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The type of gas sampling bags described as "Snout" (U.S. Patent #3,907,164) and "Aluminized Polyester" are both exclusive products of Calibrated Instruments, Inc. Aluminized polyester bags are no longer available however since the manufacturer of the material (Minnesota Mining) has discontinued making same. Our current snout type bags have incorporated some of the properties of the aluminized polyester bags that are mentioned in the report and in our opinion, are suitable for all types of gas sampling.

Evaluation of Bag Sequential Sampling Technique for Ambient Air Analysis

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■ The bag sequential sampling technique for sampling ambient air was evaluated by comparing results from bag sequential samplers and continuous analyzers. When placed side by side, carbon monoxide concentrations from the two methods did not correlate well. However, when the samples were drawn through a common header, the concentrations agreed to within ±1 ppm for at least 90% of the data points for carbon monoxide concentrations between 1 and 8 ppm. Bags constructed of polyvinyl chloride; Tedlar; layers of polyester, polyvinyl chloride, aluminum foil, polymide, and polyethylene; and aluminized polyester were tested up to 100 h for their influence on sample integrity. Only the aluminized polyester bags were satisfactory for long-term storage. Certain pump and tubing materials were found to affect the sample. The bag sampling technique has good potential for collecting ambient air samples.

With the increasing interest in pollution control, there is a much greater demand to monitor pollutant concentrations in ambient air. In most cases, the ambient concentrations are in the range of 0.01–10 ppm and are expensive as well as difficult to measure. In an attempt to overcome some of these problems, several new air monitoring techniques are being introduced. Before extensive economic and health decisions based on data from these new techniques can be made, experience dictates thorough evaluation programs.

For example, decisions must be made regarding the construction or major modification of roadways. Questions encountered include: Will the construction of a new roadway allow smoother traffic flow, thus reducing congestion on existing streets and the pollution load on the general area? Will the new roadway significantly affect the air quality in its immediate vicinity? To answer these questions, experimental measurements must be made along existing roadways, and a capability to predict air pollution levels from roadways must be developed. Of course, the prediction capability or model can be no more accurate than the data it is based upon. Thus, it is imperative that data collecting techniques must be closely scrutinized.

Most models for the dispersion of pollutants from roadways are based on experimental measurements of carbon monoxide along roadways. Carbon monoxide can be measured fairly accurately, and it is also stable.

Pollutant Sampling Methods. There are three basic methods to acquire the data necessary for model development. Intermittent Sequential Sampling (ISS) is the cheapest, least elegant technique for data collection. A single monitoring instrument is attached to a multiport header through a series of solenoid activated valves. These valves are activated by a stepping switch that allows only one port to be open at any particular time. Sequential sampling allows several locations to be intermittently monitored with only one instrument. The data obtained with this technique are rather poor for modeling purposes since no readings are simultaneous and sometimes the lag between subsequent readings at the same point is many minutes. According to probability theory, Papoulis (*1*), and Bendat and Piersol (*2*), a sampling frequency of at least twice the highest frequency of concentration variation is required to statistically reproduce the concentration. Other problems associated with the ISS technique include the long lines from the sampling points to the analyzing instrument.

Bag sequential sampling can yield an improved quality of data at a modest increase in cost if it is performed properly. Again there is only one analytical instrument, but instead of piping the sample to the instrument directly, it is pumped into a series of air-tight bags at each sample point. Thus, when filled properly, each bag can represent the averaged concentration for a given period. The bags can then be analyzed at leisure. Currently, there are two manufacturers of bag sequential samplers. One of the primary problems with the bag sequential sampling technique is the interaction of the sample with the materials of construction, that is, the tubing, pump, and storage bag. Some materials will adsorb one or more of the pollutants, carbon monoxide, hydrocarbons and nitrogen oxides, while others will desorb these compounds. In addition, the ability of the bag sequential sampler to collect a representative sample must be verified.

Continuous monitoring yields a great improvement in data quality and quantity; however, the costs also increase greatly. In this method, an analyzing instrument is located at each sampling point. For the highest quality data, the instruments can be interfaced to a digital computer or data logger which can record the instrument readings simultaneously and at any desired frequency. For carbon monoxide, the two most practical instrument types for continuous monitoring are electrochemical and chromatographic instruments. The major problems with this approach are the expense and adaptability of some instruments to operate in the ambient atmosphere.

