

**Emission Factor Documentation for AP-42
Section 9.12.2**

Wines and Brandy

Final Report

**For U. S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Emission Factor and Inventory Group**

**EPA Contract 68-D2-0159
Work Assignment No. 2-03 and 3-01**

**MRI Project No. 4602-03
and 4603-01-03**

October 1995

Emission Factor Documentation for AP-42
Section 9.12.2

Wines and Brandy

Final Report

For U. S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Emission Factor and Inventory Group
Research Triangle Park, NC 27711

Attn: Mr. Dallas Safriet (MD-14)

EPA Contract 68-D2-0159
Work Assignment No. 2-03 and 3-01

MRI Project No. 4602-03
and 4603-01-03

October 1995

NOTICE

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Contract No. 68-D2-0159 to Midwest Research Institute. It has been reviewed by the Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, and has been approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

PREFACE

This report was prepared by Midwest Research Institute (MRI) for the Office of Air Quality Planning and Standards (OAQPS), U. S. Environmental Protection Agency (EPA), under Contract No. 68-D2-0159, Work Assignment No. 2-03 and 3-01. Mr. Dallas Safriet was the requester of the work.

Approved for:

MIDWEST RESEARCH INSTITUTE

Roy Neulicht
Program Manager
Environmental Engineering Department

Jeff Shular
Director, Environmental Engineering
Department

October 1995

TABLE OF CONTENTS

	<u>Page</u>
LIST OF FIGURES	vii
LIST OF TABLES	vii
1. INTRODUCTION	1-1
2. INDUSTRY DESCRIPTION	2-1
2.1 INDUSTRY CHARACTERIZATION	2-1
2.2 PROCESS DESCRIPTION	2-1
2.2.1 Still Table Wines	2-2
2.2.2 Sweet Table Wines	2-8
2.2.3 Sparkling Wines	2-9
2.2.4 Dessert Wines	2-10
2.2.5 Brandy Production	2-11
2.3 EMISSIONS	2-12
2.4 CONTROL TECHNOLOGY	2-13
3. GENERAL DATA REVIEW AND ANALYSIS PROCEDURES	3-1
3.1 LITERATURE SEARCH AND SCREENING	3-1
3.2 DATA QUALITY RATING SYSTEM	3-2
3.3 EMISSION FACTOR QUALITY RATING SYSTEM	3-3
4. REVIEW OF SPECIFIC DATA SETS	4-1
4.1 INTRODUCTION	4-1
4.2 REVIEW OF SPECIFIC DATA SETS	4-1
4.2.1 Reference 1	4-1
4.2.2 Reference 2	4-2
4.2.3 Reference 3	4-2
4.2.4 Reference 4	4-3
4.2.5 Reference 5	4-3
4.2.6 Reference 6	4-4
4.2.7 Reference 7	4-4
4.2.8 Reference 8	4-5
4.2.9 Reference 9	4-6
4.2.10 Reference 10	4-7
4.2.11 Reference 11	4-7
4.2.12 Reference 12	4-7
4.2.13 Reference 13	4-8
4.2.14 Reference 14	4-8
4.3 DEVELOPMENT OF CANDIDATE EMISSION FACTORS	4-8
4.3.1 Ethanol	4-15
4.3.2 Other VOCs	4-15
4.3.3 Hydrogen Sulfide	4-15
4.4 SUMMARY OF CHANGES TO AP-42 SECTION	4-15
4.4.1 Section Narrative	4-15

TABLE OF CONTENTS (continued)

	<u>Page</u>
4.4.2 Emission Factors	4-15
5. PROPOSED AP-42 SECTION	5-1
APPENDIX A	A-1
APPENDIX B	B-1
APPENDIX C	C-1
APPENDIX D	D-1
APPENDIX E	E-1
APPENDIX F	F-1
APPENDIX G	G-1

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
2-1	Basic steps in still table wine production	2-3

LIST OF TABLES

<u>Table</u>		<u>Page</u>
2-1	DISTRIBUTION OF WINERIES BY STATE, 1989	2-1
4-1	SUMMARY OF FERMENTATION EMISSIONS DATA	4-9
4-2	FERMENTATION EMISSION DATA USED FOR EMISSION FACTOR ESTIMATION	4-13
4-3	SUMMARY OF CANDIDATE EMISSION FACTORS FOR FERMENTATION IN WINE PRODUCTION	4-14

EMISSION FACTOR DOCUMENTATION FOR AP-42 SECTION 9.12.2
Wines and Brandy

1. INTRODUCTION

The document *Compilation of Air Pollutant Emission Factors* (AP-42) has been published by the U. S. Environmental Protection Agency (EPA) since 1972. Supplements to AP-42 have been routinely published to add new emission source categories and to update existing emission factors. AP-42 is routinely updated by EPA to respond to new emission factor needs of EPA, State and local air pollution control programs, and industry.

An emission factor is a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant. Emission factors usually are expressed as the weight of pollutant divided by the unit weight, volume, distance, or duration of the activity that emits the pollutant. The emission factors presented in AP-42 may be appropriate to use in a number of situations, such as making source-specific emission estimates for areawide inventories for dispersion modeling, developing control strategies, screening sources for compliance purposes, establishing operating permit fees, and making permit applicability determinations. The purpose of this report is to provide background information from test reports and other information to support revisions to AP-42 Section 9.12.2, Wines and Brandy (formerly Section 6.5.2, Wine Making).

This background report consists of five sections. Section 1 includes the introduction to the report. Section 2 gives a description of the wine and brandy industry. It includes a characterization of the industry, a description of the different process operations, a characterization of emission sources and pollutants emitted, and a description of the technology used to control emissions resulting from these sources. Section 3 is a review of emission data collection (and emission measurement) procedures. It describes the literature search, the screening of emission data reports, and the quality rating system for both emission data and emission factors. Section 4 details how the revised AP-42 section was developed. It includes the review of specific data sets, a description of how candidate emission factors were developed, and a summary of changes to the AP-42 section. Section 5 presents the AP-42 Section 9.12.2, Wines and Brandy.

2. INDUSTRY DESCRIPTION

This section includes a brief description of the wine making industry, an overview of the process involved in making wines and brandy, and a discussion of the air emissions to be considered.

2.1 INDUSTRY CHARACTERIZATION¹⁻⁴

Table 2-1 shows the distribution of wineries across the United States. Although wineries are by far most prevalent in California (with 293 of a total 510 establishments), New York has 32 wineries and Washington has 27 wineries.

TABLE 2-1. DISTRIBUTION OF WINERIES BY STATE, 1989

Arizona	2	Maine	2	Pennsylvania	18
Arkansas	4			Rhode Island	1
California	293	Maryland	3	South Carolina	1
Colorado	3	Massachusetts	1	South Dakota	1
Connecticut	1	Michigan	6	Tennessee	5
Florida	1	Minnesota	1	Texas	9
Georgia	3	Mississippi	1		
Hawaii	1	Missouri	10	Vermont	1
		New Jersey	5	Virginia	10
Idaho	4	New Mexico	1	Washington	27
		New York	32	West Virginia	1
Illinois	3	North Carolina	4	Wisconsin	9
		Ohio	13		
Indiana	5				
		Oregon	19		
Iowa	3				
Kansas	1				

Source: Reference 4.

Several states actively promote the development of the wine industry through their departments of agriculture or economic development. In particular, the number of small wineries has been increasing. Between 1982 and 1987, the number of wineries with 50 or less employees grew by 48 percent, from 315 wineries to 453. The growth of small wineries has increased the dispersion of wine making emissions across the country.

The Standard Industrial Classification (SIC) code for wines and brandy is 2084. This code encompasses the production of wines, wine coolers, brandy, and brandy spirits; it also includes bonded wine cellars engaged in blending wines.

2.2 PROCESS DESCRIPTION^{5-7,9}

Wine is an alcoholic beverage produced by the fermentation of sugars in fruit juices, primarily grape juice. In general, wines are classified into two types based on alcohol content: table wines (7 percent to 14 percent alcohol, by volume) and dessert wines (17 percent to 22 percent alcohol, by volume). Table wines are further subdivided into still and sparkling categories, depending upon the carbon dioxide (CO₂) content retained in the bottled wine. Wines found in the category of still table wines are divided based on the color of the wine into three groups: red, white, and rosé (or blush). In terms of overall production, still table wines represent the vast majority of all of the wines produced in the United States. Sparkling wines are often classified by the method used to achieve the CO₂ content in the wine; the three primary production techniques are: methode champagnoise (fermented in this bottle), transfer, and bulk. In all three methods, yeasts are used to generate the CO₂ to produce the effervescence.

Dessert wines may achieve their higher alcohol content by the addition of distilled spirits (fortified wine) or by fermentation of high sugar content juices. These wines are produced in a wide range of styles, either dry or sweet, and are typically consumed in small amounts either before or after meals. Examples of dry dessert wines are dry vermouth or dubonnet; examples of sweet types are sweet vermouth, sherry, port, and madeira.

The production of still table wines is discussed in detail in the following sections, followed by more concise discussions of the production of sweet table wines, sparkling wines, dessert wines, and brandy.

2.2.1 Still Table Wines

The basic steps in vinification (wine production) include harvesting, crushing, pressing, fermentation, clarification, finishing, and bottling. A simplified process diagram outlining the basic steps in the production of still table wines is shown in Figure 2-1

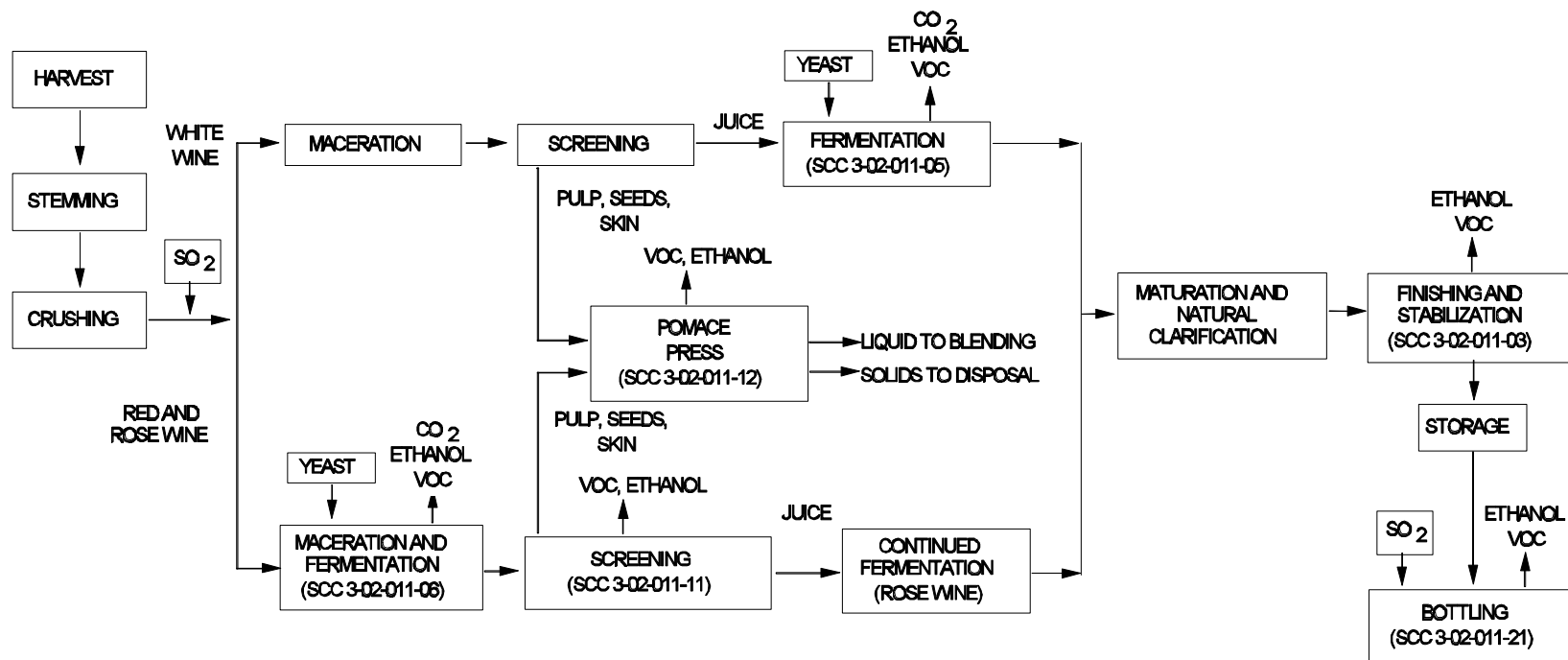


Figure 2-1. Basic steps in still table wine production.

