

# Assay and Control of Dimethyl Sulfide in Brewery Carbon Dioxide<sup>1</sup>

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## ABSTRACT

Methods were developed for assaying dimethyl sulfide (DMS) concentration in fermentor gas, activated carbon from the CO<sub>2</sub> purifier, and purified CO<sub>2</sub> and were used to characterize the pattern of DMS evolution during fermentation and removal during CO<sub>2</sub> purification. The gas chromatographic flame photometric assay procedures are based on a method described previously. DMS evolution during fermentation generally increased to a maximum during the first day then decreased to a lower but significant value at the end of fermentation. This was also the general pattern observed for the reduction of DMS in the fermentation medium. The water scrubber of the CO<sub>2</sub> purification system removed an average of 72% of the DMS from the collected fermentor gas, and the carbon purifiers removed the remainder. DMS concentration on the activated carbon was monitored at three levels in the purifier during typical purification cycles. A peak with a progressively increasing DMS concentration moved through the tower in the direction of the gas flow. Reactivation effectively reduced carbon DMS concentration to negligible levels. These observations have practical implications for CO<sub>2</sub> purification system control and management.

**Key words:** *Activated carbon, CO<sub>2</sub> purification, Dimethyl sulfide, Fermentor gas*

The quality of brewery carbon dioxide is acknowledged to have a major effect on the odor and flavor of the finished beer. During fermentation, a wide variety of compounds is evolved along with the CO<sub>2</sub>. When present in moderate concentrations, these impurities are readily removed by an efficient CO<sub>2</sub> purification system. However, abnormally high levels of impurities or an overtaxed or improperly maintained purification system can result in production of brewery CO<sub>2</sub> that is organoleptically and analytically unacceptable.

Dimethyl sulfide (DMS) is one of these many impurities. This compound is recognized as an important contributor to the odor and taste of beer. Numerous studies have dealt with the origin and control of DMS and DMS precursor (DMSP) in brewing materials (1,6,11,12) and on the fate of these compounds during brewing and fermentation (2-5, 14,18). The level of these compounds in finished beer has also been investigated (9,10). Impurities in brewery CO<sub>2</sub> have been the subject of several studies (8,17). Some controversy has existed about the degree to which DMS is evolved with the CO<sub>2</sub> during fermentation and/or storage. Drews, Bärwald, and Niefind (7) identified DMS as one of the chief volatile sulfur compounds produced during bottom-fermentations. They found that significant levels of DMS could be detected in fermentor gas soon after pitching and that DMS, along with other volatile sulfur compounds, was eliminated by the CO<sub>2</sub> stream before the end of fermentation. However, the theoretical calculations of Zangrando and Girini (16) imply that only a minimal amount of DMS would evolve with the CO<sub>2</sub>. The role of the volatile DMS as a contaminant in brewery CO<sub>2</sub> has not been explored.

We therefore studied the pattern of DMS evolution during fermentation and its removal during CO<sub>2</sub> purification. Techniques were developed for sampling fermentor gas and CO<sub>2</sub>, for extracting DMS from activated carbon taken from the CO<sub>2</sub> purification towers, and for analyzing DMS in these samples. The free DMS was measured by a gas chromatographic (GC) flame photometric detector method (9).

## EXPERIMENTAL

The GC instrumentation, conditions, and materials used for this work were basically those described previously (9). The methods for analysis of DMS and DMSP in wort and fermented beer have also been reported (10).

All fermentations studied were routine production brews. Samples from the CO<sub>2</sub> purification system were taken under normal operating conditions.

### Gas DMS Assay

Fermentor gas and CO<sub>2</sub> from the purification system were collected in gas sampling bulbs (250 ml) with Teflon stopcocks on each end and a side system sampling port (Alltech Associates Inc., No. 7013). The sampling bulbs, previously washed with chromic acid, rinsed, and filled with tap water, were filled with gas by downward displacement of the water. Ethyl methyl sulfide (EMS) internal standard was injected through the side port septum. Mixing was accomplished by inserting a 1,000-series Hamilton gastight syringe and pumping it 10 times before withdrawing an aliquot for injection into the gas chromatograph. The most common injection volume used was 2 ml; however, a 5-ml volume was advantageous at times, and a volume as great as 10 ml was used for purified CO<sub>2</sub> samples. Successive aliquots totaling as much as 30 ml from the same sampling bulb could be assayed with good reproducibility.