Previous Work. The previous work to evaluate the bag sequential sampling technique has been concentrated on sample deterioration in the bags. Ranzieri et al. (*3*) reported sample deterioration tests for bags made of mylar and aluminized polyester. The bags were filled with certified zero gas and with various span gases at concentrations up to 92 ppm. The samples in the bags were analyzed by nondispersive infrared (NDIR) analyzers after assorted time spans. The aluminized polyester bags did not affect the samples for the reported total testing time of 4–6 h. The mylar material was shown to be completely unacceptable.

Noll et al. (*4*) describe the comparison of a set of bag sequential samplers with an intermittent sequential sampling system. Five points were checked in a test at an actual roadway site. All bags were analyzed by an electrochemical analyzer, and some were reanalyzed by a nondispersive infrared analyzer. The bags were made of aluminized polyester and were used to take 15-min samples. The ISS system consisted of an NDIR tied to aluminum foil jacketed tygon lines. No significant differences in the concentration were noted. However, due to the nature of the test, variations of less than 20% were not considered significant.

Clemena (*5*) compared the sampling capabilities of two sequential samplers produced by different manufacturers. One contained aluminized polyester bags and piston-type pumps while the other contained polyvinyl chloride (PVC) bags and rubber diaphragm pumps. At a roadway site, the samplers were placed side by side along with a gas chromatograph with a flame ionization detector. The sample concentrations from the systems using aluminized polyester bags and piston pumps were all within 12% of the chromatograph readings. The concentrations from the system using PVC bags and rubber diaphragm pumps were about 50% below the chromatograph reading at carbon monoxide levels of about 20 ppm and about 20% high at concentrations of about 5 ppm.

From additional tests, Clemena concluded that the rubber diaphragm pump and tubing in the sampler were also absorbing or adsorbing the carbon monoxide from the sample.

In a limited test, Moe (6) checked sample deterioration in Tedlar and PVC bags. The bags were filled with a carbon monoxide span gas in the lab and analyzed periodically for up to 24 h with a nondispersive infrared analyzer. With 45.0 ppm span gas, the concentration in the PVC bags deviated a maximum of only 6% over the 24-h period. However, with 7.5 ppm span gas the maximum deviation was about 50% high, and the average deviation from all of the time intervals was 16% high. Due to leaks discovered in several of the Tedlar bags, the results were considered inconclusive.

Current Work. From the above discussion, it is apparent that the validity of the bag sequential sampling technique has not been established. The current work describes a complete experimental analysis of the bag sequential sampling technique. Tests of sample deterioration with various bag and sampler construction materials are also discussed.

Experimental Methods and Discussion of Results

To evaluate the bag sequential sampling technique, a series of experimental tests were designed. These tests included

- Comparison between bag samplers and continuous analyzers placed side by side
- Comparison between bag samplers and continuous analyzers sampling through a common header
- Sample deterioration with time for various bag materials
- Sample deterioration by sample passing through the bag sampler tubing and pump.

The bag samplers used in these tests consisted of 24 rubber diaphragm pumps similar to aquarium air pumps, with each pump connected to a 1.5-L bag by gum rubber tubing. The sequencing was controlled by an electronic timer programmed to run each pump for 15 min, then advance to the next. The sampler internals were sheltered in a plastic barrel about 2 ft in diameter and 4 ft high. The sample intake ports for the pumps were distributed uniformly around the barrel at a 3-ft height.

The continuous analyzers were of the electrochemical type (Ecolyzers) with a range of 0–50 ppm carbon monoxide, a span drift of ±1% of full scale per 24 h, and a zero drift of ±0.5 ppm/24 h. The continuous analyzers were read simultaneously every 10 s by a minicomputer, and the readings were logged onto magnetic cassette tape. To ensure good accuracy, the instruments were zeroed and calibrated every 2 h. The instrument readings were corrected by assuming a linear span drift between calibrations. No correction was made for zero drift which was quite small.

