

CHROM. 13,937

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### Recovery of HPLC-grade acetonitrile by spinning-band distillation\*

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(Received March 17th, 1981)

The rising cost of high-purity solvents coupled with the ethical and financial burden of waste solvent disposal have prompted us to investigate the recovery of previously used high-performance liquid chromatographic (HPLC) solvents.

The use of PTFE annular spinning-band distillation columns has been recognized as a valuable analytical technique for the separation of compounds whose boiling points are as close as  $0.5^{\circ}\text{C}^{-1-3}$ . High-speed rotation of the PTFE band against the column wall produces a thin film of condensate, highly efficient vapor liquid contact, and enrichment (rectification) with low column hold-up. Once equilibrium has been established, solvents may be distilled at rapid boiling rates and low reflux ratios to maximize sample throughput.

This paper describes the recovery of previously used HPLC-grade acetonitrile by distillation without chemical pretreatment on a thirty-plate PTFE annular spinning-band column. Using static, preconcentration, and dynamic (on-column solvent enrichment) evaluation, spectrophotometric and chromatographic data indicate 85-95% recovery of acetonitrile with purity at or near the specifications of commercially available HPLC-grade solvents.

#### EXPERIMENTAL

##### *Apparatus*

All distillations were carried out on a B/R Instrument Corporation Model 40-T, PTFE-banded still equipped with ground glass joints and PTFE sleeves.

Gas chromatographic data were obtained on a Perkin-Elmer Model 3920B all-glass dual flame ionization detection system, using Carbowax 1540 or Chromosorb 101 (ref. 4) columns.

HPLC baseline absorbance studies were carried out on a Jasco Familic 100 micro HPLC system equipped with a UVIDEC 100-II variable-wavelength detector and a reversed phase (SC-01,  $\text{C}_{18}$ ) column. Dynamic enrichment studies were carried out on a Tracor Model 950/980A gradient elution high-performance liquid chromatograph equipped with a Tracor Model 970A variable-wavelength UV detector and an ISCO Model UA-5 fixed-wavelength (254 nm) detector. The system was interfaced

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\* Presented in part at the *Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy*, Atlantic City, NJ, March 1980.

with an ISCO Model 1200 fraction collector which allowed for automatic peak separation and collection. Whatman Partisil (5% C<sub>18</sub>) or Alltech (18% C<sub>18</sub>) 25.0 cm × 4.6 mm I.D., 10- $\mu$ m particle size columns were used.

Differential pulse polarograms were obtained using a PAR Model 174A polarographic analyzer.

### *Materials*

Distilled-in-glass grade acetonitrile UV (190 nm UV cutoff) and HPLC-grade water were obtained from Burdick & Jackson Labs. (Muskegon, MI, U.S.A.). Previously used acetonitrile solvent mixtures, originally prepared using Burdick & Jackson solvents, were collected in clean, amber bottles through the cooperation of several local hospital laboratories. The mobile phases, studied for solvent recovery, included acetonitrile–4% aqueous ammonia and acetonitrile–water–acetate buffer (theophyllin or tricyclic antidepressant analyses).

### *Procedure*

All previously used mobile phase mixtures were refluxed for 24 h to ensure equilibrium, followed by distillation at a band speed of 2500 rpm and take-off rate of 125 ml/h. The first 20 ml of distillate at the appropriate boiling range (ambient barometric pressure) were discarded. Acetonitrile was distilled without chemical pretreatment as the pure solvent (81–82°C) or as a binary azeotrope acetonitrile–water (84:16) (77°C).

### *Solvent purity*

Solvent purity was determined from boiling range, refractive index, Karl Fischer titration for water, UV absorbance and fluorescence spectra, as well as from chromatographic information. The specifications of recovered acetonitrile were compared to the specifications of unused HPLC-grade acetonitrile.

Samples of recovered acetonitrile were preconcentrated by reducing 100-ml portions to 10 ml on an unheated rotary flash evaporator. The tenfold preconcentrates were then spectrophotometrically compared to samples of unused HPLC-grade acetonitrile prepared in the same way. The evaporation was done at room temperature to minimize the loss of higher boiling impurities.