### Gas Calibration

Calibration was done by preparing a series of gaseous solutions of DMS in CO<sub>2</sub> (0.2-50 µg/L for 2-ml injection volumes, 0.1-0.6 µg/L for 5-ml injection volumes, and 0.2-1.4 µg/L for 10-ml injection volumes), each containing EMS internal standard (25,6.5, and 4 µg/L, respectively). A stock solution of DMS (50 mg/L) was prepared by injecting the required volume of DMS into a gas sampling bulb filled with CO<sub>2</sub> and allowing the DMS to evaporate completely. The series of dilute solutions was prepared by injecting the required volumes of this or a 100-fold dilution stock solution into CO<sub>2</sub>-filled gas bulbs. The required amount of EMS stock solution, prepared as described for the DMS stock solution, was then injected into each bulb.

### Carbon DMS Assay

The carbon was put into airtight containers immediately after the sample was removed from the purifiers. The containers were stored in a freezer for at least 12 hr before being opened for analysis. The cold carbon (0.5 g) was weighed directly into a 125-ml Pierce Hypo-Vial, 20 ml of ethanol/water (30:70) was added immediately, and the vial was quickly sealed with a butyl rubber septum secured with an aluminum seal. The vial was shaken at low speed in an Eberback reciprocating shaker for 45 min. EMS internal standard (200 µl of a 0.1 µg/µl-solution) was injected into the vial through the septum. The vial was shaken for 15 min in an Eberback water bath shaker thermostated at 25°C. A 3-ml sample of headspace was withdrawn with a gastight syringe and 2 ml of this was injected into the gas chromatograph.

### Calibration for Carbon Assay

The calibration curve was prepared by adding standard amounts of DMS (0-240 µg/g) to a series of sealed Hypo-Vials, each containing 0.5 g of new activated carbon and 20 ml of ethanol/water (30:70). The vials were treated and the analyses performed as described for the assay.

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### Sampling of the CO<sub>2</sub> Purification System

In the Demarques purification system that was monitored, the gas flow rate is approximately 3,800 lb/hr. Fresh water is fed through the top of the water scrubber at 5–10 gal (Brit)/hr, with the bottom-to-top gas flow ensuring that the dirtiest gas is washed by the dirtiest water, which is then discharged. The twin carbon purifiers, in which the gas flow is top-to-bottom, are each charged with 1,530 lb of activated carbon and are routinely reactivated after 125,000 lb of fermentor gas has been treated. Reactivation is accomplished by a purge of hot air temperature-programmed to rise from 250 to 400° F over 4 hr and to hold at 400° F for 2 hr.

Gas samples were taken at five locations in the purification system: from the collector, after the compressor, after the water scrubber, after the carbon filters, and from the usage line. The carbon samples were taken through three sampling ports equally spaced over the height of the tower. The probe carrying the sample cup penetrated 14 in. into the carbon bed. For on-stream sampling, the unit was equipped with a valve-operated closure that prevented blow-out and premature sampling.

