Diaphragm-Type Micromanometer for Use on a Mass Spectrometer

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A diaphragm-type micromanometer is described that is capable of measuring pressures in the range of 1 to 100 microns with a sensitivity of about 0.1 micron on the 50-micron scale. The displacement of the thin diaphragm is measured by the change in mutual inductance of two coils mounted above the center of the diaphragm. The capsule is easy to assemble, and the rugged construction reduces the effects of mechanical vibration. The value of the manometer is illustrated by a comparison of the sensitivities of the isomeric heptanes, octanes, and nonanes calculated from pressures measured in two ways: First by the conventional method of measurement with a mercury manometer of the pressure of a known volume of the vapors and expanding approximately 1,000 fold, and second, by measuring with the micromanometer the pressure of the expanded gases.

I. Introduction

The amount of a sample of gas admitted to a gas-analysis mass spectrometer is usually measured with a mercury manometer on a volume of a few cubic centimeters. The sample is then expanded approximately 1,000-fold into a gas reservoir preparatory to entering the leak manifold. The method is quite inapplicable if the vapor pressure of a compound is less than a few millimeters, yet the mass spectrometer can, in principal, be used with substances having vapor pressures as low as 0.01 mm or less. Even with substances having vapor pressures of several centimeters, large errors may be introduced by the expansion method because of departures from the ideal gas laws. Taylor and Young [1] [1] have described a method of introducing liquid samples by means of a micropipet. However, it has been noted [2] that for some compounds the pressure of the vaporized liquid is considerably less than expected due to adsorption on the interior surfaces of the inlet system. Furthermore, no suitable method has been described for introducing and measuring the vapor pressure of compounds that are solids at room temperature. The above sources of error are substantially eliminated if a suitable micromanometer be attached to the reservoirs for pressure measurements on the expanded vapors.

The construction of sensitive manometers for the micron pressure range has usually taken the form of modifications of the ordinary U-tube manometer [3, 4, 5] or McLeod gage. Most of these require careful control of temperature and bulky, rigid mountings on vibration-free supports. Matheson and Eden [6] have described a sensitive manometer by using a pair of nesting diaphragms as the pressure-sensitive element. Their manometer was capable of detecting a pressure differential between the inside and outside of the capsule of 0.001 mm in the range 1 mm to 1 atm. The displacement of the

diaphragms was measured by direct coupling to a strain gage, the stiffness of which largely controlled the sensitivity of the instrument.

We have constructed a diaphragm-type manometer capable of measuring pressures in the range of 1 to 100μ with a sensitivity of about 0.1μ on the 50μ scale. The high sensitivity is due to the specially designed diaphragm and to the absence of mechanical coupling between the diaphragm and the displacement-measuring device.[2] The displacement was measured by the change in mutual inductance of two fixed, concentrically wound coils due to the approach or retreat of the conducting surface of the diaphragm.

II. The Micromanometer

A number of capsule designs were tried. Sylphons and corrugated diaphragms of the nesting type with sufficient pressure sensitivity were found to be too sensitive to ordinary building vibration to be useful. In the final design, a single diaphragm with a working diameter of 2.87 in. was made from rolled brass 0.001 in. thick. The diaphragm had 26 concentric V-shaped corrugations 0.01 in. deep with 90° angles. Figure 1 is a cross section of the capsule assembly showing relative positions of the diaphragm, probe coils, and coil support. The assembly was made in the following manner. A 0.25-in. hole was drilled in the center of a 0.08-in.-thick brass disk, B. One end of a 3-in. length of 0.50-in. outside diameter brass tubing, C, was hard soldered in position to match the hole; the other end was tapered to fit the outer member of a 12/30 standard taper glass joint. The disk was undercut 0.01 in. and the diaphragm, A, soft soldered at the periphery. The parts of the stainless steel yoke, D, were machined to 0.125-in. thickness from bar stock of the proper dimensions. The mating surfaces were carefully fitted and assem-

