

A Leaky Situation

John V. Hinshaw, Serveron Corp., Hillsboro, Oregon, USA.

In this month's "GC Connections," John Hinshaw looks into a carrier-gas leak and its effects on the chromatographic baseline.

Gas leaks in gas chromatography (GC) are the source of many and various problems for chromatographers. Leaks are wasteful when they are large and small leaks can cause a number of problems. Flow-rate calibration, for example, is inaccurate in the presence of significant leakage, and improperly calibrated detector gas flows can cause poor sensitivity or distorted peak shapes. When using flame detectors, the wrong flow-rates can make igniting or sustaining a flame difficult. Hydrogen gas leakage, if directed into an enclosed space such as a GC oven, could produce a potentially explosive mixture, although such occurrences are rare.¹

Even trace-level leaks engender chromatographic side effects that can affect results. Going beyond problems caused by inaccurate flows, these side effects can be more subtle in the instance of carrier-gas leaks. Most chromatographers who work with capillary columns are familiar with practices that reduce carrier-gas leakage to a minimum level; these practices include installing an efficient filtering system between the gas tank and the chromatograph and using new ferrules during column installation.

Gas leaks are bidirectional; if gas can leak out, then the atmosphere can diffuse in. Thus, a carrier-gas leak can enable undesirable levels of oxygen and moisture to enter a column, where they can increase detector noise and column bleed, and cause solute adsorption on damaged inner column surfaces. Left unheeded, carrier-gas leaks usually lead to poor quantitative results and a shortened column life.

Nevertheless, chromatographers who work with packed columns don't worry as

much about carrier-gas leaks. The required gas-purity levels are less stringent than those for capillary columns, for the most part, because packed columns contain much more stationary phase and are therefore less sensitive to trace carrier-gas impurities. Analysts also expect packed columns to operate at higher solute levels than do capillary columns, which makes the issues of baseline instability and detector noise less important. When working with columns that separate the components of air, chromatographers have even less concern for minor carrier-gas contamination because the columns themselves are intrinsically safe when operating with these gases. Yet, even a relatively minor carrier-gas leak can cause problems with packed columns if the conditions are right.

A High-Stepping Baseline

Recently, while working with a gas analysis system, I noticed an unusual stepped appearance in the baseline at high sensitivities. In this particular configuration, two electronic-pressure-controlled carrier-gas sources were used. During injection, a valve actuation exchanged the carrier-gas sources for each of two columns as part of an overall analysis scheme. After injection, the valve returned to its original position and restored the carrier-gas connections to their original configuration. The stepped baseline was a problem because the signal displacements corresponded with the beginning of some peaks of interest and interfered with accurate peak detection and integration. The appearance of the baseline immediately reminded me of *frontal* chromatography.

Frontal chromatography: When the amount of a substance dissolved in the carrier gas increases or decreases from one steady level to another — in contrast to sending a momentary injection pulse into a column — a moving frontal zone is created in the column. An initially sharp frontal transition spreads forward and backward into a symmetrical Gaussian shape through mechanisms similar to those that cause band spreading in elution chromatography, and elution of the front from the column exit establishes a change in signal level proportional to the change of the amount of substance passing through. The time for a front to pass through a column that retains it is related to the same distribution coefficient (*K*) that dictates the substance's elution time. Thus, I would expect to see distinct fronts for any substances separated on the columns in use as their carrier-gas concentrations increased and decreased through an analysis, and the positions of these fronts should be related to the substances' retention behaviour.

A simplification: After I realized it was a series of baseline artefacts that had caused the quantification difficulties and that a frontal chromatography effect was the likely symptom, I decided to isolate the problem. The most likely source was a leak in one of the carrier-gas supplies that was allowing more air into the carrier on one side of the system than on the other. To demonstrate that the problem was in fact caused by an instrumental effect and not by the somewhat-complex column configuration in use, I instead set up the simplified configuration shown in Figure 1. If, as I hypothesized, a leak was somewhere in one of the carrier-gas

supplies but not in the other, then switching the rotary valve from position A to position B and back would cause the same type of baseline disturbance and would also indicate which side was to blame. In essence, the trace amount of air in the carrier gas on either side would increase or decrease as the valve moved back and forth, which would cause an increasing air front to propagate along one column and a corresponding decreasing air front to pass through the other.

