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VAPOR PHASE EXTRACTION - A NEW PURIFICATION METHOD[1]

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The primary OBJECTIVE of this procedure is the purification of a non-volatile compound which is the least soluble component of a mixture when dissolved in a solvent. The compound itself possesses appreciable solubility and cannot be freed of the contaminants by filtration and washing. The procedure is based on two principles: the solvent used to extract the more soluble components is saturated in these components; the driving force for the spontaneous addition of the solvent to the mixture is determined by the difference in vapor pressure of the pure solvent and the solution formed. An advantage of the technique and the apparatus is that the optimum separation conditions may be determined without going beyond a point of no return. Furthermore, as the system is closed, there is no possibility of product loss due to manipulation or reactivity with air, water, etc.

The observation leading to the development of the vapor phase extraction method occurred in the study of the reaction of an ethereal solution of iron(III) chloride with phenyl Grignard under an atmosphere of hydrogen[2]. When the experimental conditions were such that two liquid phases were present at the end of the reaction, the less dense phase was decanted from the heavier black oil[3]. The black oil, after repeated washing with diethyl ether, solidified to a black solid which "dissolved" in tetrahydrofuran (THF) yielding an inky black solution. After part of the solution splashed on the upper walls of the evacuated container and the liquid drained away, a black solid deposit remained. Overnight, solvent vapor apparently condensed on the residue and washed away all components except an adherant yellow crystalline solid which remained on the upper walls. As a result of this observation, the vapor phase extraction method was developed. Assuming that the effectiveness of extraction measured in terms of both rate and degree was dependent on an ample source of solvent vapor and the thin layer spreading of the impure solid, the following primary requirements of extractor design should be satisfied: there should be a large volume for solvent vapor along with a large surface for solid deposition; the liquid solvent should either be close to the solid or else a large orifice should connect the reservoir containing the solvent with that containing the solid to be extracted.

The apparatus, Figure 1, is comprised of two 500-ml round bottom flasks whose necks are bent and sealed at 7. Length

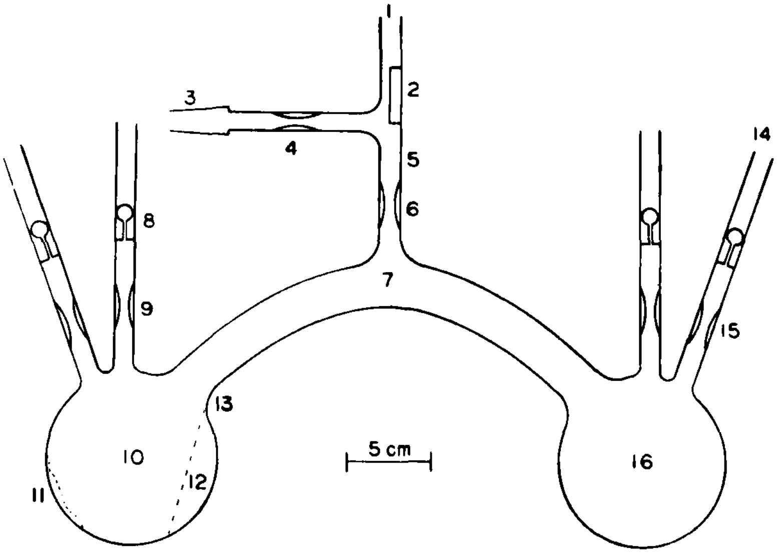

FIGURE 1

dimensions of tubing, 12 to 14 mm o.d., are a convenient minimum. Fragile bulb break seals are used rather than the hook type. Accidental breakage of the seals is avoided by sealing the tops closed when not in use[4]. Although only two such seals are required, several additional ones are present for either additional extractions or unanticipated needs. All operations are carried out with the major plane of the extractor in the vertical orientation. This plane is determined by the centers of the two bulbs and tube 7. The extractor is rotated about a horizontal axis perpendicular to this plane.

Originally the apparatus was designed for the use of extremely air and water sensitive solids. As the method employed organic solvents in an evacuated vessel for extended periods, it was essential that the apparatus be all glass and free of stopcocks and grease. Alternative designs may employ greaseless stopcocks if air leakage does not pose a decomposition problem.

