

Introduction of Measured Liquid Samples Into the Mass Spectrometer

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Several methods of introducing measured amounts of liquid samples of neohexane and of styrene into a mass spectrometer are compared by measuring the sensitivity (ion current per unit pressure) on mass peaks 71 and 104. A precision microburet and pipet made of thermometer tubing were used to introduce samples of about 0.0015 milliliter. A reproducibility of about 2 percent is obtained with the microburet and of 5 to 8 percent with the pipet. Sensitivities obtained by either method are lower than the sensitivity obtained by a direct pressure measurement using a micromanometer. They are low by 13 percent for neohexane and by 30 percent for styrene. Styrene is retained on the glass walls and in the stopcock grease, and after pumping out 20 minutes some styrene is gradually evolved.

I. Introduction

The conventional method of introducing measured gas samples into the mass spectrometer is that of measuring the pressure of the gas in a small volume of a few milliliters and then expanding the gas one thousand fold into a reservoir. For liquid samples of low vapor pressure, the method becomes very inaccurate because nearly saturated vapor does not expand as a perfect gas. The use of multiplying manometers¹ to read pressures more accurately before expansion of the gas does not remove the difficulty. For this reason, methods of introducing known volumes of liquid into the large reservoir have been investigated both here and in other laboratories.² Micromanometers have also been developed for measuring directly the pressure in the large reservoir.³ In this paper we present comparative data on sensitivities for neohexane, boiling at approximately 49° C, and styrene, boiling at 146° C, as examples of liquid samples differing considerably in physical properties. Several methods of introducing the liquids are used, and the measured sensitivities are compared with values obtained with a micromanometer. The research includes the adapta-

tion of a precision ultra-microburet⁴ available through the Emil Greiner Co. of New York, N. Y., to the use of introducing measured volumes of liquid directly into the reservoir of the mass spectrometer.

II. Experimental Details

The microburet, figure 1, consists of a capillary delivery-tube, *E*, attached to a capillary reservoir, *C*. The amount of mercury in the delivery tube is controlled by displacement of mercury from *C* by the stainless steel rod, *B*. The movement of the rod is controlled by the screw, *F*, and is indicated by the micrometer dial, *A*. The dial is graduated in one hundred divisions and can be read directly to 0.0001 ml for a buret of 0.1 ml total volume or to 0.00001 ml for a buret of 0.01 ml total volume. The liquid sample was introduced by close contact of the tip of the capillary with the surface of a Corning "fine" fritted glass disk (see footnote 2) as shown in figure 1. The disk was sealed with a layer of clean mercury.

For these experiments it was found convenient to mount the buret on a rack and pinion device (not shown in fig. 1), which permitted controlled vertical movement as well as rotation of 360° about the vertical. Careful control of the posi-

¹ For a complete discussion of pressure measuring devices, see Experimental methods in gas reactions by A. Farkas and H. W. Melville (MacMillan and Co. Ltd., London, 1939).

² R. C. Taylor and W. S. Young, Ind. Eng. Chem., Anal. Ed. **17**, 811 (1945).

³ W. S. Young and R. C. Taylor, Anal. Chem. **19**, 133 (1947).

⁴ R. Gilmont, Anal. Chem. **20**, 1109 (1948).

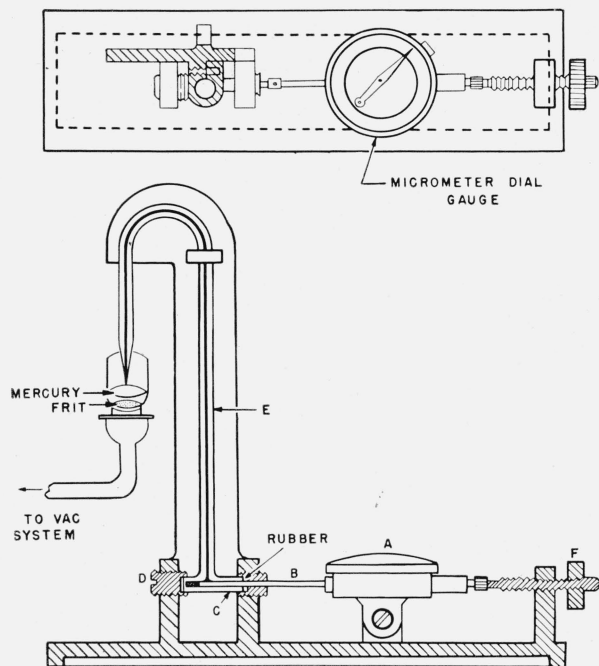


FIGURE 1. Microburet assembly.

tion of the buret by means of the rack and pinion was necessary because of the possibility of chipping the capillary tip on the porous disk.

