bottles are cleaned by the same procedure used for the cryogenic collection bottles. Before a bottle is used in the splitting system, it is also tested for background contaminants on the same chromatograph as the one used in a man-test.

There is no need to split samples obtained with the porous polymer collectors. In order to obtain four samples, one for each gas chromatograph, four samplers can be set in parallel.

Sample transfer system

Fig. 6 illustrates the sample transfer system. It consists of (1) a special gas sampling valve for shunting the carrier gas through the loop containing the gas sample,

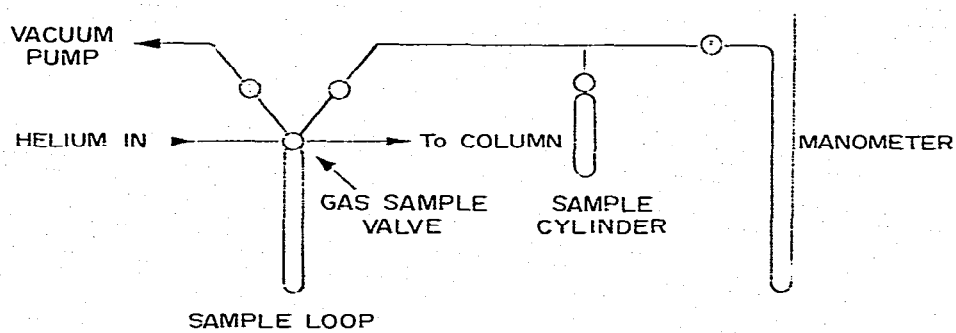

Fig. 6. Gas chromatograph sample introduction system.

(2) a stainless-steel trapping loop, between 7 and 10 ml in volume, and (3) a mercury manometer to monitor the vacuum and check for leaks in the transfer system. The transfer of the sample from the stainless-steel bottle is accomplished under vacuum. The loop system is evacuated to less than 100 μm Hg. Liquid nitrogen in a Dewar flask is placed around the loop, and the sample, warmed to 65–70° with a heat gun for 4 min, is allowed to pass slowly through the loop. Condensable gases and other contaminants are trapped at −196°.

Reduced pressure is not used to transfer effluents from the porous polymer sampler. In such a transfer, helium at a flow-rate of 20 ml/min is passed through the sampler into the loop. The sampler is simultaneously heated with heating tape at 140° for 1 h. After the transfer of sample is complete, the gas sampling valve is opened to allow the carrier gas to flow through the loop. The liquid nitrogen bath is removed and heat (100°) immediately applied to the loop to volatilize its contents. Carrier gas drives the sample into the GC column.

To make certain that part of a sample is not deposited in the tubing and connections leading from the loop to the GC column, the gas sampling valve and all tubing are maintained at a temperature of 100°. Because the loop can become contaminated when used, it is cleaned before each run by heating it to above 100° and evacuating it to 5 mm pressure for a period of at least 15 min. Following cleaning, a background chromatogram of the loop contamination is taken. As a result of these background tests, O-rings present in the gas sampling valve were found to emit contaminants that produced significant interfering peaks on chromatograms. This problem was resolved by replacing the silicon or Buna O-rings with Viton O-rings.

Calibration of the chamber

The calibration of the chamber is accomplished by introducing standard compounds with an infusion pump into the chamber at different rates. Air containing the standards is collected from the chamber with a porous polymer sampler under conditions identical to those used when air from a human subject is sampled. This technique assumes that amount of standard lost both on the walls of the chamber and that which cannot be recovered from the sampler will be identical with that amount lost by an identical compound evolved by a man in the chamber. To date, five compounds commonly found in human effluents have been quantitated: acetone, ethanol, isoprene, butanol and toluene. The procedure includes a pre-infusion flushing of the chamber with purified air for 3 h at 25 l/min to remove contaminated air that may have entered the chamber. The standard compound is infused with a pressure pump