A gas chromatograph was also used to analyze the bag samples. The principle of operation of both the gas chromatograph and electrochemical analyzers is discussed in American Society for Testing and Materials (7) and Benchley et al. (8).

Bag Sampler and Continuous Analyzer Side by Side. In this test, bag samplers with PVC bags and continuous electrochemical analyzers were placed side by side at various distances ranging from 15 to 150 ft from a 10-lane freeway. The intakes for the continuous analyzers were 4 ft above ground. The pump intakes for the bag samplers were 1 ft below the continuous analyzer intakes and between 6 in. and 3 ft away laterally, depending on which pump was running. Each day of the tests, the bag samplers were operated until all 24 bags were filled (6 h). At the end of the day, the bags were collected and analyzed by one of the electrochemical analyzers which was rezeroed and recalibrated after each 24 bags.

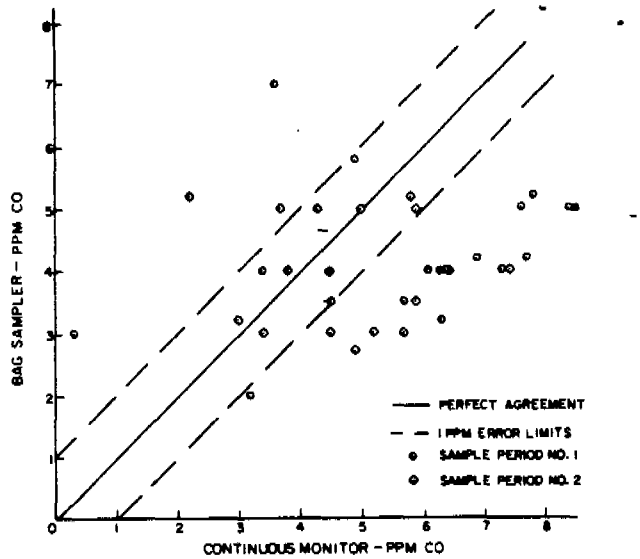

Figure 1. Comparison of bag samplers with PVC bags to nearby continuous monitors

Typical results from these tests are shown in Figure 1. Less than 30% of the points fall within ±1 ppm of the 45° line of perfect agreement, and the points were almost uniformly distributed. This indicates large random deviations which completely override any systematic deviations that may be present. The poor correlation was believed to be caused by the asymmetry of the sample ports on the sampler. Since almost no correlation was found, further tests were undertaken to ensure that the continuous analyzers were correct as well as to evaluate the bag samplers.

Bag Sampler and Continuous Analyzer with Common Intake Header. A sample header was built to deliver a common air sample to two bag samplers and two continuous monitors at the same time. The header consisted of 1-in.-diameter polyethylene tubing. The sample entered through a 2-ft-long sample intake, and then was split to serve each of the bag samplers. The sample intakes for the bag samplers which were distributed around the barrel were connected to the 1-in. polyethylene header. The sample ports for the continuous analyzers were placed in the 2-ft header intake section. The air was pulled through the header at a high rate by two vacuum pumps downstream of the bag samplers. Both vacuum pumps were adjusted to ensure a near uniform air flow through each branch of the header. To make the bag samplers completely independent of the continuous analyzers, a gas chromatograph was used to analyze the bags for these tests. Each bag was disconnected from its pump and sealed within 15 min of pump shut down to prevent any sample loss back through the pump. Tests were conducted with PVC bags and Tedlar bags in the samplers.

Two continuous analyzers were attached to the common header to test the accuracy and reliability of the continuous measurements. The continuous analyzers were read every 10 s by the minicomputer. A representative comparison of the 10-s values as a function of time for the two analyzers is shown in Figure 2. This figure also shows that the carbon monoxide concentration along roadways varies widely and at frequencies up to 2 cycles/min. A representative comparison of the 15-min averages from the two analyzers is shown in Figure 3. Based on a comparison of 101 fifteen-min averages, the standard error between the two continuous analyzers was 0.28 ppm, and the standard deviation of the error was 0.22 ppm. The values from the Tedlar bags were consistently low for both sampling days.

