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MEASUREMENT OF WORKER'S EXPOSURE TO STYRENE

Final Report

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16. Abstract (Limit: 200 words) → Studies were conducted to determine the effectiveness of personal samplers in the work place by documenting the magnitude of the variability in breathing zone concentrations of styrene (100425) within the reinforced plastics industry, determining factors which contribute to breathing zone concentrations and investigating the stability of styrene samples taken with charcoal tubes. Measurements were taken at a facility for manufacturing boats where the production process included spraying a catalyzed resin solution along with chopped fiberglass onto a mold. The average background air concentration was 18mg/m3. The personal exposure concentrations were: nose, 327mg/m3; left lapel, 365mg/m3; right lapel, 388mg/m3; and chest, 430mg/m3. Factors affecting the concentration in the breathing zone included air flow patterns, the hood face velocity, and the position of the worker relative to the hood and relative to the spray gun. Styrene, being a volatile and reactive compound, may undergo physical and chemical changes such as vaporization, oxidation and polymerization, any of which would cause underestimation if they occurred following the sample collection. Samples collected on charcoal were stable up to 4 weeks in storage. ←			13. Type of Report & Period Covered	
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I. INTRODUCTION

This grant award was received under the small grants program for research relating to occupational safety and health. The funds were used, as prescribed under the grant guidelines, for support of pre-doctoral research. This report briefly summarizes the substantial body of work completed during the period for which the project was funded. Some of the data developed under the grant have not yet been fully analyzed, but all data will be utilized in Mr. Malek's doctoral dissertation. The grant support will be acknowledged in scientific publications of this work.

The specific aims of this research are to:

- 1) Document the magnitude of the variability in breathing zone concentrations of styrene within the reinforced plastic industry.
- 2) Investigate the factors which contribute to breathing zone concentration variations.
- 3) Investigate the stability of styrene sampled with charcoal tubes for the period between sampling and analysis.

The ultimate goal of this research is to better understand how to use personal samplers in the work place and how to interpret the results in order to obtain the best possible estimate of worker exposure to volatile organic compounds.

II. SIGNIFICANT RESULTS

1. Breathing Zone Concentration Variations

A field study of breathing zone concentration variations was conducted in a boat manufacturing facility in New England. The production process involves spraying a catalyzed resin solution along with chopped fiberglass onto a mold. The spraying is performed by a gunner who is followed by two or three operators who roll the sprayed mold to insure saturation of the fiberglass with the resin solution and to expell air bubbles.

Styrene samples were collected on the gunner and the rollers, and in background air with 3M one stage diffusion monitors. The monitors were placed around the breathing zone of the test subjects as follows: Nose, left lapel, right lapel, and chest. Twenty one sets of samples were collected. The collected samples were desorbed with carbon disulfide (CS_2) and analyzed along with controls and blanks by gas chromatography with a flame ionization detector according to NIOSH method S-30.

Background styrene air concentrations are presented in Table 1. The average background air concentration was $18 \pm 7 \text{ mg/m}^3$. Results of the personal monitors are presented in Table 2. Concentration variations on individual workers were obvious with the highest concentration found at the chest. The mean (\pm standard deviation) measured styrene concentrations were: nose $327 \pm 128 \text{ mg/m}^3$; left lapel $365 \pm 104 \text{ mg/m}^3$; right lapel $388 \pm 129 \text{ mg/m}^3$; and chest $430 \pm 132 \text{ mg/m}^3$. The concentration measured by the nose sampler for an individual was about 76% of that measured by the chest sampler. Concentration variations were more

pronounced in the case of the gunners compared to the rollers.

A second set of field experiments were also carried out at the boat manufacturing plant. Samples were collected to better quantitate source terms and breathing zone variability.

2. Factors Which Contribute to the Breathing Zone Concentration Variations

Controlled spray booth experiments were carried out to estimate the relative magnitude of factors which contribute to differences between breathing zone concentrations measured on the same worker. Air flow velocity profiles and styrene air concentrations were measured with and without a mannequin placed in front of the spray booth. The experiments examined the effect of obstructing the air flow into the hood due to the presence of the mannequin. Further measurements also examined the effect of the worker's position relative to the hood and relative to the spray gun.

a. Air flow patterns:

The air flow pattern into the spray booth was studied by measuring air velocity into the hood with a hot wire anemometer and by releasing white smoke into the spray booth. The measurements were conducted in front of an unobstructed hood and with the mannequin in front of the hood which obstructed the hood.