Samples of recovered and unused HPLC-grade acetonitrile were also compared after 60 min of on-column HPLC enrichment using acetonitrile–water (30:70) mobile phase at 3.0 ml/min through a C<sub>18</sub> reversed-phase column. Impurities accumulating on the column were subsequently stripped using a step gradient of acetonitrile–water (70:30) (15 min) followed by a step gradient of 100% acetonitrile (15 min).

## RESULTS AND DISCUSSION

### *Solvent specifications*

Table I shows the comparison of specifications for recovered acetonitrile fractions and HPLC-grade acetonitrile. The percentage of water in the pure solvent samples and the binary azeotrope was verified by gas chromatographic analysis on Chromosorb 101 (ref. 4). The total yield of recovered acetonitrile, as pure solvent and/or azeotrope, ranged between 85–95% based upon the compositions of the pot

TABLE I  
SOLVENT SPECIFICATIONS

	<i>Acetonitrile</i>		
	<i>HPLC</i>	<i>Recovered, pure solvent</i>	<i>Recovered, azeotrope</i>
Boiling range (°C)	81–82	82	77–78
Refractive index at 15°C	1.3466	1.3465	—
Water, Karl Fischer	0.07%	0.08%	15.7%
Purity*	99.9%	99.9%	99.7%
UV Cutoff (nm)**	<190	<190	<190

\* Gas-liquid chromatography, 8% Carbowax 1540.

\*\* Wavelength at which absorbance equals 1.00.

charge and distillate fractions. The optimum take-off rate for acetonitrile recovery was found to be 120–140 ml/h. Column hold-up was estimated to be 1.2 ml.

Fig. 1 shows that the maximum sensitivity fluorescence spectrum of recovered acetonitrile to be virtually identical to that of unused HPLC grade acetonitrile. The differential pulse polarograms (Fig. 2) show the presence of an impurity, suspected but not confirmed to be acrylonitrile<sup>5</sup>, in HPLC-grade but substantially reduced in recovered acetonitrile. The end currents result from supporting electrolyte decomposition.

Baseline stability studies (Fig. 3) show that the recovered solvent has a slightly lower absorbance *versus* time profile but gives essentially the same response as HPLC-grade acetonitrile.

The comparison of static solvent specifications (without preconcentration, or

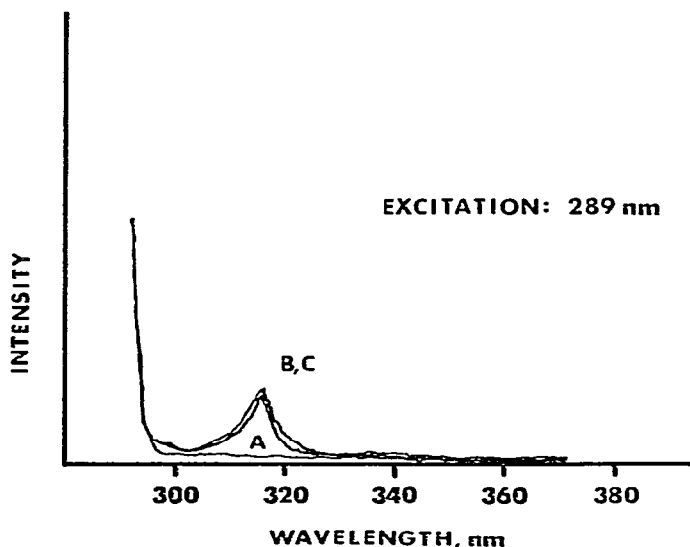


Fig. 1. Fluorescence spectra of empty cell (A), HPLC-grade acetonitrile (B), and recovered acetonitrile (C).

