RHEODYNE

TECHNICAL NOTE

Number 5

Achieving Accuracy and Precision with Rheodyne Manual Sample Injectors

Abstract. The accuracy and precision of HPLC sample injection depends on injector design and loading techniques. This article describes the performance of different Rheodyne injectors and answers the following questions:

- *How large a volume can be partially loaded into a sample loop with syringe accuracy?*
- *How much sample must be wasted to completely fill a sample loop with pure sample?*
- *What precision can be achieved by the various designs and loading techniques?*
- *How can cross-contamination be avoided?*

Manual sample injectors for HPLC transfer sample at atmospheric pressure from a syringe to a sample chamber. The chamber is then connected by valving action to the high-pressure mobile phase stream that carries the sample onto the column. There are two methods of loading the sample chamber: "complete-filling" and "partial-filling." These two techniques differ in accuracy, precision, and the amount of sample required.

Rheodyne offers several models that use only the complete-filling method. (See Table I). This method produces volumetric precision often better than 0.2% relative standard deviation. The volume injected is that of the sample loop. An excess of two to five sample loop volumes should be loaded. Sample volume is varied by changing the sample loop size.

Fig. 1. Five typical Rheodyne manual sample injectors: 7725, 8125, 7410, 7010 (with Loop Filler Port, P/N 7012), and 3725-038. Valve characterisitics are listed in Table I.

Table I. Characteristics of Rheodyne Manual Sample Injectors.

Type and Capabilities	Scale	Partial-Filling Volumes (Range)	Sample Loop Sizes (Range)	Liquid-contact Materials	Max. MPa[1]	Max. T °C	MBB[2]	Model[3]
Dual Mode Can load the loop by two methods: 1) partial-filling – syringe determines volume without wasting sample 2) complete-filling – loop determines volume by overfilling loop	Analytical	1 µL - 2.5 mL	2 µL - 5.0 mL	316 SST, Vespel[4], ceramic, PEEK	48	80°	Yes	7725, 7725i
			5 µL - 5.0 mL		48	80°	No	7125
		1 µL - 5.0 mL	2 µL - 10 mL	PEEK, Tefzel[4], ceramic	34	50°	Yes	9725, 9725i
	Micro	0.1 µL - 500 µL	5 µL - 1.0 mL	316 SST, Vespel ceramic, PEEK	48	80°	No	8125
	Preparative	100 µL - 10mL	2.0 mL - 20 mL	316 SST, PEEK	34	50°	Yes	3725(i)-038
				PEEK	28	50°	Yes	3725, 3725i
Single Mode Can load the loop by one method: complete-filling – loop determines volume by overfilling loop	Analytical	Not Applicable	5 µL - 5.0 mL	316 SST, Vespel	48	150°	No	7010
			5 µL - 10mL	PEEK, Tefzel, ceramic	34	50°	No	9010
	Micro		0.5 µL - 5.0 µL	316 SST, Vespel	48	150°	No	7410
			0.2 µL - 1.0 µL	316 SST, Vespel	48	80°	No	7520

1. This is the maximum pressure in MPa to which the valve can be adjusted. Some models are shipped from the factory set for lower pressures. 1 MPa = 10 bar = 145 psi.
2. MBB™ (Make-Before-Break) is a patented Rheodyne design that provides uninterrupted flow when switching between LOAD and INJECT. MBB provides zero sample loss, no cross-contamination and greatly reduces transient pressure shocks.
3. Models with an "i" suffix have a built-in position sensing switch. Models 8125 and 9010 each has a built-in switch.
4. Vespel and Tefzel are trademarks of E.I. DuPont.

Rheodyne Models 7125, 8125, 7725i, 9725i and 3725i-038 (see Table I) can use both the complete-filling and the partial-filling methods. With partial-filling, the volume injected is that dispensed from the syringe. Therefore, the sample volume is easily changed. The volumetric precision of partial-filling is the syringe repeatability, typically better than 1%.

Model 3725 is designed for preparative-scale liquid chromatography. Accuracy and precision are not main concerns when using preparative scale valves as sample volumes are usually larger (see Table I), and therefore, the percent relative standard deviation (%RSD) is often higher.

