## LC TROUBLESHOOTING

# Solvent Recycling

**John W. Dolan**

*We recycle milk jugs, aluminum cans, and newspapers — why not recycle LC solvents?*

A reader asked, "Why don't chromatographers recover their waste solvents to repurify and reuse?" On the surface, this sounds like a good idea — one that simultaneously reduces solvent and solvent-disposal costs — so we'll examine the prospects. We'll also look at some alternative ways to reduce liquid chromatography (LC) solvent costs. None of the techniques covered in this month's column are used by a majority of LC laboratories, but several thousand workers certainly use one or more of these techniques on a regular basis.

## SOLVENT RECYCLING

**Q:** One aspect of LC that I rarely see addressed in print is the disposal of spent mobile-phase and sample preparation solvent. Proper disposal is costly under present regulations, often costing nearly the same as the original solvent purchase. It seems to me that purification techniques such as spinning-band distillation could be used for recycling the common LC solvents. Why hasn't solvent recycling caught on in analytical laboratories?

**JWD:** Although solvent recycling seems like an environmentally wise procedure and one that should have financial advantages for the laboratory, some roadblocks make the prospects discouraging. First, one of the reasons we use acetonitrile for LC applications is its very low UV-cutoff wavelength. Acetonitrile can be used at wavelengths ≤ 200 nm on a routine basis with good results. It takes very little background absorbance under such conditions to make the solvent unusable. Because you can't control the amount of UV contaminants in the repurification feedstock, it is likely that the residual UV components would vary from batch to batch.

A second problem arises from trace residues of intentional or unintentional mobile-phase additives. Many LC methods are very sensitive to small amounts of metals, amines, salts, and other additives. Thus, you might expect retention reproducibility to vary from bottle to bottle of "remanufactured" mobile phase.

When I prepared the first draft of this column, I believed that these potential problems would prevent solvent recycling from having a reasonable chance of success, either from a scientific or economic standpoint. Since that time, however, I have reexamined my stance. In the discussion below, we'll look at several possible approaches to purifying, reusing, and recycling HPLC-grade solvents.

## PURIFYING LESSER GRADE SOLVENTS

Some laboratories lower their solvent costs by buying lesser purity solvents and distilling them before use. When I worked in a pesticide-residue laboratory, we routinely distilled hexane and some other solvents used for gas chromatography sample preparation. The solvents were nominally pure before we started, so we were just "polishing" the solvents for our particular applications. I'm not sure how common this practice is today — it depends on the availability of relatively inexpensive solvents of acceptable purity for feedstocks and on the type of contaminants that need to be removed. Whenever large volumes of solvents are being distilled, you may have to consider additional safety and environmental regulations. Purifying lesser grade solvents has particular appeal for laboratories that perform many solvent extractions during sample preparation, such as environmental analysis laboratories.

## RECYCLING USED SOLVENT

As I mentioned above, I was not very optimistic about the prospects of recycling used LC solvents — until I spoke with a company dedicated to this technology. B/R Instrument Corporation (Easton, Maryland) sent me information about an apparatus it manufactures that consists of a spinning-band distillation column packaged in such a way that users can control fraction collection, temperature set points, equilibration times, and other critical parameters through the instrument controller. Additional safety features allow vapor monitoring, venting, and fire control.

One example, taken from a technical bulletin (1), shows the potential of this recycling technique. It uses an LC waste stream consisting of 50:50 (v/v) acetonitrile–acetate buffer from a tricyclic antidepressant assay. Because of the large amount of water in the feedstock, pure acetonitrile could not be recovered. Rather, the distilled product was the 84.3:15.7 (v/v) acetonitrile–water azeotrope. The recovery was impressive: 56% of the 5-L waste-stream sample was recovered as the azeotrope, which is ~94% recovery of the acetonitrile. Of course, the "pure" acetonitrile contains 15.7% water, a fact that must be considered when preparing mobile phases.

A comparison of the recovered acetonitrile with HPLC-grade acetonitrile using UV-spectral and step-gradient tests shows that the recovered material apparently is of similar purity to the HPLC-grade solvent (Figures 1 and 2) (2).

The manufacturer claims that the system works equally well with acetonitrile, methanol, hexane, and other common LC solvents. With installations in government and government-regulated labs, B/R's spinning-band technology reportedly satisfies regulatory requirements for solvent purity.

