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CALIFORNIA AIR RESOURCES BOARD

TECHNICAL REPORT

ARB/SS-81-004

Alcohol Emissions from a Fermentation Tank

March 19, 1981

CALIFORNIA AIR RESOURCES BOARD

STATIONARY SOURCE DIVISION
1102 Q STREET, SACRAMENTO, CA 95814

David F. Todd
Dean C. Simeroth
Peter K. Ouchida

State of California

AIR RESOURCES BOARD

Alcohol Emissions from a Fermentation Tank

March 19, 1981

Issue Date: March 19, 1981

Report No. SS-81-004

Alcohol Emissions from a Fermentation Tank

Engineering Evaluation Report C-8-050, Part 2

By

Stationary Source Control Division

State of California

Air Resources Board
1102 Q Street
Sacramento, California
95814

Alcohol Emissions from a Fermentation Tank

This report presents an evaluation of emissions based on data from tests performed by the ARB staff, local districts or commercial laboratories. The data have been reviewed by the staff and are believed to be accurate; however, emissions are usually affected by process variables which are sometimes not apparent to the test personnel. The data should not, therefore, be necessarily considered typical of a specific source or industry unless the effects of such variables are taken into account.

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ALCOHOL EMISSIONS FROM A WINERY FERMENTATION TANK

SUMMARY

Wine is made by fermenting fruit juice in a large tank. As the juice ferments, it releases carbon dioxide gas through a vent or vents in the roof of the tank. Ethanol is removed from the liquid phase by the upward passage of the carbon dioxide, and the released ethanol vapor may react in sunlight to form photochemical oxidant. Ethanol has been classified by the ARB as being highly reactive. To determine the extent of emissions from a fermentation tank, the Air Resources Board (ARB) conducted a test of a 600,000 gallon steel fermentation tank at Gallo's Fresno winery September 20-21, 1978. The test was performed at the request of the Fresno County Air Pollution Control District (APCD) and the ARB Planning Division.

From the test data it was determined that this tank emitted an average of 1.87 pound of ethanol per hour during the 24-hour test. This number appears to be a minimum emission value for the following reasons:

-- The test was performed near the beginning of the two-week fermentation period; previous studies indicate that the greatest rate of emissions occur near the middle or the end of the period.

-- The figure of 1.87 pounds per hour represents average emissions over a 24-hour period; emissions during the first 2-1/2 hours were lower due to tank stabilization.

-- A white wine was in the tank, and white wines are fermented at lower temperatures than reds. This lower fermentation temperature may be expected to result in a lower alcohol loss rate.

Important additional data on emissions from wine fermentation tanks can be gained if:

-- A red wine is tested.

-- Wines with different bases are tested.

-- Tanks in the 10,000-gallon range are tested. (Many such tanks are in use.)

-- Test are conducted later in the fermentation period, or even better, at intervals during the entire fermentation period.

Additional sections of the report point out that:

-- Meteorological conditions in the Fresno area are favorable for the development of photochemical oxidant (smog).

-- Alcohol vapors of 1,000 ppm may represent a health hazard.

-- Hydrogen sulfide and mercaptans may also be emitted as a result of wine-making.

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ALCOHOL EMISSIONS FROM A FERMENTATION TANK

I. INTRODUCTION

Wine is made by fermenting fruit juice in a vessel open to the atmosphere. As the juice ferments, it releases carbon dioxide gas through a vent or vents in the tank roof. Ethanol vapors generated by fermentation are entrained with the carbon dioxide, and these vapors react in sunlight to form photochemical oxidant. Ethanol has been determined to be a highly reactive organic compound by the ARB. Oxidant is a pollutant for which a national ambient air quality standard exists. In 1978, this standard (0.12 ppm) was exceeded in Fresno County on 49 days; in the city of Fresno itself, the standard was exceeded on 39 days. Under the Clean Air Act, Fresno County is required to meet the national ambient air quality standard by 1987.

One strategy the Fresno County Air Pollution Control District (APCD) is considering to achieve the standard is to reduce organic emissions (in the form of ethanol vapors) from winery fermentation tanks. To assess the usefulness of this strategy, it is necessary to determine the magnitude of these emissions. To make this determination, an emission test was conducted on a fermentation tank at the Gallo winery at Fresno. The test was conducted by the Engineering Evaluation Branch of the Stationary Source Control Division, California Air Resources Board (ARB).

The tank tested is a white, cylindrical, welded, epoxy-lined, steel tank (number 6033), with a domed roof and built to API 650 specifications. The height of the straight wall is 40 feet, and the diamter is 50 feet; the capacity is 637,776 gallons. Height of the liquid level in the tank was about 37 feet, and the tank contained 569,000 gallons of grape juice that was fermenting into a blending white wine. The tank itself was not in a building but is exposed directly to the weather. The 24-hour test was conducted on September 20-21, 1978.

As was pointed out, the juice in the tank was fermenting to a white wine, as opposed to a red; also the tank was tested near the beginning of the fermenting period. For these reasons, which are elaborated on later in this report, the emission rates determined by the source test probably represent the minimum amount of alcohol this tank is likely to emit during the fermentation of any wine.*

Test results are discussed in the next section of this report. Other sections contain material on wine making; meteorological aspects of the air pollution problem in the Fresno area; the health effects of ethanol; and a discussion of a method that might be used to compute emissions from fermentation when the temperature of the fermenting juice is known.

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*Note: For the purposes of this reoort, the word alcohol will refer to ethanol (C_2H_5OH) only.

II. DISCUSSION OF TEST RESULTS

A. MEASURED EMISSIONS

The 24-hour test of the Gallo fermentation tank showed that the tank emitted an average of 1.87 pounds per hour of ethanol or about 0.2 percent of the alcohol that was formed by fermentation during the 24-hour period. The test results and the results of other studies on alcohol losses are presented in Table 1 and Figure 1. Figure 1, relating alcohol lost and temperature, should provide a fairly good way of predicting alcohol emissions, provided the user can determine the alcohol available. The data of Table 1 and Figure 1 include the measured alcohol loss found in this test. Figure 2 represents the emission and operating data from the test as a function of fermentation time. The rate of alcohol emissions can be seen in Figure 2G.

B. FACTORS AFFECTING TEST RESULTS

The measured emission of 1.87 pounds per hour is considered to be a minimum value for the following reasons.

1. Test Timing with Respect to Fermentation Period

   The test was conducted within three days of the start of fermentation period, a period that normally takes two weeks to complete for white wine. According to previous studies and as discussed in Section IV, the greatest alcohol loss should occur either during the middle (when there is supposed to be the greatest fermentation activity) or near the end of fermentation (when there is the greatest concentration of alcohol in the wine). In any event, it would appear the test did not occur during a period of maximum ethanol emissions.

