Source Reduction Research Partnership
Metropolitan Water District of Southern California
Environmental Defense Fund

Source Reduction of Chlorinated Solvents

Food Products Manufacture

Prepared for

Alternative Technology Division
Toxic Substances Control Program
California Department of
Toxic Substances Control

and

Pollution Prevention Research Branch
Risk Reduction Engineering Laboratory
Office of Research and Development
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Pollution Prevention Research Branch
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DISCLAIMER

The statements and conclusions of this report do not necessarily represent those of the State of California, the U.S. Environmental Protection Agency or any other contributors. The mention of any commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

PREFACE

This report is one of twelve reports that evaluate the opportunities for source reduction of chlorinated solvents in twelve specific industries. The twelve reports are part of a large-scale study sponsored by the Source Reduction research Partnership (SRRP), a joint venture by the Metropolitan Water District of Southern California and the Environmental Defense Fund. The reports cover the following industries and industrial practices:

1. Aerosols Manufacture
2. Adhesives Manufacture
3. Chemical Intermediates Manufacture
4. Dry Cleaning of Fabrics
5. Electronic Products Manufacture
6. Flexible Foam Manufacture
7. Food Products Manufacture
8. Paint Removal
9. Pesticides Formulating
10. Pharmaceuticals Manufacture
11. Solvent Cleaning
12. Textiles Manufacture

The objectives of the SRRP study include a survey and evaluation of existing and potential techniques for reducing the generation of halogenated solvent wastes, and thus their potential release into the environment, across a wide range of the industrial users of these solvents.

Each of the industry-specific reports begins with a description of the industry and processes where halogenated and solvents are used. Sources and causes of releases are described and regulatory regime discussed for waste streams of concern.

Subsequent sections focus on source reduction opportunities through chemical substitution, process modification, product substitution and recovery/reuse. For major solvent using industries, select source reduction options were analyzed for their economic feasibility.

The information in the reports was compiled and analyzed by the SRRP project staff, employed by the Partnership to carry out the project research. Each report was reviewed by industry representatives and/or other experts familiar with the specific industry and the relevant technologies and issues, and then reviewed and edited by an additional expert consultant.

The intent of the sponsors is to provide all interested parties with useful information on available and potentially available methods for source reduction of halogenated solvents, in the context of specific industries and processes, and an evaluation in context of the various source reduction options.

I. INTRODUCTION

This report is one of the several companion reports that focus on source reduction of chlorinated solvents and evaluate source reduction opportunities in a number of industries where these solvents are widely used. The five major chlorinated solvents mostly used in commerce today include trichloroethylene (TCE), perchloroethylene (PERC), 1,1,1-trichloroethane (TCA), methylene chloride (METH), and 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113). Today, only METH is used in the food industry, in processes such as decaffeination of coffee, hop extraction, and spice oleoresins extraction. Manufacturers voluntarily discontinued using TCE when a ban was proposed by the Food and Drug Administration (FDA) in 1977. None of the other chlorinated solvents is used in the food industry. This document specifically describes the use of METH as an extraction agent in the food industry and provides an assessment of the source reduction potential in that industry. The food industry uses about 3,000 metric tons of METH annually as an extraction agent. This figure is SRRP's best estimate of the level of METH used in the food industry. Chlorinated solvents are commonly sold through distributors to users, and purchase records are not available from either source.

Methods for the production of decaffeinated coffee, hop extracts, and spice oleoresin extracts have been known and commercially practiced for decades. A problem with many natural flavors and fragrances is that they are composed of a dozen or more different chemical substances, some of which are unstable--especially when heated. As a result, extraction must be performed with care. Even so, conventional gentle extraction processes still leave some essential substances behind. Extensive R&D in the past few years has promoted the use of some new technologies such as supercritical carbon dioxide extraction and liquid carbon dioxide extraction. Although more expensive than traditional separation processes, these hold significant promise for the future.

In the case of extracts or concentrated material destined for human consumption, the situation has changed dramatically over the last few years, and there is an increasing concern over the possible presence of compounds which may present a hazard to health. This concern has led to increasing regulatory requirements. In particular, there may be limits on the solvent residues remaining in foods or beverages, and there is an incentive to minimize or eliminate these residues.

In the balance of this document, the extent and processes that use chlorinated solvents in the food industry are discussed. Section II focuses on the food extraction process and provides characteristics of the industry structure. Section III describes the source reduction options that might be used to reduce the use of solvents in the industry. Finally, Section IV discusses conclusions about the future use of chlorinated solvents in the industry.

II. BACKGROUND

Solvent extraction is used in the food industry to separate or concentrate a desired component or to eliminate or reduce the concentration of an undesirable component. The most important solvent property that must be considered in the selection of an extraction solvent is the ability of the solvent to extract the required component from the raw material and produce a desired product quality.

A solvent used for food extraction should preferably be nonflammable, volatile, nontoxic while possessing the ability to selectively and efficiently extract the components of interest. The suitability of each solvent for a particular application is determined by laboratory evaluation and tasting. Many other factors such as flavor, consumer opinion, and potential government regulation also play a role in the choice of a solvent.

The United States Food and Drug Administration (FDA) regulates the solvents that can be used in food extraction (FDA, 1987). TCE and METH are the only chlorinated solvents currently approved for extraction of certain food products. Many other types of solvents, such as water and hexane, are used as extraction agents. The FDA proposed a ban on TCE in food extraction in 1977. Although never finalized, this resulted in a movement away from the chemical by the industry. Presently, METH is the only chlorinated solvent used as a food process solvent in the preparation of decaffeinated coffee, hop extracts, and spice oleoresins.

The remainder of this section discusses the various food production processes where METH is used, estimates of the amount of METH used, the amount and sources of releases from the processes, and the regulations that govern the industries.

PROCESS DESCRIPTIONS

METH is used as an extraction solvent in three food food processing applications: decaffeination of coffee and tea, hop extraction and spice oleoresins extraction. Each of these is described below.

Decaffeination of Coffee

Today, eight to ten percent of the world's coffee beans, or close to 4.4 million bags are decaffeinated annually (Sivetz, 1971). About 55 percent of this coffee is decaffeinated in Europe, 40 percent in the U.S. and the balance, elsewhere. Close to 2.7 million bags are decaffeinated in the U.S.; this represents fifteen percent of the imported coffee to the U.S. (NCA, 1989).