The addition to and the removal from the apparatus of materials is straight forward if they are not air or water sensitive. If such sensitivity is the case, special procedures utilizing the apparatus in Figure 2 are employed. The primary unit of Figure 2, designated as either the sample introduction vessel or the product receiver, is a 100- to 300-ml round bottom flask. When used as an introduction vessel, the introduction tube was sealed off at constriction 21 after the sensitive sample was initially transferred to bulb 26 by appropriate means. Transfer of the solution in bulb 26 to the vapor phase extractor is accomplished in the following manner. The extractor is clamped at 7 by a large type 3-finger clamp to a vertical ½-inch support rod which is itself clamped to a permanent vertical lattice by means of two horizontal rods. The sample introduction vessel is clamped at 25 in an inverted position to the support rod and the fragile bulb break seal 22 is sealed onto the extraction apparatus at 1 by the usual glass blowing techniques. The apparatus,

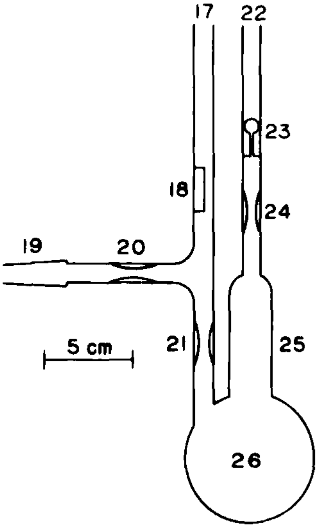

FIGURE 2

connected to a high vacuum system by the inner standard taper joint 3, is pumped down to 10^{-5} Torr and flamed out to remove the last traces of adsorbed water. Joint 3 does not lie in the major apparatus plane. If additional solvent is required, it is distilled from the vacuum line, where it is stored, to bulb 10 where it is condensed by a cold bath. The need for exclusion of mercury should be considered[5]. With the solvent condensed in 10 cooled below a temperature at which it has a significant vapor pressure, the evacuation tube is sealed off at constriction 4. The apparatus is rotated 180° or if there is a solvent in 10, to an extent that it is not decanted into tube 1. With the apparatus in the inverted vertical position, the fragile bulb break seal 23 on the sample introduction vessel is broken by the Teflon (DuPont) coated bar magnet 2. At all other times, the bar magnet is arrested by an externally taped magnet. After rotation of the apparatus 180° back to its original orientation, the bulk of the solution flows into the extractor. Quantitative transfer to the extractor of the solution trapped in 26 and also that which wets the vessel walls is accomplished by condensation of the solvent with dry ice touching the walls, coupled with appropriate hand manipulation of the support rod. Constriction 6 is washed free of solute, the solution in 10 is cooled, and the sample introduction vessel is sealed off the extractor at 6. The extractor is now easily hand manipulated. When required, it is clamped to a fixed lattice by a single 3-finger clamp at 7.

The first step in the extraction process requires that all the solution be present in bulb 10. This is accomplished by decantation and washing of the vessel walls in, for example, bulb 16 by solvent condensation with dry ice. The extractor is then oriented so that the line joining the centers of bulbs 10 and 16 is approximately 60° from the horizontal with bulb 16 the more elevated. The solvent, at a rate commensurate with the absence of splattering, is condensed in bulb 16 by a cold bath. On completion of solvent distillation, a solid adherant layer 11 remains at the "bottom" of bulb 10. The apparatus is now rotated clockwise until bulb 16 is almost directly below 10. Some solvent from 16 is condensed in the bottom of bulb 10 in a pool 12 which is retained by lip 13.

The spontaneous extraction process occurs with the entire apparatus at the same temperature. While room temperature is the most convenient, elevated temperatures could be used for high boiling solvents to hasten the process, although loss of the least soluble component into the extract solution will probably increase. The extraction process involves condensation of the solvent vapor on the solid layer 11. The solution, presumably saturated, then drains down to pool 12. The process proceeds spontaneously until either the more soluble components are washed away or that which remains is occluded by the least soluble component. This process takes at least several days. On termination of the primary extraction, the extract solution in pool 12 is decanted into bulb

16 and region 12 is washed free of the solute by solvent condensation followed by decantation. The secondary extraction, that is removal of the occluded more soluble components, is achieved after the solid in bulb 10 is redistributed on the vessel wall by repetition of the solution-evaporation process.