TABLE 1

Summary of Selected Studies on Alcohol Loss

	Study	Alcohol Content	Initial Sugar	Fermentation Temperature	Alcohol Lost*
1.	Mathieu and Mathieu		18%	95°F (35°C)	1.5%
2.	Flanzey and Boudet		18.2	95 (35)	1.2
3.	"		18.2	68 (20)	0.65
4.	"		18.2	43 (5)	0.17
5.	Warkentin and Nury	4.6-10.6%range		86 (30)	1.17
6.	"	(7.6% avg.)		80.6 (27)	0.83
7.	Zimmerman, Rossi, and Wick		21	79.7 (26.5)	0.84
8.	"		16	79.7 (26.5)	0.70
9.	Air Resources Board (using Warkentin and Nury formula)	3-4% range		52 (11)	0.3
10.	Air Resources Board (based on measured alcohol loss)	(3.5% avg.)		52 (11)	0.2

* as % of total available over the entire test or fermentation period

FIGURE 1

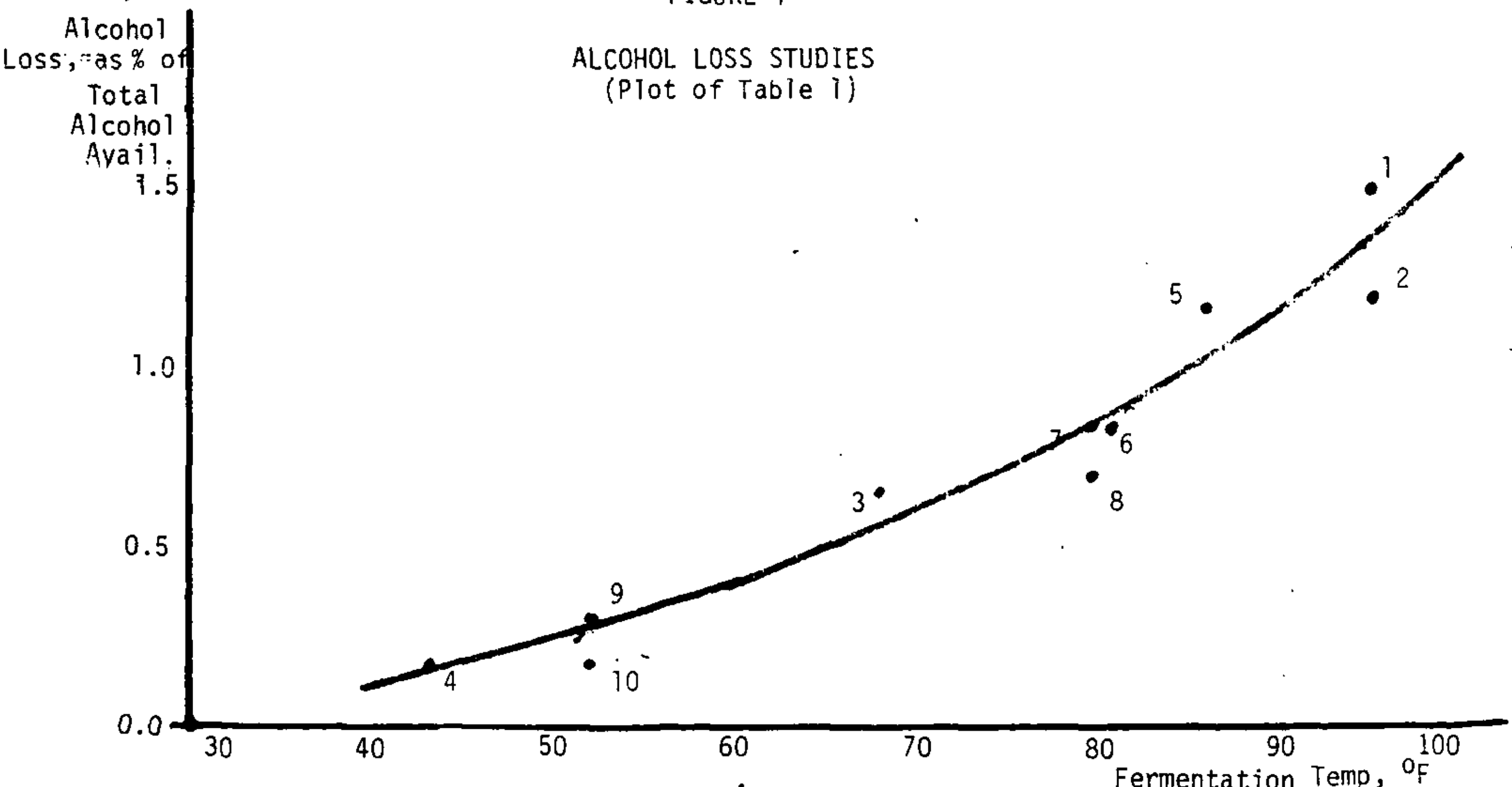


FIGURE 2

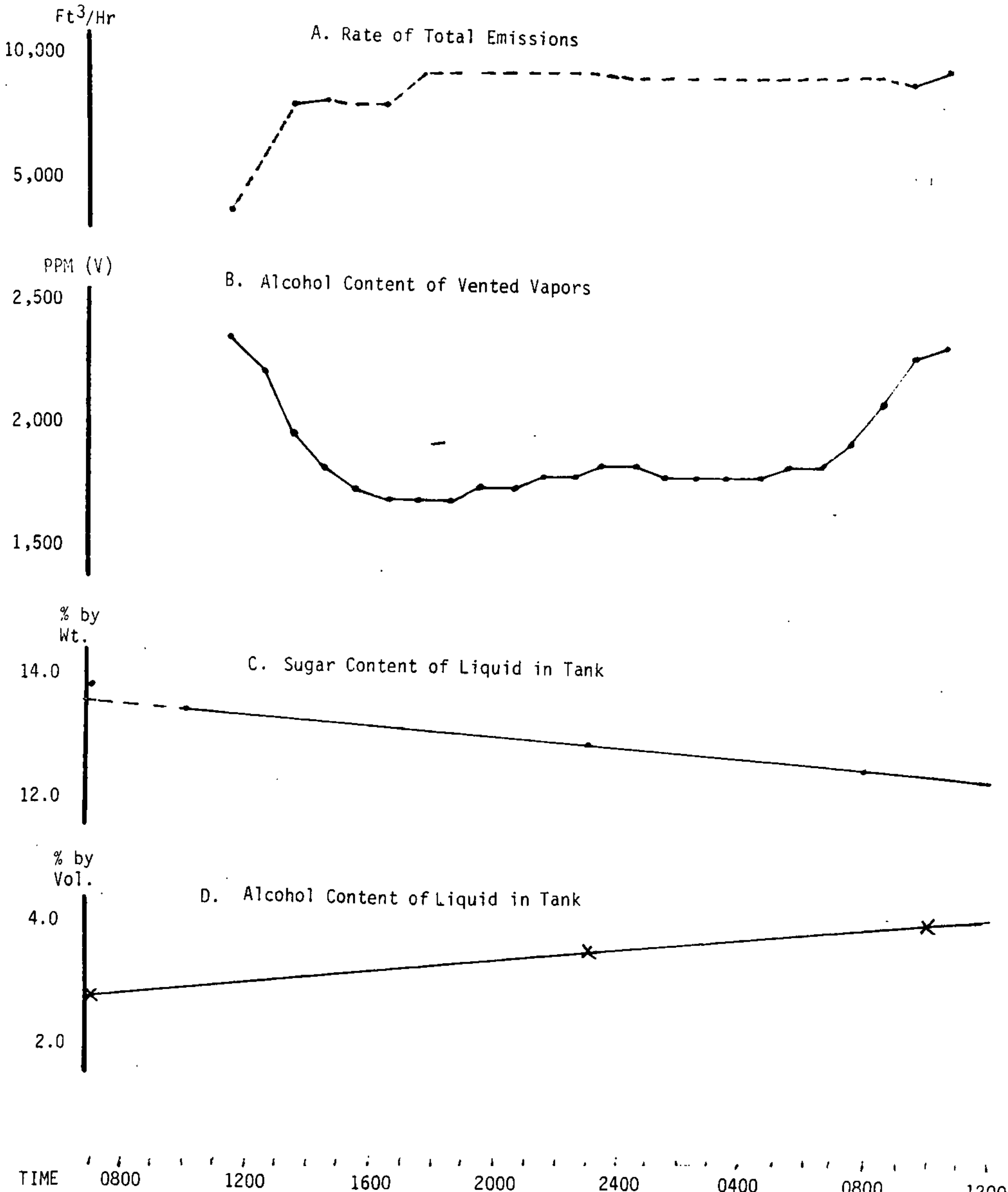
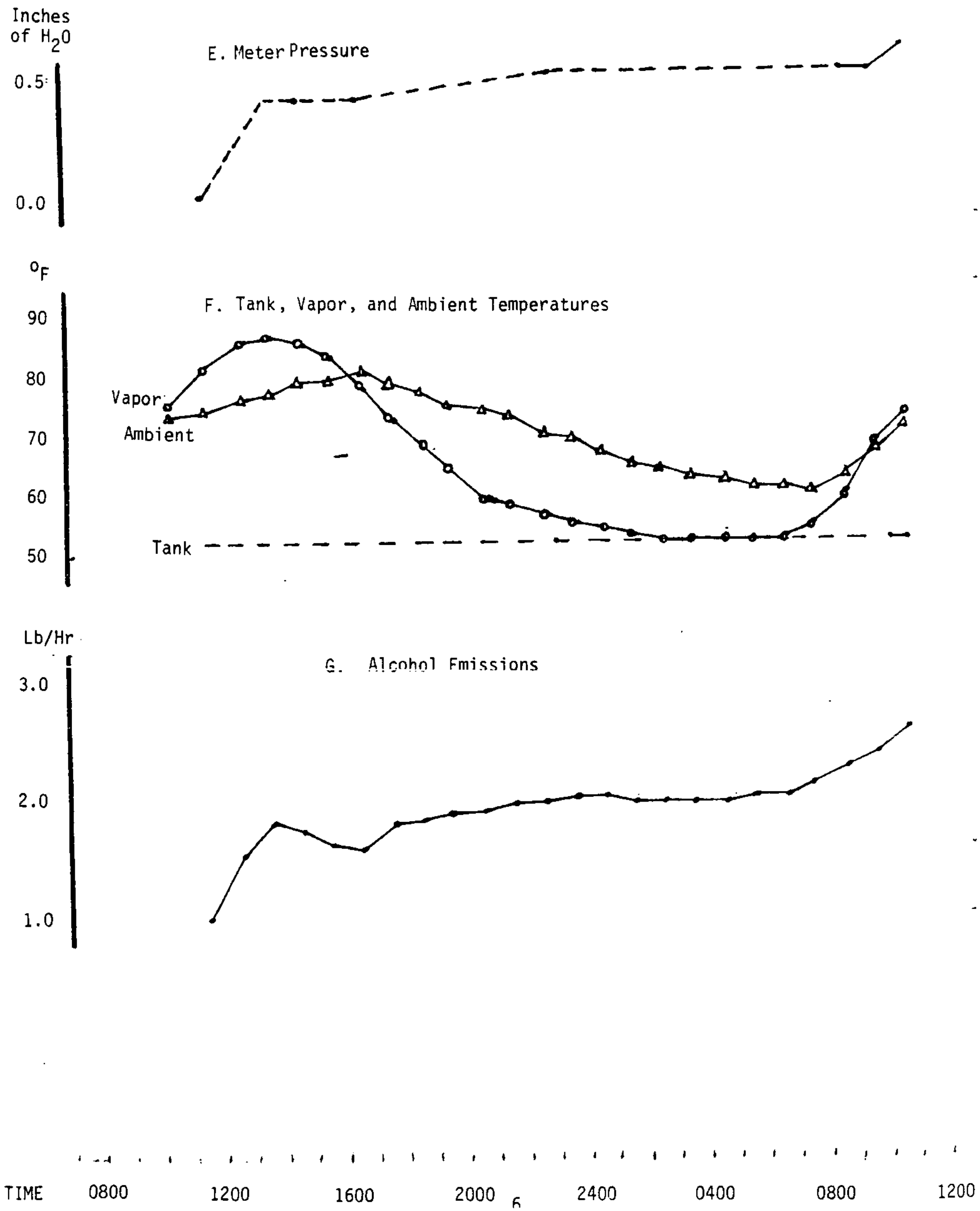

Ft3/Hr
10,000
5,000
A. Rate of Total Emissions
PPM (V)
2,500
2,000
1,500
B. Alcohol Content of Vented Vapors
% by Wt.
14.0
12.0
C. Sugar Content of Liquid in Tank
% by Vol.
4.0
2.0
D. Alcohol Content of Liquid in Tank
TIME
0800
1200
1600
2000
2400
0400
0800
1200

FIGURE 2 (Cont.)



2. Initial Pressure Stabilizing Period

A second factor tending to minimize the average measured emissions is that measurements made during an initial stabilizing period were included in the overall test average, even though these emissions were significantly lower. This stabilizing period included at least the first 2-1/2 and possibly the first 12 hours of testing. It is the time required for the pressure within the tank to equilibrate following installation of the turbine meter, used to measure gas flow, on the vent port flange. The turbine meter and adaptor effectively reduced the exit diameter for the escaping fermentation gases from 26 inches to 6 inches. This reduction caused the tank to pressurize until the rate that the gas emitted from the tank equaled the rate at which it was being evolved from the liquid. Therefore, as shown in Figure 2A, it took at least 2-1/2 hours before the flow rate for the 6-inch exit equaled that for the original 26-inch exit.

Also, at this time while the flow rate out of the tank was low, the alcohol concentration in the vented vapors was high. As the flow rate out of the tank increased during the stabilizing period, the alcohol concentration of the vented vapors decreased.

3. White Wine Versus Red Wine

Another factor working toward minimizing emissions is that the test was made during production of a white wine, which is fermented at a lower temperature to enhance its flavor. This lowered temperature also lowers the fermentation activity thus reducing alcohol loss. This relationship can be seen in Figure 1. This, of course, also results in a longer fermentation time (about two weeks for white wines as opposed to about one week for red wines). In addition, a white wine is fermented without a pomace cap. The pomace cap generally consists of the grape skins and other solids needed to color wine red. The pomace cap, coincidentally, may also enhance alcohol entrainment.