Decaffeinated coffee was first introduced to the American public as a chemically-treated product called Sanka^R, which was developed in Germany and purchased by General Foods in the 1930s. Roasted coffee beans commonly contain only 1 to 2 percent caffeine by weight. The decaffeination process removes 97 percent of the caffeine, so that a five-ounce cup of decaffeinated coffee contains from 1 to 5 milligrams of caffeine, compared with 60 to 180 milligrams in a five-ounce cup of drip-brewed coffee (NCA, 1987).

Total consumption of coffee in the U.S. is 127 billion cups each year. Between 1960 and 1970, decaffeinated coffee use increased threefold in the U.S., from 0.06 to 0.18 cups per person per day to 0.31 cups per person per day. During the same time the use of coffee fell from 22 to 17 pounds of green coffee beans per person per year. Decaffeinated coffee consumption increased from 2.37 cups per day in 1986 to 2.48 cups per day in 1987. Every day about 33 percent of U.S. coffee drinkers consume at least one cup of decaffeinated coffee. Consumption of both regular and instant decaffeinated coffee has increased in recent years, until decaffeinated now accounts for 30 percent of all instant coffee sales (CMR, 1988a).

Decaffeination was first developed commercially in Europe about 1900. In what is referred to as the "direct" method, the green coffee beans are first steamed to increase the moisture content from 20 percent to 40 percent. The heat and moisture cause the caffeine to separate from the natural complexes and move to the surface of the bean. Then the beans are contacted countercurrently with an organic solvent for 12 to 18 hours, sufficient time to extract 97 percent of the caffeine. The beans are steamed again to remove the solvent, then dried and roasted (Stefanucci et al, 1979). The solvent is recovered from the caffeine/solvent mixture by distillation in a continuous circulation evaporator. The solution is sent to the caffeine refining operations for the recovery of 99.9 percent pure pharmaceutical-grade caffeine.

In 1943, a process to extract caffeine with water was introduced. This process is referred to as an "indirect" method. In this method, water is mixed with the steamed beans to draw out the caffeine. The water is separated from the beans and then, in a separate stage, it is contacted with a decaffeinating solvent such as METH. Decaffeinated water is separated from the solvent phase and then recycled to the next batch of coffee beans. Recycled water is saturated with the amino acids and other important coffee flavors, so it is not capable of stripping these components from the beans. It also contains small amounts of METH. The caffeine is purified by water extraction, crystallization, and absorbents for use in pharmaceuticals and soft drinks.

In 1984, Nestle Company patented a process which uses a liquid water-immiscible, fatty material to extract caffeine. This process does not require the use of halogenated solvents;

instead, it relies on fatty oils composed of edible esters of fatty acids, usually glycerol esters, as extraction solvents. Such fatty oils include safflower oil, soybean oil, peanut oil, coffee oil, triolein, olive oil, and lard.

In the coffee oil decaffeination process, which employs the oils extracted from coffee beans, the coffee beans are soaked in water first. Then the beans are washed with a stream of natural coffee oils, which removes the caffeine from the surface of the beans. The decaffeinated beans are then dried and roasted.

Activated charcoal is sometimes used in Europe in the "Swiss water process". In this indirect method, beans are soaked for hours in water to draw out off the caffeine. The caffeine-rich water mixture is then run through a charcoal bed to adsorb the caffeine. The charcoal bed is pretreated to prevent adsorpton of other coffee compounds from the water. The caffeine-free mixture is concentrated and added back to the partially-dried coffee beans. The decaffeinated beans are then ready for drying, roasting, and grinding.

In each of the processes described below decaffeination is achieved using a substance that has the ability to extract caffeine from coffee beans. These include coffee oils, preheated charcoal, ethyl acetate, and METH. Water alone cannot be used to produce the final product directly, because it also extracts too much of the important flavor and aromas. The decaffeination of tea is achieved by the same methods as coffee.

Four companies produce decaffeinated coffee in the U.S.: General Foods Corporation, Procter and Gamble Company, Nestle Company, and Hills Brothers. Table 2.1 shows the decaffeinated coffee market share of these various producers. The values demonstrate that instant coffees account for about two-thirds of the decaffeinated coffee market.

General Foods--the largest producer--holds approximately 62 percent of the market. Apparently, only General Foods uses supercritical carbon dioxide for extraction of caffeine at its Houston, Texas plant and METH in the indirect decaffeination method at the Hoboken, New Jersey plant. One of the companies uses the water extraction process. Proctor and Gamble and Nestle use the ethyl acetate and natural coffee oil extraction process, respectively.

Cost information on various decaffeination processes is limited. The METH decaffeination process costs about \$0.18/pound of decaffeinated coffee, compared to \$0.40/pound for the Swiss Water Process. The price difference (\$0.22/pound of the coffee) itself, however, is only about 5 percent at the retail level (Hammitt, 1989). There also appears to be no systematic differences in the prices of coffee decaffeinated with METH or any of the other decaffeination agents. Solvent cost is not a major share of the production cost; rather, product quality and the capital cost of the processing plant are reported to be the most significant factors in selecting a decaffeination process (Hammit et al, 1989).

Hop Extraction

Hop is the blossom of the female hop plant and is added to beer for its uncharacteristic bitter taste and aroma. Hop extracts became very popular between 1966 to 1972. Today the use of hop extracts accounts for 25% of the world's supply of hops (Harold and Clarke, 1979). Hop overcomes the sweet taste of unhopped beer, plays a role in biologically stabilizing beer, and improves the head retention and body of beer. The amount of hop added to beer varies from 0.4 to 4.0 grams per liter of beer. Some hop extracts are also used in pharmaceutical production (Mitchel, 1988).

Table 2.1

DECAFFEINATED COFFEE MARKET SHARES

Brand[1]	Producer	Percent of Market[2]
	Roasted and Ground Coffees	
Brim	General Foods	15.6
Sanka	General Foods	12.3
Hills Brothers	Hills Brothers	4.7
Total		32.6
	Instant Coffees	
Sanka	General Foods	22.8
Taster's Choice	Nestle	14.0
High Point	Proctor and Gamble	11.7
Brim	General Foods	7.0
Nescafe	Nestle	5.3
Sanka Freeze Dried	General Foods	4.7
Hills Brothers	Hills Brothers	1.8
Total		67.3

SOURCE: Hollie, 1985, SRRP, 1990.

NOTE: [1] All brands listed are trademarks.

[2] The percentages do not add up to 100 because of rounding.

