ANALYTICAL GAS DESORPTION APPARATUS

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FOREWORD

The analytical gas desorption apparatus was developed by the Biotechnology Branch, Life Support Division, Biomedical Laboratory, Wright-Patterson Air Force Base, Ohio, in support of Project 6373, "Equipment for Life Support," and Task 637302, "Respiratory Support Equipment." Mr. William H. Toliver, Sr., was principal investigator for the Aerospace Medical Research Laboratories. The development began July 1964 and ended March 1965.

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This report has been reviewed and is approved.

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ABSTRACT

Volatile organic contaminants are a problem in spacecraft, evaluators, and other closed cabin atmospheres and must constantly be measured. Consequently, a chemical high vacuum system for the desorption and manipulation of desorbates from solid adsorbents was developed. Essentially, the system is provided with three provisions for trapping the contaminant depending on its volatility. The high boilers are trapped in the first section, the compounds with low vapor pressure are collected in the middle section, and the noncondensables in the third section of the apparatus.

SECTION I

INTRODUCTION

Volatile organic contaminants are a problem in spacecraft, evaluators, and other closed cabin atmospheres and must be constantly measured. The most widely used and the most productive analytical sampling procedure for volatile organic contaminants is based on their adsorption by and subsequent desorption from active carbon (ref 4). A chemical high vacuum system for the desorption and manipulation of desorbates from solid adsorbents has been developed. The fact that vapors diffuse rapidly through a vacuum is the basis of the high vacuum technique for manipulating gases. After removing most of the air and other noncondensable gases from a closed system (pressure less than 10^{-3} torr)*, the vapors from a volatile substance introduced into the system will diffuse rapidly through out the entire system. It may be quantitatively moved to any part of the system by cooling that part of the system to a temperature at which the substance has negligible vapor pressure. The kinetic energy of the vapor molecules provides the motive power for the transfer, which is made irreversibly by removing the kinetic energy at the point of cooling (ref 7). All materials that do not react with mercury or Pyrex glass at ambient temperatures can therefore be manipulated with high vacuum techniques, if at ambient temperature they have a vapor pressure greater than a few tenths of a millimeter.