2.2.1.1 Harvesting. Harvesting of grapes is usually conducted during the cooler periods of the day to prevent or retard heat buildup in the grape; if the temperature is high, the grapes must be cooled immediately after harvest to prevent flavor deterioration. During harvest, some grapes are unavoidably bruised or the skin broken resulting in release of the juice. When this occurs, oxidative degradation of the juice can begin and the juice can become contaminated with yeast or bacteria present on the grape skin. To minimize this degradation, the grapes may be field-treated with sulfite compounds after harvest. Some wineries crush the grapes in the vineyard and transport the crushed fruit to the winery.

2.2.1.2 Stemming and Crushing. Stemming and crushing are commonly conducted as soon as possible after harvest and are currently done in separate steps. Removal of the stems, leaves, and stalks prior to crushing helps control the production of undesirable compounds during subsequent production steps. For convenience and efficiency, stemming and crushing are often performed in a crusher-stemmer. The stemmer portion of the machine contains an outer perforated cylinder that allows the grapes to pass through but prevents the passage of stems, leaves, and stalks. After stemming, the grapes pass immediately to the crusher. Crushing the grapes after stemming permits fermentation to commence almost immediately and limits microbial contamination. Generally, 25 to 100 milligrams (mg) of liquified sulfur dioxide (SO₂) are added per liter of the crushed grape mass to control oxidation, wild yeasts, and spoilage bacteria.

Crushing is accomplished by any one of many procedures; the processes generally favored are (1) pressing grapes against a perforated wall; (2) passing grapes through a set of rollers; or (3) using centrifugal force. In the perforated wall process, the juice, pulp, seeds, and skin pass through the openings, are collected, and pumped to a retaining tank or vat. The roller process crushes the grapes between a pair of spiral ribbed or grooved rollers turning in opposite directions. Centrifugal crushers turn the grapes into a pulpy slurry; this process is generally undesirable because juice clarification is difficult and the seeds are commonly broken. In crushing, it is important to avoid crushing the seeds

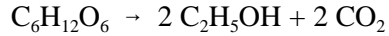
to preclude contaminating juice slurry with seed oils, which can produce rancid odors and bitter tannins. In most direct to press operations, stemming and crushing are not performed.

2.2.1.3 Maceration. Maceration is the breakdown of grape solids following crushing. The major portion of the maceration results from the mechanical crushing process. A small portion of the maceration results from enzymatic breakdown of the solids. In red and rosé wine production, the slurry of juice, skins, seeds, and pulp is termed the "must." In white wine production, the skins, seeds, and pulp are separated from the juice before inoculation with yeast and only the juice is fermented. A fermenting batch of juice is also called "must." Thus, the term "must" can refer to either the mixture of juice, seeds, skins, and pulp for red or rosé wines or only the juice for white wines. Maceration is always involved in the initial phase of red wine fermentation. Maceration temperature and duration of the process are the major factors influencing the degree of compound extraction and types of compounds released. During maceration, the temperature of the mass is adjusted and controlled to influence the types and amounts of compounds released.

2.2.1.4 Pressing. The juice from the grapes may be extracted from the "must" directly in the press. Additionally, juicers may be used to initially separate the majority of the juice from the crushed grapes by gravity flow, and the presses are used to extract the juice remaining in the pomace. There are many designs of dejuicers but, in general, they consist of a tank fitted with a perforated basket at the exit end. The "must" is introduced into the tank and juice flows through the basket into a receiving tank (sump). The "must" may be allowed to rest in the press and the juices forced out under the weight of the skins and seeds (pomace). When drainage is complete, the basket is raised to facilitate pomace discharge for transport to the press. After gravity dejuicing has occurred, the pomace is placed in the press and the remaining juice extracted. There have been several major advances in press design including the use of hydraulic force instead of muscle power, removable bottoms for easier pomace discharge, increased drainage surface area, and the design of the horizontal press and the continuous screw press. The horizontal press is used for either crushed or uncrushed grapes. The "must" is loaded at the upper raised end of the press and one or both end plates moved forward to compress the "must". Juice escapes between slats in the press cylinder; the remaining pomace cake is then removed from the lower end of the cylinder. A pneumatic press can also be used for either crushed or uncrushed grapes as well as for fermented "must." The press is filled through an elongated opening in the top and, after filling and closure, the press is inverted to allow any free-running juice to escape. Pressing occurs by one of two mechanisms: (1) the grape mass is filled into a central sack, and gas is forced between the sack and the cylinder walls to compress the mass against perforated plates in the center of the cylinder; or (2) the mass is filled between the sack and perforated cylinder walls, and gas forced into the sack presses the mass against the perforated cylinder walls. The remaining pomace cake is crumbled and removed from the cylinder.

In the continuous screw press, the "must" is pumped into the press via a hopper at one end and a fixed helical screw forces the mass into a pressing chamber where perforated walls allow the juice to escape. Pressed pomace accumulates at the opposite end of the press and is periodically discharged through a port opening. After pressing, white "must" is typically clarified prior to fermentation to retain the fruity character. The white juice is commonly allowed to settle for up to 12 hours but may be centrifuged to speed the clarification.

2.2.1.5 Fermentation. Fermentation is the process whereby the sugars (glucose and fructose) in the "must" undergo reaction by yeast activity to form ethyl alcohol (ethanol) and CO₂ according to the equation:



Based on this equation, about one percent of fermented sugar yields 0.55 volume percent of ethanol. Thus, a juice sugar content of about 16.4 percent is the minimum necessary to produce a wine with 9 volume percent ethanol. In the U.S., the sugar content of the juice is commonly measured with a hydrometer in units of degree Brix ($^{\circ}\text{B}$), which is grams (g) of sugar per 100 grams of liquid. Because sugars constitute the major component of grape soluble solids when over 18 $^{\circ}$ Brix (i.e., 18 g of sugar per 100 g of juice), this reading is a fairly accurate indicator of the capacity of the juice to produce ethanol.

Fermentation may be initiated by the addition of yeast inoculation to the "must." The fermentation process takes place in tanks, barrels, and vats of a wide variety of shapes, sizes, and technical designs. Tanks are differentiated from vats by being enclosed, whereas vats have open tops. In most of the larger wineries, tanks have almost completely replaced vats. Most fermenting tanks (termed fermentors) are straight-sided or have the form of slightly inverted cones. Since the 1950's, the move has been away from wooden tanks to primarily stainless steel tanks; however, in certain areas, lined concrete tanks are also used. In addition, fiberglass tanks are becoming more popular due to their light weight and lower cost. However, stainless steel has the distinct advantage of rapid heat transfer, which is very important for cooling the fermenting juice. The fermentation process is an exothermic reaction, and requires temperature control of the fermenting "must." Double-jacketed stainless steel tanks, circulating coolant between the inner and outer walls, can provide the required temperature control. Red wines are typically fermented at 25 $^{\circ}$ to 28 $^{\circ}$ C (70 $^{\circ}$ to 82 $^{\circ}$ F) and white wines at 8 $^{\circ}$ to 15 $^{\circ}$ C (46 $^{\circ}$ to 59 $^{\circ}$ F).

Almost all of the fermentation is conducted by the batch process; continuous fermentors are rarely used in the U.S. The size of the fermentors is based primarily on the volume of juice or "must" to be fermented. For many premium wines, fermentor volumes commonly range from 50 to 100 hectoliters (hl); 1 hectoliter equals 26.42 U.S. gallons. With standard quality wines, fewer but larger fermentors are used and common sizes range from 200 to over 2,000 hl (5,300 to 53,000 gallons). For large scale wineries, fermentor tanks with capacities in excess of 7,570 hl (200,000 gallons) are common.

During fermentation of red wines, the CO_2 released by the yeast metabolism becomes entrapped in the pomace (layer of skins and seeds) and causes it to rise to the top of the tank where it forms a cap. The entrapped CO_2 can prevent contact between the pomace and the juice, which retards the extraction of those compounds from the skins, seeds, and pulp necessary to provide the red wine with its flavor and character. When open-top vats were used for the fermentation of red wines, the pomace cap was manually submerged (punched down) to improve contact with the juice. In addition to improving color removal, punching down aerates the fermenting "must," limits growth of spoilage organisms in the cap, and helps equalize the temperature in the fermenting "must." Many U.S. wineries are replacing manual punching down by pumping the fermenting "must" over the cap ("pumping over").

For white wines, fermentors are of simple design with the main technical requirement being efficient temperature control. If not initially cool, the juice must be cooled before the yeast inoculation occurs and the fermenting juice maintained between 8 $^{\circ}$ and 15 $^{\circ}$ C (46 $^{\circ}$ to 59 $^{\circ}$ F).

Temperature is one of the most influential factors affecting the fermentation process. At the upper and lower limits, temperatures can cause yeast cell death; however, inhibiting effects are experienced well within the temperature extremes. During fermentation with no temperature control, a juice with an initial reading of 23 $^{\circ}$ Brix could increase in temperature by about 30 $^{\circ}$ C (54 $^{\circ}$ F). If this were to occur, the yeast cells would die before completing fermentation; however, this temperature rise is not realized in practice.

Because the heat is liberated over several days to weeks, some of the heat is lost with the escaping CO₂ and water vapor as well as through the walls of the tank. During fermentation, the CO₂, water vapor, and ethanol are released through a vent in the top of the tank. Heat buildup is controlled by the initial juice temperature at the beginning of fermentation, the size and shape of the fermentor, and the presence or absence of a pomace cap. The formation of CO₂ during white and rosé wine fermentation often creates sufficient agitation of the juice to maintain a uniform temperature. However, for red wines, the pomace caps can disrupt effective circulation and mixing of the "must" by the CO₂. A pomace cap-to-liquid temperature difference of 10°C (18°F) is often observed.

2.2.1.6 Malolactic Fermentation. The principal effect of malolactic fermentation is a reduction in the acidity of the fermented juice or "must." The major benefit of this fermentation step is the metabolism of a dicarboxylic acid (malic acid) to a monocarboxylic acid (lactic acid), which leads to a reduction in acidity and increased pH. Malolactic fermentation also affects the sensory characteristics of the wine. There are very diverse opinions about this step because the fermentation, to varying degrees, can improve or reduce wine quality.

2.2.1.7 Maturation and Clarification.

2.2.1.7.1 Maturation. All wines undergo a period of adjustment (maturation) prior to bottling. The process of maturation involves the precipitation of particulate and colloidal material from the wine as well as a complex range of physical, chemical, and biological changes that tend to maintain and/or improve the sensory characteristics of the wine. The major adjustments are acidity modification, sweetening, dealcoholization, color adjustment, and blending.

Acidity adjustments can be either a deacidification or an acidification. Wines may be deacidified by either physicochemical or biological means; the biological process usually involves malolactic fermentation whereas the physicochemical process includes precipitation (primarily for tartaric acid neutralization) or column ion-exchange. The methods used to sweeten wines depend on the type of wine. Sparkling wines may be sweetened with sugar, whereas still wines are sweetened by the addition of partially fermented or unfermented grape juice, termed sweet reserve.