Only the molecular sieves column would actually separate oxygen from nitrogen and generate a multiple frontal chromatography baseline profile similar to what I observed originally. The other, inert column should show a single front at its unretained peak time because it would not separate the components of air. Furthermore, the directions of the frontal displacements from the two columns would be opposites because the columns were connected differentially to a thermal conductivity detector. An increasing amount of air from the A column would create a positive signal displacement, but an increasing amount from the B column would drive the detector response down.

An Air Leak Revealed

After warming up and stabilizing the GC set-up, I programmed the rotary valve to move to the B position 1 min after the run start and then back to the A position 2 min later. Figure 2(a) shows the frontal effect obtained with this set-up, and Figure 2(b) shows a normal elution trace from a manual injection into the same system. It is evident immediately that the contaminated carrier gas comes from channel A.

In Figure 2(a), after a brief injection spike, the signal moves downward because of a new, higher level of air passing into column B from carrier supply A. Remember that increasing the air level in column B will cause the signal to move downward. At a time that corresponds to the beginning of a normal oxygen peak on the molecular sieves column, a second front passes through the detector. This second front originates from column A and represents a drop-off in the amount of oxygen in the carrier gas, which is now coming from carrier source B. The third front, which corresponds to nitrogen, further reduces the signal as the amount of nitrogen exiting the column decreases.

At the middle of the experiment, after three fronts have passed, the signal has dropped to exactly twice the size of the first front to appear. This points strongly to

Only the molecular sieves column would actually separate oxygen from nitrogen and generate a multiple frontal chromatography baseline profile similar to what I observed originally.

the first front corresponding to the same positive change in air contamination from column B — but reversed in direction by the detector — as the sum of the serial oxygen and nitrogen fronts coming from column A, the molecular sieves column, which can separate the air components.

When the rotary valve returns to its original A position 3 min into the experiment, the fronts reappear in the same order but in opposite directions. The change in air concentration first comes through the inert B column as an upward tick in the signal level, and then it appears as separate oxygen and nitrogen fronts from the molecular sieves A column.

Figure 3 provides additional confirmation that carrier channel A is the contamination source, and it also exonerates any other leak source downstream of the carrier connections to the valve. Figure 3(a) shows the same trace as Figure 2(a). Figure 3(b) shows the result when the A and B carrier connections to the valve are reversed — the frontal pattern is exactly inverted. If the air leak was located at one of the valve

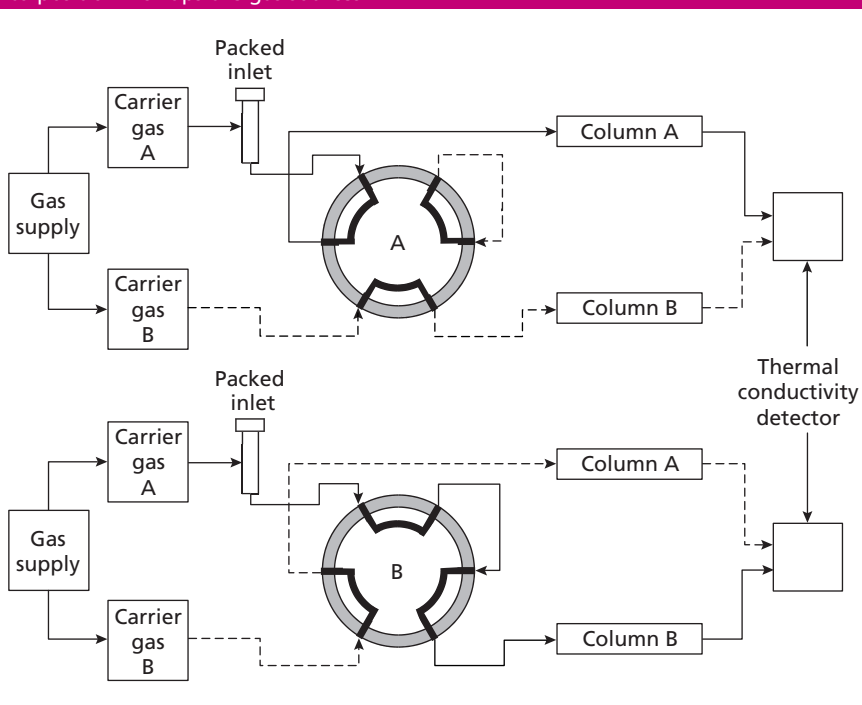
connections or in the valve itself, the pattern wouldn't change. Besides, I had already checked the gas connections from the carrier-gas sources in the oven through the valve and the columns.

