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CHARACTERIZATION OF FERMENTATION EMISSIONS FROM CALIFORNIA BREWERIES

FINAL REPORT

26 OCTOBER 1983

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Contract No. A2-073-32

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L-068-84-108

27 October 1983

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OCT 31 1983
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Mr. John V. Stier
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Dear John:

Science Applications, Inc. is pleased to submit one copy, each, of our final report and executive summary for the California Air Resources Board-sponsored project, "Characterization of Fermentation Emissions from California Breweries."

I would like to thank you and all other Anheuser-Busch personnel involved for providing us with invaluable assistance and cooperation throughout the project. Your interest has been greatly appreciated.

Sincerely,

SCIENCE APPLICATIONS, INC.

Richard D. Rapoport

Richard D. Rapoport, M.P.H.
Principal Investigator
California Brewery Project

enclosures

DISCLAIMER

The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

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This report was submitted in fulfillment of ARB contract No. A2-073-32, "Characterization of Fermentation Emissions From California Breweries." Work was completed as of 30 June 1983.

ABSTRACT

The release of volatile organic compounds (VOC) into the atmosphere by the brewing industry has recently become a matter of concern to air pollution control officials. The objectives of this study were to (1) characterize and inventory all VOC emissions from California breweries, (2) establish emission factors which are representative of each important emission source, and (3) suggest potentially applicable control technologies which can be implemented to reduce VOC emissions from breweries.

According to our telephone and mail survey of all nine California breweries, the industry in 1982 - 1983 produced at an average rate of 20.7 million barrels/year, 81 percent of which was in Los Angeles County.

To develop process-specific emission factors, we conducted a two-phase source testing program at one large and one small brewery. Data from Phase I were used to select important emission sources and to qualitatively characterize emissions therefrom. Phase II data quantitatively characterized emissions from each source using charcoal tube and distilled water/XAD-resin sampling trains followed by analyses using gas chromatography with flame ionization detection and mass spectrometry. Resulting emission factors were based on the amount of beer produced.

Total organic vapor emissions from California breweries were estimated to be 38.7 metric tons/year (42.6 tons/year). Large breweries accounted for about 93 percent of these emissions. Breweries in the South Coast air basin accounted for 75 percent of the total. Beer production contributed 0.001 percent to statewide total organic gas emissions as reported in the 1979 statewide emission inventory.

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1.1.5 Fermentation Gas Handling

(1) All large breweries carry out primary fermentation in systems closed to the ambient atmosphere; this enables fermentation CO_2 gas to be collected, purified and stored for later use.

(2) All small breweries carry out an open fermentation that results in emissions of CO_2, ethanol and other fermentation gases directly to the atmosphere.

1.2 DERIVATION OF EMISSION FACTORS

1.2.1 Definition

Because operations and processes can vary from brewery to brewery, the use of one composite emission factor to calculate brewery emissions would lead to inaccuracies. Therefore, we developed process-specific emission factors based on the mass of volatile organic compounds (VOC) emitted per 10^3 barrels of beer produced.

1.2.2 Previous Emission Factors

(1) A study by the U.S. Environmental Protection Agency (EPA) derived a hydrocarbon emission factor for spent grain drying based on a literature search only. California breweries do not dry spent grains.

(2) An EPA inspection team conducted a brief tour of a brewery and estimated VOC emissions from spent yeast disposal and "brewery operations;" the former was not based on field tests while the latter estimate was based on an average of instantaneous, readings throughout the brewery using a portable organic vapor analyzer.

1.2.3 Phase I Monitoring

The purpose of Phase I monitoring was to: (1) identify significant emission sources, (2) qualitatively characterize the VOCs emitted and (3) determine the most effective sampling and analytical technique for collecting these emissions. Tests were conducted using a variety of sampling techniques at one large and one small brewery (Anchor Brewing Co.). Samples were analyzed by gas chromatography (GC) using flame ionization detection (FID) and mass spectrometry (MS). Our results are as follows:

(1) The use of Tedlar bags, Tenax traps and a portable organic vapor analyzer (OVA) was ineffectual in collecting and/or analyzing emissions due to the high moisture content of the emission streams. Charcoal tubes and water filled impingers were effective in collecting VOC emissions at all brewery sites.

(2) After Phase I monitoring the following sites at Anchor Brewing were considered significant sources of VOCs: the mash tun, brew kettle and lauter tun stacks; hot wort tank vent; and fermentation room exhaust. Important large brewery sites included the mash cooker and brew kettle stacks, the activated carbon regeneration vent ofthe CO_2 purification system, beechwood chip washer vent; in addition to these sites, the strainmaster and rice cooker stacks and waste beer sump were considered important enough for Phase II sampling.

(3) The major species identified were ethanol, ethyl acetate, dimethyl sulfide, monoterpenes and other aldehydes and ketones.

1.2.4 Phase II Monitoring

The purpose of Phase II monitoring was to quantitatively characterize the VOCs emitted from sources identified during Phase I. Because many of the compounds identified were not readily soluble in water, XAD resin was added to the impinger sampling train; a charcoal tube sampling

train was also used. Samples were analyzed using GC/FID and GC/MS techniques.

1.2.4.1 Source Tests at Anchor

Tests at this small brewery covered all sites listed in Section 1.2.3 (2) plus the spent grain tank. Uncontrolled brew kettle stack emissions were collected. Our results were as follows:

(1) The total emission rate for Anchor Brewing was estimated to be 7.2 kg/day (15.9 lb/day); the annual emission rate was 2.5 metric tons/yr (2.8 tons/yr).

(2) The most important site sampled was the fermentation room exhaust, which contributed 93.5 percent of Anchor's total daily emission rate. Ethanol accounted for over 99 percent of the emissions from this site.

(3) The brew kettle stack emissions accounted for 4.6 percent of the daily total. Dimethyl sulfide and a c_5-aldehyde account for about 33 and 26 percent of the total from this site, respectively.

(4) Hot wort tank emissions contributed almost one percent of the brewery's daily emission rate. Myrcene, a hop oil, contributed 34 percent of the emissions from the site while a c_5-aldehyde, ethanol and dimethyl sulfide contributed 14, 12 and 10 percent, respectively.

(5) The mash tun contributed only 0.5 percent of the total daily emissions. Dimethyl sulfide accounts for 53 percent of the daily total from this site.

(6) The lauter tun stack and spent grain tank contributed a combined total of 0.4 percent to the daily total. Ethanol and dimethyl sulfide were the major species in these emissions.

1.2.4.2 Source Tests at Facility A

Tests at this large brewery included all sites listed in Section 1.2.3 (2). Our results were as follows:

(1) The total daily emission rate was 19.4 kg/day (42.7 lb/day); the annual emission rate was 7.06 metric tons/year (7.8 tons/year).

(2) The brew kettle stack had the highest VOC emission rate, accounting for 45.9 percent of the total daily emissions. Myrcene and dimethyl sulfide contributed 47 and 28 percent o the total emissions from this site, respectively.

(3) The strainmaster stack accounted for 17.8 percent of the tot emissions from the brewery. Dimethyl sulfide was the most significant component, contributing 80 percent of the total, followed by a c_5-aldehyde at 10 percent.

(4) The beechwood chip wash vent contributed 10.8 percent of t total daily emissions. Emissions consisted almost entirely ethanol.

(5) The activated carbon regeneration vent accounted for 8.7 percent of the total emissions. Ethanol and ethyl acetate contributed 77 and 13 percent of the emissions from this sit respectively.

(6) Waste beer sump emissions contributed 8.8 percent of the total emissions; ethanol was the only compound identified.

(7) The mash cooker and rice cooker stacks accounted for 7.8 an 0.2 percent of the total daily emissions, respectively. Ethanol and dimethyl sulfide were the major species identifi in mash cooker emissions, contributing 53 and 44 percent of the total from this site.

1.2.4.3 Comments on Sampling Techniques

(1) Charcoal tubes collected the greatest mass of VOCs per site all the sampling train components, followed by XAD resin an distilled water impingers.

1.2.5 Recommended Emission Factors

All emission factors were based on the amount of beer produced;

units are expressed as kg of VOC emitted per 10^3 barrels of beer produced andlb of VOC emitted per 10^3 barrels (in parentheses).

1.2.5.1 Small Breweries

(1) Mash tun stack -	0.183	(0.403)
(2) Lauter tun stack -	0.088	(0.194)
(3) Brew kettle stack -	1.711	(3.771)
(4) Hot wort tank vent -	0.361	(0.797)
(5) Fermentation room exhaust vent -	23.395	(51.578)
(6) Spent grain holding tank -	0.027	(0.060)

1.2.5.2 Large Brewery

(1) Mash cooker stack -	0.125	(0.275)
(2) Rice cooker stack -	0.002	(0.005)
(3) Strainmaster/Lauter tun stack -	0.286	(0.631)
(4) Brew kettle stack -	0.741	(1.634)
(5) Activated carbon regeneration vent -	0.300	(0.660)
(6) Beechwood chip washer vent -	0.437	(0.963)

1.3 ESTIMATION OF ORGANIC COMPOUND EMISSIONS IN CALIFORNIA

1.3.1 Emissions By Geographic Unit

(1) Annual statewide emissions of VOCs from breweries was estimated to be 38.7 metric tons/year (42.6 tons/year); on a daily basis the total was 109.5 kg/day (241.3 lb/day).

(2) Emissions from Los Angeles County accounted for 75 percent of the total annual emissions, followed by Solano - 18 percent, and San Francisco - 6 percent.

1.3.2 Emissions By State Air Basin

(1) The South Coast air basin accounted for 75 percent of the

total annual emissions from breweries.

(2) San Francisco Bay Area air basin contributed 25 percent of the total; the Sacramento Valley air basin contributed less than 1 percent.

1.3.3 Emissions By Firm Size

(1) Large breweries account for 93 percent of the total annual emissions.

1.3.4 Perspectives

(1) Estimated emissions from beer production in California constitute 0.001 percent of the statewide total organic gas (TOG) emissions, and 0.002 percent of stationary source TOG emissions as reported in the 1979 Statewide Emission Inventory.

(2) Emissions from the three large breweries in Los Angeles County (where the industry is concentrated) were estimated to account for only 0.019 percent of the total county-wide stationary source reactive organic gas (ROG) emissions based on 1979 inventory data.

(3) Currently, emissions inventory data include only fuel combustion emissions from boilers at breweries. Inclusion of brewing process emissions in the emissions inventory for Los Angeles County would result in a 10-fold increase in total ROG emissions from breweries in the county.

1.4 CONTROL TECHNOLOGY

Since estimated emissions from individual breweries are rather low, we focussed our attention upon the most important processes at small and large breweries: the fermentation room and the brew kettle, respectively.

(1) Fermentation room emissions can be controlled by activated carbon adsorption. With credit for sale or re-use of

recovered ethanol, the control cost would be on the order of $5/lb pollutant removed.

(2) Ethanol concentrations in the exhaust stream are too low for absorption to be practical.

(3) Since the majority (by weight) of the pollutants in the brew kettle stack are slightly soluble or insoluble in water, an organic solvent would be needed were absorption to be used. Annualized capital costs for an absorption and stripping system would be from $22 to $84/lb pollutant removed.

(4) Activated carbon systems would be practical for removal of brew kettle emissions, although recovery of exhaust constituents would probably not be economical. The estimated total annualized capital cost and operating cost for such a system would be about $24 per pound pollutant removed.

2.0

RECOMMENDATIONS

On the basis of our findings, we recommend:

(1) The information obtained through our survey of the California brewing industry (provided to the Air Resources Board as a separate document) and the applicable results of our source testing program should be incorporated into local emission inventories and the statewide Emission Data System. Furthermore, the ARB should establish Source Classification Codes (SCCs) for each device and major species combination at large and small breweries.

(2) Emission factors for this industry should be process-specific and be based on the amount of beer produced.

3.0
INTRODUCTION AND BACKGROUND

3.1 INTRODUCTION

3.1.1 Purpose and Objectives of the Study

The release of volatile organic compounds (VOC) into the atmosphere by the brewing industry has recently become a matter of concern to air pollution control officials. Although neither federal new source performance standards nor state and local regulations restrict VOC emissions from California breweries, these emissions are suspected of contributing to the atmospheric burden of VOC in ozone non-attainment areas of the South Coast and Bay Area Air Quality Management Districts. The four largest breweries in the state, which account for greater than 99 percent of the state's current annual beer production, are located in two ozone non-attainment areas (three in the South Coast Air Quality Management District; one in the Bay Area Air Quality Management District).

Previous studies have identified possible VOC emission sources within breweries. One study by the U.S. Environmental Protection Agency estimated VOC emissions of 10.9 pounds per thousand gallons of beer from spent grain drying operations (USEPA, 1977). The validity of this emission factor has been questioned due to the complete lack of substantiating field data. After a tour of a large brewery, representatives of the U.S. Environmental Protection Agency's (EPA) Region IX Surveillance and Analysis Division reported that generalized fugitive ethanol emissions within the brewery and yeast disposal areas totaled 23 and 40 tons per year, respectively (Lavignino and Henderson, 1979). The latter estimate was based largely on a literature review. EPA Region IX representatives have suggested that more comprehensive studies, incorporating field work, be performed.

The objectives of this study were to (1) characterize and inventory all VOC emissions from California breweries, (2) establish emission factors which are representative of each important emission source in a brewery, and (3) suggest potentially applicable control technologies which can be implemented to reduce VOC emissions from breweries. The results of this study should help air pollution agencies devise effective control strategies for

ozone reduction in non-attainment areas.

3.1.2 Outline of Research

Research under this contract was conducted between September 1982 and June 1983. The major elements of the study were as follows.

3.1.2.1 Characterization of California Breweries

Since this project was geared towards developing representative emission factors based on source tests, it was necessary to design and distribute questionnaires to all California breweries. Information provided on these questionnaires enabled us to make brewery site selections based on the fulfillment of various selection criteria. Upon meeting the criteria, one large brewery ("large" is defined as a production rate greater than 60,000 bbls/year) and one small brewery were selected from the four large and five small breweries in California. Besides serving as a site selection tool, the questionnaire provided information on various throughput measures such as grain usage and beer production rates which, in conjunction with our experimentally derived process-specific emission factors, enabled us to develop a statewide inventory of brewery emissions.

3.1.2.2 Derivation of Emission Factors

To ensure that experimentally derived would be as accurate as possible, SAI conducted "pre-test" (Phase 1) monitoring, and detailed (Phase II) source testing, and then derived emission factors. The objectives of the pre-test monitoring were to sample all potential emission sites from one large and one small brewery and then, after sample analysis, rank them by expected emissions to identify the important species emitted from each source; and to provide input for developing an effective and reliable sampling and analysis plan to be implemented during Phase II. The objectives of the Phase II monitoring were to return to the same breweries to quantify the total VOC emissions from each major brewing process source and to identify the important species emitted therefrom. Stack velocity traverses were also performed so that emission rates could be calculated for various sources. Data obtained

during Phase II monitoring were used to develop process-specific emission factors for large and small breweries based on the amount of grain used and beer produced. Throughput data supplied by all other California breweries together with experimentally derived emission factors enabled us to develop the first statewide inventory of brewery process emissions ever assembled.

After reviewing the relative importance of each emission site at the large and small brewery in terms of overall VOC emissions, we explored the applicability of various generic control technologies to brewery processes. Practical advantages and disadvantages for each technique are identified, and the costs roughly estimated for a "typical" large and small brewery.

3.2 BACKGROUND - THE BREWING INDUSTRY

United States beer production increased from 1.4×10^8 barrels/year (4.4×10^9 gallons/year) to 1.9×10^8 barrels/year (6.0×10^9 gallons/year) during 1972 - 1981 (USBA, 1982). This represents a 35.7 percent growth rate over ten years or 3.6 percent per year. Figure 3.2-1 shows beer production trends in California between 1973 and 1982. Statewide beer production increased from 8.9 million barrels to 15.0 million barrels during this period. This represents an annual growth rate of 7.6 percent per year. Based on SAI's survey of the California brewing industry (see Section 4.2), actual production in 1982 is estimated to have been 20.7 million barrels. Most of the increase from 1981 production was due to the expansion of capacity at a large southern California brewery. Figure 3.2-2 compares national and California production trends.

In April 1983, nine breweries were operating in California. Table 3.2-1 gives the names, locations and production rates of these breweries. The three large breweries in the South Coast Air Basin account for 81 percent of the state's 20.7 million barrel production in 1982. One brewery in southern California accounted for 51 percent of the state total. The remaining state production takes place largely in the Bay Area air basin.

3.2.1 Brewing Process and Technology

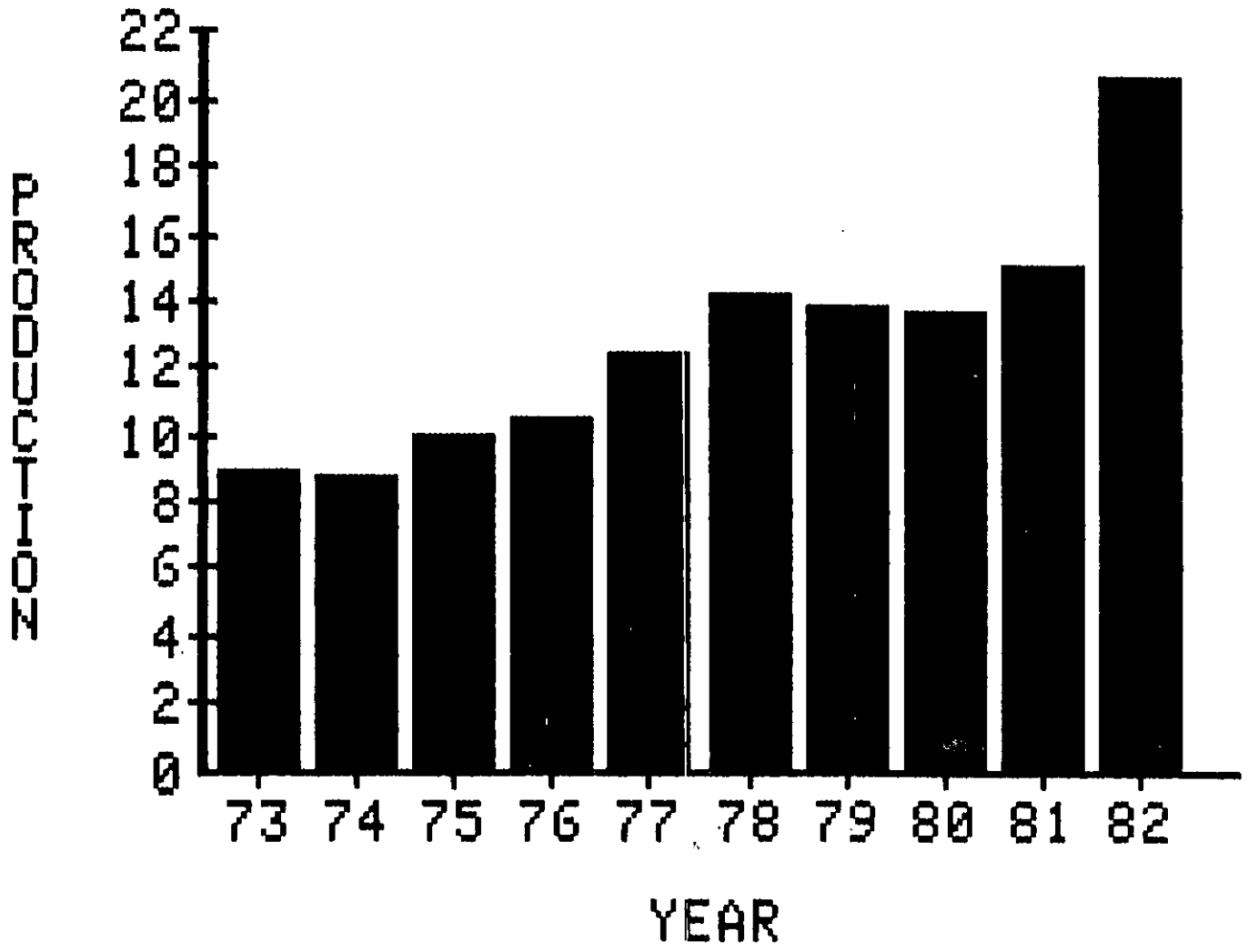


Figure 3.2-1. Production of Malt Beverages in California, 1973 to 1982 (in millions of barrels; USBA, 1982; SAI Industry Survey)

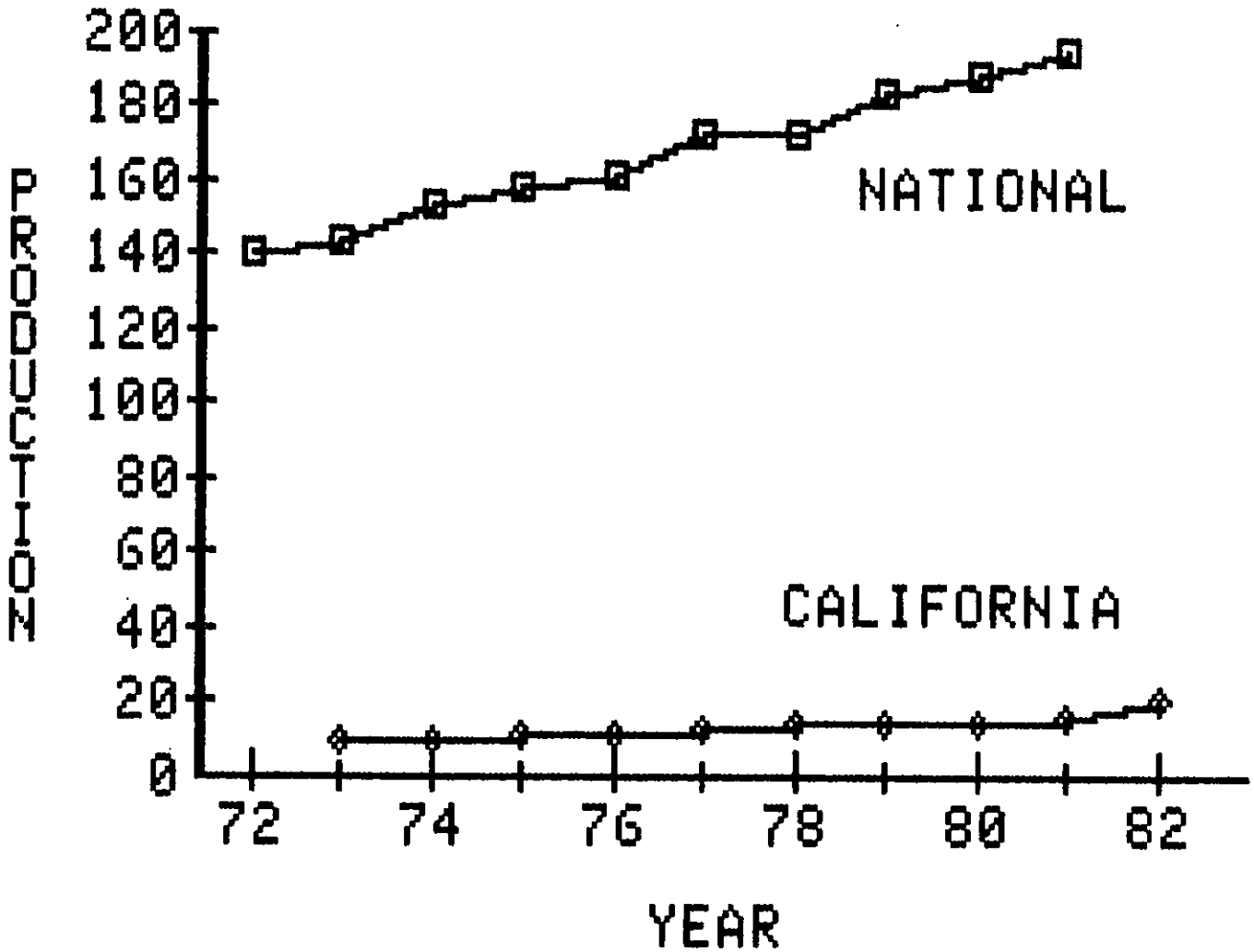


Figure 3.2-2. Beer Production in the United States and California (in million barrels)

Table 3.2-1

BREWERIES OPERATING IN CALIFORNIA

Brewery	Address & Telephone	Air Pollution Control District	Production Capacity[a] (Bbls/yr)
Anheuser-Busch Inc.	15800 Roscoe Blvd. Van Nuys, CA 91406 (213) 989-5300	SCAQMD	10,500,000
Miller Brewing Co.	15801 E. First Street Irwindale, CA 91706 (213) 969-6811	SCAQMD	4,400,000
Anheuser-Busch Inc.	3101 Majellan Road Fairfield, CA 94533 (415) 429-2000	BAAQMD	3,900,000
Jos. Schlitz Brewing Company	7521 Woodman Ave. Van Nuys, CA 91409 (213) 786-1510	SCAQMD	1,875,000
Anchor Brewing Co.	1705 Mariposa Street San Francisco, CA 94107 (415) 863-8350	BAAQMD	29,500
Sierra Nevada Brewing Co.	2539 Gilman Way Chico, CA 95926 (916) 343-3520	Butte County	2,600

Table 3.2-1

BREWERIES OPERATING IN CALIFORNIA

(cont.)