[1] Figures in brackets indicate the literature references at the end of this paper.
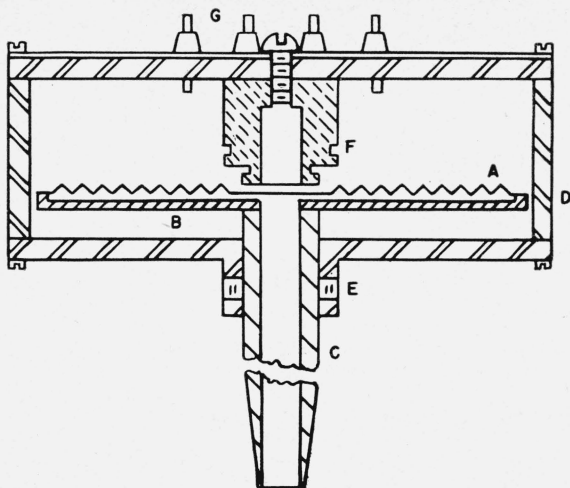
FIGURE 1. *Cross section of the pressure-sensitive element showing the relative positions of the components.*

bled with machine screws. The yoke was attached to the diaphragm support by set screws in the collar, E. The probe coils were wound on an insulating coil form, F, and mounted on the underside of the top cross bar. Electrical tie-points were provided in the form of Stupakoff through-panel insulators, G. Figure 2 shows the assembled pressure cell. The entire unit was mounted inside two glass hemispheres (not shown) sealed together by a low-vapor pressure wax. An outer 12/30 standard taper was sealed to the lower hemisphere at the pole to receive C (fig. 1). A small quantity of Apiezon grease was used to make the seal. The outer standard taper
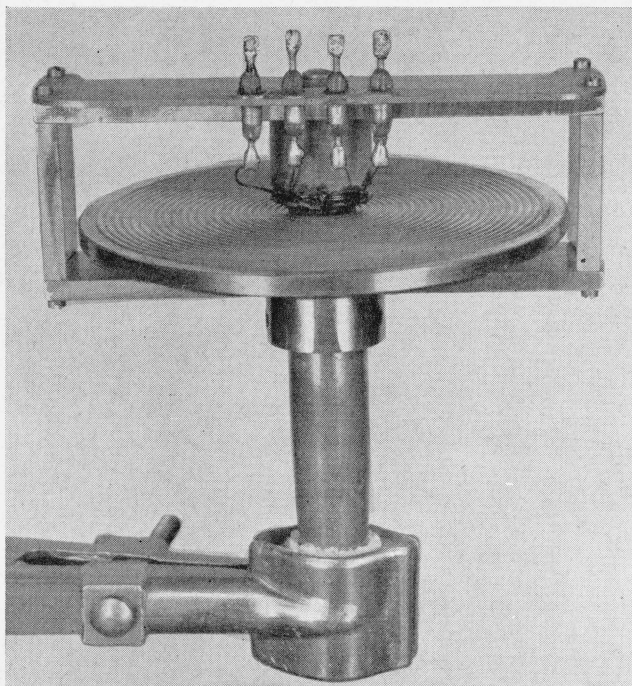

FIGURE 2. *Assembled pressure-sensitive unit.*

was connected to the inlet system of the mass spectrometer. Connection was also made to the hemisphere through an isolating stopcock to prevent damage to the diaphragm during venting and also to allow periodic checks on the zero point of the diaphragm. The cable connections for the electronic micrometer were made through a four-conductor glass press in the lower hemisphere.

The pressure sensitivity measured at the center of the diaphragm was about 2×10^{-5} in. per micron of mercury. Conservatively, the diaphragm will have satisfactory elastic properties with a permissible central deflection of 3 percent of its diameter, or 0.086 in., far in excess of any deflection contemplated in service. It was deemed unnecessary therefore to use materials with superior elastic properties, such as phosphor bronze or beryllium copper. The capsule was easy to construct, and the 0.08-in. base provided mechanical strength for handling, as well as stiffness to reduce the effect of mechanical vibration.

A detailed description of the displacement-measuring instrument utilizing the mutual inductance micrometer appears in the accompanying paper (see footnote 2). A brief description of the operation can be obtained, however, by referring to figure 1. The primary winding of the probe coil is excited with radio-frequency current. The voltage induced in the secondary is a function of the proximity of the diaphragm surface as a result of eddy currents generated in the metal. This voltage is amplified by suitable circuitry, rectified and applied to a direct-current microammeter. The gain control of the amplifier permits a wide range of scale adjustments for the output meter. It also provides a means of adjusting the calibration of the unit from the deflection of the diaphragm caused by a known pressure difference across the capsule.