This Technical Note describes the characteristics of these injectors and the loading techniques that produce the best analytical results. Some caveats: Precision values are always stated as one standard deviation or as %RSD. Keep in mind that injector precision values refer only to the injector's reproducibility when transferring sample onto the column. The precision of peak heights and areas observed with a chromatograph will typically be worse because non-injector components also contribute to non-reproducibility. Some explanations of injector behavior are simplified, but additional discussions are contained in footnotes.

Sample chambers can be a loop of tubing or a machined passageway, but we use the term sample loop for all chambers, regardless of shape.

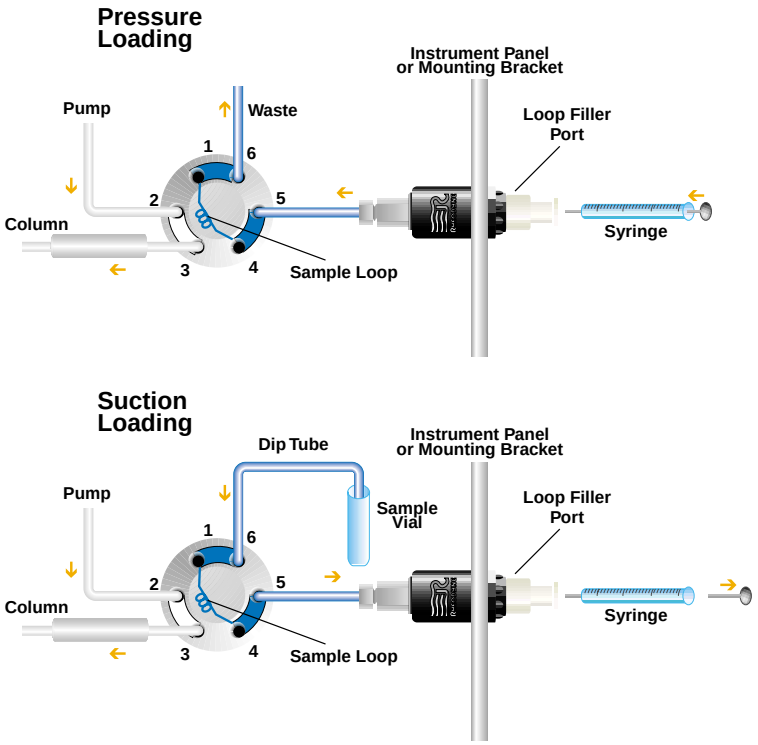

Fig. 2. Pressure loading and suction loading with P/N 7012 and 9012 Loop Filler Ports connected to Models 7010 and 9010 injectors respectively.

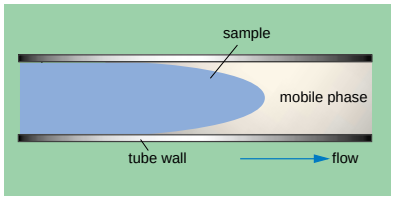

Fig. 3. Laminar flow effect.

Filling Characteristics

The mobile phase that flows through the sample loop in the INJECT position is trapped when the handle is returned to LOAD. As the next sample is loaded, pushing mobile phase ahead of it, the front of the sample becomes diluted. This happens because the fluid has a parabolic velocity profile between the tube walls. At the center of the tube the velocity is about twice the average, and at the wall the velocity is zero. This laminar flow effect is illustrated in Figure 3.

The initial fluid element (not shown) begins to elongate between tube walls and the sample distributes throughout a longer section of the tube, with the sample in the center having traveled farthest. The sample occupies about 2 µL of loop for every 1 µL loaded from the syringe. The exact distance traveled depends on the passageway geometry and the loading flow rate **(1)**.

This behavior accounts for the shape of a curve that is an important injector characteristic. Figure 4 is a plot of sample mass injected onto the column (as indicated by peak height or area) vs. volume of sample dispensed from the loading syringe. Figure 4 shows the three regions of the plot obtained when using the partial-filling technique.

1. Partial-Filling Region. When the volume dispensed is less than half the loop volume, the curve is linear. Sample has not yet reached the far end of the loop. Within this region, performance depends on the syringe and operator.

2. Nonlinear Region. When the volume dispensed is between half a loop volume and about two loop volumes, the curve is nonlinear. Sample is lost from the loop, so accuracy and precision are poor. If you dispense a volume equal to the loop size, you are in this region of inferior performance.