The centerline face velocity at the unobstructed hood entrance was 140-150 ft/min. When a smoke tube was placed at the hood entrance, in a position equivalent to a spray gun, a uniform smoke cone, or envelope,

was generated which could be seen flowing into the hood with minimum turbulence. When the mannequin was placed in front of the hood, air was deflected around the mannequin. A smoke tube held by the mannequin hand to simulate a spray gun, revealed the disturbed air flow pattern due to obstruction of air flow with stagnation of the smoke immediately in front of the mannequin. Turbulent air flow was seen around the mannequin and the air flow velocity dropped to 5-15 ft/min immediately in front of the mannequin. This calm air zone was located at the hood centerline in the area where styrene vapors would be generated by a spray gun operator.

b. The effect of hood face velocity:

Two spraying experiments were carried out, one with a centerline face velocity of 140-150 ft/min and the second at 110-120 ft/min. These were the velocities at the two airflow settings normally used at this hood. The center line velocities were measured prior to placing the mannequin in front of the spray hood. Once the mannequin was placed in front of the hood, a significant drop in the centerline air velocity was observed. In both experiments samples were collected in the breathing zone of the mannequin with 3M diffusion samplers. The results are presented in Table 3. Comparison of the nose and the chest samplers concentrations in the two experiments showed that reducing the hood velocity from 140-150 ft/min to 110-120 ft/min did not have a significant effect on the styrene concentration.

c. The effect of the worker's position relative to the hood and relative to the spray gun:

In three experiments breathing zone concentrations were measured on the mannequin with the spraying gun and the mannequin placed at different distances from the hood. Since the mannequin position in front of the hood obstructs the air flow and increases turbulence, the experiments were repeated without the mannequin. In the latter case the 3M diffusion samplers were placed on a frame in front of the hood at the same positions at which the breathing zone samplers had been located. The total amount of sprayed polyester resin solution was the same for the six experiments. The spray gun was remotely operated in order to avoid introducing any turbulence as a result of the experimental procedure.

The results of the above 6 experiments are presented in Table 14. Higher styrene air concentrations were detected in the presence of the mannequin. This can be explained by the obstruction of the air flow into the hood by the mannequin which retards effective removal of the styrene. In addition, the generated back eddies increase the contaminant (styrene) air concentrations in the breathing zone. Increasing the distance of the mannequin and the gun from the hood resulted in higher styrene air concentrations in the presence of the mannequin, probably due to uncontrolled cross drafts in the work place. Finally, increasing the distance between the mannequin and the spray gun (source of exposure) reduced the breathing zone concentrations.

3. Stability of Styrene on Charcoal

Styrene is a volatile and reactive compound that can undergo physical and chemical changes such as vaporization, oxidation, and polymerization. If any of these changes take place after air samples are collected, it will result in underestimation of styrene air concentration and the estimates of worker exposures. Since collected samples are frequently stored for periods of days, or even weeks, it was essential to ascertain that collected styrene samples remain stable for the period between sampling and analysis. Also the effect of storing at room temperature rather than refrigeration needed to be investigated.

Styrene air samples were collected in groups of eight charcoal tubes during the application of polyester resin solution in front of a spray booth. Results showed that the styrene atmosphere was decidedly nonuniform and thus not suitable for these studies. Several laboratory systems were tested and ultimately we used a vapor dilution system with a 0.12 m³ chamber designed for animal exposure studies to obtain a uniform styrene atmosphere.

Styrene vapor was generated from solutions prepared with and without methylethylketone peroxide (MEKP) which initiates styrene polymerization. The use of MEKP simulates conditions in the reinforced plastic industry while the absence of MEKP simulates the general use of a volatile organic compound such as in industrial paint operations. The styrene concentration in the chamber was monitored with a Miran infrared analyzer.

For each experiment (catalyzed and uncatalyzed) three sets of samples were collected. Each set consisted of eight charcoal tubes. The first set was analyzed immediately. The second set of samples (catalyzed and uncatalyzed) was collected and stored at room temperature. Two tubes were analyzed immediately, three tubes after two weeks and three tubes after four weeks. The third set of samples was collected and kept refrigerated and analyzed according to the same time table as the second set.