4. Possibility of a Leak During the Test

A potential cause of reduced emissions concentration was a "leak" that "seemed" to have appeared in the grab sample line. We say "seemed" because the analytical results received from the Air and Industrial Health Laboratory (AIHL) indicated an emission effluent of 15.5% oxygen and 21.5% carbon dioxide, which is not expected from a process that is essentially a carbon dioxide generator. Assuming the oxygen was from the atmosphere, calculations were made adding in a weighted value for the other atmospheric gases. The result tended to support the thought that there may have been a leak. However, high concentrations of carbon dioxide can permeate through Scotch-pak bags used to obtain the grab samples. In either case, the reported concentration of CO_2 may be low.

As a control check a mathematical analysis of the hydrocarbon analyzing system data was undertaken and compared with known results, such as the change in alcohol content within the tank, and historical information from other studies (see Appendix III, Table I, and Figure 1).

The results seemed to assure there were no leaks in the hydrocarbon analyzing system.

5. Comparison with API Estimates

The results of the ARB test were compared with emission estimates based on American Petroleum Institute (API) equations (see Appendix II). These equations are listed in API Bulletin 2523, Petrochemical Evaporation Loss from Storage Tanks, and relate emissions with the physical properties and operating conditions of the tank. This comparison was undertaken to determine the applicability of the API equations to emissions from fermentation tanks. The API breathing loss equation gives an estimate of 50 pounds per day whereas the ARB measured emission rate was 45 pounds per day.

III. SUGGESTED AREAS FOR FURTHER STUDY

A. TESTING A RED WINE

The results of the ARB test fall in the low temperature area in Table 1 and Figure 1. While there is a previous study that tends to agree with the ARB test results at the low end of the curve, there are no ARB data to reinforce the validity of the upper or higher temperature end of the curve. This is the end of the curve associated with red wines which have higher fermentation temperatures, and a majority of the earlier studies were with red wines. Also, except for the ARB data, all the information for Table 1 dates from before 1964, some even from 1938. Therefore, to verify these earlier data, a test of red wine production would either correct or reinforce the information contained in previous studies. Such a test should encompass the entire fermentation period of a red wine (about 1 week) so that the rate of carbon dioxide and alcohol emissions can also be characterized.

B. TESTING OF DIFFERENT WINE BASES

If further testing on a red wine confirms previous tests, emphasis should then be placed on testing white wines. In recent years, the consumption of white wines has increased to the extent that white varietal wine grapes are considered scarce. Emissions from wines produced by the fermentation of pears and apples should also be checked because these fruits are replacing grapes as the bases of some wines and may have a different sugar content or rate of fermentation that can affect ethanol emissions. (The undisputed single, largest selling wine made in California, Gallo's Thunderbird, is a pear base wine.)

C. TESTING OF A SMALLER TANK

A test of a tank in the 10,000 gallon range would be useful. The majority of commercial producers in the state are much smaller than Gallo, and their tanks tend to measure in the tens-of-thousands and thousands-of-gallons range as compared to the large tank tested. However, it should be pointed out that some of the data for Figure 1 came from laboratory work and of necessity required the use of small fermentation tanks, and little deviation from the field was found.

D. TESTING LATER IN THE FERMENTATION PERIOD

Because the tank tested seems to have been tested during a period of low alcohol emissions, a test during the middle and the end or, even better, the entire fermentation period might be warranted for a truer prediction of the tank's emission pattern.

IV. WINE MAKING

A. ALCOHOLIC CONTENT OF WINE

The concentration of alcohol in wine is based upon the sugar content of the grapes, extent of fermentation, and losses or additions of alcohol during fermentation, treatment, and storage.

Sugar content derives from the grapes and the pomace cap. The grapes contain 15-25 percent sugar, and the soluble solids in the pomace cap may contain 90 percent sugar. One percent sugar yields 0.55 percent alcohol by volume. In general, the theoretical chemical reaction for converting sugar to alcohol is:

$$\underset{\text{(sugar)}}{C_6H_{12}O_6} \rightarrow 2\ \underset{\text{(ethanol)}}{C_2H_5OH} + 2\ CO_2$$

According to the above equation, sugar should yield 51.1 percent alcohol by weight, but in reality sugar yields about 47 percent retained alcohol by weight. The rest of the sugar goes into lost alcohol, or other products such as glycerin, hydrogen sulfide, and methyl and ethyl mercaptans (see tables 2 and 3 from the book Table Wines.)

According to Table Wines, the concentration of retained alcohol and the nature and concentration of by-products depends upon temperature as well as yeast activity and strain, acidity, and other factors. Lower fermentation temperature yields a higher concentration of alcohol as well as producing a greater fruitiness and freshness of flavor.

TABLE 2

PRODUCTS OF ALCOHOLIC FERMENTATION, THEORETICAL AND ACTUAL, AND WITH THREE YEAST TYPES
PERCENTAGE OF FERMENTABLE SUGAR TRANSFORMED

Product	Theo-retical	In Industrial Fermentation[a]	Pasteur Data	With Champagne Wine Yeast	With Rkatsateli Wine Yeast	With Steinberg Wine Yeast
Alcohol	51.1	48.4	48.4	47.86	48.22	48.07
Carbon Dioxide	48.9	46.5	46.6	47.02	47.61	47.68
Actaldehyde	0.0	00.00 - 0.08	—	0.01	0.04	0.02
Acetic Acid	0.0	0.05 - 0.25	—	0.61	0.50	0.65
2, 3 - Butylene Glycol	0.0	—	—	0.06	0.09	0.10
Glycerin	0.0	2.5 - 3.6	3.2	2.99	2.61	2.75
Lactic Acid	0.0	0.0 - 0.2	—	0.40	0.28	0.40
Succinic Acid	0.0	0.5 - 0.7	0.6	0.020 - 0.045	—	0.015 - 0.053
Furfural	0.0	trace	—	—	—	—
Fusel Oil (higher alcohols)	0.0	0.5 - 0.35	—	—	—	—
Yeast (dry weight)	0.0	—	1.2	0.55	0.55	0.57

[a]Calculated on basis on Gay-Lussac's equation.
Sources of data: For industrial fermentations, Rahn (1932); for Pasteur data, Hewitt (1928); for type of wine yeast, Gvaladze (1936).

Reprinted from Table Wines; The Technology of Their Production (1970)

Table 3

Formation of Hydrogen Sulfide and Mercaptans During Wine Fermentation and Aging (Results in mmg per liter)

Days	Hydrogen Sulfide	Mercaptans
0	3	0
2	41	10
6	126	7
9	480	27
13	398	86
31	300	72
43	260	120
62	210	230
93[a]	73	120
180	21	150
270	30	162

[a]Date of first separation of sediment and wine.

B. FERMENTATION

Fermentation is the process that makes wine from the juices of fruits such as grapes, apples, and pears. Fermentation is the anaerobic (without free oxygen) breakdown of organic compounds by the action of microorganisms or their extracts, to products simpler than the starting substrate. With wine, this breakdown is caused by yeast. The yeast provides complicated enzymes that create alcohol, carbon dioxide gas, glycerin and other products from the sugar in the juice. The yeast acts biologically as a catalyst, and theoretically the process could be done chemically, without yeast, but would probably be less efficient and would require more drastic conditions for completion.