The buret is charged with sample in the following manner: The mercury is forced into the capillary, *E*, by turning the control knob until a drop begins to form at the tip. Then with the tip below the surface of the sample, a portion is drawn into the capillary by rotating the screw in the reverse direction. When sufficient liquid has been drawn into the capillary, the buret tip is removed from the liquid and is carefully wiped with a piece of filter paper. The buret is then brought into position above the porous disk and very cautiously lowered by means of the rack and pinion until the tip is below the surface of the mercury and makes contact with the porous surface of the fritted disk. An appropriate quantity of sample, measured by the difference between two readings of the micrometer dial, is then introduced into the vacuum manifold by forcing the mercury forward into the capillary, *E*.

Figure 2 shows a calibration curve of the volume of liquid delivered in milliliters times 100 as a function of the number of divisions read on the dial of the micrometer gauge. The calibration was done by weighing the mercury delivered from the buret.

When the desired amount of liquid has been drawn through the porous disk into the evacuated manifold, the tip and porous disk are immediately separated to prevent evaporation of additional sample into the manifold. The tip, however, is left below the surface of the mercury in order to prevent loss by evaporation from the capillary or contamination of the sample. The samples could be introduced into the mass spectrometer reservoir directly through a porous disk attached to the reservoir, or condensed with liquid nitrogen into lengths of 3-mm tubing, sealed off and stored until it was convenient to introduce them into the mass spectrometer through an appropriate break-off device. Most of the samples in this work were introduced in the latter fashion. The sample manifold, containing the porous disk and 3-mm sample tubing, was pumped out for 5 min between the introduction of successive samples through the disk. The time allowed for the sample to condense in the 3-mm tube was from 5 to 8 min, depending on the size of the sample taken.

The 3-mm tubing containing the sample was waxed into a break-off stopcock of the mass spectrometer by using accepted procedures and after evacuation of the stopcock, the end of the tubing was broken off and the liquid sample allowed to evaporate directly into the reservoir. Four minutes were allowed to establish equilibrium between the adsorbed vapor and the expanded

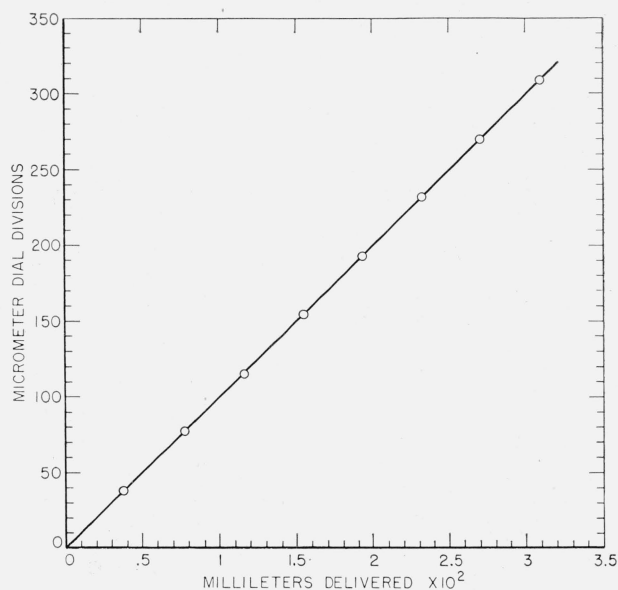


FIGURE 2. Volume calibration of the microburet.

vapor in the 2-liter reservoir. An additional 4 min were allowed after opening the reservoir to the leak before scanning over a range of $m/e=65$ to 75 for neohexane and 100 to 108 for styrene. The time allowed for evacuation between successive runs of neohexane was 10 min; for styrene, 15 to 20 min. The spectrogram was recorded in the conventional manner with a Consolidated Mass Spectrometer. Constant magnetic field was used with varying ion accelerating voltage. The energy of the electrons was nominally 50 electron volts. The magnet current was 0.675 amp. The 71 peak of neohexane was in focus at approximately 800 v, while the 104 peak of styrene was collected at approximately 600-v ion accelerating voltage.