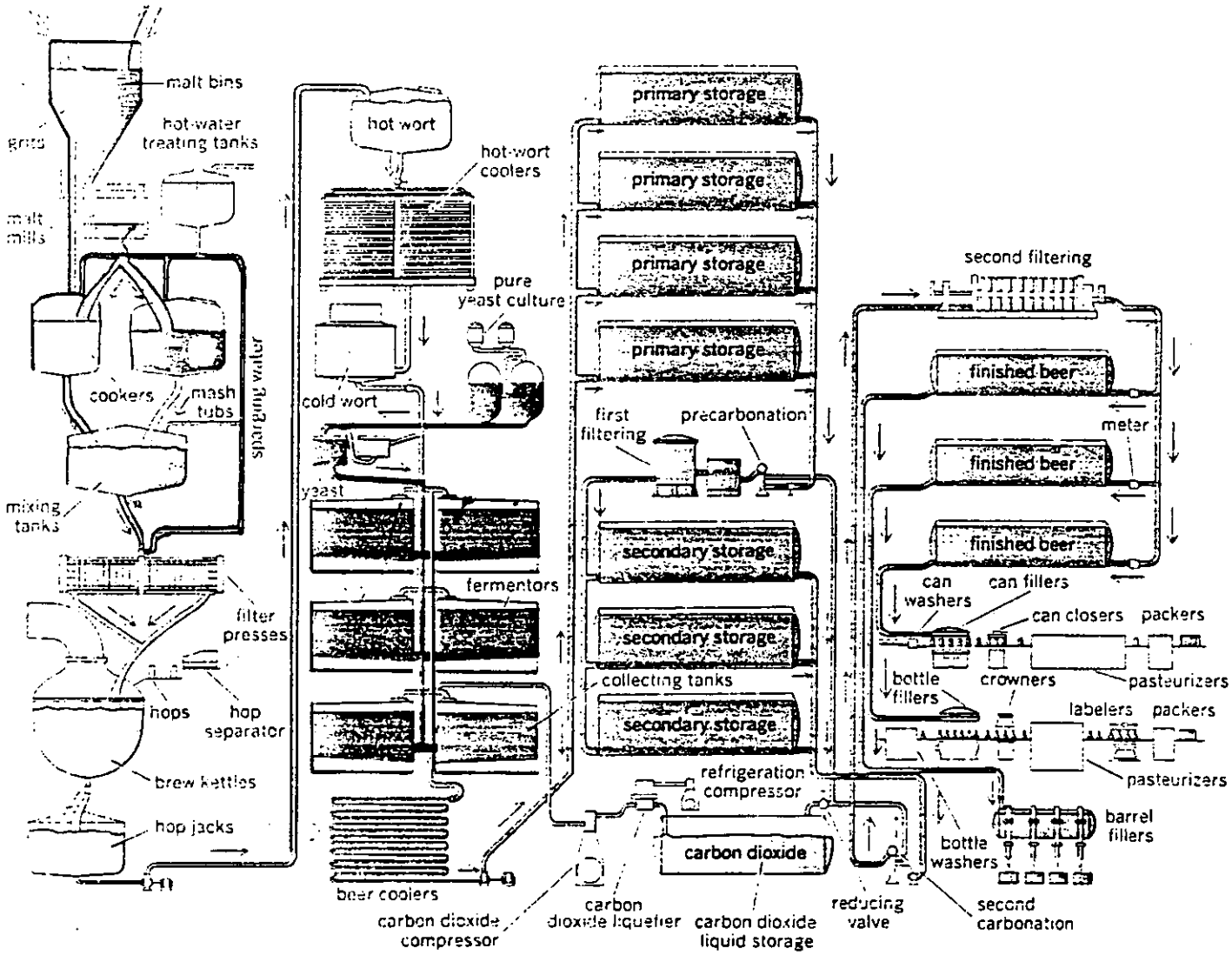
Brewery	Address & Telephone	Air Pollution Control District	Production Capacity[a] (Bbls/yr)
River City Brewing	35308 LeGrande Blvd. Sacramento, CA 95823 (916) 392-1908	Sacramento APCD	2,500
New Albion Brewing Company	20330 8-East St. Sonoma, CA 95476 (707) 938-4263	BAAQMD	350
Thousand Oaks Brewing Company	444 Vasser Ave. Berkeley, CA 94708 (415)	BAAQMD	230
Total			20,710,180

[a] Data for 1982; bbl = barrel (1 bbl = 31 gallons)

Figure 3.2-3 outlines the production of beer from malting to packaging. The production process begins with barley malting. In California, breweries do not produce their own malt; rather they obtain it from independent malt houses. First, barley is placed into large water-filled steeping tanks where the grain is softened. The contents of these tanks are transferred to germination tanks where the softened barley (malt) is detained for about one week. The germination process is terminated by transferring the malt to a drying kiln. The barley malt is crushed into a flour by a malt grinder and is now ready for the brewing process. Large breweries in the state crush their own malt while most small breweries purchase the flour. Malt is the source of starch-splitting and protein-splitting enzymes.

The conversion of starch to fermentable sugars occurs during the process called mashing. The three main methods of mashing are "double mash," "decoction" and "infusion." In California the large breweries employ the double mash method which uses additional sources of starch (adjuncts) such as rice or corn. In this system, adjuncts are cooked in a cereal cooker for about one hour at temperatures between 40 and 100°C (104 and 212°F). The mixture is then combined with the malt in a separate vessel called the mash tun. This transfer raises the temperature of the malt mixture from about 40 to 70°C (104 to 158°F) over an additional 40 minutes. The temperature of the mash is then raised to 80°C (176°F) after 20 minutes (Dougherty, 1977). These times and temperatures are approximate and will differ from brewery to brewery. Decoction involves boiling portions of the mash in a separate vessel and then transferring it back to the main mash tun thereby raising the temperature of the main mash. Raising the mash to a final temperature of 75°C (167°F) is usually achieved after three decoction cycles (Yates, 1979). In the infusion process, the ground malt and water are mixed so as to obtain a selected temperature of between 65 to 75°C (149 and 167°F) which is maintained constant for about one hour; time of mashing is set to allow complete conversion of all starch. In principle, the various mashing methods differ only in the way the temperature is raised; the higher the temperature of conversion, the faster is the reaction, but the lower the quantity of fermentable sugar formed.

After mashing is complete, the extract (called "wort") is separated



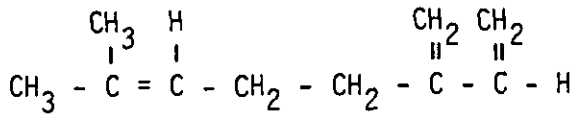
Source: Mrak and Phaff, 1977

Figure 3.2-3. Flow Chart of the Brewing Process

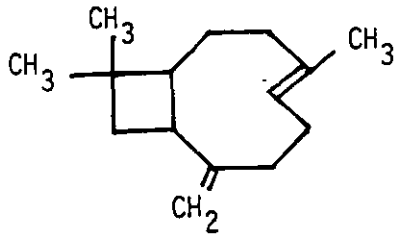
from the insoluble grain residues in a straining tank with a perforated false bottom called a "lauter tun." The grain residues settle uniformly on the false botttom and act as a filter through which the wort flows. Mash filters using polyproylene fibers are sometimes used in place of a lauter tun. A device called the "strainmaster" is a variation of the lauter tun and is used by large breweries in California. Once the process is complete the spent grains are transferred to holding tanks. California breweries do not dry their spent grains; the wet grains are stored briefly on-site and then sold to cattle feed processors.

As the wort is strained in the lauter tun, the brew kettle is simultaneously filled. Wort is boiled in the brew kettle for about 90 to 120 minutes. The objectives of boiling are to: (1) arrest further enzymatic conversion of starch to sugar; (2) sterilize the wort; (3) precipitate out undesired hydrolyzed proteins; (4) concentrate the wort by evaporation of water; and (5) hasten chemical changes affecting flavor development. The addition of hops during boiling result in the formation of iso-alpha acids in the wort. Besides imparting the characteristic bitter flavor to the beer, iso-alpha acids have a sterilizing bacteriostatic effect on a wide range of bacteria and also contribute to foam stability as a result of their strong surface active properties. Hops contain as many as 200 identified oils and resins including the terpenes myrcene, and b-caryophyllene (shown in Figure 3.2-4) (Lickens, 1983; Hudston, 1977). These natural hydrocarbons have the potential for being photochemically reactive. Myrcene, in particular, is 28,540 times more reactive than methane (equals 1) based on its reaction with the hydroxyl radical (OH) (McRae, 1982; Winer, et al, 1976). Even though many of these compounds contribute to flavor development (the iso-alpha acids) and bacteriostatic properties, a large number of undesired volatile organic compounds must be boiled off to the atmosphere to prevent off-flavor development in the final product (Hudston, 1977).

When boiling is finished, hops are filtered out by passing the wort through a strainer; wort is collected and detained in the hot wort tank where the insoluable matter is allowed to settle out as "trub." The wort is then cooled to a proper fermentation temperature between 7 and 12°C (45 and 54°F) by means of open coolers which expose it to the surrounding air during cooling, or by closed coolers that shelter it from the atmosphere (Strauss, 1977); most breweries in the state employ the latter.



Myrcene

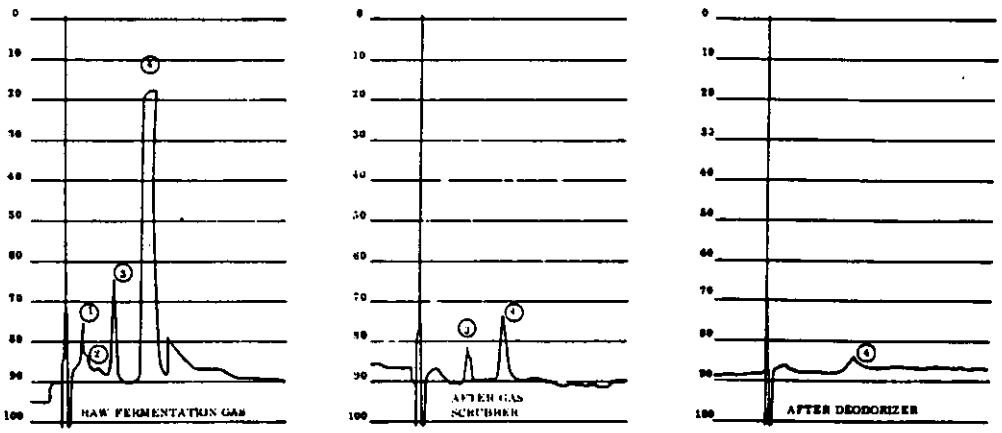


β - Caryophyllene

Figure 3.2-4. Structure of Some Common Hop Oil Terpenes

As the wort is cooled and aerated it is transferred to the fermenters. Yeast is injected directly into the transfer lines during the filling process. In California, bottom fermenting yeasts such as Saccharomyces uvarum are used most commonly in the production of lager beers while top fermenting yeasts (Saccharomyces cerevisiae) are used for producing ales, porters and stout brands. Bottom fermentation usually proceeds at temperatures between 5 and 10°C (41 and 50°F). The exact course of the fermentation process varies from brewery to brewery and also depends on the type of beer produced. Fermentation can take place either in tanks open to the atmosphere or in closed tanks designed to collect evolving carbon dioxide (CO_2) for use later in the brewing process. In the latter design, the fermenters are open to the atmosphere through a passive roof vent during filling and the first few hours of fermentation.

When all the oxygen is displaced from the tank and the CO_2 concentration is at the required level the tank is closed so that the CO_2 (and all other fermentation gas) is run through a CO_2 purification and collection system. Organic gas impurities are removed from the CO_2 gas by a water scrubber followed by an activated carbon bed. Gruber (1974) conducted a study to determine the amount of organic gas impurities in collected CO_2 after various purification steps. Figure 3.2-5 shows gas chromatograms of CO_2 gas before and after gas scrubbing in the packed water tower and deodorization by three activated carbons beds. The large first peak is caused by reignition of the hydrogen flame which was extinguished during CO_2 gas sample injection. The study examined four known organic gas impurities: acetaldehyde, acetone, ethyl acetate and ethanol. Most of the gases are removed during water scrubbing. The waste water from the scrubber, containing most of the organic impurities, is disposed of directly to an industrial sewer. The impurities remaining in small concentrations, mainly ethanol and ethyl acetate, are captured by the activated carbon bed. After purification CO_2 is compressed and stored in liquid state. The activated carbon bed is periodically recharged with hot air at 204°C (400°F). Most of the volatiles are driven off the activated charcoal during the first few hours of regeneration (Stier, 1983). Many fermenters, each containing brews at various stages of fermentation, are hooked up to the system at any given time.



Summary of Results of Quantitative Estimation of Trace Impurities

All results are in Parts per Billion — gm. x 10^{-9}/cc.

Components	#1 Acetaldehyde	#2 Acetone	#3 Ethyl Acetate	#4 Ethyl Alcohol
Raw Fermentation Gas	5	3	30	1070
After CO_2 Scrubber	2	Faint Trace	21	290
After Deodorization	—	—	—	4

Figure 3.2-5. Gas Chromatographic Analysis of CO_2 Fermentation Gas at Various Stages of Purification (from Gruber, 1974)

The length of the primary fermentation period varies between three to seven days depending on the type and style of beer production. Once the primary fermenters are emptied, most breweries reclaim a portion of the viable spent yeast for use in a later brew. The remaining spent yeast is either autolyzed and sold to animal feed processors, disposed of in industrial sewers or distilled to recover ethanol for future sale, as one California brewery does. Beer is then transferred to storage tanks where secondary fermentation takes place.

Secondary fermentation is enhanced by the immediate addition of a small portion of freshly fermenting wort in the aging tanks. The aging process takes place for two or more weeks at temperatures less than 5°C (41°F). Beechwood chips are sometimes added to increase the surface area, thereby allowing more complete fermentation with flocculent yeasts. Chips must be washed and sterilized prior to use in a subsequent brew. Old chips are deposited directly into a dumpster for later removal. Two large breweries in the state use beechwood chips in their aging processes.

Finally, the beer is filtered by centrifugation or diatomaceous earth filters and prepared for bottling. Once bottles and cans have been filled and crowned, they are pasteurized at 60°C (140°F) for a short time, and then labelled and packaged.

3.2.2 Potential Emission Sites

Prior to designing our sampling plan, we identified several potential emission sites in the brewing process by reviewiwng the literature, and holding discussions with representatives from the brewing industry, EPA and local air pollution control districts. These sites include:

- Mash cooker stack
- Lauter tun/Strainmaster stack
- Brew kettle stack
- Hot wort tank vent
- Wort cooler stack
- Fermenters and/or CO_2 filtration system during activated carbon

regeneration

- Beechwood chip washer vent
- Bottling
- Spent grain disposal
- Other (yeast disposal, diatomaceous earth disposal, tank and barrel transfer, spills, and leaks)

A few of the above sites were later deemed insignificant after our preliminary investigation and were omitted from the final source testing plan; our justification will be discussed later in the report (see Sections 5.1.1 and 5.1.2). Spent grain drying activities, which are potential sources of particulate matter and gaseous hydrocarbons, were left out of our analysis since no California brewery dries its spent grains.

3.2.2.1 Vented Emission Sites

Process exhaust streams are intentionally emitted through uncontrolled stacks and/or vents at the first seven sites listed above. In California, two breweries do have controls on brew kettle stacks to either recirculate process steam exhaust or control odors (see Section 4.2). Emissions from the mashing process consist mainly of water vapor, but also contain measurable amounts of volatile organic compounds evolving from the cooking of barley malt and adjuncts (rice, corn, etc.). Lauter tun process exhaust streams should contain species similar to mashing emissions since the process only involves straining with no addition of raw materials. In the brew kettle many volatile organic compounds contained in hop oils and resins are lost to the atmosphere during wort boiling. The exhaust stacks for the above three sites are fan-assisted (at large breweries) and usually near one another on the roof of the brewhouse. The species emission profile from the hot wort tank should be similar to that of wort boiling since only a transfer is involved between the two sites; this transfer results in hot wort tank working losses. All large breweries in the state have systems which collect, purify and store CO_2 from the primary fermentation process. One component of this system, the activated carbon bed, releases adsorbed VOC impurities during periodic hot-air bed regeneration. Breweries typically have a two-bed system whereby one system is in use while the other is being regenerated. Emissions are vented directly through a stack to the ambient atmosphere. In smaller

breweries, primary fermentation takes place in open tanks; no CO_2 collection takes place. Depending on brewery fermentation room design, emissions can be vented to the atmosphere through room air conditioning exhaust ports or passive roof vents, or unintentionally through windows and doors as fugitive emissions. Emissions from beechwood chip recycling are vented directly from the hot water washer to the atmosphere through short stacks located on the roof. Other intentionally vented sources include by-product (spent yeast and grain) holding tanks. Emissions from these sources occur as working losses during tank transfer.

3.2.2.2 Fugitive Emissions

Fugitive emissions occur during final wet disposal of the spent grains to hauling trucks. Emissions from bottling operations result from beer spillage during the filling of cans, bottles and kegs. Most of the waste beer is drained to sanitary sewers or sumps, thus reducing potential evaporative emissions. Other fugitive emissions sources include beechwood chip disposal bins, miscellaneous spills and leaks.

3.3 REGULATORY FRAMEWORK

3.3.1 Federal Regulation

The U.S. Environmental Protection Agency has no New Source Performance Standards (NSPS) for the brewing industry and no regulatory measures are currently being considered (Walsh, 1981).

3.3.2 State and Local Regulations

Under the Clean Air Act Amendments of 1977, each state is to formulate and receive EPA approval for a State Implementation Plan (SIP) for preventing significant deterioration of air quality where federal primary ambient air quality standards are currently met and for achieving the standards in current non-attainment areas. Activities and regulations relating to federal ambient standards generally fall within one of two arenas--Prevention of Significant Deterioration and Non-Attainment.

3.3.2.1 Prevention of Significant Deterioration

Under the Prevention of Significant Deterioration (PSD) provisions

of the Clean Air Act, three classes of "clean air" areas were created, a clean area being one in which the federal ambient standards for SO_2, total suspended particulate matter, carbon monoxide, NO_x, hydrocarbons and ozone are met. In each classification, air quality is permitted to deteriorate by a prescribed maximum increment above the baseline condition existing at the time of the first permit application in a clean air area. These increments must be shared by all present and future sources in and around each air quality control region.

3.3.2.2 Non-attainment

Any air quality control region in which the federal ambient standards are violated is designated as a non-attainment area. Construction of new or modified facilities in these areas is governed by EPA's emission offset policy, unless the state's SIP is adequate to manage non-attainment areas. Under this policy, major sources must meet the following requirements before a construction permit may be issued:

- Emissions from the proposed facility must be more than offset by reduced emissions from existing sources, resulting in a positive net air quality benefit and reasonable further progress toward attainment of the ambient standard. A portion of "excess" offset credit may be banked for future use by the applicant, but interpollutant tradeoffs are not permitted.
- The proposed facility must have the Lowest Achievable Emission Rate.
- Any other major sources within the state which are owned by the applicant must be in compliance with applicable emission standards or compliance schedules.

3.3.2.3 Local District Regulations

California's local air pollution control districts' responses to the PSD and non-attainment regulatory obligations vary from county to county. Here we will discuss the regulations that may apply to the emissions of interest in districts having the largest concentration of breweries.

South Coast Air Quality Management District (SCAQMD)

Three breweries are located in the SCAQMD. The District has no

specific rules covering ethanol emissions from breweries. However, these emissions may fall under Rule 442, "Usage of Solvents" (SCAQMD 1978), which requires reduction of organic solvent emissions by 85 percent or by various absolute amounts depending upon the process used and the photoreactivity of the substances.

Bay Area Air Quality Management District (BAAQMD)

Four breweries are located in the BAAQMD. The District has no specific regulation regarding ethanol emissions. However, this type of emission may fall into the miscellaneous category, Regulation 8 - Rule 2, which requires that emissions of organic compounds (including gases) into the atmosphere not exceed 300 parts per million and 15 pounds per day (DeBoisblanc, 1981).

Sacramento County Air Pollution Control District

Currently, there is one small brewery in Sacramento County. The District has no regulation regarding ethanol emissions. However, this type of emission may fall into the "Organic Solvent Use" rule number 25 (Nixon, 1981), which states that reactive hydrocarbon emissions may not exceed three pounds per hour.

Butte County Air Pollution Control District

One small brewery has been identified in this district. According to one local air pollution official, there are no regulations restricting VOC emissions. The district does rely on regulations in the Clean Air Act which are applicable (Schacht, 1981).

3.4 REFERENCES

Deboisblanc, William, Bay Area Air Quality Management District, San Francisco, California. Personal communication (18 November 1981).

Nixon, Bruce, Sacramento Air Pollution Control District, Sacramento, California. Personal communication (20 November 1981).

Dougherty, J.J. 1977. "Wort production," in The Practical Brewer, Master Brewers Association of the Americas, Madison, WI, pp. 99-116.

Hudston, H.R. 1977. "Wort boiling," In The Practical Brewer, Master Brewers Association of the Americas, Madison, WI, pp. 117-127.

Gruber, J.D. 1974. "One important brewery utility - carbon dioxide," Master Brewers Assocation of the Americas Technical Quarterly 11(4):276-285.

Lavignino, G., and D. Henderson. 1979. "SIP inspection report," Surveillance and Analysis Division, U.S. Environmental Protection Agency, Region IX, September 13, 1979. CDS Number: 00147.

Lickens, S.T. 1963. "The nature of hop oils," Canadian Beverage Review, August, pp. 20-31.

McRae, G.J. 1982. "Background notes on: the development of a technique for assessing the accuracy of emissions inventories," Working Paper (unpublished), March 9.

Mrak, E.M. and H.J. Phaff. 1977. "Malt beverages," Encyclopedia of Science and Technology, 7:91-93, McGraw-Hill Publishing Company, New York.

Schacht, B., Senior Air Quality Specialist, Butte County Air Pollution Control District, Orville, California. Personal communication (20 November 1981).

South Coast Air Quality Management District (SCAQMD). 1978. "Rule 442. Usage of solvents," Rules and Regulations, El Monte, California.

Stier, John, Environmental Engineer, Anheuser-Busch, Inc., St Louis, Missouri. Personal communication (19 May 1983).

Strauss, K.M. 1977. "Wort cooling," in The Practical Brewer, Master Brewers Association of the Americas, Madison, WI, pp. 147-159.

United States Brewers Association, Inc. (USBA). 1982. Brewers almanac. Washington, D.C., p. 8.

U.S. Environmental Protection Agency. 1977. Determining input variables for calculation of impact of new source performance standards: Worksheets for food and agriculture industries, EPA-450/3-76-018c.

Walsh, Bob., U.S. Environmental Protection Agency, Research Triangle Park, Emission Standards and Engineering Division, North Carolina. Personal communication (18 November 1981).

Winer, A.M., Lloyd, A.C., Darnall, K.R. and J.N. Pitts, Jr. 1976. "Relative rate constants for the reaction of the hydroxyl radical with selected ketones, chloroethenes, and monoterpene hydrocarbons," Journal of Physical Chemistry, 80(14):1635-1639.

Yates, S. 1979. "World brewing methods and beer styles," Chemistry and Industry, 15 December.

4.0

CHARACTERIZATION OF CALIFORNIA BREWERIES

Two of the main goals of this study were to develop process-specific emission factors and to assemble a statewide inventory of brewing process emissions. To achieve these goals, SAI designed and distributed questionnaires to all California breweries to obtain information about their brewing processes. This information was used to select representative breweries for source testing and to establish a data base from which statewide brewery emissions could be calculated. This chapter outlines the methods used and the results obtained from our survey. The final section summarizes our rationale for selecting the test breweries.

4.1 METHODS

A list of currently operating California breweries was obtained from the Federal Bureau of Alcohol, Tobacco and Firearms. Each brewery was contacted by telephone to verify the address and proper contact. During the conversation, the respondent was asked to provide the desired information over the telephone; if he was unwilling to do so, a survey packet containing a cover letter and questionnaire (Figures 4.1-1 and 4.1-2, respectively) was sent to the relevant party. Some breweries did not initially respond to question No. 8, as they felt it would require divulging their closely guarded brewing recipes. The question was then re-worded to ask for the total amount of grain (barley, adjuncts, grain) used per barrel. This alternative was acceptable to all but one brewery.

Brewery site selection was based on how well the following criteria, in descending order of importance, were satisfied:

- The brewery should contain all or nearly all of the processes common to the industry;

<date>

<gender> <first name> <middle name> <last name>
<title>
<company>
<address>

Dear <gender> <last name>:

Science Applications, Inc. (SAI) is under contract to the Research Division of the California Air Resources Board (CARB) to characterize fermentation emissions from California breweries. This letter is to confirm our telephone conversation of <date> which clarifies SAI's request for information. The objectives of our research are (1) to inventory all volatile organic compound (VOC) emissions (principally ethanol) from breweries, (2) establish emission factors which are representative of each emission source in a brewery and (3) to suggest potentially applicable control technologies which can be designed to reduce VOC emission from breweries.

As part of our research, we will be required to perform source tests at one large brewery and one small brewery in California. To ensure that our site selections are representative of the California brewing industry, we are conducting an information gathering survey of many breweries in the State. It would be a great help to our selection process if you would take a few moments to fill out the enclosed questionnaire pertaining to aspects of your production processes. Science Applications, Inc. is required to preserve in strict confidence all information designated "trade secret" which is obtained from business entities during performance of this contract and may not retain, disclose, or in any other manner use such information except to report it to duly authorized members of the Air Resources Board staff. The ARB will maintain the confidentiality of trade secret data and of any information exempt for any reason from legal requirements for disclosure. Attached are copies of our authorization letter from the CARB and a secrecy agreement which we have signed with that agency. If you feel that any of the information you report to us should be deemed a trade secret please so state.

This request for data is a formal one made by the CARB pursuant to Section 41511 of the California Health and Safety Code and Section 91100, Title 17 of the California Administrative Code which authorizes the CARB, or its duly appointed representative, to require submission of air pollution related information from owners and operators of air pollution emission sources. Please identify <u>any</u> information you consider to be proprietary in nature (e.g. trade secrets) and restrictions you request to be placed upon its dissemination. We will handle such requests consistent with the requirements

Figure 4.2-1. Letter Accompanying Written Questionnaire

set down in the California codes outlined above. This type of agreement has been use successfully in conducting surveys of over 1000 firms and we have never been faced with litigation in these matters. Further information on ARB policy may be obtained from the ARB research contract monitor, Mr. Joseph Pantalone, whose telephone number is (916) 323-1535. Our contract number is A2-073-32.

If you need further information please contact me at the address and phone number at the bottom of the page.

Thank you very much for assisting us in this survey. We will let you know as to the results of our site selection process.

Sincerely,

SCIENCE APPLICATIONS, INC.

Richard D. Rapoport, M.P.H.
Principal Investigator

/m

enclosures

Figure 4.2-1. Letter Accompanying Written Quesionnaire (cont.)

SCIENCE APPLICATIONS, INC./CALIFORNIA AIR RESOURCES BOARD
CALIFORNIA BREWERY INDUSTRY QUESTIONNAIRE

INSTRUCTIONS: Please fill out the entire questionnaire. If answers need clarification, use the other side of the sheet, with reference to the question number. Please return the questionnaire as soon as possible.

Company Name: _____

Address: _____, City: _____, Zip: _____

Person To Contact: _____, Title: _____

Telephone No.( ) _____

1. How many employees are currently working at the brewery? _____

2. What is your current operating cycle? _____ Hours/Day; _____ Days/Week; _____ Weeks/Year

3. What percentage of your annual production operations occurs during the following seasons: _____ % Winter; _____ % Spring; _____ % Summer; _____ % Fall (total should = 100 percent).