The bitter substances in the hop, which are a combination of many complex organic compounds, can be extracted using a solvent. Although the FDA allows use of other extraction solvents such as isopropanol and methanol, about forty percent of hop extraction is done with METH, and the balance mainly with hexane (SRI, 1985).

The extraction process is quite simple. The bales of the plant are shredded. Then the hop cones are extracted with organic solvent in either a batch or continuous extractor. The solution is then heated to recover the solvent for recycle and the hop resins. A second extraction of the spent hops with hot water yields a water extract, often referred to as "tannins", which is then mixed with resins to produce a "standard" extract. This "standard" extract is the one usually used in America. Although the FDA allows up to 2.2 percent solvent in hop extracts, the solvent residue in "standard" extract is generally less than 1 percent (SRI, 1985). Indeed, virtually all the solvent is believed to be removed in the first few minutes of kettle boiling. Hop extracts are not recommended for use in cold hopping, which involves the addition of hops to cold storage beer.

Hop extracts are added in a variety of different manners to the boiling wort (Grant, 1977). Wort is the main raw material of beer and contains the enzymatic degradation products of barley's starch and protein. Hop extracts provide a higher amount of essential bitter substances and offer a standard level of bitterness (SRI, 1985).

The addition of hop extracts facilitates commercial production of beer. The acids and resins are preisomerized in the resultant extract. This eliminates the need to add these substances at the boiling stage, and they can be added to the finished beer directly. Preisomerization not only provides a good yield of bitter substance, but also prevents the loss of acids and resins during fermentation.

Two types of hop extracts are processed and used: "standard" or "kettle" extracts, and "isomerized" or "post-fermentation" extracts. The "standard" process uses METH and the "isomerized" process does not. Of 195 million barrels of beer produced annually, about 40 million use isomerized and the rest use raw hops; as a result less than five percent of the beer is produced using the "standard" method (SRI, 1985).

Although methods for production of hop extracts have been known for over a century, commercial use of hop extracts is not widely accepted. Brewers, particularly in Germany and Japan, believe that hop extracts negatively affect the quality of their product. As a result, the use of hop extracts has been inhibited in these countries.

Although hop extracts are produced by a number of general extractors, there are four major producers in the U.S.: John I. Hass, Inc., a hop product manufacturer; Hopstract, a joint venture of two hop producers (S.S. Setiner and Louis Von Horst); Kalsec, Inc., a producer of spices such as oleoresins and essential oils; and Pfizer, Inc., a manufacturer of dairy and beer products such as cheese cultures and mashing enzymes (SRI, 1985). Pfizer has adopted liquid carbon dioxide extraction. Hopstract uses METH, and has also installed a supercritical carbon dioxide extraction system.

Spice Oleoresins

The U.S. is the largest importer of spices, accounting for approximately one-fourth of the total produced. Imports supply 80 percent of U.S. consumption needs, and the remainder comes from domestic production spices. Most flavor companies sell their products worldwide, which emphasizes the need for global standards and labeling on such products. Of the approximately 1,000 companies worldwide, 12 flavor companies account for 50 percent of the marketplace. Production of any type of spice oleoresin and its quantities varies significantly from year to year, depending on the market needs and food industry trends. For example, in the early 1960s and 70s, the use of essential oils was phased out, but in recent years its use has been expanded (SRI, 1985). In general, the U.S. consumption of spice oleoresins has increased but domestic production is believed to have decreased, primarily because of industry's transfer of production to overseas, close to the spice sources.

The essential oils carry the aroma of the spice in a concentrated form. The essential oils are volatile, and do not contain the nonvolatile constituents which are responsible for the characteristic taste of certain spices. To isolate the nonvolatile compounds, the spices have to be extracted with a volatile solvent. A viscous semisolid or sometimes solid residue (oleoresin) is obtained after careful evaporation of the solution in vacuum, (SRI, 1985).

Oleoresins have lately achieved great importance in the food industry. They offer many advantages over straight spices, including cleanliness and uniformity of flavor from lot to lot. This is especially important when foods are produced by an automated process. The use of oleoresins permits better distribution of flavor and a standardization of the flavor level that is difficult to obtain with straight spices. Moreover, oleoresins, when properly prepared, are almost free of bacteria, molds and spores, which is a major advantage over crude spices and aromatic herbs, especially in prepared foods. Because of their high concentration, a few kilograms of oleoresins (or in many cases, of essential oils, where the nonvolatile portion is of minimal significance to the total flavor) can replace many kilograms of natural spices. Oleoresins are often added to the food product in a diluted form, usually on a dry edible carrier, such as table salt or dextrose. These products, commonly known as dry solubles, are usually equivalent in performance to the corresponding natural spice. The users of oleoresins are primarily industrial producers of canned and processed foods and beverages and spice blenders. Oleoresins are not sold for home use because of their high potency.

Oleoresins are produced by two different methods: the continuous (one-step) process, and the batch (two-step) process. In the continuous process, raw spice is pulverized until the required particle size distribution is reached, and then percolated with a volatile solvent like METH. The solvent extracts the active ingredients which impart aroma and taste to the spice. The solution is then boiled and vacuum distilled to remove all but small quantities of the solvent. The resulting product is called oleoresin, which is either incorporated into a blend or diluted. In the batch process, the spice is subjected to steam under pressure, which volatilizes the aromatic principals. The spice is then dried and percolated with solvent to remove the flavor principals. Afterwards the aromatic principals--the essential oils and flavors--are combined and form oleoresins.

The solvent used in oleoresin extraction depends on the type of the spice that is to be extracted. For example, ginger and tumeric cannot be extracted using a chlorinated solvent. Non-solvent methods are also used to recover essential oils. These include vacuum distillation, steam distillation, and adsorption. Disadvantages of these methods are that they usually have low yield, form degradation products, and result in a different flavor than the original spice.

The major U.S. oleoresin producers are: Kalsec, Inc.; McCormick-Stange Flavor Company; Fries & Fries, Division. of Mallinckrodt, Inc.; and Fritzche Dodge & Olcott, Inc. There are many smaller operators who are also involved in the production of oleoresins on a small scale (SRI, 1985). Only two companies, Fries & Fries and Fritzche Dodge & Olcott, reported the use of METH in the 1987 toxic release inventory (TRI) data. Since the reporting threshold was 10,000 pounds of use annually, there may be other firms that use METH for this purpose but were not required to report. The American Spice Trade Association says that none of its members west of the Mississippi River use chlorinated solvents in their processes (Burns, 1988).