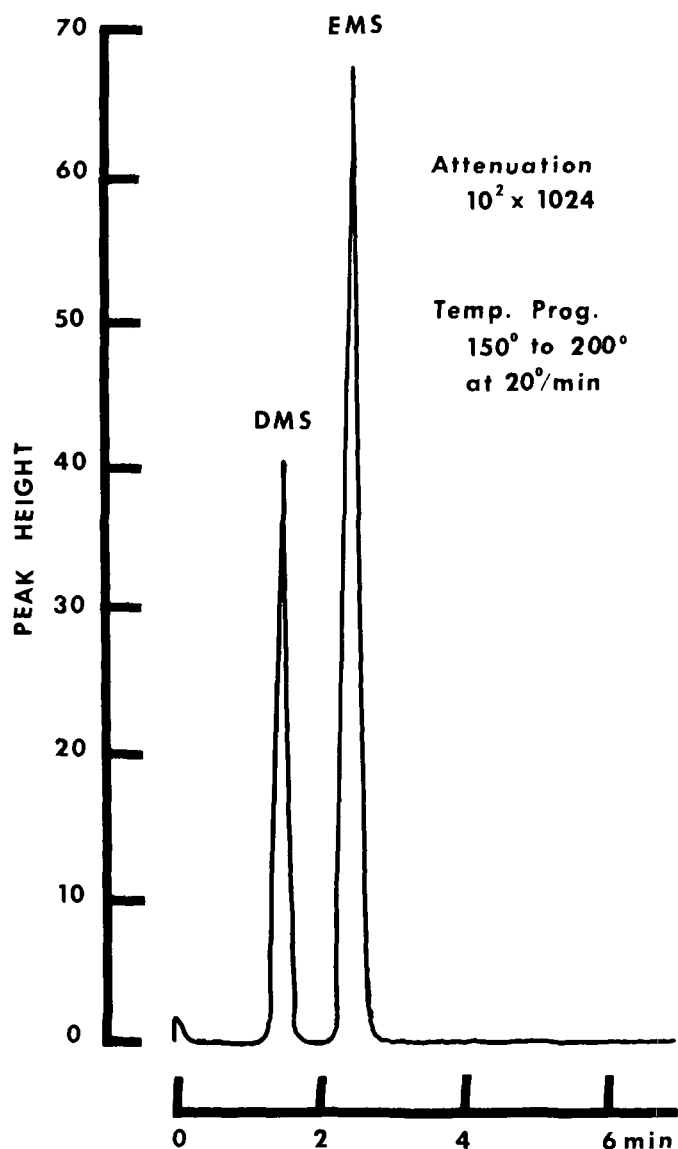


Fig. 1. Typical assay chromatogram for dimethyl sulfoxide (DMS) in a standard CO<sub>2</sub> solution. EMS = ethyl methyl sulfide, internal standard.

### RESULTS AND DISCUSSION

The typical chromatogram for a standard DMS solution containing EMS internal standard (Fig. 1) is representative of those for samples of fermentor gas, purified CO<sub>2</sub>, and headspace from activated carbon extractions.

The DMS concentration was calculated by multiplying the square root of the ratio of DMS peak height ( $h_D$ ) to EMS peak height ( $h_E$ )— $(h_D/h_E)^{1/2}$ —by the response factor obtained from the calibration curve. Calibration curves for DMS in CO<sub>2</sub> and DMS on carbon were derived by plotting  $(h_D/h_E)^{1/2}$  versus concentration of added DMS. Figures 2 and 3 show the calibration curves for 2-ml and 10-ml GC injection volumes of CO<sub>2</sub>. Figure 4 presents the

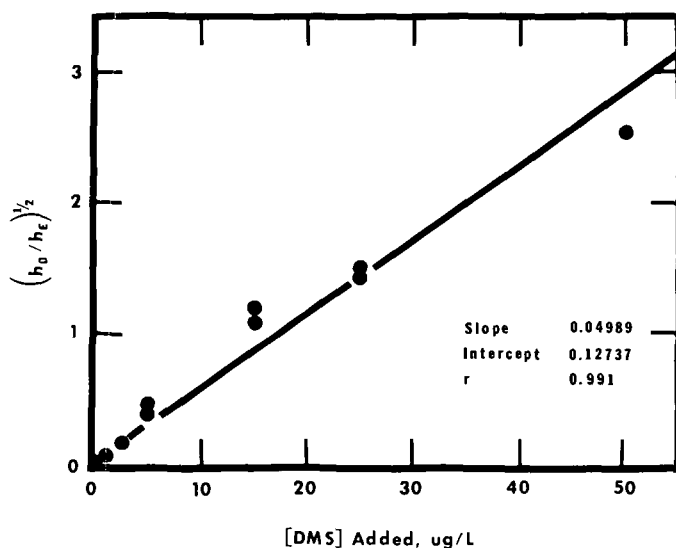


Fig. 2. Calibration curve for the assay of dimethyl sulfide (DMS) in CO<sub>2</sub>, using a 2-ml injection volume. The straight line was fitted by linear regression analysis, using  $(h_D/h_E)^{1/2}$  as the dependent variable and added DMS concentration as the independent variable.  $h_D$  = DMS peak height,  $h_E$  = internal standard peak height.