Table 5 presents styrene air concentrations of two sets of charcoal tubes, one collected from catalyzed and the second from uncatalyzed styrene. Both sets were analyzed immediately to test the uniformity of the generated styrene atmosphere inside the test chamber. The average styrene air concentration from uncatalyzed and catalyzed experiments was $340 \pm 7 \text{ mg/m}^3$ and $509 \pm 11 \text{ mg/m}^3$ respectively. These results demonstrated the uniformity of the generated styrene atmosphere. Table 6 presents the results from the experiments with uncatalyzed and catalyzed styrene with the charcoal tubes stored at room temperature. The mean concentrations were $453 \pm 11 \text{ mg/m}^3$ and $480 \pm 12 \text{ mg/m}^3$ respectively. Table 7 presents similar results except samples were refrigerated up to four weeks. Mean concentrations were: uncatalyzed $481 \pm 10 \text{ mg/m}^3$ and catalyzed $461 \pm 9 \text{ mg/m}^3$.

Statistical Evaluation

The results from the collected samples (N=48) were evaluated using a nested (hierarchical) analysis of variance procedure. Three sets of styrene air concentrations measured in mg/m^3 were nested within three

cross factors namely:

- A. Atmosphere (A): 1) catalyzed, 2) uncatalyzed.
- B. Time of Analysis (T): 1) immediately, 2) after two weeks, 3) after four weeks.
- C. Storage Temperature: 1) refrigerated, 2) room temperature.

The collected 48 samples can be divided into 14 subgroups as a result of the three cross factors. The subgroups are presented in Table 8. It is obvious from Table 8 that numerous subgroups are missing either due to the limited number of samples that can be collected in each set or because it was impractical to collect some subgroups. Tables 9 and 10 present the results of the nested ANOVA. In Table 9, the total sum squares (ss) considers the deviation of each sample from the grand mean of all samples. The total degrees of freedom (DF) = $N-1$. The among all subgroups (ss) considers the variability due to subgrouping within groups. The among subgroups DF equals the number of subgroups - 1. The error considers the within subgroup variability and the error (ss) and DF are obtained by difference:

$$\text{Error ss} = \text{Total ss} - \text{Among all subgroups ss}$$

$$\text{Error DF} = \text{Total DF} - \text{Among all subgroups DF}$$

Using the information in Table 9, the null hypothesis is tested first that no difference occurs among the three sets of measured styrene air concentrations. The F value is calculated as follows:

$$F = \frac{\text{MS sets}}{\text{MS error}} = \frac{10,112}{117.8} = 85.8$$

$$\text{MS error} \quad 117.8$$

The F value leads to rejection of the null hypothesis and this is consistent with the experimental conditions since styrene air concentration was kept uniform within each set of samples but not from one set to another.

Next the null hypothesis is tested that atmosphere (A), storage time (T) and storage temperature (R) have no effect on styrene air concentrations.

$$F(A) = \frac{\text{MS Atmosphere}}{\text{MS Samples}} = \frac{41,360}{10,111} = 4.09$$

$$\text{MS Samples} \quad 10,111$$

$$F(T) = \frac{\text{MS Time}}{\text{MS Samples}} = \frac{3,864}{10,111} = 0.36$$

$$\text{MS Samples} \quad 10,111$$

$$F(R) = \frac{\text{MS Temperature}}{\text{MS Samples}} = \frac{228}{10,111} = 0.2$$

$$\text{MS Samples} \quad 10,111$$

The null hypothesis cannot be rejected in each case and this indicates that styrene samples collected on charcoal tubes are stable up to one month without effect due to atmosphere (catalyzed and uncatalyzed), or the storage temperature (room temperature vs. refrigeration) or the length of storage up to one month.

CONCLUSION

This work studied the measurement of worker inhalation exposure to styrene vapor in the reinforced plastic industry. It was demonstrated

that styrene samples collected on charcoal were stable for up to 4 weeks of storage. It was also shown that significant variations existed in air concentrations within the worker's breathing zone. The variations may be attributed to the creation of turbulent eddies and an almost quiescent zone which result from obstruction of air flow into the hood by the presence of the worker. The distance between the worker and the spray gun (source) was an important factor in determining the breathing zone concentrations.