SECTION II

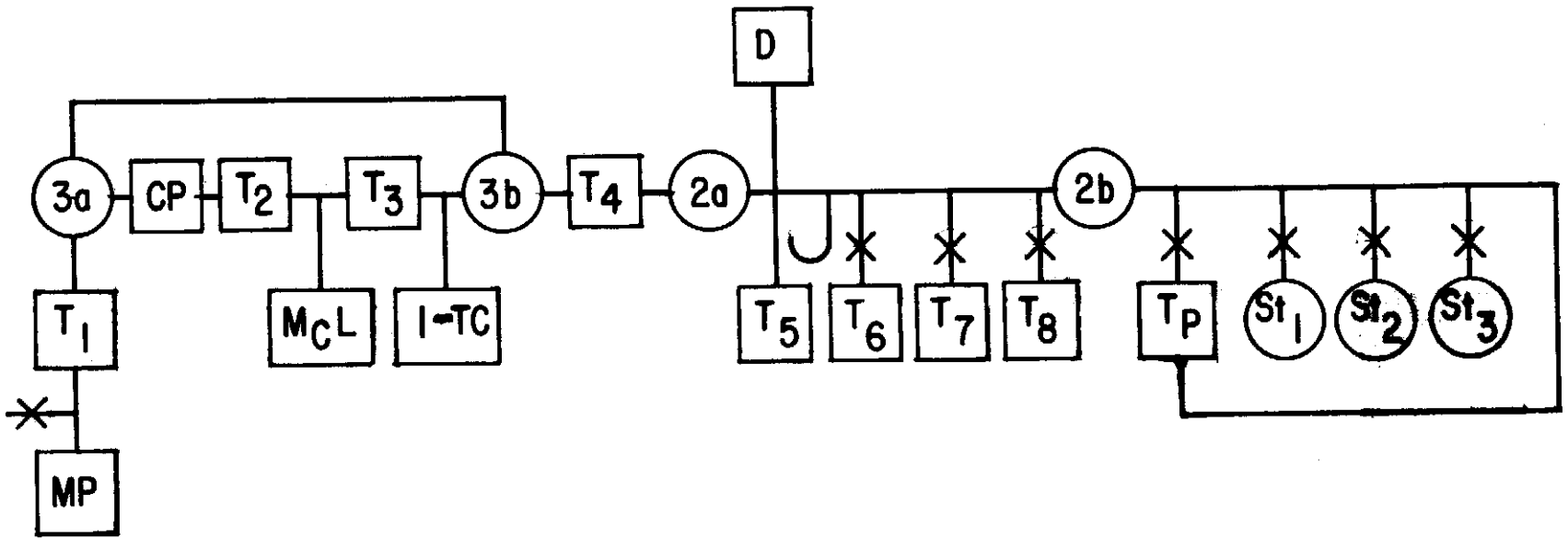
HIGH VACUUM SUBSYSTEM

This system has been divided into two major parts: (1) the high vacuum subsystem, and (2) the gas sample manipulation subsystem. Figure 1 shows a diagram of the high vacuum analytical gas desorption system. The system is fabricated principally of fragile glass containing mercury and therefore a skeletal support to reduce strain and provide protection is necessary. The components of the high vacuum subsystem are described from the high to the low vacuum side.

MECHANICAL FOREPUMP

A mechanical forepump (fig 2), Welch series 1402, DuoSeal, 2-stage, vented exhaust, with open motor was used to back the mercury diffusion pump in the system. Guaranteed vacuum with vent closed is 0.1 micron. With the vent open it is slightly higher——about 1 micron. The free air capacity is 140 liters per minute at 525 rpm. The mechanical forepump operates continously and irreversibly, sweeping gas from

*1 torr = 1 mm Hg



MP - Mechanical Forepump
X - Stopcock
T - Trap
3 - Special Threeway Stopcock
CP - Mercury Diffusion Pump (Condensation Pump)
McL - McLeod Gage
I-TC - Ionization - Thermocouple Gage
2 - Special 2-Way Stopcock
D - Desorption Tube and Furnace
J - Manometer
T_p - Topler Pump Gasometer System
St - Storage Tubes

FIGURE 1

Analytical Gas Desorption Apparatus

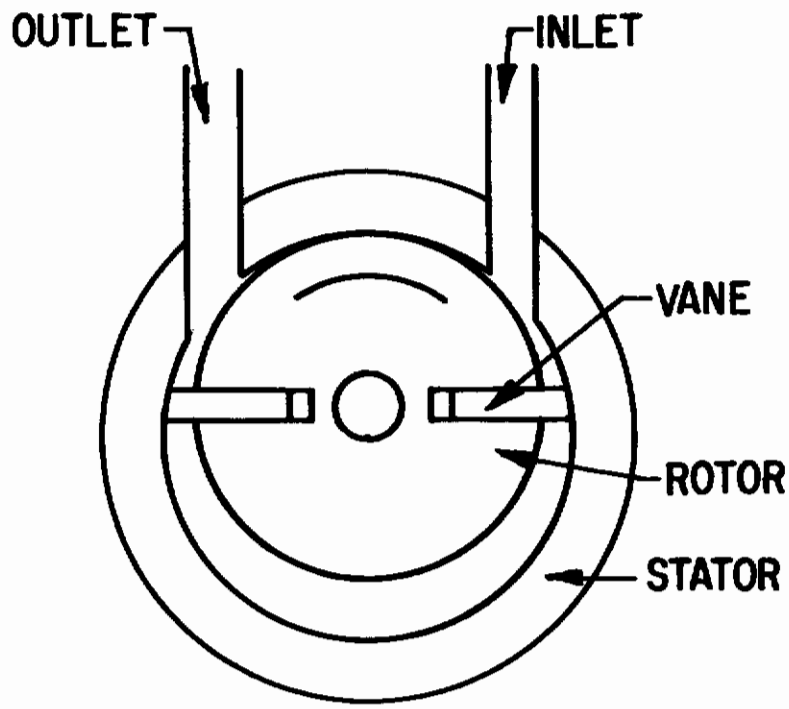


FIGURE 2

Mechanical Forepumps

an inlet to an outlet, under protection of an oil seal. The cylinder rotates eccentrically about the axis which coincides with the center of the casing. The pump has ports separated by an oil seal of only 1/10,000-inch clearance between a cylinder that rotates on center and the stationary part or stator. The air is not swept out by the cylinder itself, but rather by vanes, mounted in the cylinder, which are held constantly against the stator inner wall by springs. The pump operates at a high oil bath temperature and has the advantage of a more rapid removal of volatile contaminants by evaporation; and the disadvantage of making the oil more likely to deteriorate by oxidation. Operating at high vacuum the pump is relatively quiet and is capable of preventing the oil from being forced back into the inlet port when the pump is off.