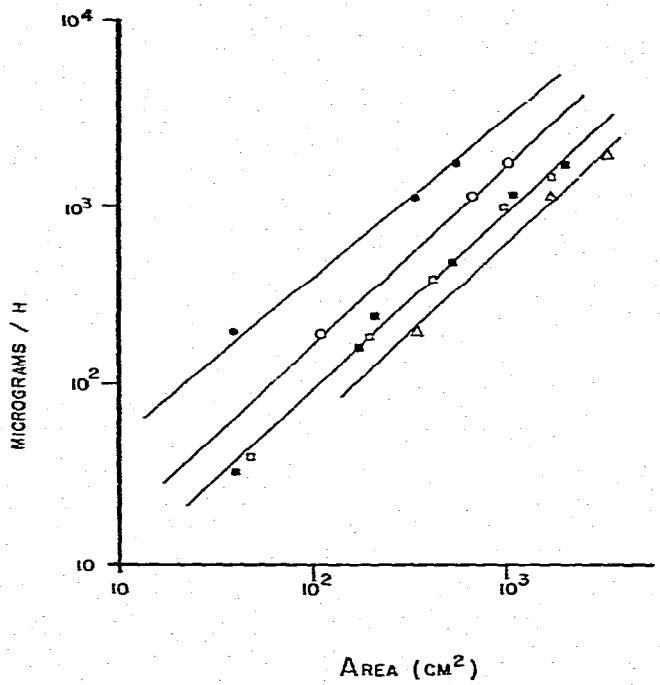

Fig. 7. Calibration curves for compounds introduced into metabolic chamber, trapped by porous polymer collector and analyzed by a gas chromatograph. ●, Ethanol; ○, acetone; ■, isoprene; □, butanol; △, toluene.

at a constant rate into a heated inlet to assure that the test material is completely vaporized before it enters the chamber. Infusion is continued for at least 1 h before sample collection is initiated. Approximately 1 h is required at a flow-rate of 25 l/min for equilibration of the chamber. Infusion rates can be varied by changing the rate of infusion and/or by changing the size of the Hamilton syringe used. Samples coming from the chamber are collected on porous polymers at the rate of 2 l/min for 25 min. These samples are analyzed on the gas chromatograph, as previously described. The area under the GC peak for each compound is plotted against infusion rate on log–log paper. A linear relationship was obtained for the five compounds studied (Fig. 7). Total efficiencies for these compounds ranged from 40 to 75%.

ANALYTICAL SYSTEMS

Three gas chromatographs and a mass spectrometer were used to analyze each sample. Four different phases were used in the gas chromatographic columns (two in the Perkin-Elmer gas chromatograph): (1) 28% Pennwalt 223 in 5% potassium hydroxide for separation of amines; (2) Chromosorb 101 for acidic compounds; (3) Carbowax packed in a column of an F & M Model 5750 (No. 1) instrument, used for its overall polar characteristics and its ability to resolve low-molecular-weight alcohols; and (4) a dinonyl phthalate (DNP) column for separating compounds of intermediate polarity in an F & M Model 5750 (No. 2) instrument. Columns were either 6 or 24 ft. of 1/8-in., standard-wall, stainless-steel tubing (Table I). The F & M Model 5750 (No. 1) and Perkin-Elmer instruments were equipped with flame and electron capture detectors, and the F & M Model 5750 (No. 2) with flame and thermal conductivity detectors. In the F & M Model 1, the splitting ratio for flame ionization to electron capture detection was 200:1; for Model 2, the splitting ratio of flame ionization to thermal conductivity was 1:1.

A fourth gas chromatograph, an F & M Model 500, with a thermal conductivity detector was reserved for the analysis of permanent gases. Molecular sieve 5A, Porapak Q, silica gel and/or charcoal were used as stationary phases to separate compounds like such as nitrogen, oxygen, carbon dioxide, carbon monoxide and hydrogen sulfide.