QUANTITY OF METH CONSUMED

About 3,000 mt of METH is consumed in the food industry annually. In decaffeination of coffee, one source estimates the use of METH to be between 680 mt and 3,180 mt (SRI, 1985). Since 1985, the use of METH in the decaffeination of coffee has decreased substantially. The one U.S. coffee manufacturer that uses METH--General Foods Corporation--has installed a supercritical carbon dioxide unit at one plant. SRRP staff estimates that 200 mt of METH is used at the Hoboken, New Jersey plant of General Foods.

The amount of solvent used for hop extraction also depends greatly on the solvent use procedures. About five percent of the U.S. beer market uses METH-extracted hops. Typically, six pounds of solvent is used to extract one pound of raw hop. Assuming that 12 to 13 million pounds of raw hops are extracted in the U.S. (SRI, 1985), and that only five percent of that is extracted using METH, about 1,750 mt of METH is used in the industry.

No estimates of the amount of METH or other solvents used in the spice industry could be found by the SRRP staff. U.S. production of spice oleoresins is estimated to be about 1,000 metric tons per year. Sources estimate that 10 to 20 percent of U.S. spice extraction uses METH (SRI, 1985). SRRP estimates that about 1,000 mt of METH is used for spice extraction.

SOURCES OF RELEASES IN THE FOOD INDUSTRY

The METH used in the coffee industry is released as an atmospheric emission and as a wastewater containment. In coffee extraction, water is mixed with the steamed beans to draw out the caffeine. The water then undergoes liquid-liquid extraction with METH, causing some of the METH to dissolve and/or become entrained in the water. The resultant water/METH mixture contains 100 ppm (0.01 percent) to 10,000 ppm (1 percent) METH (TRI, 1987). The total amount of METH released in decaffeination industry is estimated at about 200 mt.

The FDA requires that residues of METH in hop extraction not exceed 2.2 percent. Losses in hop extraction are about 1 pound of METH per 100 to 200 pounds of dry hops extracted (SRI, 1985). Using the assumptions presented above for METH consumption, only 291 mt of hops is extracted using METH. Losses of 1 pound of METH per 100 to 200 pound of dry hops would imply that 4,200 pounds or about 2 mt of METH is lost annually in hops extraction. This means that virtually all the METH is left in the hops after extraction. The residueS that contain METH would have to be handled as hazardous waste because of the METH content. Some of the METH can be recovered through distillation of the spent hops. The extent to which distillation and recycling are practiced in the industry is not known. It is likely that no water releases occur. No toxic release inventory data were reported in the Standard Industrial Code for hop extract manufacturing (SIC 5149) in 1987 (TRI, 1987).

In spice extraction, the total residues of chlorinated solvents must not exceed 30 ppm in the oleoresin product.

Some solvent will be left in the spent spice, which may require that spent spices be handled as hazardous waste. Water releases occur in the spice industry when the spices are steamed prior to extraction, or when the solvent goes through liquid-liquid extraction or condensation. There are no data on the magnitude of the releases in the spice industry.

The toxic release inventory data for the Standard Industrial Classification code for spices (SIC Code 2987) lists two companies using METH in 1987. Fries & Fries in Cincinnati, Ohio reported one mt of air releases, and no water or waste releases. Fritzsche Dodge & Olcott in Clifton, New Jersey reported 27 mt of air releases and seven mt of water releases to the POTW.

REGULATORY REGIME

The FDA has methods for the determination of residual solvents in spice extracts, such as oleoresins, and has limited the concentrations of specific solvents permitted. Under the food additive regulatory authority, the FDA has approved the use of ethyl acetate, TCE, and METH for coffee decaffeination. Ethyl acetate has been approved for decaffeination in accordance with good manufacturing practices. The trace levels of ethyl acetate remaining in decaffeinated coffee with ethyl acetate are claimed to be lower than those found naturally in many fruits (e.g., apples, peaches, pears, cherries). Ethyl acetate is generally recognized as safe (GRAS) for use in food as a flavoring agent (NCA, 1987).

Residues of METH cannot exceed 10 ppm in roasted or instant coffee, and residues of TCE cannot exceed 25 ppm in ground and 10 ppm in instant coffee. The National Coffee Association reports that METH residues in coffee are about 0.1 ppm (NCA, 1987).

In November 1986, California voters passed the Safe Drinking Water and Toxic Enforcement Act (Proposition 65). The Governor was required to publish a list of chemicals known to the state to cause cancer or reproductive toxicity no later than March 1, 1987, and was charged with updating the list annually. For chemicals so listed, warnings are required 12 months after listing of knowing and intentional exposures, and knowing discharges are prohibited 20 months after listing. There are several exemptions in the Act. The first one requires no warning if exposures to listed carcinogens would result in a risk lower than the level of "no significant risk", or if exposure to the listed reproductive toxicants is less than one one thousandth of the no-observable effect level. The level of risk may be determined in a variety of ways including quantitative risk assessment, application of routes of exposure, specific regulatory levels which pose no significant risk, or by application of levels based on state and federal standards. In cases where concentration levels are higher than levels listed, clear and reasonable warnings have to be posted on the product.

Both METH and TCE have been listed as chemicals known to the state to cause cancer. The "no significant risk" level set by regulatory standards is 50 micrograms per day for METH and 60 micrograms per day for TCE.

III. SOURCE REDUCTION OPPORTUNITIES

This section examines a variety of source reduction options. They fall into the general categories of chemical substitution, process modification, recovery and recycling, and equipment modification. Each of these categories is discussed in turn below.

CHEMICAL SUBSTITUTION

A number of solvents are approved for use and are currently being used in the food industry. These are listed in Table 3.1 together with several of their properties such as flash point, lower and upper explosive limits, boiling point, and vapor pressure. Prices of these solvents are shown in Table 3.2. It has been reported that solvent price is not the major factor in solvent choice (Hamitt, 1989).

As Table 3.1 indicates, many of the solvents permitted for use or used in the food industry are flammable. As the tables show, the chlorinated solvents are generally less expensive than the flammable solvents and do not require explosion-proof equipment. Costs of transportation and handling may also be higher for flammable solvents.

