ENSR

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January 14, 1994

Mr. Michael Koerber
Lake Michigan Air Directors Consortium
2350 E. Devon Ave., Suite 242
Des Plaines, IL 60018

Re: Carbonyl Bag Sampling

Dear Mike:

Enclosed is a write up of the Bag/Cartridge sampling comparison for carbonyl compounds. The results are the same as those Kosky Fung described, i.e. there is no significant difference between ambient concentrations determined from the bags or the cartridges.

Maybe there is something going on in the atmosphere to cause higher concentrations aloft, but seeing the same results for formaldehyde and acetone does not give me a warm fuzzy feeling.

Dick and I looked at the formaldehyde maps I plotted a year and a half ago and there is some spatial pattern aloft similar to the surface distribution of concentrations. Over in Michigan, the air to surface ratio is down to 1.5 to 2 on July 17 and 18. Are we really sure that Battelle did not make a mistake in sample values?

I am glad this comparison came out to show no difference, but you still have some work to do to find the cause of the differences. I may even think about this one now and again in retirement. Call me if anything is unclear.

Very truly yours,

Norm Bowne(kf)
Norman E. Bowne

NEB/kwf
Attachment

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BAG SAMPLING

FOR

CARBONYL COMPOUNDS

A Comparative Study of Bag Samples

and

Cartridge Samples

for

Lake Michigan Air Directors Consortium
2350 East Devon
Des Plaines, IL 60018

Norman E. Bowne, CCM

ENSR Consulting and Engineering
95 Glastonbury Boulevard
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January 12, 1994

BACKGROUND

Carbonyl compounds are important in the creation of ozone because they are highly reactive. Air samples for these compounds are collected at the ground by drawing air at approximately one liter per minute through a cartridge filled with a substrate coated with DNPH. Two commercially available cartridges are used, one with a carbon substrate, C-18 and the other with a silica gel substrate. Samples were collected at ground level for two-hour periods during the Lake Michigan Ozone Study, LMOS. The same sampling system is not appropriate for aircraft where the purpose of the sampling is to determine the spatial variability of concentrations. Tedlar bags were used to collect samples in a matter of seconds from air intakes directly into the bags. After the airplane landed, the bags were pumped out through the cartridges. Air concentrations of formaldehyde were significantly different aloft when compared to the surface observations during the LMOS. Typical surface concentrations were 3 to 10 ppbC, while aircraft concentrations ranged from 10 to 20 ppbC. Similar ratios were observed for the other carbonyl compounds.

Ambient concentrations of volatile organic compounds, VOC, in the C4 to C10 range are determined from analysis of air collected in polished summa canisters. These compounds are analyzed directly rather than after processing to remove the sample from the cartridge substrate. Comparison of VOC concentrations for aircraft samples compared to surface samples for several species indicated an increase near 10 percent , but none approached the factor of two or three found for the carbonyl compounds. We speculated that the bag sampling procedure for carbonyls was introducing a bias into the measurements.

A sampling program was planned for the southeastern Michigan area for the summer of 1993, although without the bag sampling in the aircraft. LADCO decided to sponsor a brief experiment to see if bag sampling at the ground showed similar results. A protocol was developed and sampling was carried out at the ENSR office in Westmont, IL west of Chicago.

PROTOCOLS

Aircraft Protocol

The forty liter Tedlar bags were prepared approximately one hour prior to takeoff using the following procedure.

1. Fill each bag partially with Ultra-Zero air and evacuate. Perform three times.

2. Attach each bag to the regulator output from a Nitric Oxide cylinder and introduce a 1 to 2 second burst of gas into the bag.

3. Place the Tedlar bag into a black plastic garbage bag and place aboard the aircraft.

Attach the sample bag to the ram air Teflon sampling line in the aircraft at sampling time. Three minute grab samples were collected. Return the Tedlar bag to the black garbage bag for storage immediately after sampling.

Upon landing the Tedlar bag samples were pumped through a DNPH coated silica gel cartridge, one per bag. During the pumping process, the bag was exposed to diffused light, This task occurred within 30 minutes after landing. The third last bag was not pumped out until two hours after landing.

