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An Improved Exponential Dilution
Flask for Gas Chromatography

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The usefulness of the exponential dilution flask for calibration of gas chromatographic detectors and preparation of dilute gas samples has been discussed by Lovelock (1), Williams and Winefordner (2), and Oberholtzer and Rogers (3). In the glass version of the design of Winefordner, serious wear occurs at the glass-metal bearing. As a result, a mixture of glass and metal dust collects at the bottom of the flask and necessitates regular cleaning and repair. The critical alignment of the stirring mechanism makes replacement of this bearing a very difficult task.

To overcome those problems, we have designed a three-piece flask which has been found to compare favorably with those previously reported. Moreover, this design facilitates cleaning, and wear of the contacting surfaces is reduced.

EXPERIMENTAL

Construction of the Dilution Flask. Figure 1 shows the dilution flask with both a Teflon stirrer and a glass stirrer. The exterior of the flask (item 1) was constructed from 54-mm Pyrex tubing. The bottom half of the flask was prepared by flanging one end followed by blowing a flat surface 41-mm below the flange. The top half was prepared in a similar manner except, in this instance, a domed surface was blown 41-mm above the flange. The gas inlet and outlet were constructed from 6.4-mm o.d. tubing with 8-mm o.d. tubing for the syringe injection port. After

annealing, the flanges were ground and lapped on a glass plate to give a close fit of the joint.

The Teflon stirrer (item 2) was constructed from an annular Teflon washer, 25.4-mm o.d. X 12.7-mm i.d. X 6.4-mm thick; a 38.1-mm X 6.4-mm Teflon coated stirring bar; and a 1.6-mm Teflon sheet of trapezoidal shape with a height of 50.8-mm and parallel sides of 25.4-mm and 44.4-mm, respectively. The 25.4-mm side of the Teflon sheet was knotted as shown in the figure. The washer was machined so that one-half the width of the stirring bar could be imbedded into it. Perpendicular to the stirring bar a second slot 1.6-mm wide X 3.2-mm deep was machined for fastening the Teflon sheet. A minimum of epoxy cement was used to bond all points of contact.

The glass stirrer (item 3) was constructed from 7-mm glass tubing and 3.2-mm glass plate. The glass tubing was used to form a 38.1-mm X 38.1-mm cross. A 31.8-mm X 4.8-mm magnet was sealed into one arm of the cross. The glass plate was attached to the adjacent arm of the cross such that the stirrer had dimensions of 44.4-mm wide X 44.4-mm high.

A very light coat of Dow Corning Silicon High Vacuum grease was applied to the outside edge of the flange to insure tight sealing of the flask. The flanges were clamped together with an aluminum collar, formed from two pieces of aluminum plate 3.2-mm thick. The glass inlet and outlet

tubes were connected to the stainless steel gas lines using Cajon, 4UT-6-100-316, Ultra Torr to Swagelok, Unions (Crawford Fitting Co.).

Other Apparatus. The digitally controlled chromatographic system has been discussed in detail (3). Gas samples were introduced into the dilution flask by means of a Carle Model 2014 Sampling Valve using a Model 2050 Pneumatic Actuator (Carle Instruments, Inc., Anaheim, Calif.). The flask was immersed in an air bath, thermostated at 35.0 ± 0.1 °C. The magnetic stirring mechanism of the flask was driven by a Sargent Magnetic Stirrer, S-76409 (E. H. Sargent and Co.).

Procedure. The gas samples consisted of a binary mixture of methane in helium, and they were prepared according to the method described by Guiochon, et. al. (4). The concentration of methane in the mixture was 1390 ppm. A 3.92-ml sample of gas was introduced into the 121.5-ml exponential dilution flask. This resulted in an initial concentration of ~~44.8~~ ppm methane, assuming that complete mixing occurred instantly.