The neohexane was Phillips "pure" grade. The purity as stated by the manufacturer was not less than 99 mole percent.

The styrene was obtained from the University of Akron and had no detectable impurities of over 0.1 mole percent as determined by the mass spectrometer.

III. Experimental Results

1. Neohexane

Maximum deflections were obtained with neohexane when 0.0015 ml was expanded into the 2.2-liter reservoir. Table 1 lists the results obtained for a number of samples measured and introduced as described above. The first column gives the number of divisions indicated by micrometer dial of the buret. The second column gives the ion intensity of the $m/e=71$ ion as scale divisions of the spectrogram. The third column gives the sensitivity or the number of scale divisions per micron of sample pressure in the reservoir. The sample pressure is calculated from the following relation:

$$p = 7.6 \times 10^5 k \left(\frac{vd}{M} \right),$$

where p = pressure in microns;

k = ratio of molar volume of the vapor to the volume of the reservoir;

v = volume of sample in milliliters;

d = density of liquid sample;

M = molecular weight of compound.

TABLE 1. Sensitivity of neohexane using microburet and 2.2-liter reservoir

Microburet divisions	Ion intensity	Sensitivity divisions/micron	Mean sensitivity	Percentage deviation
15	1870	19.73	-----	-1.8
15	1917	20.23	-----	+0.6
15	1914	20.20	-----	+ .5
15	1870	19.73	-----	-1.8
15	1921	20.27	-----	+0.8
15	1870	19.73	-----	-1.8
16	2047	20.25	-----	+0.7
16	2016	19.95	-----	- .8
16	2067	20.45	-----	+1.7
17	2201	20.50	-----	+2.0
17	2153	20.05	20.10±.23	-0.3

The fifth column gives the percentage deviation from the mean sensitivity.

In several experiments the pressure in the reservoirs was measured with a diaphragm-type micro-manometer, to be described in a later publication. The reproducibility of the pressure readings was usually better than ± 1 percent of the value when calibrated with *n*-butane, using the mass spectrometer as the calibrating instrument.

Table 2 lists the data obtained by pipetting a number of samples of neohexane directly into the mass spectrometer reservoir and into the 3-mm

TABLE 2. Sensitivity of neohexane

Pipet	Divisions	Ion intensity	Sensitivity (div-micron)	Percentage deviation from mean
Calibrated thermometer pipet and porous disk with 2.2-liter mass spectrometer reservoir.	39.3	865	18.3	-5.2
Do.....	19.9	473	19.8	-2.6
Do.....	24.4	594	20.3	+5.2
Do.....	49.6	1119	18.8	-2.6
Mean sensitivity (pipet).....			19.3	-----
Mean sensitivity (micromanometer).....			23.1	-----
Calibrated thermometer pipet and porous disk with 3-mm gas-sampling manifold.	70	1682	20.9	-3.7
Do.....	77	2024	22.9	+5.5
Do.....	137	a 3140	20.0	-7.8
Do.....	138	a 3626	22.9	+5.5
Mean sensitivity (pipet).....			21.7	-----

a Calculated from the 57+ peak.

sampling manifold through a porous disk using a length of calibrated thermometer tubing. Column one gives the number of scalar divisions of the thermometer tubing; other columns are similar to those of table 1.

Five minutes of evacuation removed 99.9 percent of the neohexane from the reservoir as indicated by measurement of the 71^+ peak. If the reservoir were then isolated from the pumps, the background of the 71^+ ion did not increase during thirty minutes.

2. Styrene

Approximately 0.0015 ml of liquid expanded into a 4.2-liter reservoir was found to be suitable for mass spectrometric measurements of the 104 peak of styrene. Table 3 summarizes the data for the 2.2- and 4.2-liter volumes. Column two gives the volume of liquid in terms of divisions of the micrometer dial of the buret. Column three gives the ion intensity of the 104 peak in scale divisions. Column four gives the sensitivity as the number of scale divisions per micron of sample pressure in the reservoir. The calculations are similar to those for neohexane. The fifth and sixth columns give the mean sensitivity, and percentage deviations, respectively.

Table 4 gives the sensitivity data of styrene obtained by pipetting the liquid from a calibrated thermometer tubing directly into the reservoir and into the 3-mm gas sampling manifold through a porous disk.