4. What is your current production rate? _____ Barrels/Year; _____ Barrels/Week; _____ Barrels/Day.

5. What are the chances of your breweries business picture changing in the next five years (i.e., planned expansions or slowdowns)?
   ____ High, ____ Medium, ____ Low

6. Are there definite plans to change (modernize) existing plant process technologies in the next five years? Yes _____; No _____

7. What types of beer are produced at your brewery? (e.g., lager stout, lite, ales, etc.) For each type of beer, please give its percent contribution to your total annual production given in question 4.

   _____

Figure 4.2-2. California Brewery Industry Questionnaire

8. How many pounds of the following raw materials are used to produce one barrel (31 gallons) of your beer?

Brewer's Malt _____
Malt Adjuncts _____
Hops _____
Yeast _____

9. What types of control devices are in place to prevent emissions from escaping into the ambient air; in what process streams are they located: (e.g. controls on fermentation tanks, storage tanks, slurry disposal tanks, exhaust streams from mashing and wort boiling, waste beer, and any others)

_____
_____
_____
_____
_____

10. Do you use beechwood chips? Yes_____, No_____

11. What are the current methods of disposal for:
Spent Grains:

_____
_____

Spent Yeast:

_____
_____

Trub:

_____
_____

Figure 4.2-2. California Brewery Industry Questionnaire (cont.)

Beechwood chips (or other, if applicable)

_____

_____

12. For each of the disposal catagories listed in question 11, how many pounds are disposed of per barrel of beer produced (If per barrel figures are unavailable, use disposal per year.)
Spent Grains _____, Spent Yeast _____, Trub _____,
Beechwood Chips _____

13. What types of filters are used after mashing:
_____ Lauter Tuns
_____ Plate-and-Frame Filters
_____ Other; please specify _____

14. For your major products, how long is the: fermentation cycle? _____Days
aging cycle? _____Days

15. Is fermentation carried out in an open system? ___Yes; ___No

16. What types of filters are used during and after fermentation: (e.g., CO_2 filtration, pad filters, diatomaceous earth, centrifugation, others)?

_____

_____

17. Beers are packaged in _____cans, _____bottles, _____kegs

18. Thank you very much for completing the questionnaire. Please use the enclosed, self addressed, stamped envelope and send to:

Science Applications, Inc.
California Brewery Project
1900 Avenue of the Stars, Suite 900
Los Angeles, California 90067

Figure 4.2-2. California Brewery Industry Questionnaire (cont.)

- Raw materials and production processes should be representative of large (or small) breweries;
- The brewery should be located in a non-attainment area for ozone;
- The level of sophistication of existing control technology should be representative of the industry;
- Production capacity should be representative of large (or small) breweries in California;
- Waste disposal systems should be representative of the industry;
- The brewery's production capacity and process technology should not be expected to change significantly during the next five years; and
- The level of cooperation from brewery representatives should be adequate.

4.2 RESULTS

To obtain information from the breweries, it was necessary to insure the confidentiality of "trade secret" information pertaining to various throughputs and other process data. Therefore, information so designated will not appear in this report. The following discussion of industry characteristics does not include any trade secret data.

4.2.1 Temporal Operating Cycles

Large breweries in the state brew 24 hours per day, 365 days per year, with the exception of one brewery which brews 5 days per week. Small breweries operate on a more flexible schedule, varying between 8 and 12 hours per day, 5 days per week; bottling operations occur 1 or 2 days per week. Production volumes vary seasonally as follows:

Season	Average Percent of Annual Production
Winter	23.2
Spring	24.5
Summer	26.7
Fall	25.6
	100.0

The seasonal percent differences were statistically significant at the 95 percent confidence level.

4.2.2 Existing Air Pollutant Controls

Air pollutant emissions other than those from fuel combustion are not deliberately controlled in this industry. However, some control is achieved as the result of certain brewery operations. Anchor Brewing, for example, uses a tower packed with polyethylene beads to condense steam coming off the brew kettle; the condensed water scrubs out odorous hydrocarbons. A large brewery recirculates and condenses steam boiled off from the brew kettle, thus providing some air pollutant control.

4.2.3 By-products Handling

All breweries in the state sell their spent grains, wet, to animal feed processors or local farmers. Buyers pick up the spent grains as often as 14 times a day at some of the larger breweries and once a week or more at the smaller facilities. Disposal methods for spent yeast vary among breweries. Most breweries reclaim a small portion of the spent yeast for use in later brews and deposit the remainder in industrial sewers or septic tanks. One brewery autolyzes its spent yeast before removal by a contract buyer while another recovers entrapped ethanol using an on-site distillation

system; still bottoms are shipped out with the spent grains. Trub is usually hauled away with the spent grains. One small brewery uses it as a landscaping fertilizer. Facilities disposing of beechwood chips do so in sanitary landfills. It should be noted that we did not choose to consider wastewater by-products in our survey.

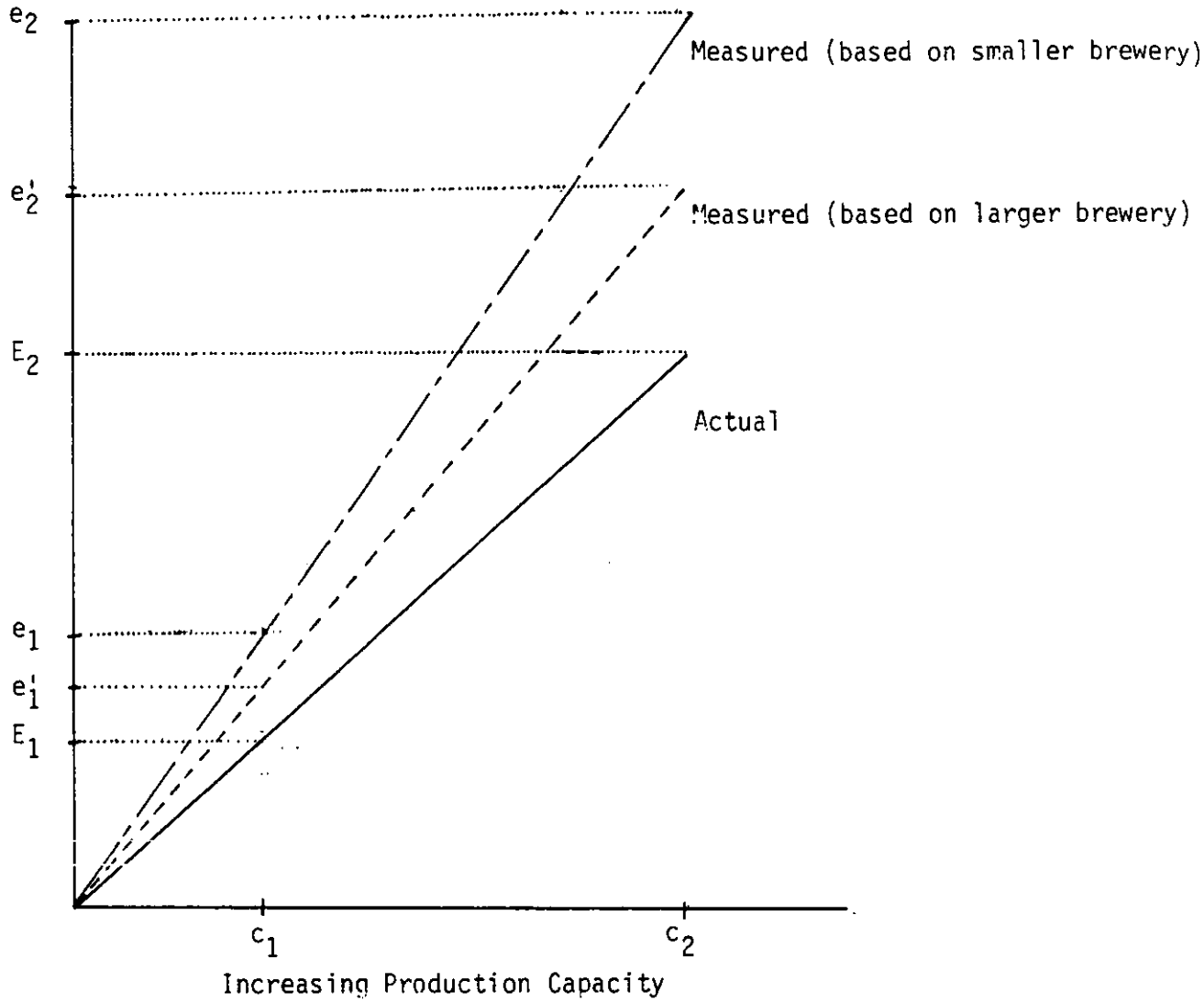
4.2.4 Fermentation Gas Handling

All large breweries in the state have activated carbon adsorption systems which collect, purify and store CO_2 fermentation gas from a primary fermentation process closed to the atmosphere (discussed in Section 3.2.1); small breweries do not. When the activated carbon bed is regenerated with hot air after a period of continuous operation, volatile organic compounds (mainly ethanol) are released into the atmosphere. One brewery carries out regeneration every other day for 24 hours, another brewery carries out regeneration every 7 days for 17 hours. Regeneration schedules depend on system CO_2 collection and storage capacities.

4.3 BREWERY SELECTION RATIONALE

Anchor Brewing in San Francisco was selected for testing as the small brewery. Anchor met most of the criteria outlined earlier except for its production capacity which is nearly 11 times greater than the next-largest small brewery. We purposely made this selection because the error involved in extrapolating emissions from a large to a small brewery would be smaller than the converse situation, as illustrated by Figure 4.2-3. If a smaller brewery were selected for source testing, extrapolating up to a large, untested facility would lead to a much greater error in estimating emissions.

Representatives of Facility A requested that we keep their identity confidential. This facility met all of the criteria more completely than other large breweries in the state.



E_1, E_2 = actual emission rate from small and large breweries, respectively

e_1 = measured emission rate

e_2 = extrapolated emission rate estimate based on small brewery

e_1' = extrapolated emission rate estimate based on large brewery

e_2' = measured emission rate

c_1, c_2 = production capacity at small and large breweries, respectively

Figure 4.2-3. Hypothetical Results of Extrapolating Emission Rates Based on Measurements From Either a Large or Small Brewery

5.0

DERIVATION OF EMISSION FACTORS

Air pollution control agencies and the industries they regulate are faced continually with the problem of estimating pollutant emissions in the absence of hard, site-specific scientific data. A very common practice is to assume that emissions are a fixed fraction of the material consumed, processed, produced, stored or disposed of by the facility. These fractions, whose scientific bases range from "engineering judgement" to comprehensive field and laboratory studies, are called emission factors. In the case of the brewing industry, emission factors can be expressed as mass of volatile organic compound (VOC) emitted per unit mass of grain fermented, or, alternatively, per barrel of beer produced. Because operations and processes vary from brewery to brewery, the use of only one composite emission factor to quantify total VOC emissions for emissions inventory purposes may not be appropriate. Therefore, the use of process-specific emission factors based on measured emission data and process data is vital for reliable emission estimates.

5.1 PREVIOUS EMISSION FACTORS

Before this project, the U.S. Environmental Protection Agency (1977) estimated an emission factor for spent grain drying operations based on process data which assumed that one percent by weight of the spent grain is emitted as hydrocarbon. Assuming the grain loses 20 percent of its weight during processing, for every pound of spent grain, 1.25 pounds of raw grain are initially required. Therefore, each 1.25 pounds of raw grain input emits 0.01 pounds of hydrocarbons, and the emission factor would be 16 pounds of hydrocarbons per ton of grain handled. To convert this figure to pounds per thousand gallons of beer produced, a grain throughput estimate of 1.36 pounds of grain used per gallon of beer (42.3 pounds per barrel of beer) is factored in (Shreve, 1977). The emission factor then becomes 10.9 pounds per thousand gallons of beer. Since no California breweries dry their spent grain,

however, this emission factor is not applicable to the state brewing industry.

Lavignino and Henderson (1979) conducted tests at one brewery and reported fugitive ethanol emissions within the brewhouse and yeast disposal area totalling 23 and 40 tons per year, respectively. The first estimate was obtained by averaging instantaneous concentration readings taken at various locations using a portable organic vapor analyzer. An emission rate was calculated by multiplying the concentration by the maximum air conditioning intake flow rate. Yeast disposal emissions were calculated by assuming that spent yeast contains two percent by weight ethanol, and that this entire fraction evaporates from the total amount of yeast used at the brewery in one year. Besides being based only on process data, this estimate does not take into account the various spent yeast storage and disposal methods used by state breweries (see Section 4.2.1).

Given the inapplicability of these emission factors, a conclusive source testing program was warranted. Our program was conducted in two parts: the pre-test monitoring (Phase I) and quantitative source testing (Phase II). The purpose of Phase I monitoring was to identify important emission sources, qualitatively characterize the volatile organic compounds (VOCs) emitted from these sources and to determine the most efficient methods for Phase II sampling and analysis. The purpose of the Phase II testing was to quantitatively characterize the VOCs emitted from important sources identified during Phase I testing. Source testing was conducted at one small and one large brewery in California. (The large brewery wishes to remain unidentified.) The rationale for their selection is discussed in Section 4.2.2.

5.2 PHASE I MONITORING

The following section will describe the test protocols used at both breweries during the pre-test monitoring phase, followed by a brief description and discussion of the sampling results.

5.2.1 Sampling Procedures

The purpose of the initial survey was to identify not only the significant emission sources within the breweries selected for sampling, but also to qualitatively characterize the volatile organic compounds (VOCs) emitted. Furthermore it was necessary to try a variety of sampling techniques in order to select the most appropriate means for quantifying VOCs during Phase II monitoring activities.

The following sampling devices were used during the initial site inspection at Anchor Brewing Company in San Francisco and at Facility A:

- Tedlar bags
- Charcoal tubes
- Tenax traps
- Water-filled impingers
- The Foxboro Model 128 Organic Vapor Analyzer (OVA) for identifying point sources and general areas of VOC release.

Given our understanding before the project of the likely nature of brewery VOC emissions, we believe that these devices, or combinations thereof, would be the most appropriate. Their suitability in the high moisture, high temperature environment of many brewery processes had to be evaluated.

5.2.1.1 Tedlar Bag Sampling

Samples of whole gas were collected from various sources using 8-liter Tedlar bags contained in polyethylene carboys. The carboy lid contained one part which was attached to the Tedlar bag and another which was open to the inside of the carboy. The Tedlar bag was filled with sample gas by applying a vacuum to the carboy through the open port.

A sampling probe consisting of 1/4-inch stainless steel and teflon tubing was used where necessary. A Gast Model MDA oil-less diaphragm vacuum pump was used to evacuate the carboy, at a flow rate of approximately 1 L/min. The sampling time was about eight minutes at each of the sites sampled. Following sample collection the inlet port to the Tedlar bag was capped with a teflon-lined septum cap, and the carboys were sent to the SAI Laboratory in La Jolla, California.

5.2.1.2 Charcoal Tube Sampling

Gas samples were collected using charcoal tubes available through SKC Inc. The tubes were packed with front and backup sections of activated charcoal, containing 400 and 200 mg of charcoal, respectively. Gas was sampled through two tubes in series using a Dupont Model P200A portable air sampling pump at a flow rate of about 50 ml/min. The pumps were calibrated to the stated flow using a bubble flow meter and checked before and after each sample collection.

A 1/4-inch stainless steel and teflon sampling probe was used at most sites. In addition, drying tubes containing 250 mg of sodium sulfate (SKC, Inc.) were used upstream of the charcoal tubes to help remove moisture at one of the sampling sites. Drying tubes were used because of the anticipated problems associated with the analysis of wet charcoal tube, as will be discussed in Section 5.2.3.3. Following sample collection, the charcoal tubes were capped, placed in water-tight plastic bags and shipped in ice to the SAI Laboratory.

5.2.1.3 Tenax Trap Sampling

Gas samples were also collected using Tenax traps consisting of 1/8-inch stainless steel tubing packed with 100 mg of Tenax GC sorbent. Dupont Model P200A pumps were calibrated to sample at a flow rate of approximately 20 ml/min; the calibration procedure was the same as described for charcoal tube sampling. Tenax trap sample volumes ranged between 0.3 and 0.6 L. Following sample collection the traps were capped, placed in water-tight plastic bags, and shipped in ice to the SAI Laboratory.

5.2.1.4 Impinger Train Sampling

Water-filled impingers were also used to sample the various gas streams for VOC at the breweries. The sampling train consisted of 1/4-inch stainless steel and teflon tubing used as a sampling probe; two 25-ml midget impingers each filled with 20 ml of deionized water; a midget impinger filled

with silica gel to dry the gas before entering the pump; and an MSA portable vacuum pump set to sample at a flow rate of approximately 1 L/min. The flow was monitored during the sampling period using a rotameter which had been previously calibrated using a bubble flow meter. Following sample collection, impinger contents were transferred to 40 ml glass vials, placed in water-tight plastic bags and stored in ice during shipment to the SAI Laboratory.

5.2.1.5 OVA Sampling

The Foxboro Model 128 OVA uses a flame ionization detector to detect the presence of organic vapors delivered to it by means of a small diaphragm sampling pump. When used in the survey mode to detect total organic hydrocarbons, it has a linear working range of 0 to 10,000 ppmv organic vapor and a response time of approximately two seconds. The instrument was calibrated at the sampling sites using certified methane-in-air gas standards available through MG Burdett Gas Products Co. It was used mainly during the initial site visits to monitor certain point and fugitive sources within the breweries.

5.2.1.6 Field QA/QC Procedures

Charcoal tube and Tenax trap field blanks were generated by handling blank tubes and traps in a manner identical to the samples. Impinger train field blanks were generated by transferring 20 ml of deionized water to an impinger, transferring the water to a 40-ml glass vial, and then shipping the vial to the laboratory in the same ice chest as the samples.

5.2.2 Analytical Procedures

This section describes the extraction and analysis procedures used in handling samples collected from Anchor Brewing Co. and Facility A during Phase I monitoring.

5.2.2.1 Tedlar Bag Samples

The gaseous contents of the Tedlar bags were analyzed directly using packed column gas chromatography with flame ionization detection (GC/FID). A 10-ml aliquot of each sample was transferred and injected into the injection port of the gas chromatograph using a 10-ml gas tight syringe. A Hewlett Packard 5730A gas chromatograph equipped with a 3388A Integrator and flame ionization detector was used for the analyses. Table 5.2-1 lists the column, oven temperature program, gas flow rates, and other GC conditions used in the analysis of the Tedlar bag contents.

5.2.2.2 Charcoal Tube Samples

Charcoal tube contents were analyzed using solvent desorption of the charcoal followed by packed column GC/FID analysis of the extracts. Charcoal from the front and back tubes was transferred to 3.5 ml glass vials with teflon-lined septum caps. Then 1.5 ml of either 1 percent 2-butanol in carbon disulfide or 1 percent tetrahydrofuran in carbon disulfide were added to the samples. The use of two solvent mixtures for desorption of the samples was called for due to the high water content of some of the samples. The samples which had water entrained in the charcoal (determined by visual observation) were desorbed with the tetrahydrofuran mixture while the remaining samples were desorbed with the 2-butanol mixture. Following a minimum desorption period of one hour, sample extracts were analyzed by packed-column GC/FID using the conditions listed in Table 5.2-1. Some of the sample extracts were re-analyzed after additional desorption time (maximum ~ 36 hours) and no increase in the desorbed components was measured. Thus the one hour minimum desorption time was determined to be sufficient.

Charcoal tube field blanks were analyzed in the same manner as the samples. In addition, desorption efficiency samples were generated and analyzed using both of the solvent mixtures described above. The desorption efficiencies for ethyl alcohol and ethyl acetate were determined by spiking charcoal tubes with various known amounts of the two compounds, and then analyzing the tubes in the same manner as the sample tubes. Both dry charcoal tubes and tubes saturated with deionized water were spiked and analyzed using the methods described above.

Table 5.2-1

GC/FID CONDITIONS USED IN THE ANALYSIS OF TEDLAR BAG AND CHARCOAL TUBE SAMPLES

Parameter	GC/FID
Column dimensions	6-ft x 2-mm ID, glass
Column packing	0.1% SP-1000 on 80/100 Carbopack C
Column temperature program	$70^{o}C$ for 2 minutes $8^{o}C$/minute to $220^{o}C$ $220^{o}C$ for 10 minutes
Injection port temperature	$250^{o}C$
Detector temperature	$250^{o}C$
Carrier gas	Nitrogen
Carrier gas flow	20 ml/minute
Detector gases and flows	Hydrogen -- 30 ml/min Air -- 240 ml/min

The gas chromatograph used in these analyses was calibrated each day with standards prepared in both of the solvent mixtures described above. The standards prepared for calibration contained ethyl alcohol and ethyl acetate and were prepared volumetrically using the pure solvents. A three-point calibration curve was established at the beginning of the analyses to check the linearity of the GC/FID. The calibration was checked at the beginning of each day and after every 10 sample analyses.

5.2.2.3 Tenax Trap Samples

Tenax trap samples were analyzed directly by heat desorption onto a capillary column followed by temperature programmed gas chromatography with mass spectrometer detection (GC/MS). The tenax traps were heat desorbed by placing the trap in the heated jacket of a Tekmar LSC 2 purge-and-trap device which was interfaced to the injection port of a Finnigan 4000 GC/MS. Due to the high water content of the tenax traps it was not possible to analyze these samples. Upon heat desorbing the samples, the capillary column became plugged with water, which made it impossible to complete the analyses.

5.2.2.4 Impinger Train Samples

Impinger train contents were analyzed (1) directly, by packed column GC/FID for volatile constituents, and (2) following solvent extraction by capillary column GC/FID for semi-volatile components. Direct analysis was performed on the samples using the Hewlett Packard 5730A GC with the 3388A Integrator. The GC analysis conditions are presented in Table 5.2-2. The GC/FID was calibrated in this mode using ethyl alcohol and ethyl acetate standards prepared in deionized water.

The impinger train contents were extracted using EPA Method 625 extraction techniques described in the 3 December 1979 Federal Register. In summary, the samples were extracted three times at neutral pH with methylene chloride. The extracts were combined and dried over sodium sulfate, and concentrated to an appropriate volume for GC/FID analysis. The GC/FID analyses of the impinger train extracts were performed on a Hewlett Packard

Table 5.2-2

GC/FID CONDITIONS USED IN THE DIRECT ANALYSIS OF IMPINGER TRAIN CONTENTS

Parameter	GC/FID
Column dimensions	3-ft x 4-mm ID, glass
Column packing	3% Carbowax 20M/0.5% H_3PO_4 on 60/80 Carbopack B
Column temperature program	$70^{o}C$ for 2 minutes $16^{o}C$/minute to $160^{o}C$ $160^{o}C$ for 10 minutes
Injection port temperature	$250^{o}C$
Detector temperature	$250^{o}C$
Carrier gas	Nitrogen
Carrier gas flow	60 ml/minute
Detector gases and flows	Hydrogen -- 50 ml/minute Air -- 500 ml/minute

Table 5.2-3

GC/FID CONDITIONS USED IN THE ANALYSIS OF IMPINGER TRAIN EXTRACTS

Parameter	GC/FID
Capillary column dimensions	30-m x 32-mm ID, fused silica
Liquid phase	DB5
Film thickness	0.25 micrometers
Column temperature program	45°C for 5 minutes 3.5°C/minute to 280°C 280°C for 10 minutes
Injection port temperature	280°C
Detector temperature	350°C
Carrier gas	Helium
Detector gases and flows	Hydrogen -- 30 ml/minute Air -- 240 ml/minute
Makeup gas and flow	Nitrogen -- 30 ml/minute
Splitless injection volume	1 microliter

5840A gas chromatograph equipped with a capillary inlet system and a fused silica capillary column. The capillary column GC/FID analysis conditions are presented in Table 5.2-3.

Prior to analyzing samples the GC/FID was calibrated using a series of even and odd n-alkanes from nC-8 through nC-32. The calibration standard was prepared gravimetrically in hexane from the pure compounds. The instrument was recalibrated daily or after every 10 sample analyses.

5.2.2.5 GC/MS Sample Analysis Procedures

To facilitate the identification of unknown components in the sample extracts, a representative selection of extracts was analyzed by packed and capillary column GC/MS. Charcoal tube extracts were analyzed using packed column GC/MS techniques while impinger content extracts were analyzed using capillary column GC/MS techniques. A Finnigan Model 4000 computer-controlled GC/MS system was used for the analyses of the selected extracts. Prior to sample analyses the mass calibration of the GC/MS was checked and adjusted using decafluorotriphenyl phosphine. The mass was calibrated using a computer-stored reference table of the calibration compound. The GC/MS was further calibrated using the same standards as were used for the calibration of the GC/FID in the analyses described above.

The mass spectrometer was operated in the electron impact ionization mode using conventional parameters. Typically, one- to two-second scans from mass 30 to mass 450 (amu) were obtained, and data acquisition was initiated at the beginning of the GC temperature programming run. Ion source potentials were optimized for sensitivity, and the electron multiplier was operated at appropriate voltages for optimal signal to noise.

Charcoal tube extracts were analyzed by injecting 2 microliters of sample onto a 6-ft x 2-mm ID glass column packed with 0.1 percent SP-1000 on 80/100 Carbopack C. The GC oven was held isothermal at 70°C for 2 minutes and was then programmed to 220°C at 8°C/min. The effluent from the GC was transferred directly to the mass spectrometer via an all-glass transfer system utilizing a glass jet separator.

Impinger extracts were analyzed by splitless injection of 1 microliter of sample onto a 30-m x 0.25-mm ID DB5 fused silica capillary column. The GC oven was held isothermal at 30°C for 5 minutes and was then programmed to 275°C at 5°C/min. The effluent from the GC was transferred directly to the mass spectrometer as described above for packed column analyses.

The mass spectrometer was interfaced to a computer system to allow acquisition of continuous mass scans for the duration of the chromatographic program. The computer system was also equipped with mass storage devices for saving all data from GC/MS runs. Software was available to allow searching of any GC/MS run for specific ions and plotting the intensity of the ions versus time or scan number.

5.2.3 Phase I Tests at Anchor Brewing Company

Emission measurements were made on the morning and afternoon of 20 December 1982. Weather conditions consisted of intermittent rain, an air temperature of about 55°F (13°C) and moderate winds from the south between 10 to 25 miles/hr (4 to 11 meters/sec).