Additional tests with two continuous analyzers and two bag samplers both containing PVC bags, sampling through a common header were performed (Figure 4). The results showed that all points were within a ±1 ppm limit except a few in the 5–6 ppm range where the bag samples gave low values. Based on a comparison of 98 fifteen-min averages between the continuous analyzer and the bag sampler, the standard error was 0.41 ppm, and the standard deviation of the error was 0.39 ppm. To check the consistency between the two bag samplers, the results from the samplers were plotted against each other as shown in Figure 5. This plot shows that Bag Sampler No. 2 gave higher values than Sampler No. 1 about 80% of the time. From a comparison of 44 fifteen-min averages between the two bag samplers, the standard error was 0.54 ppm, and the standard deviation of the error was 0.55 ppm.

Sample Deterioration with Bag Materials. The influence of bag material on sample deterioration was tested by filling bags made from different materials with calibration gas containing carbon monoxide, nonmethane hydrocarbons, and methane. The samples in the bags were analyzed immediately after filling and after 24, 48, and 100 h by a gas chromatograph. The bag types were polyvinyl chloride (PVC), Tedlar, "Snout", and "aluminized polyester". The "snout" bags were constructed of layers of polyester, polyvinyl chloride, aluminum foil, polymide, and polyethylene whereas the "aluminized polyester" bags were constructed of layers of polyester and aluminum. The snout bags were purged six times with zero air before being filled with span gas. The purge gas was left in the bags for several hours during each purge. All bags were stored in a controlled environment between analyses. A summary of

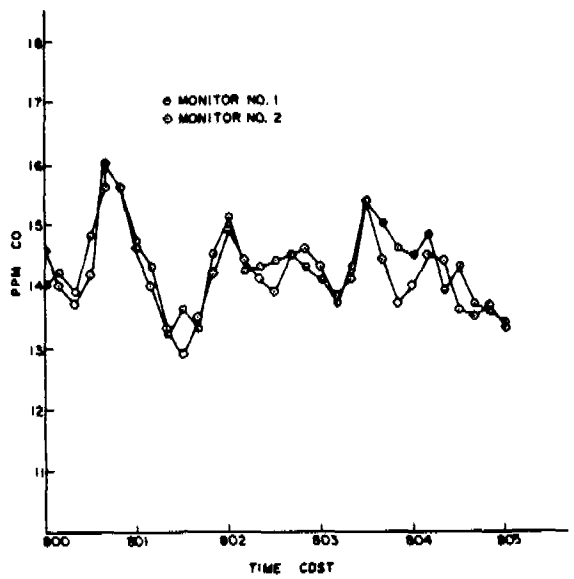

Figure 2. Comparison of two continuous monitors on common header as a function of time

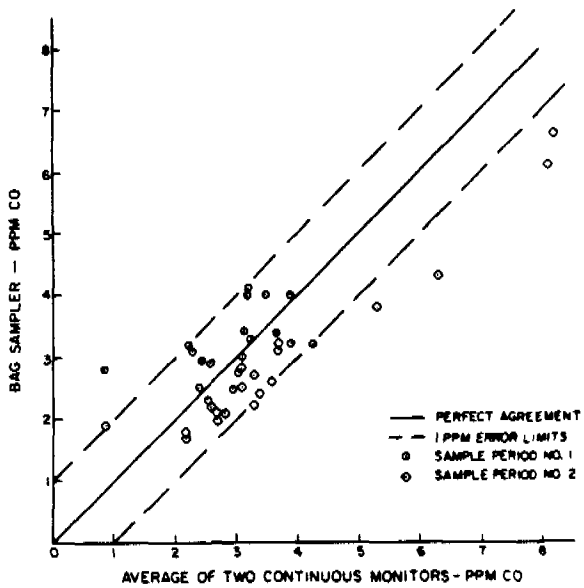

Figure 4. Comparison of bag sampler with PVC bags and continuous monitor on common header

