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Instability of Formaldehyde Air Samples Collected on a Solid Sorbent

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In May, 1980, an article appeared in the American Industrial Hygiene Association Journal which described a new method for sampling and analysis of formaldehyde vapor in air. Recent experiments have shown that samples collected according to this method (currently designated as NIOSH P&CAM 318) are unstable. This paper describes some of these experiments and presents data which show that ambient temperatures and storage times in excess of one week contribute to sample loss.

Introduction

In May of 1980, an article was published in this journal which presented details of a new sampling and analytical method for formaldehyde.⁽¹⁾ The method described a procedure for collection of formaldehyde vapor on a specially treated charcoal. Analysis is performed using ion chromatography after oxidizing the formaldehyde to formate. The method (which is currently designated as NIOSH P&CAM 318) has the advantage of using a solid sorbent for collection of the vapor thus making the method attractive for personnel sampling.⁽²⁾

At NIOSH, this has been the method of choice for a large number of field study projects. The original work with this method was done with a treated charcoal obtained from Barneby-Cheney Co. Subsequent to publication of the original work, SKC Inc. manufactured the sorbent tubes for commercial sale, first with charcoal obtained from Barneby-Cheney, and later with a charcoal which SKC themselves treated.

This later lot of charcoal (lot 115) was used in a laboratory study comparing three sampling and analytical methods for formaldehyde. In addition to method P&CAM 318, method P&CAM 125 (the chromatropic acid method), and a method which collects formaldehyde on silica gel coated with 2,4-dinitrophenyl hydrazine⁽⁵⁾ were compared. The results of this study showed good agreement among the methods.⁽³⁾

Among further experiments performed by NIOSH to evaluate formaldehyde sampling and analytical methods, was a comparison of the performance of three methods in sampling the atmosphere of a formaldehyde production

facility. One of the methods compared in this study was method P&CAM 318. The lot of charcoal used in this study was #124 and was obtained from SKC. The second method compared was method P&CAM 354. This method is based on reaction of the formaldehyde vapor with N-benzyl-ethanolamine which is coated onto a solid support. The resulting oxazolidine of formaldehyde is desorbed and quantitated using gas chromatography.⁽⁴⁾ The third method compared is based on the reaction of formaldehyde with 2,4-dinitrophenyl hydrazine coated onto silica gel. The resulting hydrazone of formaldehyde is quantitated using liquid chromatography.⁽⁵⁾ The details of this study will not be presented here; however a summary of the results is shown in Table I for the two days of sampling. These results indicated that the concentration of formaldehyde as determined by method P&CAM 318 was significantly lower than that determined by the other two methods investigated. In addition, quality control samples submitted to the analytical laboratory with the field samples showed similar low results.

In an effort to isolate the cause of the low results noted above, we have performed additional experiments to investigate the inter-laboratory variation and stability characteristics of method P&CAM 318.

Experimental

In the first experiment, a set of 30 formaldehyde samples were collected from a test atmosphere during three collection runs. These thirty samples were divided into five groups and each group received a different treatment. One group of

TABLE I
Summary of Field Study Comparing Three Formaldehyde Sampling and Analytical Methods

Day	Method	Mean Concentration ($\mu\text{g/L}$)	Standard Deviation ($\mu\text{g/L}$)	Number of Samples
1	P&CAM 318 ⁽²⁾	2.89	1.55	4
1	P&CAM 354 ⁽⁴⁾	4.59	0.57	7
1	Coated Silica Gel ⁽⁵⁾	4.74	0.75	7
2	P&CAM 318	0.75	0.18	5
2	P&CAM 354	1.11	0.18	8
2	Coated Silica Gel	1.53	0.25	7

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TABLE II
Summary of Experiment to Study Various Treatments of
Samples Collected According to Method P&CAM 318

Grouping ^A	Average of 2 Samples ($\mu\text{g/L}$)	Collection Run	Treatment ^B
	24.0	1	2
	22.9	1	1
	18.7	1	3
	18.2	1	4
	10.4	3	1
	10.1	3	2
	9.5	2	1
	9.3	2	2
	8.7	3	3
	7.1	2	3
	6.8	1	5
	6.4	2	4
	5.7	3	4
	2.9	2	5
	2.7	3	5

^AMeans connected by vertical lines are not significantly different.