The blending of wine from different varieties is a long established practice in many wine regions. Blending individual varietal wines is especially important in the production of fortified and sparkling wines and also in the production of standard quality table wines in which consistency of character is most important. In the production of many premium table wines, blending is performed, but the wines are usually from the same geographical area or vineyard. The basic result of blending is an improvement in the fragrance and flavor of the finished wine.

2.2.1.7.2 Clarification. Following the fermentation process, a preliminary clarification step is used to remove the sediment from the wine. This step is commonly accomplished by decanting the wine from one vessel to another, called racking, to separate the sediment (lees) from the wine. Sediment consists principally of yeast and bacterial cells, grape cells, precipitated tannins, proteins, and tartrate crystals. If left in contact with the wine, the lees may cause the production of off-colors or microbial spoilage. Current racking practices range from manually decanting wine from barrel to barrel to highly sophisticated, automated, tank-to-tank transfers. In all cases, separation occurs with minimal agitation to avoid resuspending the particulate matter. The residue from racking may be filtered to recover wine otherwise lost with the lees or used "as is" for brandy production. Racking is generally more effective in clarifying wine matured in small barrels or kegs (cooperage) than in large tanks. In addition to racking, other means

of clarification include centrifugation and filtration. Centrifugation often replaces racking when early bottling is desired or if the wine is heavily laden with particulate matter.

2.2.1.8 Stabilization and Finishing. Stabilization and finishing steps involve procedures designed to produce a permanently clear wine with no flavor faults. These steps entail various stabilization procedures, additional clarification (fining), and a final filtration prior to bottling. Aging the wine for a period of months or years is a common stabilization technique used for many red wines and some white wines. During the aging process in red wines, the excess tannins are gradually oxidized or combine with aldehydes and precipitate. In addition, the color of the wine shifts from red towards brown and the wine becomes less bitter and astringent. In the aging of white wines, ester formation increases and the wine darkens in color to a yellow or gold. Ester formation during aging of white wine generates much of the fragrance in the wine.

White oak has traditionally been the material of choice for the barrels used to age wine, but currently its usage is reserved primarily for the production of premium white and red wines and some fortified wines. Vessels used to store and age wine, termed cooperage, are produced in a wide range of sizes, depending on their intended use. Wine, placed in well-made barrels, bunged tight, and rotated so the wine covers the bung, is exposed to air only during procedures such as racking or topping off barrels. Limited exposure to air is designed to restrict oxidation of the wine and microbial spoilage. Water and ethanol are lost through the barrel surfaces and a partial vacuum develops in the space created by the loss of the ethanol and water. Each barrel is periodically opened and topped off with wine to fill the void created by the ethanol and water loss.

Cooperage constructed from materials other than wood has many advantages and is less expensive to maintain. Stainless steel is often preferred, but fiberglass and concrete are also used. Concrete tanks require a coating of paraffin wax, glass, or epoxy resin to prevent excessive seepage of calcium from the concrete/cement into the wine and to prevent corrosion of the tank walls by the wine. Fiberglass tanks possess less strength than steel and are more difficult to cool and clean.

In addition to aging, other stabilization procedures are used, such as tartrate stabilization, which prevents formation of crystalline deposits in bottled wine, protein stabilization, polysaccharide removal and stabilization, oxidative casse (haziness) stabilization, metal casse stabilization, and microbial stabilization. Sulfur dioxide may be added at various stages in wine production to prevent microbial growth and oxidation.

Finishing (fining) agents that bind or absorb particulate matter are commonly used to accelerate the precipitation of suspended material in wine. Primary fining agents include activated charcoal, albumin, bentonite, casein, gelatin, kieselsol (an aqueous solution of silicon dioxide), isinglass, polyvinylpyrrolidone (PVPP), and tannin. The aggregates formed by the fining agents are generally sufficiently large enough that they quickly precipitate; if not, filtration or centrifugation is used.

Prior to bottling, a final clarification step is used to remove any remaining suspended material and microbes in the wine. This step involves only physical means of clarification and generally consists of a filtration procedure. With the development of new filters and support systems, filtration is currently classified into four categories. Conventional filtration employs depth-type fibrous filters that remove particles down to about one micrometer in diameter. Other filtration techniques are based on membranes and, depending upon the size range of the membrane perforations, are classified as microfiltration, ultrafiltration, or reverse osmosis/dialysis.

2.2.1.9 Bottling. Wooden vessels were the primary means for wine storage and transport for centuries, but glass bottles replaced barrels. Due to some disadvantages, bottles are sometimes being replaced by new containers, such as bag-in-box, for many standard quality, high volume wines. Glass bottles are still the container of choice for the premium quality wines and for sparkling wines. To protect the wine against microbial spoilage, and to limit oxidation, the wine is adjusted to a final level of 50 mg/L of sulfur dioxide before filling. Glass bottles are filled either by a siphoning (or gravity) feed or by use of pressure (or vacuum). Siphoning and gravity feeding are the simplest but slowest methods, so the pressure or vacuum fillers are more appropriate for rapid, automated filling lines. Regardless of the method, precaution is taken to minimize contact with air during filling and thereby reduce oxidation. This is accomplished by flushing the bottle with inert gas before filling or flushing the headspace with inert gas after filling.

For the bag-in-box container, the bag collapses as the wine is removed, but because the empty volume is not filled with air, wine can be periodically removed over several weeks or months without noticeable loss in quality. In its current form, the packaging protects wine from oxidation by air for nine months or longer. To minimize contact with air during filling, the bags are placed under vacuum before filling and the headspace charged with an inert gas after filling.

2.2.2 Sweet Table Wines

The most famous of the sweet wines are those made from noble-rotted, *Botrytis*-infected grapes. These wines are produced to a limited extent in the United States. The mature grapes are left on the vine to develop the *Botrytis* mold and to hopefully develop the desired noble rot instead of the destructive bunch rot. The mold acts to loosen the grape's skin so moisture loss occurs rapidly and the sugar concentration in the grape increases. The grapes are then selectively picked, followed by pressing, and fermentation. Fermentation is a slow process, however, because of the high sugar content and the use of SO₂ to retard the growth of undesirable molds and microorganisms.

Botrytis can also be induced by spraying harvested fruit with a solution of spores and holding the fruit at warm, humid conditions for 24 to 36 hours to permit the spores to germinate and penetrate the fruit. Next, cool dry air is passed over the fruit to induce partial dehydration and restrict invasion. After 10 to 14 days, the fruit is pressed and fermented.

Nonbotrytized sweet wines are also produced. Drying is probably the oldest procedure used to produce sweet wines. It involves allowing the grapes to dehydrate on mats or trays in the shade for weeks or months and then crushing the grapes and fermenting the concentrated juice. Heating or boiling is also used to concentrate juice or semisweet wines. When the method of freezing is used, the juice becomes concentrated as water is extracted to form ice crystals. By harvesting and pressing the grapes while they are frozen, most of the water remains in the press as ice and the concentrated juice is largely undiluted. The simplest and most easily controlled method used is the addition of unfermented grape juice (sweet reserve) to dry wine or stopping the fermentation prior to conversion of all the grape sugar to ethanol.

2.2.3 Sparkling Wines

Most sparkling wines obtain CO₂ supersaturation by a second alcoholic fermentation, typically induced by adding yeast and sugar to dry white wine. Sparkling wine owes much of its development to a series of events that occurred in the 1700s, including major improvements in the manufacture of glass, reintroduction of cork bottle-closures to France, and an unusually long period of cold weather in Europe.

Rather than producing inferior red wines during this cold spell, Don Perignon introduced techniques that culminated in the production of champagne. There are three principal methods of sparkling wine production: the methode champagnoise, the transfer method, and the bulk method.

2.2.3.1 Methode Champagnoise. Although both red and white grapes may be used, most sparkling wines are white. The grapes are harvested earlier than those used for table wines, and pressed whole without prior stemming or crushing to extract the juice with a minimum of pigment and tannin extraction; this is important for producing white sparkling wines from red-skinned grapes. Primary fermentation is carried out at approximately 15°C (59°F) and bentonite and/or casein may be added to aid the process. Inoculation with selected yeast strains helps avoid production of undesirable volatiles by indigenous yeasts.

The blending of wines produced from different sites, varieties, and vintages distinguishes the methode champagnoise. Before preparing the blend (*cuvée*), the individual base wines are clarified and stabilized. Aging typically takes place in stainless steel but occasionally takes place in oak cooperage. Blending is based on sensory evaluation of the wines concerned.

The secondary fermentation requires inoculation of the *cuvée* wine with a special yeast strain. A concentrated sucrose solution is added to the *cuvée* just prior to the yeast inoculation, which, upon fermentation, produces a pressure appropriate for sparkling wine (about 6 atmospheres [atm]). About 4.2 g of sugar is required to produce 2 g of CO₂ (most sparkling wines contain about 15 g of CO₂). The wine is then bottled, capped, and stacked horizontally at a stable temperature, preferably between 10° and 15°C (50° and 59°F), for the second fermentation. After fermentation, the bottles are transferred to a new site for maturation and stored at about 10°C (50°F).

Riddling is the technique used to allow removal of the yeast sediment (lees). The process involves loosening and suspending the cells by manual or mechanical shaking and turning, and positioning the bottle to move the lees toward the neck. Automated riddling takes 1 week to 10 days, while manual riddling can take from 3 to 8 weeks. After riddling, the bottles may be left neck down for several weeks in preparation for sediment removal.

Disgorging takes place about a year after bottling. The bottles are cooled to about 7°C (45°F) and the necks immersed in an ice/CaCl₂ or ice/glycol solution (about -20°C [-4°F]) to freeze the sediment. Cooling also increases the solubility of the CO₂ and reduces the likelihood of gushing upon opening the bottle. The disgorging machine rapidly removes the cap on the bottle, allowing for ejection of the frozen yeast plug. The mouth of the bottle is quickly covered and the fluid level is adjusted. Some sparkling wines receive a sucrose solution dissolved in high quality white wine and/or brandy to achieve the sweetness desired; this solution is referred to as the *dosage*. Small quantities of sulfur dioxide or ascorbic acid may be added to prevent subsequent in-bottle fermentation and limit oxidation.

Once the volume adjustment and other additions are complete, the bottles are sealed with special corks, the wire hood is added, and the bottles agitated to disperse the additions. The bottles are then decorated with their capsule and labels and stored for about 3 months to allow the corks to set in the necks.

2.2.3.2 Transfer Method. With advancements in automated riddling and yeast encapsulation, the advantages of the transfer method have been virtually negated. The preparation of sparkling wine is identical to the methode champagnoise up to the riddling stage.

During aging, the bottles are stored neck down. When the aging process is complete, the bottles are chilled below 0°C (32°F) before discharge into a transfer machine and passage to pressurized receiving tanks. The wine is usually then sweetened and sulfited, clarified by filtration, and sterile filtered just before bottling.

2.2.3.3 Bulk Method. In this method, fermentation of the juice for the base wine may proceed until all the sugar is consumed or be prematurely terminated to retain sugars for the second fermentation. The yeast is removed by centrifugation and/or filtration. Once the cuvée is formulated, the wines are combined with yeast additives and, if necessary, sugar. The second fermentation takes place in stainless steel tanks similar to those used in the transfer process.

Removal of the lees takes place at the end of the second fermentation by centrifugation and/or filtration, carried out at isobarometric pressure to maintain the level of CO₂. Sugar and sulfur dioxide content are adjusted just before sterile filtration and bottling.

2.2.3.4 Other Methods. Other methods of production of sparkling wine include the "rural" method and carbonation. The rural method involves prematurely terminating the primary fermentation by repeatedly removing the yeasts by filtration. Then, a second in-bottle fermentation converts the residual sugars to CO₂, and the remaining yeast is removed by riddling and disgorging. The injection of CO₂ under pressure at low temperatures is the least expensive and the least prestigious method of producing sparkling wines.

2.2.4 Dessert Wines

Dessert wines are classified together because of their elevated alcohol content. They usually have wine spirits added at some stage in their production. Among the most common dessert wines are sherries and ports.