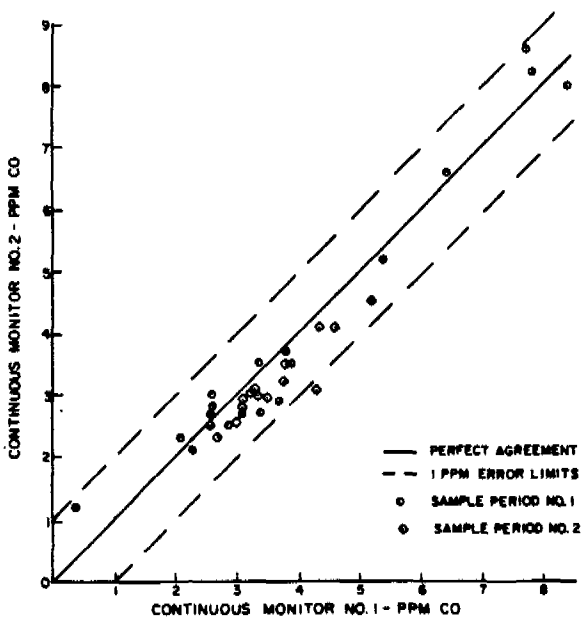

Figure 3. Comparison of two continuous monitors on common header

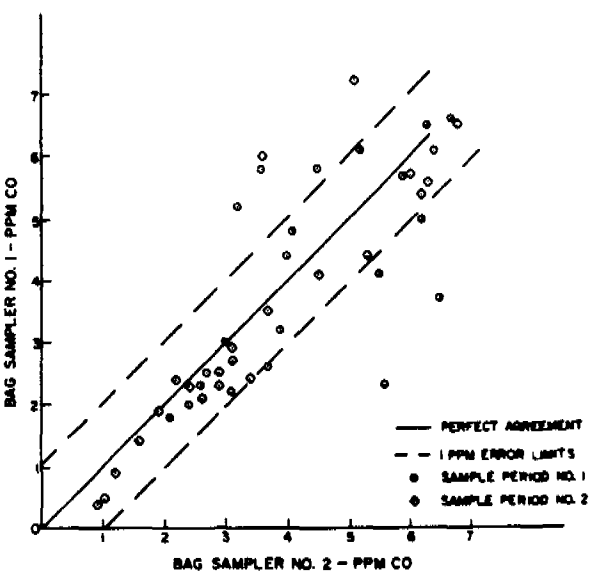

Figure 5. Comparison of two bag samplers with PVC bags on common header

the results from the carbon monoxide tests is shown in Table I for the four bag types, and a summary from the nonmethane hydrocarbon tests is shown in Table II. The results showed that:

- PVC bags are good only for short-term (less than 10–15 h) sample storage for both carbon monoxide and nonmethane hydrocarbons.
- Tedlar bags are poor for sample storage of ambient air concentration levels.
- Snout bags are excellent for long-term sample storage of carbon monoxide. However, for nonmethane hydrocarbons, the snout bags are completely unacceptable.
- Aluminized polyester bags are excellent for long-term sample storage of both carbon monoxide and nonmethane hydrocarbons. The concentration variations for both gases were within the accuracy of the chromatograph at all times in the 100-h tests.
- All of the bag materials tested except the aluminized polyester appear to give off nonmethane hydrocarbons during the first 24–48 h resulting in an increase in the concentration. This is followed by a long-term decay where the hydrocarbons are apparently reabsorbed or readsorbed by the bag material.

Sample Deterioration Due to Pump and Tubing. The effect of bag sampler rubber diaphragm-type pumps and gum rubber connecting tubing was tested. PVC bags were filled with nominal 10 ppm span gas and attached to the pump intakes on a sampler. The calibration gas flowed through the tubing and diaphragm pump by action of the diaphragm pump. The gas was collected in other PVC bags and then analyzed by a gas chromatograph. The results are shown in Table III. The pumps and tubing contributed significantly to the system error, causing drifts as large as 0.6 ppm in the observed carbon monoxide values.

Summary and Conclusions

Extensive tests have been performed to evaluate the bag sequential sampling technique for sampling ambient air. When placed side by side, carbon monoxide concentrations from bag samplers and continuous electrochemical analyzers did not correlate well. However, when the samples to the bag samplers and continuous analyzers were drawn through a common header, the concentrations agreed to within ±1 ppm for at least 90% of the data points.