5.2.3.1 Facility Description

The brewery is housed in a three-story structure in the Potrero Hill district of San Francisco, which is largely residential on the south, and commercial/industrial on the notheast and west. Of the small breweries in California, Anchor's production capacity of around 29,500 bbls/year makes it the largest. During a five-day work week, the brewery produces an average of 2 brews/day, 4 days/week, with the remaining day spent bottling.

Figure 5.2-1 is a detailed flow diagram of the brewing process at Anchor. A general discussion of the brewing process is given in Section 3.2.1. The facility brews three brands of beer: steam beer, porter and ale. Steam beer is brewed in essentially the same process used by other small breweries, with the exception of slightly increased primary fermentation

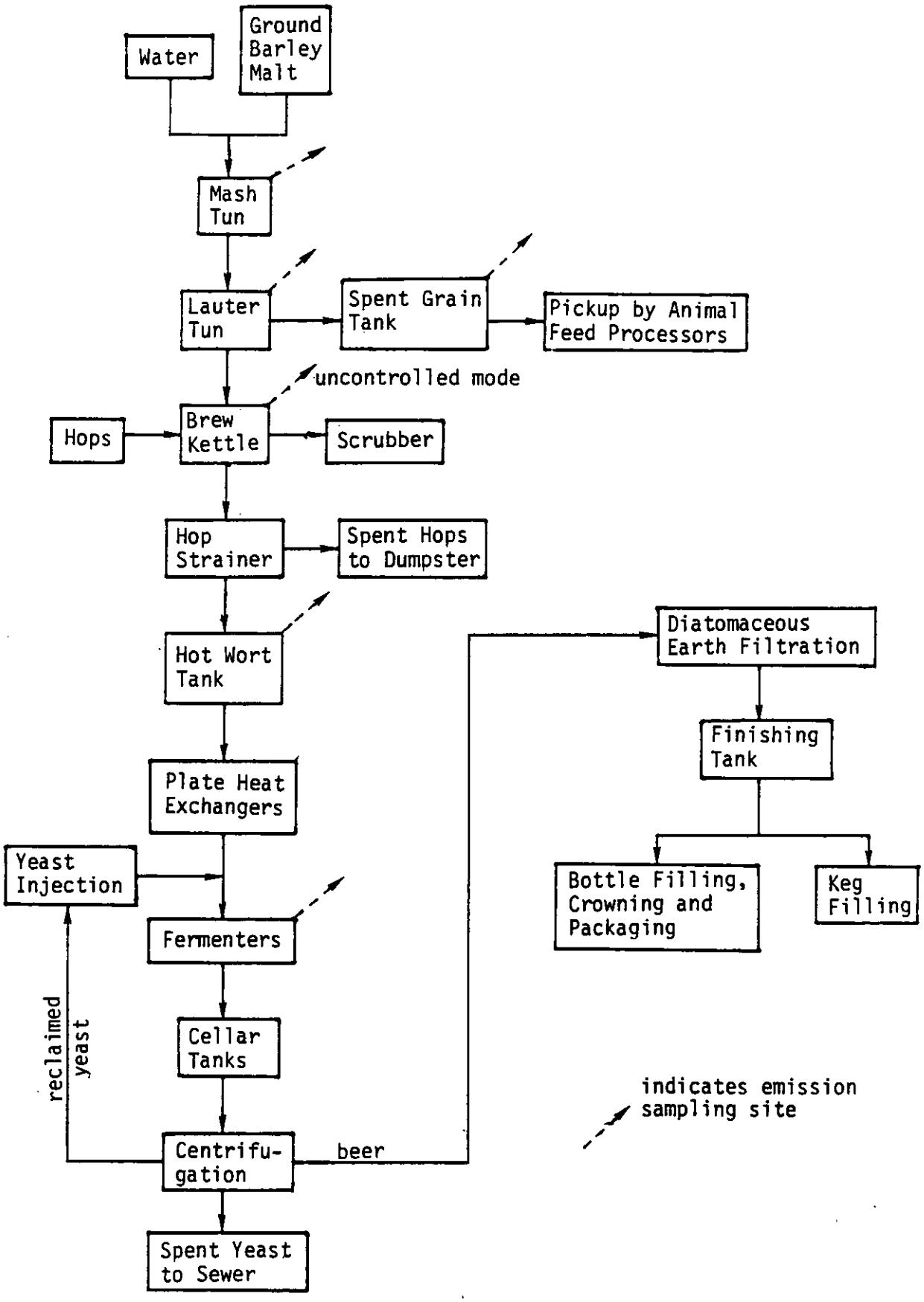


Figure 5.2-1. Brewing Process Flow Diagram - Anchor Brewing Company

temperatures and a carbonation method carried out entirely by "krausening" (induced secondary fermentation in closed cellar tanks). Anchor uses no adjuncts in its beer.

Mashing, spent grain filtration and wort boiling take place near each other in the brew house. Wort is cooled in a plate-heat exchanger which shelters it from the atmosphere. Fermentation takes place in a separate, closed room containing 20-by-30 ft shallow, open fermenting vessels. The room has its own air-conditioning system which maintains a fairly constant temperature and flow rate into and out of the room. Bottling occurs in a separate part of the building. Windows in this area are kept closed during bottling to maintain clean conditions. Waste and spilled beer is drained to the municipal sewer. Spent grains are screw-conveyed from the lauter tun to a closed tank outside the facility and hauled away about once a week by a cattle feed processor. Spent hops are placed outside in a dumpster. About a third of a brew's spent yeast is reused as seed in another brew while the remaining portion is drained to the municipal sewer.

5.2.3.2 Emission Points

Through discussion with brewery personnel, literature reviews and a visual inspection of the facility, we identified six potentially important emission sources. Figure 5.2-2 illustrates the configuration of, and the sampling points (denoted by the dot) for, each emission source. Figure 5.2-3 shows a top-view schematic layout of the locations of each source. All of the important emissions we identified are intentionally vented to the atmosphere. Emissions from the mash tun, lauter tun and brew kettle stacks occur mainly by convection as they do not have exhaust blowers. Emissions from the hot wort tank and spent grain tank occur as working losses during material transfer. The brew kettle stack scrubber and fermentation room exhaust vents are blower assisted.

During Phase I, we sampled controlled emissions from the brew kettle scrubber while during Phase II, the scrubber was turned off so that we could sample brew kettle emissions in a totally uncontrolled mode. We did not sample emissions from the spent grain holding tank during Phase I because of

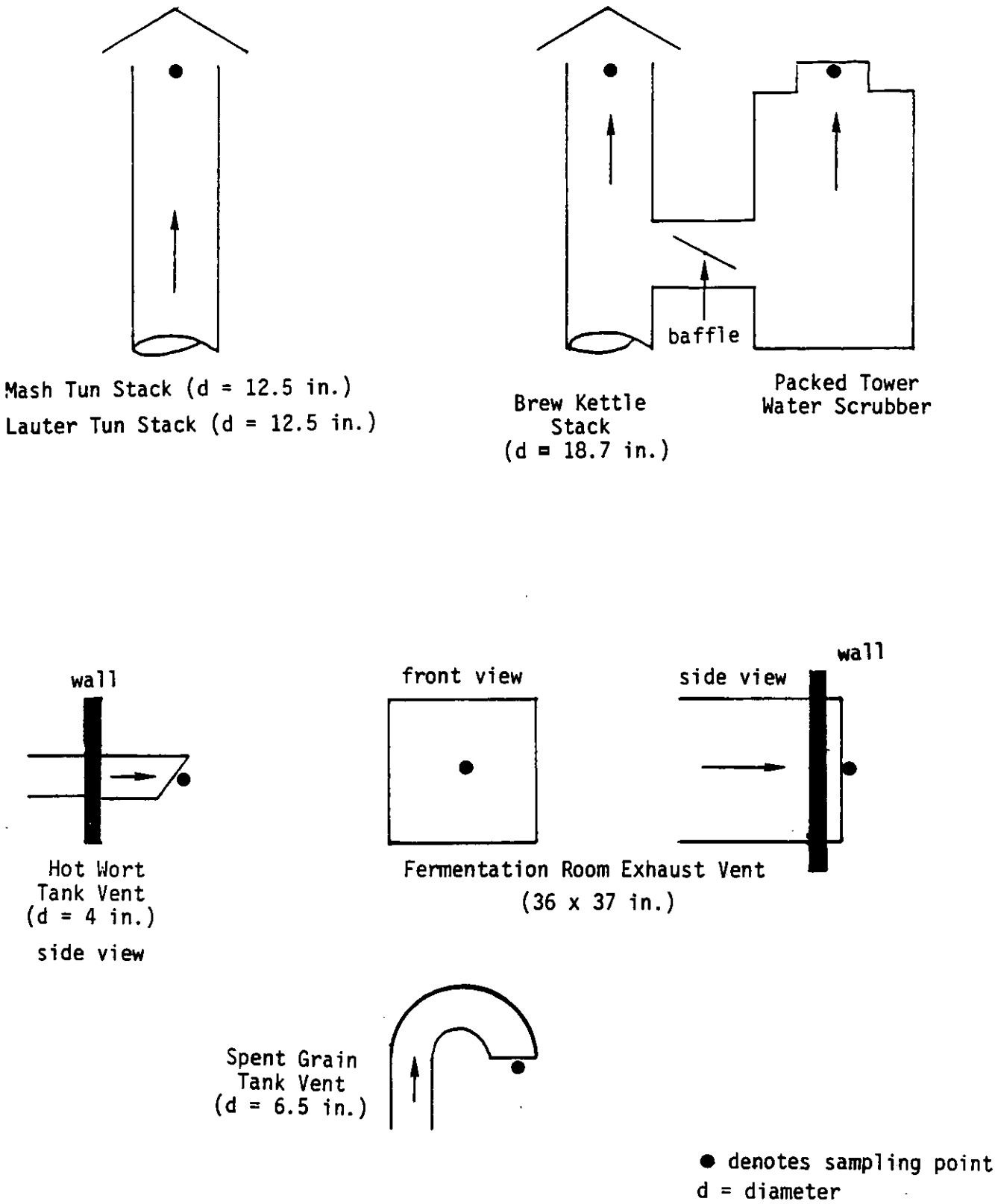
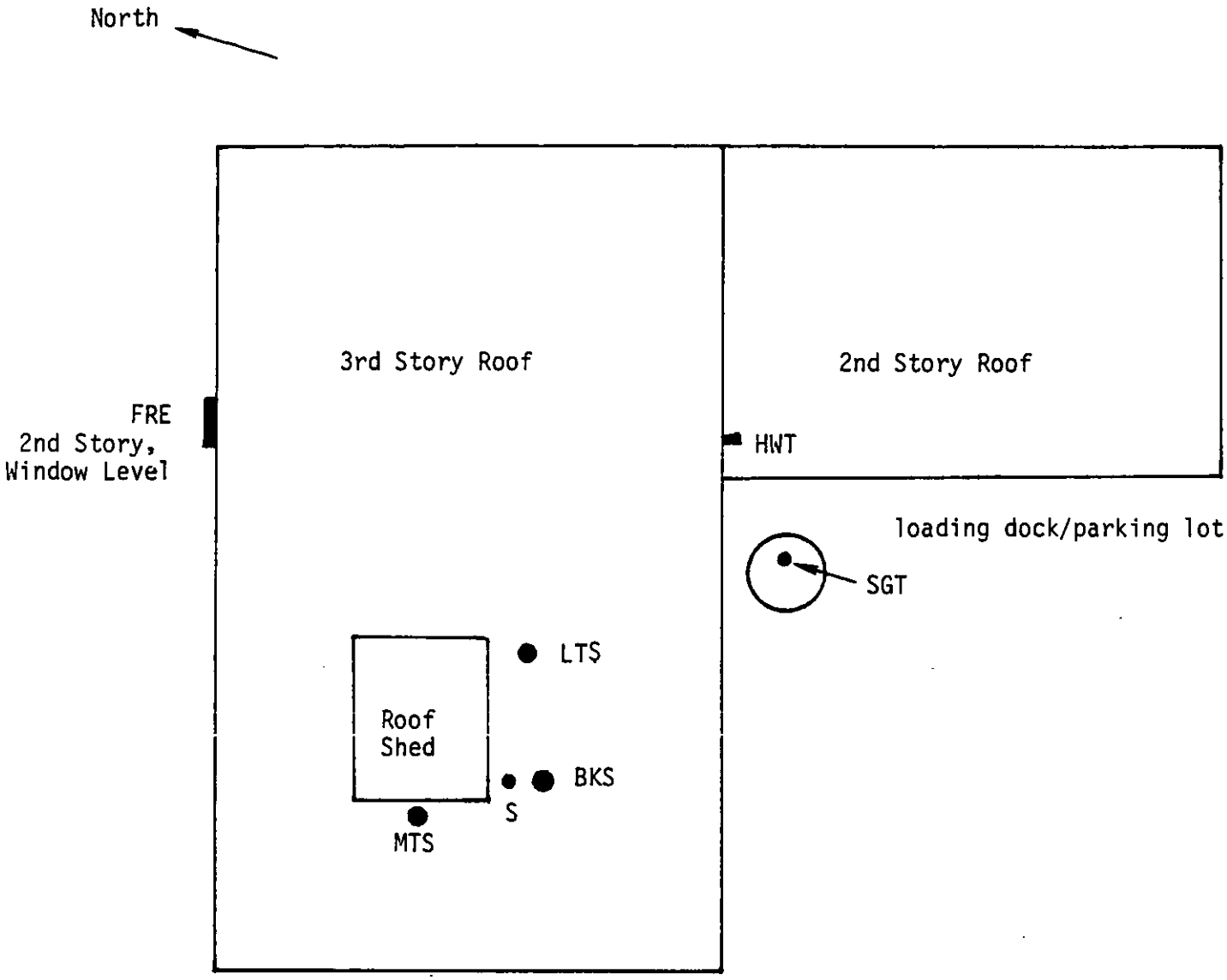


Figure 5.2-2. Configuration of Exhaust Stacks and Vents at Anchor Brewing Co.



MTS - mash tun stack
LTS - lauter tun stack
BKS - brew kettle stack
S - brew kettle scrubber

HWT - hot wort tank vent
FRE - fermentation room exhaust vent
SGT - spent grain tank vent

Figure 5.2-3. Plant Layout at Anchor Brewing Company (not to scale)

safety problems created by the foul weather; sampling at this site was carried out during Phase II. Anchor Brewing does not dry spent grains.

5.2.3.3 Results and Discussion

In this section Phase I sampling results for Anchor Brewing Co. are discussed. It should be emphasized that these results are qualitative in nature, and that concentration results reported here are listed only to give an indication of the approximate levels of VOC found at each of the sampling sites.

Tedlar Bag Analyses

The analyses of the Tedlar bag samples by the GC/FID procedures described above showed no detectable components. After sampling, the Tedlar bags contained condensed moisture, which probably sequestered any VOCs present in the samples. Due to the high water vapor content of the sampled stack gases and the possible instability of organic compounds in the Tedlar bags, this device was not used during Phase II monitoring.

Charcoal Tube Analyses

The analytical procedure for charcoal tubes entailed the use of two desorption solvents depending on the amount of water present in the sample. The results of desorption efficiency testing using each of the solvent mixtures is presented in Table 5.2-4. From the results it is apparent that the presence of water in the sample interferes with the analysis. The recovery of ethyl alcohol from charcoal saturated with water was only 15 percent using the tetrahydrofuran/carbon disulfide mixture, whereas when dry charcoal is used the recovery of ethyl alcohol is 65 percent using the 2-butanol in carbon disulfide mixture. No ethyl alcohol was recovered from wet charcoal using the 2-butanol/carbon disulfide mixture. The need to remove water vapor from the gas stream prior to the charcoal tube thus became apparent. In the later sampling, the gas was cooled and dried as it passed through a dry impinger in an ice bath upstream of the charcoal tubes. The results of this sampling technique will be discussed further in Sections 5.3.4 and 5.3.5.

Table 5.2-4

DESORPTION EFFICIENCIES OF ETHYL ALCOHOL AND ETHYL ACETATE FROM CHARCOAL USING TWO DIFFERENT SOLVENT MIXTURES

Compound	Percent Desorption Efficiency[a]	
	1% 2-butanol[b]	10% tetrahydrofuran[b]
ethanol	65 ± 5 (n=2)	15 ± 1 (n=3)[c]
ethyl acetate	102 ± 19 (n=2)	99 ± 23 (n=3)[c]

[a] Mean ± standard error

[b] In carbon disulfide

[c] Charcoal was saturated with deionized water prior to spiking

Quantitative data presented here (and for all other sampled Phase I sites) should not be used for comparison with Phase II results. These data are not necessarily quantitatively accurate and are included only to provide background for Phase II sampling and analytical protocol development. The results of charcoal tube sample analyses for Anchor Brewing Co. are shown in Table 5.2-5. Measured concentrations for the mash tun stack are presented for cases in which sodium sulfate drying tubes were absent and present upstream of the charcoal tubes. The absence of drying tubes, in line, resulted in lower levels of ethyl alcohol measured at the site. This may be due to the interfering effects of the small amount of water vapor present in the gas stream. Without a drying tube inline the water vapor would have occupied adsorption sites on the charcoal, thereby decreasing the adsorption of the ethyl alcohol. Therefore it is important to remove as much of the water as possible when using charcoal. There was some question as to whether ethanol would adsorb onto sodium sulfate and therefore be missed in our analysis. It is difficult to determine how much, if any, ethanol was lost on the sodium sulfate but it would appear from our Phase I results that its beneficial effects as a dessicant outweigh its negative effects as a potential organic gas adsorbent. Since the potential interferences from sodium sulfate desiccant were unknown when we were designing the sampling train for Phase II monitoring, the dry impinger procedure described above was used instead. This procedure appeared to remove the water vapor from Phase II charcoal tube samples such that any potential interferences from either the water vapor or sodium sulfate dessicant were eliminated.

Fermentation room exhaust emissions showed the highest concentration of ethyl alcohol of all the sites sampled at Anchor Brewing Co. The hot wort tank vent also showed relatively high concentrations of ethyl alcohol and ethyl acetate.

Impinger Train Analyses

The results of direct analysis of impinger train contents for VOCs are presented in Table 5.2-6. The ethyl alcohol content of the mash tun exhaust using this method is in good agreement with that analyzed from

Table 5.2-5

RESULTS OF CHARCOAL TUBE ANALYSIS BY GAS CHROMATOGRAPHY/ FLAME IONIZATION DETECTION, ANCHOR BREWING COMPANY, PHASE I SAMPLING[a]

Site	Concentration (mg/m^3)	
	Ethanol	Ethyl Acetate
Mash Tun Stack[b]	43 ± 6	ND
Mash Tun Stack[c]	60 ± 1	ND
Fermentation Room Exhaust Vent	180	ND
Hot Wort Tank Vent[d]	126 ± 6	21

ND - not detected

[a] Quantitative data presented here should not be used for comparison with Phase II results.

[b] Mean ± standard error; based on 3 replicate analyses; sampling train without sodium sulfate drying tube

[c] Mean ± standard error; based on 3 replicate analyses; sampling train with sodium sulfate drying tube.

[d] Mean ± standard error; based on 2 replicate analyses; ethyl acetate only found in one sample.

Table 5.2-6

RESULTS OF DIRECT ANALYSIS OF IMPINGER TRAIN CONTENTS USING GAS CHROMATOGRAPHY/FLAME IONIZATION DETECTION, ANCHOR BREWING COMPANY, PHASE I[a]

Site	Ethanol (mg/m^3)
Mash Tun Stack	51
Lauter Tun Stack	ND
Hot Wort Tank Vent[b]	162 ± 20
Brew Kettle Stack[c]	17

ND - not detected

[a] Quantitative data presented here should not be used for comparison with Phase II results.

[b] Mean ± standard error; based on two replicate analyses

[c] Sample taken from brew kettle stack scrubber (controlled mode)

charcoal tubes. Emissions from the hot wort tank vent had higher concentrations of ethyl alcohol than were measured by the charcoal method. No ethyl acetate was detected at any of the sites using this method.

Table 5.2-7 lists the compounds identified in the impinger train extracts analyzed by GC/MS. Several alcohols, aldehydes, ketones, and various unidentified species were present. The concentration data, although tentative, indicated that the hot wort tank vent exhaust had the highest concentration of these semi-volatile components among the sampled sites. The mash tun stack exhaust also showed a relatively high concentration of semi-volatile species. Brew kettle stack emissions were sampled through a scrubber with a stated control efficiency of 95 percent for odorous hydrocarbon. This sampling site yielded the second lowest concentration of semi-volatile organics for all sampled sites.

OVA Sampling Results

The high water content in the gas streams limited the use of OVA. We initially attempted to use the OVA to estimate VOC levels in the spent grain tank exhaust during transfer of grains to the tank. Since the location of the tank made sampling at the exhaust port difficult, we used the OVA to sample the air in the exhaust plane. While we sampled, water began to condense in the lines of the instrument, making further sampling with the OVA impossible. As a result, future OVA sampling activities were limited to exhaust locations low in water vapor content.

5.2.4 Phase I Tests at Facility A

Emission measurements were made on the morning and afternoon of 21 December 1982. Weather conditions consisted of light to moderate rain, an air temperature of about 58°F (14°C) with moderate winds from the southwest at 10 to 15 mi/hr (4 to 7 m/sec).

Table 5.2-7

RESULTS OF IMPINGER EXTRACT ANALYSES BY GAS CHROMATOGRAPHY/ MASS SPECTROMETRY, ANCHOR BREWING COMPANY, PHASE I SAMPLING[a]

Site	Species	Concentration (mg/m^3)
Mash Tun Stack	methyl butanol	0.62
	pentanol	0.04
	hexanol	0.12
	hexanal	0.01
	phenyl acetaldehyde	0.02
	others	0.02
	subtotal	0.83
Brew Kettle Stack[b]	furan methanol	0.03
	phenyl ethanol	0.04
	phenyl acetaldehyde	0.03
	furfural	0.02
	hexadecanoic acid	0.02
	others	0.05
	subtotal	0.19
Hot Wort Tank Vent	furan methanol	0.30
	phenyl ethenol	0.10
	methyl ethyl pentanone	0.20
	furfural	0.50
	phenyl acetaldehyde	0.40
	triazolopyridinone	0.20
	others	0.57
	subtotal	2.27
Lauter Tun Stack	others	0.05

[a] Quantitative data presented here should not be used for comparison with Phase II results.

[b] Controlled emission mode

5.2.4.1 Facility Description

The brewery, surrounded mainly by open range and farmland and commercial establishments, currently operates 24 hours/day, 365 days/year, and produces 15 brews per day.

The brewery can be divided into three main sections. In the brewhouse, where mashing and wort boiling take place, air conditioning is passive in nature. The fermentation area, housing the alpha tanks and the aging tanks, contains an air conditioning system which keeps the air very cool; hence this area is closed to outside ambient air so that cool inside air may be conserved. The filling and packaging facility is a warehouse-type structure which has no forced-air conditioning. Several hatches on the roof can be opened to supply passive cooling during emergencies; an array of roof fans are regularly used to supply passive cooling air.

Figure 5.2-4 gives a detailed process flow diagram of brewing at Facility A. The brewery uses the double-mash method wherein rice and barley malt are first cooked separately, then combined in the mash tun and cooked for several more minutes. Spent grains from this process are conveyed to a transfer facility outside the brewery. Trucks arrive about 13 times per day to haul away the material in open container trailers with dimensions of 8 x 38 ft and 8 x 27 ft (Cooper, 1983). After boiling, wort is cooled to fermenting temperature and aerated by gravity flow through several vertical tubes contained in a tower which extend down through water and glycol cooling sections. Figure 5.2-5 is a schematic of this device. Aeration is achieved when sterile air is forced up through the vertical tubes in countercurrent flow to the descending wort. Evaporation gases are exhausted to the atmosphere through a stack.