The Perkin-Elmer Model 900 gas chromatograph was combined with a Consolidated Electrodynamics Corp. (CEC) Model 21-491 mass spectrometer (Fig. 8). A molecular separator was not used. Approximately 3 ml of the carrier gas flow (30 ml/min) was directed into the mass spectrometer; 85% went to the flame ionization detector, and 5% into the electron capture detector. The CEC Model 21-491 mass spectrometer was selected for its excellent resolution, sensitivity, ability to reproduce ion fragmentation patterns, and capability of handling 3-ml volumes. The efficacy of the gas chromatograph–mass spectrometer system was verified with standard gas mixtures. *n*-Hexane and *n*-heptane were blended in helium and chromatographed. The effluent was monitored on the gas chromatographic recorder and also by following ion production with the mass spectrometer focused on *m/e* 57. Within an experimental error of $\pm$ 1 sec, the gas chromatograph signal maximum occurred simultaneously with the ion production maximum. A scan speed of 3 sec for approximately 2½ octaves provided adequate signal resolutions. Inlet pressures of $5 \cdot 10^{-6}$ torr provided adequate signal response without decay resulting from molecule–ion reactions. Under ideal

TABLE I

GAS CHROMATOGRAPHS USED IN SEPARATING EFFLUENTS

Property	*Perkin-Elmer 900*	*Perkin-Elmer 900*	*F&M Model 5750 (No. 1)*	*F&M Model 5750 (No. 2)*
Columns				
Type, length	6 ft. of $^1/_8$-in SS*	6 ft. of $^1/_8$-in. SS*	24 ft. of $^1/_8$-in. SS*	24 ft. of $^1/_8$-in. SS*
Phase (%)	Pennwalt 223 (27%) + 5% KOH	Chromosorb 101	Carbowax 1000 (7%)	Dinonyl phthalate (7%)
Support	60–80 mesh Gas-Chrom R	60–80 mesh	60–80 mesh Chromosorb AW	60–80 mesh Chromosorb AW
Detectors (splitting ratio)				
Flame	85%	85%	99.5%	50%
Electron capture	5%	5%	0.5%	—
Thermal conductivity	0**	0**	—	50%
Operating conditions				
Temperature	Isothermal at 30° for 4 min, programmed at 4°/min to 180°, held for 15 min	Programmed at 10°/min from 100° to 230°	Isothermal at 40° for 6 min, programmed at 4°/min to 140°, held for 18 min	Isothermal at 40° for 6 min, programmed at 4°/min to 120°, held for 22 min
Gas flow-rate (ml/min)	33	30	30	33

* SS = stainless steel.

