

Extraction and Concentration of Volatiles from Dilute Aqueous and Aqueous-Alcoholic Solution Using Trichlorofluoromethane

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A method for extraction and concentration of volatiles from dilute aqueous and aqueous-alcoholic solution using trichlorofluoromethane (Freon 11) is described. Results are given for the recoveries of 1-alkanols, 2-alkanones, and ethyl alkanooates between 2 and 12 carbon number from water and 10% ethanol in a 17-hour extraction. Between 70 and 100% of volatiles of between 5 and 12 carbon number are recovered. The main advantage of the solvent is the high efficiency of

extraction of alcohols of C₅ and above and the low efficiency for C₄ alcohols and below, which makes it particularly well suited to alcoholic beverages and other materials in which ethanol is a major volatile constituent. By treatment of the Freon 11 extracts with propylene glycol, 80 to 90% of the higher alcohol but relatively little of the ester and carbonyl is removed, allowing these compounds to be concentrated further. Other advantages of the method are discussed.

The different methods employed for extracting and concentrating food volatiles from aqueous solutions have recently been discussed by Forss *et al.* (1967). These workers and Whitfield and Shipton (1966) favor refluxing the aqueous solution through a cold condenser into a liquid nitrogen trap under reduced pressure. This method gave a concentration of about 400-fold, with yields of over 80% for 1-alkanols, 2-alkanones, and ethyl alkanooates boiling below 175° C., but the recoveries of higher-boiling compounds were lower (Forss *et al.*, 1967). To achieve a further concentration of 200-fold, a second step of vacuum sublimation was used. These methods are inconvenient when dealing with solutions with high concentrations of ethanol, because the removal of ethanol by a second stage distillation or sublimation results in a further loss of volatiles.

The usual method for isolating volatile flavor compounds from alcoholic beverages is by extraction with an organic solvent. A solvent is required which will not extract ethanol, but will extract other volatile compounds in good yield. Boidron (1966) compared the gas chromatograms obtained after extraction of a wine with several of the commonly used solvents. Disadvantages of some solvents were impurities, low extraction efficiency, extraction of ethanol, water, and pigments. Of the solvents tested, *n*-pentane was the most satisfactory. However, to obtain good recoveries of volatiles, a 240-hour extraction period was necessary. Also, the pentane extract would have to be dried afterwards, and many low-boiling compounds would be lost during evaporation of the pentane.

Wines contain up to 300 p.p.m. of isopentyl and other higher alcohols (Rankine, 1967). Thus, even if ethanol is not extracted, the factor of concentration possible is limited by the amount of higher alcohol present unless these alcohols can be separated from the other minor components in the extracts. Suffis and Dean (1962) partially separated alcohols from hydrocarbons, car-

bonyls, and esters by shaking with equal volumes of carbon tetrachloride and propylene glycol.

A commercial process for extracting fruit flavors employing chlorofluorocarbon solvents was developed by Stanley *et al.* (1963). Safrin and Strobl (1964) also used chlorofluorocarbons in extracting perfume fragrance components. Schiede and Bauer (1967) developed a method of extracting food flavor compounds using a pressure-tight apparatus in which trichlorofluoromethane (Freon 11) was the preferred solvent. These commercial methods of flavor extraction are stated to yield products with the same flavor as the original sample of food, yet contain essentially no water or alcohol. However, the efficiency of extraction of individual compounds from dilute solution has not been reported. Palmer (1967) has used Freon 11 in studies on the volatiles in bananas, and it has also been used as a solvent in the column chromatography of different classes of flavor compounds (Murray and Stanley, 1968).

The present investigation was conducted to test the suitability of Freon 11 as a solvent for use in the analysis of food flavors, particularly those containing high concentrations of alcohol, such as alcoholic beverages. The results of trial extractions of 1-alkanols, 2-alkanones, and ethyl alkanooates from water and 10% aqueous ethyl alcohol in model systems are presented, together with a method of removing higher alcohols from the Freon 11 extracts using propylene glycol, which allows the remaining esters and carbonyl compounds to be concentrated further.

EXPERIMENTAL

Procedure for Testing Recoveries of Volatiles from Water or 10% Ethanol. Freon 11 was obtained from a local refrigeration company and was redistilled once prior to use. The test solutions for extraction were solutions in water or 10% aqueous ethyl alcohol of 1-alkanols, 2-alkanones, or ethyl alkanooates of between 2 and 12 carbon number. The concentration of each component was 1.0 p.p.m. (v./v.). Reference solutions of the same mixtures in Freon 11 were also prepared,

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Table I. Percentage Recoveries of Alcohols, Ketones, and Esters from Water or 10% Ethanol

Carbon Number	1-Alkanols		2-Alkanones		Ethyl Alkanoates	
	Water	10% Ethanol	Water	10% Ethanol	Water	10% Ethanol
2	0					
3	0		0			
4	9		19		51	
5	68	47	65		72	
6	86	73	72	66	78	71
7	87	76	78	73	81	78
8	93	83	81	78	82	83
9			82	81	84	86
10	100	92	84	85	85	88
11			91	95		
12			95	105		

having a concentration of 500 p.p.m. of each component, plus diethyl succinate, which was used as an internal standard.

