



Project Summary

A Test Method for the Measurement of Methanol Emissions from Stationary Sources

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Methanol was designated under Title III of the Clean Air Act Amendments (CAAA) of 1990 as a pollutant to be regulated. The U.S. Environmental Protection Agency (EPA), through a contract with Research Triangle Institute (RTI), has developed a test method for the measurement of methanol emissions from stationary sources. The methanol sampling train (MST) consists of a glass-lined heated probe, two condensate knockout traps, and three sorbent cartridges packed with Anasorb 747. The Anasorb samples were desorbed with a 1:1 mixture of carbon disulfide and N,N-dimethylformamide. All samples were analyzed by gas chromatography with flame ionization detection.

Following laboratory testing, field tests of the MST and the National Council of the Paper Industry for Air and Stream Improvement (NCASI) sampling method for methanol were conducted at two paper and pulp mills. In accordance with EPA Method 301, two pairs of trains were run in parallel for six runs, collecting a total of 24 samples by each method. During each run, half of the trains were spiked with a known amount of methanol. The sampling location at the first field test was an inlet vent to a softwood bleach plant scrubber where the methanol concentration was about 30 ppm. The average percent recovery of the spike was 108.3% for the MST method and 81.6% for the NCASI method. Although neither method showed significant bias at the 95% confidence level, the biases of the two methods were significantly differ-

ent. A second field test was conducted at the vent of a black liquor oxidation tank where the methanol concentration was about 350 ppm. The average percent recovery of the spike was 96.6% for the MST method and 94.2% for the NCASI method. The biases of the two methods were not significantly different for the second field test. The MST had a practical quantitation limit (PQL) of about 3 ppm for a 20-L sample. Samples were shown to be stable for at least 2 weeks after collection.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Under Title III of the CAAA of 1990, 189 toxic chemical species will be regulated for stationary source emissions. Methanol is one of the pollutants to be regulated. EPA, through a contract with RTI, has developed a test method for the measurement of methanol emissions from stationary sources.

A literature search was conducted to review the sampling and analysis methods currently used to measure methanol. Based on the information obtained from this literature search, the MST was developed and evaluated in the laboratory. The MST consists of a glass-lined heated probe, two condensate knockout traps in an ice bath, and three sorbent cartridges packed with Anasorb 747. A 1:1 mixture



of carbon disulfide and N,N-dimethylformamide is used to desorb the Anasorb samples. The knockout traps, used to remove water vapor, also collect a significant amount of methanol if water is present. Condensate and desorption samples are analyzed by gas chromatography with flame ionization detection.

A field evaluation of the MST and the NCASI sampling method for methanol was conducted at two pulp and paper mills in accordance with EPA Method 301 procedures. The first field test location was an inlet vent to a softwood bleach plant scrubber where the methanol concentration was about 30 ppm. A second field test was conducted at the vent of a black liquor oxidation tank where the methanol concentration was about 350 ppm. Both methods met the criteria for precision and bias as set forth in Method 301.

Experimental Approach

Laboratory Testing Apparatus

A dynamic dilution system was used for mixing methanol and diluent humidified nitrogen. The components were mixed in a 1-L Kimak* dilution flask. Flow rates of the test gas and the humidified nitrogen were regulated with Tylan mass flow controllers. The gas mixture was passed from the dilution flask to a three-port manifold, both of which were enclosed in an insulated, temperature-regulated box. A cylinder containing 250 ppm methanol was used as the test gas and was diluted to the desired concentration using this dynamic dilution system.

The MST, shown in Figure 1, consists of a heated sampling probe, two condensate traps in an ice bath, three Anasorb 747 (SKC) sorbent cartridges, and a pump. (However, the results from the field tests would later show that only two Anasorb cartridges are necessary.) Each condensate trap is an empty half-stem impinger. The first sorbent cartridge contains 5 g of Anasorb and the backups contain 1.5 g of Anasorb each.

Laboratory Experiments

The Occupational Safety and Health Administration (OSHA) recently promulgated a method for measuring methanol in the workplace (OSHA Method 91) that uses Anasorb 747 (SKC) as the collection medium. Although OSHA Method 91 was written for methanol as a non-stationary

source, a literature review indicated that Anasorb was the most promising sorbent and the results outlined below show that Anasorb was highly efficient in collecting methanol.