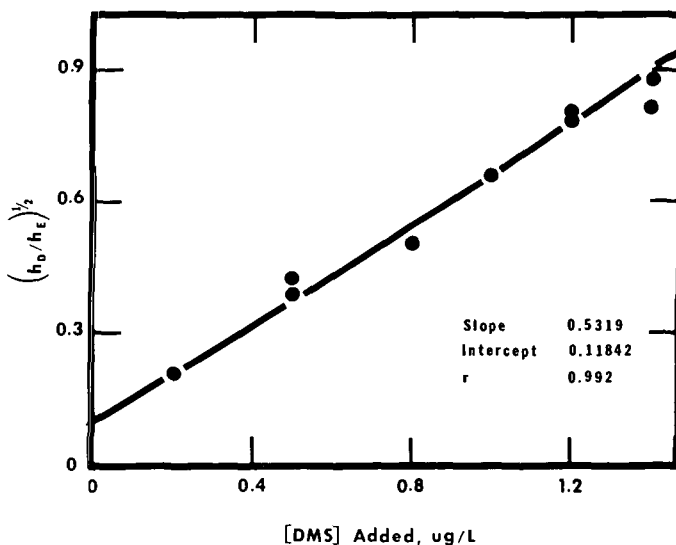


Fig. 3. Calibration curve for the assay of dimethyl sulfide (DMS) in CO<sub>2</sub>, using a 10-ml injection volume. The straight line was fitted by linear regression analysis.  $h_D$  = peak height of DMS,  $h_E$  = peak height of internal standard.

calibration curve for DMS on carbon. The reciprocal of the slope of the straight line was the response factor used in the sample calculations.

The limit of detection, defined as that concentration of DMS required to give a peak height equal to twice the standard deviation of the background, was determined, for the DMS-in-CO<sub>2</sub> assay, to be 0.2 µg/L with a 2-ml injection volume and 0.05 µg/L with 10 ml. Relative standard deviations for DMS solutions of 5, 15, and 25 µg/L were 7, 4, and 3%, respectively, from 10 replicate analyses of each. Recovery of DMS added to fermentor gas at concentrations ranging from 5 to 30 µg/L averaged 84%. The DMS-on-carbon method had a limit of detection level of 0.2 µg/g. Average recovery of DMS added to carbon over a range of 12–200 µg/g was 96%. The method precision was good. Relative standard deviations of 5, 2, and 3% were determined for carbon spiked to DMS levels of 20, 120, and 200 µg/g, respectively, from 10 replicate analyses of each. The relative standard deviation for the assay of DMS on carbon from the CO<sub>2</sub> purifier containing 100 µg/g was 8.7%, also from 10 replicate analyses.

#### DMS Evolution During Fermentation

The pattern of DMS evolution was studied in several fermentations. Figures 5 and 6 present the patterns observed during typical commercial fermentations of ale and lager beers, respectively. Figure 7 shows the pattern exhibited in a commercial ale fermentation that was accelerated by overpitching and elevating fermentation temperatures.