3. Complete-Filling Region. When the volume dispensed is several loop volumes, the mass injected is independent of the volume dispensed. The loop contains only pure sample, undiluted by residual mobile phase.

Now consider loading with single mode injectors. A loop filler port is used, in which case sample must pass through a connecting passage before it reaches the loop. Alternatively, as in Model 7520, an internal passage loads the sample chambers. Laminar flow again accounts for their behavior. The relationship between volume dispensed and mass injected for single mode injectors is shown in Figure 5.

Figure 5 differs from Figure 4 in all three regions: i) The curve is offset to the right because sample first must travel through the connecting passage. This region of the plot in Figure 5 is called the Offset Volume Region. This region shows the offset (error) between the volume dispensed from the syringe and the volume that enters the loop. ii) The curve is not linear because the first sample entering the loop is dilute; it is the sample traveling down the center of the connecting passage. iii) The region of complete-filling is reached later, especially when small loops are used, because the connecting passage must also be flushed.

Therefore, single mode injectors can achieve high precision only by using the complete-filling method. The following discussion shows how these filling characteristics affect accuracy, precision, and cross-contamination.

Accuracy

Often it is not necessary to know the actual volume injected onto the column, since errors are usually constant, the same during calibration and analytical runs. However, when absolute accuracy is required, the following precautions are necessary.

Partial-Filling. Partial-filling with accuracy is only practical with dual mode injectors. A safe rule is to assume that the linear region (in Figure 4) extends only to 50% of the loop volume.

Complete-Filling. A "complete loop volume" is only injected if enough sample is loaded to flush out the residual mobile phase. Table II lists the volume of sample that must be transferred from the syringe into various injectors to achieve 95% of the maximum. The actual volume contained must be determined by experimental measurement **(2)**. This is because stated volumes on loops are nominal (errors can be as high as 30% in small loops). Also, in the case of external loops, the same loop on different injector models will inject different volumes. This is because the volume includes internal injector passages, whose volumes differ among models.

Table II. Approximate Load Volumes in µL for 95% of Maximum Sample Mass **(1)**.

Loop Volume (µL)	7520	7410(2)	7010 & 9010	7125, 7725, & 9725
0.2	3			
0.5	4	40		
1	7	25		
2		25		
5		30	35	15
10			40	25
20			55	40
50			95	80

(1) These are approximate values intended to show the relative volumes required. Actual volumes will depend on operator technique (see Footnote 1).

(2) The 7410 and 7010/9010 data applies when using Models 7012/9012 Loop Filler Ports with the standard (0.3 mm ID) connecting tube containing about 7 µL. Fill volumes can be reduced by using a tube with smaller diameter.

Precision

The reproducibility of peak height and peak area in LC depends on (a) injector precision, (b) stability of flow rate, mobile phase composition, temperature, and (c) detector and integrator sensitivity fluctuations. When non-injector components are the major source of variations, different injectors, operators, or loading techniques are indistinguishable. When non-injector contributions are carefully controlled, the differences can be significant. The section on page 6 discusses non-injector contributions. The injector contributions are discussed below.

Partial-Filling. As shown in Figure 4, the syringe volume dispensed and sample mass injected are linearly related in the partial-filling region of dual mode injectors. The precision of the injector is simply that of the syringe. Consider a 25 µL syringe with fifty divisions. If the plunger can be set with a precision of 0.1 division, the result is the Syringe Volumetric %RSD shown in Table III. As the loaded volume becomes smaller, the relative error of the constant 0.1 division setability becomes larger.