The desorption efficiency of methanol from Anasorb was determined at three different loadings. A primary methanol standard (94.8 µg/mL) was prepared by diluting 3 mL methanol to 25 mL with deionized water. Five grams of Anasorb were placed in three separate vials and were then spiked separately with 3 µL, 6 µL, and 9 µL of the methanol standard. The Anasorb in each vial was desorbed with 30 mL of CS₂/DMF. Each Anasorb sample was calibrated with a corresponding secondary methanol standard, prepared by spiking 3 µL, 6 µL and 9 µL of the primary standard into separate vials containing 30 mL of solvent.

Several spiking tests were conducted to determine the recovery efficiency of the MST. A heated stainless steel tee, with a septum in one arm, was placed between a port on the dilution system and the MST. The dilution system was set to a temperature just above 100°C, and the diluent nitrogen contained 20% water by volume. The sample flow rate was 1 L/min for all runs. At the beginning of each run, approximately 5 µL of methanol was injected at the tee.

Field Testing and Method Validation

Field testing of the MST was conducted at three different sites. The primary objective of the field testing was to obtain an estimate of the precision and accuracy of the method under field conditions. A secondary objective was to compare the MST to the NCASI method (shown in Figure 2) for sampling methanol. In accordance with EPA Method 301, a field test of a method consisted of four trains run in parallel for six runs (24 samples total). The four trains were run as two pairs, with the two probes of each pair taped together and inserted perpendicular to the flow of gas in the vent (or stack).

Field Site A: TMP Mill

The first field site was the stack from an atmospheric cyclone at a thermomechanical pulping mill. Source data provided by the mill indicated that the methanol concentration was around 100 ppm. The first run of the presurvey was stopped after 30 seconds because condensing steam had filled the condensate knockout traps and the Anasorb cartridges, and water was threatening the sampling pump. The temperature of the stack gas was measured

at 212°F, indicating that the gas was nearly all water. Because neither method was suitable under the prevailing conditions, a second field site was necessary.

Field Site B: Softwood Bleach Plant Scrubber

The second field site was a 3-foot-diameter inlet vent to a softwood bleach plant scrubber at a pulp and paper mill. The site was downstream from a fan that created a strong positive pressure. The vent gas temperature was just above 130°F. Sampling Trains 7 and 10 were exposed to direct sunlight whereas Trains 11 and 14 were shaded. To prevent breakthrough problems due to sunlight, the sorbent tubes for Trains 7 and 10 were shielded from the sun with a moist rag. The heated probes were placed about 18 in. into the vent and each sample was collected at a rate of 1.0 L/min for 20 min.

On the first day of sampling, seven NCASI runs were performed. Each NCASI train consisted of two impingers (one dry and one filled with 20 mL of deionized water) and a silica gel tube. The methanol sampling train was tested on the second day of sampling. Each pair of trains was alternately spiked with 6 µL of a methanol standard. Thus, each spike contained about 569 µg methanol, approximately the same amount collected during each run. The spikes were injected with a 10-µL syringe immediately after the start of a run.

Field Site C: Black Liquor Oxidation Tank

The third field site was a 3-foot-diameter exhaust vent from a black liquor oxidation tank at a pulp and paper mill. The vent gas temperature was about 170°F. Six NCASI runs were performed on the first day of sampling. Each NCASI train consisted of a single impinger (filled with 20 mL deionized water) and a silica gel tube. Because the presurvey indicated a high methanol concentration (~350 ppm), all runs were conducted at a flow rate of 0.5 L/min for 20 min. Each pair of trains was alternately spiked with 4 µL (3,170 µg) of neat methanol, which was equivalent to a methanol spike concentration of 244 ppm for a 10-L sample volume. The spikes were injected with a 10-µL syringe 6 to 8 min. after the start of a run. The four probes were placed in a single 3-in.-I.D. port because there was no second port that was perpendicular to the first port. The methanol sampling train was tested on the second day of sampling. Each methanol sampling train consisted of two condensate traps and three sor-