Overall, the pattern of DMS evolution followed that of the CO<sub>2</sub> and paralleled other fermentation changes such as pH and apparent extract. The DMS evolution in the fermentor gas generally followed the reduction of DMS in the fermentation medium except in the latter stages, at which medium DMS concentrations increased. In general, the concentration of DMS in CO<sub>2</sub> increased to a maximum, usually during the first day of fermentation, then decreased to a considerably lower, yet still significant, value at the end of fermentation. This observation suggests that DMS evolution during fermentation is a mass-transfer phenomenon. Zangrando and Girini (16) calculated the theoretical removal of a number of substances from beer, using both activity coefficients and diffusion and mass-transfer coefficients. According to those calculations, only 1 µg/L of DMS would be removed from a beer containing 200 µg/L during passage of 0.5 kg of CO<sub>2</sub> at 0°C and one atmosphere pressure. They also

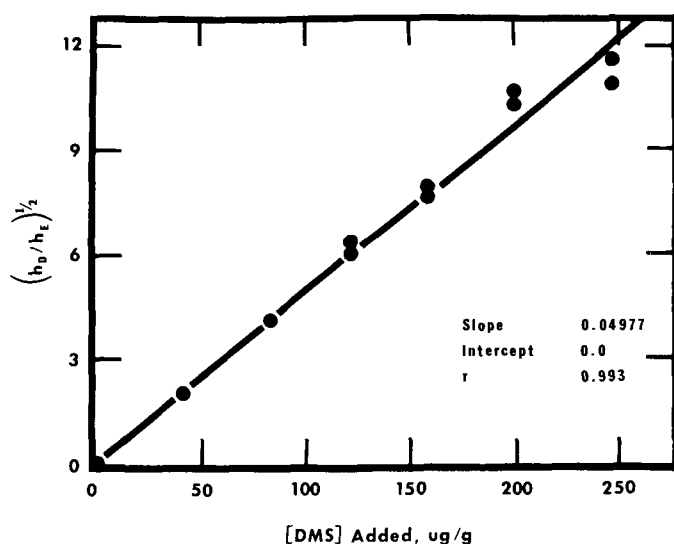


Fig. 4. Calibration curve for the assay of dimethyl sulfide (DMS) on carbon. The straight line was fitted by liner regression analysis.  $h_D$  = peak height of DMS,  $h_E$  = peak height of internal standard.

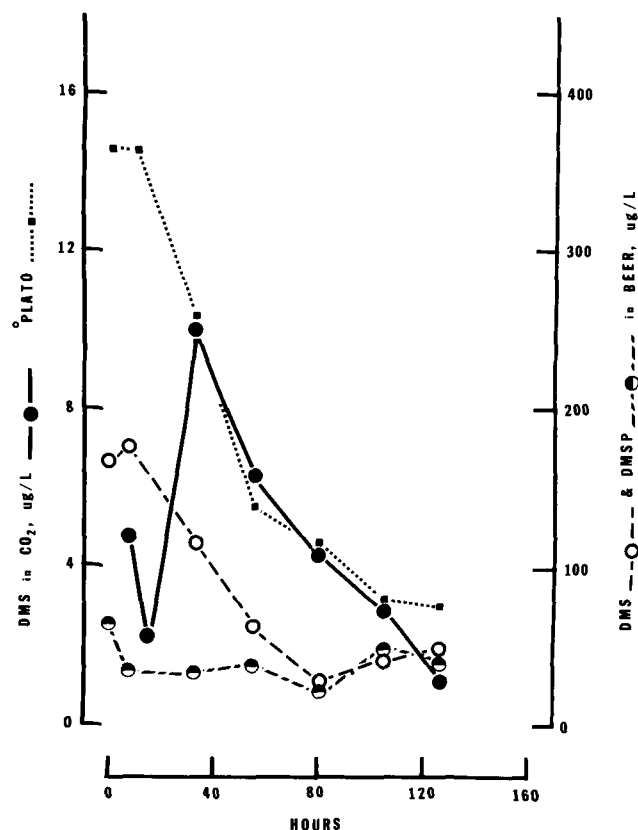


Fig. 5. Dimethyl sulfide (DMS) evolution during a typical commercial ale fermentation. DMSP = dimethyl sulfide precursor.