2.2.4.1 Sherry. Baking is the most popular technique for producing sherries in the United States. Both white and red grapes are used because baking destroys the original color of the wine. Grapes are crushed and stemmed, and sulfur dioxide is added as soon as possible to control bacteria and oxidation. The maximum amount of juice is separated from the skins and the juice is transferred to fermentors. The juice is inoculated with starter and fermented at temperatures of 25° to 30°C (77° to 86°F). Usually the "must" is fermented until all of the sugar is consumed or to a low sugar content and then allowed to settle before fortification.

The new wine is then pumped from the fermentor or settling tank to the fortification tank. High proof spirits are added to the sherry material, or shemat, to raise the alcohol content to 17 to 18 percent by volume and then the wine is thoroughly mixed. The wine is then clarified and filtered before baking.

Slow baking occurs when the wine is stored in barrels exposed to the sun. More rapid baking is achieved through the use of artificially heated storage rooms or heating coils in barrels or tanks. Heating induces the formation of a wide variety of compounds, including furfurals, caramelization compounds, and browning by-products, and promotes the oxidation of ethanol to acetaldehyde. Air or oxygen may be bubbled through the heated wine to accelerate oxidation.

After baking, the sherry is cooled, clarified, and filtered. Maturation is then required and is usually carried out in oak barrels; aging can last from 6 months to 3 years. Various lots of sherry may then

be blended. Baked wines are usually sweet, a result of the addition of fortified grape juice to a base wine or residual sugar resulting from the early termination of fermentation by fortification.

2.2.4.2 Ports and Portlike Wines. Port wines are produced by the premature termination of fermentation by addition of brandy. When red grapes are used to produce ports, the major problem in production is the extraction of sufficient color. The extraction can be aided by mixing the juice and pomace, heating, adding SO₂, and using highly pigmented varieties of grapes. Port can be produced by baking, but with a shorter baking time than baked sherries.

When the fermenting "must" is run off (separated from the pomace by gravity), it is fortified with wine spirits containing about 77 percent alcohol. The first press fraction for red port is fortified to the same level as the free-run and may be kept separate for independent aging or blended with the free-run. Most white ports are fortified when half the original sugar content has been fermented. However, semidry and dry white ports are fortified later in the process.

The type and duration of aging depend on the style of wine desired. Slight fortification after each racking compensates for alcohol evaporation from the cooperage, and blending is used to achieve the desired properties of the wine. The final blend is left to mature in oak cooperage for several months prior to fining, filtration, stabilization, and bottling.

2.2.5 Brandy Production

Brandy is an alcoholic distillate or mixture of distillates obtained from the fermented juice, mash, or wine of grapes or other fruit (e.g., apples, apricots, peaches, blackberries, or boysenberries). Brandy is produced at less than 190° proof and bottled at a minimum 80° proof. (In the United States, "proof" means the ethyl alcohol content of a liquid at 60°F, stated as twice the percent ethyl alcohol by volume.) Two types of spirits are produced from wine or wine residue: beverage brandy and "wine spirits." Beverage brandy is distilled at 170° proof or lower from the fermented juice or mash of whole fruit, reduced to 102° to 130° proof for aging, and further reduced to 80° to 100° proof for bottling. Wine spirits include all spirits eligible for addition to wines: neutral spirits (190° or more proof), neutral brandy (171° to 189° proof), and brandy (140° to 170° proof).

In brandy production, the grapes or other fruit are pressed immediately after crushing. There are major differences in the fermentation process between wine and brandy production. Pure yeast cultures are not used in the fermentation process for brandy. Brandy can be made solely from the fermentation of fruit or can be distilled from the lees leftover from the racking process in still wine production or the pomace cap that is leftover from red still wine fermentations.

Distillation generally starts immediately after the fermentation and continues until all newly fermented wine is distilled. Nearly all U.S. producers use continuous column distillation, usually with an aldehyde section, instead of pot stills. For a detailed discussion of the distillation and aging of distilled spirits, which include brandy and brandy spirits, refer to AP-42 Section 9.12.3, Distilled and Blended Liquors.

After distillation, the brandy is aged in oak casks. Aging time can vary from 3 to 15 years or more. During aging, some of the brandy seeps through the oak and evaporates, so brandy is added periodically to compensate for this loss. Caramel coloring may also be added during aging to give the

brandy a characteristic dark brown color. After aging, the brandy may be blended and/or flavored, and then chilled, filtered, and bottled.

2.3 EMISSIONS^{5,7-8}

Ethanol is the primary volatile organic compound (VOC) emitted during the production of wines and brandy. Acetaldehyde, methane, n-propyl alcohol, n-butyl alcohol, sec-butyl alcohol, isobutyl alcohol, and isoamyl alcohol are also generated and emitted but in much smaller quantities compared to ethanol. In addition, a large number of other compounds are formed during the fermentation and aging process. It is the presence of these compounds that gives wines and brandy complex aroma and flavor.

Prior to fermentation, small amounts of liquified sulfur dioxide (SO₂) are often added as a preservative to the grapes after harvest and to the juice or "must;" SO₂ emissions can occur during these steps. Except for these potential emissions, there is little potential for emissions prior to the fermentation step in wine production.

During fermentation, large volumes of CO₂ are produced from the yeast metabolism of the sugars present in the juice or "must;" a general CO₂ production rate of approximately 260 milliliters per gram (ml/g) of glucose or fructose has been cited. This emission represents a volume greater than 50 times the volume of juice fermented. The escape of CO₂ is estimated to remove about 20 percent of the heat generated during fermentation. Ethanol loss was previously believed to occur through entrainment of the liquid droplet in the escaping CO₂, but recent studies indicate that evaporation is the major mechanism for ethanol loss. Ethanol droplets are formed and leave the "must" surface but either fall back into the "must" or impinge on the sides or top of the tank. The upward velocity of the CO₂ is not sufficient to carry the droplets out of the tank. In addition, other VOCs are also evolved through evaporation or entrainment in the CO₂ produced during fermentation; the extent of loss of those compounds depends on the temperature of the juice or "must," rate of CO₂ evolution, initial sugar concentration, and the size and shape of the fermentation tank.

Ethanol loss during fermentation has been estimated to be in the range of 0.1 to 1.5 percent of the ethanol produced, but this level varies considerably with the temperature of the "must" and the degree of sugar utilization. Losses of higher alcohols and monoterpenes occur at about the same rate. For some compounds, such as ethyl acetate and other esters, the losses can range up to 25 percent of the quantity produced during the fermentation. Selected examples of specific compounds formed during the fermentation of a Riesling wine include isoamyl acetate, isobutyl acetate, hexyl acetate, 1-hexane, ethyl n-hexanoate, ethyl n-octanoate, ethyl n-butanoate, and ethyl n-decanoate. Selected examples of other types of compounds formed and potentially emitted during fermentation include a variety of acetates, monoterpenes, higher alcohols and acids, and aldehydes and ketones. Emissions generally become negligible after fermentation stops because the production of CO₂ ceases and the liquid temperature decreases. Small quantities of dissolved CO₂ and ethanol may escape from the wine during subsequent processing steps. If the wine is aged in oak barrels, some small levels of ethanol loss may occur through the sides of the barrel. Other potential sources of emissions are the screening of the pomace from the juice (drag screen), the pomace pressing where the residual red wine is extracted from the pomace following fermentation, and the wine bottling process. There are very limited data available on emissions from these fugitive sources.

Except for harvesting the grapes and possibly unloading the grapes at the winery, there is essentially no potential for particulate (PM) emissions from this industry. Any PM emissions are expected to be negligible.

2.4 CONTROL TECHNOLOGY

Emission control methods are not currently used in the production of wines and brandy. Several potential systems have been studied to control emissions from the fermentation tanks. These studies were conducted at wineries or universities in California, primarily by the California Air Resources Board (CARB). The five systems under study were (1) carbon adsorption; (2) water scrubbing; (3) condensation; (4) catalytic incineration; and (5) temperature control. Of the five systems, temperature control is probably the least effective and has operational disadvantages. Control efficiency for the condensation system is lower than the remaining three systems, and water scrubbers present a problem due to the generation of significant quantities of contaminated wastewater that must be directed to a treatment facility. None of these systems are currently used at wineries in California. Continuing discussions are being conducted between the wine industry and CARB concerning the potential applicability of some type of emission control system.

Disposal of the dealcoholized solution (less than 0.05 percent alcohol by volume) produced from the still constitutes one of the major problems of the brandy industry. This problem results from the high percentage of material in solution or suspension and the difficulty of decomposition of the material. One solution is centrifugation and sale of the solids for uses such as fertilizer or feedstock. Another method of disposal is the use of shallow ponds in sandy fields. The ponds, not more than 6 inches deep, are filled in succession, and each is allowed to dry for 6 days. This method of disposal is a potentially small source of emissions from the evaporation of the residual ethanol and other VOCs due to the pre-evaporated nature of the still waste water. Deep ponding is not allowed as a method of disposal.

REFERENCES FOR SECTION 2

1. K. Shea, *Food, Beverages and Tobacco: Current Analysis*, Standard & Poor's Industry Surveys, Standard & Poor's Corporation, March 19, 1992.
2. J. M. Farren et al., *U.S. Industrial Outlook '92*, U.S. Department of Commerce, 1992.
3. *1987 Census of Manufactures: Beverages*, U.S. Department of Commerce, Bureau of Census, 1988.
4. *1989 County Business Patterns*, U. S. Department of Commerce, Bureau of Census, 1991.
5. R. S. Jackson, *Wine Science: Principles and Applications*, Academic Press, San Diego, CA, 1994.
6. M. A. Amerine, *Wine*, in *Kirk-Othmer Encyclopedia of Chemical Technology*, Third Edition, Volume 24, John Wiley and Sons, New York, 1984.
7. J. A. Heredia, "Technical Assessment Document on Ethanol Emissions and Control from California Wineries." Master of Science Dissertation, California Polytechnic State University, San Luis Obispo, CA, June 1993.
8. G. C. Miller, J. M. Amon, and R. F. Simpson, "Loss of Aroma Compounds in Carbon Dioxide Effluent During White Wine Fermentation," *Food Technol. Aust.*, 39(5):246-249, 1987.
9. M. A. Amerine, et al., *Technology of Wine Making*, Fourth Edition, AVI Publishing Company, Westport, CT, 1980.

3. GENERAL DATA REVIEW AND ANALYSIS PROCEDURES

3.1 LITERATURE SEARCH AND SCREENING

Data for this investigation were obtained from a number of sources within the Office of Air Quality Planning and Standards (OAQPS) and from outside organizations. The AP-42 background files located in the Emission Factor and Inventory Group (EFIG) were reviewed for information on the industry, processes, and emissions. The Factor Information and Retrieval (FIRE), Crosswalk/Air Toxic Emission Factor Data Base Management System (XATEF), and VOC/PM Speciation Data Base Management System (SPECIATE) data bases were searched by SCC code for identification of the potential pollutants emitted and emission factors for those pollutants. California's Air Resource Board provided test reports from several facilities in their state.

Information on the industry, including number of plants, plant location, and annual production capacities, was obtained from the *Census of Manufactures, U. S. Industrial Outlook* and other sources. The Aerometric Information Retrieval System (AIRS) data base also was searched for data on the number of plants, plant location, and estimated annual emissions of criteria pollutants. A number of sources of information were investigated specifically for emission test reports and data. The EPA library was searched for test reports. Using information obtained on plant locations, State and Regional offices were contacted about the availability of test reports. Publications lists from the Office of Research and Development (ORD) and Control Technology Center (CTC) were also searched for reports on emissions from the wine and brandy industry. In addition, representative trade associations, including the Wine Institute, were contacted for assistance in obtaining information about the industry and emissions.