To determine the influence of bag materials on samples, calibration gas was placed in the bags and then analyzed after 0, 24, 48, and 100 h. The results showed that polyvinyl chloride bags are satisfactory for sample storage up to about 15 h, whereas Tedlar bags are, in general, unsatisfactory for sample storage. Bags consisting of layers of polyester, polyvinyl

Table I. Carbon Monoxide Sample Deterioration with Time in Bags of Various Materials

Bag material	PVC	Tedlar	Snout [a]	Aluminized polyester
No. of bags tested	10	10	5	3
Concn of calibration gas used to fill bags, ppm	9.0	9.0	8.2	8.2
0 h after filling, av ppm	8.9	8.5	8.2	8.0
Av deviation, ppm	−0.12	−0.5	0	−0.17
Av sqd deviation, ppm^2	0.056	0.352	0.012	0.030
24 h after filling, av ppm	8.5	7.5	8.0	7.9
Av deviation, ppm	−0.50	−1.5	−0.18	−0.30
Av sqd deviation, ppm^2	0.306	4.2	0.048	0.097
48 h after filling, av ppm	8.4	6.8	8.3	8.2
Av deviation, ppm	−0.63	−2.2	0.10	−0.03
Av sqd deviation, ppm^2	0.497	7.7	0.010	0.010
100 h after filling, av ppm	7.9	5.2	8.0	7.7
Av deviation, ppm	−1.2	−3.8	−0.18	−0.50
Av sqd deviation, ppm^2	1.5	17.8	0.066	0.25

[a] Consists of layers of polyester, polyvinyl chloride, aluminum, polymide, and polyethylene.

Table II. Nonmethane Hydrocarbons Sample Deterioration with Time in Bags of Various Materials

Bag material	PVC	Tedlar	Snout [a]	Aluminized polyester
No. of bags tested	10	10	5	3
Concn of calibration gas used to fill bags, ppm	7.3	7.3	9.5	9.5
0 h after filling, av ppm	7.4	7.5	13.3	9.6
Av deviation, ppm	0.02	0.06	3.8	0.1
Av sqd deviation, ppm^2	0.010	0.172	15.8	0.016
24 h after filling, av ppm	8.0	8.6	15.5	9.8
Av deviation, ppm	0.60	1.15	5.9	0.30
Av sqd deviation, ppm^2	0.390	2.52	39.1	0.090
48 h after filling, av ppm	7.5	8.7	15.7	9.6
Av deviation, ppm	0.07	1.3	6.2	0.10
Av sqd deviation, ppm^2	0.055	3.83	41.9	0.017
100 h after filling, av ppm	6.6	8.3	15.4	9.4
Av deviation, ppm	−0.80	0.90	5.9	−0.10
Av sqd deviation, ppm^2	0.680	4.0	38.4	0.017

[a] Consists of layers of polyester, polyvinyl chloride, aluminum, polymide, and polyethylene.

Table III. Sample Deterioration Due to Pump and Tubing Materials [a]

	Nonmethane hydrocarbons	Methane	Carbon monoxide
Gas concn to pump, ppm	10.3	10.0	9.0
Five-min av exit concn			
Pump No. 1, ppm	10.3	9.5	8.7
Pump No. 2, ppm	9.9	9.1	8.4
Pump No. 3, ppm	10.0	9.1	8.4
Pump No. 4, ppm	10.5	9.8	8.9

[a] Rubber diaphragm pump and gum rubber tubing.

chloride, aluminum foil, polymide, and polyethylene are excellent for long-term storage of carbon monoxide, but completely unacceptable for nonmethane hydrocarbons. Aluminized polyester bags consisting of a layer of polyester on both sides of an aluminum layer are excellent for long-term storage of both carbon monoxide and nonmethane hydrocarbons. Tests also show that rubber diaphragm pumps and gum rubber tubing can have a significant (0.6 out of 10 ppm) impact on ambient air samples.

In conclusion, the bag sequential sampling technique is a good method to collect samples of ambient air economically when used with the proper precautions.

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