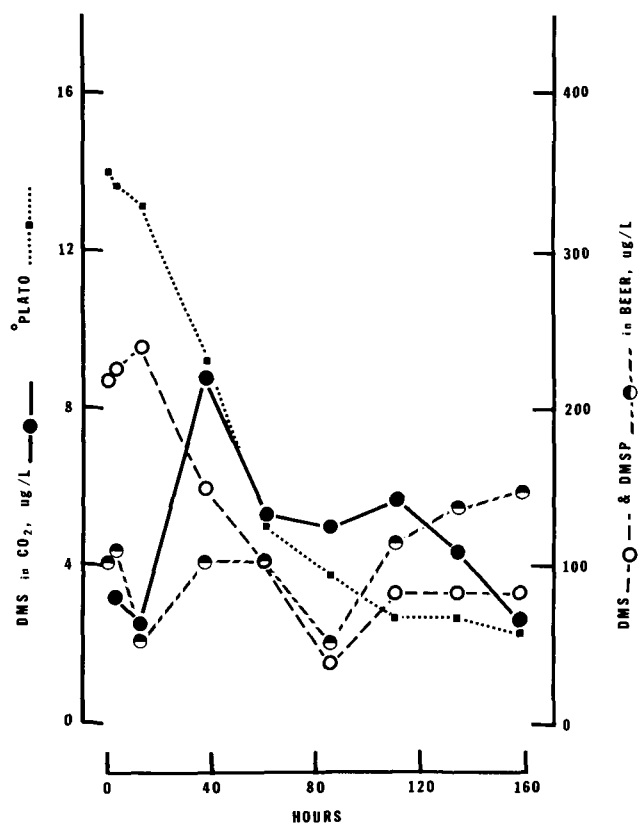


Fig. 6. Dimethyl sulfide (DMS) evolution during a typical commercial lager fermentation. DMSP = dimethyl sulfide precursor.

compared the theoretical removal of water, ethanol, and hydrogen sulfide with experimentally observed loss of these compounds from laboratory-, pilot plant-, and brewery-scale fermentations and found that these were very similar. They did not examine the removal of DMS in these experiments, and we did not attempt to extend their calculations to DMS reduction in our studies. However, we did find that a significant proportion of wort DMS was removed during brewery-scale fermentations—a 64–72% reduction, with a mean of 69%, for nine fermentations—under normal operating conditions. Accelerated fermentations exhibited a more rapid expulsion of DMS in the initial stages, followed by a sharper decrease in evolution but a relatively high DMS concentration at termination of fermentation.

As much as 90% of the DMSP was removed during the first 12 hr of fermentation, presumably due to absorption by the yeast (14). All fermentations studied exhibited a subsequent small but significant increase in DMSP concentration, a phenomenon that has been observed previously (15).

In addition to the major patterns just described, a number of minor, unexplained changes in fermentor gas DMS concentrations and DMS and DMSP concentrations in the fermenting medium were noted in some of the fermentations. These are undoubtedly due to the complexity of the system and the lack of direct experimental control over many factors. Carefully controlled laboratory and pilot plant experiments would be required to obtain data without these deviations.

From the observed fermentor gas DMS concentrations, the wort and fermenting medium DMS and DMSP concentrations, and the calculated volumes of CO<sub>2</sub> that evolved, approximate mass balances for the DMS and DMSP changes were determined. The amount of DMS evolved in the CO<sub>2</sub> was calculated to be