The zero air was Scott Specialty Gases "Ultra Zero Ambient Monitoring Zero Air" with THC < 0.05 ppm; Co < 0.05 ppm; H_2O < 5ppm; CO_2 315 to 385 ppm and O_2 content 20 to 21 percent.

The Nitric Oxide cylinder concentration was 10 ppm.

The cartridges were shipped to the laboratory for analysis with the canisters. All surface site shipments occurred at the same time. All cartridges were refrigerated before and after use.

The Nitric Oxide is introduced to quench any ozone reactions that might take place after sampling to preserve the carbonyl molecules.

Surface Sampling Protocol

Bags were obtained from Aerovironment, the same supplier used in 1991, and were treated in the same manner as for the aircraft flights, i.e. filled and evacuated three times with zero air, then given a 1 to 2 second shot of Nitric Oxide and stored in a dark place.

Air samples were collected in tedlar bags for analysis of carbonyl compounds. Air was pumped into the bags through an Oregon State (Professor Rasmussen) supplied VOC/Carbonyl sampling system at a rate of 1 liter per minute. Two bags were used for each hour. Simultaneously, a cartridge was collected in the standard manner for Carbonyl sampling, drawing the air through an ozone scrubber then over the DNPH substrate in the cartridge. Silica gel substrates were used in general to match the 1991 sampling protocol. Air was drawn out of the bags through silica gel cartridges coated with DNPH for analysis, plus one case using a C-18 cartridge. Three standard samples were drawn over CC-18 cartridges in parallel with the bags and silica gel samples for comparison. Blank bag samples were prepared and pumped over silica gel cartridges for analysis. Cartridges were stored in a refrigerator before and after sampling. They were sent to the analysis laboratory, Atmospheric Analysis and Consulting (Dr. Sucha Parmer) for analysis with the Southeast Michigan Ozone Study samples.

In general the aircraft sampling conditions were simulated on the ground with the differences of pump filling the bags rather than filling with ram air. In addition, we obtained twice as much air sample over the cartridge by combining two bags from the same hour. Analysis was at a different laboratory in 1993, but the methods used were the same.

RESULTS

The spreadsheet, Table 1, lists the basic data for the compounds that were above detection limit from the cartridges. Formaldehyde, acetaldehyde, acetone and butyraldehyde were the only species with air concentrations above the laboratory detection limit. Concentrations of acrolein, propionaldehyde, crotonaldehyde and benzaldehyde were below the detection limit. That was consistent with the results obtained during the 1991 study.

Air concentrations for the two days sampled in Westmont were at the low end of concentrations seen during the LMOS project, but formaldehyde concentrations on the cartridge were eight to ten times the blank level, butyraldehyde and acetaldehyde were three to four times the blank level, and acetone was about three times the blank level. These levels are lower than desired for comparison because they are so close to blank levels for the laboratory. However, they are in the range of observations from the 1991 study.

Table 2 lists the cartridge concentration by species and type of cartridge for the nine tests. Average values are shown as well as the blank. Four plots of the bag versus silica gel cartridge follow the table.

Formaldehyde

Figure 1 shows the formaldehyde comparison. The scatter is fairly large, but there seems to be no bias. Certainly the average values of the bag and silica gel cartridge are not significantly different. The C-18 cartridge does appear to measure less formaldehyde, both from the bag to cartridge, (solid square in the figure) and comparison of the three cartridge samples in Table 2. The C-18 cartridge concentration was 80 percent of the silica gel concentration for the three simultaneous samples.

Acetaldehyde

Figure 2 shows the plot for acetaldehyde; bias appears to be present. The average value of the bag concentration is 25 percent higher than the cartridge. The C-18 cartridge concentration is 15 percent higher than the silica gel cartridge. The results are limited be the fact that the maximum concentration was less than four times the average blank level.