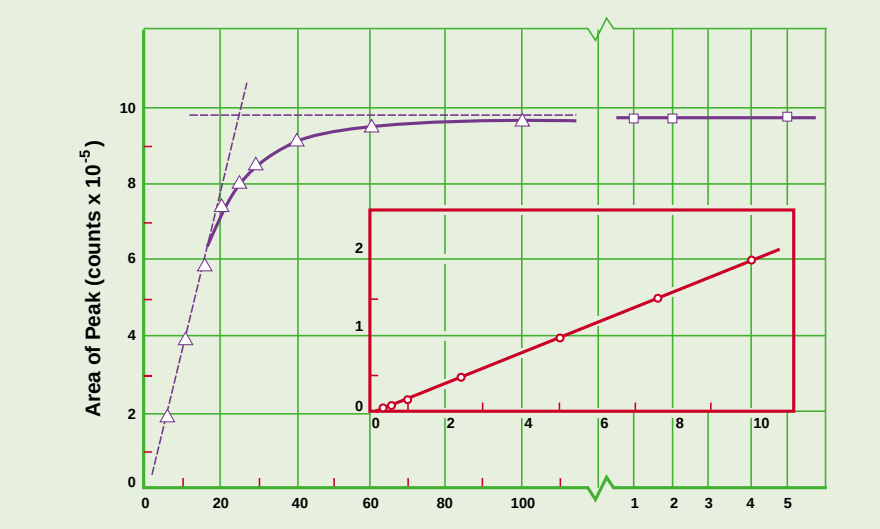

Fig. 4. Characteristic plot of the sample mass injected onto the column (area of peak) vs. the volume of sample dispensed from the loading syringe for dual mode injectors such as Model 7125 with a 20 µL sample loop. Data were obtained using three syringe sizes: 10 µL (0), 100 µL (Δ), and 5 mL (□). The linear regression straight line best fit to the 10 µL syringe data is shown (—). The straight line correlation coefficient is 1.0000. Departure from linearity starts around 15 µL, i.e., at about 60% of the actual loop volume. The injector was flushed (INJECT position) with 0.5 mL of solvent after each injection.

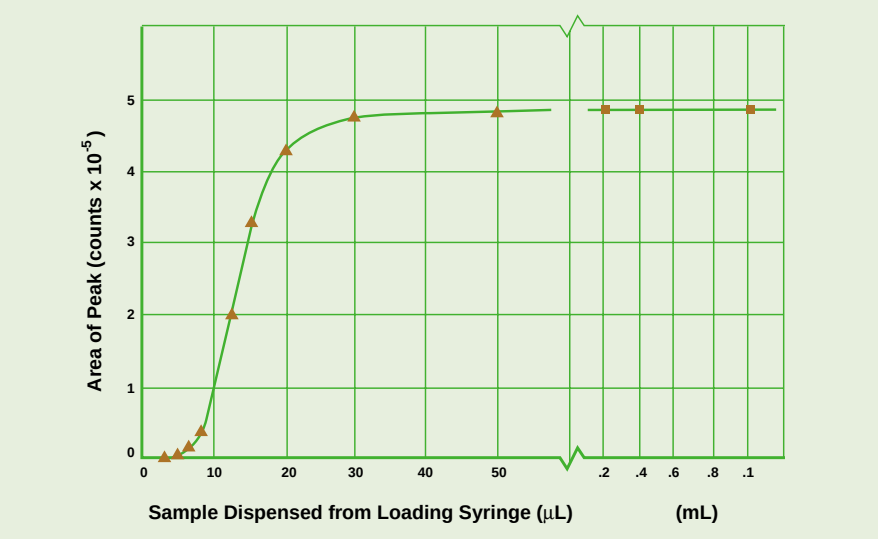

Fig. 5. Characteristic plot of sample mass injected onto the column (area of peak) vs. the volume of sample dispensed from the loading syringe for single mode injectors such as the Model 7010 injector with a 5 µL sample loop and a Model 7012 Loop Filler Port (0.3 mm ID connecting tube). The first 5 µL of sample loaded does not become injected, because it has not yet reached the sample loop. After 5 µL the sample starts to enter the loop. After about 8 µL a nearly linear region is reached. At about 15 µL some sample has reached the far end of the loop and the contained mass increases nonlinearly. At about 30 µL the loop contains 95% of the maximum. After 200 µL the addition of sample causes very little increase in mass contained in the loop.

Table III. Chromatograph Peak Height % RSD.

Loaded Volume:	20 µL	10 µL	2 µL
Syringe Volumetric %RSD:	0.25	0.5	2.5
Peak Height %RSD:	0.2	0.3	1.5

The chromatograph Peak Height %RSD in Table III was experimentally determined using a 25 µL syringe and a 50 µL sample loop on a Model 7125 Injector.

Special equipment (see page 6) kept non-injector contributions to height and area precision below 0.05% RSD. The chromatograph values are essentially due to the injector alone. Results varied with different syringes, loops, and operators, but the values in the table are typical.