** 10% is directed into the mass spectrometer.

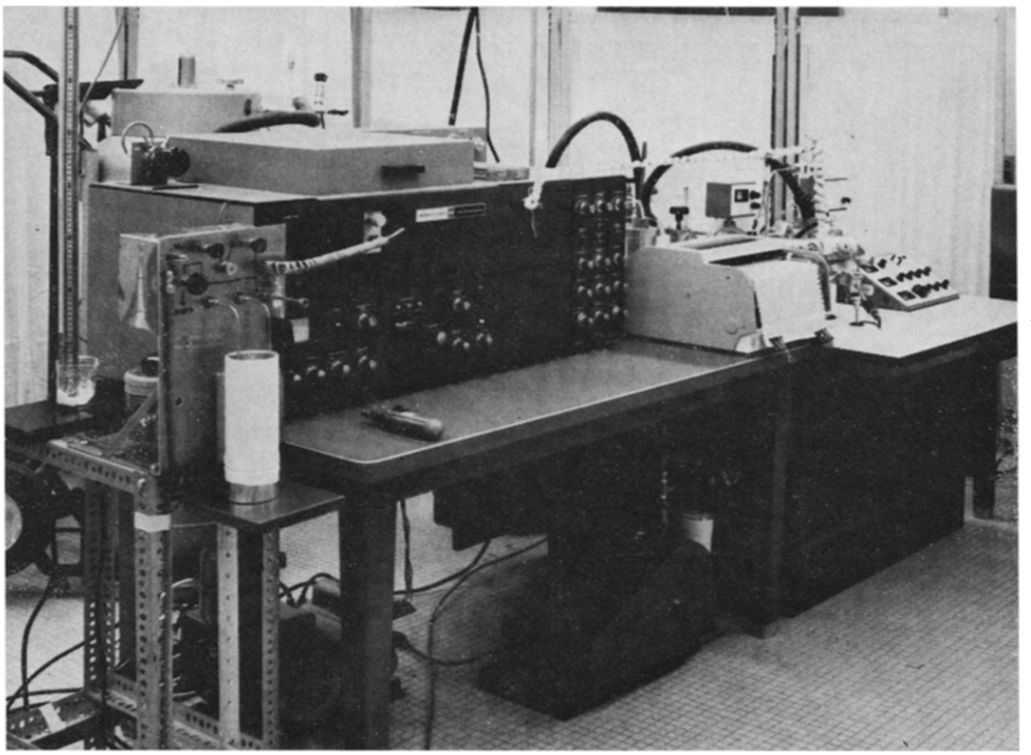

Fig. 8. Gas chromatograph combined with a mass spectrometer.

conditions, the spectrum of a 10-ng amount of material can be obtained. This is about the lowest limit of sensitivity of the gas chromatographic instruments.

An instrument log was prepared for recording data of analysis, sample identification, ionization setting (filament), sensitivity setting of electron multiplier, recorder response, chart speed and mass spectrometer scan speed. Sensitivity responses for both ionization and electron multiplier settings were used to evaluate the mass spectrometer performance. Over 325 compounds were classified for GC–MS operations on the Pennwalt column as to compound name, molecular weight, retention time, mass to charge (m/e) peaks and m/e abundance patterns. Retention times for 100, 235 and 330 standard compounds were determined in the DNP, Chromosorb 101 and Carbowax columns, respectively. Tetrahydrofuran was chosen as an internal standard to obtain relative retention times.

In each man-experiment, at least three retention times were obtained. A background spectrum was made on the carrier gas entering the mass spectrometer at zero time and at selected intervals during the analysis. The mass and relative amounts of each fragment were entered on a data sheet and the background was subtracted. As in most cases each peak of a gas chromatogram contained more than one component, a pattern analysis sheet was drawn, showing mass number to indicate functional groupings, and a numerical value from +1 to +4 to indicate the abundance of the mass fragment. Total analysis of a sample run required about 40 h.

TABLE II
COMPOUNDS IDENTIFIED IN HUMAN EFFLUVIA

Hydrocarbons
- Methane
- Ethane
- Propane
- Pentane
- Hexane
- Heptane
- Decane
- Undecane
- Dodecane
- 2-Methylpropane
- 2,2,4-Trimethylpentane
- 2,3-Dimethylhexane
- 2,2,4-Trimethylhexane
- Cyclopropane
- Cyclopentane

Unsaturated hydrocarbons
- Isoprene
- Butene
- Hexene-1
- Hexene-2
- Octene-1
- Octene-2
- Nonene
- 2,5-Dimethyl-1,5-hexadiene
- Decene
- Butadiene-1,3
- Propadiene
- 2-Methylbutene-2
- 2-Methyl-1-pentene
- 4-Methyl-1-pentene
- 2-Ethyl-1-butene
- Propyne
- Hexyne-1
- Hexyne-2
- Heptyne-2
- Nonyne
- 1-Hydroxybutene-2
- 1-Hydroxybutene-1
- Butene-1,4-diol
- Pinene
- Camphene
- Cyclohexene

Alcohols
- Methanol
- Ethanol
- Propanol
- Isopropanol
- Butanol-1
- Isobutanol
- Butanol-2
- *sec.*-Butanol
- *tert.*-Butanol
- Pentanol-1
- Pentanol-2
- Hexanol
- 2-Methyl-1-pentanol
- 4-Methyl-2-pentanol
- 2-Ethylbutanol
- Heptanol
- 2-Ethylhexanol
- Ethylene glycol
- Glycidol
- 2-Ethoxyethanol
- 3-Methyl-1,2-cyclopentanediol

Acids
- Lactic acid
- Pyruvic acid

Amines
- Ammonia
- Methylamine
- Ethylamine
- Dimethylamine
- Diethylamine
- Propylamine
- Butylamine
- Amylamine

Ketones
- Acetone
- Butanone-2
- Pentanone-3
- 4-Methyl-2-pentanone
- Heptanone-4
- Allylacetone
- Mesityl oxide
- Cyclohexanone
- Octanone-2

