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Freeze-Concentration of Dilute Aqueous Solutions

SIR: The study of the aqueous environmental chemistry of trace amounts of organic and inorganic compounds in natural waters often requires that these solutes be concentrated to analytically detectable amounts. Freeze-concentration is an attractive procedure for solvent removal since the low temperatures would tend to minimize losses due to volatility and chemical reactivity.

The present study was undertaken to evaluate the effectiveness of progressive freezing as a method of solute concentration in dilute aqueous solutions. The procedure employed was reported by Shapiro (3) where he claims greater than 99% recoveries after concentrations of as much as 20-fold in volume. No sample data, however, were reported.

EXPERIMENTAL

Dilute solutions of Rhodamine B (E. I. du Pont) and NaCl were employed in the present study. Rhodamine B concentrations were determined spectrophotometrically at a wavelength of 554 m μ on a Perkin-Elmer Model 202 recording spectrophotometer. Both 10- and 2-cm. cells were used. A base line method was adopted to compensate for background absorption. Chloride was determined potentiometrically according to the method outlined in "Standard Methods" (1).

Sample solutions were prepared by sizeably diluting aliquots of a known working solution with glass-distilled water. The initial concentration was calculated from the dilution factor.

RESULTS AND DISCUSSION

For investigations of natural waters, a method of solute concentration ideally should effect complete solute recovery, in sufficient quantity, without altera-

tion. These criteria essentially dictate that the method be evaluated in terms of the efficiency of recovery with respect to initial solute concentration and degree of concentration.

In the present study, distilled water solutions were prepared with the smallest solute concentration possible with the analytical procedure used. Theoretically, this approach should furnish the efficiency of the experimental crystallization process with a minimum of solute interaction.

During the course of the study, it was found that the best procedure for sample preparation was to prepare a working solution whose concentration was sufficiently great to permit an accurate analysis and then to dilute an aliquot to the volume desired. The aliquot would approximate the volume of concentrate expected. By this means, it was possible to prepare initial solutions whose concentrations could not otherwise be analyzed, and whose concentrates could be determined in the more accurate analytical ranges.

Chloride. Three series of runs each at chloride levels of 1.2, 2.6, and

5.0 mg. per liter were made to determine the efficiency of the chloride concentration process. The results are presented in Table I.

Examination of the data presented indicates that for the nine samples, after an approximately nine-fold concentration of 2.2 to 2.5 liters, chloride recoveries were essentially complete. Recovery efficiencies appear to be independent of initial chloride levels. The over-all variation in recoveries ranging from 97.7 to 102.7% is within the experimental error of the analytical procedure used. These results are in accord with the previously given data of Himes *et al.* (2) in the completeness of the recovery. Together they show that chloride can be effectively concentrated by progressive freezing throughout the milligram to gram range of concentration.

Rhodamine B. A number of replicate runs were made with Rhodamine B at initial concentrations varying from approximately 10 to 55 μ g. per liter. The results of these studies are presented in Table II.

Examination of the data presented in

Table I. Chloride Recovery Data

Volume		Chloride		
Initial, ml.	Final, ml.	Added, mg.	Recovered, mg.	Recovery, %
2200	275	2.60	2.67	102.7
2200	290	2.60	2.54	97.7
2200	285	2.60	2.62	100.8
2100	350	5.49	5.41	98.5
2100	202	5.49	5.54	100.9
2100	186	5.49	5.44	99.1
2200	195	10.98	11.04	100.5
2200	265	10.98	10.96	99.8
2200	275	10.98	11.10	101.1

Table II. Rhodamine B Recovery Data

Volume		Concn. factor, X	Rhodamine B		
Initial, ml.	Final, ml.		Added, μ g.	Recovered, μ g.	Recovery, %
5000	515	9.7	122	106.6	87.6
5000	1325	3.8	122	108.7	89.0
5000	890	5.6	115	100.6	87.8
5000	555	9.0	115	99.9	87.2
5000	890	5.6	115	94.3	82.3
5000	1250	4.0	115	103.8	90.3
5000	650	7.7	92	86.5	94.2
5000	760	6.6	91	75.2	82.4
2200	297	7.4	108.8	91.2	83.8
2200	223	9.9	108.8	98.8	90.8
2200	305	7.2	108.8	97.7	91.6

Table II shows that Rhodamine B recoveries were poorer than those of chloride without exception and were more variable. The over-all variability of the 11 samples ranged from recoveries of 82.3 to 94.2%. Although the initial Rhodamine B concentrations were considerably lower than those of the chloride samples, the degree of solute concentration was less, averaging seven-fold as against nine-fold with chloride.

Freezing runs were ended when cloudiness, most probably due to occlusion as discussed by Himes *et al.* (2), appeared around the upper portions of the core. The cloudiness was accompanied by numerous entrained

bubbles and, in the case of Rhodamine B, a pink coloration. Reduced core size, increased solute concentration, and limited agitation because of splashing would all contribute to solute entrapment.

The process of entrapment by constitutional super-cooling indicates that solute losses should be proportional to solute concentration in the bulk fluid. Assuming such losses to be nonspecific, the reduced efficiency of recovery with Rhodamine B would indicate a relative build-up of the compound at the surface of the ice. Recovery efficiency, therefore, appears to be more a function of the nature of the solute than of its

concentration. One might also note that in the core analysis presented by West (4), there is an increase in color of 5 times in the concentrate but a simultaneous increase in chloride of 8.7 times. Thus, Shapiro's (3) contention that "any easily measured parameter such as conductivity or optical absorbance will serve to indicate the recovery of the whole" is undoubtedly overstated.

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