Yeast is injected as the wort enters large, rectangular primary fermentation vessels called "alpha" tanks. The tanks have vents which are open to the ambient atmosphere for the first 30 hours of fermentation. Each of these vents is connected to a header which conduct flow to a single roof vent. As each brew reaches the 30-hour point, the fermenter vent is switched

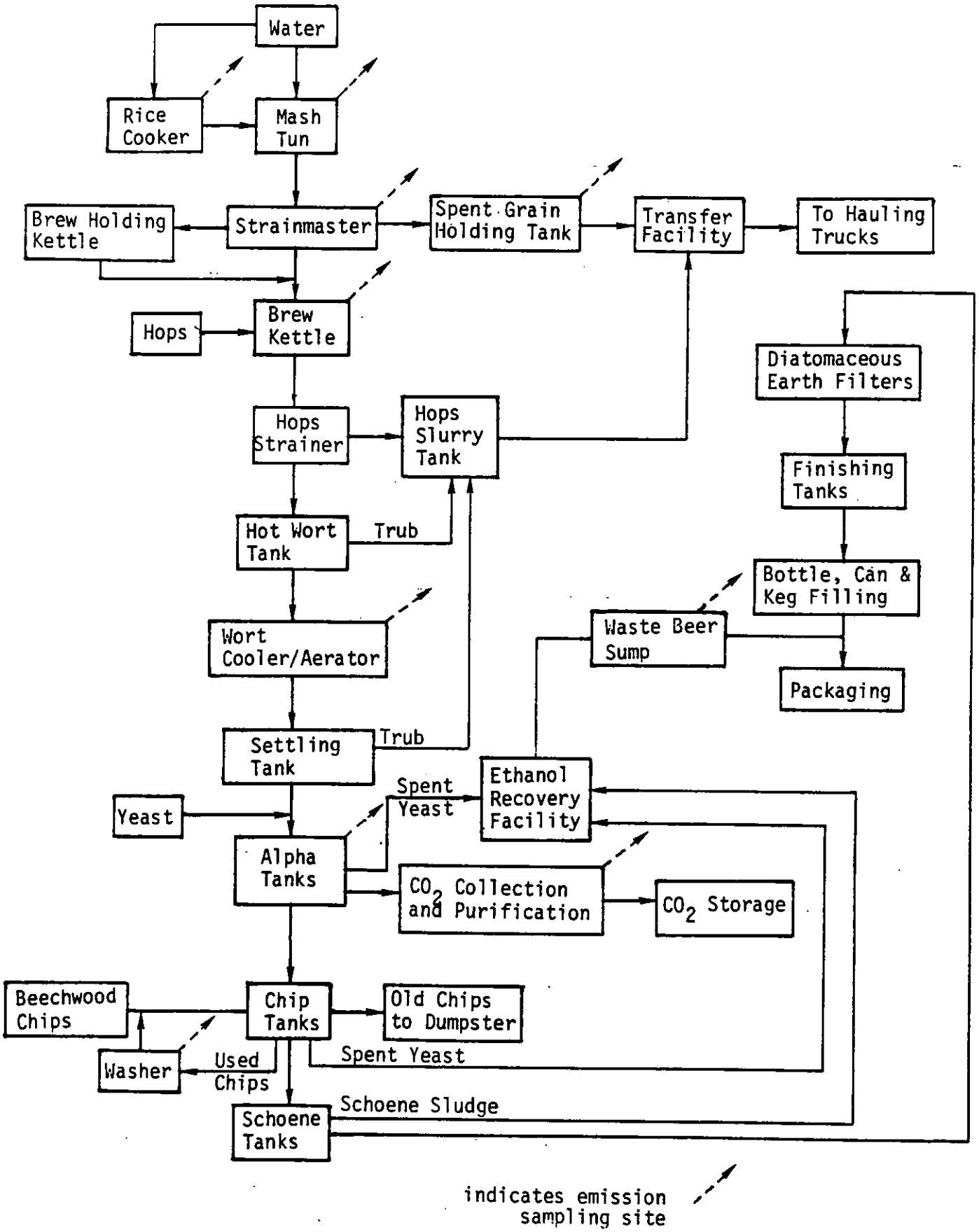


Figure 5.2-4. Brewing Process Flow Diagram - Facility A

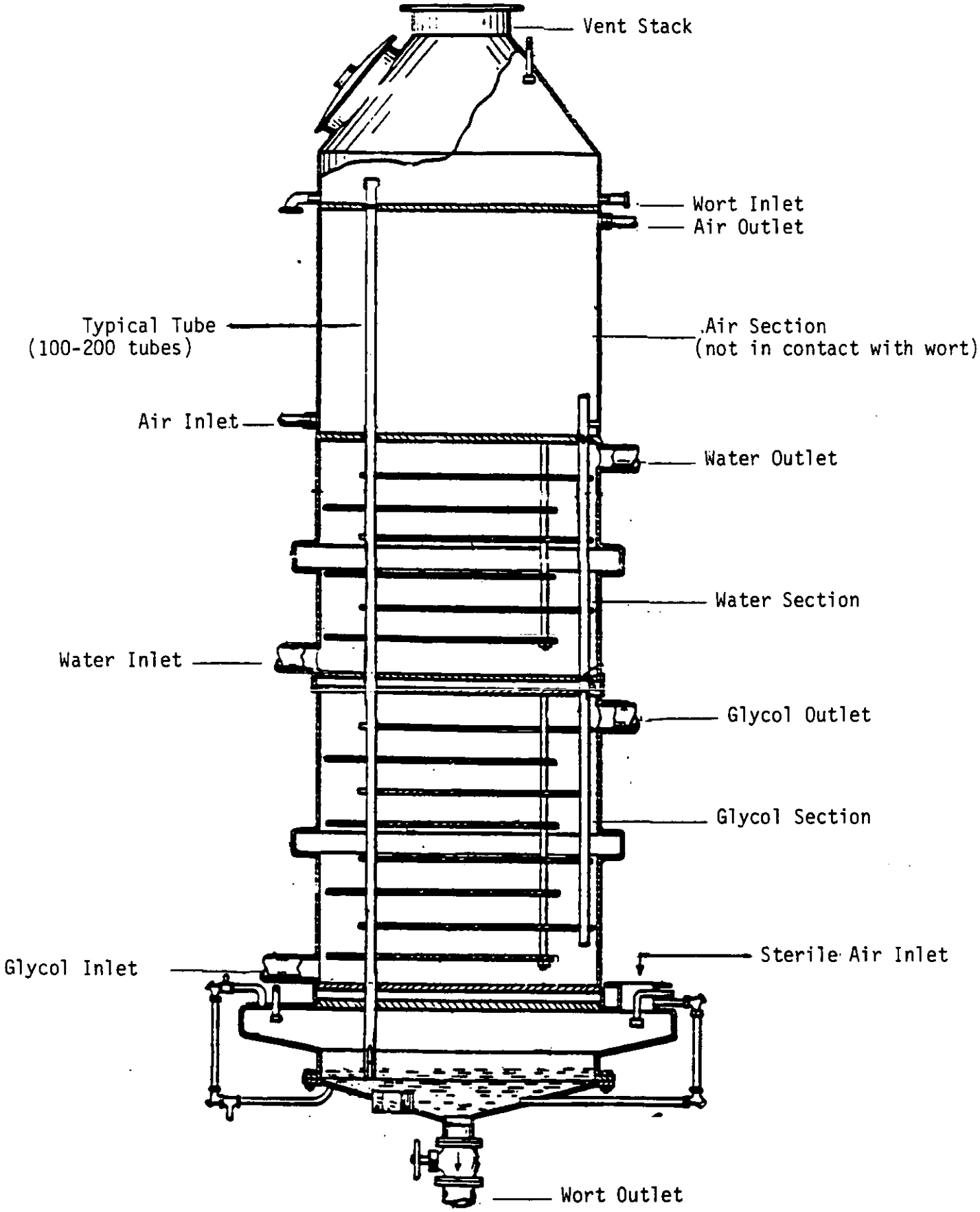


Figure 5.2-5. Schematic of a Wort Cooler Aerator

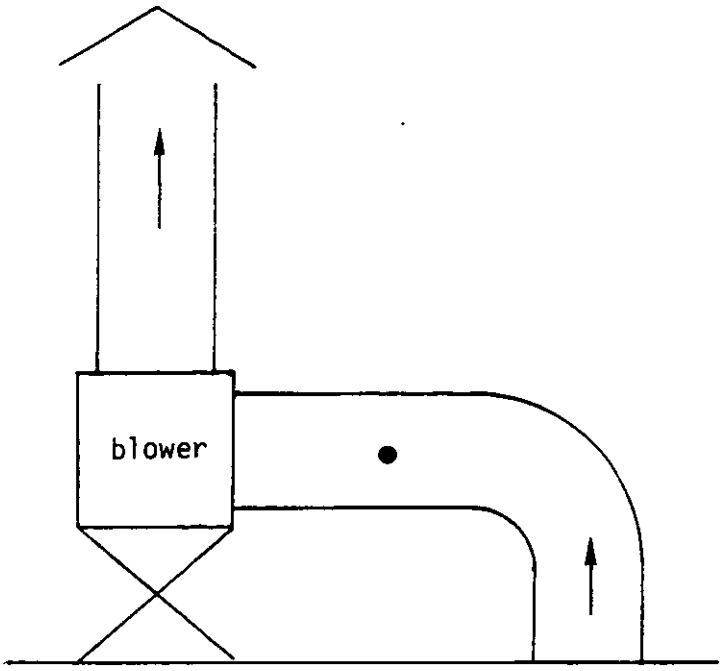
from the open to the closed position, thereby preventing the escape of fermentation gases to the ambient atmosphere. Carbon dioxide (and other volatiles) from fermentation are then passed through a CO_2 purification and collection system that includes a water scrubber followed by an activated carbon bed. (This system is described in Section 3.2.1.) The beds are regenerated for 24 hours, every day, with most of the volatiles being driven off to the atmosphere during the first four to five hours. At Facility A, two activated carbon beds are connected in parallel so that when one is being regenerated, the other is on-line. The brewery uses 49 alpha tanks, seven of which may be hooked up to the purification system at one time. These tanks contain brews at various stages of fermentation.

After primary fermentation is complete, the brew is pumped to horizontal, cylindrical "aging" tanks where beechwood chips are presented to enhance secondary fermentation. Once the alpha tanks and chip tanks are emptied, the spent yeast is drawn off the bottom and pumped to a distillation system (the only one of its kind in the state) which recovers ethanol for use as a boiler fuel or sale. When the aging tanks are emptied, beechwood chips are placed in torpedo-shaped containers and recycled in chip washers using hot water and steam. Vents from the washers are located on the roof. Old chips are deposited, unwashed, in a disposal bin in a garage-like structure in the brewery. Waste beer from filling operations is drained to an underground sump used as a holding tank before the waste is pumped to the distillation system.

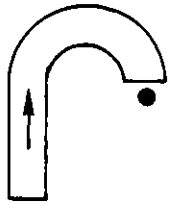
5.2.4.2 Emission Points

Through discussions with brewery personnel, literature reviews and a visual inspection of the facility we identified several potentially important emission sources. Figure 5.2-6 illustrates the configuration of, and sampling points (denoted by the dot) for, each emission source. The following sites were considered to be of secondary importance and hence, because of time constraints, were not sampled during Phase I testing:

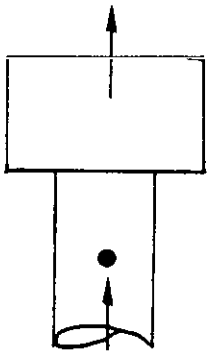
- Rice Cooker Stack
- Strainmaster Stack



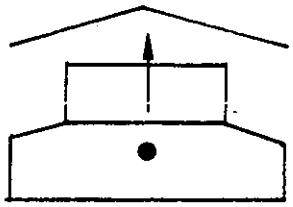
Rice Cooker Stack - II
Mash Cooker Stack - I,II
Brew Kettle Stack - I,II
Strainmaster Stack - II



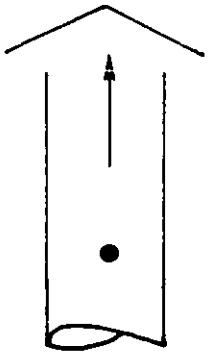
Alpha Tank Vent - I
CO_2 Purification System -
Activated Carbon Rengeneration Vent - II



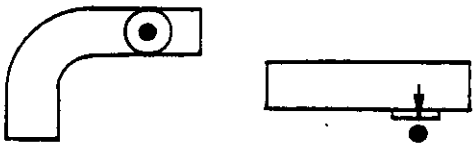
Wort Cooler/Aerator Stack - I



Beechwood Chip Washer Vent - I,II
(side view)



Spent Grain Holding Tank - I



Waste Beer Sump Vent - II
(side view) (top view)

● denotes sampling point
I = Phase I sampling site
II = Phase II sampling site

Figure 5.2-6. Configuration of Exhaust Stacks and Vents at Facility A

- Filling Area Roof Ventilation Ducts
- Waste Beer Sump Vent
- Spent Grain Disposal Facility
- Beechwood Chip Disposal Area

These sites were screened using the OVA during Phase II sampling to determine if more testing was warranted (see Section 5.3.5).

Because of a scheduling problem, we were unable to sample emissions during activated carbon regeneration from the CO_2 purification system; rather, we sampled emissions from the vent connected to the fermentation tanks open to the ambient atmosphere. The flow rate from the vent was negligible; emissions resulted from breathing losses. All of the remaining sites shown in Figure 5.2-6 have blower-assisted stacks or vents.

5.2.4.3 Results and Discussions

In this section, Phase I sampling results for Facility A are discussed. The problems encountered during sampling and analysis are very similar to those encountered at Anchor.

Tedlar Bag Analyses

Tedlar bag samples were analyzed using GC/FID analysis techniques described in Section 5.2.2. The analyses again showed no detectable components in the samples. As with the samples from Anchor Brewing Company, Tedlar bags also contained condensed moisture.

Charcoal Tube Analyses

The results of charcoal tube analyses from Facility A are presented in Table 5.2-8. Ethyl alcohol and ethyl acetate were the two major components identified at the sites sampled using this sampling and analysis technique. As would be expected ethyl alcohol was highest in concentration at the alpha tank vent. Brew kettle stack emissions contained the greatest concentration of ethyl acetate and also contained large amounts of ethyl

Table 5.2-8

RESULTS OF CHARCOAL TUBE ANALYSES BY GAS CHROMATOGRAPHY/ FLAME IONIZATION DETECTION, FACILITY A, PHASE I SAMPLING[a]

Site	Concentration (mg/m^3)	
	Ethanol	Ethyl Acetate
Brew Kettle Stack	22	69
Mash Tun Stack	ND	ND
Beechwood Chip Washer Vent	4	21
Alpha Tank Vent[b]	317	ND

ND - not detected

[a] Quantitative data presented here should not be used for comparison with Phase II results.

[b] Sample represents tank breathing loss emissions while open to atmosphere; Phase II sample taken from activated carbon regeneration vent.

alcohol. Unlike at Anchor Brewing Company, the mash tun stack at Facility A showed no detectable ethyl alcohol in the exhaust gases. The beechwood chip washing vent had measureable but relatively low concentrations of both ethyl alcohol and ethyl acetate.

Impinger Train Analyses

Table 5.2-9 presents the results of direct analysis of impinger train contents using GC/FID techniques described above. Only ethyl alcohol was detectable in the samples using this technique. Ethyl alcohol levels measured using impingers and the charcoal tubes are only within about a factor of five of each other. However it should be emphasized that these results are by no means quantitative and represent only a qualitative analysis of brewery emission sources.

The results of analysis of the impinger train content extracts are listed in Table 5.2-10. The major species identified by GC/MS analysis from brew kettle emission samples include alcohols, aldehydes, ketones and other miscellaneous compounds. Analyses showed that the mash tun stack contained the greatest concentration of semi-volatile organics. The wort cooler stack and the spent grain holding tank exhaust showed no measureable emissions with the exception of one compound identified from the former.

5.3 PHASE II MONITORING

The purpose of Phase II monitoring was to quantitatively characterize the VOCs emitted from sources identified during Phase I monitoring. The following section describes the test protocols used at both breweries during the second site visit, followed by a description of the exhaust points and a discussion of our sampling results.

5.3.1 Sampling Procedures

As a result of our experience in Phase I testing, the following methods were deemed most appropriate and were modified where necessary for

Table 5.2-9

RESULTS OF DIRECT ANALYSIS OF IMPINGER TRAIN CONTENTS USING GAS CHROMATOGRAPHY/FLAME IONIZATION DETECTION, FACILITY A, PHASE I SAMPLING[a]

Site	Ethanol (mg/m^3)
Brew Kettle Stack	10
Mash Tun Stack	18
Beechwood Chip Washer Vent	22
Wort Cooler Stack	ND
Spent Grain Holding Tank Stack	4

ND - not detected

[a] Quantitative data presented here should not be used for comparison with Phase II results.

Table 5.2-10

RESULTS OF IMPINGER EXTRACT ANALYSES BY GAS CHROMATOGRAPHY/ MASS SPECTROMETRY, FACILITY A, PHASE I SAMPLING[a]

Site	Species		Concentration (mg/m^3)
Brew Kettle Stack	furan methanol		0.04
	hexanol		0.05
	phenyl ethanol		0.20
	myrcene		0.12
	β-caryophyllene		0.05
	others		0.11
		subtotal	0.57
Mash Cooker Stack	hexanol		0.70
	pentanol		0.20
	others		0.10
		subtotal	1.00
Wort Cooler Stack	phenyl ethanol		0.01
Spent Grain Holding Tank Vent	none detected		

[a] Quatitative data presented here should not be used for comparison with Phase II results.

Phase II monitoring:

- Charcoal tubes;
- Impinger and XAD sorbent tube sampling train; and
- The Foxboro Model 128 OVA for area and point source measurements.

The first two sampling methods were designed to differentiate between lower molecular weight volatile compounds and medium to higher molecular weight semi-volatile compounds. The lower molecular weight volatile compounds are most effectively sampled and analyzed using charcoal tubes, while medium and higher molecular weight semi-volatile compounds are more amenable to sampling and analysis using water-filled impingers and an XAD sorbent tube as the sample collection media.

5.3.1.1 Charcoal Tube Sampling

The charcoal tube sampling method used during Phase II monitoring was modified slightly from that described in Section 5.2.1. The sampling train, shown in Figure 5.3-1, consisted of 1/4-inch stainless steel and teflon tubing used as a sampling probe to allow access to sampling ports. The probe was attached to a Dudley bubbling tube submerged in an ice bath which acted to cool the sampled gas and trap out moisture before it reached the charcoal tube. The Dudley tube was attached to two charcoal tubes connected in series followed by the sampling pump. The pump was calibrated, as described previously, both before and after each sample collection. Sample flow rates ranged from 60 to 75 ml/min. Sample volumes ranged from 0.58 to 11.2 liters.

Following the sampling period the sampling probe and Dudley tube were rinsed with organic-free deionized water which was transferred to an amber glass vial; all samples, including charcoal tubes, were stored in ice and shipped to the SAI Laboratory for analysis.

5.3.1.2 Impinger - XAD Sampling Train

The impinger sampling train, shown in Figure 5.3-2, was redesigned for Phase II monitoring. A sampling probe consisting of 1/4-inch stainless

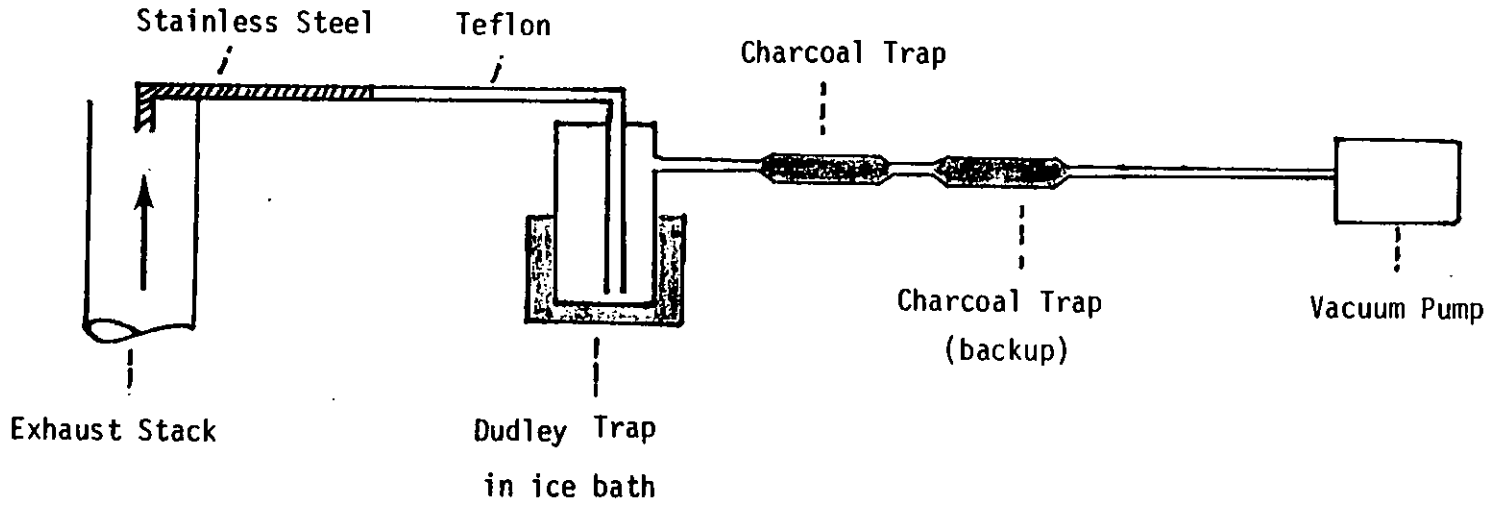


Figure 5.3-1. Charcoal Tube Sampling Train Used at Anchor Brewing Co. and Facility A

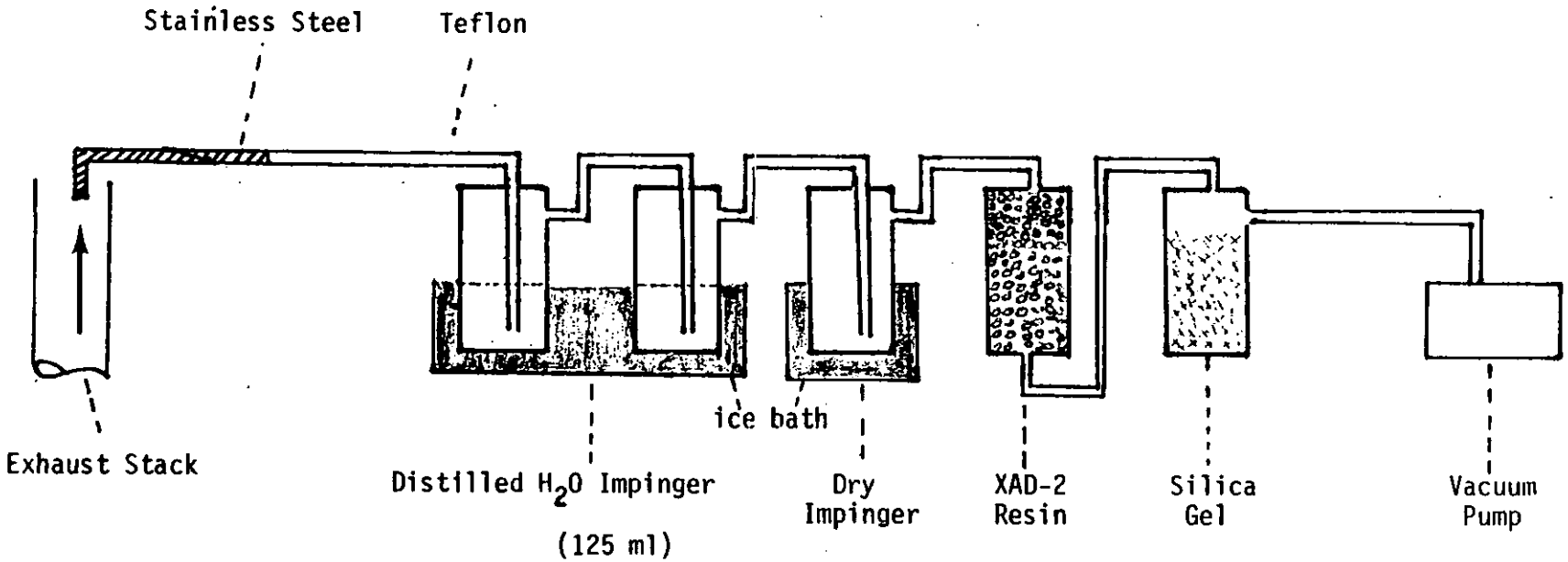


Figure 5.3-2. Impinger - XAD Resin Sampling Train Used at Anchor Brewing Co. and Facility A

steel and teflon tubing was connected to three 125-ml all glass impingers connected in series; the first two contained 75-ml of organic free deionized water and the third was empty. The three impingers were kept in an ice bath during sampling. The empty impinger was connected upstream of a glass tube containing about 3.5 grams of an equal mixture of XAD-2 and XAD-7 resins. During Phase I analysis, we discovered that many of the identified compounds were not readily soluble in water. Therefore, a tube of XAD resin was added to trap out any compounds which may not have been absorbed in distilled water. The XAD resin mixture was held in place in the glass tube with glass wool. The use of both XAD-2 and XAD-7 increased the range of polarity of compounds attracted to the adsorbents. The XAD tube was connected to an impinger filled with silica gel to dry the gas prior to its passage through a rotameter and sampling pump. The rotameter was used to monitor the sampling rates, which ranged between 0.8 and 2.3 L/min. The rotameter had been previously calibrated using a large volume bubble flow meter. A Sierra Model 244 MCM constant air flow sampler pump was used to pull gases through the sampling train.

Following sampling, the impinger contents were transferred to 125-ml amber glass bottles. The sampling probe was rinsed with deionized water and combined with the impinger contents. XAD resin and the glass wool used to hold the resin in place were transferred from the glass tube to a glass vial with a teflon lined septum cap. Sample bottles and vials were stored in an ice chest and shipped to the SAI Laboratory for analysis.

5.3.1.3 Stack Exhaust Flow Rate Determinations

A Kurz Model 415M hot-wire anemometer was used to perform stack velocity traverses at Anchor Brewing Company. Traverses were taken at various diameters along two perpendicular traverse paths. Measurements were taken near the location of the sampling probe at the top of the stack. Several readings were taken during each sampled cycle enabling us to calculate 95-percent confidence intervals for the flow rate. It was not necessary to perform velocity traverses at Facility A because staff engineers provided stack flow rate data for all sampled sites based on the manufacturer's specifications for individual blowers. These data, however, were corrected to reflect higher sampling temperatures.

5.3.1.4 OVA Sampling

The OVA was used to screen several sites at Facility A, including the distillation system, beechwood chip disposal bins, waste beer sump, and filling room roof vents, to determine if more extensive sampling was warranted during Phase II. The instrument was calibrated using certified methane-in-air gas standards available from MG Burdett Gas Products Co.

5.3.1.5 Field QA/QC Procedures

Prior to field sampling a method blank of the deionized water used in the impinger train was analyzed to verify that the water was free from interferences. Field charcoal and impinger water blanks were generated in the same manner as described under the field QA/QC procedure for Phase I monitoring. XAD field blanks were generated by transferring XAD resin to the sampling tubes and then to one of the vials used for XAD sample storage. Prior to use the XAD resin mixture was cleaned by Soxhlet extraction for 24 hours with methanol followed by Soxhlet extraction with methylene chloride for 24 hours.

5.3.2 Analytical Procedures

5.3.2.1 Charcoal Tube Samples

Charcoal tube contents were analyzed using the same procedures outlined in Section 5.2.2 with one exception. Since all charcoal samples were visibly dry, one percent 2-butanol in carbon disulfide was the only desorption solvent used.

The sampling probe and Dudley tube rinses were analyzed directly by packed column GC/FID for volatile constituents using the Hewlett Packard 5730A GC with the 3388A Integretor. The GC analysis conditions were presented in Table 5.2-2. The GC/FID was calibrated in this mode using ethyl alcohol and ethyl acetate standards prepared in deionized water.

5.3.2.2 Impinger - XAD Samples

The impinger train contents were extracted and analyzed using methods described earlier in Section 5.2.2. XAD resin samples were extracted using standard Soxhlet extraction techniques. The XAD was transferred to a Soxhlet extraction thimble and extracted for 24 hours with methylene chloride. The methylene chloride was dried by passage over sodium sulfate and was then concentrated to an appropriate volume for GC/FID analysis. The capillary column GC/FID analysis conditions were presented in Table 5.2-2.

5.3.2.3 GC/FID Sample Analysis Procedures

The GC/MS procedures used for analysis of samples collected during Phase II monitoring were identical to those described in Section 5.2.2. XAD extracts were analyzed using the capillary column GC/MS methodology.

5.3.2.4 Laboratory QA/QC Procedures

Laboratory method blanks were processed in the same manner as the samples to insure against laboratory contamination. Fortified (spiked) charcoal, water, and XAD samples were analyzed to validate the accuracy of the analytical procedures.