On completion of the extraction process and thorough washing of the region 12 and the connecting tube to bulb 16, all the extract solution is collected in bulb 16. An inverted product receiver, Figure 2, suitably supported by the aluminum rod-clamp method cited previously, is sealed onto the extractor fragile bulb break seal 14. To later facilitate solvent distillation and avoid solution transfer from the product receiver, the tube joining 14 to 21 is bent about 15^{o} in a gentle curve of 15 to 20 cm radius. The bend lies in the major apparatus plane and is oriented away from the adjacent fragile bulb break seal. Methods and conditions of extract removal are similar to the sample introduction operations. The receiver via joint 19 is evacuated to 10^{-5} Torr and flamed out. Joint 19 is sealed off at the constriction 20, the fragile bulb break seal 14 is opened by magnet 18, and the extract solution is poured into receiver 26 by rotation of the apparatus. Bulb 16 is washed free of all extract by solvent condensation and decantation. The apparatus is then oriented so that the solvent in 26 can be condensed and retained in bulb 16. It is essential that no extract solution flow back into 16 at this stage. After the solvent is distilled back into 16, constrictions 15 and 21 are sealed off. The extracted solid in bulb 10 is transferred to a receiver in like manner. This order of product transfer minimizes the possibility of accidental recontamination of the purified product in bulb 10.

The modified extractor shown in Figure 3 is useful for optimization of the solvent volume. The extractor receiver bulb is now a 50-ml calibrated centrifuge tube 32 and the two "bulbs" 29 and 32 are physically separated by use of an inverted Stock

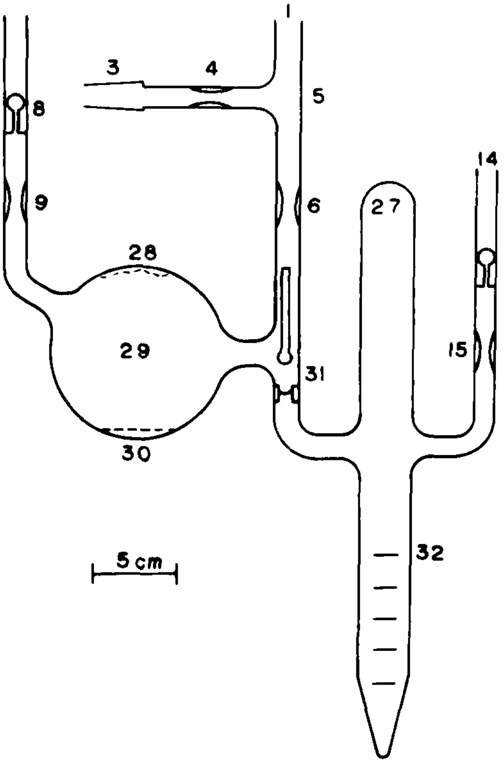

FIGURE 3

half valve 31 which is readily manipulated or arrested in the open position by an external magnet[6]. With this apparatus, solvent quantities are both more easily controlled and varied. On termination of the preliminary extraction in bulb 29, the solution is decanted into 32, new solvent is condensed in 29, and an additional extraction is carried out. Suitable manipulations are accomplished by rotation about a horizontal axis, both parallel to and perpendicular to the major apparatus plane. Reservoir 27 holds the contents of 32 when the apparatus is inverted. The solid is initially deposited in region 28 and the solvent extract pool collects in region 30.

A more versatile apparatus was designed and utilized for the application of the complimentary purification methods of vapor phase extraction and filtration. The need for the apparatus became apparent when the hydride reaction products resulted in one liquid phase rather than two[3]. The vast quantities of contaminates removed by extraction with diethyl ether in the two phase case could not be removed in the one phase case prior to vapor phase extraction.

The basic unit of the apparatus comprises of three 500-ml round bottom flasks whose necks are bent and sealed to glass tubing in the manner shown in Figure 4, a side view, and Figure 5, a top view. Liquid fractions are transferred by rotation of the apparatus about a horizontal axis perpendicular to the plane defined by the center of the connecting tube and the centers of the two bulbs involved in the transfer. If convenient, liquid

