Drying of Grossly Wet Ether Extracts

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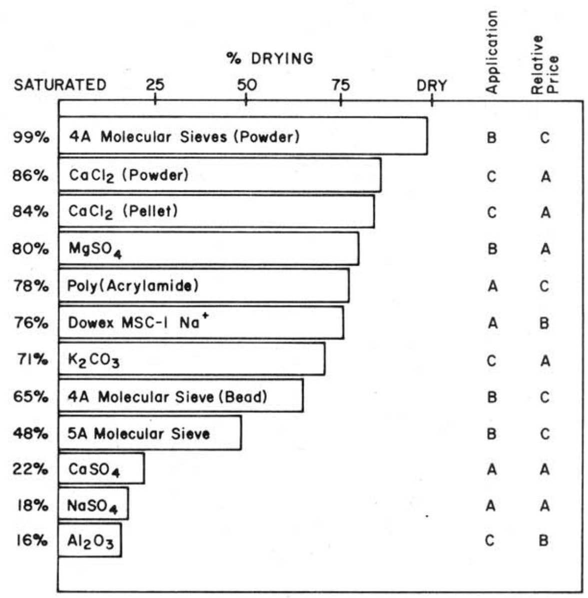
Problems arising in the drying of organic extracts are routinely faced in undergraduate laboratories; thus, the dissemination of new information concerning desiccants or improved procedures which can be adopted by teaching laboratories as exemplified by a recent report in THIS JOURNAL (*1*) are to be welcomed.

Our previous work (*2–6*) has been concerned with the ultimate efficiency of desiccants in the drying of reagents and solvents containing relatively small amounts of water and has provided quantitative information for the researcher. However, the drying of grossly wet organic extracts, as routinely encountered in student preparations, presents a new facet of the problem. The results below were obtained using our radiotracer method (*2–6*) and give information concerning the speed and efficiency of desiccants in the drying of water saturated diethyl ether.

The following points are worth highlighting. First, of the ultimate drying obtainable after 6 hr, for most desiccants at least 80% of this value has already been attained after 15 min. In one case, i.e., powdered molecular sieve, the extent is >99%. This result strongly endorses the customary practice of relatively short drying times. The only exceptions to this are the bead forms of Molecular Sieves, which although characterized by high ultimate efficiency are relatively slow in drying bulk quantities of water. Presumably, penetration of the internal labyrinthine canals is rate determining in these cases.

Sodium and calcium sulfates ("Drierite") are both surprisingly ineffective, more particularly so in the light of the august recommendations (*7*) and other exhortations (*8*) which have appeared on their behalf. In the case of calcium sulfate, this may be attributable to the very limited capacity for water absorption, i.e., ~5% w/w, which is exceeded at these desiccant loadings.

Of the more active desiccants, it should be noted that there is little difference in the rate of drying by powdered and granular $CaCl_2$, presumably indicating the highly porous nature of the granule form. The applications of this desiccant are, of course, subject to the usual limitations imposed by functional group considerations. Magnesium sulfate and ion exchange resin are fairly efficient, have wide application, and are particularly advantaged in that the dry solutions produced can be decanted easily from the desiccant. On the other hand, although this was not always true for powdered molecular sieve, the siccative *par excellence* in this study, we found that this desiccant was easily voided by gravity filtration through a glass wool plug. It was striking that the potency of sieves in



Application: A No limitation
B Wide applicability, but may cause dehydration in sensitive compounds
C Chemically incompatible with some solutes

Relative Price: A Inexpensive
B Moderate
C expensive

Extent of drying after 15 min (10% w/v desiccant).

[1] This article is Part 6 of "Desiccant Efficiency in Solvent and Reagent Drying."

Desiccant Efficiency [a] in Drying of Water Saturated [b] Diethyl Ether

Desiccant [c,d]	Residual Water Content (mg/g) 15 min	30 min	60 min	360 min
$MgSO_4$	2.9(7.4)	2.8(6.8)	2.5(6.3)	1.8(3.6)
$CaSO_4$ (Drierite)	11.4	9.2	10.2	10.7
$CaCl_2$ (Pellet)	2.4	2.1(2.1)	1.9(2.1)	0.39(0.85)
$CaCl_2$ (Powder)	2.1	1.4	0.46	0.24
Ion Exchange Resin (Dowex MSC-1 Na^+ form)	3.5(8.4)	2.4(7.4)	2.4(5.3)	1.2(3.4)
Molecular Sieve-5A (Bead)	7.7	4.9	3.2	0.40
Molecular Sieve-4A (Bead)	5.2	3.0	1.0	0.29
Molecular Sieve-4A (Powder)	0.092(0.84)	0.076(0.61)	0.027(0.44)	0.095(0.37)
Na_2SO_4	12.0	12.0	11.8	10.4
K_2CO_3	4.3(4.8)	3.8(4.2)	3.3(4.7)	1.6(3.1)
Poly(acrylamide)	3.3(6.1)	2.8(5.0)	2.6(4.9)	1.9(3.1)
Al_2O_3	12.3	12.8	13.4	13.0

[a] Static drying with intermittent shaking. Drying temperature 22°C.
[b] Initial water content approximately 14.7 mg/g.
[c] Desiccants activated at 350°C overnight except Drierite (220°C); Ion Exchange Resin (140°C) and Poly(acrylamide) (no activation).
[d] Desiccant loading. 10% w/v and 5% w/v (values in parenthesis).

this form was such as to cause a noticeable temperature rise in the ether solution. As noted earlier In THIS JOURNAL (*1*) poly(acrylamide) is a useful desiccant, but the marked tendency of the granules to swell in ethereal suspensions, in our view, constitutes a serious drawback to its use.

While dilute ether extracts of compounds containing weakly or nonpolar functionalities would be expected to show broadly similar drying patterns to those noted here, it must of course be emphasized that deviations will almost certainly occur with the increasingly polar or hydrophilic nature of the solute.

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