Welch DuoSeal Oil was selected as having the required viscosity, low vapor pressure, and chemical stability to insure efficient operation and freedom from unnecessary noise and oil vapors.

The connection between the pump and the glass portion of the apparatus is made with heavy-walled rubber tubing. Worm-screw band clamps are used to secure a good vacuum tight joint.

A vent stopcock is placed in the line between the first trap (T_1) and the mechanical pump. Both of these components are insurance to restrain the oil if the conventional means fail.

Two pumps are needed to operate in series. The mechanical forepump produces a rough vacuum necessary for operation of a diffusion or condensation pump capable of producing the desired high vacuum.

MERCURY DIFFUSION PUMP

A mercury diffusion pump produces the high vacuum for the apparatus. Diffusion or condensation pumps irreversibly entrain in a stream of vapor the gas molecules diffusing from the system. The vapor carries the gas molecules to an area where they diffuse into the forepump and are ejected to the atmosphere. The vapor is condensed and returned to a boiler where is is again evaporated and continuously recycled past the entrainment point. Langmuir (ref 3) invented the most useful type of diffusion pump, the condensation pump, which condenses the vapor immediately after it passes the point of entrainment.

To increase pumping speed, many variations of the basic design have been developed. High boiling organic oils have been used. The oil-filled pumps are reputed to be faster, but because of the possibility of oxidation and contamination, a mercury diffusion pump is preferable for this apparatus. The mercury condensation pump is limited to a vacuum of 2.4×10^{-3} torr, or the vapor pressure of mercury at room temperature when it is used without a cold trap. Vacua of 10^{-6} torr can be obtained if a cold trap if liquid air is used as the refrigerant.

The forepump should have a pumping rate which prevents the backup of gas in the line between it and the condensation pump. Application of Boyle's law shows that the forepump should have a rate greater than

$$S_F = \frac{S_C \quad P_C}{P_F}$$

where

S_F = pumping rate of the forepump.

S_C = pumping rate of the condensation pump.

P_F = working pressure of the forepump.

P_C = working pressure of the condensation pump.

Thus a condensation pump with a rate of 50 liters/sec at 10 torr requires a forepump of 5×10^{-3} liters/sec at 10^{-1} torr. However, because of tubing restrictions and gas evolution from the tubing, this pump factor should be increased a magnitude of 10.

The Analytical Gas Desorption Apparatus can be pumped from a pressure of 1 atmosphere of dry air to a vacuum better than 10^{-5} torr in 20-30 minutes, if properly conditioned and if the minimum stopcock restriction is not less than 3-4 mm.

Trap T_2 is placed in the system to contain mercury vapors and increase pumping rate as indicated above.

Traps T_1, T_2, and T_3 are selected as the type 1 (fig 3) of common use and availability, and are suitable for protecting a pump against vapors. However, a disadvantage of this type of condensation trap (fig 4) is that it cannot be adequately conditioned because the inner tube surfaces are not accessible to direct heating, and the ring seal is liable to fissure if strongly heated.

After obtaining the high vacuum it is helpful to know its magnitude. The semi-quantitative, coarse measure of the vacuum of the system (pressures greater than 10^{-3} torr), is performed by a McLeod gage; and the fine, quantitative measure of the vacuum is performed by the thermocouple-ionization gauge (TC: 0-2000 millitorr,* ionization: 1×10^{-3} torr to 2×10^{-9} torr).

McLEOD GAGE (ref 2)

A modified McLeod Gage was selected; stopcocks are oblique bore to aid in retarding mercury and isolating the gage. The double scale is calibrated 5 torr 2×10^{-5} torr. The gage is easily operated, rugged and has a wide pressure range. The accuracy is of the order of ± 0.5% absolute.