For centuries, grape juice has been fermented into wine, but it was not until the ninteenth century that the fermentation process was understood and explained by Louis Pasteur. Before then, the yeast that grows naturally on the skin of the fruit generally caused the fermentation process. Any yeast, including bread yeast, can be used to ferment the juice into wine; however, varying yeasts will cause varying tastes in the wine, so most wineries prefer using their own laboratory grown yeasts. Other yeasts, such as those occurring on the fruit or those that are air-borne, are considered contaminants. Thus, any material, such as the juice, anti-foam agents, or air, is sterilized before entering the fermentor, as is the fermentation tank itself. (Because of the high volume of CO_2 exiting the large test tank, there is little chance of contaminated air entering a fermentation tank.)

According to Table Wines and the Encyclopedia of Chemical Technology, SO_2 gas is often used at a rate of 50-200 mg/l of storage as the sterilizing agent to prevent growth and competition of undesirable organisms in the fermentation tank. Most of the SO_2 is combined with other materials or vented with the escaping air from the fermentation tanks as the tank is filled with juice.

There are a number of ways to obtain SO_2 gas. Probably the best and most common in recent years is to use liquified SO_2, although salts that produce either SO_2 or aqueous solutions of SO_2 may also be used. The problem with SO_2 is that not only is it an air pollutant itself, but if in its formation there is any free sulfur created (or free sulfur in the juice), then hydrogen sulfide and mercaptans (which are also air pollutants) can be formed. Table 3, which shows emissions of hydrogen sulfide and mercaptans, was adapted from Table Wines and is the work of Cantarelli who followed the formation of hydrogen sulfide and mercaptans during fermentation and aging. As Table 3 indicates, the production of mercaptans does not significantly increase until after the fermentation period (about 1 week long) and at that time the wine is stored in a closed container where the mercaptans are not an air pollution problem.

Besides sterilizing, SO_2 also increases the extraction of color and soluble material from the skins.

The fermentation process has a fairly narrow optimum temperature range. However, the process also generates a significant amount of heat so the fermenting juice needs to be continuously cooled. Because of this optimum temperature range, fermentation time and temperature at different wineries should be similar, about 1 week at around 70°–80°F for reds and about 2 weeks at about 55°F for whites. Also, fermentation tanks are only 70 percent to 90 percent full during fermentation. (They are filled after fermentation if they are also used for storage as is often the case with Gallo's tanks.)

C. ALCOHOL LOSSES

A number of studies have been made of alcohol loss because of entrainment with escaping carbon dioxide (CO_2) during fermentation. The losses reported either by calculation or by actual measurement range from less than 0.1 percent to over 10 percent. Some of the more reliable measurement studies have been listed in Table 1 and plotted in Figure 1 -- along with the ARB test at Gallo. The amount of alcohol lost during fermentation is apparently economically unimportant to most wine makers.

From Figure 1 it can be seen that the amount of alcohol entrained with the carbon dioxide is largely proportional to the temperature of the fermentation tank. As an example, losses at 95°F are about double those at 80°F. However, Zimmerman, Rossi, and Wick have determined that alcohol entrainment also increases with the alcohol concentration within the wine, agitation of the fermenting liquid, the presence of a pomace cap, and the rate at which carbon dioxide is produced. Also, Zimmerman, Rossi, and Wick believe the maximum alcohol loss occurs during the middle of fermentation because they believe there is a maximum of activity at that time.

V. METEOROLOGICAL CONDITIONS IN THE FRESNO AREA

The climate and meteorological conditions of the San Joaquin Valley -- including Fresno County -- are favorable for the accumulation of air pollutants and the production of oxidants. At the present, few air pollutants are emitted by large industries, for the area is dominated by agricultural and light industrial operations. But light industry, agriculture, and transportation do contribute pollutants, and some of these sources are increasing in number, or have increased rapidly in recent years, especially in Fresno County. One such growing industry is the wine industry.

As determined by County estimates and ARB Air Quality Maintenance Planning estimates, volatile organic emissions from wineries in the form of ethanol are significant, especially in terms of tons per day (see Tables 4 and 5). Fermentation is considered to be the major source of ethanol (a highly reactive organic compound) and fermentation along with the grape harvest and crush and distillation, covers only about 16 weeks during late summer and fall. By coincidence, late summer and early fall are favorable for smoggy weather in Fresno County because of the great abundance of sunny days and warm temperatures.

According to ARB meteorological data, the summertime wind direction in Fresno County is typically from the west-northwest, so Gallo's Fresno winery tends to be downwind of the city of Fresno. However, there are numerous wineries up and down the San Joaquin Valley, making it one of the largest wine producing areas in the state. Many of these wineries are upwind of Fresno County. Because

Table 4

Estimated Hydrocarbon Emissions
for Fresno County

1976

Area Sources	County Tons/Yr	County Tons/Day	AQMP Study Area Tons/Yr	AQMP Study Area Tons/Day
1. Pesticides	1821	4.99	456	1.25
2. Chemical	29	.08	29	.08
3. Surface Coating	634	1.74	634	1.74
4. Road Construction	127	.35	127	.35
5. Wood Processing	5	.01	5	.01
6. Incinerators	<1	<.01	<1	<.01
7. Other Waste Burning	40	.11	40	.11
8. Petroleum Marketing	813	2.23	609	1.67
9. Aircraft	53	.15	53	.15
10. Railroads	37	.10	18	.05
11. Roofing	42	.65	32	.49
12. Architectural Coatings	1606	4.40	1205	3.30
13. Dry Cleaning	639	1.74	445	1.22
14. Degreasing	112	.31	84	.23
15. Wineries	918	18.36*	459*	9.18
16. Industrial Fuel Combustion	10	.03	7	.02
17. Commercial Fuel Combustion	10	.03	7	.02
18. Domestic Fuel Combustion	19	.05	15	.04
Subtotal	6912	35.3	4225	19.92

* Emissions occur mainly during late summer and early fall when fermenting occurs.

TABLE 5

COUNTYWIDE EMISSION PROJECTIONS: Reactive Hydrocarbons (Tons/Day)

	Area Sources	1976	1980	1982	1985	1987	1990	1995
1.	Pesticides	4.99	5.29	5.44	5.64	5.74	5.99	6.34
2.	Chemical	.08	.09	.10	.12	.13	.14	.17
3.	Surface Coating	1.74	2.00	2.14	2.37	2.52	2.77	3.22
4.	Road Construction	13.58	14.26	14.67	15.35	15.75	16.43	17.52
5.	Wood Processing	.01	.01	.01	.01	.02	.02	.02
6.	Incinerators	.01	.01	.01	.01	.01	.01	.01
7.	Other Waste Burning	.11	.12	.12	.12	.13	.13	.14
8.	Petroleum Marketing	2.23	2.34	2.41	2.52	2.59	2.70	2.88
9.	Roofing	.07	.07	.08	.08	.08	.08	.09
10.	Architectural Coatings	4.40	4.62	4.75	4.97	5.10	5.32	5.68
11.	Dry Cleaning	1.45	1.52	1.57	1.64	1.68	1.75	1.87
12.	Degreasing	.31	.36	.38	.42	.45	.49	.57
13.	Wineries	11.39	12.07	12.42	12.87	13.10	13.67	14.47
	Subtotal	40.36	41.75	44.09	46.11	47.29	49.49	52.97

it is possible for pollution from the San Francisco Bay Area to impact Fresno, it is also reasonable to believe that ethanol emissions from these wineries could also impact on Fresno. In addition, it is just as likely that Gallo and nearby wineries may affect the air quality in Tulare and Kern Counties as well as some valleys and lower elevations of the Sierras.