To screen out unusable test reports, documents, and information from which emission factors could not be developed, the following general criteria were used:

1. Emission data must be from a primary reference:
 - a. Source testing must be from a referenced study that does not reiterate information from previous studies.
 - b. The document must constitute the original source of test data. For example, a technical paper was not included if the original study was contained in the previous document. If the exact source of the data could not be determined, the document was eliminated.
2. The referenced study should contain test results based on more than one test run. If results from only one run are presented, the emission factors must be down rated.
3. The report must contain sufficient data to evaluate the testing procedures and source operating conditions (e.g., one-page reports were generally rejected).

A final set of reference materials was compiled after a thorough review of the pertinent reports, documents, and information according to these criteria.

3.2 DATA QUALITY RATING SYSTEM¹

As part of the analysis of the emission data, the quantity and quality of the information contained in the final set of reference documents were evaluated. The following data were excluded from consideration:

1. Test series averages reported in units that cannot be converted to the selected reporting units;
2. Test series representing incompatible test methods (i.e., comparison of EPA Method 5 front half with EPA Method 5 front and back half);
3. Test series of controlled emissions for which the control device is not specified;
4. Test series in which the source process is not clearly identified and described; and
5. Test series in which it is not clear whether the emissions were measured before or after the control device.

Test data sets that were not excluded were assigned a quality rating. The rating system used was that specified by EFIG for preparing AP-42 sections. The data were rated as follows:

A — Tests that were performed using sound methodology and reported in enough detail for adequate validation. These tests do not necessarily conform to the methodology specified in EPA reference test methods, although these methods were used as a guide for the methodology actually used.

B — Tests that were performed by a generally sound methodology but lack enough detail for adequate validation.

C — Tests that were based on an untested or new methodology or that lacked a significant amount of background data.

D — Tests that were based on a generally unacceptable method but may provide an order-of-magnitude value for the source.

The following criteria were used to evaluate source test reports for sound methodology and adequate detail:

1. Source operation. The manner in which the source was operated is well documented in the report. The source was operating within typical parameters during the test.

2. Sampling procedures. The sampling procedures conformed to a generally acceptable methodology. If actual procedures deviated from accepted methods, the deviations are well documented. When this occurred, an evaluation was made of the extent to which such alternative procedures could influence the test results.

3. Sampling and process data. Adequate sampling and process data are documented in the report, and any variations in the sampling and process operation are noted. If a large spread between test results

cannot be explained by information contained in the test report, the data are suspect and are given a lower rating.

4. Analysis and calculations. The test reports contain original raw data sheets. The nomenclature and equations used were compared to those (if any) specified by EPA to establish equivalency. The depth of review of the calculations was dictated by the reviewer's confidence in the ability and conscientiousness of the tester, which in turn was based on factors such as consistency of results and completeness of other areas of the test report.

3.3 EMISSION FACTOR QUALITY RATING SYSTEM¹

The quality of the emission factors developed from analysis of the test data was rated using the following general criteria:

A — Excellent: Developed from A- and B-rated test data taken from many randomly chosen facilities in the industry population. The source category is specific enough so that variability within the source category population may be minimized.

B — Above average: Developed from A- or B-rated test data from a "reasonable number" of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industries. The source category is specific enough so that variability within the source category population may be minimized.

C — Average: Developed from A-, B-, and/or C-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. In addition, the source category is specific enough so that variability within the source category population may be minimized.

D — Below average: The emission factor was developed only from A-, B-, and/or C-rated test data from a small number of facilities, and there is reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of the emission factor are noted in the emission factor table.

E — Poor: The emission factor was developed from C- and D-rated test data, and there is reason to suspect that the facilities tested do not represent a random sample of the industry. There also may be evidence of variability within the source category population. Limitations on the use of these factors are footnoted.

The use of these criteria is somewhat subjective and depends to an extent upon the individual reviewer. Details of the rating of each candidate emission factor are provided in Section 4.

REFERENCE FOR SECTION 3

1. *Technical Procedures for Developing AP-42 Emission Factors and Preparing AP-42 Sections*, EPA-454/B-93-050, Office of Air Quality Planning and Standards, U. S. Environmental Protection Agency, Research Triangle Park, NC, October 1993.

4. REVIEW OF SPECIFIC DATA SETS

4.1 INTRODUCTION

This section describes how the revised AP-42 section on wines and brandy was developed. First, descriptions of data sets reviewed for this revision are presented, followed by a discussion of how candidate emission factors were developed from the data.

4.2 REVIEW OF SPECIFIC DATA SETS

Fourteen references were obtained for use in developing revised emission factors from red and white wine fermentation. The references are reviewed in the following subsections.

4.2.1 Reference 1

This reference contains calculations performed in 1979 by EPA to develop an equation to estimate ethanol emission factors for red and white wine fermentations. This estimating equation was published in the 1980 AP-42 Section 6.5.2. The equation is based on data from a 1964 article by Zimmerman, Rossi, and Wick and the data in Reference 2. The emission factor is expressed as pounds ethanol lost per 1,000 gallons of wine produced and is based on the fermentation temperature (°F) and initial sugar content (°Brix). A correction factor for ethanol emissions due to the pomace cap in red wine production is included in the equation.

To develop the emission factor equation, the data sets were plotted and a °Brix correction factor was developed so an ethanol emission factor could be calculated based on any initial sugar content. The original data was then converted to °F and a temperature function calculated. These two functions were then combined to give a relationship for any combination of initial sugar content and fermentation temperature for any white wine. A red wine correction factor was added to the equation to account for the additional emissions from the fermenting pomace cap. The emission factors estimated by this equation agreed with the Zimmerman, et al. data within ± 3.3 percent for all data points and was within 1 percent of the Reference 2 test result. The final equation is as follows:

$$EF = (0.135T - 5.91) + (B - 20.4)(T - 15.21)(0.0065) + C \quad (4-1)$$

where:

EF = emission factor, lb ethanol lost/1,000 gal wine made

T = fermentation temperature, °F

B = initial sugar content, °Brix

C = 0 for white wine, 2.4 lb/1,000 gal for red wine

This equation assumes the emission factor is linearly related to temperature and sugar content, but is based on a small data set. If either relationship is nonlinear, the equation has limitations. Also, the equation has a low temperature cutoff in applicability; for 18°Brix juice, the applicable range only extends down to 3.6°C (38.5°F). The data in this reference are rated D because they were based on mathematical equations. The data were not used in emission factor development because the equation was based on data from 1964 and overestimates emissions compared to the recent test results.

4.2.2 Reference 2

This reference presents the results of a source test conducted at E&J Gallo Winery, Fresno, California, in September 1978, by CARB to determine the VOC concentration in the gas vented directly to the atmosphere from a white wine fermentation tank. The tank tested was an epoxy lined steel tank with a 24,142 hl (637,776 gal) capacity. The test was conducted during the first 3 days of the fermentation process and there was no control device in use.

The exhaust gas stream was sampled using a condenser train with Greenburg-Smith type impingers in an ice bath. Volatile organic compounds (VOC) in the exhaust was measured continuously, using a flame ionization detector at the tank vent hatch; grab samples were also collected in double-ended flasks. Moisture content was determined by EPA Method 4, and CO₂, carbon monoxide (CO), and oxygen (O₂) concentrations were measured by analyzing grab samples. Volatile organic compounds were reported as lb/hr/tank for white wine fermentation. The emission rate that was obtained is specific to the tank geometry, product, and process conditions. Ethanol emissions were reported as lb/hr/tank.

The data were only collected at the beginning of the fermentation process; if the data had been collected in the middle of the process, for example, a higher emission rate may have been obtained. It was noted that the CO₂ concentrations measured may have been lower than the actual concentrations due to possible migration through the sampling bag material. The O₂ concentrations measured, however, may have been higher than the actual concentrations because the sampling line was not secure, allowing for leaks. This would also affect the CO₂ results. The data in this reference were not used in emission factor development.

4.2.3 Reference 3

This reference is a report containing the results of a test on a white wine fermentation tank at United Vintners winery, Reedley, California, in October 1980. The test was conducted by the CARB to determine an ethanol emission rate from the tank during a complete fermentation cycle. The cycle lasted 216.5 hours, but the test was conducted only during the final 159 hours (73 percent of the fermentation process).

The tank tested was constructed of stainless steel and had a capacity of 40,130 hl (106,000 gal). All emissions measurements were taken at the tank vent hatch. Ethanol, O₂, and CO₂ concentrations were continuously measured. Total organic compounds were measured with a flame ionization detector and converted to ethanol; O₂ was measured using an oxygen analyzer with a paramagnetic detection system; and CO₂ was measured with a nondispersive infrared detector. Grab samples were also taken in 2 liter glass flasks and analyzed for TOC, ethanol, O₂, CO₂, SO₂, H₂S, and methyl mercaptan.

Ethanol emissions were presented as ppm, lb/hr, and lb/gal of juice fermented. Data for the other gaseous constituents were presented as ppm in the fermentation exhaust gas. An ethanol emission factor was developed in this report based on the AP-42 equation (Eq. 4-1), which compared closely to the measured emission rate. The data in this report are rated D. Test data, process data, and emission factor calculations for ethanol are provided in Appendix A. The sampling and analysis methods used for ethanol in this test deviated from current methods, no test data sheets were provided for CO₂, SO₂, H₂S, or methyl mercaptan, no analytical methods were identified for gaseous constituents other than ethanol and CO₂, no data were presented for the THC correction factor to ethanol, and a fluctuation in power source affected the

operation of the continuous analyzers for a 24 hour period but the data were not excluded. For these reasons, the results of this test were not used in emission factor development.

4.2.4 Reference 4

This report presents an evaluation of emissions based on data from tests performed by CARB, local districts, or commercial laboratories. Test results were compared with emission estimates based on American Petroleum Institute (API) aboveground storage tanks breathing loss equations. No original data are presented and, therefore, the report was not used for emission factor development.

4.2.5 Reference 5

This reference is a report containing the results of ethanol emissions tests performed on four fermentation tanks and various processing and storage operations at three California wineries in 1981 by EAL Corporation. The tests were performed for CARB as a result of the board's determination that ethanol emissions from winery production and storage may significantly contribute to the formation of ozone through photochemical smog reactions. The tests were conducted using a sampling train with Greenburg-Smith type impingers, and ethanol collected in the impingers was analyzed by gas chromatography. Fermentation exhaust flow rate from the tank was measured by a turbine meter (totalizer). All processes tested were uncontrolled.

At the first location, United Vintners, Madera, tests were conducted for both red and white wine fermentation. For the white wine test, a stainless steel tank with a 13,249 hl (350,000 gal) capacity was monitored. The tank of must was a combination of 2 days of crushing; the fermentation process lasted for 172 hours. The test report states that this fermentation batch was less than ideal and did not follow typical fermentation behavior. For the red wine test, a 4,845 hl (128,000 gal) stainless steel tank was monitored. An initial red wine test was aborted after a pressure buildup and sudden release of fermenting must. A second test was completed without similar incident. During the test, the cover was periodically opened to release pressure built up in the tank. This fermentation lasted for only 26 hours.

At the second location, United Vintners, Oakville, a tank emissions test was conducted for red wine fermentation and fugitive emissions tests were conducted for barrel storage, screen separation, transportation of fermented lees to pressing, and bottling operations at UV Inglenook (UV Oakville does not have a bottling facility). The first test conducted was invalidated because no measurable exhaust data were obtained. The second test was conducted in a 341 hl (9,000 gal) epoxy lined concrete tank for red wine fermentation. The fermentation lasted only 77 hours.

At the third location, Robert Mondavi, Oakville, a tank emissions test was conducted for white wine fermentation in a 227 hl (6,000 gal) stainless steel tank. On days 1 through 4 of the test, exhaust volumetric flow was undetectable because of the small fermentation volume, so a more sensitive dry test meter was used. Fermentation lasted 512 hours. That test length resulted from fermentation process problems near the end of the process, resulting in an unusually slow decrease in sugar content. Fugitive emissions were monitored from the aeration process. In this process, the fermented juice is allowed to splash from a hose into a trough to remove undesired volatile compounds from the wine prior to storage.

