

GPC: Use of Automatic Weighing to Determine Elution Volumes

GERHART A. MOEBUS, JOHN A. CROWTHER, EDWARD G. BARTICK, and JULIAN F. JOHNSON, *Institute of Materials Science and Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268*

Synopsis

An automatic balance has been designed, constructed, and tested for continuous determination of the weight of the eluent in chromatography. This balance is considerably more precise than the frequently used automatic siphons. As the elution volume for any molecular species is independent of flow rate over a considerable range, the balance can be used with relatively inexpensive pumps, and thus highly precise constant volume pumps are not required.

INTRODUCTION

The two variables that are measured in gel permeation chromatography are the concentration of material emerging from the column and the elution volume at a given point. The elution volume is commonly measured by use of a siphon or by using a constant-volume pump and making the determination as a function of time.

There have been a number of reports of significant errors encountered, particularly in high-speed GPC, using automatic siphons.^{1,2} Procedures for minimizing these errors have been described.^{1,3,4} The disadvantage of the precision volumetric pumps is that to obtain the desired reproducibility requires precision workmanship, and the cost of such pumps is therefore relatively high.

It is a well-established phenomenon that the elution volume for a given molecular species of a given polymer in a given solvent at a given temperature does not vary with flow rate (although the resolution does). It therefore seems reasonable to suppose that if a precise, inexpensive way of determining the elution volume were available, a relatively inexpensive pumping mechanism could be used as the small variations in flow would be of no concern.

An obvious solution to this is to automatically weigh the eluted material. Automatic weighing balances are commercially available in a wide variety of configurations, precision, and accuracy.⁵ It is desirable to have a balance whose capacity can be readily changed over a wide range to make possible its use with both high-speed and conventional GPC instruments. With this in mind, a balance was designed for the specific requirements of this case.

BALANCE DESIGN

Figure 1 is a schematic of the circuitry of the balance, and Figure 2 shows a photograph of the balance itself. The cantilever arm design was selected because

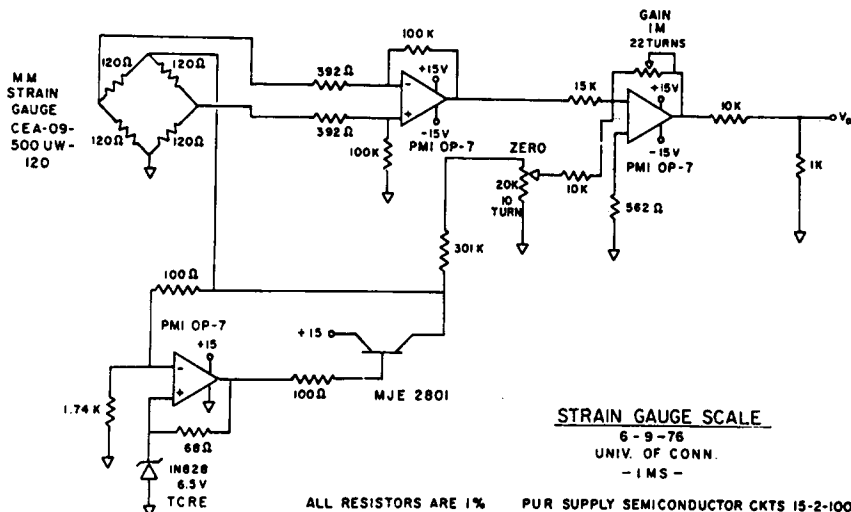


Fig. 1. Schematic of the balance circuitry.