VI. HEALTH EFFECTS OF ETHANOL

The minimum identifiable odor limit for ethanol (CH_3CH_2OH) is 350 ppm. The vapor threshold limit -- that limit where 8 hours of inhalation may result in undesirable effects -- is 1,000 ppm. Exposures of 5,000 to 10,000 ppm may result in eye irritation and irritation of mucous membranes of the upper respiratory tract. If exposures of levels of 5,000 to 10,000 ppm are continued for an hour or longer, drowsiness or stupor may result (see Table 6). Concentrations of this order have an intensely disagreeable odor, but most people can become acclimatized to exposure in a short time.

Intoxication due to inhalation is rare, and there is no evidence that inhalation will cause cirrhosis of the liver. Also, ethanol is not a cumulative poison; it completely oxidizes in the body to form carbon dioxide and water.

The ARB has listed ethanol as a Class 3, highly reactive, organic compound (see Table 7). Reactive organics are those that have been determined to react photochemically with nitrogen oxides to produce oxidants. Oxidants can cause haze, eye irritation, harmful human health effects, and, importantly to agricultural areas, plant damage.

TABLE 6

Ethyl Alcohol Vapor Concentration and Its Effects in Humans

Concentration		
mg/l of air	ppm/vol. in air	Effects in Humans
10 - 20	5,300 - 10,640	some transient coughing and smarting of the eyes and nose, which disappear after 5-10 min; not comfortable but tolerable
30	15,960	continuous lacrymation and marked coughing; could be tolerated but with discomfort
40	21,280	just tolerable for short periods
> 40	> 21,280	intolerable and suffocating for even short periods

Source: Encyclopedia of Chemical Technology (1972)

The above concentrations are unlikely to occur outside of facilities dealing with ethanol and therefore are mainly an industrial safety problem

TABLE 7

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Reactivity Classification of Organic Compounds

Class I (Low Reactivity)	Class II (Moderate Reactivity)	Class III (High Reactivity)
C_1 - C_2 Parafins	Mono-tert-alkyl-benzenes	All other aromatic hydrocarbons
Acetylene	Cyclic Ketones	
Benzene	Alkyl acetates	All Olefinic hydrocarbons (including partially halogenated)
Benzaldehyde	2 - Nitropropane	
Acetone	C_3 + Paraffins	Aliphatic aldehydes
Methanol	Cycloparaffins	Branched alkyl Ketones
Tert-alkyl alcohols	n-alkyl Ketones	Cellosolve acetate
Phenyl acetate	N-methyl pyrrolidone	Unsaturated Ketones
Methyl benzoate	N, N-dimethyl acetamide	Primary & secondary C_2 + alcohols (incl. ethanol)
Ethyl Amines	Alkyl Phenols*	
Dimethyl Formamide	Methyl phthalates**	Diacetone alcohol
Perhalogenated Hydrocarbons		Ethers
		Cellosolves
Partially halogenated paraffins		Glycols*
Phthalic Anhydride**		C_2 + Alkyl phthalates**
Phthalic Acids**		Other Esters**
Acetonitrile*		Alcohol Amines**
Acetic Acid		C_3 + Organic acids + di acid**
Aromatic Amines		C_3 + di acids anhydrides**
Hydroxyl Amines		Formin** (Hexa methylene-tetramine)
Naphthalene*		
Chlorobenzenes*		Terpenic hydrocarbon
Nitrobenzenes*		Olefin oxides**
Phenol*		

*Reactivity data are either non-existent or inconclusive, but conclusive data from similar compounds are available; therefore, rating is uncertain but reasonable.

**Reactivity data are uncertain.

VIII. CAN EMISSIONS BE COMPUTED BASED ON GRAPES?

For this test, no attempt was made to relate emissions to the variety or condition of the grapes. Our reasons are as follows. The alcohol content of wine is based upon a number of factors including the sugar content of the grapes. Sugar content in turn is greatly influenced by many factors, among them sunshine and rain. Thus, the sugar and, therefore, the alcohol content will vary from year to year. However, varieties of grapes also have different sugar content, so the quality of the final product can be made consistent throughout the years by mixing appropriate varieties. Thus, calculating emissions for different types of grapes may be extremely difficult. So, rather than "pounds of alcohol per ton of grapes", a better expression seems to be "pounds of ethanol per hour" for specific tanks or "percent of total alcohol available" as used by the industry in general.

However, to calculate emissions relative to weight of crushed grapes, the following information may be used. Twelve to 18 pounds of grapes yield 4 to 6 bottles (fifths) of wine. That means about 35 tons of grapes yields 5,500 gallons.

For product quality the minimum alcohol content is 9 percent by volume; the maximum for table wines, by law, is 14 percent with a 1.5 percent deviation allowed. By state law, sugar cannot be added to table wines (this increases alcohol content during fermentation), so these numbers, in general, are probably good throughout the industry in California for table wines. Thus, as an example, if the above 5,500 gallons has an alcohol content of 12 percent by volume, then about 660 gallons of the wine is alcohol. If this wine had been fermented at 80°F, then the alcohol loss is probably 5.3 gallons (665 total gallons available x 0.8 percent from Figure 1) or 34.5 pounds (6.533 pound per gallon, from Appendix V, Table 3). This means that the fermentation of 35 tons of grapes under the above conditions could emit 34.5 pounds of ethanol or about 1 pound per ton of grapes.

The above example, however, can be compared with the test of Gallo by increasing the gallonage in the example 100 times. If that were done, then the alcohol emissions based upon one pound per ton of grapes would be 3,500 pounds. On the other hand, given the emission rate of about 2 pounds per hour from the source test and a fermentation time of 15 days, the Gallo tank seems to emit only about 720 pounds. While the grape tonnage should be about the same for both, the difference between 720 pounds and 3,500 is substantial, and yet each emission is valid for its given conditions. The main reason for this emission difference is that the emissions from the source test are based on a 52°F fermentation temperature and the above example is based on an 80°F fermentation temperature. Other reasons may include conditions affecting the source test stated in Section II B of this report, but now we have a very good illustration of the problem involved using tons of grapes as the basis for emissions.