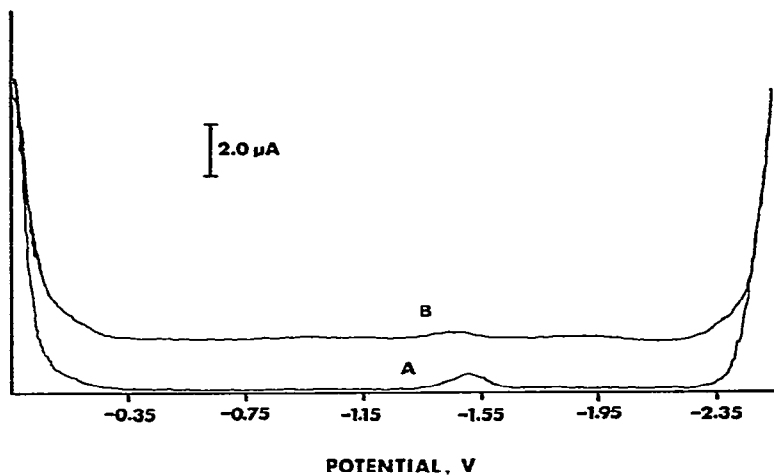


Fig. 2. Differential pulse polarograms of HPLC-grade acetonitrile (A) and recovered acetonitrile (B). Supporting electrolyte: 0.05 M tetrabutylammonium iodide; rate: 10 mV/sec, drop-time: 0.5 sec. Curves A and B manually offset 2.0  $\mu$ A.

enrichment of impurities) suggests that the purity of recovered, previously used acetonitrile is at or near that of commercially available HPLC-grade acetonitrile. However, this comparison does not adequately indicate the presence of impurities which may become potential contaminants in an HPLC determination.

#### *Solvent preconcentration and enrichment*

Fig. 4 illustrates the effect of preconcentrating impurities on the UV spectra of acetonitrile samples. Although the static spectra show nearly identical absorbance, the spectra of the tenfold preconcentrates show that the unused HPLC-grade has higher absorbance in the 210–225 nm region which could result in “ghost” peaks during an HPLC analysis.

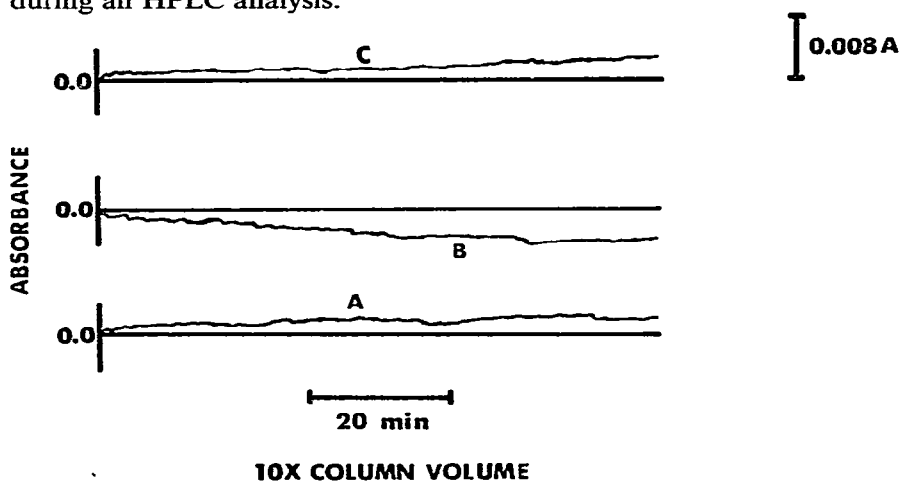


Fig. 3. Chromatograms of 100% HPLC-grade acetonitrile (A), recovered acetonitrile (B), and A rerun (C). Detector: 210 nm; column:  $C_{18}$  reversed phase; flow-rate: 4  $\mu$ l/min.