Although all the solvents that are listed are approved by the FDA, several pose serious disadvantages because of their toxicity. TCE use was discontinued by the industry because of regulatory scrutiny. It is unlikely that TCE will be used in the future. Ethylene dichloride has a very low workplace exposure level. Hexane, ethyl acetate, and isopropanol are also acutely toxic. Ethanol and acetone exhibit the lowest toxicity in long-term animal studies. Practically all potential METH substitutes are precursors to photochemical smog. Their use is regulated by EPA and local air pollution control districts under the Clean Air Act.

Table 3.1

PROPERTIES OF SOLVENTS FOR FOOD PROCESSING

PROPERTY	CRITICAL FUNCTION	METHYLENE CHLORIDE	ETHYLENE DICHLORIDE	TRICHLORO-ETHYLENE	METHA
Material extracted	Extraction ability	Coffee Hops Spices	Spices	Coffee Spices	Hops Spic
Flash point, C	Safety	None	13	None	
Explosive limits, % by volume in air	Safety				
Lower		None	6.2	None	
Upper		None	15.9	None	
Boiling point, C	Recoverability	40	84	87	
Vapor pressure, Hg @ 25 C	Recoverability	436	82	47	
Molecular Weight	Recoverability	85	99	131	
OSHA TWA, ppm	Toxicity	500^d	50	50	
Permissable residues	Toxicity				
Coffee		10 ppm	--	10-25 ppm	
Hop extracts		2.2%	--	2.2%	
Oleoresins		30 ppm	30 ppm	50 ppm	

Table 3.2

PRICES OF FOOD GRADE SOLVENTS

Solvent	Price (per kg)
METH	.62
Ethylene Dichloride	.35
TCE	.85
Methanol	1.14
Ethanol (Ethyl Alcohol)	4.55
Isopropanol	3.61
Acetone	.64
Ethyl Acetate	.97
Hexane	1.63
Natural Coffee Oil	4.40

Source: CMR, 1989c, Hammitt et al, 1989.

Decaffeination of Coffee

The three potential METH substitutes in Table 3.1 for decaffeination include TCE, ethyl acetate and natural coffee oil. [Ed. Note - Supercritical and liquid CO_2 extraction is discussed under process modifications.] TCE is not likely to be adopted again for extraction in the future.

Ethyl acetate has been used by one of the coffee manufacturers to extract caffeine and is considered the most likely potential METH substitute. The ethyl acetate process draws off the caffeine when applied either directly or indirectly to coffee beans or coffee liquids. Ethyl acetate is then removed by heating and evaporation. The chemical is currently approved by the FDA for coffee extraction (FDA, 1987).

Natural coffee oil is used to extract caffeine by the Nestle Company. This method has many advantages; the end product has consistent quality and the method produces a 99.7 percent caffeine-free product. However, the high cost of development and implementation of this chemical substitute, which requires completely different equipment, have been a deterrent to its wide use.

Hop Extraction

Raw hop, added to beer for the flavor, is a potential substitute for hop extract. In the U.S., only one major brewer relies solely on hop extraction as a source of hop flavor. Most companies use a combination of both raw and extract hops.

Other alternative solvents have been permitted by FDA and are used in the industry. As Table 3.1 indicates, these alternatives include methanol, ethanol, isopropanol and hexane. It is estimated that 60 to 65 percent of extraction is done using hexane. However, METH is a more efficient extraction solvent than hexane and technically a more desirable one (SRI, 1985). Ethanol would be suitable for this use, but is reported to have lower extraction capability than hexane. In the food industry, any chemical substitution technique would involve plant modifications and process changes. This effort could be very costly since all modifications must be in compliance with related laws and regulations in the U.S. and overseas.

Spice Oleoresin Extraction

Solvents currently approved for spice extraction include: TCE, methanol, ethanol, isopropanol, acetone, hexane, and ethylene dichloride. Any conversion would require product tasting and testing. Characteristics such as solvent boiling point and toxicity will also affect selection of alternatives. TCE and ethylene dichloride apparently are most similar to METH, whereas hexane, acetone and alcohols will be suitable substitutes for METH only in some uses (SRI, 1985).

Extraction equipment for spice oleoresins is custom designed and may be built for use with one or more solvents. Facility design can require a larger investment when flammable solvents are used. A company considering switching from METH to any replacement solvent must consider other factors such as the cost of acquiring explosion-proof equipment and other handling costs. Furthermore, change to a flammable solvent may not be allowed by local zoning ordinances.

PROCESS MODIFICATION

Under this category, two extraction methods are considered. Both techniques--supercritical fluid extraction and liquid extraction--utilize carbon dioxide (CO_2). The greatest advantage of carbon dioxide for the food industry is that the chemical is a gentle extraction agent. It is also nontoxic, inert, and nonflammable. Carbon dioxide is readily available in large quantities and at high purity. It is probably the cheapest solvent next to water; its present price is only about $0.03 per pound.

Supercritical Fluid Extraction (SFE)

Supercritical fluid extraction using carbon dioxide (CO_2) is under consideration by the food industry as a potential process substitution method for solvent extraction. Supercritical fluids are fluids that have been heated and pressurized to beyond their critical point. These fluids possess physical and chemical properties that are between those of liquids and gases, making them particularly good solvents. High density provides unique solvent properties, while high diffusivity provides improved mass transfer characteristics, and therefore, rapid extraction.

A typical SFE process uses a batch extraction vessel, in which the feed contacts with a supercritical fluid. The fluid extracts the solute from the feed, then goes to a second vessel where the pressure is released. This causes the to drop out, as CO_2 returns to its normal vapor state. The relatively clean solvent is then repressurized and recycled. This process is similar to the carbon dioxide liquid extraction process discussed later, except the pressures and the fluid diffusivity are higher and the fluid's density and viscosity are lower, enabling more rapid extraction and phase separation (SRI, 1985).

The advantages of supercritical fluid extraction technology as a viable separation technique include: tightening government regulations on solvent residues and pollution control, and consumer concern over the use of chemical solvents in the manufacture of foods and leftover residues in the food. Other advantages of SFE are good selectivity for some compounds and the essentially complete separation that can be attained. Despite these advantages, carbon dioxide SFE has not been used until recently in the food industry, because its use requires costly high pressure vessels and high energy costs for pressurization.

Decaffeination of Coffee. Extraction of caffeine from coffee using SFE is currently practiced commercially in Europe. The first U.S. plant to adopt the process started operation in Houston in September, 1988. The capacity of this plant--General Foods Corp's Maxwell House Coffee Company--is about 50 million pounds of coffee per year. At the General Foods plant, extraction is performed at 90 to 100 degrees C and a pressure of 3,000 to 4,000 pounds per square inch (CE, 1988).