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

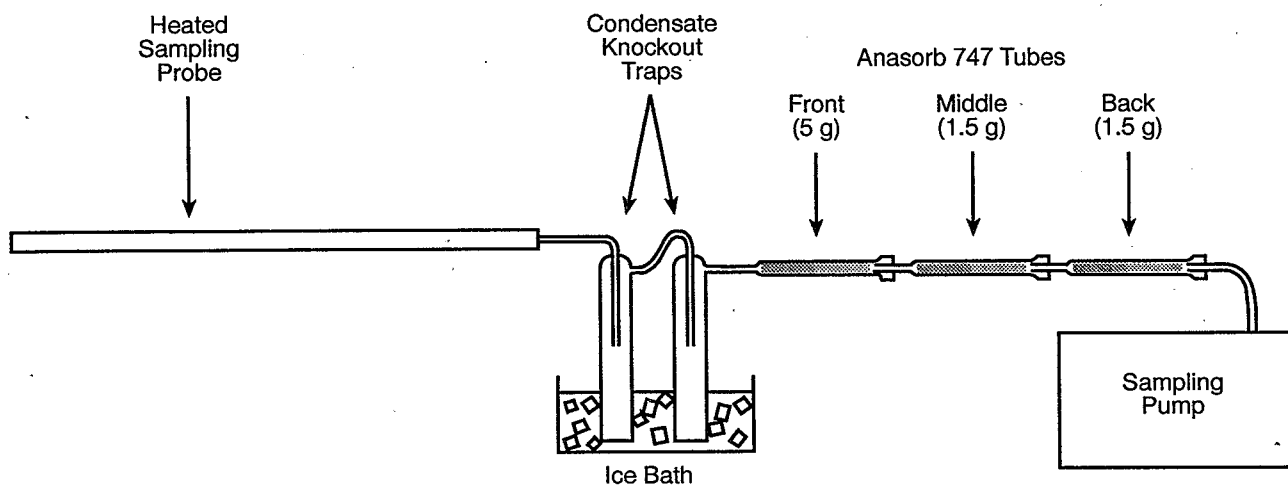


Figure 1. Methanol sampling train.

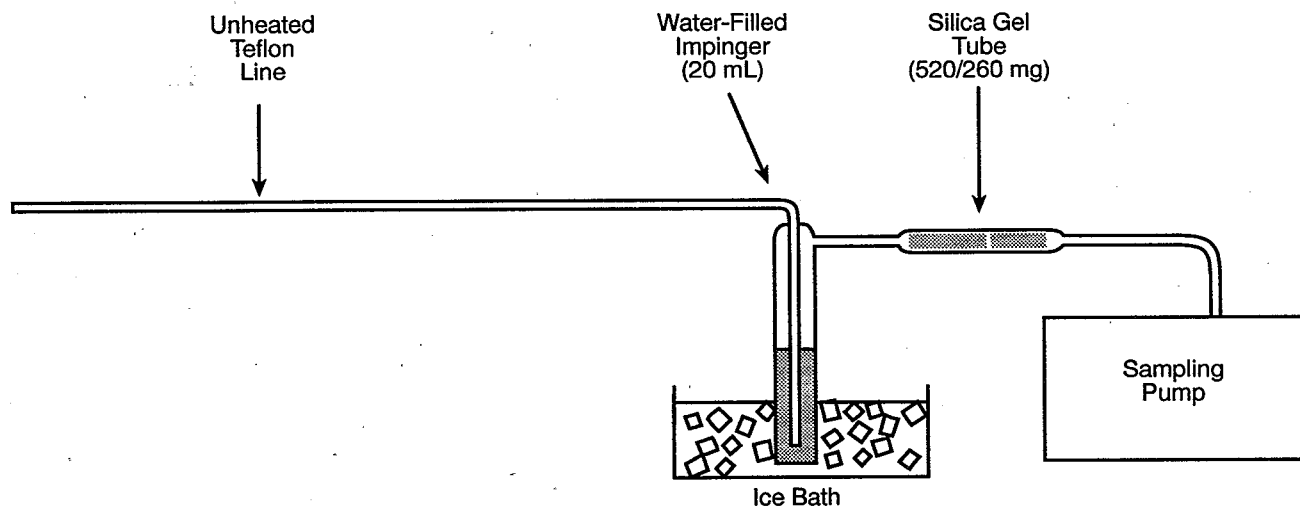


Figure 2. NCASI sampling train for methanol.

bent tubes containing 5, 1.5, and 1.5 g of Anasorb, in that order.

Results and Discussions

Laboratory Evaluation

The average overall recovery (desorption efficiency) of methanol from Anasorb for the three samples was $98.1 \pm 1.7\%$. The three vials that were spiked with 3 μL , 6 μL , and 9 μL of methanol had respective overall recoveries of 95.8, 98.5 and 100.0%.