## DIRECT RECYCLING

When routine isocratic methods are used, some workers recycle the mobile phase directly for a dramatic reduction in solvent consumption. A large batch (for example, 10–20 L) of mobile phase can be prepared for use with the method. The waste line from the detector is directed back into the reservoir. If the

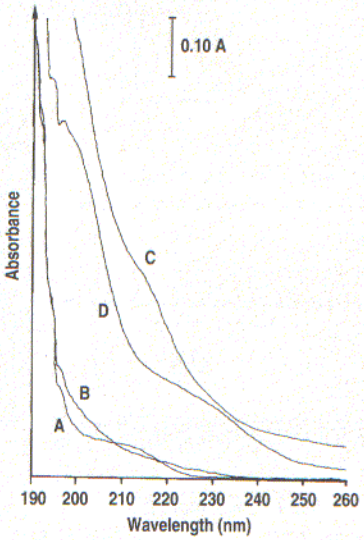

**FIGURE 1:** Spectral comparison of acetonitrile recovered from an LC waste-stream sample with HPLC-grade acetonitrile. UV spectra: A = HPLC-grade acetonitrile, B = recovered acetonitrile, C = 10-fold concentrate of A, D = 10-fold concentrate of B. (Reprinted with permission from reference 2.)

reservoir is stirred continuously, the impurities are diluted out and fed onto the column at a steady rate. Over time, contaminants build up on the column and eventually cause a wavy baseline, but if you carefully control how long the solvent is used, you can successfully reduce solvent consumption by recycling it in this manner. Of course, this technique does not work for gradient methods.

## USING LESSER PURITY SOLVENTS

An alternative that will work for certain applications is purchasing a grade of solvent that is not as pure as HPLC grade. For example, if your application uses UV-absorbance detection at 280 nm, perhaps ACS-grade methanol will provide satisfactory results. Once again, this should be limited to isocratic applications. You should be on the lookout for signs of contaminant buildup, such as undulating baselines or drifting retention times.

## THE BOTTOM LINE

You can see that several possibilities allow you to reduce your solvent cost and consumption. Distillation of spent mobile phase is not as widely used as the other techniques mentioned, but it may become much more popular as the environmental issues related to waste disposal cause increased disposal costs and liability.

Before using any of these techniques, be sure to perform an audit of all the costs associated with the analysis of your samples. For example, if a method uses an 80% acetonitrile mobile phase at 1 mL/min, a run is made every 15 min, and 4 L of acetonitrile costs \$80, then solvent costs for each sample would be only \$0.24 (\$20/L × 80% × 0.015 L/sample). My guess is that the actual total cost per sample, however, is in the \$10–40 range, depending on how much sample preparation is required, what equipment costs are involved, and how much labor is associated with the sample from preparation through reporting. If your per-sample costs are influenced by such factors, eliminating the mobile-phase expense completely would have an insignificant impact on your total costs.

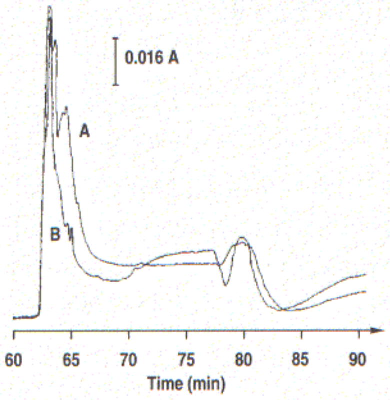

**FIGURE 2:** Chromatograms of HPLC-grade acetonitrile and recovered acetonitrile. Column: 25 cm × 4.6 mm, 10-μm $d_p$ C18; gradient: 30% acetonitrile in water for 60 min, step to 70% acetonitrile in water at 60 min, then step to 100% acetonitrile at 75 min; flow rate: 3 mL/min; detection: UV absorbance, 210 nm. Curves: A = HPLC-grade acetonitrile, B = acetonitrile–water azeotrope recovered from distillation. (Reprinted with permission from reference 2.)

Finally, I think a word of defense for the HPLC-grade solvent manufacturers is in order. I worked closely with one of these vendors in a previous job and found that the solvent-purification process is not a simple one. First, they start off with the best feedstock available and then proceed to purify it further. Each lot of solvent must pass a large battery of tests before it is released. The tests often include UV and IR spectroscopy and chromatography, plus tests for particulates, trace levels of water, and other specific contaminants. A solvent manufacturer's routine set of quality control tests may well exceed the capabilities of most LC laboratories.

In 20 years of working in LC, only once have I encountered solvent that I could prove was bad. A batch of methanol contained a trace impurity that appeared only near the UV cutoff under gradient conditions with a specific buffer system. When I brought this to the attention of the manufacturer, the manufacturer took a sample from the same lot, confirmed the problem, and added my test to its normal testing protocol. I'm sure that I couldn't maintain the same track record if I purified my own solvents.

To address the environmental issues properly, you may want to check with your waste disposal service to see how it discards your spent solvent. The company that we use blends our solvents with other flammables to fuel a manufacturing process. This makes more sense to me than burying the waste in a barrel somewhere for my grandchildren to worry about.

## CALL FOR FEEDBACK

In my experience, the techniques discussed in this column are not widely applied. I would appreciate feedback from users of these techniques — what do you like or dislike about them? If you have used one of these techniques in the past, or if you have considered it and decided that it was not a good choice, let me know about your experiences, too. If there is sufficient interest, we may pursue this topic further in a future "LC Troubleshooting" column.

## REFERENCES

(1) "Application Note #4" (B/R Instrument Corporation, Easton, Maryland, 1981).
(2) R.M. Katusz, L. Bellew, J.A. Mangravite, and R.F. Foery, *J. Chromatogr.* **213,** 331–336 (1981).

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