*1 millitorr = 1 micron Hg

This gage is based on Boyles Law, the inverse relationship of pressure and volume of gases. A known volume of gas is isolated and compressed into a smaller known volume at readable pressure.

IONIZATION-THERMOCOUPLE GAGE

A combination ionization-TC gage was selected for this system. Ionization and TC gages are molecular gages, so called because they depend on the number of gas molecules or properties of these molecules. They require an electrical circuit for measuring pressure.

The TC gage works on the principle of a change of resistance of a heated filament with a change in thermal conductance caused by gas molecules in the gage. The temperature of the hot filament is read by an auxilliary thermocouple that is welded to the filament. The TC gage has a simple electronic circuit with a constant current source for the filament.

The ionization gage is essentially a triode and works on the principle of indicating the pressure as a function of plate current when electrons emitted from a hot filament in the tube are accelerated to an electrode, the grid, and the positive ions formed by the collision of these electrons and gas molecules are collected on a third electrode, the plate. The quantity of ions formed is directly proportional to the number of gas molecules in the tube and thus the plate current is a direct function of the pressure.

Thus with the McLeod and I-TC gages, the analytical gas desorption apparatus can cover the ranges 5 torr to 2×10^{-5} torr, 0-2000 millitorr, and from 1×10^{-3} torr to 1×10^{-9} torr. The McLeod gage measures the pressures too high for the I-TC gage to handle safely and also serves as a check on the proper functioning of I-TC gage.

The Ionization-TC gage is placed between Trap T_3 and a special threeway stopcock 3b. This completes the high vacuum subsystem. High purity mercury and Apiezon N grease are used where appropriate in the system. All stopcocks from mercury sources are oblique-bore; all tubing from mercury sources is inclined at least 30 C to resist condensed mercury drippage into the vacuum system.

Between special stopcocks 3a and 3b there is a bypass that can be used to rough pump the sample manipulation subsystem without breaking the vacuum in the high-vacuum subsystem.

No vacuum reservoir is incorporated in this system. The subsystem is 36 inches wide x 48 inches high (measured from table top) and 11 inches deep. Both special three way stopcocks are easily manipulated, simultaneously. The bypass provides flexibility and provides a site for modification or extension (vacuum). Quantitative pressure measurements are readily made over a wide range. No dial gages or manometers are necessary.

Trap T_4 (fig 1) prevents contamination of the high vacuum subsystem and the rough vacuum bypass. Stopcock 2a is the beginning of the gas desorption, vapor fractionation, gas manipulation units of the gas handling subsystem.

SECTION III

SAMPLE MANIPULATION SUBSYSTEM

The function of this subsystem is to produce a desorbate of condensable and noncondensable gases, measure its volume, and produce as nearly as possible a sample species with integrity.

DESORPTION UNIT (ref 5)

This unit (D) consists of a course grit tubular fritted glass center, to contain and restrain the solid adsorbent. This restraining inner tube is contained in a gas tight envelope open to the system. A thermometer well is located in the top side of the unit. The joint of this component fits into a unit with a long spout that is connected to a liquid collection tube that has a graduated centrifuge tube incorporated in the bottom. The first two components above in this unit have drip spouts to avoid contact of desorbed liquids with high temperature sealing grease, thus high boilers can be collected and measured.

CONDENSABLE GAS UNIT

Compounds of different volatility may be separated by condensation-fractional distillation. If a mixture is selectively condensed and warmed to a temperature at which all but one compound have negligible vapor pressures, that compound can be quantitatively distilled from the mixture.

The condensable vapor must pass through the trap in such a manner that it is cooled to the temperature of the trap; but the condensed vapors must not be entrained with any of the noncondensable gases. Traps T_6, T_7, and T_8 were selected with this consideration in mind; in addition low gas velocity and low turbulence were considered.

Trap T_6 is type 2 trap (fig 3) and T_7 and T_8 are type 3 traps. The wide side of T_6 is used next in line from T_5 anticipating liquid condensate. Traps T_7 and T_8 are used where vapors can approach from only one side. Of course the traps are annealed.

The fractionation procedure is designed to separate compounds with vapor pressure differentials on the order of 0.5 mm when the component of next lowest volatility is cooled to negligible vapor pressure. The principle of condensation-fractional distillation is based on the separation of a polycomponent mixture as if it were a binary mixture.