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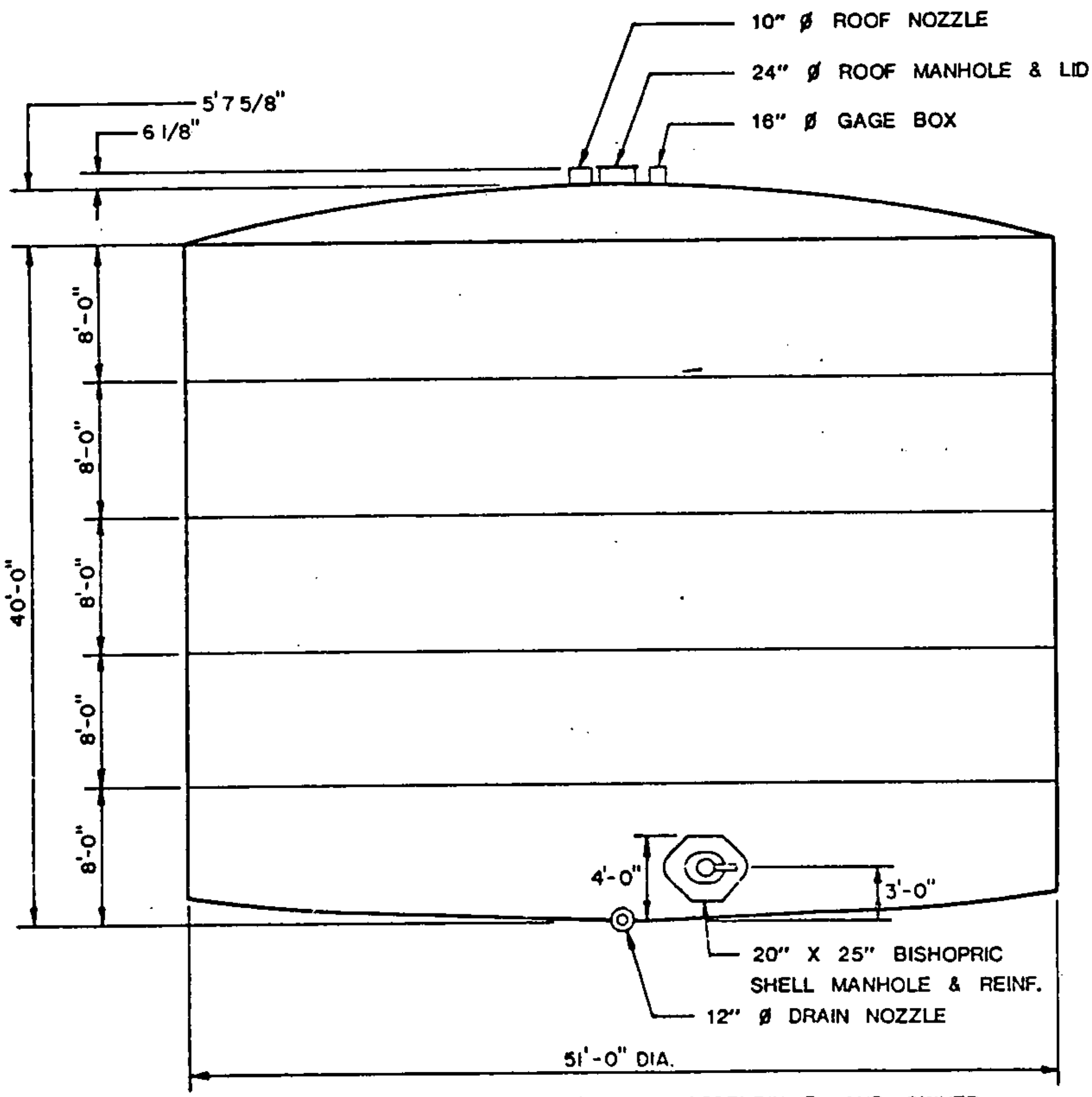
APPENDIX I

Test Tank Schematic

GALLO

600,000 GALLON STEEL FERMENTATION AND STORAGE TANK



BUILT TO CONFORM TO API 650, APPENDIX D, AND OWNER.

ELEVATION

NOT TO SCALE

APPENDIX II

API Equations and Estimates

Alcohol Loss Calculations

Based on API Breathing Loss. Equations in API Bulletin 2523

$$L = \frac{24}{1000} \left(\frac{P}{14.7 - P}\right)^{0.68} D^{1.73} H^{0.51} T^{0.50} F_p C$$

L = Breathing loss in barrels per year

L = L x 42 x 0.13368 x 49.4 = L x 277.36 = loss in lb. per year

P = True vapor pressure 2.345 psia

D = Tank diameter = 50'

H = Average outage (ht. of vapor space) including roof correction = 4.72'

T = Avg. daily temp. differences ^{0}F = 80 - 60 = 20^{0}F

F_p = Paint factor = 1.00 (tank white & paint in very good condition)

C = small tank factor = 1.00 (tank diameter greater than 30')

$$L = \frac{24 \times 277.36}{1000} \left(\frac{2.345}{14.7-2.345}\right)^{0.68} 50^{1.73} \; 4.72^{0.51} \; 20^{0.50}$$ = 18,450 lb/yr. = 50 lb/day

(measured loss was 45 lb/day)

Note 1: API equations are for standard oxygen/nitrogen atmosphere and wine fermentors have a CO_2 atmosphere.

Note 2: 18,450 lb/yr. of emissions is a convenience number fitted to the API equation and in no way reflects actual or estimated emissions from a single fermentor.

APPENDIX III

Check of Measured Data

Check of ARB Data

A. Relating ARB measured CO_2 volume out of tank to Gallo's measured change in alcohol content of tank.

Total gas out turbines (for 24 hr.) = 204,220 ft^3

1) Assume 100% CO_2 measured by turbine

2) Assume CO_2 density = 0.1236 lb/ft^3 @ turbine

CO_2 0.1236 lb/ft^3 x 204,220 = 25,250 lb of CO_2 produced during test

3) Assume alcohol produced @ 1 mole (46 lb) alcohol/1 mole (44 lb) CO_2

Alcohol produced during 24 hr. test:

46/44 x 25, 250 lb CO_2 = 26,400 lb of alcohol

Alcohol % (V) produced during 24 hr. test:

$$\frac{\text{26,400 lb of Alc x 0.15 gal/lb.}}{\text{569,000 gal. of juice in fermentor}} = 0.7\% \text{ (v)}$$

(This agrees somewhat with data from Gallo which indicates about a 1% (v) change in alcohol -- See Figure 2D. The difference may be explained by the orifice reduction trapping CO_2 in the tank as seen by tank pressure build-up.)

B. Relating ARB measured CO_2 volume out of tank with historical alcohol loss information.

4) Assume (wt. Alc. removed)/(wt. CO_2 removed) = (partial press alc. x mole wt. Alc)/(partial press. CO_2 x mole wt CO_2) from Alcohol Losses During Fermentation (Warkentin & Nury) is valid.

Partial Pressures @ 20°C (Warkentin & Nury)

Alc. % (V)	Alcohol	Water	CO_2 (=760 - 2.345 - 17.55)
3.5*	2.345	17.55	740.105

*Average alcohol content during 24 hr. test.