There are two types of beans that are currently decaffeinated, roasted coffee beans and green coffee beans. Roasted coffee beans can be subjected to a multistep process to produce decaffeinated coffee beans or caffeine-free instant coffee. Prior to decaffeination, roasted coffee beans or rough ground coffee is first extracted with dry supercritical carbon dioxide to extract the soluble aromatics and coffee oils, avoiding loss of these flavor components. Then decaffeination is carried out by wet carbon dioxide (the carbon dioxide is passed through a water scrubber to dissolve some water). In both steps, pressure reduction separates the solute from the extracting fluid, which is recompressed and recycled. The soluble aromatics and coffee oils can be redeposited on the decaffeinated coffee beans by reversing the fluid flow cycle.

Decaffeinated instant coffee can be prepared by treating the decaffeinated rough ground coffee with water and spray or freeze-drying the aqueous extract.

In the decaffeination of green coffee beans, one variation consists of charging the beans, which have been presoaked in water, into a pressure vessel and extracting with carbon dioxide at pressures of 160 to 220 atmospheres. The caffeine dissolves in the supercritical carbon dioxide, and the caffeine-rich carbon dioxide stream is routed into a washing tower. In the washing tower, water at 70 to 90 degrees C acts as an entrainer for caffeine, and the stripped carbon dioxide is recycled. The caffeine is subsequently recovered by distillation.

A system innovation involves replacing the water scrubber with activated carbon to adsorb the caffeine. The green coffee beans can also be mixed directly with activated carbon pellets, which fill the space between the beans. This extraction is performed at 90 degrees C and 220 atmospheres pressure. The caffeine, dissolved in the supercritical carbon dioxide, diffuses out of the beans and is directly adsorbed by the charcoal. The decaffeinated beans are then separated from the charcoal by sieving (Caragay, 1981).

<u>Hop Extraction.</u> Supercritical extraction of hops is currently performed in Germany and the United States. Hopfenextraktion, a company in Halertan, West Germany has used the carbon dioxide SFE process at a 5,000 ton per year plant for the extraction of hops (The Economist, 1982). One U.S. hop extractor, Hopstract, has recently begun to use this process as well.

Prior to extraction, the hops are milled to rupture the microscopic lupulin gland, in which the active ingredients are stored. Supercritical carbon dioxide is passed through a bed of hops and becomes saturated with flavor and aroma substances. The carbon dioxide is then depressured to separate the hop extracts, then recompressed and recycled through the hop bed (The Economist, 1982).

Other Applications. SFE is suitable for extracting oil from oil seeds, deodorizing oils and fats, preparing spice extracts, extracting food coloring from plant material, preparing flavors and aroma oils, and separating vegetable fats and oils. In the perfume and fragrances industry, carbon dioxide is attractive for processing thermally-labile natural products such as jasmine, chamomile, and other delicate essences. A large number of natural products have been extracted with supercritical carbon dioxide, as shown by Table 3.3. In the U.S., Pfizer, Inc., a New York based pharmaceutical company, uses SFE to extract flavor components. At the Pfizer plant in Grasse, France, a number of SFE processes are tested and then commercialized.

Carbon dioxide extraction also allows separation of different substances from the same material. For example, at low pressure, extraction of pepper yields an aromatic but non-pungent oil that can be used in both perfumes and flavors. At high pressures, the extraction results in the pepper's highly pungent substance (The Economist, 1982). Experiments with more delicate fragrances, such as lilac, have shown that the carbon dioxide extraction product results in a truer scent than other methods.

Table 3.4 summarizes a range of possible processing applications of SFE. Several additional applications of carbon dioxide supercritical extraction are reported to be under investigation. These include removal of gums from soy oil for lecithin recovery, extraction of oils from corn germ, extraction of oil from avocados, extraction of sunflower and rapeseed oils, extraction of oils and flavors from fermented seaweed and recovery of oil from cottonseed, wheat, and sorghum (Rizvi et al, 1986).

Table 3.3

SOME NATURAL PRODUCTS EXTRACTED WITH SUPERCRITICAL CARBON DIOXIDE

Natural Product	Constituents Extracted
Black pepper	Essential oil, piperine
Chili pepper	Essential oil, capsaicine alkaloids
Cloves	Essential oil, eugenol
Cinnamon	Essential oil, cinnamic aldehyde, eugenol
Nutmeg	Essential oil, trimyristin
Caraway	Limonene, carvone, triglycerides
Sesame seeds	Sesamin, triglycerides
Vanilla pods	Essential oil, vanillin
Peppermint leaves	Essential oil, menthol, menthone
Roses	Essential oil, geraniol, citronellal
Chamomile flowers	Essential oil, matricin, herniarin, a-bisabolol, "ene-yne dicycloethers"

SOURCE: Caragay, 1981.

Table 3.4

Current and Potential Applications of SFE Technology in Food Technology

Application	Supercritical	Status	Comment
Coffee decaffeination	Carbon dioxide	Commercialized in West Germany and the U.S.	Removes more than 97% of caffeine with no loss of aroma; batch process
Flavor agents extraction from hops	--	Commercialized in West Germany, England, and United States	Extract alpha acids from hops
Cholesterol removal	Carbon dioxide	Pilot plant	Removes 20-90 percent of cholesterol from butter, beef tallow, lard, and egg yolks at 40 to 80 degrees °C, 2,000 to 2,500 pounds per squqre inch.
Nicotine recovery	--	Pilot plant	Removes nicotine from tabacco
Peptide synthesis	Carbon dioxide	Laboratory	
Recovery of citrus oils	Carbon dioxide	Laboratory	Recovery citrus oils from peelings.

Source: Muller Associates Inc., 1988; CE, 1988.

Practical Application. an SFE system consists of four basic components, a solvent compressor or pump, an extractor, a temperature/pressure control system, and a separator or adsorber.

In the fixed bed method isothermal and isobaric conditions are used. Solutes are extracted from their natural matrix in the extractor, and subsequently removed from the solvent stream, by adsorbing onto activated carbon or other suitable material (Rizvi et al, 1986).

Carbon dioxide produces a high value product and it can be used for low volume as well as high volume production. It has been estimated that carbon dioxide extraction could reduce the energy requirements for extracting fermentation broths by as much as 80 percent. The current high cost of setting up a plant may decline as the technology is more widely adopted.

