LC Troubleshooting

Recycling Revisited

John W. Dolan

Readers offer mixed reviews of approaches to solvent recycling.

One of last year's "LC Troubleshooting" columns (1) covered several aspects of solvent recycling for liquid chromatography (LC). Two primary modes of recycling are used to reduce solvent consumption in HPLC laboratories. The simplest involves routing the waste solvent back into the mobile-phase reservoir for direct reuse. This technique is limited to isocratic separation conditions. An alternative involves collecting waste solvent and distilling it to recover pure solvents for later reuse. This technique can be applied to any chromatographic method and is limited primarily by the availability of high-quality distillation equipment and the economics of the process.

This topic pushed the "hot button" for a lot of readers — a surprising number provided feedback about their experiences with solvent recycling. I have organized some of this feedback into the case studies discussed in this column, commenting on the examples where appropriate.

CASE 1: DIRECT RECYCLING

Reader: We purchased a Waters QA1 (Millipore Corporation, Waters Chromatography Division, Milford, Massachusetts) several years ago. This instrument is designed for routine, repetitive analysis and can recycle solvents directly. Although we were skeptical at first, we tried recycling our solvents from a quantitative psoralen analysis by normal-phase LC. We have been pleased with the results. Just to check, we run a blank after each batch of samples to be sure the baseline is clean.

We suspected that the main problem would be buildup of contaminants on the column, but instead we had to contend with preferential evaporation of the more volatile solvent. To compensate for the loss, we add back small amounts of the more volatile solvent, usually once a month.

We use 1 L of mobile phase and change it completely every two months. Although we run only about 25 samples during this time, the savings is substantial. Because the main problem is evaporation, not contamination, we could probably run more samples before changing the solvent. Even so, our approach is satisfactory because we are saving both solvent and money and are reducing the impact on the environment.

JWD: Evaporative loss of the more volatile mobile-phase component is one of the primary drawbacks of direct recycling. This loss is greater with the volatile solvents used for normal-phase work than with reversed-phase solvents, whose volatility is generally lower. Evaporative loss can be minimized by using a very small (for example, 1-mm) hole for a reservoir vent and by using larger reservoir volumes. A larger reservoir (for example, 4 L) will also help dilute contaminants so that the mobile phase can be used longer before unacceptable baselines are encountered.

CASE 2: RECYCLE AND FLUSH

An article sent in by another reader (2) describes a modification of the direct recycling technique discussed in Case 1. The assay was for anticonvulsant drugs and used a C18 column and an acetonitrile–methanol–phosphate buffer mobile phase with detection at 214 nm. To avoid unnecessary contamination of the mobile phase, the system was equilibrated with ~35 mL of mobile phase, which was diverted to waste before recycling the solvent into the mobile-phase reservoir. After use, the column was flushed with another 35 mL of a strong solvent to wash unwanted contaminants to waste. An 800-mL batch of mobile phase was used for 3–4 weeks before it was discarded. The authors summarized their findings as follows (2):

> Recycling the mobile phase did not cause any drifting of the baseline. The retention times increased somewhat as the mobile phase got older. However, there was no indication of the separation deteriorating. Generally, when an 800-mL portion of mobile phase had been used for six to eight sessions, it had received about 110 injections of 250 μL, the volume had been reduced to 300–400 mL, and the retention times had increased about 10%. The mobile phase was then discarded. Recycling reduced the consumption of mobile phase from about 400 mL a day to about 100 mL a day.

These workers also experienced selective evaporation of the mobile phase, as demonstrated by the drifting retention times. Depending on the magnitude of the drift and the allowable limits for adjusting the method, you can compensate for such drift by running standards more frequently, adjusting the mobile-phase composition as in Case 1, or making a new batch of mobile phase. One encouraging aspect of this report is that the baseline was acceptable even at the low wavelength of 214 nm.

CASE 3: SAVING CLEAN MOBILE PHASE

An alternative to routing the entire waste stream back into the mobile-phase reservoir is to save only the clean mobile phase and discard the contaminated mobile phase. At first, this process might seem to require Maxwell's demon, but an *LC•GC* article (3) described a timed switching valve that can be used to accomplish the task. With this device, the system recycles "clean" waste solvent directly to the reservoir whenever bands are not being eluted from the column. The valve timer is set to divert the effluent stream to waste during the elution of sample peaks. The authors provided the following observations (3):

> For a modest initial cost, this system can save a significant amount in solvent cost. Our own system realizes a minimum solvent savings of 50%. Continual degassing of the mobile phase by helium maintains the solvent's stability. Also, little unspent mobile phase is wasted, and small 1-L solvent reservoirs can be used. Finally, the system is ready to use with minimum time delays for column equilibration. This more efficient use of time and equipment has also led to increased column life.