Acetone

Figure 3 shows acetone results similar to those for acetaldehyde. The bag concentrations average 18 percent higher than the silica gel cartridge, but again the average values are only three times the blank level and the maximum is only four times the blank. The C-18 cartridge

values were 23 percent higher than the silica gel cartridge concentration for the three simultaneous samples.

Butyraldehyde

Figure 4 shows that butyraldehyde concentrations are essentially the same for all sample comparisons. The average concentration values are all the same to the second decimal and the scatter is large for only one sample. These sample concentrations are all at least three times the blank level.

CONCLUSIONS

Formaldehyde and butyraldehyde concentrations from air samples collected in Tedlar bags, pretreated in the same manner as aircraft sampling bags, were not significantly different from air sample concentrations collected on cartridges in the normal carbonyl sampling train. Concentrations of acetaldehyde and acetone both appeared to be 20 percent higher from the bags, but the average concentrations were not more than three times the blank level of the cartridges. There were no concentrations that differed by the typical factor of three seen in the 1991 aircraft versus surface concentration comparisons.

Table 1 Lake Michigan Ozone Study
Bag Comparison Data 1993

No.	Date	Start	End	Type Cart	Vol	Hold Time	Laboratory Results uG/sample				Air Concentration ppbC				
							Formald	Acetald	Acetone	Butyral	Formald	Acetald	Acetone	Butyral	
1	17 Aug 93	730	830	SG	60		0.4679	0.3004	0.8756	0.1522	2.4306	1.5605	3.9383	0.5733	
2	17 Aug 93	730	830	BAG(2)SG	60	0	0.4469	0.3205	0.8849	0.1575	2.3216	1.6649	3.9801	0.5932	
3	17 Aug 93	900	1000	SG	60		0.5219	0.3606	0.9117	0.2650	2.7112	1.8732	4.1006	0.9981	
4	17 Aug 93	900	1000	C18	60		0.4183	0.3959	1.0746	0.3204	2.1730	2.0566	4.8333	1.2068	
5	17 Aug 93	900	1000	BAG(2)C18	60	30	0.4117	0.3953	1.1175	0.2551	2.1387	2.0535	5.0263	0.9608	Held in black plas
6	17 Aug 93	1010	1110	SG	60		0.5263	0.3408	1.0075	0.2650	2.7340	1.7704	4.5315	0.9981	
7	17 Aug 93	1010	1110	BAG(2)SG	60	60	0.5697	0.4517	1.1344	0.2742	2.9595	2.3465	5.1023	1.0328	Held in black plas
8	17 Aug 93	1115	1145	BLANK BAG	30	0	0.0500	0.1526	0.3199	0.0600	0.5195	1.5855	2.8777	0.4520	HC free zero air
9	17 Aug 93	1210	1310	SG	60		0.7958	0.4549	1.1944	0.2799	4.1340	2.3631	5.3722	1.0542	
10	17 Aug 93	1210	1310	BAG(2)SG	60	60	0.5631	0.3417	1.0089	0.1637	2.9252	1.7751	4.5378	0.6166	Held in black plas
11	17 Aug 93	1325	1425	C18	60		0.4152	0.3880	1.0679	0.1849	2.1569	2.0156	4.8032	0.6964	
12	17 Aug 93	1325	1425	SG	60		0.6422	0.4211	0.9938	0.1943	3.3361	2.1875	4.4699	0.7318	
13	17 Aug 93	1325	1425	BAG SG	60	60	0.5567	0.4914	1.3800	0.2327	2.8919	2.5527	6.2070	0.8765	Held in black plas
14	17 Aug 93	1445	1545	SG	60		0.6385	0.4265	1.0591	0.2286	3.3169	2.2156	4.7636	0.8610	
15	17 Aug 93	1445	1545	BAG SG	60	30	0.7627	0.4752	1.2851	0.2076	3.9621	2.4686	5.7801	0.7819	Held in black plas
16	18 Aug 93	731	831	SG	60		0.6197	0.3878	1.0531	0.2235	3.2192	2.0145	4.7366	0.8418	
17	18 Aug 93	731	831	BAG SG	60	0	0.5942	0.5954	1.1602	0.2003	3.0868	3.0930	5.2183	0.7544	
18	18 Aug 93	845	945	SG	60		0.6008	0.4312	1.1234	0.2980	3.1210	2.2400	5.0528	1.1224	
19	18 Aug 93	845	945	BAG SG	60	0	0.6940	0.6274	1.3573	0.3276	3.6052	3.2592	6.1049	1.2339	
20	18 Aug 93	1030	1130	C18	60		0.5621	0.4995	1.2383	0.2141	2.9200	2.5948	5.5696	0.8064	
21	18 Aug 93	1030	1130	SG	60		0.5938	0.3291	0.8354	0.1641	3.0847	1.7096	3.7575	0.6181	Held in black plas
22	18 Aug 93	1030	1130	BAG SG	60	60	0.7389	0.6062	1.3004	0.2104	3.8384	3.1491	5.8489	0.7925	
23	18 Aug 93	1145	1220	BLANK BAG	30		0.0500	0.1253	0.3558	0.0600	0.5195	1.3018	3.2006	0.4520	HC free zero air
24	18 Aug 93			C18 SHIP			0.0500	0.1201	0.4683	0.0600	0.2597	0.6239	2.1063	0.2260	
25	18 Aug 93			SG SHIP			0.0500	0.0400	0.2699	0.0600	0.2597	0.2078	1.2140	0.2260	Sealed cartridge
26	18 Aug 93			SG SHIP			0.0500	0.1932	0.3207	0.0600	0.2597	1.0036	1.4424	0.2260	Cartridge exposed,
				LAB BLANK			0.1699	0.1469	0.3289	0.0600	0.8826	0.7631	1.4793	0.2260	
				LAB BLANK			0.1699	0.1469	0.3289	0.0600	0.8826	0.7631	1.4793	0.2260	