SFE has yet to become a widely-employed commercial technology in the food industry. The extractive properties of supercritical fluids have stimulated extensive R & D in the past few years. The use of technology in many areas is developing rapidly, with some plants already commercialized and others still in the pilot plant or laboratory stage. Two applications which did not prove economically viable were extraction of pepper and production of limonin (Muller, 1988).

Today use of SFE is limited not only because of the high capital cost but also because of a lack of understanding of the theoretical basis of the process, and an absence of engineering data and scale up technology. A major problem is that fundamental knowledge of the supercritical process is relatively limited and complicated. Until suitable predictive models are developed, the application potential will occur only on a case by case (or a trial and error) basis (Rizvi, et al, 1986). Manufacturers of supercritical extraction processes are hesitant to discuss the economics of various SFE systems because they say system characteristics vary with each process. There are also other key technical hurdles that need to be resolved before SFE use can become widespread. Some people claim, for instance, that supercritical carbon dioxide is such a good solvent that it eats through elastomeric seals and parts (CE, 1985). Although capital costs may be high, operating costs are usually lower than those of competing processes. In spite of the implementation barriers, there are a number of patents in food related applications. These are listed in Table 3.5.

Liquid Carbon Dioxide Extraction (LCDE)

LCDE, like SFE, appears to be a very suitable solvent system for the extraction of flavoring materials. The use of

Table 3.5

Food Related Supercritical Fluid Process Patents

Process	Country	Number	Date
Extraction of flavor	Germany	2,127,611.9	1971
	France	2,140,096	1973
	Canada	989,662	1976
Extraction of oils from oilseeds	Germany	2,127,596	1972
	Germany	2,363,418	1972
	Austria	331,374	1972
	Holland	7,207,441	1972
Extraction of animal or vegetable fats	U.S.	3,939,281	1976
	Britain	2,032,789	1980
	U.S.	4,280,961	1981
	U.S.	4,331,695	1982
Fractionation of fats and oils	Holland	8,104,820	1983
Decaffeination of coffee	Germany	2,005,293.1	1970
	Germany	2,357,590	1975
	Britain	2,014,425	1979
	U.S.	4,168,324	1979
	U.S.	4,308,291	1981
	U.S.	4,331,694	1982
	U.S.	4,348,422	1982
	U.S.	4,344,974	1982
Concentration of coffee aroma	U.S.	4,328,255	1982
Production of hops extract	Britain	1,328,255	1972
	Canada	987,250	1972
	France	2,140,097	1973
	Germany	2,127,618.6	1973
	Britain	2,026,539	1980
	U.S.	4,218,491	1981
	U.S.	4,278,012	1984
	U.S.	4,507,329	1984
Deodorization of fats and oils	Austria	347,551	1972
	Germany	2,332,038	1974
	Germany	2,441,152	1975
	U.S.	3,969,382	1977
	U.S.	4,156,688	1979

Source: Rizvi, et al, 1986

liquid carbon dioxide as an extraction agent is not new. The earliest investigations and patent requests took place about 30 to 40 years ago (Harold and Clarke, 1979).

The basic difference between supercritical and liquid carbon dioxide processes is the use of significantly higher pressures and temperatures to effect extraction in the case of supercritical extraction. The principal advantage of supercritical carbon dioxide extraction over liquid carbon dioxide appears to be a more rapid, more efficient and less selective extraction. It has, however, been demonstrated that the use of liquid carbon dioxide, although selective, removes all the hop components significant in brewing, including acids, essential oils, and soft resins. The yield is greater than 95 percent and the extract is similar to the type obtained with hexane, in that hard resins and poly-phenolic materials are excluded (Harold and Clarke, 1979). Stability tests conducted to date on hop extract produced from liquid carbon dioxide indicate that the stability of the extract under normal storage conditions is at least as good as, if not better than, extracts produced by other solvents (Harold and Clarke, 1979).

The economics of hop extraction with liquid carbon dioxide will vary from location to location. In addition to the system cost, the economics will be influenced by the cost of hops and the cost of carbon dioxide. Investigations have shown that the cost of constructing a plant to produce extract using METH would be comparable to the cost of a similar capacity plant using liquid carbon dioxide (Harold and Clarke, 1979). An advantage of the liquid carbon dioxide process is that it operates at subcritical conditions, means lower energy cost. It has been reported that the production costs of hop extraction using supercritical carbon dioxide would be two to five times greater than with conventional extractions (Harold and Clarke, 1979).

Table 3.4

FOOD-RELATED SUPERCRITICAL FLUID PROCESS PATENTS

Process	Country	Number	Date
Extraction of flavor	Germany	2,127,611.9	1971
	France	2,140,096	1973
	Canada	989,662	1976
Extraction of oils from oilseeds	Germany	2,127,596	1972
	Germany	2,363,418	1972
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Extraction of animal or vegetable fats	U.S.	3,939,281	1976
	Britain	2,032,789	1980
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	France	2,140,097	1973
	Germany	2,127,618.6	1973
	Britain	2,026,539	1980
	U.S.	4,218,491	1980
	U.S.	4,278,012	1981
	U.S.	4,507,329	1984
Deodorization of fats and oils	Austria	347,551	1972
	Germany	2,332,038	1974
	Germany	2,441,152	1975
	U.S.	3,969,382	1977
	U.S.	4,156,688	1979

Source: Rizvi, et al, 1986.

Despite all the developments in the use of liquid carbon dioxide technology, there are only a few commercial applications of the process, in Australia, the U.S.S.R. (Harold and Clarke, 1979) and, most recently, in the U.S. The only commercial liquid carbon dioxide plant in the U.S. belongs to Pfizer, Inc., which has reportedly built a hops extraction plant in Sydney, Nebraska (CMR, 1989b).

PRODUCT SUBSTITUTION

Substitutes for decaffeinated coffee include roasted chicory, chick peas, cereals, fruit and vegetable products. Such products have been used in coffee-consuming countries and are usually priced lower than coffee. Consumers generally prefer to use these substitutes as other beverage sources rather than as coffee substitutes.

Chicory contains no caffeine and on roasting develops an aroma comparable to that of coffee. It provides a darker than normal coffee brew, and can also be dried for instant use. In the U.S., chicory is used as a flavor additive to coffee, rather than as a coffee substitute.