A commercial version of this device is now available (4) (Figure 1). The unit intercepts the detector signal and shunts the effluent to waste

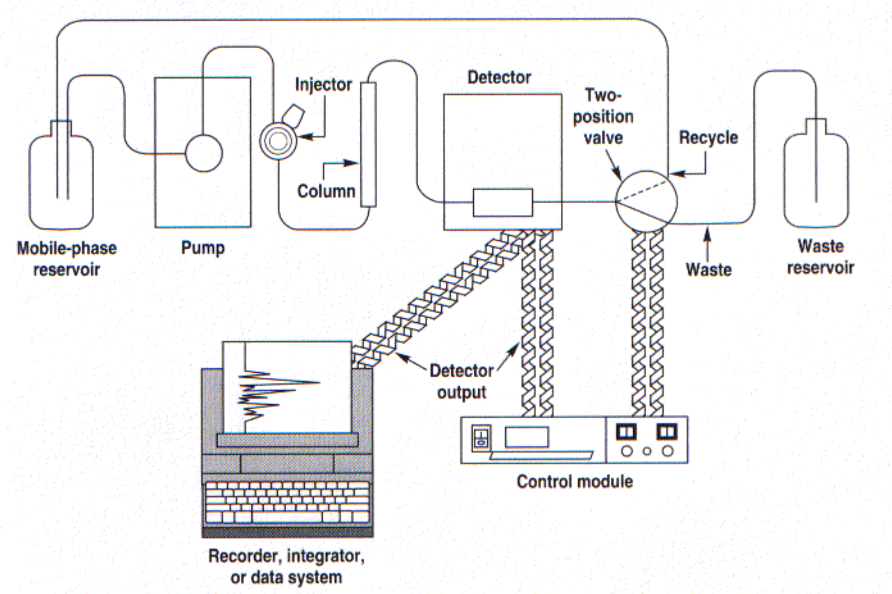

FIGURE 1: Schematic of an automated solvent recycling module installed in an LC system. (Courtesy of Alltech Associates, Deerfield, Illinois.)

whenever the baseline exceeds a user-set threshold.

CASE 4: LIMITED BY CONVENIENCE

Reader: Five years ago, our lab was analyzing soil and vegetables for residues of a novel insecticide. We used a reversed-phase column and UV detection at 255 nm with a 75:30 (v/v) acetonitrile–water mobile phase. We distilled the aqueous acetonitrile as the azeotrope and reused it in the same analytical method. We didn't face any problems with the quality of the distilled solvent mixture, and the result was quite economical.

However, the fact that recycled acetonitrile was used for only one method in one lab at our facility brings us to reality. It requires discipline to keep and distill waste solvents, and often time limitations make opening a new bottle faster than distilling used solvents. Hence, recycling is an organizational rather than a quality problem.

JWD: Convenience is perhaps the biggest stumbling block in the widespread recovery of mobile phase through distillation. In addition, although solvent distillation may save a major portion of solvent expenses, the reality that solvent costs generally account for ≤1% of per-sample analysis costs (1) may discourage widespread use of this technique.

CASE 5: LIMITED BY REGULATION

Reader: For several years I used a published technique (5) to recover acetonitrile wastes by distillation over phosphoric anhydride (P_2O_5). After two distillations, I recovered an acetonitrile–water azeotrope of ~95% acetonitrile. A check on the true composition was made by comparing retention times for standards between the azeotrope and true 95% acetonitrile–water as a mobile phase. The azeotropic mixture was adjusted by adding acetonitrile or water if the retention times did not match. Otherwise, the optical and chromatographic properties of the recovered solvent were comparable to those of new solvents, and the use of recovered solvent saved a lot of money.

Convenience is perhaps the biggest stumbling block in the widespread recovery of mobile phase through distillation.

In a second lab, I proposed to build a similar solvent recovery apparatus, but after comparing the cost of the equipment with that of fresh acetonitrile, the management vetoed my proposal.

In my present laboratory, the safety regulations are so strict that the added expense of explosion-proof cabinets, automatic temperature control, and foolproof venting make the cost of building such an apparatus prohibitive in light of the modest cost savings derived from solvent recovery.

FINDING THE "BEST" METHOD

These examples illustrate the tradeoffs involved when making an effort to recycle mobile phase. What is the best technique for your laboratory? It depends on many factors. In a laboratory where solvent costs represent a significant portion of operating expenses, recovery by distillation may be the best choice. Such might be the case when preparative separations consume large quantities of solvent. On the other hand, the cost of solvents in many laboratories is a small portion of the per-sample costs. In such situations, direct recycling using manual or automated techniques may be used primarily for convenience. Direct recycling also saves some of the time normally spent preparing mobile phase. Some users, however, find that additional uncertainties about the quality of recycled mobile phase coupled with the low cost contribution of fresh solvents fail to justify any practice other than a single use of solvents in LC separations.

ACKNOWLEDGMENTS

I would like to thank all the readers who took the time to submit their comments, especially A. Alertsen, A. Hruza, H. Kühne-Thu, P. Sperl, and R. Sütfeld.

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