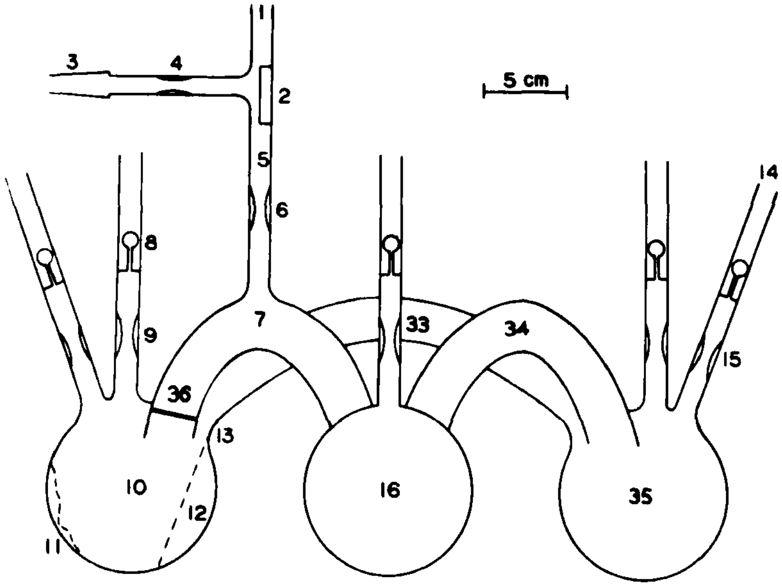

FIGURE 4

should not be in the third bulb because of accidental transfer to the lowest bulb. A coarse sintered disk 36, 25 mm o.d., positioned as close to bulb 10 as possible, is used for the secondary objective of purification by filtration. As compromise is inevitable in the design of this multifunctional apparatus, it is not intended to replace the superior filtration apparatuses previously described[7,8].

The transfer of samples and solvents to and from the 3-bulb apparatus requires that it be clamped at 7 to a principal support rod 37. When the rod is vertical and the major apparatus plane (defined by the centers of the three bulbs) is horizontal, a torque is produced which tends to twist the apparatus toward the vertical position. The horizontal position is stabilized by use of a second three finger clamp at 33, Figure 5. This clamp is fastened to the vertical section of a bar 41 which is bent in the

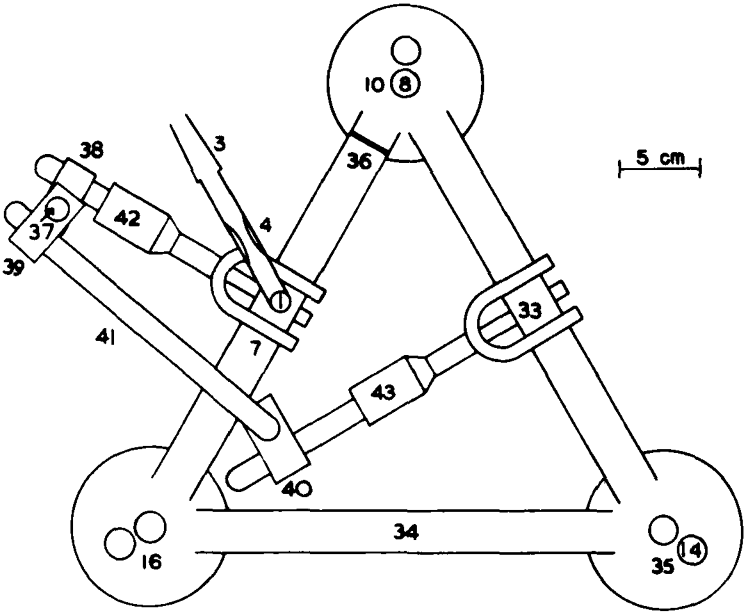

FIGURE 5

shape of the letter U and oriented so that the two parallel arms are horizontal. The extremities of the two horizontal arms are secured to the principal support rod 37 by standard 90° clamp holders 39. The vertical section of this auxiliary rod lies within the apparatus perimeter. The introduction sample bulb, Figure 2, is clamped over tube 1 in the inverted position by a three finger clamp which is connected to the principal support rod 37. In Figure 5, the rectangular sections 38, 39, and 40 are intended only to symbolize clamp holders. When the apparatus is not connected to either a sample receiver or the vacuum line via the inner standard taper joint 3, it is readily hand manipulated.