Two potential spice oleoresins substitutes have been identified (SRI, 1985). One is the spice itself, and the other is a synthetic chemical that captures the flavor characteristics of the spice. Cinnamaldehyde, for example, is a synthetic chemical with characteristics very similar to cinnamon. The spice itself is usually not a satisfactory substitute, especially for large volume uses. Original spices do not have consistent flavor, are contaminated with microorganisms, do not disperse uniform flavor, and are difficult to store and handle in large volumes.

The increasing number of materials available today and an improvement in flavor characteristics have led to the wider use of synthetic flavor products. Synthetics include: benzyl acetate (fruity raspberry and cherry) for candies and soft drinks; cinnamaldehyde (cinnamon) for candies; chewing gum and baked goods; menthol (mint); vanillin (vanilla) for ice cream, baked goods and candies; engenol (clove) for candies and condiments; 5-methylthiophen-2-carboxyaldehyde (almond); and diallylsuffide (garlic). Synthetic materials account for much of the flavoring used in the U.S. For example, vanillin accounts for over 90 percent of all vanilla flavoring used (CMR, 1988a). The price of synthetic vanillin ranges from $6.50 to $7.30 per pound, whereas the price of natural vanilla products can range from $15 per pound for Javan Vanilla to $35 per pound for Bourbon. Natural vanillin, extracted directly from vanilla beans, is priced around $1,000 per pound (CMR, 1988b).

Bioengineering research to obtain flavoring from plant tissue culture rather than beans or seeds is also underway. Cells from the plant are placed in a culture and grown in a nutrient medium the way bacterial cells are grown for medical research. The extracted cells then function as miniature factories for the production of the spice flavoring (CMR, 1988a). This technology is presently being demonstrated in vanilla flavoring. Scientists believe that the research being performed on vanilla is based on the totipotency of the cells and can be applied to virtually every plant. The technological advances in the area of vanilla research are ultimately expected to be applicable to other flavorings, especially essential oils from tropical countries and popular domestic fruits. The technology seems to offer great potential as an alternative source for natural flavoring.

RECOVERY AND REUSE

It is believed that the METH used in the industry is captured, recovered and reused as a part of the process. Solvent recovery techniques discussed in the companion document for intermediates use may be applicable in the food industry as well.

IV. CONCLUSIONS

Consumer demands for safer decaffeination processes and general health consciousness have caused companies to convert away from solvent and invest in the supercritical carbon dioxide extraction process. Liquid carbon dioxide is also a promising alternative. Many companies have already started the switch to these processes, despite the limited technical and empirical data on these processes. For example, General Foods has recently installed a supercritical carbon dioxide decaffeination process at its Houston plant (CE, 1988).

A number of source reduction options have been identified in this document that could reduce or eliminate the use of METH in the food industry. These source reduction options are summarized in Table 4.1; they fall into the general categories: chemical substitution, process modification, and product substitution. The table lists the advantages and disadvantage of each identified option. Many options are being used or are under investigation by the industry. The food industry has traditionally practiced solvent control and recovery because of the nature of the processes involved. For example, in the oleoresin extraction process, atmospheric releases result in loss of the aromatic component of the spice; to preserve the product such releases are stringently controlled (Burns, 1988).

The potential for alternative chemical solvents to replace METH in the food industry is not high. This reflects the fact that all the potential substitutes have at least one serious drawback that make their widespread use limited. Many solvents--ethanol, hexane, and ethylene dichloride, for instance--are currently used in the food industry. Ethanol and hexane are flammable and ethylene dichloride is toxic. Ethyl acetate and natural coffee oil are considered by the U.S. Food and Drug Administration (FDA) to be safer substitutes, but they are expensive.

The product substitutes for coffee and flavors would not have significant potential to completely replace decaffeinated coffee, hops, or spice oleoresins extracts, even if they were acceptable as equivalents. Previous experiences suggest consumers have not readily accepted coffee substitutes. The synthetic substitutes are commonly more expensive than the extracted material. Bioengineered flavors are years away from full commercialization. Such products have little potential for replacing METH-based processing and require many years to implement.

The same trend seems to have occurred for the hop extraction. While recent trends to lighter, milder and more widely acceptable beers have drastically reduced hopping rates compared to those of twenty or thirty years ago, there is still a very important place for hop flavors in the taste of beer. There are no product substitutes for this ingredient. Hopstract, one of the biggest U.S. hop extraction companies, has installed a carbon dioxide supercritical extraction system. Pfizer, Inc. has installed a liquid carbon dioxide process for hop extraction.

Table 4.1

SOURCE REDUCTION OPTIONS
FOR DECAFFEINATION PROCESS
(FOOD INDUSTRY)

OPTION	ADVANTAGES	DISADVANTAGES
METH SUBSTITUTES		
TCE	Non-flammable	Toxic/carcinogenic
Ethyl Acetate	Low boiling point, good	Flammable
Natural Coffee Oil	Consistent product quality	High operating cost
Process Modification		
Supercritical CO_2	Comm. good prod quality	High energy cost, high investment
Liquid CO_2 extract'n	Lowest waste generation	Not demonstrated for caffeine
Coffee Substitutes	Commercially practiced	Lack of consumer acceptance

Tale 4.2

SOURCE REDUCTION OPTIONS FOR HOPS EXTRACTION

OPTION	ADVANTAGES	DISADVANTAGES
CHEMICAL SUBSTITUTE		
Methanol	Non-carcinogen	Flammable
Ethanol	Non-carcinogen	Flammable, less efficient than hexane
Isopropanol	Non-carcinogen	Flammable
Hexane	Widely used in commercial practice	Flammable, less efficient than METH
PROCESS MODIFICATION		
Supercritical Fluid Extract	Commercially-practiced	High investment and Operating Costs
Liquid CO_2	Cost comparable to METH extraction	
PRODUCT SUBSTITUTION		
No substitutes reported		

Table 4.3

SOURCE REDUCTION OPTIONS
FOR SPICE EXTRACTION

OPTION	ADVANTAGES	DISADVANTAGES
CHEMICAL SUBSTITUTES		
TCE		Carcinogen
Methanol		Flammable
Ethanol		Flammable
Isopropanol	Widely used	Flammable
Hexane		Flammable
Ethylene dichloride		Carcinogen
PROCESS MODIFICATION		
Supercritical Fluid Extraction	Demonstrated for some essential oils	High invest High operating cost
Liquid CO_2		Not demonstrated for spices
PRODUCT SUBSTITUTIONS		
Synthetic flavors	More consistent flavor	
Natural Spices		Very high cost of spices for large volume uses

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