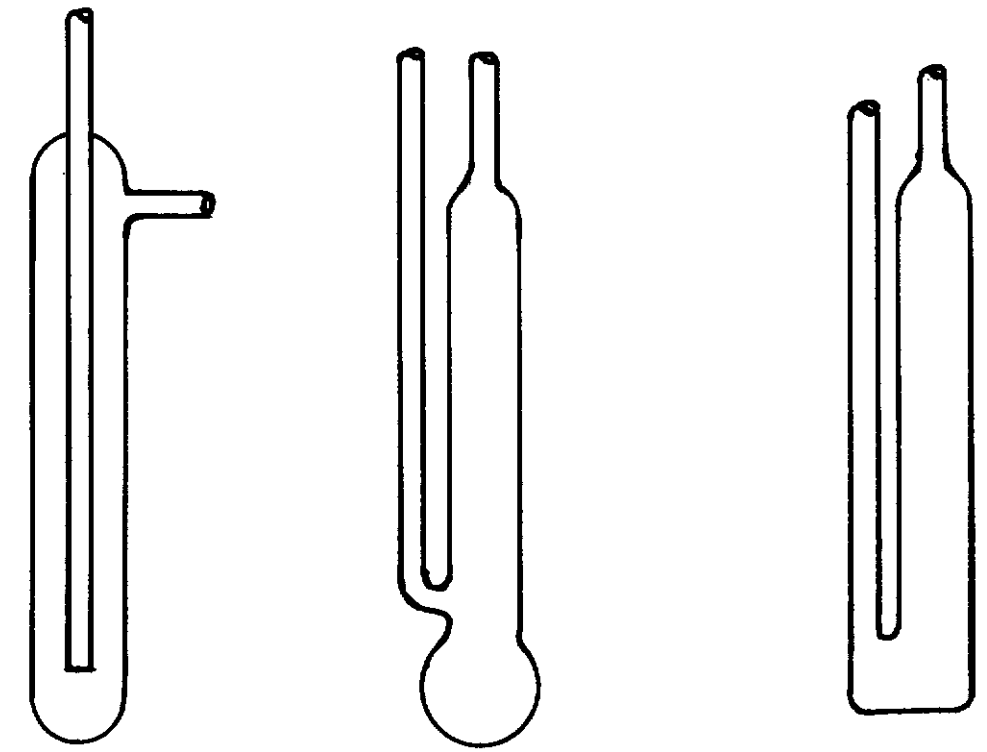


FIGURE 3

Condensation Traps

Thus with the use of various temperature coolants and the manometer, fractions of about 1 mm integrity can be obtained of condensable gases. Volumes from 1 to 10^{-4} ml can be measured in a microval (ref 6). In this manner the midboilers can be separated and measured. The low boilers are manipulated in the following unit.

NONCONDENSABLE GAS UNIT

Gases that cannot be entirely condensed by liquid nitrogen coolant must be manipulated through the system by pumping from place to place. The most common noncondensable gases in boiling point order are helium, hydrogen, neon, nitrogen, carbon monoxide, and methane. Residual water vapor and carbon dioxide can also be manipulated by this unit.

The Toepler pump pumps the noncondensable gases into any desired vessel, i.e., a gasometer for volume measurement and a storage tube for later analysis.

The principle of the Toepler pump is based upon filling an evacuated chamber with noncondensable gas, then filling the chamber with mercury, and driving the gas into the desired vessel. The mercury is withdrawn and the cycle initiated again. The speed of pumping is a function of the volume of the Toepler chamber and the volume of the system.' The pump operates automatically every 2-4 minutes in this system. The gasometer is based on the design of Barr and Auhorn (ref 1).

SECTION IV

APPARATUS SUPPORT

A rack and table combination support the apparatus. The table top is high enough to work from conveniently and for the location of the mechanical pump below. The top is plywood and is covered with cement asbestos to resist burns, permit easy modification, and to reduce the cost. The vertical and horizontal rods of the rack are adjustable for versatility in placement of the components. The top, side and supporting framework is double 1-3/4 inch steel channel assembled back to back. Provisions are made for mounting two electrical conduits, water, air, and gas.

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