^BTreatment groups:

1. Independent analysis by P&CAM 354
2. Immediate analysis at NIOSH
3. Immediate analysis at contract laboratory
4. Analysis after 2 weeks at ambient temperature
5. Analysis after 2 weeks at elevated temperature

samples was collected and analyzed according to P&CAM 354. This group of samples, designated as treatment group #1, was used as a "reference" to which the other treatment groups were compared. The other four groups of samples were collected according to P&CAM 318. One of these groups (treatment group #2) was analyzed immediately in our laboratory, one group (treatment #3) was sent to our contract laboratory for immediate analysis, one group (treatment #4) was stored for two weeks at ambient temperature before analysis in our laboratory and the last group (treatment #5) was stored for two weeks at elevated temperature (40 °C) before analysis in our laboratory.

In a second experiment performed concurrently, a set of ten samples collected from a test atmosphere was split. Half were sent to our contract laboratory and returned to our laboratory. The other half remained in our laboratory until the first half was returned at which time all ten samples were analyzed according to P&CAM 318. This experiment was intended to establish whether factors involved in shipping collected samples were involved with sample loss.

To further evaluate these and other stability factors a set of 16 samples collected according to P&CAM 318 from a test atmosphere was divided and treated according to a predetermined experimental design. The factors investigated included:

1. Time — Samples were stored for either one week or one month.
2. Light — Some samples were exposed to sunlight for one day, while all others were kept in the dark.
3. Pressure — Some samples were exposed to a reduced pressure (640 mm Hg) for 6 hours to simu-

late the reduced pressure in an airplane cargo hold, while the rest were kept at ambient pressure.

4. Storage temperature — Some samples were stored at refrigerator temperatures while the rest were stored at room temperature.
5. Humidity — All samples were collected from a dry atmosphere of formaldehyde vapor. Some of the collected samples were spiked with approximately 50 μL of water to investigate any effects which humidity might have on sample stability.

Results

The results of the first experiment are summarized in Table II. Analysis of variance techniques were used to examine these data. This analysis showed strong effects due to both "collection run" and "treatment" as well as a strong interaction between these two factors. Since generation of a quantitative atmosphere of formaldehyde vapor is difficult with the generation technique we used, it was therefore not too surprising that the concentration during collection run 1 was higher than in later collection runs. In Table II group means which are connected by vertical lines are not statistically different. As can be seen, within every run, the results obtained by treatments 1 and 2 (immediate analysis by our laboratory and analysis via the independent method) are not significantly different. Within each run, however, results obtained by our contract laboratory are approximately 25% lower. Also the results of samples stored for two weeks at ambient temperatures were approximately 25% lower. The samples which were stored for two weeks at elevated temperature were approximately 75% lower than samples analyzed immediately. These results indicate that time and storage temperature are critical in causing sample loss. It is not clear from these data, however, that time and temperature are the only shipping factors that may cause sample loss.

The results of the second experiment showed a statistically significant difference between samples which were not transported and those which were transported to our contract laboratory and returned. These results are in conflict with what was expected at the time. The average concentration determined from samples which were shipped was 5.85 $\mu\text{g/L}$ while the average concentration determined from samples which were not shipped was 4.99 $\mu\text{g/L}$. It was anticipated that the samples which were transported to the contract laboratory would be lower than those which

TABLE III
Summary of Results of Experiment on
Stability of Samples Collected
According to P&CAM 318

Temperature	Time	Mean ^A Recovery	Standard Deviation
Ambient	1 Month	0.52	0.06
Ambient	1 Week	0.85	0.07
Refrigerator	1 Month	1.02	0.18
Refrigerator	1 Week	1.16	0.06

^AMean of 3 to 5 samples.

remained in our laboratory if there was indeed sample loss caused by shipping. Instead, the samples which remained in our laboratory were lower than those which were transported. It was noted that the samples which remained in our laboratory were stored at ambient temperature in a rather warm office (daytime highs of 30 °C). These results tend to support the conclusions of the first experiment; that a significant cause of the sample loss was temperature.

The results of the third experiment are summarized in Table III. A reference method⁽⁴⁾ was used to calculate the amount of formaldehyde collected and "recovery" values were then calculated for each sample. Analysis of these data showed that reduced recovery was observed both when samples were stored for one month before analysis and when samples were not kept refrigerated. The other factors studied (light, reduced pressure, and humidity) had no significant effect on recovery.

Conclusions

These experiments indicate that samples collected according to method P&CAM 318 on SKC lot #124 charcoal are unstable. Refrigeration of samples after collection tends to increase stability, but the limits of storage time and tempera-

ture are not known. We believe that the temperature at which collected samples are shipped and stored is a critical factor in causing sample loss with this method and further, that this loss cannot be adequately controlled at this time. Therefore, we at NIOSH have abandoned the use of P&CAM 318. We now recommend and use P&CAM 354 for monitoring worker exposure to formaldehyde.

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