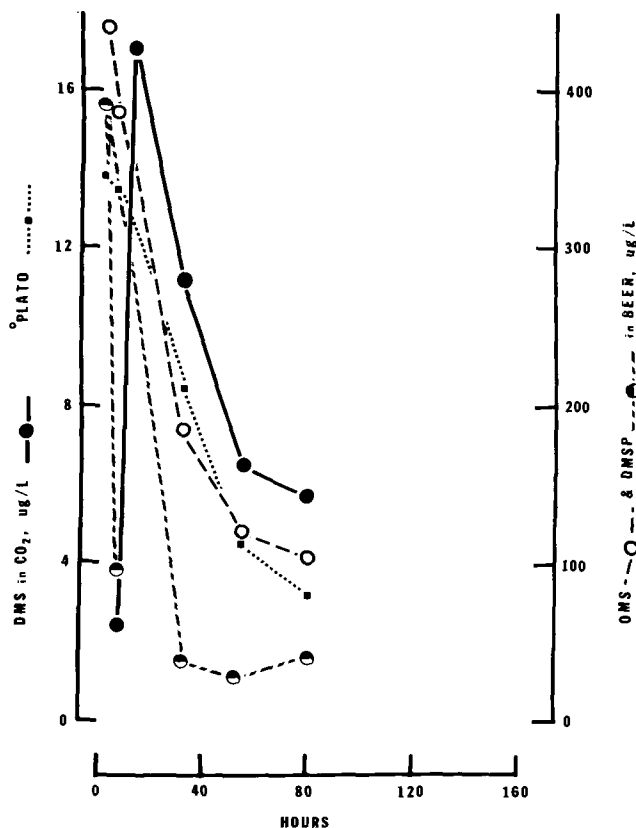


Fig. 7. Dimethyl sulfide (DMS) evolution during commercial ale fermentation accelerated by overpitching and fermenting at elevated temperatures. DMSP = dimethyl sulfide precursor.

approximately equal to the amount lost from the medium during fermentation. Such calculations may thus be of practical value in sizing CO<sub>2</sub> purification systems and/or estimating activated carbon reactivation cycles.

#### Removal of DMS During CO<sub>2</sub> Purification

Table I shows the concentrations of DMS in CO<sub>2</sub> taken from the five sampling points in the purification system. The efficiency of the system was demonstrated by the removal of 99.7% of the DMS carried by the collected fermentor gas. Although DMS is highly insoluble in water, the water scrubber removed as much as 83% of this compound, with an average reduction of 72%. The DMS remaining in the CO<sub>2</sub> after the water wash was reduced to zero by the carbon purifiers in all but three sets of samples analyzed. These infrequent breakthroughs of low concentrations of this compound emphasize the need for constant and adequate maintenance measures. This effective removal of DMS is similar to that reported by Gruber (8) for removal of acetaldehyde, acetone, ethyl acetate, and ethyl alcohol from fermentor gas by a Wittmann CO<sub>2</sub> purification system.

#### DMS Levels on Carbon from CO<sub>2</sub> Purifiers

Table II gives the DMS concentrations found in samples of carbon taken from the purifiers before and after reactivation. The reactivation program did not return the DMS level to zero although the new carbon used to charge the purifiers did give a zero value when determined by the same method. This might simply be a result of inadequate purging time during the hot air reactivation of the towers. Also, the DMS might be so strongly bound to the carbon sites, or the sites so well protected, that the DMS is not released even by a long purge of hot dry air, whereas with the conditions of the assay in which the medium is aqueous ethanol

TABLE I  
Dimethyl Sulfide (DMS) in CO<sub>2</sub> Purification System<sup>a</sup>

Location	DMS ( $\mu\text{g/L}$ of CO <sub>2</sub> )	
	Mean <sup>b</sup>	Range
Collector	9.18 <sup>c</sup>	5.95–11.30
After compressor	9.40 <sup>c</sup>	7.35–11.45
After water scrubber	2.60 <sup>c</sup>	1.35–5.10
After carbon purifier	0.04 <sup>d</sup>	0–0.15
Usage line	0.03 <sup>d</sup>	0–0.13

<sup>a</sup>Samples over two intervals of two weeks each; throughput of gas ranged from 600 to 123,000 lb at time of sampling.

<sup>b</sup>Each point sampled 14 times.

<sup>c</sup>GC injection volume: 2 ml.

<sup>d</sup>GC injection volume: 10 ml.

TABLE II  
Dimethyl Sulfide (DMS) on Carbon from CO<sub>2</sub> Purifiers<sup>a</sup>

	DMS ( $\mu\text{g/g}$ )	
	Mean	Range
Before Reactivation <sup>b</sup>		
Top	3.3 <sup>c</sup>	1.9– 4.7
Middle	14.7 <sup>c</sup>	4.0– 40.0
Bottom	134.0 <sup>c</sup>	8.0–298.1
After Reactivation <sup>d</sup>		
Top	4.1 <sup>e</sup>	2.6– 5.0
Middle	3.4 <sup>e</sup>	1.4– 4.6
Bottom	3.9 <sup>e</sup>	1.6– 4.9

<sup>a</sup>Gas flow from top to bottom.