Fortified charcoal samples were analyzed using identical procedures as for the samples to obtain desorption efficiencies for ethyl alcohol and ethyl acetate. The desorption efficiencies were determined by spiking three charcoal traps with between 0.16 and 0.90 mg of each of the compounds. These traps were analyzed in the same manner as the samples using 1 percent 2-butanol in carbon disulfide as the desorption solvent.

Blank water and XAD resin were fortified with 1-hexanol, 2-heptanone, octanal, and benzaldehyde and were analyzed in the same manner as the samples. The spiking amounts were about 0.4 to 0.5 mg of each component added to 150 ml of blank water and to 3.6 grams of blank XAD resin.

5.3.3 Results of Sampling Train Efficiency Tests

Table 5.3-1 presents the results of charcoal tube desorption efficiency runs for ethanol and ethyl acetate. The concentration of these two compounds in actual field samples were adjusted for their respective desorption efficiencies as indicated in Table 5.3-1, and the concentration of other components in the samples were similarly adjusted using the average desorption efficiency of ethanol and ethyl acetate. Table 5.3-2 presents results of fortified water and XAD resin extraction efficiency runs using known quantities of four compounds. The concentration results for impinger samples were adjusted for the average extraction efficiency (82.3 percent) of the four test compounds from fortified water. Similarly, the concentrations reported for XAD resin samples were adjusted for the average desorption efficiency (66.9 percent) of the four test compounds from fortified XAD.

5.3.4 Tests at Anchor Brewing Company

Emission measurements were made during the mornings and afternoons of 10 March and 11 March 1983. Weather conditions the first day consisted of overcast skies with intermittent sprinkles, an air temperature of about 61°F (16°C), and light to moderate winds from the south. The second day was partly cloudy, with an air temperature of 65°F (18°C) and light winds from the southeast.

5.3.4.1 Emission Points

During the two days, we were able to sample all the sites shown in Figure 5.2-2. Brew kettle emission sampling was conducted in the main uncontrolled stack with the scrubber turned off.

5.3.4.2 Results and Discussion

The following section discusses Phase II sampling results from Anchor Brewing Company. Table 5.3-3 summarizes site-specific VOC concentrations and associated emission rates. The general equation used to calculate daily emission rates was:

Table 5.3-1

DESORPTION EFFICIENCIES OF ETHANOL AND ETHYL ACETATE FROM CHARCOAL USING ONE PERCENT 2-BUTANOL IN CARBON DISULFIDE - PHASE II

Compound	Desorption Efficiency[a] (%)
ethanol	46 ± 2
ethyl acetate	93 ± 2

[a] Mean ± standard error (n=3)

Table 5.3-2

RESULTS OF ANALYSIS OF FORTIFIED BLANK WATER AND BLANK XAD RESIN USING METHYLENE CHLORIDE EXTRACTION TECHNIQUES - PHASE II

Compound	Extraction Efficiency From Blank Water (%)	Desorption Efficiency From Blank XAD (%)
1-hexanol	91.1	77.3
2-heptanone	83.1	58.6
octanol	69.9	66.7
benzaldehyde	85.0	65.0
Average	82.3	66.9
Std. Deviation	8.9	7.8

Table 5.3-3

VOC CONCENTRATION AND EMISSION RATES AS A FUNCTION OF PROCESS SITE, ANCHOR BREWING

Site	Concentration (mg/m^3)	Process Cycle Time (min)[a]	Emission Rate[c] (kg/day)	Emission Rate[c] (kg/yr)
Mash tun stack	104.71	155	0.04 ± 0.01	7.29 ± 2.36
Lauter tun stack	29.50	145	0.02 ± 0.00	3.52 ± 1.01
Brew kettle stack[d]	173.78	90	0.33 ± 0.06	68.30 ± 13.27
Hot wort tank vent	299.05	40	0.07 ± 0.02	14.43 ± 4.98
Fermentation room exhaust vent	211.53 62.20	1440[b] 1440	6.74 ± 0.75	2,459.28 ± 272.39
Spent grain tank vent	5.10	20	>0.01	1.08
Total			7.21 ± 0.84[e]	2,553.90 ± 294.01[f]

[a] Length of one cycle; emission rates based on two cycles per day, 208 days/yr except where noted.

[b] 24 hour per day cycle 365 days/yr; emission rate based on first sample.

[c] Exhaust flow rates (95-percent confidence intervals) from Tables 5.3-4 to 5.3-10.

[d] Uncontrolled mode.

[e] 15.88 ± 1.85 lbs/day.

[f] 5,630.77 ± 648.18 lbs/year.

$$\text{emission rate, kg/day} = \left[\begin{pmatrix}\text{concentration in}\\ \text{the sample, mg/m}^3\end{pmatrix}\left(10^{-6}\ \text{kg/mg}\right)\begin{pmatrix}\text{exhaust flow}\\ \text{rate, m}^3\text{/min}\end{pmatrix} \times \begin{pmatrix}\text{process cycle}\\ \text{time, min}\end{pmatrix}\begin{pmatrix}\text{number of}\\ \text{cycles per day}\end{pmatrix}\right] \quad (5.3\text{-}1)$$

The concentration in the sample was calculated using the following equation:

$$C_i = \frac{m_{c,i}}{V_c} \quad (5.3\text{-}2)$$

$$C_i = \frac{m_{I,i} + m_{x,i}}{V_I} \quad (5.3\text{-}3)$$

where C_i is the concentration of species i, m and V are the mass collected and volume sampled, respectively; and c, I, and x denote charcoal tubes, water impingers, and XAD resin, respectively. Total reported concentrations represent the sums of all individual species concentrations. In two minor cases, both sampling trains (charcoal and impinger/XAD) trapped out a common compound. To avoid double counting, data from the sampling train which collected more of the compound was included in our analyses while data from the sampling train that collected less was deleted.

Fermentation Room

By far the most important site was the fermentation room exhaust stack which accounted for 93.5 percent of Anchor's total daily emission rate. Tables 5.3-4 and 5.3-5 show species profiles for both sample runs. The first run was used to calculate an emission rate since the operating conditions were most representative of long-term conditions. In both runs, ethanol accounted for more than 99 percent of the total emissions. The category of "unidentified" refers to compounds whose identification could not be characterized, but do contribute a fraction of the total emitted VOCs. It will be shown later that the (open) fermentation emission factor is the highest of all site-specific emission factors developed for the state brewing industry.

Brew Kettle Stack

The brew kettle stack, whose species profile is shown in Table 5.3-6, is the second most significant source, accounting for 4.6 percent of

Table 5.3-4

SPECIES PROFILE - FERMENTATION ROOM EXHAUST VENT, RUN #1, ANCHOR BREWING[a]

Compound	Concentration (mg/m^3)	Percent of Total Concentration	Emission Rate[b] g/hr	(oz/hr)	kg/yr	(lbs/yr)
ethanol	210.00	99.30	278.71	(9.83)	2,441.50	(5,382.58)
ethyl acetate	1.40	0.64	1.86	(0.07)	16.29	(35.91)
unidentified	0.13	0.06	0.17	(0.01)	1.49	(3.28)
Total	211.53	100.00	280.74	(9.91)	2,459.28	(5,421.77)

[a] represents emissions from one 3-day-old brew and two 2-day-old brews.

[b] exhaust flow rate (95-percent confidence interval; d.f. = 17) = 22.12 $\pm$ 2.45 actual m^3/min; cycle time = 1,440 min/day, 365 days/year.

Table 5.3-5

SPECIES PROFILE - FERMENTATION ROOM EXHAUST VENT, RUN #2, ANCHOR BREWING[a]

Compound	Concentration (mg/m^3)	Percent of Total Concentration	Emission Rate[b]			
			g/hr	(oz/hr)	kg/yr	(lbs/yr)
ethanol	62.00	99.70	82.29	(2.90)	720.86	(1,589.22)
unidentified	0.20	0.30	0.26	(0.01)	2.28	(5.03)
Total	62.20	100.00	82.55	(2.91)	723.14	(1,594.25)

[a] represents emissions from two 2-day-old brews and one new brew.

[b] exhaust flow rate (95-percent confidence interval; d.f. = 17) = 22.12 $\pm$ 2.45 actual m^3/min; cycle time = 1,440 min/day, 365 days/year.

Table 5.3-6

SPECIES PROFILE - BREW KETTLE STACK, ANCHOR BREWING[a]

Compound	Concentration (mg/m^3)	Percent of Total Concentration	Emission Rate[b] g/day	(oz/day)	kg/yr	(lbs/yr)
dimethyl sulfide	56.00	32.22	105.84	(3.73)	22.01	(48.52)
C_5-aldehyde	46.00	26.47	86.94	(3.07)	18.08	(39.86)
acetaldehyde	26.00	14.96	49.14	(1.73)	10.22	(22.53)
C_5-aldehyde	19.00	10.93	35.91	(1.27)	7.47	(16.47)
myrcene	9.00	5.18	17.01	(0.60)	3.54	(7.80)
ethanol	4.00	2.30	7.56	(0.27)	1.57	(3.46)
others	9.78	5.63	18.48	(0.65)	3.84	(8.47)
unidentified	4.00	2.30	7.56	(0.27)	1.57	(3.46)
Total	173.78	99.99	328.44	(11.59)	68.30	(150.57)

[a] Uncontrolled mode

[b] Exhaust flow rate (95-percent confidence interval; d.f. = 21) = 10.50 ± 2.04 actual m^3/min; average two cycles (90 minutes each) per day; brewing 4 days/week, 52 weeks/year.

the total daily emissions from the small brewery. It should be noted that these data represent uncontrolled emissions; during normal operations, Anchor uses a scrubber to reduce odorous hydrocarbons. Emissions from this site will be lowered by the stated control efficiency factor of 0.95 for emission inventory purposes (see Section 6.2). Figure 5.3-3 shows gas chromatograms for impinger and XAD resin extracts from the brew kettle stack sample. The chromatograms illustrate the large number of compounds detected. However, the compounds found in greatest quantity were recovered from the charcoal tube sample. These, and all subsequent, chromatograms include the residence times, in minutes, for each peak (sample constituent) eluted from the GC column. Dimethyl sulfide (DMS) accounts for about a third of the total emissions while the C_5-aldehyde represents about 26 percent of the total. DMS in beer has been ascribed to several causes including the heat decomposition of S-methyl-L-methionine during wort boiling (Anderson et al., 1971). Two compounds are reported as "C_5-aldehydes" since positive identifications could not be confirmed. As expected, myrcene, a hop oil, was also present in the sample. The category of "other" represents a number of positively identified compounds, all of which were in relatively low quantities.

Hot Wort Tank

Working emissions from filling of the hot wort tank, shown in Table 5.3-7, account for almost one percent of the total daily brewery emissions. Since only a transfer is involved, brew kettle and hot wort tank emissions have many compounds in common. Figure 5.3-4 shows gas chromatograms for impinger and XAD resin extracts from the hot wort tank. Comparisons of chromatograms from the brew kettle and hot wort tank show that the two sites share many of the same compounds. Again, many of the major compounds from the hot wort tank were collected on the charcoal tube sample. Ethanol's presence was probably due to contamination by fermentation-inducing organisms in the wort or from fermenting residues adhering to process equipment. This same explanation may apply to the presence of ethanol (and other fermentation products) in samples taken at sites preceding actual fermentation operations. Analysis also identified the presence of β-caryophyllene, a volatile hop oil which is expected to evaporate during wort boiling and transfer. Furfural, a compound resulting from the dehydration of pentose sugars found in cooking grain mixtures, was also identified in the sample.

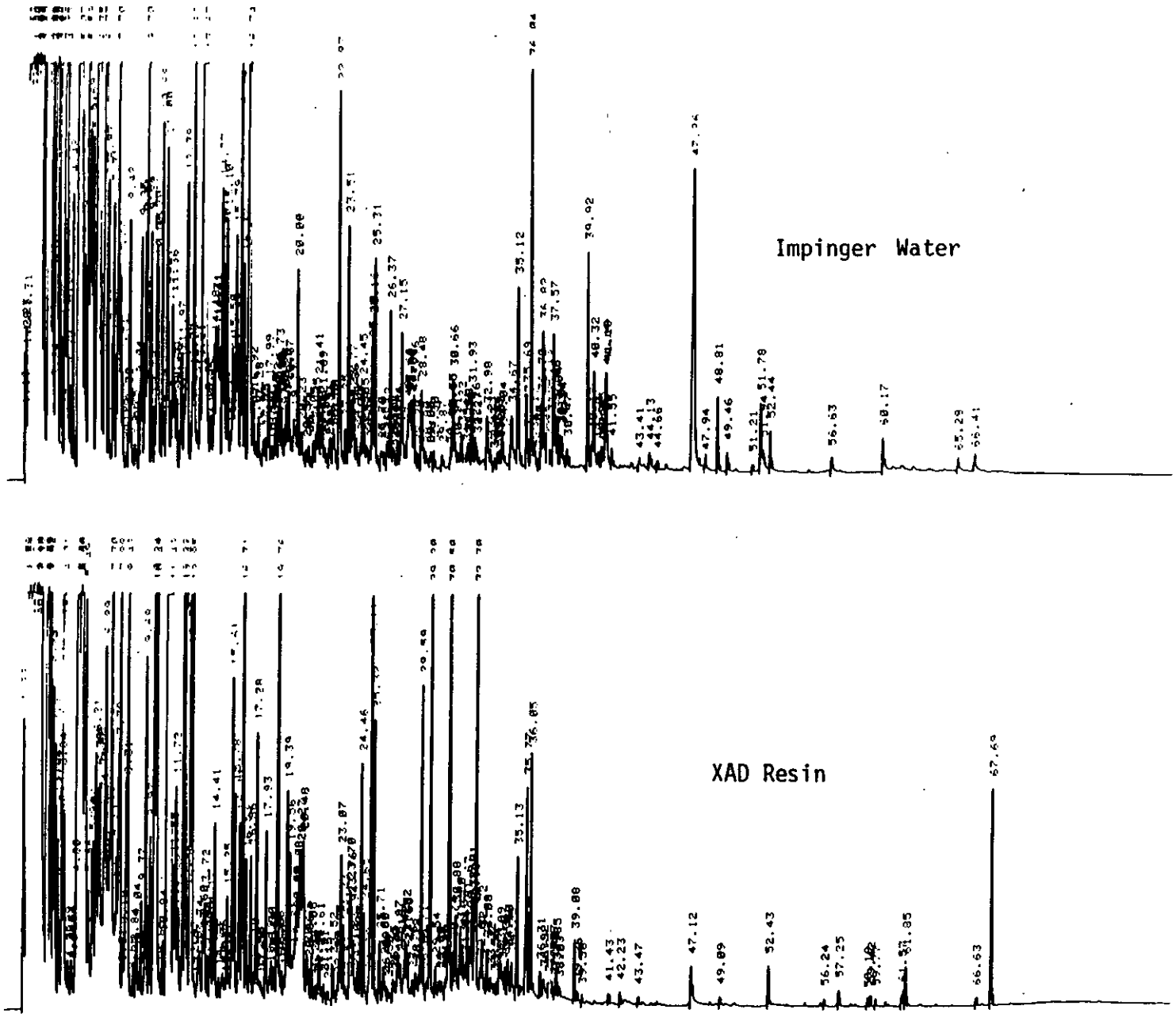


Figure 5.3-3. Gas Chromatograms of Impinger and XAD Resin Sample Extracts From the Brew Kettle Stack -- Anchor Brewing Company

Table 5.3-7

SPECIES PROFILE - HOT WORT TANK VENT, ANCHOR BREWING[a]

Compound	Concentration (mg/m^3)	Percent of Total Concentration	Emission Rate[b] g/day	(oz/day)	kg/yr	(lbs/yr)
myrcene	103.00	34.44	23.90	(6.84)	4.97	(10.96)
C_5-aldehyde	41.00	13.71	9.51	(0.33)	1.98	(4.36)
ethanol	35.00	11.70	8.12	(0.29)	1.69	(3.73)
dimethyl sulfide	31.00	10.37	7.19	(0.25)	1.50	(3.31)
acetaldehyde	16.00	5.35	3.71	(0.13)	0.77	(1.70)
B-caryophyllene	11.00	3.68	2.55	(0.09)	0.53	(1.17)
C_5-aldehyde	9.30	3.11	2.16	(0.08)	0.45	(0.99)
furfural	7.20	2.41	1.67	(0.06)	0.35	(0.77)
phenyl acetaldehyde	5.40	1.81	1.25	(0.04)	0.26	(0.57)
cyclic hydrocarbons	4.50	1.50	1.04	(0.04)	0.22	(0.48)
others	24.35	8.14	5.65	(0.20)	1.17	(2.58)
unidentified	11.30	3.78	2.62	(0.09)	0.54	(1.19)
Total	299.05	100.00	69.37	(2.44)	14.43	(31.81)

[a] Working emissions

[b] Exhaust flow rate (95-percent confidence interval; d.f. = 20) = 2.90 ± 1.00 actual m^3/min; average two cycles (40 minutes each) per day, 4 days/week, 52 weeks/year.

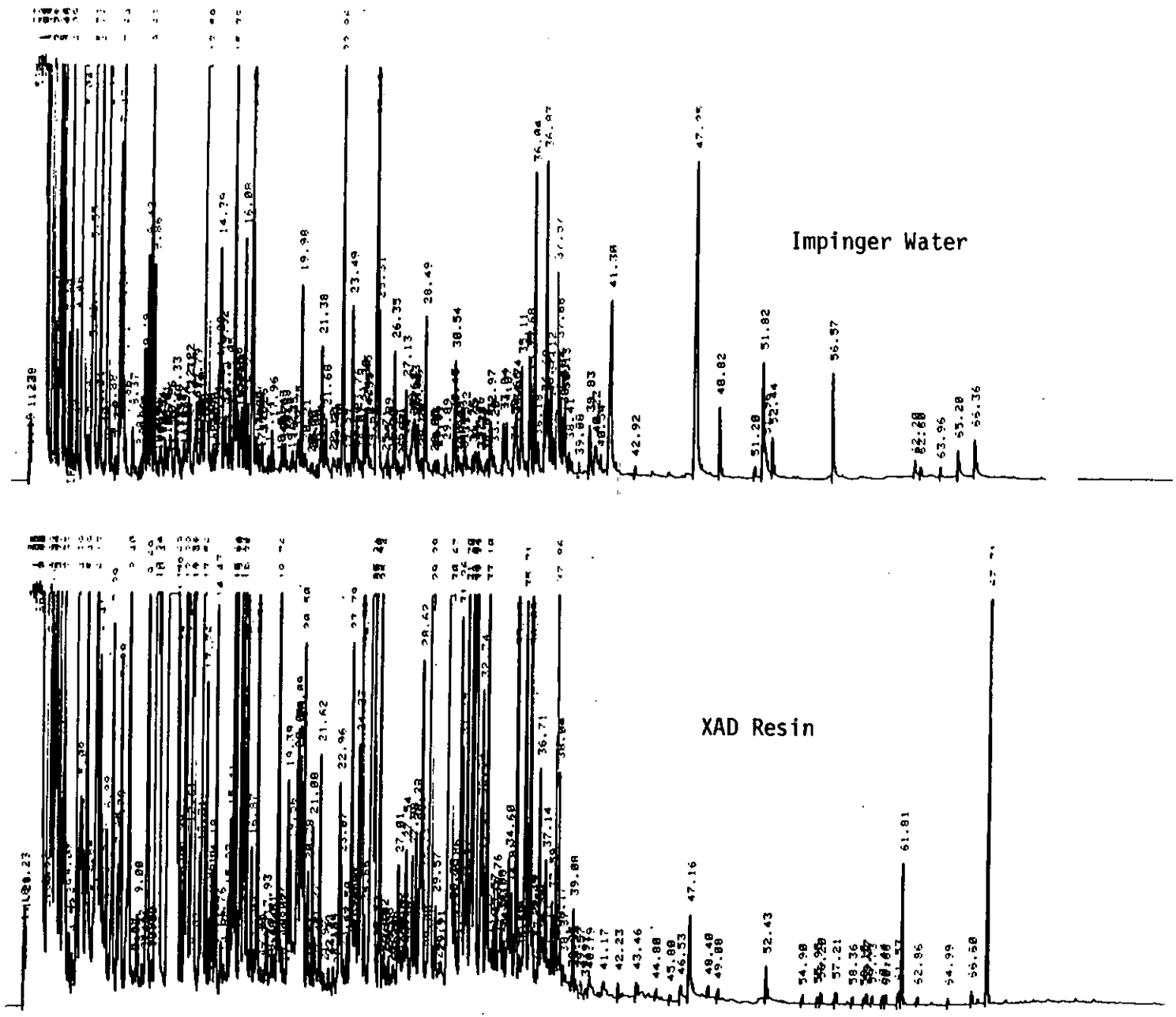


Figure 5.3-4. Gas Chromatograms of Impinger and XAD Resin Sample Extracts From the Hot Wort Tank Vent -- Anchor Brewing Company

Mash Tun and Lauter Tun

The mash tun and lauter tun stacks were among the minor sources sampled at the small brewery. Together they account for less than one percent of the total daily brewery emissions. Species profiles for the mash tun and lauter stacks, shown in Tables 5.3-8 and 5.3-9, reveal many of the same compounds. Since the lauter tun is only a filtering device following mashing, the two sites would be expected to have similar profiles. DMS shows up in both the mash tun and lauter tun for the reasons discussed earlier. As seen in Figure 5.3-5 the chromatograms for the mash tun sample revealed fewer gaseous compounds in the emission stream. Only a relatively small amount of ethanol was present in spent grain tank emissions, as shown in Table 5.3-10.

5.3.4.3 Comments on Sampling Techniques

The Dudley tube in the charcoal tube sampling train shown in Figure 5.3-1 worked well to prevent moisture from entering the charcoal tube. Most of the major compounds identified from each site, including DMS, ethanol, ethyl acetate and C_5 aldehydes, were collected and analyzed from charcoal tubes while most of the compounds included in the catagories of "others" and "unidentified" were collected in the impinger/XAD resin sampling train. Heavy, semi-volatile compounds such as myrcene and β-caryophyllene, both of which are highly photochemically reactive, were collected mainly on the XAD column. The higher molecular weight alcohols and aldehydes, all of which were present in relatively small quantities, were found in impinger extracts. Charcoal tubes collected the greatest mass of VOCs per site of all the other sampling train components, followed by XAD resin and the distilled water impingers. This finding is due, in part, to the selection of the solvent used to extract the compounds from the impinger water and XAD resin samples. This solvent probably masked some of the lower molecular weight compounds during GC/FID sample analysis. The charcoal tube was used because its analysis would reveal lower molecular weight compounds (such as ethanol) masked by the impinger/XAD analyses.

Table 5.3-8

SPECIES PROFILE - MASH TUN STACK, ANCHOR BREWING

Compound	Concentration (mg/m^3)	Percent of Total Concentration	Emission Rate[b] g/day	(oz/day)	kg/yr	(lbs/yr)
dimethyl sulfide	56.00	53.48	18.75	(0.66)	3.90	(8.60)
C_5-aldehyde	23.00	21.97	7.70	(0.27)	1.60	(3.53)
C_5-aldehyde	15.00	14.33	5.02	(0.18)	1.04	(2.29)
ethanol	4.60	4.39	1.54	(0.05)	0.32	(0.70)
C_5-alcohol	2.70	2.58	0.90	(0.03)	0.19	(0.42)
others	2.82	2.69	0.95	(0.03)	0.20	(0.44)
unidentified	0.59	0.56	0.20	(0.01)	0.04	(0.09)
Total	104.71	100.00	35.06	(1.23)	7.29	(16.07)

[a] Exhaust flow rate (95-percent confidence interval; d.f. = 20) = 1.08 ± 0.35 actual m^3/min; average two cycles (155 minutes each) per day; brewing 4 days/week, 52 weeks/year.

Table 5.3-9

SPECIES PROFILE - LAUTER TUN STACK, ANCHOR BREWING

Compound	Concentration (mg/m^3)	Percent of Total Concentration	Emission Rate[a] g/day	(oz/day)	kg/yr	(lbs/yr)
ethanol	16.00	54.24	9.19	(0.32)	1.91	(4.21)
dimethyl sulfide	5.90	20.00	3.39	(0.12)	0.71	(1.57)
C_5-aldehyde	3.70	12.54	2.12	(0.07)	0.44	(0.97)
C_5-aldehyde	2.30	7.80	1.32	(0.05)	0.27	(0.59)
acetaldehyde	1.60	5.42	0.92	(0.03)	0.19	(0.42)
Total	29.50	100.00	16.94	(0.59)	3.52	(7.76)

[a] Exhaust flow rate (95-percent confidence interval; d.f. = 10) = 1.98 ± 0.57 actual m^3/min; average two cycles (145 minutes each) per day, 4 days/week, 52 weeks/year.