At this point, I was convinced that gas from carrier channel A contained a higher level of air contamination than carrier channel B. The problem became isolating the leak source.

Finding the Leak

I had already used a sensitive electronic leak detector, one of the many sold by chromatography supply companies, to determine that the valve fittings and other fittings inside the GC oven were not leaking significantly. I started at the back of the instrument and worked my way forward across several in-line tee fittings that distribute the carrier gas from the gas filters to the bulkhead fittings where it enters the instrument. I found that each metal-to-metal swaged fitting showed evidence of a slight helium leak when examined at the leak detector's highest

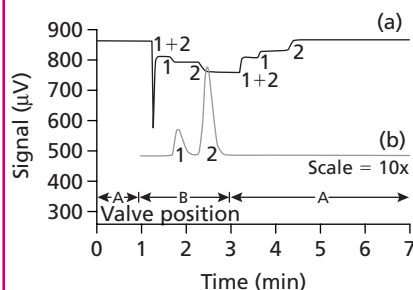
Figure 1: Gas chromatography configuration. In valve position A, carrier gas from pressure controller A (solid line) feeds the molecular sieve column and carrier gas from pressure controller B (dashed line) feeds the inert column. Rotating the valve to position B swaps the gas sources.



sensitivity setting. The leak detector indicator would move slightly when the detector's probe was placed squarely onto the back of any of the fitting nuts. However, all the fittings but one showed very nearly the same small deflection.

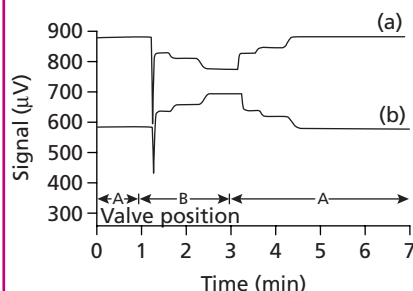
The bulkhead fitting for carrier gas A gave a considerably larger leak detector deflection. I tightened the nut one-eighth of a turn but this did not reduce the leak detector response. Suspecting that I might have found the problem, I shut off the carrier gas at the tank regulator and

Figure 2: Chromatographic traces showing (a) frontal chromatography effects obtained by actuating the valve as shown and (b) normal elution chromatography at a 10-times less sensitive setting, obtained by manually injecting 10 μL of air. Column A: molecular sieves 5A; column B: Chromosorb G A/W; oven temperature: 70 °C; carrier gas: He (30.0 psig) on both sides; detection: thermal conductivity at 100 °C with a 120 mA filament current. The column flow-rates match within ± 0.4 mL/min.



Peaks: 1 = oxygen, 2 = nitrogen.

Figure 3: Traces obtained (a) before (same as Figure 2(a)) and (b) after the carrier-gas connections were reversed at the rotary valve. Carrier A was connected to port 4 and carrier B was connected to port 6 (see Figure 1).



removed the fitting from the bulkhead. I was surprised to find that the front ferrule slid off the tubing easily after removal. It appeared that the fitting hadn't been assembled correctly in the first place; the tubing seemed to have slid back approximately 0.125 in before tightening. Figure 4 shows two views of the fitting that I removed from the bulkhead union.

I decided to simplify the carrier connections to the instrument as well, so I reinstalled the carrier supply with a single tee fitting to take carrier gas to the A and B carrier inlets. Make-up gas, which was unnecessary in this configuration, was disconnected from the carrier source. When I rechecked with the leak detector, I found only very slight, and roughly equal, responses at all five fitting nuts.

Not so fast: Optimistically, I purged the system with carrier gas, restored normal operation and allowed the baseline to stabilize. However, I was surprised to find that the frontal baseline profile had not changed at all. On the computer screen, I could superimpose the profile after

changing the bulkhead fitting with one from before and see almost no difference. Strangely, it seems that even though the carrier A bulkhead fitting was assembled incorrectly and had a significant leak, it was not the source of the fronting baseline profile. What, then, was the cause?

