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Laboratories and Demonstrations

Simple Procedures for Quantification and Reuse of Common Organic Solvent Mixtures

PATRICK H. DUSSAULT and **KEVIN R. WOLLER**
Department of Chemistry
University of Nebraska–Lincoln
Lincoln, NE 68588-0304, USA

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A recycling protocol is described for the recovery and reformulation of common solvents in teaching and research laboratories. Recovery of mixed solvents is shown to be facilitated by the use of solution density as a convenient and accurate assay method. The procedure is explicitly illustrated for mixtures of ethyl acetate/hexane. An effective procedure is also reported for recovery of wash acetone.

Spent wash acetone and recovered solvents from liquid chromatography represent serious waste management issues for academic teaching and research programs. Chromatography experiments in organic teaching labs, even with microscale procedures, can generate ten or more liters of spent solvent while a number of the research groups in our department generate 20 to forty liters of spent ethyl acetate/hexane (EA/Hex) on a weekly basis. Attempts to initiate an effective recycling program within our research group were initially frustrated by the lack of an accurate and straightforward method for quantification of the re-

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cycled solvent. Comparison of the Rs of standard analytes on thin-layer chromatography was of limited accuracy, while GC or NMR analysis was complicated by the presence of multiple hexane isomers. We report the use of solution density as an inexpensive, fast, and accurate (±1%) method for assay of EA/Hex mixtures which should be applicable to a variety of binary solvent mixtures. Likewise, wash acetone is used in copious quantities in nearly all laboratories, and we also report a simple procedure for repurification and assay of recovered acetone. The combination of these two procedures has cut solvent consumption in our laboratories nearly in half.

Procedure–EA/Hex

Recovered solvent is transferred into a 4-L "drying bottle" along with a small amount of $MgSO_4$. The dried solution is decanted into a 5-L distillation flask fitted with a solvent distillation head. A few boiling chips are added and the solvent is directly distilled into a clean bottle. An inexpensive electrical cut-off timer (Dayton/Grainger) is placed between the transformer and the heating mantle as a safety device to prevent baking out the pot; typical distillation cycles are approximately four hours. The mass of a 100-mL aliquot of the cooled (23 °C) distillate is measured in a tared volumetric flask and compared against the values shown in Table 1.

The values in Table 1, which reflect volume % EA, are based upon Eqs. 1–3, assuming $d_{EA} = 0.894\ gmL^{-1}$ and $d_{Hex} = 0.664\ gmL^{-1}$ [1]. A number of volumetrically prepared standards were found to agree with the calculated values to within an absolute error of +1% [2].

$$\text{Mass}_{100mL} = (0.894\ g/mL)(\%\ EA) + [(0.664\ gmL^{-1})(100 - \%\ EA)] \quad (1)$$

$$\text{Mass}_{100mL} = 0.230(\%\ EA) + 66.44\ g \quad (2)$$

$$\%\ EA = (\text{Mass}_{100mL} - 66.4\ g)/0.230 \quad (3)$$

Substitution of density values allows extension to other binary mixtures whose components display nearly ideal mixing and have significant density differences. For example, the procedure allows highly accurate quantification of methanol/methylene chloride mixtures.

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TABLE 1. Correlation Chart for $Mass_{100mL}$ Recycled EA/Hex (v/v)

Mass (g)	% EA	Mass (g)	% EA	Mass (g)	% EA
66.4	0	74.2	34	82.0	68
66.9	2	74.7	36	82.5	70
67.4	4	75.2	38	83.0	72
67.8	6	75.6	40	83.4	74
68.0	8	76.1	42	83.9	76
68.7	10	76.5	44	84.3	78
69.2	12	77.0	46	84.8	80
69.7	14	77.5	48	85.3	82
70.1	16	78.0	50	85.7	84
70.5	18	78.4	52	86.2	86
71.0	20	78.8	54	86.6	88
71.5	22	79.3	56	87.1	90
71.9	24	79.7	58	87.5	92
72.4	26	80.2	60	88.0	94
72.9	28	80.7	62	88.5	96
73.3	30	81.1	64	88.9	98
73.8	32	81.6	66	89.4	100

Reformulation–EA/Hex

As a practical matter, we have found that the perceived difficulty in reformulating mixtures is a major barrier to the use of recycled solvents. Each student is therefore provided with the reformulation chart shown in Table 2.