Table 2 LMOS Carbonyl Cartridge/Bag Comparison

Bag Sampling Study - LMOS

Data listed are uG/sample from cartridges

Acetone

	SG	Bag	C18	
	0.8756	0.8849		
	0.9117	1.1175	1.0746	Bag sampled on C18 cartridge
	1.0075	1.1344		
	1.1944	1.0089		
	0.9938	1.38	1.0679	
	1.0591	1.2851		
	1.0531	1.1602		
	1.1234	1.3573		
	0.8354	1.3004	1.2383	
Average	1.0060	1.1810		
Blank	0.3207	0.3558	0.4683	

Butyraldehyde

	SG	Bag	C18	
	0.1522	0.1575		
	0.265	0.2551	0.3204	Bag sampled on C18 cartridge
	0.265	0.2742		
	0.2799	0.1637		
	0.1943	0.2327	0.1849	
	0.2286	0.2076		
	0.2235	0.2003		
	0.298	0.3276		
	0.1641	0.2104	0.2141	
Average	0.2301	0.2255		
Blank	<.06	<.06	<.06	

Table 2 LMOS Carbonyl Cartridge/Bag Comparison

Bag Sampling Study - LMOS

Data listed are uG/sample from cartridges

Formaldehyde

	SG	Bag	C18	
	0.4679	0.4469		
	0.5219	0.4117	0.4183	Bag sampled on C18 cartridge
	0.5263	0.5697		
	0.7958	0.5631		
	0.6422	0.5567	0.4152	
	0.6385	0.7627		
	0.6197	0.5942		
	0.6008	0.694		
	0.5938	0.7389	0.5621	
	0	0		
Average	0.6008	0.5931		
Blank	<.05	<.05	<.05	

Acetaldehyde

	SG	Bag	C18	
	0.3004	0.3205		
	0.3606	0.3953	0.3959	Bag sampled on C18 cartridge
	0.3408	0.4517		
	0.4549	0.3417		
	0.4211	0.4914	0.388	
	0.4265	0.4752		
	0.3878	0.5954		
	0.4312	0.6274		
	0.3291	0.6062	0.4995	
Average	0.3836	0.4783		
Blank	0.1932	0.1253	0.1201	