I moved on to the electronic pressure controllers for the A and B carrier gases. I checked them as best as I could using the leak detector, but I was unable to perform a thorough leak check because these pressure controllers are sealed and self-contained. However, I found no obvious problems with the leak detector. I also performed a pressure-drop test by installing no-hole ferrules at the gas connections just before the oven, pressurizing the lines to 70 psig, and then setting the pressures back to zero. In both instances, the pressure readouts dropped by less than 0.1 psig in 5 min.

Finally, I began to suspect the packed-column inlet that was in the carrier A path; I observed no corresponding inlet in the carrier B path. The inlet had not been included in the pressure-drop test. A quick leak check revealed no obvious problems. I changed the septum anyway but this change also failed to make any difference in the baseline profile. With the new unpunctured septum installed, a pressure-drop test that included the inlet lost 0.2 psig in 5 min — not as good as without the inlet, but not enough to arouse much suspicion. Nevertheless, I proceeded to remove the packed-column inlet from the carrier-gas stream by running a new gas line directly from the rotary valve to the carrier-gas pressure controller module.

When I ran the frontal chromatography baseline test, the sizes of the fronts were reduced approximately 100 times. Figure 5 compares the initial results with the profile obtained after removing the packed-column inlet. Interestingly, the small residual fronts move upward, not downward as before, which indicates that whatever small leakage or contamination remained after removing the inlet was in the B side carrier supply, not the A side supply.

This result is difficult to explain. Hypothetically, a gas-tight in-line inlet could add some air to the carrier-gas stream by diffusion across and around the septum. However, the sizes of the frontal profiles seem too large for this scenario; they were only 50 times or so smaller than the oxygen and nitrogen peaks from a 10 μL injection.

Figure 4: Incorrectly assembled gas fitting. This fitting was removed from the rear carrier-gas bulkhead connection for carrier gas A.

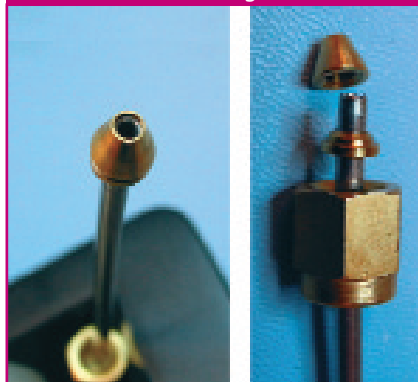
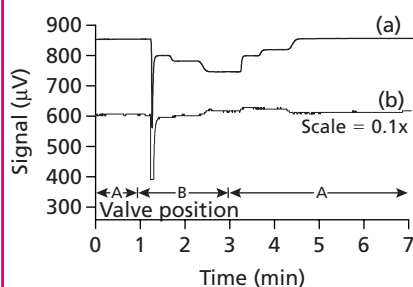


Figure 5: Frontal profiles (a) before (same as Figure 2(a)) and (b) after removing the packed-column inlet from the carrier-gas A path.



Conclusion

The search for carrier-gas leaks sometimes leads to unusual or unexpected sources. A packed-column inlet seemed to introduce a significant amount of air into the carrier-gas stream on one side of a gas analysis system, yet an obviously incorrectly installed and leaking bulkhead fitting seemed not to be a significant air-leak source at all. By working through several hypotheses until each was proven incorrect, until only the obscure answers remained, the problem was eventually eliminated. However, the root cause of the problem — the reason for a significant amount of air in the packed inlet — remains unknown.

Reference

1. J.V. Hinshaw, *LC•GC Eur.*, **15**(9), 582–587 (2002).

“GC Connections” editor **John V. Hinshaw** is senior staff engineer at Serveron Corp., Hillsboro, Oregon, USA, and a member of the Editorial Advisory Board of *LC•GC Europe*.

Direct correspondence about this column to “GC Connections,” *LC•GC Europe*, Advanstar House, Park West, Sealand Road, Chester CH1 4RN, UK, e-mail: dhills@advanstar.com

For an on-going discussion of GC issues with John Hinshaw and other chromatographers, visit the Chromatography Forum discussion group at <http://www.chromforum.com>