The average overall recovery efficiency (Table 1) of the methanol spike from the front (3 g), middle (1.5 g), and back (1.5 g) Anasorb cartridges was $97.3 \pm 2.6\%$. A comparison of Runs 1 and 3 with Run 2 of the spiking tests indicates there was substantial breakthrough on the front Anasorb cartridge when 60 L of sample was collected. When the sample volume was reduced to 30 L, there was little breakthrough. In Run 4, breakthrough was eliminated by increasing the amount of Anasorb in the front tube from 3 to 5 g.

Field Testing and Method Evaluation

Field Site B: Softwood Bleach Plant Scrubber

The presurvey results at the softwood bleach plant scrubber vent gave concentrations that were very similar. A major concern with the presurvey data was breakthrough of methanol on the sorbent tubes. The breakthrough may have been due to elevated temperatures at the site because the ambient temperature was 97°F and the MST was exposed to sunlight, resulting in a dry gas meter temperature of 114°F.

The paired trains for NCASI and MST methods showed very good precision. The average spike recovery for the MST was

considerably higher than for the NCASI method: 108.3% compared to 81.6%. The methods had nearly identical average unspiked concentrations, but the average spiked concentration of the MST was higher than the average spiked concentration of the NCASI method. The reason for this difference is unknown. Both methods had similar, and rather high, standard deviations of spike recoveries. The high standard deviation of the spike recoveries was due to a bias that existed between the two pairs of trains. Trains 11 and 14 gave results that were consistently about 6% higher than the results from Trains 7 and 10. As a result, when pair 11 and 14 was spiked, there was a high spike recovery, and when pair 7 and 10 was spiked, there was a low spike recovery. The spike recovery for pair 11 and 14 averaged about 25% higher than the spike recovery for pair 7 and 10. This discrepancy was found for both methods and the cause is unknown. Because of the precision between the paired trains, it is unlikely that there was a leak problem.

The data obtained by both methods were homogenous and a linear regression of train pair differences versus concentration showed there was no dependence on concentration. A statistical analysis following EPA Method 301 procedures showed that the precision of paired trains was not statistically different for the two methods tested and that no significant bias was found with the MST and the NCASI methods at the 95% confidence interval.

A small amount (0.1%) of methanol broke through the front Anasorb tube in spiked field test samples and a negligible amount broke through in unspiked field test samples. This result was significant because of the breakthrough problems that occurred during the presurvey. Apparently the extreme heat at the presurvey did cause breakthrough, but the corrective measures (i.e., shielding the tubes from

the sun with a wet cloth) taken during the field test were adequate to solve the problem.

Field Site C: Black Liquor Oxidation Tank

The results for the presurvey at the black liquor oxidation tank indicated a methanol concentration between 300 and 400 ppm. The vent gas temperature ranged between 170°F and 190°F for the three runs. Because the ambient temperature was measured at 107°F, the Anasorb tubes were protected from the sun and heat by a wet cloth. Several unidentified compounds were found in the Anasorb samples, indicating the presence of compounds other than methanol in the vent gas matrix.

The paired trains for each method showed good precision, although there was substantial bias between Trains 3 and 9 for the NCASI method. Train 9 collected an average of 35 ppm more methanol than Train 3. The average spike recovery for the MST was slightly higher than for the NCASI method, 96.6% to 94.2%. Both methods had a similar standard deviation of the spike recovery, 8.7% for the NCASI method and 9.8% for the MST method.

Concentration data for both methods were homogenous at the 95% confidence level, and a linear regression of train pair differences versus concentration showed there was no dependence on concentration. A statistical analysis conducted according to EPA Method 301 procedures showed that the precision of paired trains was not significantly different for the two methods at the 95% confidence level and both methods were found to be accurate because neither had a statistically significant correction factor for its bias. No methanol broke through the first Anasorb tube even though the methanol level in the spiked samples was almost 600 ppm. This field test showed that a third Anasorb tube is probably unnecessary for the MST method if the sorbent tubes are properly shielded from excessive heat.

Analytical Instrumentation and Performance Evaluation

Analytical Systems

The majority of the samples from the laboratory evaluation were analyzed on a Hewlett-Packard 5890 Series I gas chromatograph (GC) equipped with a flame ionization detector (FID). A 30-m DB-Wax megabore column was used for the analysis. The temperature program started at 50°C and increased by 10°C/min to a final temperature of 140°C. The temperature

Table 1. Percent Recovery of Methanol Spike

Run	Volume Sampled (L)	Condensate Traps (%)			Anasorb Cartridges (%)				Total Recovery (%)
		Front	Back	Total	Front	Middle	Back	Total	
1	60	45.2	3.9	49.1	28.6	—	18.8	47.4	96.5
2	30	44.0	0.4	44.4	45.2	4.6	0.0	49.8	94.2
3	60	51.0	5.0	56.0	17.8	19.0	4.4	41.2	97.2
4	60	44.5	1.6	46.1	51.7	3.6	0.0	55.3	101.4
Average recovery									97.3
Standard deviation									2.6

program was shortened when water analyses were performed.