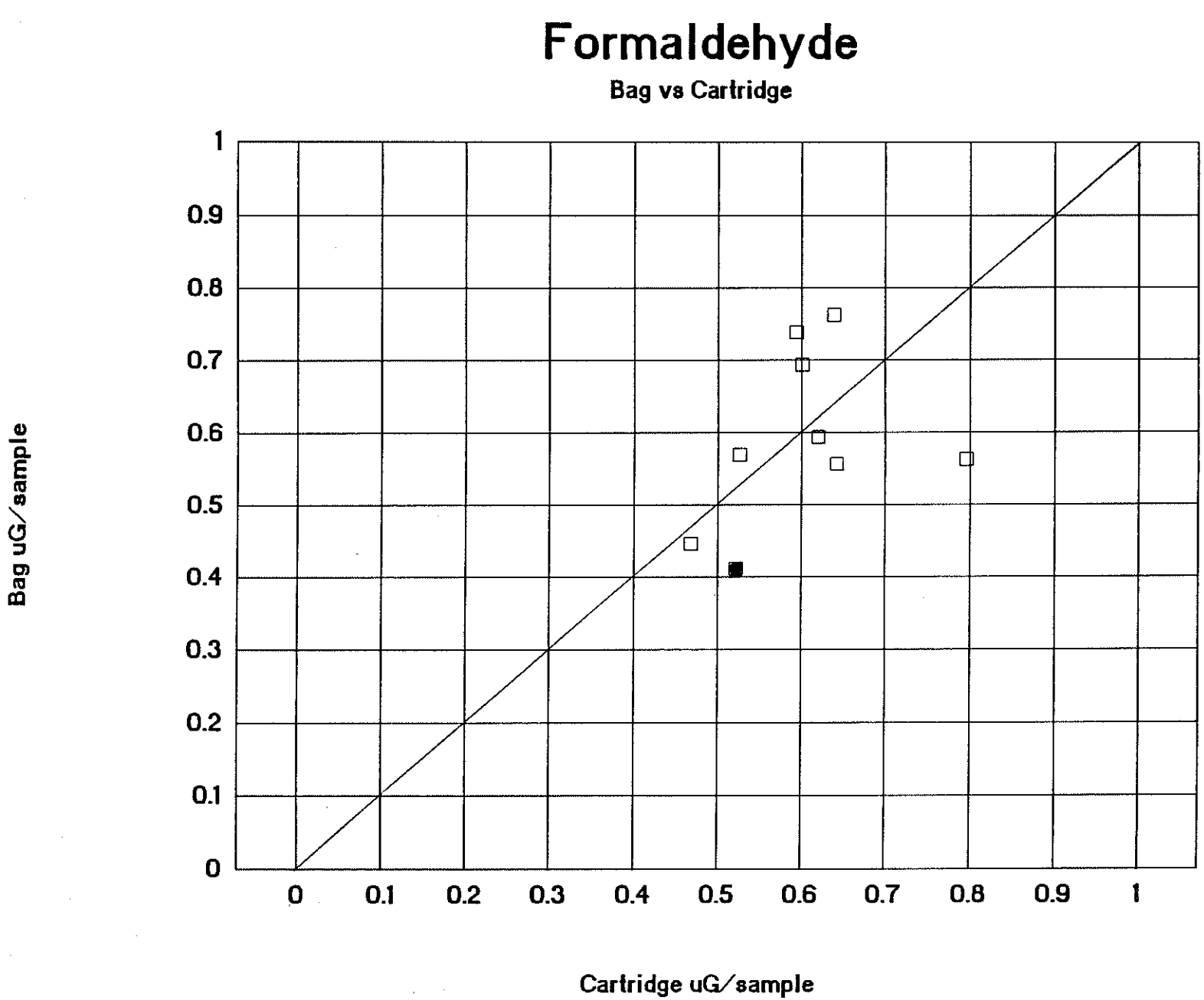

Figure 1. Comparison of formaldehyde recovery from 60 liters of ambient air.