For all four of the tank tests, ethanol emissions were presented in ppm, lb/hr, and cumulative pounds. Emission factors were developed for the fermentation process, based on gallons of juice fermented and tons of grapes crushed. The fugitive emissions data were presented in mg/m³, g/hr, and ppm. Fugitive

emission factors were developed for the drag screen separator, pomace press, and bottling processes based on the UV Oakville data. No emission factors were developed for barrel storage. The data in this test report are rated C. Pertinent test data, process data, and emission factor calculations are provided in Appendix B. The sampling and analysis methods used in this study do not reflect current technology, and there were several process problems and inconsistencies. The ethanol emission factors developed for red wine at both Madera and Oakville (United Vinters) were considerably higher than emission factors for red wine developed from more recent tests. For white wines, there were problems with the fermentation processes in all of the tests. For these reasons, the results in this report were not used in emission factor development for the fermentation process.

4.2.6 Reference 6

This reference is a 1983 journal article by R. Boulton and L. Williams that discusses a computer model developed to quantify evaporative losses for batch alcoholic fermentations. The model is used to illustrate the effects of inoculum level, sugar utilization, must temperature, non-isothermal conditions, and cap temperature on evaporative ethanol losses. A master correlation is presented for estimation of losses under any combination of temperature and sugar utilization during entire isothermal batch fermentations. The estimating equation is as follows:

$$\log(E_{\text{lost}}/[S_o - S]^2) = K_4 - K_5/(T+273) \quad (4-2)$$

where:

- E_{lost} = ethanol emitted (g/L)
- S_o = initial sugar concentration (g/L)
- S = final sugar concentration (g/L)
- T = fermentation temperature ($^{\circ}\text{C}$)
- K_4, K_5 = constants, 6.682 and 2,552

Validation comparisons were performed and indicated that the model does a reasonable job of simulating fermentation and evaporative ethanol loss behavior, both qualitatively and quantitatively. When compared with the AP-42 equation, it was found that the AP-42 equation generally underestimates ethanol losses, especially at lower temperatures. A simple model, which probably underestimates ethanol losses, was also developed to take into account the effects of the pomace cap on red wine fermentation ethanol emissions. It was shown that an increase in cap to liquid temperature differential resulted in an increase in vapor phase ethanol concentrations and total ethanol emissions. The data derived in this reference were based on mathematical equations. The data were not used for emission factor development because the emission factors calculated using the equation were consistently higher than data obtained from more recent tests for both red and white wines.

4.2.7 Reference 7

This report presents an estimate of emissions from four 53 hl (1,400 gal) wine fermentation tanks using three ethanol control techniques. Although the tanks are described as pilot scale units, many wineries in the Napa, Sonoma, and Mendocino county areas use fermentation tanks of approximately this size for the production of premium wines, so emissions obtained from this test would be representative of these wineries. Each of the three control devices was connected to a tank, and the fourth tank was used as a reference tank. The study was performed in September 1987 as part of a demonstration program, conducted by CARB with assistance from California State University (CSU) at Fresno. The program was

developed to evaluate methods of reducing emissions from winery fermentation tanks as a response to CARB's consideration of a Suggested Control Measure (SCM) for these emissions. The control technologies studied were scrubbing, carbon adsorption, and catalytic incineration; all were pilot scale units sized for the 53 hl (1,400 gal) tanks. Four tests were conducted in each tank: two red and two white wine fermentations.

The wet scrubber unit used tap water to remove ethanol from the gas stream vented from the fermentation tank. Carbon dioxide, ethanol, and make-up air were all pulled into the unit at a constant flow rate. The water with the removed ethanol was collected at the bottom of the unit and recycled back to the top of the column. During the process, some of the water was bled off for disposal and fresh make-up water added.

The carbon adsorption unit had two beds and used activated carbon to adsorb and hold the ethanol emissions pumped from the fermentation tank, using make-up air to provide a constant flow rate. Upon reaching saturation, the exhaust was routed to the second bed and the first bed was desorbed with steam. The steam and ethanol were cooled, condensed, and then disposed. Carbon adsorption provides for the control of ethanol emissions from the fermentor to the atmosphere but does not provide for the overall control of ethanol to the environment. The ethanol is present in the condensation water and, depending upon subsequent treatment, could evaporate from the water before the treatment process degrades the ethanol.

The catalytic incinerator used a ceramic catalyst to incinerate ethanol emissions from the fermentation tank. Once again, make-up air was used to provide a constant flow rate; the gas was heated prior to incineration and then vented to the atmosphere.

Sampling was performed at the inlet and outlet of each control device and the outlet of the reference tank. Ethanol, O₂, CO₂, and CO were measured continuously, according to CARB Method 100. Moisture content was measured using CARB Method 4, and grab samples were taken using bags for volatile organics and specimen jars for liquids.

Several problems were experienced with the scrubber, including water pump failure, excess water flow rates, high pressure drop, and water carryover. The incinerator experienced only a few problems with low outlet temperatures, and the carbon beds experienced periodic breakthrough conditions. From the ethanol concentrations at the inlet and outlet of the control device, a control efficiency was calculated for the scrubber, catalytic incinerator, and carbon adsorber. All of the control devices were able to reach peak efficiencies of over 90 percent in each test, despite the problems encountered. The data in this report are rated C. Pertinent test data, process data, and emission factor calculations are provided in Appendix C.

4.2.8 Reference 8

This paper contains the results of a study conducted in response to the findings of the tests in Reference 7. Scrubbing and catalytic incineration as methods of ethanol emissions control from fermentation tanks were determined to be infeasible due to disposal and cost factors. This study was conducted to further evaluate the operational efficiency of the emission collection hoods and charcoal adsorption unit discussed in Reference 7. The tests were again conducted by the CARB and CSU. Two 53 hl (1,400 gal) fermentation tanks were utilized in two red and two white wine tests; one tank served as the uncontrolled reference tank and one tank was controlled.

Fermentation emissions were collected from the controlled tank by a capture hood. The exhaust was chilled to remove as much water as possible before passing through one of two carbon adsorption beds and then vented to the atmosphere upon exiting the bed. Steam was used to regenerate the saturated bed and adsorbed volatiles freed from the charcoal were condensed into a stainless steel reservoir. During fermentation, it was necessary to switch between the two beds several times.

Ethanol concentration in the gas stream was measured continuously using flame ionization detection, in accordance with CARB Method 100. Sampling was performed at the outlet of the reference tank and at the inlet and outlet of each adsorption bed and control efficiencies generated for the four tests. Data for one of the red wine fermentations were not presented, due to measurement and collection problems. Data for one white wine test were not used for emission factors because the fermentation temperature for one test was 26.7°C (80°F), which is much higher than normal white wine fermentation temperatures. The control efficiencies for the other three tests were all above 98 percent. The data presented in this report are rated B; no raw data sheets were included. Pertinent test data, process data, and emission factor calculations are provided in Appendix D.

4.2.9 Reference 9

This study culminated a 3-year investigation of ethanol emissions control technology that included the studies discussed in References 7 and 8. Testing was conducted in September of 1990 at E&J Gallo's Fresno, California, winery using a 7874 hl (207,000 gal) fermentation tank and a carbon adsorption unit. The study was conducted to further examine ethanol emissions in order to develop ethanol emission factors and to determine the feasibility and requirements of the carbon adsorption system. A detailed cost analysis of implementing carbon adsorption systems was presented as part of the report.

The design of the adsorption system was based on the pilot test design in Reference 8 and contained a tank vent hood, ducting system, and carbon adsorption unit. Three white and five red wine fermentation cycles were tested. Total organic compounds were monitored using a flame ionization detector at the inlet and outlet of the adsorption system only during runs 6, 7, and 8. For runs 1 through 5, only the concentration of ethanol in the carbon adsorption condensate was measured. Gas evolution rates during fermentation were higher than expected, but alcohol removal efficiencies for the adsorber were over 97 percent. After ethanol emissions reached 50 ppm or after 20 hours, the unit initiated a regeneration cycle. The emissions were then condensed and a comprehensive chemical analysis was performed using gas chromatography. Constituents other than ethanol, such as acetaldehyde, were also measured in the analysis but no evaluation of the data was presented. This is the only reference cited that presented data for emissions of hydrogen sulfide and VOCs other than ethanol from the fermentation process.

Problems experienced during the test included failure of fan parts and shut-down of the analyzer system due to loss of fuel, loss of ignition, moisture in the sample line, or sample pump failure. Plugging of condensate withdrawal lines also resulted in incomplete regeneration cycles during fermentations 4 and 5. The results show that the amounts of alcohol collected per 1,000 gallons of wine fermented were close to the amounts predicted by the pilot studies carried out in 1987 and 1988.

For runs 1 through 5, the ethanol concentrations were measured only in the aqueous condensate from the carbon adsorption unit. Ethanol concentration at the outlet of the adsorber was less than 50 ppm. The data represent only the ethanol captured by the adsorber and not the total quantity released during fermentation. Use of these data would underestimate the total quantity of ethanol released. If the adsorber collection efficiency had been measured, the total quantity released during fermentation could be calculated

but these data were collected only during runs 6, 7, and 8. Since the inlet and outlet concentrations at the adsorber were measured only during runs 6, 7, and 8, these three runs were used in emission factor calculations. The ethanol emissions data in this report are rated A. Pertinent test data, process data, and emission factor calculations are provided in Appendix E.

4.2.10 Reference 10

This report is a more detailed presentation of the data from the fermentation runs 6, 7, and 8 in the study discussed in Reference 9. No new data are presented; therefore, this reference was not used in the development of emission factors.

4.2.11 Reference 11

This reference is a memorandum from Gallo to the San Joaquin Valley Unified Air Pollution Control District (SJVUAPCD) concerning the protocol and results of the study in Reference 9. The SJVUAPCD provided only copies of the analytical data sheets that contain data for hydrogen sulfide, acetaldehyde, other selected VOCs emitted during the test, the volume of condensate for each fermentation, and the calculations of the average content of hydrogen sulfide and acetaldehyde emitted during the fermentations. The results for hydrogen sulfide obtained in Reference 9 showed considerable variation. Two red wine fermentation tests showed no hydrogen sulfide emissions while the other three showed levels that ranged from 0.0023 to 0.0035 lb/1,000 gal of fermenting "must." According to the Wine Institute, hydrogen sulfide formation depends upon several factors including fermentation temperature, yeast strain, yeast nutrients, sulfur dioxide levels in the fermenting "must," and the level of elemental sulfur applied to grapes for mildew prevention. This latter factor, elemental sulfur application, varies from region-to-region, variety-to-variety, and year-to-year. The variation in hydrogen sulfide emissions is the result of the nature of the fermentation process and the presence or absence of certain compounds and not poor test protocols or analyses. No protocol or sampling and analysis information is provided in this reference; only the final emissions data are provided. The emissions data presented in this reference are rated C. The emission data and emission factor calculations are provided in Appendix F.

4.2.12 Reference 12

This reference is a Master of Science dissertation on ethanol emissions and control from California wineries presented to the faculty of the Civil/Environmental Engineering Department of California Polytechnic State University at San Luis Obispo in June 1993. This document compiles the results of studies conducted in California on ethanol emissions from wineries and options for control of ethanol emissions during wine fermentation. An estimate of total uncontrolled ethanol emissions from wineries in California and emission factors for red and white wines are presented, as is an assessment of control technologies and their costs. The report compares predicted emissions to source test results for the tests in References 3, 5, 7, 8, and 9. Predicted emissions were calculated using both the Boulton computer model (Eq. 4-2) and the 1980 AP-42 equation (Eq. 4-1) and the results compared to the source test data. Because no new data were presented, this reference was not used for emission factor development.

4.2.13 Reference 13

This document is a memorandum from the Wine Institute to CARB that contains comments on Reference 12. The memorandum states that fermentation emissions for both white and red wines were overestimated because of the inclusion of three erroneous data points, and discusses several other errors

that led to an underestimation of the costs of implementing the proposed control technology. The document also states that the calculation used for the required total number of fermentor tanks in a winery is an underestimation. It presents revised estimates of statewide uncontrolled ethanol emissions from wineries based on the revised emission factors and production figures. This reference was not used for emission factor development.