III. Operational Details

The manometer was operated with the capsule connected to the inlet reservoir. The pressure in the sphere enclosing the capsule was maintained at approximately 10^{-5} mm of mercury. Zero adjustment was made when the reservoir was evacuated on the same vacuum line. Calibration of the micromanometer was obtained by using the mass spectrometer as a pressure-measuring instrument in the following manner. With the reservoir open to the leak manifold, a pressure of approximately 50 mm of *n*-butane measured with a mercury manometer was metered into the gas pipet provided as an integral part of the inlet system of the Consolidated mass spectrometer. This sample was then expanded 1,000 fold into the reservoir. The gain control of the micromanometer was adjusted for a reading on the output meter corresponding numerically to the exact pressure in microns calculated from the manometer reading and the known expansion ratio. The $m/e=$ 43 peak of the *n*-butane mass spectrum was then scanned by the mass spectrometer in the conventional manner. A portion of the gas in the reservoir was pumped out, the micromanometer reading was
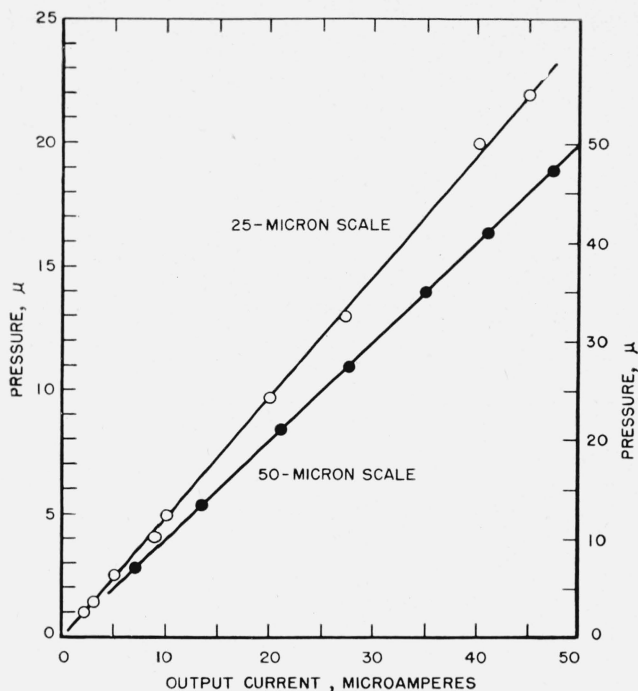
FIGURE 3. *Calibration curves of the micromanometer for full-scale sensitivities of 25 and 50 microns.*

The left-hand ordinate refers to the open circles. The right-hand ordinate refers to the solid circles.

noted, and the 43 peak again scanned. Further repetitions of this procedure resulted in data illustrated by the lower curve in figure 3, in which the ordinates are computed from the initial pressure and the peak heights recorded by the mass spectrometer. The upper curve was obtained in a similar manner when the gain was adjusted for full-scale deflection of the output meter with a pressure of 25μ in the reservoir. At full sensitivity a pressure of approximately 10μ was sufficient to give full-scale reading on the micromanometer. The noise level for the 50-μ scale was approximately 0.1μ and was principally the result of vibration from pumps and other equipment mounted in the vicinity of the cabinet housing the inlet system. Temperature variations of 3 to 4 deg in the ambient room temperature had no effect on the performance. Zero drifts over 8-hour periods were less than 1μamp, and day-to-day adjustments of the full-scale calibration were of the same order. The capsule has been found to be fully protected against a pressure differential of 1 atm applied to the outside of the capsule. No test has been made for large excess pressure on the inside. Pressures of a few tenths of a millimeter have had no effect on the mechanical zero.

Except for the pressure measurements, the sensitivities of various compounds were obtained by using conventional techniques on a Consolidated mass spectrometer. The approximate amount of sample required was introduced into the inlet reservoir. The reservoir was opened to the leak, and 1 minute later the exact pressure indicated by the micromanometer was noted and the sweep started.