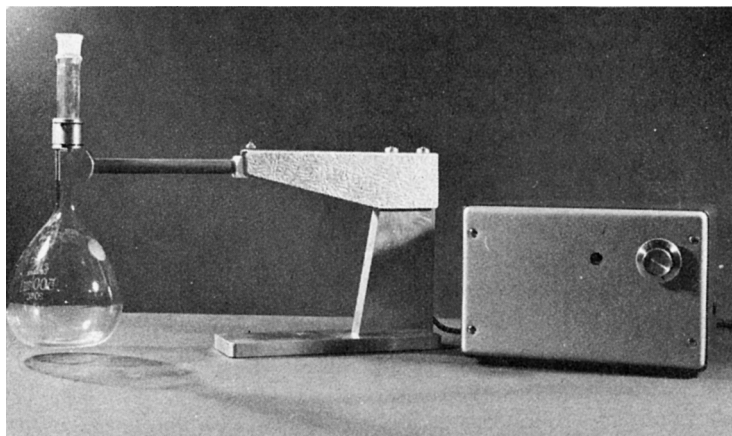


Fig. 2. Photograph of balance.

this balance is also used with a high-temperature GPC operating in the differential mode.⁶ This requires that the eluted solvent and polymer be maintained at elevated temperatures to prevent precipitation; thus, the balance arm must of necessity extend into the thermostatted oven.

The measuring principle consists of the use of four strain gauges mounted in an additive configuration on the cantilever arm. The strain gauges are connected in a bridge circuit which is supplied with a stable excitation voltage. The signal is then transmitted into an operational amplifier operating in the differential mode which senses an electrical imbalance when a mechanical deflection is applied to the arm. The resulting signal is transmitted into an operational amplifier operating in the inverting mode which acts as a buffer and gain amplifier and produces the signal to be read.

The same stable voltage supply used for the bridge is also used as an offset voltage for easy taring. The display device may be any suitable precision potential-measuring instrument such as a digital voltmeter or a conventional potentiometric recorder with or without a range changing device.

PERFORMANCE

The performance of the balance is dependent on many factors, both those inherent in the construction of the balance itself and those which are a result of the display methods employed. Some of the balance variables are the beam thickness, the stress which may be applied to the beam without exceeding its elastic limit, the beam material, and the length of the beam. The variables found in the display methods include the range of voltages which can be measured and the precision which can be obtained by the measuring device. These factors were considered in order to design a balance with optimum characteristics in the 0–400 g range.

Performance tests were conducted using a 3½-digit digital voltmeter and a Varian A-25 recorder. Tests were conducted on the balance for stability, reproducibility, and linearity. The gain potentiometer was set to give approximately a 1-volt signal when a 400-g load was placed on the balance arm. A pan was constructed which hung freely from the balance grip on which the various weights were placed. The pan weighed 17.7970 g as weighed on a Mettler H 15 analytical balance.

The Varian A-25 recorder was used to determine the baseline stability over a 24-h period. The results show that the long-term stability was good to ± 0.02 mV, which corresponds to ± 0.01 g with the given gain setting. This test was conducted with no loading on the arm.

The recorder was then replaced by the 3½-digit digital voltmeter, and visual inspection of the resulting noise indicated measurements could be discriminated to approximately ± 0.02 mV ($\sim \pm 0.01$ g). Ohaus "Sto-A-Weigh" weights were weighted on a Mettler H 15 analytical balance, and the results showed that the stated weights were all within the 0.01-g tolerance needed to test the balance.

A linearity test was conducted using the weights mentioned previously and the digital voltmeter as the potential measuring device. The balance was tared to zero with the sample pan in place, using the tare potentiometer, and 30 different weights from 400 to 0.03 g were placed on the pan and the resulting signal recorded. The results for 19 weights from 10 to 400 g may be seen in Figure 3. A least-squares analysis of the data resulted in the following coefficients: slope, 2.4985; intercept, -6.4891×10^{-3} ; std. dev. slope, 5.403×10^{-5} ; std dev. int., 7.485×10^{-3} ; and correction coefficient, $9.999999935 \times 10^{-1}$. These results show the excellent linearity of the new strain gauge balance.

A similar linearity test was conducted with several weights, only this time a 295-g weight was tared to zero and the other weights were added to this. The results demonstrated that the weight tared had no influence on the linearity or value of signal as long as the tare weight and test weights together do not exceed the elastic limit of the beam material.