4.2.14 Reference 14

This document is a memorandum from CARB to San Joaquin Valley Unified Air Pollution Control District (SJVUAPCD). It includes CARB revised emission factors for red and white wine, based on the most recent source test data. A revised cost effectiveness estimate is also presented, based on these new emission factors and a CARB winery tank usage survey. A copy of this memorandum is presented in Appendix G.

4.3 DEVELOPMENT OF CANDIDATE EMISSION FACTORS

TABLE 4-1. SUMMARY OF FERMENTATION EMISSIONS DATA^a

Table at end of document

TABLE 4-1. (continued)

Table at end of document

TABLE 4-1. (continued)

Table at end of document

TABLE 4-1. (continued)

Table at end of document

summarizes the test data from the references presented in Section 4.2, Table 4-2 summarizes the test data
TABLE 4-2. FERMENTATION EMISSION DATA USED FOR EMISSION FACTOR ESTIMATION^a

Wine type	Pollutant	Control device	Number of runs	Data rating	Emission factor		Ref. No.
					g/hl	lb/1,000 gal	
Red	Acetaldehyde	None	5	C	0.032	0.0027	11
Red	Ethanol	None	8	C	71	5.9	7
Red	Ethanol	None	2	B	53	4.4	8
Red	Ethanol	None	2	A	43	3.6	9
Red	Hydrogen sulfide	None	5	C	0.020	0.0017	9
Red	Isoamyl alcohol	None	5	C	0.17	0.014	11
Red	Isobutyl alcohol	None	5	C	0.043	0.0036	11
Red	Methanol	None	5	C	0.030	0.0025	11
Red	n-Butanol	None	5	C	0.00066	5.5e-05	11
Red	n-Propanol	None	5	C	0.041	0.0034	11
Red	sec-Butanol	None	3	C	0.00054	0.000045	11
Red	Ethanol	Carb. Adsorption	1	C	4.8	0.40	7
Red	Ethanol	Carb. Adsorption	1	B	0.86	0.072	8
Red	Ethanol	Carb. Adsorption	2	A	0.53	0.044	9
Red	Ethanol	Cat. Incineration	2	C	13	1.1	7
Red	Ethanol	Wet Scrubber	2	C	0.67	0.056	7
White	Acetaldehyde	None	3	C	0.0086	0.00072	11
White	Ethanol	None	8	C	26	2.2	7
White	Ethanol	None	2	B	18	1.5	8
White	Ethanol	None	1	A	22	1.8	9
White	Hydrogen sulfide	None	1	C	0.017	0.0014	9
White	Isoamyl alcohol	None	3	C	0.061	0.0051	11
White	Isobutyl alcohol	None	3	C	0.0083	0.00069	11
White	Methanol	None	3	C	0.0077	0.00064	11
White	n-Propanol	None	3	C	0.028	0.0023	11
White	Ethanol	Carb. Adsorption	2	C	1.4	0.12	7
White	Ethanol	Carb. Adsorption	1	B	0.33	0.027	8
White	Ethanol	Carb. Adsorption	1	A	1.6	0.13	9
White	Ethanol	Cat. Incineration	2	C	1.8	0.15	7
White	Ethanol	Wet Scrubber	2	C	0.99	0.083	7

^aEmission units are in terms of weight per unit volume of fermented juice produced.
 1 lb/1,000 gal = 11.98 g/hl.

that were used in developing the emission factors, and Table 4-3 presents the emission factors for red and

TABLE 4-3. SUMMARY OF CANDIDATE EMISSION FACTORS FOR FERMENTATION IN WINE PRODUCTION^a

Wine type	Pollutant	Control device	EMISSION FACTOR RATING	Emission factor range		Emission factor		Ref. Nos.
				g/hl	lb/1,000 gal	g/hl	lb/1,000 gal	
Red	Acetaldehyde	None	E	NA	NA	0.032	0.0027	11
Red	Ethanol	None	C	43-71	3.6-5.9	55	4.6	7,8,9
Red	Hydrogen sulfide	None	E	0-0.042	0-0.0035	0.020	0.0017	9
Red	Isoamyl alcohol	None	E	NA	NA	0.17	0.014	11
Red	Isobutyl alcohol	None	E	NA	NA	0.043	0.0036	11
Red	Methanol	None	E	NA	NA	0.030	0.0025	11
Red	n-Butanol	None	E	NA	NA	0.00066	0.000055	11
Red	n-Propanol	None	E	NA	NA	0.041	0.0034	11
Red	sec-Butanol	None	E	NA	NA	0.00054	0.000045	11
Red	Ethanol	Carb. Adsorption	C	0.53-4.8	0.044-0.40	2.0	0.17	7,8,9
Red	Ethanol	Cat. Incineration	E	NA	NA	13	1.1	7
Red	Ethanol	Wet Scrubber	E	NA	NA	0.67	0.056	7
White	Acetaldehyde	None	E	NA	NA	0.0086	0.00072	11
White	Ethanol	None	C	18-26	1.5-2.2	22	1.8	7,8,9
White	Hydrogen sulfide	None	E	NA	NA	0.017	0.014	9
White	Isoamyl alcohol	None	E	NA	NA	0.061	0.0051	11
White	Isobutyl alcohol	None	E	NA	NA	0.0083	0.00069	11
White	Methanol	None	E	NA	NA	0.0077	0.00064	11
White	n-Propanol	None	E	NA	NA	0.028	0.0023	11
White	Ethanol	Carb. Adsorption	C	0.33-1.6	0.027-0.13	1.1	0.092	7,8,9
White	Ethanol	Cat. Incineration	E	NA	NA	1.8	0.15	7
White	Ethanol	Wet Scrubber	E	NA	NA	0.99	0.083	7

^aEmission factor units are weight per unit volume of fermented juice produced. NA = not applicable; only one test. 1 lb/1,000 gal = 11.98 g/hl.

white wine fermentation that were developed using these data. Data from tests dated prior to 1988 were not used because the analytical methods were inconsistent with current methods. Tests conducted from 1988 to present use of an analytical method designed by CARB specifically to measure emissions from wine fermentation tanks. A 1982 test provided the only data available regarding fugitive emissions from wineries. Ethanol emission factors of 6.0 g/hl (0.5 lb/1,000 gal) of juice for the screening of the pomace from the fermented red juice (drag screen), 9.1 g/907.2 kg (0.02 lb/ton) of pomace for the pomace press, and 1.2 g/hl (0.1 lb/1,000 gal) wine for white wine bottling were calculated from a small data set.

Emission factors were developed by grouping the data from similar combinations of source, pollutant, and control device, discarding inferior data sets, and averaging the emission factors derived from each set. In some cases, data were available from multiple tests on the same source. In such cases, the emission factors from the tests on that source were averaged first, and the resulting factor was then averaged with the factors from other similar sources. The following paragraphs describe how the data presented in Table 4-2 were used to develop the candidate emission factors in Table 4-3.

Candidate emission factors for controlled and uncontrolled emissions from red and white wine fermentations were developed from several references. The pollutants measured were ethanol, acetaldehyde, hydrogen sulfide, isoamyl alcohol, isobutyl alcohol, methanol, n-butanol, n-propanol, and sec-butanol.

4.3.1 Ethanol

Data from three tests were used to develop an emission factor for uncontrolled ethanol emissions from red and white wine fermentations. Candidate average emission factors of 4.6 lb/1,000 gal of red wine fermented and 1.8 lb/1,000 gal of white wine fermented were developed and given C ratings.

Data from three tests were used to develop ethanol emission factors for red and white wine fermentations controlled by carbon adsorption. Candidate average emission factors of 0.17 lb/1,000 gal for red and 0.092 lb/1,000 gal for white wine were developed and given C ratings. Data from one C-rated test were used to develop ethanol emission factors for red and white wine fermentations controlled by catalytic incineration and fermentations controlled by wet scrubbers. These four factors were given E ratings.

4.3.2 Other VOCs

Data from one C-rated test were available for acetaldehyde, isoamyl alcohol, isobutyl alcohol, methanol, n-butanol, n-propanol, and sec-butanol emissions from uncontrolled red and white wine fermentations. These data were used to develop candidate emission factors, which were given E ratings.

4.3.3 Hydrogen Sulfide

Data from one C-rated test were available for hydrogen sulfide emissions from uncontrolled red and white wine fermentation. These data were used to develop candidate emission factors, which were given E ratings.

4.4 SUMMARY OF CHANGES TO AP-42 SECTION

4.4.1 Section Narrative

The section narrative was revised to include a more detailed process description for wine production and discussion of emissions and controls. The revised section also includes a process description for brandy production. A process flow diagram for a typical wine making facility was also added.

4.4.2 Emission Factors

The emission factor tables for the AP-42 section were completely revised to incorporate the emission factors developed from the new test data. The previous version of the section presented ethanol emission factors for two specific cases and an equation to estimate ethanol emissions from all other cases for both red and white wine fermentations. The revised section presents emission factors for ethanol, hydrogen sulfide, isoamyl alcohol, isobutyl alcohol, methanol, n-propanol, n-butanol, and sec-butanol for both red and white wine fermentations. The previous AP-42 section presented factors for uncontrolled emissions only. The revised section presents ethanol emission factors for controlled and uncontrolled wine fermentations.

REFERENCES FOR SECTION 4

1. Notes and calculations of an emission factor relationship by William Sahlie, U. S. Environmental Protection Agency, Research Triangle Park, NC, March 1979.
2. *Source Test Report, Emissions from a Fermentation Tank at E&J Gallo Winery*, Report No. C-8-050, California Air Resources Board, October, 1978.
3. *Evaluation Test to Measure Ethanol Emissions from a 106,000 Gallon Fermentation Tank*, Report No. C-80-071, California Air Resources Board, October, 1980.
4. *Alcohol Emissions from a Fermentation Tank*, Report No. ARB/SS-81-004, C-8-050 Part 2, California Air Resources Board, March 1981.
5. *Characterization of Ethanol Emissions from Wineries*, Report from EAL Corporation to California Air Resources Board, July 19, 1982.
6. L.A. Williams and R. Boulton, "Modeling and Prediction of Evaporative Loss During Wine Fermentations," *Am. J. Enol. Vitic.*, Vol 34:234-242, 1983.
7. *Ethanol Emissions and Control for Wine Fermentation and Tanks*, Report # ARB/ML-88-027, California Air Resources Board, April, 1988.
8. D.F. Todd, et al., "Ethanol Emissions Control from Wine Fermentation Tanks Using Charcoal Adsorption: A Pilot Study," California Air Resources Board, published by California Agricultural Technology Institute, March 1990.
9. *Ethanol Emissions Control from Wine Fermentation Tanks Utilizing Carbon Adsorption Technology*, Akton Associates, Martinez, CA, June 1991.
10. J. A. Heredia, "Ethanol Emissions Control from Wine Fermentation Tanks Using Charcoal Adsorption," Project No. C90-086, California Air Resources Board, October 1992.
11. Memorandum to Maria Lima, SJVUAPCD, Fresno, CA, from Arthur Caputi, Jr., E&J Gallo Winery, Modesto, CA, December 14, 1992.
12. J. A. Heredia, "Technical Assessment Document on Ethanol Emissions and Controls from California Wineries," Master of Science Dissertation, California Polytechnic State University, San Luis Obispo, June 1993.
13. Memorandum to Nelson Chan, Air Resources Board, Sacramento, CA, from Arthur Caputi, Wine Institute, San Francisco, CA, February 24, 1994.
14. Memorandum to Mark Boese, SJVUAPCD, Fresno, CA, from Dean Simeroth, California Air Resources Board, Sacramento, CA, November 1, 1994.