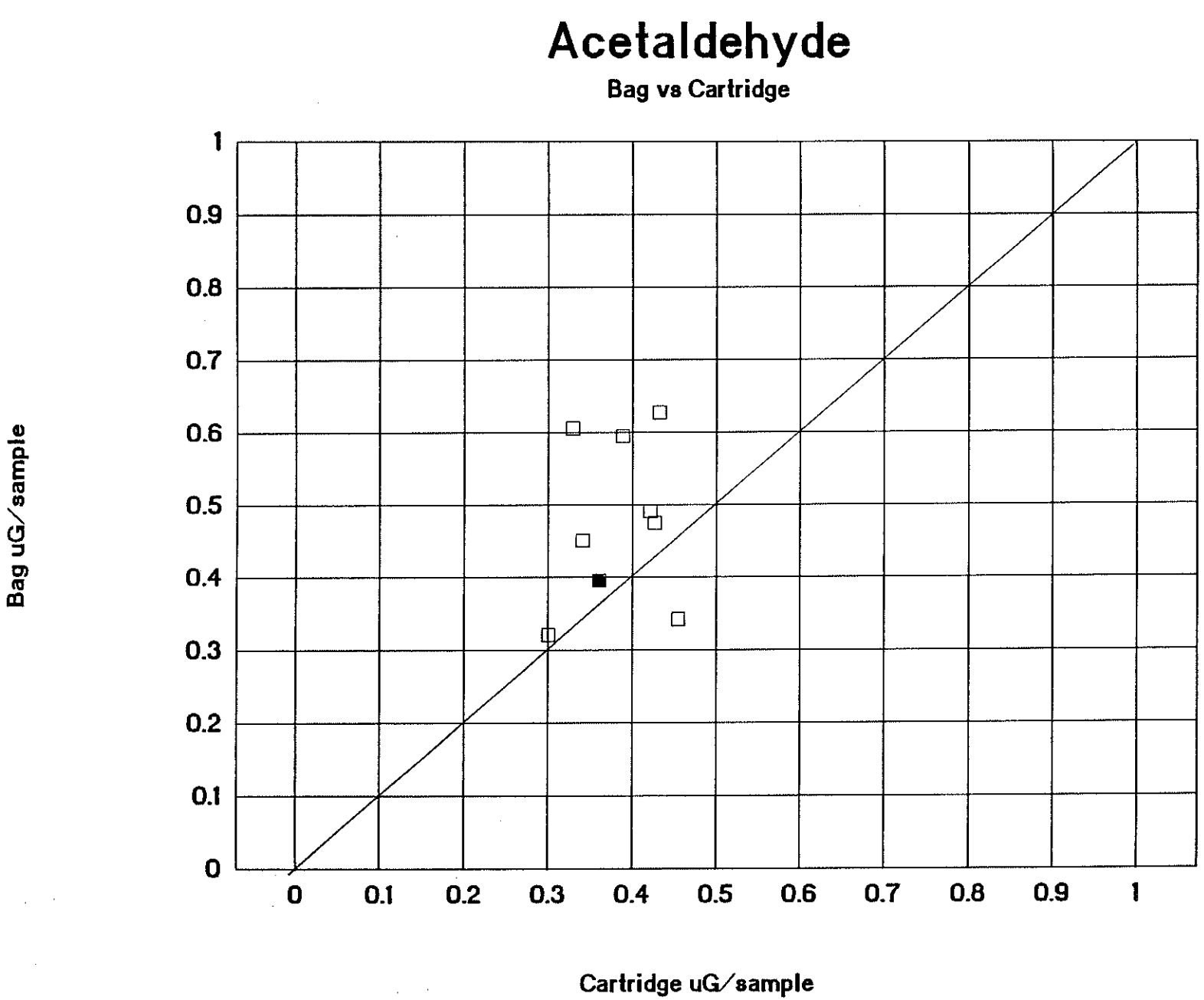

Figure 2. Comparison of acetaldehyde recovery from 60 liters of ambient air.