We conclude that partially loading the dual mode injectors should produce an injector precision in the range of 0.2 to 2% RSD, depending on how much of the syringe full scale is used, and on operator care.

Complete-Filling. Figure 4 shows that if enough sample is loaded the loop will contain almost pure sample. The zero slope of the line eliminates the syringe as a factor. The volumetric precision should be good because of the mechanical stability of the sample loop. The contained sample mass precision will then be governed by the stability of sample density. Table IV shows the precision that results from a density coefficient of 0.1% per °C **(3)**.

Table IV. Volumetric Precision Based on Density Coefficient.

Temperature Stability:	0.1°C	0.5°C	1°C
%RSD of Injected Mass:	0.01	0.05	0.1

Using the special equipment, we loaded 350 µL of sample into a 5 µL loop on a dual mode injector, thermostated at ±0.1°C. The observed chromatograph peak height precision was 0.03% RSD, so we can state that the injector was at least this good (see page 6).

Figure 4 shows that smaller load volumes will produce poorer precision. The slope increases as less sample is loaded, resulting in an increasing contribution by the syringe non-reproducibility. Our experiments show that in the load-volume range of roughly half to two loop volumes, the precision is often even worse than that of the syringe itself **(4)**. So if enough sample is available, it is good practice to load with more than two loop volumes. An injector precision of about 0.1% RSD is typical when a dual mode injector is loaded with about five loop volumes.

This behavior is representative of loops in the 5 µL to 200 µL range on most Rheodyne injectors. However, injectors with smaller chambers – Models 7410 and 7520 – provide less precision, even when a large excess of sample is used. Values are typically in the 0.2 to 2% range, when loaded with 95% of the maximum sample mass (Table II). This difference from larger volume injectors is apparently due to operator skill and subtle variations in manual loading. The dimensional stability of the micro-loops is good, as indicated by the 0.05% RSD observed when loaded under automatic control **(5)**.