TABLE 4-1. SUMMARY OF FERMENTATION EMISSIONS DATA^a

Date	Source	Wine type	Pollutant	Control device	Fermentation temp. (°F)	Initial brix (°B)	Data rating	Emission factor		Ref. No.
								g/hl	lb/1,000 gal	
1991	Gallo	Red	Acetaldehyde	None	73	23	C	0.025	0.0021	11
1991	Gallo	Red	Acetaldehyde	None	72	23.2	C	0.012	0.0010	11
1991	Gallo	Red	Acetaldehyde	None	74	23	C	0.014	0.0012	11
1991	Gallo	Red	Acetaldehyde	None	73	22.8	C	0.072	0.0060	11
1991	Gallo	Red	Acetaldehyde	None	74	22.6	C	0.041	0.0034	11
1982	UV, Madera	Red	Ethanol	None	83	23	C	93	7.8	5
1982	UV, Oakville	Red	Ethanol	None	72	22.4	C	126	10.5	5
1988	CSU Tank 1	Red	Ethanol	None	78	24.1	C	92	7.7	7
1988	CSU Tank 1	Red	Ethanol	None	80	25.4	C	84	7.0	7
1988	CSU Tank 2	Red	Ethanol	None	78	23.9	C	145	12	7
1988	CSU Tank 2	Red	Ethanol	None	78	24.8	C	79	6.6	7
1988	CSU Tank 3	Red	Ethanol	None	79	23.9	C	35	2.9	7
1988	CSU Tank 3	Red	Ethanol	None	76	25.1	C	65	5.4	7
1988	CSU Tank 4	Red	Ethanol	None	81	25.5	C	44	3.7	7
1988	CSU Tank 4	Red	Ethanol	None	75	24.3	C	22	1.8	7
1990	CSU Tank 1	Red	Ethanol	None	80	21	B	51	4.3	8
1990	CSU Tank 2	Red	Ethanol	None	80	21	B	54	4.5	8
1991	Gallo	Red	Ethanol	None	72	23.	A	34	2.8 ^b	9
1991	Gallo	Red	Ethanol	None	74	23	A	26	2.2 ^b	9
1991	Gallo	Red	Ethanol	None	73	23	A	35	2.9 ^b	9
1991	Gallo	Red	Ethanol	None	74	22.6	A	48	4.0 ^c	9
1991	Gallo	Red	Ethanol	None	73	22.8	A	38	3.2 ^c	9
1988	CSU Tank 2	Red	Ethanol	Carb. Adsorption	78	24.8	C	4.7	0.40	7
1990	CSU Tank 2	Red	Ethanol	Carb. Adsorption	80	21	B	0.86	0.072	8
1991	Gallo	Red	Ethanol	Carb. Adsorption	73	22.8	A	0.38	0.032 ^c	9
1991	Gallo	Red	Ethanol	Carb. Adsorption	74	22.6	A	0.67	0.056 ^c	9
1988	CSU Tank 1	Red	Ethanol	Cat. Incineration	80	25.4	C	2.5	0.21	7
1988	CSU Tank 1	Red	Ethanol	Cat. Incineration	78	24.1	C	24	2.0	7
1988	CSU Tank 3	Red	Ethanol	Wet Scrubber	76	25.1	C	0.65	0.054	7

TABLE 4-1. (continued)

Date	Source	Wine type	Pollutant	Control device	Fermentation temp. (°F)	Initial brix (°B)	Data rating	Emission factor		Ref. No.
								g/hl	lb/1,000 gal	
1988	CSU Tank 3	Red	Ethanol	Wet Scrubber	79	23.9	C	0.69	0.058	7
1991	Gallo	Red	Hydrogen sulfide	None	72	23	C	0	0	9
1991	Gallo	Red	Hydrogen sulfide	None	74	23	C	0	0	9
1991	Gallo	Red	Hydrogen sulfide	None	73	23	C	0.035	0.0029	9
1991	Gallo	Red	Hydrogen sulfide	None	73	22.8	C	0.028	0.0023	9
1991	Gallo	Red	Hydrogen sulfide	None	74	22.6	C	0.042	0.0035	9
1991	Gallo	Red	Isoamyl alcohol	None	73	23	C	0.14	0.012	11
1991	Gallo	Red	Isoamyl alcohol	None	72	23.2	C	0.11	0.0092	11
1991	Gallo	Red	Isoamyl alcohol	None	74	22.6	C	0.31	0.026	11
1991	Gallo	Red	Isoamyl alcohol	None	73	22.8	C	0.19	0.016	11
1991	Gallo	Red	Isoamyl alcohol	None	74	23	C	0.097	0.0081	11
1991	Gallo	Red	Isobutyl alcohol	None	72	23.2	C	0.026	0.0022	11
1991	Gallo	Red	Isobutyl alcohol	None	73	22.8	C	0.053	0.0044	11
1991	Gallo	Red	Isobutyl alcohol	None	73	23	C	0.043	0.0036	11
1991	Gallo	Red	Isobutyl alcohol	None	74	22.6	C	0.068	0.0057	11
1991	Gallo	Red	Isobutyl alcohol	None	74	23	C	0.026	0.0022	11
1991	Gallo	Red	Methanol	None	74	22.6	C	0.028	0.0023	11
1991	Gallo	Red	Methanol	None	74	23	C	0.029	0.0024	11
1991	Gallo	Red	Methanol	None	73	22.8	C	0.026	0.0022	11
1991	Gallo	Red	Methanol	None	73	23	C	0.026	0.0022	11
1991	Gallo	Red	Methanol	None	72	23.2	C	0.041	0.0034	11
1991	Gallo	Red	n-Butanol	None	72	23.2	C	0.00087	7.3e-05	11
1991	Gallo	Red	n-Butanol	None	73	23	C	0.00044	3.7e-05	11
1991	Gallo	Red	n-Butanol	None	74	22.6	C	0.00062	5.2e-05	11
1991	Gallo	Red	n-Butanol	None	73	22.8	C	0.00048	4.0e-05	11

TABLE 4-1. (continued)

Date	Source	Wine type	Pollutant	Control device	Fermentation temp. (°F)	Initial brix (°B)	Data rating	Emission factor		Ref. No.
								g/hl	lb/1,000 gal	
1991	Gallo	Red	n-Butanol	None	74	23	C	0.00086	7.2e-05	11
1991	Gallo	Red	n-Propanol	None	74	22.6	C	0.031	0.0026	11
1991	Gallo	Red	n-Propanol	None	74	23	C	0.053	0.0044	11
1991	Gallo	Red	n-Propanol	None	73	22.8	C	0.028	0.0023	11
1991	Gallo	Red	n-Propanol	None	72	23.2	C	0.060	0.0050	11
1991	Gallo	Red	n-Propanol	None	73	23	C	0.031	0.0026	11
1991	Gallo	Red	sec-Butanol	None	73	22.8	C	0.00072	6.0e-05	11
1991	Gallo	Red	sec-Butanol	None	74	23	C	0.00029	2.4e-05	11
1991	Gallo	Red	sec-Butanol	None	74	22.6	C	0.00062	5.2e-05	11
1991	Gallo	White	Acetaldehyde	None	59	20	C	0.0095	0.00079	11
1991	Gallo	White	Acetaldehyde	None	56	20	C	0.0049	0.00041	11
1991	Gallo	White	Acetaldehyde	None	57	21.6	C	0.012	0.00097	11
1980	UV, Reedley	White	Ethanol	None	53	20.5	C	18	1.5	3
1982	RM, Oakville	White	Ethanol	None	60	23.5	C	17	1.4	5
1982	UV, Madera	White	Ethanol	None	56	23	C	31	2.6	5
1988	CSU Tank 1	White	Ethanol	None	59	20.1	C	14	1.2	7
1988	CSU Tank 1	White	Ethanol	None	57	22.3	C	41	3.4	7
1988	CSU Tank 2	White	Ethanol	None	57	22.3	C	47	3.9	7
1988	CSU Tank 2	White	Ethanol	None	59	20.1	C	17	1.4	7
1988	CSU Tank 3	White	Ethanol	None	57	20.1	C	7.4	0.62	7
1988	CSU Tank 3	White	Ethanol	None	57	22.3	C	41	3.4	7
1988	CSU Tank 4	White	Ethanol	None	59	20.1	C	6.5	0.54	7
1988	CSU Tank 4	White	Ethanol	None	57	22.3	C	41	3.4	7
1990	CSU Tank 1	White	Ethanol	None	55	21	B	18	1.5	8
1990	CSU Tank 1	White	Ethanol	None	80	21	B	46	3.9 ^d	8
1990	CSU Tank 2	White	Ethanol	None	80	21	B	40	3.3 ^d	8
1990	CSU Tank 2	White	Ethanol	None	55	21	B	17	1.4	8
1991	Gallo	White	Ethanol	None	56	20	A	28	2.3 ^b	9

TABLE 4-1. (continued)

Date	Source	Wine type	Pollutant	Control device	Fermentation temp. (°F)	Initial brix (°B)	Data rating	Emission factor		Ref. No.
								g/hl	lb/1,000 gal	
1991	Gallo	White	Ethanol	None	59	20	A	17	1.4 ^b	9
1991	Gallo	White	Ethanol	None	57	21.6	A	22	1.8 ^c	9
1988	CSU Tank 2	White	Ethanol	Carb. Adsorption	57	22.3	C	1.1	0.092	7
1988	CSU Tank 2	White	Ethanol	Carb. Adsorption	59	20.1	C	1.7	0.14	7
1990	CSU Tank 2	White	Ethanol	Carb. Adsorption	80	21	B	0.055	0.0046 ^d	8
1990	CSU Tank 2	White	Ethanol	Carb. Adsorption	55	21	B	0.32	0.027	8
1991	Gallo	White	Ethanol	Carb. Adsorption	57	21.6	A	1.6	0.13 ^c	9
1988	CSU Tank 1	White	Ethanol	Cat. Incineration	57	22.3	C	0.44	0.037	7
1988	CSU Tank 1	White	Ethanol	Cat. Incineration	59	20.1	C	3.2	0.27	7
1988	CSU Tank 3	White	Ethanol	Wet Scrubber	57	20.1	C	1.32	0.11	7
1988	CSU Tank 3	White	Ethanol	Wet Scrubber	57	22.3	C	0.66	0.055	7
1991	Gallo	White	Hydrogen sulfide	None	57	21.6	C	0.017	0.0014	9
1991	Gallo	White	Isoamyl alcohol	None	59	20	C	0.034	0.0028	11
1991	Gallo	White	Isoamyl alcohol	None	56	20	C	0.072	0.0060	11
1991	Gallo	White	Isoamyl alcohol	None	57	21.6	C	0.078	0.0065	11
1991	Gallo	White	Isobutyl alcohol	None	57	21.6	C	0.0095	0.00079	11
1991	Gallo	White	Isobutyl alcohol	None	56	20	C	0.010	0.000*84	11
1991	Gallo	White	Isobutyl alcohol	None	59	20	C	0.0052	0.00043	11
1991	Gallo	White	Methanol	None	57	21.6	C	0.0032	0.00027	11
1991	Gallo	White	Methanol	None	56	20	C	0.009	0.00078	11
1991	Gallo	White	Methanol	None	59	20	C	0.011	0.00088	11
1991	Gallo	White	n-Propanol	None	59	20	C	0.019	0.0016	11
1991	Gallo	White	n-Propanol	None	56	20	C	0.036	0.0030	11
1991	Gallo	White	n-Propanol	None	57	21.6	C	0.029	0.0024	11

^aEmission units are in terms of weight per volume of fermented juice produced; 1 lb/1,000 gal = 11.98 g/hl.

^bThese values are based on the amount of ethanol in the condensate collected from the adsorber. No collection efficiencies were determined so these values represent only the quantity removed by the control device and understate the actual uncontrolled emissions.

^cThese values have been calculated using collection efficiencies to estimate emissions.

^dThese values not used because fermentation temperature exceeded the temperatures normally used for white wine fermentation.