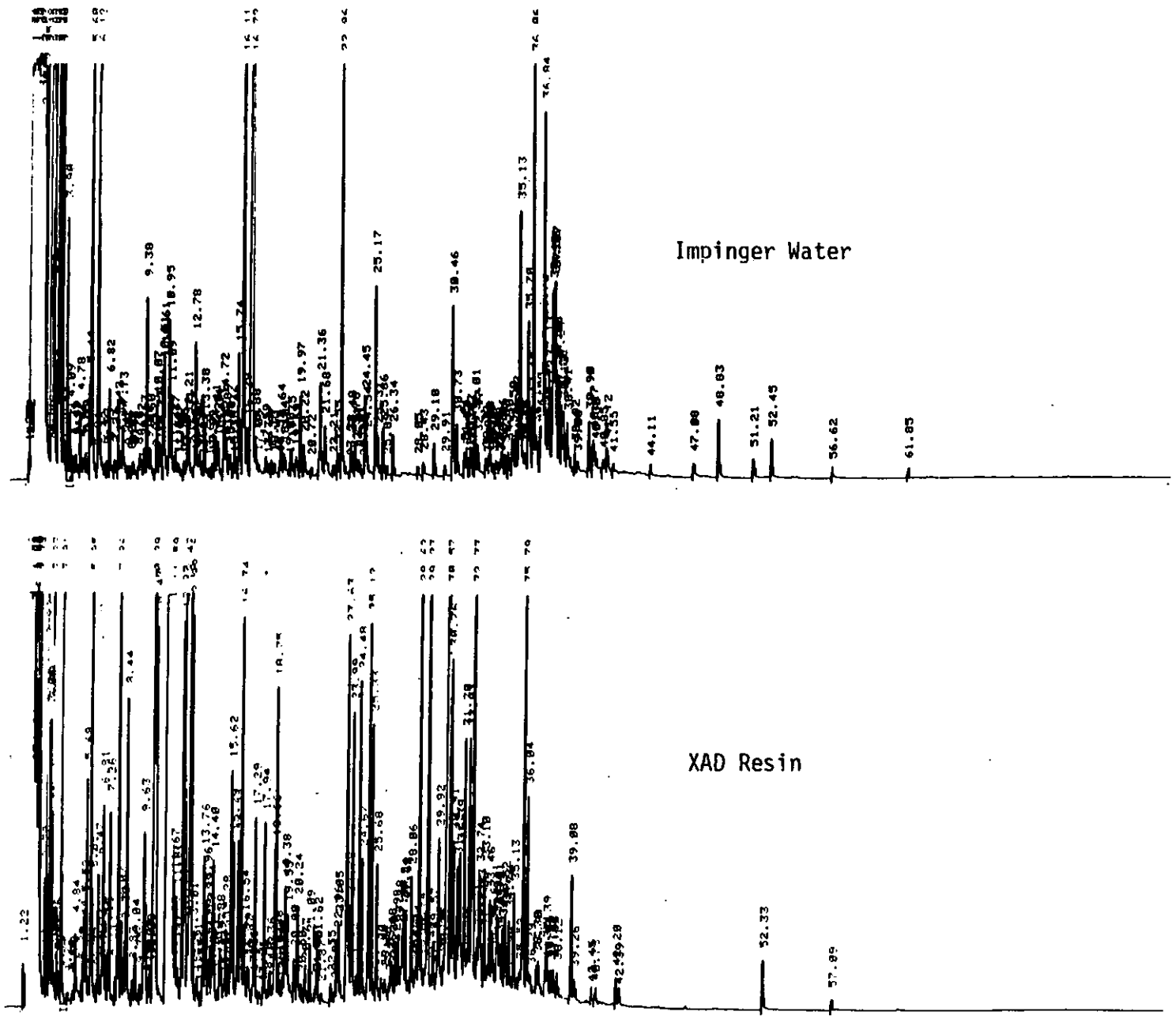


Figure 5.3-5. Gas Chromatograms of Impinger and XAD Resin Sample Extracts From the Mash Tun Stack -- Anchor Brewing Company

Table 5.3-10

SPECIES PROFILE - SPENT GRAIN HOLDING TANK, ANCHOR BREWING

Compound	Concentration (mg/m^3)	Percent of Total Concentration	Emission Rate[a]			
			g/day	(oz/day)	kg/yr	(lbs/yr)
ethanol	5.10	100.00	5.21	(0.18)	1.08	(2.39)

[a] Exhaust flow rate > 25.53 actual m^3/min (beyond range of hot-wire anemometer); average two cycles (20 minutes each) per day, 4 days/week, 52 weeks/year.

5.3.5 Tests at Facility A

Emission measurements were made on the mornings and afternoons of 8 and 9 March 1983. Weather conditions on the first day consisted of partly cloudy skies, an air temperature of about 70°F (21°C) and light winds from the southwest. The second day's weather conditions were almost identical.

5.3.5.1 Emission Points

In view of our Phase I sampling results, we decided not to retest emissions from the spent grain holding tank and the wort cooler stack. As mentioned in Section 5.2.4.2, during Phase I, breathing loss emissions were sampled directly from a vent connected to a maximum of seven alpha tanks, each containing brews at various stages of fermentation. Emissions from this vent were not sampled during Phase II since volumetric flow rates were negligible relative to other major vented sources; emissions resulted from breathing losses. Attempting to estimate total VOC emissions from breathing losses from one individual brew and then scaling up to seven would be a complex task. Emission data from one alpha tank, over an entire fermentation cycle would be required. Because of the physical layout of this system, it was not possible or desirable at the time to sample emissions from one alpha tank. Literature searches encompassing individual fermentation emission characteristics did not provide alternate sources of data. The sites sampled during Phase II were as follows:

- Rice cooler stack
- Mash tun stack
- Strainmaster stack
- Brew kettle stack
- CO_2 purification system
  - Activated carbon regeneration vent
- Beechwood chip washer vent
- Waste beer sump.

OVA Screening Results

As mentioned in Section 5.2.4.2, several secondary sites were screened using the OVA to determine if further testing was warranted. Of those sites tested, only the strainmaster and rice cooker stacks and the waste beer sump required further testing. In using the OVA, background concentrations of ethanol were established by taking several readings in the staff parking lot which was far away from any significant VOC sources. Numerous readings were taken at each secondary source; if readings were significantly above background, then extra testing was initiated. The filing room exhaust ducts and the beechwood chip disposal area were found to emit VOC concentrations at or around background.

Emissions from spent grain disposal were not sampled directly; however our analysis will show that emissions from this site are negligible.

5.3.5.2 Results and Discussion

Table 5.3-11 summarizes site-specific VOC concentrations and associated emission rates. Concentrations were calculated using Equations 5.3-2 and 5.3-3. Emission rates for all sites except the activated carbon regeneration unit were calculated using Equation 5.3-1.

The emission rate for the CO_2 purification system during activated carbon regeneration was calculated as follows. According to Stier (1983), "most of the volatiles" are driven off during the first four or five hours of regeneration when the desorption temperature is about 250°F. (Information was unavailable as to exactly what percentage is driven off during this period.) All volatiles are eventually desorbed after the 24-hour regeneration cycle is complete. We will assume that "most of the volatiles" means 90 percent of the mass adsorbed on the activated carbon. This assumption was considered reasonable by a brewing industry representative (Stier, 1983); information on desorption rate as a fuction of temperature was not available. The total mass of VOCs emitted during one regeneration cycle is calculated by the following equation:

Table 5.3-11

VOC CONCENTRATION AND EMISSION RATES AS A FUNCTION OF PROCESS SITE, FACILITY A

Site	Concentration (mg/m^3)	Exhaust Flow Rate (actual m^3/min)	Process Cycle Time (min)[b]	Emission Rate kg/day	(lbs/day)	mt/yr	(tons/yr)
Mash tun stack	6.19[a]	134.20	120[f]	1.50	(3.30)	0.55	(0.60)
Rice cooker stack	0.28	141.39	45	0.03	(0.06)	0.01	(0.01)
Brew kettle stack	49.26	133.78	90	8.89	(19.62)	3.25	(3.58)
Strainmaster stack	96.59	94.82	25	3.44	(7.58)	1.25	(1.38)
Activated carbon regeneration vent	467.72 52.86	10.76	1440[e]	1.68[d]	(3.70)	0.61	(0.67)
Beechwood chip washer vent	25.37	98.45	60[c]	2.10	(4.63)	0.77	(0.84)
Waste beer sump	120.00	9.9	1440[e]	1.71	(3.77)	0.62	(0.69)
Total				19.35	(42.66)	7.06	(7.77)

[a] Average of two cycles; standard error = $\pm$ 0.76

[b] 15 brews/day, 365 days/yr

[c] 14 cycles/day

[d] Estimate based on first sample; see Section 5.3.5.2 for calculations

[e] One cycle

[f] Facility operates two mash tuns; one brew's mashing cycle overlaps another in time.

$$\text{total VOC emitted per cycle, kg} = \frac{\left(\begin{matrix}\text{measured concentration}\\ \text{in the sample, mg/m}^3\end{matrix}\right)\left(\begin{matrix}\text{exhaust flow}\\ \text{rate, m}^3\text{/min}\end{matrix}\right)(300\text{ min})}{(0.9)(10^6\text{ mg/kg})} \quad (5.3\text{-}4)$$

Crawford (1976) shows that the ratio between the concentration of a pollutant in the desorption stream and its concentration in the input to an adsorber system is constant and is less than one. From this, we may infer that the VOC concentration in the emission stream is fairly constant during the first four to five hours of regeneration, after which 90 percent of the total mass has been emitted (desorbed). Since our emissions testing covered the first two hours of regeneration, we can assume that the measured concentration was fairly constant over five hours.

During the course of the project, a question was raised in regards to the possibility of estimating the amount of VOCs (mainly ethanol) absorbed in the water scrubber component of the CO_2 purification system. These data could have been used to inventory the amount of VOCs disposed in the sewer system. This estimation was not possible because to do so would have required sampling the raw fermentation gas entering the scrubber to determine the inlet VOC concentration. With this information and data collected at the regeneration vent a control efficiency for the scrubber could have been derived. Also, volumetric flow rates which are needed to calculate mass flow rates in the system, are not readily available.

Brew Kettle Stack

The brew kettle stack showed the highest VOC emission rate, accounting for 45.5 percent of the total daily emissions. Table 5.3-12 presents the species profile for this site. Upon comparing brew kettle stack emissions from Facility A and Anchor Brewing (see Figures 5.3-3 and 5.3-6) we find that they have many compounds in common. At Facility A, myrcene and dimethyl sulfide (DMS) account for 75 percent of the total emissions. All of the major compounds identified were collected on the charcoal except for myrcene and β-caryophyllene, which were collected on the XAD. The presence of ethanol at this site (and the mash cooker) was probably due to contamination by fermentation inducing organisms in the wort or from fermenting residues adhering to process equipment.

Table 5.3-12

SPECIES PROFILE - BREW KETTLE STACK, FACILITY A

Compound	Concentration (mg/m^3)	Percent of Total Concentration	Emission Rate[a] kg/day	(lbs/day)	kg/yr	(lbs/yr)
myrcene	23.00	46.69	4.15	(9.16)	1,516.16	(3,342.57)
dimethyl sulfide	14.00	28.42	2.53	(5.57)	922.88	(2,034.61)
ethanol	1.90	3.86	0.34	(0.76)	125.25	(276.12)
C_5-aldehyde	1.70	3.45	0.31	(0.68)	112.06	(247.06)
B-caryophyllene	1.10	2.23	0.20	(0.44)	72.51	(159.86)
acetaldehyde	1.10	2.23	0.20	(0.44)	72.51	(159.86)
aliphatic hydrocarbons	0.69	1.40	0.12	(0.27)	45.48	(100.28)
others	3.82	7.75	0.69	(1.52)	251.81	(555.16)
unidentified	1.95	3.96	0.35	(0.78)	128.54	(283.39)
Total	49.26	99.99	8.89	(19.62)	3,247.20	(7,158.19)

[a] Exhaust flow rate = 133.78 actual m^3/min; 15 cycles (90 minutes each) per day.

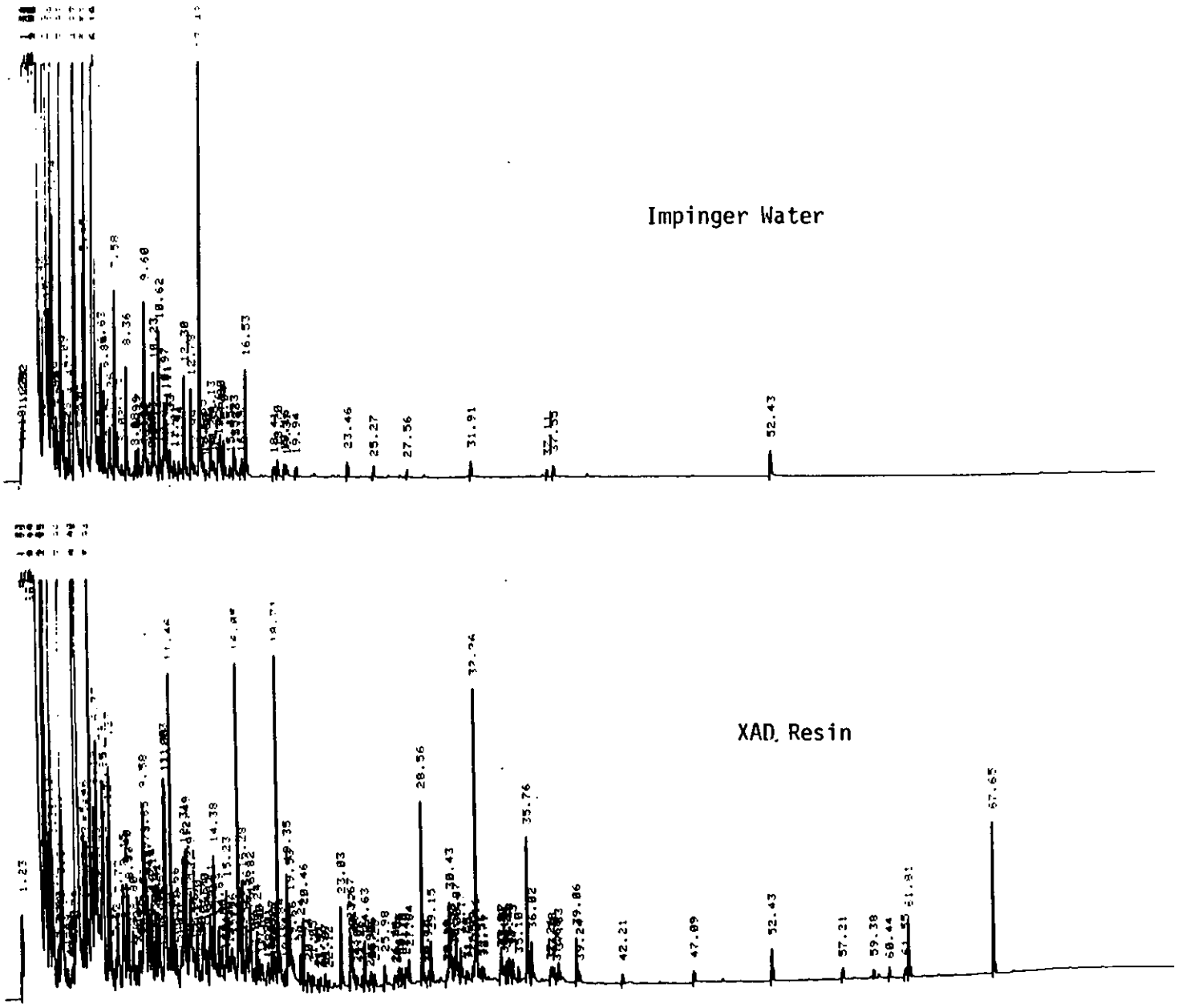


Figure 5.3-6. Gas Chromatograms of Impinger and XAD Resin Sample Extracts From the Brew Kettle Stack -- Facility A

Strainmaster Stack

The strainmaster stack, whose species profile is shown in Table 5.3-13, was the second most important source, contributing 17.6 percent of the total daily brewery emissions. This site was the single largest source of DMS emissions at the brewery; DMS accounted for 79.7 percent of the emissions from this site. All the major compounds identified were collected on charcoal.

Beechwood Chip Washer Vent

The beechwood chip washer vent contributed 10.7 percent of the total daily emissions; ethanol accounted for over 98 percent of the total emissions from this site, as shown in Table 5.3-14. A description of the analytical method discussing the quantification of VOC emissions is found in Section 5.3.2.

Activated Carbon Regeneration Vent

Emissions from the activated carbon regeneration vent, shown in Table 5.3-15, represent 8.6 percent of the total emissions from the brewery. Table 5.3-16 shows results of emissions testing during the last 1.5 hours of the regeneration cycle. Only concentrations are shown. We originally intended this test to encompass another regeneration period during the first hours of the cycle, but a scheduling mixup resulted in our sampling the wrong time period. Comparing the two runs we find that a small percentage of the volatiles (mainly ethanol) do remain after five hours of regeneration.

Waste Beer Sump

The waste beer sump was initially screened using the OVA. Readings were high enough above background to warrant further sampling. Since ethanol was assumed to be the predominant constituent in the exhaust stream, only charcoal tubes were used for sample collection. Results of the sampling, shown in Table 5.3-17, confirmed this assumption. Sump VOC emissions contributed 8.6 percent of the daily total from the brewery.

Table 5.3-13

SPECIES PROFILE - STRAINMASTER EXHAUST STACK, FACILITY A

Compound	Concentration (mg/m^3)	Percent of Total Concentration	Emission Rate[b] kg/day (lbs/day)	kg/yr (lbs/yr)
dimethyl sulfide	77.00	79.72	2.74 (6.04)	999.34 (2,203.18)
C_5-aldehyde	9.80	10.14	0.35 (0.77)	127.19 (280.40)
acetaldehyde	4.80	4.97	0.17 (0.38)	62.30 (137.34)
others	4.68	4.85	0.17 (0.37)	60.74 (133.91)
unidentified	0.31	0.32	0.01 (0.02)	4.02 (8.87)
Totals	96.59	100.00	3.44 (7.58)	1,253.59 (2,763.70)

[a] Stack flow rate = 94.82 actual m^3/min; 15 cycles (25 minutes, each) per day.

Table 5.3-14

SPECIES PROFILE - BEECHWOOD CHIP WASHER VENT, FACILITY A

Compound	Concentration (mg/m^3)	Percent of Total Concentration	Emission Rate[a]			
			kg/day	(lbs/day)	kg/yr	(lbs/yr)
ethanol	25.00	98.54	2.07	(4.56)	754.62	(1,663.65)
unidentified	0.37	1.46	0.03	(0.07)	11.17	(24.62)
Total	25.37	100.00	2.10	(4.63)	765.79	(1,688.27)

[a] Exhaust flow rate = 98.45 actual m^3/min; 14 cycles (60 minutes each) per day, 365 days/year.

Table 5.3-15

SPECIES PROFILE - CO_2 PURIFICATION SYSTEM, ACTIVATED CARBON REGENERATION VENT, RUN #1 FACILITY A[a]

Compound	Concentration (mg/m^3)	Percent of Total Concentration	Emission Rate[b] g/day	(oz/day)	kg/yr	(lbs/yr)
ethanol	360.00	76.97	1,291.20	(45.55)	471.29	(1,039.01)
ethyl acetate	59.00	12.62	211.61	(7.46)	77.24	(170.28)
C_7-ester	13.00	2.78	46.63	(1.64)	17.02	(37.52)
C_5-alcohol	11.00	2.35	39.45	(1.39)	14.40	(31.75)
dimethyl sulfide	8.00	1.71	28.69	(1.01)	10.47	(23.09)
others	14.52	3.10	52.08	(1.84)	19.01	(41.91)
unidentified	2.20	0.47	7.89	(0.28)	2.88	(6.35)
Total	467.72	100.00	1,677.55	(59.17)	612.31	(1,349.91)

[a] Run #1 taken during the first two hours of the cycle.

[b] Exhaust flow rate = 10.76 actual m^3/min (9.10 standard m^3/min at 68°C), 365 cycles/year; see Section 5.3.5.2 for calculations.

Table 5.3-16

SPECIES PROFILE - CO_2 PURIFICATION SYSTEM, ACTIVATED CARBON REGENERATION VENT, RUN #2, FACILITY A[a]

Compound	Concentration (mg/m^3)	Percent of Total Concentration
ethyl acetate	24.00	45.40
ethanol	11.00	20.81
C_5-alcohol	8.70	16.46
C_7-ester	3.44	6.51
dimethyl sulfide	2.70	5.11
unidentified	1.96	3.71
others	1.06	2.00
Total	52.86	100.00

[a] Run #2 taken during last 1.5 hours of the cycle.

Table 5.3-17

SPECIES PROFILE - WASTE BEER SUMP, FACILITY A

Compound	Concentration (mg/m^3)	Percent of Total Concentration	Emission Rate[a]			
			kg/day	(lbs/day)	kg/yr	(lbs/yr)
ethanol	120.00	100.00	1.71	(3.77)	624.41	(1,376.59)

[a] Exhaust flow rate = 9.9 actual m^3/min; one cycle (1,440 minutes) per day.

Mash and Rice Cookers

Mash cooker emission results are shown in Table 5.3-18. Concentration data were derived from two different sampled cycles. The major constituents emitted from this site were ethanol (53 percent) and DMS (44 percent). As described earlier, the presence of ethanol in the sample probably result from the fermentation of grain residues adhering to the walls inside the stack. Emissions from this site represented 7.7 percent of the total brewery VOC emissions.

The rice cooker stack was a very minor source of VOC emissions as shown in Table 5.3-19. Hexanal and the unidentified compounds were collected on XAD and in the impinger water, respectively.

Spent Grain Disposal

Emissions from the spent grain disposal facility were not directly measured during Phase II monitoring, but it was still necessary to determine if this site contributed significantly to total daily VOC emissions from breweries. To analyze the emissions from the disposal facility, we assumed that its species profile would be very similar to that of the strainmaster stack profile (see Table 5.3-13). As is shown in Figure 5.2-4, the flow of spent grains from the strainmaster to the disposal facility is interrupted only by a temporary holding tank. Since dimethyl sulfide (DMS) was the primary constituent in strainmaster exhaust, we focused on analysis of emissions of this specie.

The first step was to determine the amount of DMS originally present in the grains. Before proceeding to estimate this quantity, we begin with the assumption that the barley malt contains an average of 10 ppm methyl methionine by weight (Dickenson, 1979). From stoichiometry, conversion of all of this results in the formation of 3.8 ppm of DMS (assuming that none enters the beer during processing). An additional 5 ppm of DMS may already be present in the original grain (Dickenson, 1979). A maximum of 8.8 ppm, by weight, of the chemical would therefore be available for emissions. Each

Table 5.3-18

SPECIES PROFILE - MASH COOKER STACK, FACILITY A

Compound	Concentration[a] (mg/m^3)	Percent of Total Concentration	Emission Rate[b] kg/day	(lbs/day)	kg/yr	(lbs/yr)
ethanol	3.30 ± 0.10	53.31	0.80	(1.76)	290.95	(641.43)
dimethyl sulfide	2.75 ± 0.65	44.43	0.66	(1.46)	242.46	(534.53)
hexanal	0.03 ± 0.00	0.48	0.01	(0.02)	2.64	(5.83)
unidentified	0.11 ± 0.01	1.78	0.03	(0.06)	9.70	(21.38)
Total	6.19 ± 0.76	100.00	1.50± 0.10	(3.30± 0.22)	545.75± 67.01	(1,203.17± 147.73)

[a] Mean ± standard error (n = 2)

[b] Exhaust flow rate = 134.20 actual m^3/min; 15 cycles (120 minutes each) per day; totals represent mean ± std. error.

Table 5.3-19

SPECIES PROFILE - RICE COOKER STACK, FACILITY A

Compound	Concentration (mg/m^3)	Percent of Total Concentration	Emission Rate[a] g/day	(oz/day)	kg/yr	(lbs/yr)
hexanal	0.18	64.29	17.18	(0.61)	6.27	(13.82)
unidentified	0.10	35.71	9.54	(0.34)	3.48	(7.68)
Total	0.28	100.00	26.72	(0.95)	9.75	(21.50)

[a] Exhaust flow rate = 141.39 actual m^3/min; 15 cycles (45 minutes each) per day, 365 days/yr.

brew uses an average of 38,000 lb of grain, so that the original mass of DMS is estimated to be (38,000 lb)(8.8×10^{-6}) = 0.334 lb.

The mash cooker and strainmaster stack are the two sites which have the potential of emitting DMS prior to spent grain transferral to the disposal facility. (Actually, some DMS does remain in the beer after filtering in the strainmaster.) The maximum mass of DMS emitted at these two sites, as derived from Tables 5.3-13 and 5.3-18, is estimated by multiplying the DMS concentration in the emissions at both sites by their respective stack flow rates and cycle times.

The mash cooker and strainmaster are estimated to emit 0.098 lb (0.044 kg) and 0.402 lb (0.182 kg) per brew, respectively. The sum of masses of DMS emitted from these sites is, therefore, 0.500 lb, which is greater than the original 0.334 lb calculated to be originally present in the grains. Even with the large amount of variability expected in these calculations the potential for significant emissions from spent grain disposal is small. This conclusion is also strengthened somewhat by the Phase I results of spent grain holding tank emission tests. Emissions from this site were so negligible that further Phase II testing was deemed unwarranted (see Section 5.2.4).

5.3.5.3 Comments on Sampling Techniques

From the results of Phase II sampling at the large and small breweries, charcoal tubes collected the highest percentage of VOC on a total mass basis from all the major sites. Major compounds such as ethanol, DMS, acetaldehyde, ethyl acetate, and other C_5-aldehydes were all identified from charcoal tube analyses. However, XAD resin was also valuable for collecting constituents such as myrcene, β-caryophyllene and other higher molecular weight compounds.

5.4 DERIVATION OF EMISSION FACTORS

5.4.1 Anchor Brewing

The following equation is used to calculate all process-specific emission factors:

$$\text{emission factor (lbs VOC } 10^3\text{/bbl beer produced)} = \left[\frac{\left(\begin{matrix}\text{VOC concentration}\\ \text{in the sample, mg/m}^3\end{matrix}\right)\left(\begin{matrix}\text{exhaust flow}\\ \text{rate, m}^3\text{/min}\end{matrix}\right)}{(4.54 \times 10^5 \text{ mg/lb})} \times \frac{\left(\begin{matrix}\text{process cycle}\\ \text{time, min}\end{matrix}\right)(1000)}{\left(\begin{matrix}\text{amount of beer produced}\\ \text{per cycle, bbls}\end{matrix}\right)}\right] \quad (5.4\text{-}1)$$

It is not possible to present emission factors based on grain throughput, as to do so would permit derivation of confidential information. Table 5.4-1 presents the parameters and process-specific emission factors as calculated from Equation 5.4-1. Uncertainty ranges for emission factors are based on 95 percent confidence intervals calculated for exhaust flow rate measurements. The spent grain tank emission factor is expressed as an inequality due to the exceedence of the anemometer measurement range. The fermentation room exhaust emission factor is based on Run #1 (see Table 5.3-15), as this particular measured cycle is most representative of normal operating conditions.

At 23 kg VOC emitted per 1000 bbl of beer, the fermentation room exhaust vent was the single highest source of VOC per barrel of any site measured during the study. This emission factor is almost 14 times greater than that of the brew kettle stack, the next highest emission factor.