When mixing up (e.g., 2% EA $\longrightarrow$ 8% EA), equation 4 is used to calculate the percentage of recycled solvent required with the remainder being ethyl acetate. (x =% EA desired, y =% EA in recycle)

$$\% \text{ Recycle Used} = [(100 - x)/(100 - y)] * 100 \qquad (4)$$

TABLE 2. Reformulation Chart

% EA in Recycle	% Ethyl Acetate Desired											
	1	**2**	**5**	**10**	**15**	**20**	**25**	**30**	**35**	**40**	**45**	**50**
2	50.0	——	96.9	91.8	86.7	81.6	76.5	71.4	66.3	61.2	56.1	51.0
4	25.0	50.0	99.0	93.8	88.5	83.3	78.1	72.9	67.7	62.5	57.3	52.1
6	16.7	33.3	83.3	95.7	90.4	85.1	79.8	74.5	69.1	63.8	58.5	53.2
8	12.5	25.0	62.5	97.8	92.4	87.0	81.5	76.1	70.7	65.2	59.8	54.3
10	10.0	20.0	50.0	——	94.4	88.9	83.3	77.8	77.2	66.7	61.1	55.6
12	8.3	16.7	41.7	83.3	96.6	90.9	85.2	79.6	73.9	68.2	62.5	56.8
14	7.1	14.3	35.7	71.4	98.8	93.0	87.2	81.4	75.6	69.8	64.0	58.1
16	6.3	12.5	31.3	62.5	93.8	95.2	89.3	83.3	77.4	71.4	65.5	59.5
18	5.6	11.1	27.8	55.6	83.3	97.6	91.5	85.4	79.3	73.2	67.1	61.0
20	5.0	10.0	25.0	50.0	75.0	——	93.8	87.5	81.3	75.0	68.9	62.5
22	4.6	9.1	22.7	45.5	68.2	90.9	96.2	89.7	83.3	76.9	70.5	64.1
24	4.2	8.3	20.8	41.7	62.5	83.3	98.7	92.1	85.5	79.0	72.4	65.8

white area: use this percent recycled solvent, add remainder in hexane
gray area: use this percent recycled solvent, add remainder in ethyl acetate

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Likewise, to mix down (e.g., 16% EA $\longrightarrow$ 10% EA) equation 5 is used to calculate percentage recycled solvent required with the remainder being hexane.

$$\% \text{ Recycle Used} = (x * 100)/y \tag{5}$$

The table can, of course, be applied to any binary solvent mixture.

Procedure–Acetone

Each washing station in the lab is equipped with a wide-mouth funnel and a bottle labeled "wet acetone". Care must be taken to avoid accidental inclusion of other solvents. A small amount of acetone is initially used to remove residual organics from glassware and is discarded into a bottle or drum labeled "spent organic solvent". The glassware is then washed with detergent and the wet glassware is rinsed with acetone over the "wet acetone" recovery bottle.

The wet acetone, typically containing 20% water, is then decanted into a dedicated five liter distillation apparatus fitted with a 60×2 cm tube filled with glass rings. A few boiling chips are added and the acetone is distilled directly into a clean bottle; a timer is used as a safety measure as described above. The distilled acetone, which typically contains 2–3% water, is perfectly suitable for wash/rinse acetone [3].

Clean Up–EA/Hex

Additional distillations can be conducted in the same apparatus once the pot has cooled, each cycle requiring approximately 4 h. Residue is minimal and cleaning is required only after dozens of distillations. High-boiling pot residue, boiling-chips and $MgSO_4$ (from the drying bottle) are separated and accumulated in labeled containers for eventual pick-up by hazardous materials specialists.

Clean Up–Acetone

The high water content of the wet acetone necessitates frequent (each three to four distillations) removal of pot residue into a bottle labeled "Acetone still bottoms". The pot residue is usually a clear or lightly colored liquid containing 45–55% water/acetone. Once full, the bottle is assayed by specific gravity and tagged for removal by hazardous materials specialists.

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Conclusions

A density-based recycling–reformulation protocol, illustrated here for EA/Hex, offers a fast and accurate method for assay and reformulation of binary solvent mixtures. Combined with a convenient protocol for recovery of wash acetone, the recycling program has reduced the waste stream of our laboratory by twenty to 40 L in an average week.

Notes

1. The numbers in Table 1 are based upon density values experimentally obtained in our laboratories at 23 °C. However, the density of hexane can vary slightly (0.65–0.67) depending upon source. Furthermore, the solution densities, and therefore the values in Table 1, are altered for measurements at higher or lower temperatures. For example, based upon the altered densities of EA (0.888 gmL^{-1}) and Hex (0.656 gmL^{-1}), a 71.5 g aliquot of solvent at 30 °C corresponds to 25% EA/hex, rather than the 22% indicated by the values in Table 1.

2. The measurement error of ±1% (v/v) is most serious for mixtures containing low concentrations of one component. In our laboratory, recycled solvent typically consists of 20–30% EA/Hex.

3. Due to nonideal mixing, we employ empirically determined masses for water/acetone mixtures (volume % water diluted to 100 mL with acetone): 2% (79.2 g); 4% (80.2 g); 10% (82.0 g); 20% (85.3 g), 50% (91.9 g).