The solutions were extracted continuously in downwards displacement extractors (Quickfit, Cat. No. 400 RDL D). In this apparatus, the solvent stream is split up by a sintered disk into fine droplets which descend through the aqueous sample. After the droplets coalesce beneath the sample, the extracted volatiles are carried over into the distilling flask. Seventy-five milliliters of Freon 11 were placed in the bottom of the extractors and also in the 250- or 500-ml. distilling flasks. Five hundred milliliters of the freshly made test solutions were placed above the Freon 11 in the extractors, and water or 10% ethanol (about 100 ml.) was added until the Freon 11 was about to overflow into the distilling flask, which was heated in a bath at 35° C. Contrary to the manufacturer's recommendation, the extractors worked most efficiently—i.e., the smallest solvent droplets were obtained—if the aqueous solution was allowed to rise up through the sintered disk at the start of the extraction. The extractors were kept cool by placing them in a water bath at 10° C. After extracting for 17 hours, 1 ml. of a solution of diethyl succinate in Freon 11 (0.5 μ l. per ml.) was added to the extract in the distilling flasks. The Freon 11 remaining in the body of the extractor was discarded. The flasks were then fitted with Vigreux columns and the extracts concentrated in a water bath at 30° C. in a room at 4° C. The evaporation rate was kept at 0.5 to 1.0 ml. per minute by partially surrounding the Vigreux column with an insulating jacket and by adjusting the depth of the flask in the water. When the volume of the extract was 0.5 to 1.0 ml., the flask was removed from the water bath and the jacket from the Vigreux column to allow the solution in the condenser to drain. One to 2 μ l. of the concentrated extracts and of the reference solutions were chromatographed and the percentage recoveries of each component calculated from the peak heights relative to that of diethyl succinate. Each sample was chromatographed three times.

The gas chromatography column was a 50-foot \times 0.02-inch i.d. support coated open tubular column (Perkin Elmer Co.) with Ucon oil (LB-550-x) stationary phase. The nitrogen flow rate was 4 ml. per minute. The temperature was held at 40° C. for 2.5 minutes and then increased at 10° C. per minute to 170° C. A flame ionization detector was used.

Removal of Higher Alcohols from Freon 11 Extract Using Propylene Glycol. Two-milliliter aliquots of the reference solutions, containing 500 p.p.m. of each component in Freon 11, were placed in a small glass-stoppered tube and shaken vigorously for 2 minutes with an equal volume of propylene glycol. The mixture was allowed to settle for 5 minutes, and 1 ml. of the lower (Freon 11) layer was transferred to a dry tube. Equal aliquots of a suitable internal standard solution were then added to the propylene glycol-treated solutions and to 1 ml. of the untreated solutions. For alcohols and ketones the internal standard used was linalool, and for the esters, 1-heptanol. Traces of propylene glycol remaining in the Freon 11 layer were removed by passing through a dry filter paper. The percentage of each component remaining in Freon 11 after propylene glycol treatment was then determined by comparison of the chromatograms obtained from these solutions.

RESULTS

The percentage recoveries of the alcohols, ketones, and esters are given in Table I. The efficiency of extraction increased sharply between C₄ and C₅, and increased with increasing carbon number. It was not possible to measure recoveries of compounds below C₅ from 10% ethanol because the peaks were obscured by impurities from the ethanol.

Shaking Freon 11 solutions with an equal volume of propylene glycol results in removal of most of the higher alcohol, but relatively little of the ketone or ester (Table II). When Suffis and Dean (1962) partitioned

Table II. Percentage of Total Alcohol, Ketone, or Ester Remaining in Freon 11 Layer after Shaking with Propylene Glycol

Carbon Number	1-Alkanols	2-Alkanones	Ethyl Alkanoates
2	0		
3	2	42	40
4	3	60	59
5	6	76	71
6	9	76	79
7	13	84	89
8	17	90	95
9		95	98
10	24	98	104
11		100	
12		101	

alcohols between carbon tetrachloride and propylene glycol, the percentage of total alcohols (C₂ to C₈) found in the carbon tetrachloride ranged from 12 to 32%. Using Freon 11, the comparable figures were 0 to 17%. The proportions of carbonyls and esters remaining in Freon 11 were similar to those found by Suffis and Dean using carbon tetrachloride.

DISCUSSION

The advantages of Freon 11 as a solvent for recovery and concentration of volatile compounds from dilute aqueous or aqueous-alcoholic solutions are as follows:

The sharp increase in extraction efficiency of alcohols above C₄ allows between 70 and 100% of the higher alcohols, esters, and ketones to be recovered in an overnight extraction, while ethanol remains in the aqueous phase. Treatment of the Freon 11 extracts with propylene glycol removes higher alcohols, which are the major components of Freon 11 extracts of wines and many fruit juices. This permits esters and other minor components remaining in the Freon 11 to be concentrated by a further 5- to 10-fold. This is also useful as a preliminary step in the identification of alcohols.

The efficiency of extraction increases with increasing carbon number, whereas methods involving steam distillation, vacuum distillation, or sublimation favor the lower-boiling compounds.

In gas chromatography, Freon 11 produces a relatively small flame ionization detector response. It elutes rapidly and, compared with many solvents, is relatively free from impurities. Miscibility with water is so low that no drying of the Freon 11 extracts is necessary.

Freon 11 does not extract anthocyanin pigments, but others, particularly carotenoids, are extracted. In such cases, an aqueous distillate containing the volatiles has to be prepared. Another possible disadvantage is the

loss of low-boiling compounds which may be of importance in the flavor of certain foods. The boiling point of Freon 11 is 23.7° C. and its density is 1.5 grams per ml. The solvent is nontoxic, nonexplosive, noninflammable, and virtually odorless (Stanley *et al.*, 1963).

Volatiles from wines, fruit juices, and homogenates of dried fruit have been extracted using either direct extraction of the clarified solution or an aqueous distillate prepared using a rotary evaporator at 35° C. under reduced pressure. These preparations have the odor typical of the starting materials and are now being analyzed using combined gas chromatography-mass spectrometry.

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