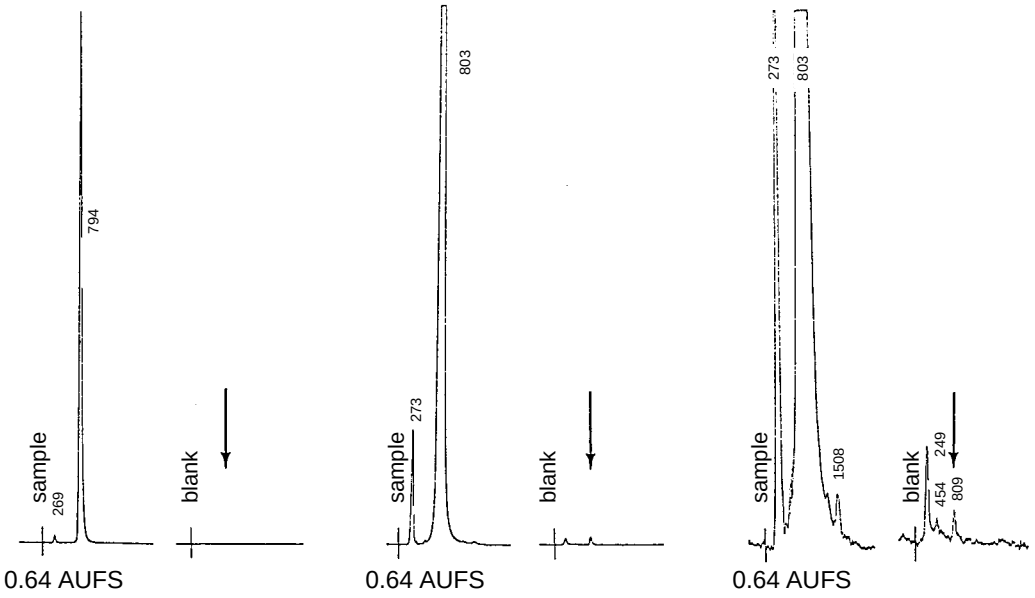

Fig 6. These chromatograms show Model 7125's small cross-contamination from one sample to the next when the needle port is not flushed between injections. (Sample carryover can be completely eliminated by flushing.) A 10 µL syringe injection (into a 20 µL loop) of concentrated sample was followed by a 10 µL injection of mobile phase (usually the blank), without an intermediate flush of the needle port. This was done at three different detector sensitivities. The units of the retention time printed out on the peaks are 0.1 seconds. Thus the retention time of the major sample component is 80 seconds (varies from 79.4 to 80.9 seconds in this series of runs). In the experiment at 0.64 AUFS the cross contamination cannot be observed. When the sensitivity is increased to 0.04 AUFS the small cross contamination can be seen. At a sensitivity of 0.0025 AUFS the contamination can be measured, 0.02% or 2 nL absolute. At this high sensitivity, contaminants in the blank are observable. Conditions: 4.6 mm x 10 cm Hypersil ODS 5 µm column; water-acetonitrile, 1:1 mobile phase; 2 mL/min flow rate; 40°C temperature; 254 nm detector wavelength.

Cross-Contamination

Mobile phase automatically flushes out the sample loop while in the INJECT position, unless the injector is returned to LOAD prematurely **(6)**. However, the connecting passage between needle and loop still contains sample and must be flushed before every injection. Small, well swept passages, require less flushing solvent. Rheodyne's dual mode injectors are special cases because they have no connecting passage. Even though it has been designed to eliminate the trapped volume, we would expect there to be a very small amount of cross contamination if the injector is not flushed between injections. This is because of sample traces left on the surface of the needle seal and rotor seal, and in the liquid left in the needle port. We have made many direct measurements of this by injecting a blank after a normal sample, without an intermediate flush. Figure 6 shows typical results. The carryover is only observable when the sample concentration is very high and the detector is operated at a sensitive range.

We found that the amount of contamination varies with conditions, and even from one particular injector to the another. For example, with water as mobile phase and sample solvent, the cross contamination was 0.004 µL, but with heptane as mobile phase and sample solvent the cross contamination was 0.001 µL. Contamination was always less than 0.01 µL, which represents less than 0.1% for a 10 µL injection. Users of the 7125, 7725, and 8125 who want to use the valves without flushing should actually check the cross contamination under the particular conditions at hand if there is any concern about its magnitude. The peak height that results from the sample should not exceed the linear range of the detector, or the cross contamination will be overstated. It is good practice to flush the 7125, 7725, and 8125 every five or ten injections to prevent the possible build-up of contaminants and to keep both needle port and vent line full of solvent **(7)**.

Summary

The partial-filling method uses syringe readings to determine the injected volume of sample. These readings are accurate only within the linear region of the load volume curve. With this filling method, linearity extends from zero to about half a loop volume since there is no internal connecting passage.

Precision with partial-filling is about 1% RSD. It depends on the syringe and operator technique. With Models 7125 and 7725, when 5 µL is dispensed with care from a 10 µL syringe into a loop 10 µL or larger, a precision of injected sample mass of about 0.4% RSD will result. The observed precision of peak height and area will be larger due to non-injector chromatograph components.

The complete-filling method uses the sample loop to determine the injected volume. When the volume must be known exactly, it must be experimentally determined. Excess sample is required to fill the loop completely with undiluted sample. With Models 7125 and 7725, about 15 µL is required to fill a 5 µL loop with 95% of the maximum contained sample mass.

Precision with complete-filling is about 0.1% RSD. Micro-scale sample loops may have a slightly higher % RSD. For example, when 25 µL dispenses into a 5 µL loop, Models 7125 and 7725 both have a precision of injected sample mass of about 0.1% RSD. The observed peak precision will be less due to non-injector components.

Cross-contamination can be avoided by flushing needle ports properly. Dual mode injectors can often be used without flushing after each injection, but it is good practice to flush after every few injections.

Footnotes

(1) The dispersion of sample in straight tubular passages is flow rate dependent. At practical rates of loading, the interaction of diffusion with the parabolic velocity profile causes dispersion to increase with increased flow rate. Sample dispensed more quickly from a syringe will travel further along the passages. This flow dependence can contribute significantly to loss of accuracy and precision, unless the operator uses consistent loading technique. The following factors depend on the loading flow rate: (a) The offset volume, the point at which sample enters the loop from a connecting passage, (b) the volume at which the linear region is exceeded, and (c) the volume at which the loop is filled with a specific percentage of its maximum contents.