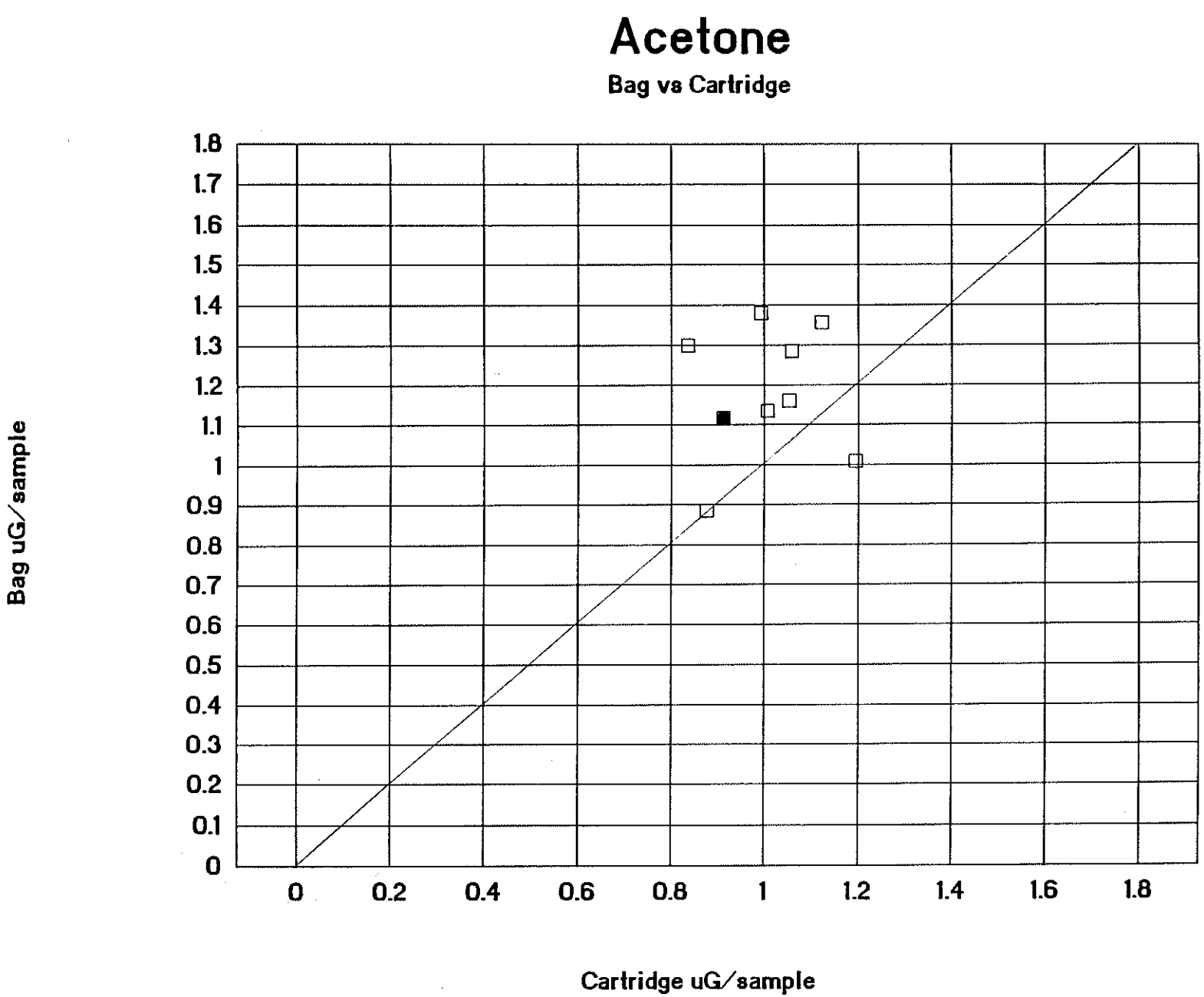

Figure 3. Comparison of acetone recovery from 60 liters of ambient air.