The field test samples were analyzed on a Hewlett-Packard 5890 Series II GC equipped with an FID and a Hewlett-Packard 7673 autosampler. A 30-m DB-624 megabore column was used to analyze all samples for the field test at Site B. For the field test at Site C, a 60-m Supelcowax-10 column was used to analyze Anasorb samples and a 30-m DB-624 megabore column was used to analyze the water samples.

Performance Evaluation

The single sample method was used to estimate the analytical limit of detection (LOD) and limit of quantitation (LOQ) for water and CS₂/DMF samples. For each solvent, a methanol solution at a concentration about 1.5 times the estimated LOQ was analyzed eight or nine times to determine a value for *s*, the approximate standard deviation at the lowest level of measurement. From this determination the LOD was calculated as 3*s* and the LOQ as 10*s*. Both methanol standards were prepared at a concentration of 0.95 µg/mL. The CS₂/DMF samples had an analytical LOD of 0.20 ng and a LOQ of 0.69 ng while the water samples had an analytical LOD of 0.15 ng and a LOQ of 0.50 ng. The analysis was performed with the analytical system used for the analysis of field test Site B samples.

The linearity of the analytical system used for the field test samples was evaluated with CS₂/DMF and water standards. A primary standard was prepared by diluting 3 mL methanol to 25 mL with deionized water, resulting in a methanol concentration of 94.8 µg/mL. Six standards of each solvent were prepared by spiking various amounts of solvent with the primary standard. These solutions ranged in

methanol concentration from 4 to 35 µg/mL. Each solution was analyzed three times and the FID response was shown to be linear over a methanol concentration range of 5 to 85 µg/L for CS₂/DMF samples and 4 to 76 µg/mL for water samples.

Quality Control

Sample Stability

Sample stability tests were performed for Anasorb, silica gel, and water. Samples were analyzed on the day they were spiked (Day 0) and on Days 1, 3, 7, and 14 following spiking. Three spiked samples and one blank of each medium were analyzed on each day. The recovery for each day represented the average of three tubes analyzed and blank corrected. Samples in water and silica gel were shown to be stable for at least 2 weeks while the Anasorb samples were shown to be stable for at least 1 week. Other Anasorb samples were found to have a recovery of about 90% after 2 weeks. The recovery of methanol from Anasorb was 107% after 1 week. The recovery of methanol from water was 96% after 2 weeks and 111% of methanol was recovered from silica gel after 2 weeks.

Conclusions and Recommendations

A laboratory evaluation of the MST showed that Anasorb had a desorption efficiency for methanol of $98.1 \pm 1.7\%$. Samples taken where methanol was collected on the Anasorb or in the condensate knockout trap were found to be stable for up to 2 weeks. The analytical system used to measure methanol had a limit of quantitation of 0.5 ppm, and the MST method had a quantitation limit of 3 ppm.

The MST and NCASI methods both met the guidelines specified by EPA Method

301 in both field tests. Both methods showed very good precision, which was not significantly different at the 95% confidence level. Although neither method showed significant bias, the biases of the methods were significantly different at the 95% confidence level for the first field test. The disparity in the biases of the methods is evident from the spike recovery values. Only 81.6% of the spike was recovered using the NCASI method, while 108.3% of the spike was recovered with the MST method. The reason for this difference is unknown; however, the heated glass-lined probe and injection port used in the MST may have been more efficient at transporting methanol than the unheated Teflon sampling line and injection port recommended by the NCASI method.

The bias between methods that was seen in the field test at Site B was not found in the field test at Site C. The average percent recovery of the spike was 96.6% for the MST method and 94.2% for the NCASI method. The precision of paired trains was not significantly different for the two methods at the 95% confidence level.

An advantage of the MST is that the composition of the emission source can be determined by using a mass spectrometric detector to analyze the desorbed Anasorb samples. Emissions at Field Site B were considered clean because no compounds other than methanol could be detected. Field Site C had a more complex emission matrix and provided important information about the capabilities of the MST method. Field Site C also had a high methanol concentration, which helped determine the capacity of the MST method.

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