When passages are short, curved, or change diameter abruptly, the dispersion mechanism becomes complex. The dispersion flow dependence can be quite different from that described above. The practical consequences are the same; injector behavior depends on the rate at which sample is loaded into the loop.

All discussions in this Technical Note assume that the loop always contains mobile phase prior to loading and that the sample is introduced without air bubbles. However, two other techniques are sometimes used. 1) The mobile phase is displaced by air before the sample is loaded. The amount of sample required to load the loop completely is reduced, since there is nothing to dilute the sample. 2) Three or four small segments of air are placed in the front of the sample. These segments reduce mixing as the sample passes through the loop, so less sample is required to fill a given volume. This is not recommended for partial-filling because the air will be injected and can cause artifact peaks at high detector sensitivity. With complete-filling the segments must be completely removed from the loop to insure high precision. When suction loading is used (Figure 2), the air segmentation is achieved by withdrawing the dip tube from the sample momentarily a few times as the sample starts into the tube.

(2) The actual volume injected into the column by the complete-filling technique includes internal valve passages. The injected volume can be experimentally determined as follows. Plot peak height or area vs. loaded volume, as in Figure 4. Be sure all points are within the linear range of the detector. Extrapolate the ascending linear part of the curve upward and the horizontal part to the left. At the intersection of these two extrapolated lines, drop a perpendicular to the volume axis. The volume thus found is that actually injected.

When there is an offset volume, as in Figure 5, the offset must be subtracted to determine the correct volume. The offset volume is determined by extrapolating the ascending linear part of the curve down to the volume axis.

(3) Density changes per degree centigrade are about 0.02% for water, 0.1% for most organic solvents, and intermediate values for aqueous-organic mixtures. These density changes are considerably larger than the changes in contained volume of a sample loop due to the thermal expansion. For example, steel has a cubic coefficient of expansion of about 0.004% per degree centigrade. Therefore, it is fluid density changes that govern the precision of sample mass injected from a completely filled sample loop. However, the presence of gas bubbles can cause very poor precision.

(4) In the complete-filling method, a point is reached during dispensing of the sample, when the front of the sample reaches the end of the loop (beginning of the nonlinear region, Figure 4). As more sample is dispensed, some of it passes out of the loop into the vent line, where it cannot become injected onto the column, For a given volume dispensed, the amount of sample lost from the loop depends on the flow rate of loading. This is because the distance that the sample travels down the loop depends on the dispensing flow rate, as discussed in Footnote (1).

As the load volume becomes large, in excess of two loop volumes, the sensitivity of this effect to flow variations diminishes. In the limiting case of very large load volumes, the loop is essentially 100% full of sample (no residual mobile phase), and the sample mass contained in the loop is immune to loading flow rate changes.

(5) Model 7520 with a 1 µL sample loop produced excellent peak height and area precision even with small sample load volumes, when loaded under automatic control. This control consisted of the following: a needle was fastened to the needle port, and connected via a Teflon tube to a helium-pressurized sample reservoir. An automatic on-off valve was placed in this line to control the time during which sample could flow, and thus the total volume of sample loaded. The time duration was computer controlled. Volumes of 6 µL and more could be loaded with 0.05% RSD. Volumes of 3 µL produced 0.2% RSD, which still compares favorably with the precision achieved by hand loading this volume. Factors which may play a role in the exceptional precision achieved under automatic control include: a) constant sample delivery flow rate, see Footnote (4), b) constant orientation of the needle in the port, leading to constant sample transfer characteristics (convective mixing, etc.), c) absence of micro bubbles that may enter the needle port during insertion and withdrawal of the needle in hand operation.

(6) In the INJECT position the sample is flushed out of the loop and onto the column. But, just as it requires several loop volumes to displace all the mobile phase when loading, several loop volumes of mobile phase must pass through the loop to flush out all of the sample. The number of volumes passing through the loop per unit time is simply: (mL/min) ÷ (mL/loop) = loops/min. For example, a 10 µL loop in a system running at 1 mL/min turns over 100 loop volumes per minute. A 0.2 µL loop at 10 µL/min has 50 volumes per minute. Leaving the handle in the INJECT position for 30 seconds will therefore flush the sample loop adequately under most conditions.