Studies of the flask behavior were carried out with helium flow rates of 99.0 and 10.2 ml/min respectively. The precision with which more dilute samples could be prepared by using the dilution flask method was studied over a two

decade concentration range, 41.5 ppm to 0.7 ppm. A 50-cm X 0.32-cm i.d. stainless steel column packed with 5% SE-30 on Chromasorb G was used to retain and spread the peaks.

RESULTS

For any single run at the 99.0 ml/min or 10.2 ml/min flow-rate, the relative standard deviation of the slope of the $\ln$ area vs time plot was less than 0.001%, which corresponded to less than +0.5% relative standard deviation in the concentration. However, the relative standard deviation of individual samples on duplicate runs depended on the flow-rate of the diluting gas. At the 99.0 ml/min flow-rate, the effluent from the dilution flask was sampled at 18-sec intervals over a 300-sec period. The concentration of the effluent of the flask after the first 18 seconds was 33 ppm. The relative standard deviation of five duplicate runs at this concentration was $\pm 0.65\%$. However, the relative standard deviation increased with the number of intervals until it reached $\pm 2.0\%$ at 3 ppm. Oberholtzer and Rogers (3) reported similar results in that at 6 ppt, concentration of the first sample in their series, the relative standard deviation was $\pm 0.40\%$, and it increased to $\pm 4.4\%$ at 0.2 ppm.

At the 10.2 ml/min flow-rate, the digital controller was programmed to sample the effluent of the dilution flask at 2-min intervals over a 20-min period. The relative standard deviation of five duplicate runs at the 20 min interval was $\pm 1.6\%$. As in the case of the 99.0 ml/min

flow-rate, an increase in the relative standard deviation with decreasing concentration was observed; however, after 20 minutes the relative standard deviation was only $\pm 1.8\%$. Therefore, the increase in the relative standard deviation with time of dilution was less at the 10.2 ml/min than at the 99.0 ml/min flow-rate over a comparable concentration range.

DISCUSSION

The dilution behavior of the flask was comparable to those flasks previously reported. However, the present design has several significant advantages over the earlier ones. First, wear of the contacting surfaces has been minimized, as evidenced by the absence of noticable wear after three months of continuous use. Second, not only have alignment problems of the stirring mechanism been eliminated, but also the entire process of dismantling and reassembling the flask has been greatly facilitated. Thus, the flask is inexpensive to construct and easy to maintain.

The excellent fit of the $\ln$ area vs time plots indicated efficient mixing of the gases in the flask. It is apparent that part of the error between duplicate runs is dependent on the reproducibility of flushing the gas samples from the sample loop into the flask. This is indicated by comparison of the relative standard deviation of the first

samples taken from a series of runs at each flow-rate -- 1.6% and 0.65% at the 10.2 ml/min and 99.0 ml/min flow-rate, respectively.

The reason for the different increases in the relative standard deviation with decreasing concentration at the two flow-rates may be due to the inability of the flow controller to reestablish the same flow-rate after interruption of flow during sampling. At the higher flow-rate, the pressure build-up may result in a non-reestablishment of the same flow-rate each time the flow is interrupted. This would have little effect on the initial samples but would greatly magnify the error over long periods of dilution. At the lower flow-rate, there would be less pressure build-up upon switching; therefore, the flow controller should more closely reestablish the flow-rate observed prior to sampling. This is reflected by the small increase in the relative standard deviation with decreasing concentration at the lower flow-rate.

We have constructed a flask which has several practical advantages over those previously reported. Also our observations show that it should be possible to obtain better precision at the lower concentration range by injecting smaller samples followed by dilution at lower flow-rates.

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References

1. J. E. Lovelock, Anal. Chem., 33, 162 (1961).
2. H. P. Williams and J. D. Winefordner, J. Gas Chromatog., 4, 271 (1966).
3. J. E. Oberholtzer and L. B. Rogers, Anal. Chem., 41, 1234 (1969).
4. L. Angely, E. Levart, G. Guiochon, and G. Peslerbe, Anal. Chem. 41, 1446 (1969).

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FIGURE CAPTION

Figure 1. Exponential dilution flask with Teflon stirrer
and glass stirrer.