The principal advantage of the 3-bulb apparatus is that any combination of the vapor phase extraction and the filtration-decantation purification methods may be carried out without need for the intermediate transfer of a product to a second apparatus. By either of these purification methods, the least soluble component of a mixture is concentrated in one bulb and the more soluble one in another. One of the two purification methods, utilizing the vacant bulb, is then carried out on one of the two previously concentrated fractions. After examination of these products to determine the necessity for further purification, the products in two of the bulbs are combined. If additional purification is necessary, the process is repeated utilizing either method and the vacant bulb. Not only may the least soluble component of a mixture be separated from the more soluble ones, but the converse is also possible when suitable conditions prevail. In the purification techniques outlined subsequently, products may be removed from the closed system by the sample withdrawal technique at any time. Subsequently, either the same solvent can be used for further purification of the remaining mixture or a different solvent can be added and its solution-extraction properties evaluated.

When the objective is the purification of the least but still moderately soluble component of a mixture, a double vapor phase extraction process is used. Initially the starting mixture which may contain substantial amounts (>50%) of the more soluble impurities is subject to vapor phase extraction in bulb 10. After decanting the extract solution to the intermediate bulb 35, the solvent is evaporated and the residue (in bulb 35) is examined for the least soluble component if its properties, for example color, so permit. The residue in bulb 35 is then subjected to vapor phase extraction. The resultant extract solution is transferred to the final bulb 16 and the solid residue is redissolved and returned to the initial bulb 10. During the second extraction, there may also be spontaneous extraction of the products in bulb 10. By careful decantation manipulation this extract solution is retained in bulb 10 when the extract solution in bulb 35 is poured into the final bulb 16. By repetition of the double extraction process, the least soluble component is progressively purified and the loss into the extract solution is minimized. Compromise between degree of purification and product loss into the extract solution may be inherent in the process. Loss of the least soluble component into the extract solution is related to duration of the operation when there is moderate solubility. The two stage vapor phase extraction process is more suitable for purification of moderately soluble compounds whereas the single stage extraction is satisfactory for less soluble compounds.

The 3-bulb apparatus can be utilized for the removal of a less soluble contaminate from a more soluble compound. Loss of the latter corresponds to its solubility in about 120% of the solvent required to initially produce a saturated solution of the contaminate. The purification process comprises of two types of operation which are designated as the primary stage A and the secondary stage B. In stage A, all the products in bulb 10 are dissolved. The solvent is then evaporated until the solution is almost saturated in the contaminate. During the process, the bulk of the more soluble component precipitates. After filtration of this solution into bulb 16, a fraction of the liquor containing the contaminate will continue to wet the purified precipitate in bulb 10. Stage B comprises of two solution operations. Solvent is condensed in bulb 10, the products are dissolved, and the solvent evaporated to the same extent as in stage A. This solution is decanted to bulb 35 and further concentrated by solvent evaporation to 20% of the volume initially in 35. Eighty percent of the more soluble compound precipitates and the remaining solution is decanted into bulb 16. The solid in bulb 35 is re-dissolved and returned to bulb 10. The objective of the first part of stage B is maximum removal of the contaminate from bulb 10 which is achieved by a relatively large solvent volume. In the second part, maximum recovery of the more soluble component is the primary objective. The operations are based on the assumption that the amount of wetting liquor retained on the solid in bulbs 10 and 35 after filtration-decantation is proportional to the quantity of the solid. Each stage of the purification process results in contaminate reduction by approximately an order of magnitude. If further purification is required, stage B is repeated. Stage A is omitted if the contaminate quantity produces such a small amount of saturated solution that a relatively large fraction continues to wet the solid after filtration.

Utilization of the 3-bulb apparatus for vapor phase extraction of large quantities (>50 g) of initial material containing a large fraction of more soluble impurities may be accomplished by a first stage filtration which is intended to concentrate the impurities in solution. A second stage vapor phase extraction on the undissolved products remaining in the initial bulb further concentrates the least soluble compound.

Another successfully used procedure employing any of the three apparatuses is a cold temperature vapor phase extraction which is carried out by depositing the raw solid products on the upper portions of the vessel and then placing a piece of dry ice next to the material to be extracted. The solvent condenses, forms a saturated solution at low temperature and then drains to a pool at the vessel bottom. The intent of citing the previous examples is to indicate the variety of manipulations possible with the 3-bulb apparatus. Since each experiment has its own unique problems, no attempt is made to be more specific in the application of the apparatus.