(7) The loading syringe is removed from Models 7125, 7725, and 8125 needle ports in the INJECT position. As the needle withdraws it sucks about 1 µL of whatever is in the vent line into the needle seal. This material is subsequently pushed into the sample loop when the next sample is loaded, unless the needle port is flushed prior to returning to LOAD. In the partial-loading method the material becomes injected onto the column. If the material is mobile phase, no artifacts are produced. But if the material is a different solvent or air, artifact peaks may be produced, especially at high detector sensitivity and low UV wavelengths. These problems are avoided by flushing the needle port with mobile phase after each injection, or at least frequently enough to keep the vent line and needle port full. A Needle Port Cleaner not a needle, should be used for flushing since this flushes the entire length of the port.

Models 7125, 7725, and 8125 are most efficiently flushed while in the INJECT position, since the flush solvent exits via a vent line and does not pass through the sample loop. Flushing in the LOAD position fills the sample loop with flush solvent. This should cause no problem with the complete-filling method since most or all of it will be displaced by the sample. But with partial-filling some of the flush solvent will become injected. Unless the flush solvent is exactly like the mobile phase (trace contaminants, oxygen content, etc.), it may cause artifact peaks.

Dependence of Analytical Precision on Variations in Flow Rate, Composition, Temperature, and Experimental Methods.

The reproducibility of peak area and peak height depends on the stability of flow rate, mobile phase composition, column temperature, and the precision of the injector. This section summarizes the relative importance of the non-injector variables. It applies only to concentration-sensitive detectors (UV, refractive index and to some extent electrochemical). Reference: "Variables Affecting Precision and Accuracy in HPLC," S.R. Bakalyar and R.A. Henry, *J. Chromatogr*. 126, 327 (1976).

Flow Rate. Peak area is inversely proportional to flow rate; a 1% flow rate decrease causes a 1% area increase. Peak height is somewhat immune to flow changes, the dependence being due to the effect of flow rate on column efficiency. A 1% flow rate decrease usually causes <0.3% peak height increase. However, height can be affected when the time constant of the detector/data system is slow compared to the speed of peaks.

Mobile Phase Composition. Peak area is relatively unaffected by changes in composition. A decrease in B modifier causes an increase in peak width and a corresponding decrease in peak height. The area is unchanged. The different composition can change detector response, but this effect is usually small.

Peak height is very dependent on mobile phase. A 1% (absolute) decrease in B modifier causes height decreases in the range of 1 to 10%, depending on the mobile phase and capacity factor of the peak.

Temperature. Peak area is only slightly affected by temperature changes, the mechanism being the temperature dependence of detector response. Peak height is affected because of the temperature dependence of retention and column efficiency. The dependence varies widely among different compounds and mobile phases. A decrease of one degree Celsius typically causes an increase in retention time of about 2%, and a corresponding decrease in peak height. Solutes with secondary equilibria, such as acidic or basic compounds can be much more sensitive to temperature changes.

Table V summarizes how peak height and area typically change with a small incremental decrease in flow rate, composition and temperature. It shows that flow rate control is most important when area is used to quantify, while composition control is most important when height is used.

Table V. Variations in Conditions Affecting Peak Area and Height.

	Flow Rate	Composition	Temperature
	-1%	-1%B	-1°C
Area	+1%	0 to ±1%	0 to ±1%
Height	<+0.3%	-1 to -10%	0 to ±2%

Experimental Methods. In the experimental work, non-injector contributions to total chromatograph precision were suppressed in order to make the differences between injectors more apparent. The chromatograph was modified to reduce the random flow fluctuations to <±0.1% and the cyclic noise to <±0.5%. Composition variance was eliminated by using pure water or a premixed binary solvent as mobile phase. Two types of columns were used: packed columns operated at about 3000 psi, and inert open capillary tubes that produce a single peak. Column temperature was controlled to <±0.1°C.

By these means the precision of the total chromatograph (injector plus non-injector contributions) was 0.05% RSD for peak area and 0.03% RSD for peak height, for the best case injector. Flow rate fluctuations are probably responsible for the larger area value, since area is more flow dependent, and since the composition and temperature variations were very small. (When flow rate was allowed to drift, the area %RSD changed much more than the peak height %RSD). Therefore, we used peak height precision as the most accurate indicator of injector precision. %RSD values an order of magnitude larger should be expected with most chromatographs.

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