TABLE 3. Sensitivity of styrene using the microburet and 2.2- and 4.2-liter reservoirs

Reservoir volume	Microburet divisions	Ion intensity	Sensitivity	Mean sensitivity	Percentage deviation
<i>Liters</i>					
2.2	7	1494	29.48	-----	+2.25
2.2	7	1482	29.24	-----	+1.42
2.2	7	1482	29.24	-----	+1.42
2.2	7	1458	28.77	-----	-0.21
2.2	7	1389	27.41	28.83	-4.93
4.2	15	1584	27.85	-----	-4.16
4.2	15	1665	29.27	-----	+0.72
4.2	15	1665	29.27	-----	+0.72
4.2	15	1650	29.01	-----	-0.17
4.2	15	1653	29.06	-----	00
4.2	15	1641	28.85	-----	-0.72
4.2	15	1683	29.59	-----	+1.82
4.2	15	1668	29.32	-----	+0.89
4.2	15	1668	29.32	29.06	+0.89

TABLE 4. Sensitivity of styrene

Pipet	Divisions	104 ⁺ Ion intensity	Sensitivity (div./micron)	Percentage deviation from mean
Calibrated thermometer pipet and porous disk with 2.2-liter mass spectrometer reservoir.	24.2	1104	33.1	+4.4
Do.....	45.5	2037	32.5	+2.5
Do.....	43.4	1686	28.2	-11.0
Do.....	45.5	2073	32.9	+3.8
Mean sensitivity (pipet).....			31.7	-----
Mean sensitivity (micromanometer).....			40.9	-----
Calibrated thermometer pipet and porous disk with 3-mm gas sampling manifold.	46	2529	30.7	+13.7
Do.....	56	2916	29.1	+7.8
Do.....	61	2924	26.8	-0.7
Do.....	69	^a 3202	24.9	-7.8
Do.....	71	^a 3114	23.6	-12.6
Mean sensitivity (pipet).....			27.0	-----

^a Calculated from the 103⁺ peak.

A sample of styrene stored in the reservoirs for less than 1/2 hr, decreased to about 0.1 percent of the original sample, (in terms of peak height) in 5 min of pumping and to 0.05 percent in 20 min. If the reservoir were then isolated from the pumps, the background peak of the 104⁺ ion increased to about 3 percent of the original peak height in 1 hr, as indicated in figure 3. In a similar experiment, a sample of styrene was stored in the reservoirs for 16 hr, during which time no decrease in pressure was observed. At the end of that time, a pump-out curve was obtained that was quite similar to that shown in figure 3 with an increase of the 104⁺ peak (after isolation of the reservoirs from the pumps) of approximately 3 percent of the original peak height in 1 hr. Thus the amount of styrene desorbed is nearly independent of the length of time it is stored in the reservoirs.

TABLE 5. Summary of results

Experimental method	Sensitivity (div./micron)	
	Neohexane	Styrene
Buret into 2.2-liter reservoir.....	20.1 ±0.23	28.83 ±0.59
Buret into 4.2-liter reservoir.....	-----	29.1 ±0.44
Pipet into reservoir.....	19.3 ±0.75	31.7 ±1.7
Pipet into sample manifold.....	21.7 ±1.25	27.0 ±2.3
Micromanometer.....	23.1 ±0.4	40.9 ±0.8

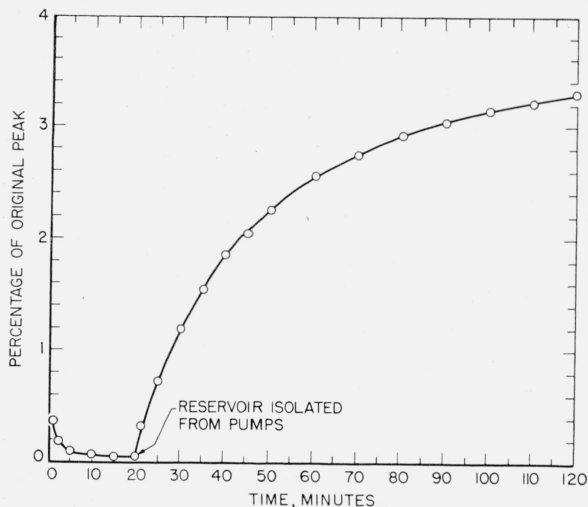


FIGURE 3. Styrene desorption in reservoir after pumping for 20 minutes.