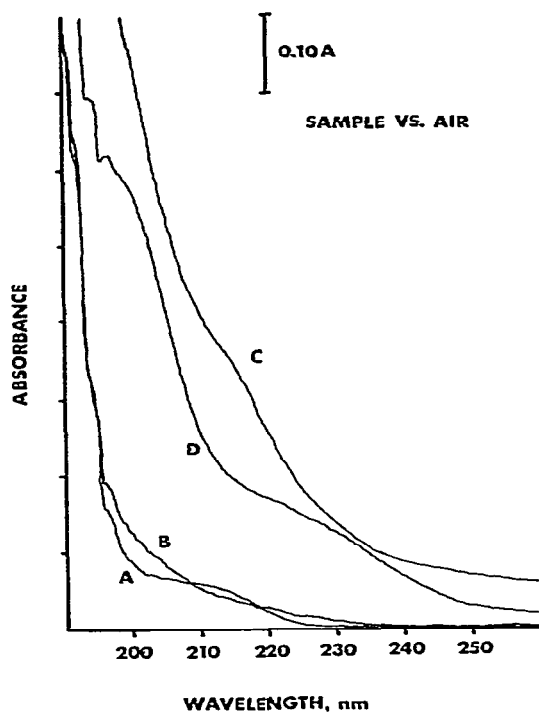


Fig. 4. Ultraviolet spectra of HPLC-grade acetonitrile (A), recovered acetonitrile (B), tenfold preconcentrate of A (C), and tenfold preconcentrate of B (D).

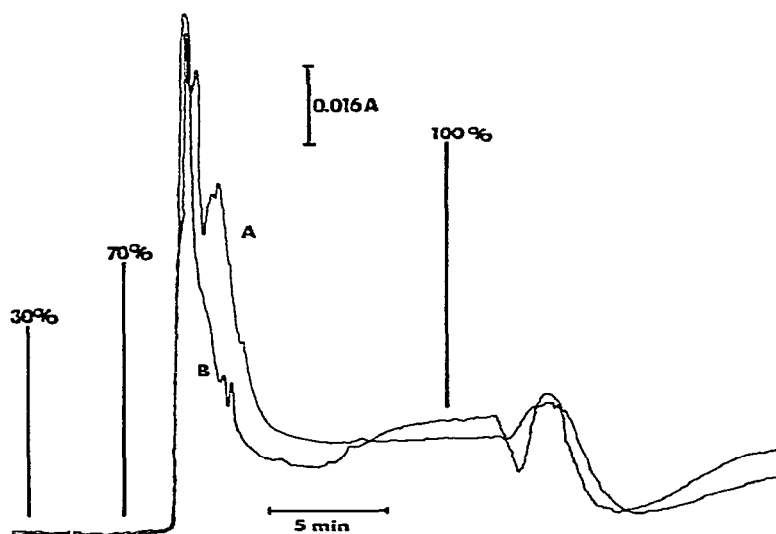


Fig. 5. Chromatograms of HPLC-grade acetonitrile (A) and recovered acetonitrile (B). Detector: 210 nm; column: Whatman C<sub>18</sub>; solvent program: 30% A or B (60 min) step gradient to 70% A or B (15 min), step gradient to 100% A or B (15 min); flow-rate: 3.0 ml/min.

A more useful assessment of the purity of the recovered acetonitrile can be made by determining the on-column enrichment of impurities during the course of a chromatographic run. Fig. 5 shows that the recovered acetonitrile has a lower level of impurities when compared to unused HPLC-grade acetonitrile after enrichment using acetonitrile–water (30:70) (60 min) followed by step gradients of acetonitrile–water (70:30) (15 min) and 100% acetonitrile (15 min) at 210 nm.

We feel that solvents with sufficient purity for re-use in most HPLC analyses can be recovered using spinning-band distillation. For acetonitrile, both static and dynamic evaluation of the recovered solvent, distilled without prior chemical treatment<sup>6</sup>, demonstrates the feasibility of recovering previously used HPLC mobile phases.

In our laboratory, we are now studying the recovery of 2,2,4-trimethylpentane, tetrahydrofuran, methanol, hexane, methylene chloride, dimethyl formamide, and dimethyl sulfoxide by spinning-band distillation. These data should be of interest to high-volume and preparative HPLC users.

#### ACKNOWLEDGEMENT

We thank G. E. Clement, H. R. Drott and J. J. Fenton for their help in providing used acetonitrile mobile phases and R. R. Roark for his valuable knowledge and experience in spinning-band distillation.

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