Aldehydes
- Methanal
- Ethanal
- Propanal
- Pentanal
- Heptanal
- 2-Ethylhexanal
- Valeraldehyde
- Crotonaldehyde

Heterocyclics
- Furfuraldehyde
- Furfuryl alcohol
- Pyrrolidine
- Pyrrole
- Butylpyrrole
- Benzothiazole
- Benzothiophene
- 2,3-Dimethylpiperidine
- Benzofuran
- Tetrahydrofurfuryl alcohol
- Thiophene

Aromatics
- Toluene
- *p*-Cumene
- *p*-Cymene
- Benzene
- Aniline
- Mesitylene
- Ethylbenzene
- Styrene
- Vinylpyridine
- Methylpyridine
- *o*- and *p*-xylene
- Cinnamyl alcohol
- Phenylhexane

Esters
- Methyl furoate
- Amyl acetate
- Allyl acetate
- Methyl butyrate
- Methyl acetate
- Butyl butyrate

Nitriles
- Acetonitrile
- Butylnitrile
- Hexylnitrile
- Allylnitrile

Sulfur compounds
- Methyl mercaptan
- Butyl mercaptan
- Amyl mercaptan
- Hexyl mercaptan
- Heptyl mercaptan
- Isothiocyanates*

Ethers
- Dimethyl ether
- Diallyl ether

Halogenated hydrocarbons
- Dichlorobutane

* Derivative.

RESULTS AND DISCUSSION

A number of systems have been developed with which one can collect, identify and measure total volatile effluents from man at trace levels, in the range of 10^{-7} g. To date we have identified 135 components of human effluvia, all of which are listed in Table II. Two to three times the number of effluents were seen as peaks on chromatograms or mass spectra, but could not be identified. Thirteen of the sixteen male subjects were Caucasian: three were Negro. No attempts were made to correlate individual effluents with race, diet, etc., as the initial studies on human subjects yielded a minimum of data; later studies gave much more data. Five compounds commonly found in the effluvia of all subjects have been quantitated in the system: isoprene, acetone, ethanol, butanol and toluene. Total efficiencies for these compounds ranged from 40 to 75%. Rates of emission are given in Table III.

TABLE III

RATES OF EMISSION OF FIVE HUMAN EFFLUENTS

Compounds	*Rate of emission (μg/h)*		
	Subject No. 1	*Subject No. 2*	*Subject No. 3*
Ethanol	25	58	100
Isoprene	425	251	270
Acetone	360	240	470
Butanol	16	26	41
Toluene	0.6	14	13

From the chemical view, a large number of ketones and alcohols were anticipated and found to be present in the effluvia of man. The large numbers of unsaturated and branched-chain hydrocarbons were not expected. Nor was isoprene expected to be one of the most common effluents of man. A large number of cyclic alkanes and alkenes, aromatic hydrocarbons, the five- and six-carbon sulfhydryl and cyano compounds, and a variety of heterocyclic compounds were also found.

Eight experiments were run under a cryogenic collection system and eight with the porous polymer collectors (the latter system is preferred because of its simplicity and sensitivity). If the retention times for an unknown effluent determined from three chromatograms were identical with values reported for a known standard, the compound was reported as definitely present. Most compounds were identified by two retention time values and mass spectrometry, or, in justifiable cases, by analysis of the mass spectra data alone by comparison to reference spectra in the literature. A variation of $\pm 10\%$ was arbitrarily set for each retention time. In a single run there were about 40 peaks in each of three gas chromatograms. Consequently, approximately 120 retention times or relative retention times were obtained; at least 40 mass spectra (plus numerous backgrounds) were recorded in a single run.

Because of the extensive amounts of data acquired in a single test, an investigator required over 40 h to analyze visually the data from each run. If one is to make additions to programs in the relatively new fields of olfactronics or orthomolecular medicine, effluents from the test subject's diet must be separated from his

total emissions. The use of a data acquisition system and a computer programmed to analyze GC and MS data becomes a necessity.

Perhaps the most useful application of our basic research effort lies in the field of medicine. As human odors must, *a priori*, originate from biological processes, the nature of the effluents emitted by man might provide signals indicative of impending or active disease states.

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