IV. Experimental Results

Table 1 summarizes the sensitivities (ion current of maximum peak per unit of pressure) of the octane isomers relative to n-butane obtained in two ways. First, the pressure of a known volume of vapor was measured with a mercury manometer and the vapor expanded 1,000-fold into a reservoir. Second, the pressure of the expanded vapors was measured with the micromanometer attached to the reservoir, the latter opened to the leak. Columns one and two, respectively, give the names and vapor pressures of the 18 isomeric octanes. Column three gives the relative sensitivities calculated from the pressures of the substance and n-butane measured by a mercury manometer [7]. The fourth column gives the relative sensitivites calculated from the pressures measured with the micromanometer [8]. Column five gives the ratio, R, of the relative sensitivities obtained by the two methods. The greatest value for R (1.9) is found in n-octane, which also has the lowest vapor pressure. The values of R apparently decrease with increasing vapor pressure in a rather uniform manner for molecules with few side chains. Similar data [8] were obtained for all of the heptane isomers and the nonane isomers. As expected, the effect was smallest for the heptanes. For n-heptane (vapor pressure, 46 mm) the value of R was 1.15. For the other heptanes (vapor pressures up to 100 mm) the average value of R was 1.02. On the other hand, n-nonane (4.3 mm) gave a value for R of 2.4, whereas 2,2,4,4-tetramethyl pentane (20.0 mm) gave a value for R of 1.5. That factors other than vapor pressure are operative for some molecules is indicated in table 1 by the low value of R (1.2) for 2,2,3,3-tetramethyl butane as compared with compounds of similar vapor pressure; for example, 2-methyl heptane ($R=1.5$) and 4-methyl heptane ($R=1.4$). Another paper [2] reports some measurements made by introducing measured volumes of liquid cyclo-

TABLE 1. *Octane sensitivity by manometer and micromanometer for 50-volt electrons*

Compound	Vapor pressure [a]	Sensitivity at maximum peak [b]		$R=S_1/S_2$
		S_1, manometer	S_2, micromanometer	
n-Octane	14.8	2.66	1.44	1.9
2-Me heptane	20.6	2.02	1.30	1.5
3-Me heptane	19.5	1.73	1.21	1.4
4-Me heptane	20.5	2.30	1.67	1.4
2,2-Me₂ hexane	34.0	2.98	2.41	1.2
2,3-Me₂ hexane	23.4	1.76	1.52	1.8
2,4-Me₂ hexane	30.4	1.53	1.29	1.2
2,5-Me₂ hexane	30.4	1.68	1.35	1.2
3,3-Me₂ hexane	28.6	1.71	1.43	1.2
3,4-Me₂ hexane	21.6	1.51	1.14	1.3
3-Et hexane	20.0	2.65	1.81	1.5
2,2,3-Me₃ pentane	32.3	2.42	1.86	1.3
2,2,4-Me₃ pentane	49.4	2.73	2.33	1.2
2,3,3-Me₃ pentane	27.0	1.95	1.41	1.4
2,3,4-Me₃ pentane	27.0	2.15	1.56	1.4
2-Me, 3-et pentane	23.9	2.14	1.61	1.3
3-Me, 3-et pentane	23.0	2.31	1.68	1.4
2,2,3,3-Me₄ butane	20.5	2.63	2.12	1.2

[a] Vapor pressure in millimeters of mercury at 25° C. Selected values of properties of hydrocarbons, NBS Circular 461 (1947).
[b] Relative to sensitivity of n-butane 43 peak (ion current/micron).

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hexane and liquid styrene into the reservoir of the mass spectrometer by means of a micropipet. In these experiments the pressure of the vapor measured by the micromanometer was always less than that computed from the amount of liquid introduced. For cyclohexane and styrene the descrepancy was about 13 percent and 30 percent, respectively, and was caused at least in part by adsorption on the walls of the reservoir.

It is often noticed that the pressure of some reactive gases and of some highly polar molecules gradually decreases on standing in the reservoir. In such cases satisfactory measurements are only obtained after waiting until a constant pressure is attained. A great advantage of the micromanometer is that continuous monitoring of the pressure in the reservoir is possible, and such changes are immediately visible and do not escape notice.

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V. References

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