<sup>b</sup>After passage of 125,000 lb of gas.

<sup>c</sup>Average of five days' samples.

<sup>d</sup>Hot air purge: temperature raised from 250 to 400° F during 4 hr and held at 400° F for 2 hr.

<sup>e</sup>Average of four days' samples.

TABLE III  
Dimethyl Sulfide (DMS) on Carbon During  
Operation of CO<sub>2</sub> Purification System

CO <sub>2</sub> Processed <sup>a</sup> (lb)	DMS <sup>b</sup> (μg/g)		
	Top	Middle	Bottom
30,040	0	7.1	1.7
32,000	14.9	1.5	2.4
56,950	2.0	150.1	2.5
82,960	2.6	162.0	3.0
125,000	2.4	2.4	10.7

<sup>a</sup>Through one purification tower at time of sampling.

<sup>b</sup>Duplicate assays performed on each sample.

rather than hot air, the compound becomes accessible for displacement. In any event, although DMS is analytically present in the carbon after reactivation, values averaging 3.9 μg/g even at the lowest sampling port, this adsorbed DMS is apparently so strongly bound that its concentration in the purified CO<sub>2</sub> at the start of the next cycle is negligible.

The data collected from sampling the CO<sub>2</sub> purifiers during operation is given in Table III. These show that the carbon towers exhibit a chromatographic effect, in that the concentration of DMS appears to move through the purifiers in the direction of the gas flow, that is from top to bottom. Smisek and Cerny (13) explained a similar phenomenon where activated carbon was used to recover gasoline from natural gas. Theoretically an equilibrium mixture consisting of all the hydrocarbons present should build up in the carbon, but in practice the adsorption process never reaches equilibrium. In passing through a bed of carbon, the lower hydrocarbons quickly saturate the bed and are successively replaced in the direction of flow by the more easily adsorbed higher compounds. This process continues until the lower hydrocarbons break through, at which time their concentration in the outgoing gas increases rapidly. Our data from on-stream sampling indicates that such a system exists in the carbon purifiers; water, ethanol, hydrogen sulfide, and other impurities in high concentration would be preferentially adsorbed, thus displacing the major concentration of DMS from the top (14.9 μg/g at 32,000 lb) to the middle (162 μg/g at 83,000 lb) and eventually to break-through. The concentration of 10.7 μg/g after 125,000 lb of CO<sub>2</sub> had been passed indicates that the expected maximum concentration of DMS had passed the bottom sampling port and that break-through was imminent or had already occurred. The ranges of concentrations of DMS before reactivation in the three sampling areas investigated, as seen in Table II, are consistent with this hypothesis; due to the nature of the collection system, which involves numerous fermentors in varying stages of fermentation, an unknown and uncontrollable variation is found in the concentration of DMS, and other volatiles, in the fermentor gas delivered to the purification system.

In the system we monitored, the routine of reactivation after 125,000 lb of fermentor gas has been processed was established and

is still controlled by the "trap and smell" method in which the CO<sub>2</sub> coming out of the purifier is bubbled through distilled water that is then evaluated organoleptically and declared "clean" or "unclean." Our studies confirm the validity of this approach, suggesting at the same time the possibility that DMS is the major compound responsible for the unclean odor. If, in fact, DMS is the major compound responsible for the unclean odor and is the first organoleptically significant compound to break through the carbon bed, then DMS could be used as a break-through indicator compound. Analysis for DMS at the purifier outlet would be a more sensitive, simpler, and faster method for monitoring CO<sub>2</sub> quality than either the subjective "trap and smell" method or the chemical analysis of CO<sub>2</sub> impurities by potassium dichromate (17) or potassium permanganate.<sup>2</sup> We are presently trying to adapt this method to the practical control and management of CO<sub>2</sub> purification systems throughout our chain of breweries.

<sup>2</sup>Unpublished data.

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