The techniques were employed in the separation of the non-volatile solid products formed by the reaction of iron(III) chloride with phenyl magnesium bromide under an atmosphere of hydrogen[3]. The least soluble component in tetrahydrofuran (0.002 M) was the yellow crystalline solid $Mg_4Br_{3.4}Cl_{0.6}H_6Fe(THF)_8$ (YCS). Purification of the YCS by the single stage vapor phase extraction method was adequate when the bulk of the contaminates had been removed previously by liquid-liquid extraction with diethyl ether. In the absence of the etheral treatment, the purification method required utilization of the 3-bulb apparatus. All the black component and the bulk of the white ones were removed by the two stage vapor phase extraction method. The remainder of the white contaminates were removed by the filtration method discussed in the reference[3]. It was curious that despite the slight solubility of the YCS in both THF and diethyl ether that the massive contamination by the very soluble black component could not be diminished by the filtration process. The solublity of the YCS in a solution containing the contaminate was enhanced by more than an order of magnitude. A more soluble (relative to the YCS) white crystalline solid was freed of the black contaminates by a combination of the filtration and the vapor phase extraction processes. It was freed of the YCS by the filtration process. The light dispersing and magnetic properties of the black component indicated that it was colloidal iron. Despite many manipulations, the colloidal iron could not be coagulated and filtered from the THF.

I have presented here the laboratory observations leading to the discovery of the vapor phase extraction method. Much work is required to establish both its utility and its limitations. While it is not expected to be widely applicable, there will arise cases where its application is crucial. As with the filtration-precipitation purification process, vapor phase extraction is to a first approximation dependent upon the solubility of the compounds to be separated. The two purification techniques, filtration and vapor phase extraction complement each other. Filtration is preferred if the product can be freed of more soluble contaminates by washing and if the degree of loss by solution is compatible with the experimental objectives. The degree of product loss is a function of solubility and quantity of both the sought compound and the impurities and also of the quantity of the solvent. As the solubility of the sought compound increases, filtration becomes less suitable. Filtration is also unsuitable if the impurity is an adherant oil which cannot be washed from the precipitate without excessive precipitate solution. As filtration becomes less suitable, vapor phase extraction becomes more useful. Vapor phase extraction is useful in the purification of slightly to moderately soluble compounds both in the presence and absence of an adherant contaminating oil. Vapor phase extraction is also useful when the apparent solubility of the sought compound is enhanced by the contaminates.

Loss of the least soluble component into the extract solution, rate, and to a degree duration of the extraction process is a function of component solubility and vapor pressure difference between the bulk solution in bulb 16 (or pool 12) and the solution in direct contact with the solid 11. Solubility can be controlled by solvent selection and perhaps a judicious choice of a mixed solvent. Rate and process duration, directly related to vapor pressure differences, may be regulated by both temperature and total solvent quantity. In the case of the iron hydride purification, solute concentration in the bulk extract solution did not rise to the extent that it significantly inhibited by vapor pressure lowering the spontaneous condensation of the solvent on the mixture 11. It was observed that loss of hydride into the extract solution was highest initially. When the contaminants were removed, there appeared to be no further hydride solution over a period of months. Apparently in the initial stages, the more soluble impurity so diminished the vapor pressure of the solvent that there was an appreciable rate of condensation on the solid which resulted in solution of the hydride as well as the more soluble contaminants. When the contaminants were washed away, solution of the pure hydride did not sufficiently lower the vapor pressure of the solvent to permit spontaneous condensation. Alternatively, the enhanced solubility effect may have been the major factor.

Samples subject to vapor phase extraction in a 500-ml flask should not exceed about 10 grams. While this quantity does not produce a thin layer, if it does not "cake" but rather forms a somewhat porous mass, complete purification is feasible. A principal quantity limiting factor is determined by the tendency of the material to adhere to the vessel wall. The effects of the secondary problem, occlusion, can be eliminated by several solid redistribution extractions. A similar apparatus comprised of a 1- or 5-liter bulb, corresponding to bulb 10 here, and a 500-ml extract receiver bulb 16, could be used for larger samples.

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1. Figures 1, 2, and 3 and a portion of the text referring to the 2-bulb extractor are reproduced by permission of the American Chemical Society. Figures 4 and 5 are reproduced by permission of Elsevier Press. Original accounts of the vapor phase extraction method are found in the following references:
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