25,250 lb. CO_2 from above = 11,453 kg

569,000 gal. juice = 2,154,000 liters

CO_2 removed: $\frac{11,453 \text{ kg}}{2,154,000 \text{ l.}}$ = 0.532 g/100 ml

0.532 x (2.345 x 46)/ (740.10 x 44) = 0.00176 g alcohol loss (according to Warkentin & Nury formula)

or $\frac{(0.00176 \times 100)}{\frac{46}{44}(0.532) + .002}$ = <u>0.3% of total available</u>

This appears in agreement with historical information. (see Figure 1)

C. Relating ARB measured alcohol loss to historical alcohol loss information

Measured alcohol loss during 24 hr. test = 2 lb/hr. x 24 hr. = 48 lb.

Alcohol made during test = 26,400 lb.

During 24 hr. test: $\frac{48 \text{ lb alcohol lost}}{26,400 \text{ lb made}}$ = 0.2% lost relative to the amount of alcohol made.

(This figure is <u>not</u> "percent lost of total available" but "percent lost of alcohol produced" during the 24 hour test.)

APPENDIX IV

Composition of a Grape Must

COMPOSITION OF A GRAPE MUST[a]

Content	Range %	Content	Range, %
water	70-85	citric	0.01 - 0.05
carbohydrates	15-25	succinic	T
dextrose	8-13	latic	0
levulose	7-12	acetic	0.00 - 0.02
pentoses	0.08 - 0.20	formic	-
arabinose	0.05 - 0.15	*propionic*	0
rhamnose	0.02 - 0.04	butyric	0
xylose	T	gluconic	?
pectin	0.01 - 0.10	glucuronic	?[b]
inositol	0.02 - 0.08	glyceric	?
alcohols and related compounds		glyoxylic	?
		a-ketoglutaric	T
ethyl	T	mesoxalic	?
methyl	0.0	mucic	T[b]
higher	0.0	pyruvic	T
2, 3-butylene glycol	0.0	saccharic	?[b]
acetoin	0.0	amino	0.01 - 0.08
glycerol[b]	0	pantothenic	T
sorbitol	T	quinic	0
diacetyl	0.0	p-coumaric	T
aldehyde	T	shikimic	T
organic acids	0.3 - 1.5	sulfurous	0
tartaric	0.2 - 1.0	carbonic	T
malic	0.1 - 0.8		

Content	Range %	Content	Range, %
polyphenol and related compounds		humin	0.001 - 0.002
		amide	0.001 - 0.004
anthocyans	T	ammonia	0.001 - 0.012
chlorophyll	T	residual	0.01 - 0.02
xanthophyl	T	mineral compounds	0.3 - 0.5
carotene	T	potassium	0.05 - 0.25
flavonol		magnesium	0.01 - 0.025
quercetin	T	calcium	0.004 - 0.025
quercetrin	T	sodium	T - 0.20
rutin	?	iron	T - 0.003
tannins	0.01 - 0.10	aluminum	T - 0.003
catechin	T	manganese	T - 0.0051
gallocatechin	T	copper	T - 0.0003
epicatechin gallate	T	boron	T - 0.007
gallic acid	T	rubidium	T - 0.0001
ellagic acid	T	phosphate	0.02 - 0.05
chlorogenic acid	T	sulfate	0.003 - 0.035
isochlorogenic acid	T	silicic acid	0.0002 - 0.005
caffeic acid	T	chloride	0.001 - 0.010
p-coumarylquinic acid	T	fluoride	T
nitrogenous compounds		iodide	T
total	0.03 - 0.17	carbon dioxide	T
protein	0.001 - 0.01	oxygen	T
amino	0.017 - 0.110		

[a]Source: M.A. Amerine and M.A. Joslyn, Table Wine, the Technology of Their Production, Univ. California Press, Berkeley, 1970.

[b]Except more for botrytised grapes.

APPENDIX V

Physical Properties of Ethyl Alcohol

TABLE 1

Physical Properties of Ethyl Alcohol (21-29)

Property	Value
Freezing point, ^{o}C	-114.1
normal boiling point, ^{o}C	+78.32
critical temperature, ^{o}C	243.1
critical pressure, atm	63.0
critical volume, l/mole	0.167
critical compressibility factor, z,	
in PV = znRT	0.248
density,[b] d_4^{20}	0.7893
refractive index, n_d^{20}	1.36143
$\Delta n_D/\Delta t$, 20 - $30^{o}C$, per ^{o}C	0.000404
surface tension, at $25^{o}C$, dyn/cm	23.1
viscosity,[c] at $20^{o}C$, cP	1.17
solubility in water, at $20^{o}C$	miscible
heat of vaporization, at normal boiling point, cal/g	200.6
heat of combustion, at $25^{o}C$, cal/g	7092.9
heat of fusion, cal/g	25.0
flammable limits in air,	
lower, % by vol.	4.3
uppper, % by vol.	19.0
autoignition temperature, ^{o}C	793.0
flash point, open-cup, ^{o}F	70.0
specific heat, at $20^{o}C$, cal/(g)(^{o}C)	0.579
thermal conductivity, at $20^{o}C$,	
J/(sec)(cm^2)(^{o}C/cm)	0.00170
dipole moment. liq at $25^{o}C$, esu	1.70×10^{-18}

[a]See Table 2 [b]See Table 3 [c]See Table 4

TABLE 2

Vapor Pressure of Ethyl Alcohol

Temperature, °C	Pressure, mm Hg	Temperature, °C	Pressure, mm Hg
0.0	12	90	1,187
10	24	100	1,696
20	44	110	2,356
30	79	130	4,320
40	134	150	7,326
50	221	170	11,856
60	351	190	18,178
70	541.5	210	26,821
78.3	760[a]	230	38,176
80	812	240	45,504
		243.1	47,850[b]

[a]Normal boiling point [b]Critical point 62.96 atm.

NOTE: For low range (10-1500 mm) the following Antoine equation can be used:

$$\log_{10}P = 8.21337 - 1652.05/(231.48 + t)$$

where P = pressure, mm Hg; t = temperature, °C.

TABLE 3

Density of Ethyl Alcohol

Temperature, °C	Density, g/ml	Temperature, °C	Density, g/ml
-110	0.9027	-10	0.8147
-100	0.8937	0	0.8063
-90	0.8846	+5	0.8021
-80	0.8757	10	0.7979
-70	0.8668	20	0.7893
-60	0.8580	25	0.7850
-50	0.8492	30	0.7808
-40	0.8405	40	0.7720
-30	0.8319	50	0.7630
-20	0.8233	60	0.7548

NOTE: Density is computed as follows:

$$d\frac{t}{4} = 0.80632 - 0.00085365\,t - 0.00000001\,t^2 - 0.000000002\,t^3$$

where average deviation = ± 0.00014; t = temperature, °C.

TABLE 4

Viscosity of Ethyl Alcohol

Temperature, ^{o}C	Viscosity, cP	Temperature, ^{o}C	Viscosity, cP
0	1.82	40	0.81
10	1.40	50	0.68
20	1.17	60	0.58
25	1.06	70	0.50
30	0.97	80	0.43

Latent Heat of Vaporization. This constant can be calculated by using the following equation:

$$l_v = 226.27059 - 0.23412409\ t - 0.00119984\ t^2$$

where l_v is cal/g, t = ^{o}C, average deviation is $\pm$ 0.24.

Source Encyclopedia of Chemical Technology (1972)