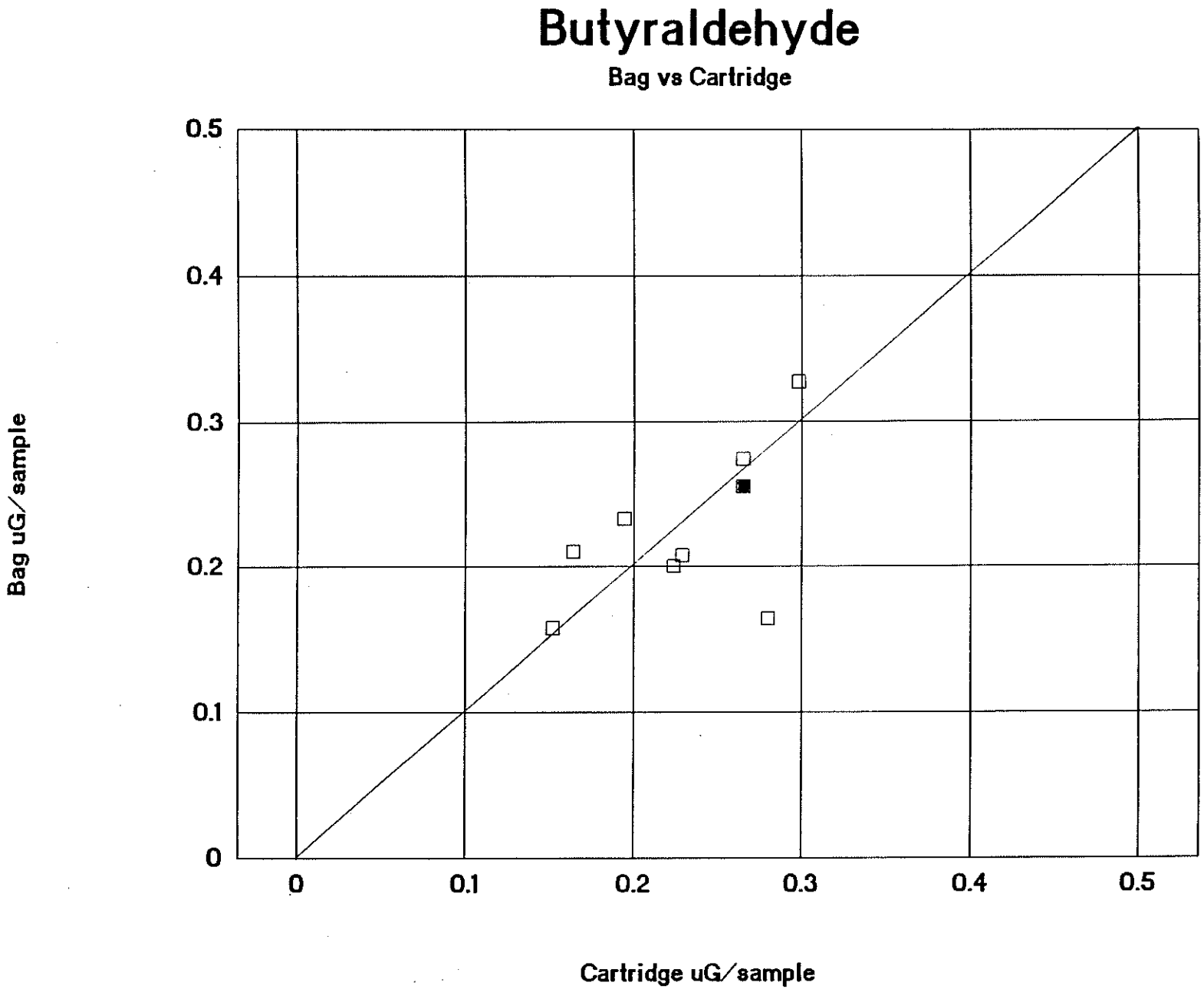

Figure 4. Comparison of butyraldehyde recovery from 60 liters of ambient air.