5.4.2 Facility A

Equations 5.3-2, 5.3-3 and 5.4-1 were used to calculate emission factors for all sites except the activated carbon regeneration vent. An emission factor for the waste beer sump was not derived because no other

Table 5.4-1

EMISSION FACTOR CALCULATIONS FOR ANCHOR BREWING[a]

Parameter	Process Site					
	Mash Tun Stack	Lauter Tun Stack	Brew Kettle Stack	Hot Wort Tank Vent	Fermentation Room Exhaust Vent[b]	Spent Grain Holding Tank
VOC Concentration in the Sample, mg/m^3	104.71	29.50	173.78	299.05	211.53	5.10
Exhaust Flow Rate, m^3/min	1.08 ± .35	1.98 ± .57	10.50 ± 2.04	2.90 ± 1.00	22.12 ± 2.45	>25.53
Process Cycle Time, min	155	145	90	40	1440	20
Amount of Beer Per Cycle, bbls	96	96	96	96	288	96
Emission Factor, kg VOC/10^3 bbl	.183 ± .059	.088 ± .025	1.711 ± .332	.361 ± .125	23.395 ± 2.591	>.027
(lb VOC/10^3 bbls)	(.403 ± .130)	(.194 ± .056)	(3.771 ± .733)	(.797 ± .275)	(51.578 ± 5.713)	(>.060)

bbls = barrels of beer (31 gallons/barrel)

[a] Uncertainty ranges based on 95-percent confidence interval for exhaust flow rate measurements.

[b] Based on Run #1

brewery in the state uses one. Table 5.4-2 presents the parameters and process-specific emission factors for Facility A.

The emission factor for the activated carbon regeneration was derived by calculating the total emissions per cycle using Equation 5.3-4 and then dividing the result by the amount of beer produced from that cycle. In this case seven fermenters, each containing 800 barrels of beer, pass their emissions through the system during one cycle. Therefore, the amount of beer produced is (800)(7) = 5600 bbls.

The amount of beer produced per beechwood chip washing cycle was estimated as follows:

$$\text{amount of beer per cycle, bbls} = \frac{(3 \text{ torpedoes/cycle})(800 \text{ bbls/brew})}{(7 \text{ torpedoes/brew})} = 343 \text{ bbls.}$$

The amount of beechwood chips recycled from one brew is enough to fill seven torpedoes. The washer can hold a maximum of three torpedoes per cycle.

At 0.7 kg VOC emitted per 1000 bbls of beer, the brew kettle stack had the highest emission factor derived from Facility A. This emission factor is still only about 3 percent of fermentation room exhaust emission fator derived for the small brewery.

5.5 REFERENCES

Anderson, R.J., Howard, G.A., and J.S. Hough. 1971. Proceedings of the european brewing convention congress, 253 pps.

Cooper, Stan, Newhall Land and Farming, Dixon California. Personal communication (16 May 1983).

Crawford, M. 1976. Air pollution control theory. Macgraw-Hill Book Company, New York.

Dickenson, C.J. 1979. "Dimethyl sulphide in malting and brewing," Chemistry and Industry, 15 December.

Lavignino, G., and D. Henderson. 1979. "SIP inspection report," Surveillance and Analysis Division, U.S. Environmental Protection Agency, Region IX, September 13, 1979. CDS Number: 00147.

Table 5.4-2

EMISSION FACTOR CALCULATIONS FOR FACILITY A

Parameter	Process Site					
	Mash Cooker Stack	Rice Cooker Stack	Strainmaster Stack	Brew Kettle Stack	Activated Carbon Regeneration Vent	Beechwood Chip Washer Vent
VOC Concentration in the Sample, mg/m^3	6.19 ± 0.76	0.28	96.59	49.26	467.72	25.37
Exhaust Flow Rate, m^3/min	134.20	141.39	94.82	133.78	10.76	98.45
Process Cycle Time, min	120	45	25	90	NA	60
Amount of Beer Per Cycle, bbls	800	800	800	800	5600	343
Emission Factor kg VOC/10^3 bbl	0.125 ± 0.015	0.002	0.286	0.741	0.300	0.437
(lbs VOC/10^3 bbls)	(0.275 ± 0.034)	(0.005)	(0.631)	(1.634)	(0.660)	(0.963)

NA - not applicable

Shreve, N.R. 1977. Chemical Process Industries. Fourth edition, McGraw-Hill Publishing Company.

Stier, John, Environmental Engineer, Anheuser-Busch, Inc., St. Louis, Missouri. Personal communication (19 May 1983).

U.S. Environmental Protection Agency. 1977. Determining input variables for calculation of impact of new source performance standards: Worksheets for food and agriculture industries, EPA-450/3-76-081C.

6.0

ESTIMATION OF ORGANIC COMPOUND EMISSIONS IN CALIFORNIA

The last step in our assessment of the brewing industry in California was to estimate emissions of volatile organic compounds (VOCs) from all breweries in the state.

6.1 METHODOLOGY

Emissions from each brewery identified by our questionnaire survey were calculated by multiplying individual production rates by the various emission factors. Our general methodology is described in the next section. Special adjustments were made for Anchor Brewing and Facility A. These departures from the general methodology are described in Section 6.1.2.

6.1.1 General Methodology

The general equation for the emissions from a facility was:

$$\text{emissions, lb/yr} = \left[\left(\text{annual beer production, bbls}\right) \times \left(\frac{(\text{mash tun EF}) + (\text{lauter tun EF}) + \ldots}{1000}\right)\right] \qquad (6.1\text{-}1)$$

where EF = process-specific emission factor in lbs VOC emitted per 10^3 bbls of beer produced.

Equation 6.1-1 expands to include all applicable process-specific emission factors (EF) for the large and small breweries (only two are shown in the equation). Emissions from the small and large breweries were calculated using emission factors developed from tests at Anchor Brewing

Company and Facility A (See Tables 5.4-1 and 5.4-2), respectively. The "strainmaster" emission factor was used to estimate emissions from large breweries using lauter tuns. The emission profile from a lauter tun and a strainmaster are not expected to be significantly different. The rice cooker emission factor was used to estimate emissions from breweries using different adjuncts such as corn or other cereals. Since this emission factor is already very small compared with other sites, any variability in emissions from non-rice adjunct cooking would not significantly alter total estimated emissions. The beechwood chip emission factor was applied only to those facilities in the state which use the process.

Finally, daily and hourly emissions were calculated for each brewery by dividing the emission estimate by the appropriate time unit. For example, a plant emitting 1 ton/year operating 10 hours/day, 260 days/year would have the following short term emissions:

$$\text{Daily emissions} = \frac{(1\ \text{ton/year})(2000\ \text{lbs/ton})}{(260\ \text{days/year})} = 7.7\ \text{lbs/day}$$

$$\text{Hourly emissions} = \frac{(7.7\ \text{lbs/day})}{(10\ \text{hours/day})} = 0.77\ \text{lbs/hour}$$

Annual emissions aggregated by geographic region, production process and firm size are presented in Section 6.2. Data on individual firms, including daily and hourly emissions are contained in a separate document. To protect confidentiality, the latter has been made available only to the Air Resources Board.

6.1.2 Method for Anchor Brewing and Facility A

Unlike the method used to calculate emissions from breweries not sampled during the project, annual emission rates for Anchor Brewing and Facility A were estimated from source tests; results are shown in Tables 5.3-3 and 5.3-11, respectively. For the purposes of constructing an appropriate estimate of yearly emissions from Anchor, we applied a 95-percent control efficiency factor to brew kettle emissions which reflects the water scrubber manufacturer's stated efficiency for controlling "odorous" hydrocarbons.

6.1.3 Speciation Methodology

Annual emission rates were estimated for each compound identified in our source tests. Weighted mass fractions were estimated for each compound and then multiplied by total industry emissions to give an average total for that compound. These weighted percentages take into consideration the preponderant amount of certain species (e.g. ethanol) emitted by small breweries. The procedure for determining the weighted percentages was as follows.

The total annual emission rates for each species found at Anchor Brewing and Facility A were calculated from data in Tables 5.3-4 through 5.3-10 and Tables 5.3-12 through 5.3-19, respectively. To determine the weighted average emission rate for species i from the two breweries, the following equation was used:

$$\overline{E}_i = \frac{\begin{pmatrix}\text{total emissions}\\ \text{for species i}\\ \text{at Anchor}\end{pmatrix}\begin{pmatrix}\text{total VOC}\\ \text{emissions}\\ \text{from Anchor}\end{pmatrix} + \begin{pmatrix}\text{total emissions}\\ \text{for species i}\\ \text{at Facility A}\end{pmatrix}\begin{pmatrix}\text{total VOC}\\ \text{emissions}\\ \text{from Facility A}\end{pmatrix}}{\begin{pmatrix}\text{sum of VOC emissions}\\ \text{from Anchor and Facility A}\end{pmatrix}}$$

where $\overline{E}_i$ = weighted average emission rate for species i. A total average weighted emission rate ($\overline{E}_T$) was calculated by summing together all speciated totals from the two facilities. The weighted fraction for species i (P_i) was determined by dividing $\overline{E}_i$ by $\overline{E}_T$. To determine total industry emissions of species i, total industry VOC emissions were multiplied by P_i.

6.2 RESULTS

6.2.1 Emissions By Geographic Unit

According to our estimates, 39 metric tons/yr (43 tons/yr) of reactive hydrocarbons were emitted from brewing operations in California. Table 6.2-1 shows estimated emissions by county. Los Angeles County, where the large brewing industry is concentrated, accounted for 75 percent of the total emissions; one brewery in this county contributed over 51 percent of

Table 6.2-1

ESTIMATED EMISSIONS FROM THE BREWING PROCESS: DISTRIBUTION BY COUNTY

County	Estimated Emissions				Percent of State Total[b]
	kg/day	(lb/day)	mt/yr[a]	(tons/yr)	
Alameda	0.03	(0.06)	0.01	(0.01)	0.03
Butte	0.32	(0.71)	0.07	(0.07)	0.18
Los Angeles	82.42	(181.69)	28.99	(31.95)	74.93
Sacramento	0.41	(0.91)	0.06	(0.07)	0.15
San Francisco	6.90	(15.20)	2.49	(2.74)	6.44
Solano	19.35	(42.66)	7.06	(7.77)	18.25
Sonoma	0.04	(0.10)	0.01	(0.01)	0.03
Totals	109.47	(241.33)	38.69	(42.62)	100.01[c]

[a] mt = metric tons

[b] Percentage based on annual emissions

[c] Discrepancy in total percentage is due to rounding.

the total emissions in the state. The small brewing industry, defined as those with capacities less than 60,000 bbls/yr, is located entirely in northern California and accounts for 7 percent of the total emissions. Distribution of emissions by state air basin is shown in Table 6.2.2. Again, the preponderance of emissions are in southern California. It is interesting to note that even though the small brewing industry accounts of only 0.2 percent of the state's annual production capacity, it contributes 7 percent of the total emissions. This inequity is primarily due to the relatively high fermentation room exhaust emission factor derived from the Anchor Brewing tests. This emission factor represents emissions from primary fermentation in an environment open to the ambient atmosphere. At large breweries in the state, fermentation takes place in a closed system environment which greatly reduces potential emissions from this brewing step.

6.2.2 Distribution of Emissions By Number of Firms

Our results show that the bulk of the emissions from beer production are concentrated among the large breweries. As seen in Figure 6.2-1, about 75 percent of the large breweries account for only 25 percent of the total emissions. On the other hand, only about 10 percent of the breweries (= 1 brewery) account for over fifty percent of the total.

6.2.3 Distributions of Emissions By Process Site

Table 6.2-3 shows that the brew kettle stacks emit over 40 percent of the total emissions in the state, followed by strainmaster/lauter tun stacks (16 percent), activated carbon regenerators (15 percent) and beechwood chip washers (14 percent). Open fermenters in the small brewing industry contribute almost 7 percent of the total VOC emissions from breweries in California.

6.2.4 Distribution of Emissions By Species

As shown in Table 6.2-4 ethanol was the major pollutant emitted from California breweries based on weighted percentages derived from the

Table 6.2-2

ESTIMATED EMISSIONS FROM THE BREWING PROCESS:
DISTRIBUTION BY AIR BASIN

Air Basin	Estimated Emissions				Percent of State Total[b]
	kg/day	(lb/day)	mt/yr[a]	(tons/yr)	
Sacramento Valley	0.73	(1.62)	0.13	(0.14)	0.34
San Francisco Bay Area	26.32	(58.02)	9.57	(10.53)	24.74
South Coast	82.42	(181.69)	28.99	(31.95)	74.93
Totals	109.47	(241.33)	38.69	(42.62)	100.01[c]

[a] Metric ton

[b] Percentage based on annual emissions

[c] Discrepancy in total percentage is due to rounding

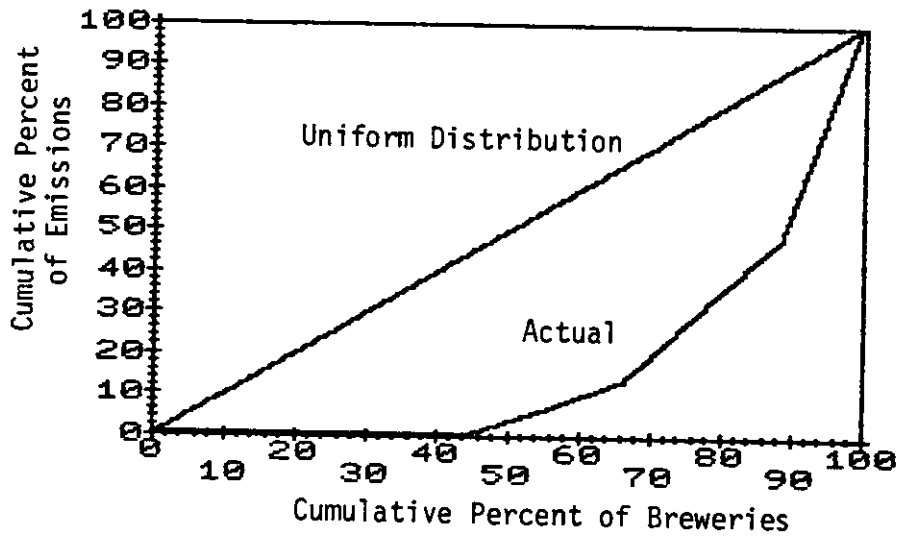


Figure 6.2-1. Lorenz Curve For the Distribution of Emissions From Beer Production in California

Table 6.2-3

ESTIMATED EMISSIONS FROM BREWING: DISTRIBUTION BY PROCESS SITE

Site		Estimated Emissions mt/yr	(tons/yr)
Small Breweries			
Mash tun stack		0.01	(0.01)
Lauter tun stack		-	-
Brew kettle stack		0.01	(0.01)
Hot wort tank vent		0.02	(0.02)
Fermentation room exhaust		2.60	(2.87)
	subtotal	2.64	(2.91)
Large Breweries			
Mash cooker stack		2.65	(2.91)
Adjunct cooker stack		0.04	(0.05)
Strainmaster/lauter tun stack		6.05	(6.67)
Brew kettle stack		15.68	(17.28)
Activated carbon regeneration vent		5.65	(6.22)
Beechwood chip washer vent		5.36	(5.90)
Waste beer sump		0.62	(0.68)
	subtotal	36.05	(39.71)
Totals		38.69	(42.62)

Table 6.2-4

ESTIMATED EMISSIONS FROM THE BREWING PROCESS:

DISTRIBUTION BY SPECIES

Compound	Weighted Percentage[a]	Emissions mt/yr	(tons/yr)
ethanol	39.49	15.28	(16.84)
dimethyl sulfide	27.38	10.59	(11.68)
myrcene	19.03	7.36	(8.12)
others	4.18	1.62	(1.78)
c_5-aldehydes	3.14	1.21	(1.34)
unidentified	2.02	0.78	(0.86)
acetaldehyde	1.74	0.67	(0.74)
ethyl acetate	1.04	0.40	(0.44)
β-caryophyllene	0.91	0.35	(0.39)
aliphatic hydrocarbons	0.57	0.22	(0.24)
c_7-esters	0.21	0.08	(0.09)
c_5-alcohols	0.18	0.07	(0.08)
hexanal	0.11	0.04	(0.05)
Total[b]	100.00	38.67	(42.65)

[a] See Section 6.1.3 for methodologies used to estimate weighted percentages.

[b] Emission rates differ from Table 6.2-1 to 6.2-3 because of rounding.

Anchor Brewing and Facility A emission profiles (see Section 6.1.3). Ethanol accounted for 39.5 percent of the total VOC emissions in the state, followed by dimethyl sulfide (27.4 percent) and myrcene (19.0 percent).

6.3 PLACING BREWERY EMISSIONS IN PERSPECTIVE

Estimated emissions from beer production in California constitute 0.001 percent of the statewide total organic gas (TOG) emissions, and 0.002 percent of stationary source TOG emissions as reported in the 1979 Statewide Emission Inventory (CARB, 1981). To really place our emissions in perspective, however, it is necessary to compare them with emissions from specific geographical areas. Consider, for example, Los Angeles (L.A.) County. According to the Final 1979 Emissions Inventory (SCAQMD et al., 1982), stationary sources in L.A. County emit 469 tons/day of reactive organic gases (ROG). Our estimate of daily emissions from the three breweries in the county is 0.091 tons/day, or about 0.019 percent of the total.

Currently available inventory data for breweries centered around TOG and NO_x emissions from fuel combustion for steam generation and TSP emissions from baghouse activities. In the Final 1979 Emissions Inventory, ROG emissions from boilers at L.A. County breweries totaled 3.6 tons/year. This figure does not reflect facility expansions that have taken place since 1979. The inclusion of brewing process emissions would result in a 10-fold increase in total emissions from breweries.

6.4 REFERENCES

California Air Resources Board (CARB). 1981. Emission Data System, 1979 Statewide emissions by process by activity. Sacramento, California.

South Coast Air Quality Management District, Southern California Association of Governments. 1982. Draft air quality management plan, 1982 revision, appendix no. IV-A, final 1979 emissions inventory for the South Coast Air Basin, El Monte, California, July 1982.

7.0

CONTROL OF IMPORTANT EMISSION SOURCES FROM BREWERIES

As has been demonstrated in Chapters 5 and 6, volatile organic compound (VOC) emissions from non-combustion processes in breweries are relatively small. A comprehensive review of emission control technologies and costs was therefore not warranted. Instead, we have focussed our attention upon the processes which are responsible for the highest percentage of brewery emissions - the fermentation room at Anchor Brewing Company and the brew kettle at Facility A - in order to review practical control alternatives.

7.1 FERMENTATION ROOM EMISSION CONTROL

Emissions from the fermentation room at Anchor Brewing Company's San Francisco plant are comprised chiefly of ethyl alcohol. The logical control point would be the roof vent, since emissions from individual fermenting tanks are channeled through it. In the following discussion, we assume a flow of 22.1 m^3/min (780 cfm) and 5382 lb/yr through this vent. Since ethanol has a commercial value, perhaps the most cost-effective approach would be to use carbon adsorption, since substantial adsorbate recovery is possible. Adsorption technology is well advanced and, indeed, is used in many breweries for CO_2 purification.

In a recent ARB-sponsored study of ethyl alcohol emissions from wineries, Fielder and Bumala (1982) reported a purchase and installation cost of $35,000 for a carbon adsorption system with low-pressure steam adsorption, to be applied to a flow of 270 cfm of exhaust air. While capital costs are not linearly related to air flow rate, we can assume for the purposes of our first-cut analysis that they are. The cost of a system capable of handling 780 cfm would thus be about $100,000. Assuming an interest rate of 18 percent for borrowed capital, a ten-year equipment life and annual costs of 6 percent for maintenance labor and materials, and 5 percent for taxes and

insurance, we find that annualized costs of the equipment are approximately $30,000. The costs of labor, electricity, and replacing spent carbon must be added, but they are much smaller than the annualized capital cost. At the end of 1982, the maximum list price for ethyl alcohol was $1.97/gallon, or 30 cents per pound (Greek, 1982). Recovery and subsequent sale of the annual emissions of ethanol would bring the brewery about $1,600 per year. Net control costs would therefore be a minimum of $28,400, or about $5.28/lb recovered.

Absorption with water as the scrubbing medium is another possibility, since ethanol is highly soluble in water. However, the concentration of ethanol in the fermentation room exhaust stream (about 100 ppmv) probably makes this method inefficient; absorption is usually considered when the VOC concentration is about 200 to 300 ppmv (Standifer, 1980). The low pollutant concentration also makes incineration prohibitively expensive.

7.2 BREW KETTLE EMISSION CONTROL

Brew kettle emissions from Facility A consist of a variety of volatile organic compounds. About 76 percent of the emissions, by mass, consist of compounds which are barely soluble or insoluble in water (myrcene, dimethyl sulfide, and miscellaneous aliphatic hydrocarbons), so that a water-based scrubber system would not likely be practical. Use of organic solvents would therefore be necessary if absorption were to be the means of control, although disposal of spent solvent and VOC emissions from solvent losses may be major problems. A rough estimate of the costs of emission control by organic solvent absorption may be obtained from cost curves presented by Standifer (1980). The installed capital cost for a complete absorption and stripping system with a VOC removal efficiency of 99.0 percent, treating an air flow rate of 4,700 acfm (the flow rate at Facility A) would be between $360,000 and $1.4 million in December 1979 dollars. According to the Council of Economic Advisers (1982), capital costs increased by 30.8 percent from December 1979 to August 1982. The present capital cost for the system would therefore be more like $470,000 to $1.8 million. Using

the assumptions presented in Section 7.1, the annualized capital cost would therefore be between $160,000 and $600,000 per year, or about $22 to $84 per pound of pollutant removed. Since these figures are already so high, we did not attempt to estimate operating and maintenance costs.

Pollutant removal by activated carbon adsorption is another possibility. From cost curves developed by Basdekis and Parmele (1980), we estimated a December 1979 installed capital cost of $257,000; in August 1982 this cost would be $336,000. Annualized capital costs, using the aforementioned assumptions, would be $112,000. For most of the brew kettle pollutants, the operating capacity of activated carbon is typically 8 lb/100 lb carbon. Thus, to remove the estimated 7160 lb/yr of pollutants would require about 89,500 lb of carbon. In a previous SAI analysis (Rogozen, 1982), the price of activated carbon was assumed to be $1.60 per pound. Assuming carbon replacement every five years, the annual cost would be about $28,600. Combined steam and electrical costs would be of the same order of magnitude as the carbon costs. The total capital and operating cost for this approach would therefore be about $170,000, or about $24 per pound of pollutant removed.

7.3 REFERENCES

Basdekis, H.S. and C.S. Parmele. 1980. "Control device evaluation: carbon adsorption," in Organic chemical maufacturing. Vol. 5: Adsorption, condensation, and absorption devices. Prepared by IT Enviroscience for U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Emission Standards and Engineering Division, Research Triangle Park, North Carolina, EPA-450/3-80-027.

Council of Economic Advisers. 1982. Economic indicators, September 1982. Prepared for the Joint Economic Committee, 97th Congress, 2nd Session, p.22.

Fielder, D.R. and P.A. Bumala. 1982. Characterization of ethanol emissions from wineries. Prepared by EAL Corporation for the California Air Resources Board, Contract No. A0-071-31.

Greek, B.D. 1982. "Slump hit major solvents hard this year," Chemical and Engineering News 60(51):26-29.

Rogozen, M.B. 1982. Control techniques for organic gas emissions from fiberglass impregnation and fabrication processes. Prepared by Science Applications, Inc. for the California Air Resources Board, Contract No. A9-120-30, SAI-068-83-01.

Standifer, R.L. 1980. "Control device evaluation: gas absorption," in Organic chemical manufacturing. Vol. 5: Adsorption, condensation, and absorption devices. Prepared by IT Enviroscience for U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Emission Standards and Engineering Division, Research Triangle Park, North Carolina, EPA-450/3-80-027.

APPENDIX A

OTHER COMPOUNDS IDENTIFIED FROM SOURCE TESTS

Table A.1 gives a detailed, site-specific list of compounds included in the category of "others" given in Chapter 5 species profiles for Anchor Brewing and Facility A. It should be noted that the presence of some of these compounds may have resulted from the use of silicone and teflon tubing in the sampling trains. All compounds listed in Table A.1 were present in extremely low concentrations relative to compounds identified in the species profiles.

Table A.1

OTHER COMPOUNDS IDENTIFIED FROM SOURCE TESTS[a]

Compound
FACILITY A
Brew Kettle Stack (7.75)
hexanal
heptanal
propanoic acid, c_5 ester
cyclic hydrocarbon ($C_{10}H_{16}$)
dimethyl-methylene bicycloheptane
c_9 ester
aliphatic hydrocarbon
methyl-methylethenyl cyclohexene
nonanal
c_{11} ester
cyclic hydrocarbons ($C_{15}H_{24}$)
dihydromethyl furan
furan methanol
c_6 alcohol
dimethyl furanone
c_8 ketone
phenyl ethanol
Strainmaster Stack (4.85)
hexanal
heptanal
nonanal
c_6 alcohol

CO_2 Purification System (3.10)

acetic acid, butyl ester
butanoic acid, ethyl ester
myrcene
acetic acid, c_7 ester
acetic acid, c_8 ester

ANCHOR BREWING

Brew Kettle Stack (5.63)

methyl-butanoic acid, methyl ester
hexanal
sulfinyl-bis methane
heptanal
c_8 ester
cyclic hydrocarbon ($C_{10}H_{16}$)
dimethyl-methylene bicycloheptane
propanoic acid, pentyl ester
c_9 ester
aliphatic hydrocarbon
methyl-methylethenyl cyclohexene
heptanoic acid, methyl ester
nonanal
pentanoic acid, c_5 ester
octanoic acid, methyl ester
methyl-methylene octadiene-one
c_{11} ketone
c_{10} acid, methyl ester
dihydro furan
dihydromethyl furanone
furfural
hexenal
furanyl ethanone
c_6 ketone
benzaldehyde
phenyl ethanol

Hot Wort Tank (8.14)

dihydromethyl furan
hexanal
furancarboxaldehyde
hexenal
heptanal
c_8 ester
cyclic hydrocarbon
benzaldehyde
dimethyl-methylene bicycloheptane
methyl-methylene octadiene
c_9 ester
aliphatic hydrocarbon
methyl-methylethenyl cyclohexene
benzene acetaldehyde
phenyl ethanone
methyl-pentenyl furan
nonanal
pentanoic acid, c_5 ester
octanoic acid, methyl ester
nonenoic acid, methyl ester
nonanoic acid, methyl ester
undecanone
decenoic acid, methyl ester
decanoic acid, methyl ester
cyclic hydrocarbons
furanmethanol
c_6 ketone
furanyl ethanone
dimethyl-benzene methanol
hydroxy-methoxy benzaldehyde

Mash Tun Stack (2.69)

c_6 ketone
hexanal

furfural	furfural
heptanal	heptanal
C_{11} alkane	C_{11} alkane
nonanal	nonanal
hexenal	hexenal
cyclohexen-one	cyclohexen-one
phenyl acetaldehyde	phenyl acetaldehyde

[a] Numbers in parentheses adjacent to site name represent the percent of the total VOC concentration measured at the site.