Reproducibility tests carried out demonstrate that the balance is reproducible to within the noise level of 0.02 mV (0.01 g).

These tests indicate that the balance has sufficient precision, linearity, and stability to substantially increase the precision of elution volume (weight) measurements over the conventional siphon. The fact that the elution weight and elution volume may be readily interconverted through the solvent density allows one to report results in either fashion. It also reduces the necessity for extremely precise pumping systems for analysis run on time as is the current practice with high-speed LC.

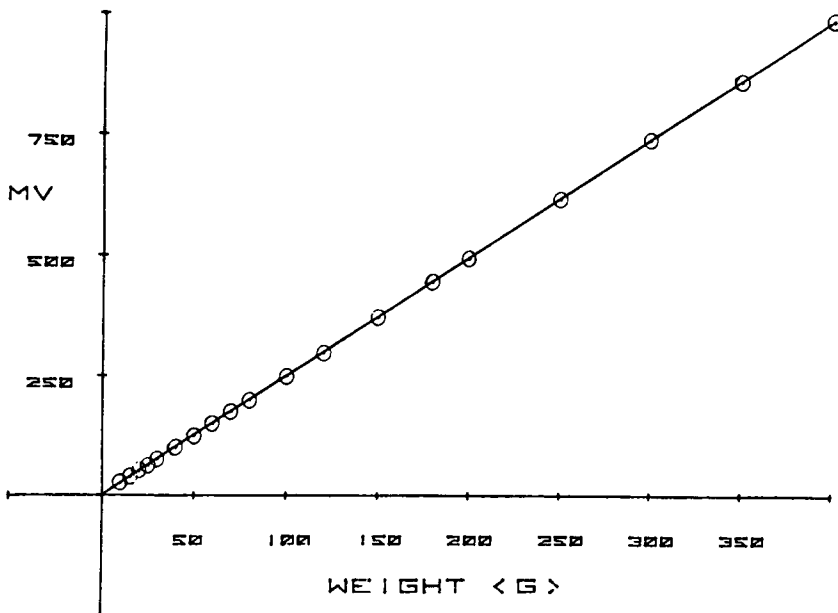


Fig. 3. Signal results for 19 weights from 10 to 400 g.

One concern at high temperature particularly has been in evaporation from siphons. Use of a volumetric flask as the collection vessel provides a long diffusion path. The effect of evaporation was studied using *o*-dichlorobenzene in an oven maintained at 140°C for 74 hr. The results show that over the 74-hr time period, approximately 2.8-g solvent evaporated. The evaporation rate of 0.038 g/hr is small enough to neglect in almost all applications.

In summary, the automatic balance described provides a simple, inexpensive, precise way of determining elution weights over a wide range suitable for both high-speed and conventional chromatography including high-temperature operation. Its disadvantage in high-temperature operation is that the receiver must be emptied before each run without disturbing the temperature control. This problem was overcome in the current case by installing $\frac{1}{8}$ -in. stainless-steel tubing into the flask which is connected to a vacuum flask outside the thermostatted oven. The solvent was then easily siphoned away before the next injection was made.

A portion of this work was supported by the National Science Foundation Grant CHE 75-01915.

References

1. D. D. Bly, W. W. Yau, and H. J. Stoklosa, *Anal. Chem.*, **48**, 1256 (1976).
2. D. D. Bly, H. J. Stoklosa, J. J. Kirkland, and W. W. Yau, *Anal. Chem.*, **47**, 1810 (1975).
3. G. N. Patel, *J. Appl. Polym. Sci.*, **18**, 3537 (1974).
4. A. W. Wolkoff and R. H. Larose, *J. Chromatogr. Sci.*, **14**, 51 (1974).
5. R. O. Leonard, *Anal. Chem.*, **48**, 879A (1976).
6. J.-Yi. Chuang, J. F. Johnson, *J. Appl. Polym. Sci.*, **17**, 2123 (1973).

Received August 8, 1978