A summary of the results obtained is given in table 5. Column 1 gives the experimental method of introducing samples, columns 2 and 3 give the average sensitivities for neohexane and styrene, respectively. The average deviation from the mean is given in each case.

With no special precautions, a reproducibility usually better than 2 percent has been attained for introducing pure neohexane or pure styrene through a porous disk by means of a microburet with a capillary diameter of 0.8 mm.

No significant difference in results was obtained between direct introduction of the sample into the reservoir of the mass spectrometer or condensing and sealing in a separate capsule, which later was opened into the inlet system of the mass spectrometer. This suggests that known amounts of liquid samples can be prepared and stored for future use if the usual precautions are taken to prevent polymerization or decomposition.

Some decrease in precision occurs when liquid volumes less than 0.0015 ml are introduced with the buret or pipet. This is not a function of the uncertainty of reading the buret or pipet scale alone since the use of a microburet with a capillary diameter of 0.3 mm and about 10 times the linear scale for the same interval as the larger buret, resulted in a 3-fold decrease in precision. The increased ratio of surface of the buret walls to volume of liquid delivered provides greater opportunity for variation in the amount of sample retained by the buret or pipet. The elliptical

cross-sectional area of the thermometer tubing was estimated as slightly less than that of the smaller buret. It is interesting therefore to note that the precision of the pipet is considerably lower than that of the 0.8 mm buret and generally lower than the value given above for the 0.3 mm buret.

Although errors are probably introduced as the result of varying amounts of liquid retained by the pipet or buret walls, a more serious source of error is the sorption of vapor in the reservoir. This is suggested by the larger difference between the sensitivities of styrene and neohexane calculated when the pipet and the micromanometer were used. Apparently styrene is strongly adsorbed in the reservoir, both on the walls and in the lubricant, and this causes a lower sensitivity when computed from the amount of liquid introduced. The micromanometer of course measures only the vaporized fraction and should give the true sensitivity. The large adsorption of styrene is substantiated by the pump-out behavior since, even after 20 min of pumping, there is still sorbed material equivalent to at least 3 percent of the original amount of sample introduced. Although a similar experiment on neohexane shows a negligible amount remaining in the reservoir after 5 min of pumping, some sorption probably occurred since there is a small but apparently real difference between the sensitivities computed from the buret and micromanometer reading. The pump-out behavior of styrene indicates that in comparing sensitivities of successive samples of styrene and similar compounds, sufficient pump-out time must be allowed between the introduction of successive samples to prevent accumulation of the sample in the reservoirs. It is not sufficient simply to pump until a low pressure is indicated.

If it is assumed that the difference between the sensitivity for styrene as measured by the microburet and by the micromanometer comes from adsorption on the walls alone, then from table 5 a fraction of about 0.3 of the liquid sample is adsorbed. It happens that this amount of styrene is nearly equal to the amount in a monomolecular layer over the surface of the reservoir. This is probably fortuitous, as the amount sorbed increases with the pressure as shown in table 4. A liquid neohexane sample gives a sensitivity 13 percent less than a gas sample. In this case it is not certain whether there is some

adsorption or whether there is some loss of liquid because of wetting of the walls of the pipet or buret. Further research is planned in the effort to determine the nature of the sorption on the walls and in the lubricant in this region of the inlet system of the mass spectrometer.

Obviously mixtures of styrene and less strongly adsorbed compounds will change composition in an unpredictable manner depending on the relative amounts and characteristics of the components of the mixture when introduced into the reservoir, unless the walls have been exactly pretreated with similar mixtures immediately beforehand.

Other laboratories have reported use of heated inlet systems at temperatures in the neighborhood of 150° C. This undoubtedly will decrease the

effects noted above but will make difficult the use of a micromanometer of the type described by Young and Taylor or the one used in the present research. In addition, problems of increased rate of polymerization of compounds such as styrene are posed by higher temperatures.

The authors gladly acknowledge indebtedness to valuable discussions on liquid sample introduction contributed by different members of various laboratories at the Chicago and New York meetings of Consolidated mass spectrometer users.

We also wish to express our thanks to Leo A. Wall for occasional advice and help.

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