TABLE 1

BACKGROUND STYRENE AIR CONCENTRATIONmg/m³

<u>SAMPLE NO.</u>	<u>LOCATION</u>	<u>mg/m³ styrene</u>
1	outside upper mold area	20
2		12
3		17
4		23
5	outside lower mold area	5
6		22
7		25

 \bar{X} = 18

sd = 7

n = 7

TABLE 2

BREATHING ZONE CONCENTRATION VARIATIONSSTYRENE AIR CONCENTRATIONSmg/m³

<u>SAMPLE NO.</u>	<u>JOB</u>	<u>NOSE</u>	<u>LEFT LAPEL</u>	<u>RIGHT LAPEL</u>	<u>CHEST</u>
1	Roller	375	385	449	510
2	Gunner	298	369	368	549
3	Roller	762	687	800	815
4	Gunner	157	206	181	251
5	Roller	352	386	368	451
6	Roller	263	306	269	341
7	Gunner	200	232	223	245
8	Roller	248	300	438	474
9	Roller	367	415	486	565
10	Roller	362	381	356	491
11	Gunner	262	290	292	280
12	Roller	311	340	340	359
13	Gunner	284	333	360	346
14	Roller	325	354	394	400
15	Gunner	144	345	367	356
16	Roller	506	533	559	600
17	Roller	314	298	348	337
18	Gunner	247	280	293	340
19	Roller	449	506	531	533
20	Roller	346	368	355	402
21	Roller	302	343	368	381
	\bar{X}	327	365	388	430
	sd	128	104	129	132

TABLE 3

THE EFFECT OF FACE VELOCITY
ON STYRENE AIR CONCENTRATIONS

Styrene air concentrations in mg/m³

<u>Hood face velocity</u>	<u>Nose</u>	<u>Right Lapel</u>	<u>Left Lapel</u>	<u>Chest</u>
140 - 150 ft/min	7.4	10.4	9.0	12.0
100 - 120 ft/min	7.8	12.0	12.6	12.4

TABLE 4

THE EFFECT OF THE WORKER'S POSITION
ON STYRENE AIR CONCENTRATIONS

<u>Experiment</u>	<u>Styrene air concentrations mg/m³</u>			
	<u>Nose</u>	<u>Chest</u>	<u>Right Lapel</u>	<u>Left Lapel</u>
Mannequin & gun at hood entrance	34	42	48	42
Same without mannequin	15	30	26	22
Mannequin & gun 15" from the hood	29	56	62	51
Same without mannequin	18	26	23	16
Mannequin 15" away from the hood and gun at hood entrance	20	34	28	27
Same without mannequin	8	11	9	11

TABLE 5

UNIFORMITY OF THE TEST CHAMBER STYRENE ATMOSPHEREmg/m³

<u>SAMPLE NO.</u>	<u>UNCATALYZED STYRENE</u>	<u>CATALYZED STYRENE</u>
1	342	501
2	331	496
3	329	506
4	342	523
5	353	513
6	337	525
7	339	509
8	347	495
n	= 8	8
\bar{X}	= 340	509
sd	= 7	11

TABLE 6

STABILITY OF STYRENE ON CHARCOAL
SAMPLES STORED AT ROOM TEMPRATURE

mg/m³

<u>SAMPLE NO.</u>	<u>TIME OF ANALYSIS</u>	<u>UNCATALIZED</u>	<u>CATALIZED</u>
1	IMMEDIATELY	451	473
2	IMMEDIATELY	477	492
3	TWO WEEKS	442	460
4	TWO WEEKS	459	489
5	TWO WEEKS	455	499
6	FOUR WEEKS	455	480
7	FOUR WEEKS	446	475
8	FOUR WEEKS	438	473
		n = 8	8
		\bar{X} = 453	480
		sd = 11	12

* TIME BETWEEN SAMPLE COLLECTION AND ANALYSIS





































TABLE 7

STABILITY OF STYRENE ON CHARCOALREFRIGERATED STORAGEmg/m³

<u>SAMPLE NO.</u>	<u>TIME OF ANALYSIS</u>	<u>UNCATALYZED</u>	<u>CATALYZED</u>
1	IMMEDIATELY	483	450
2	IMMEDIATELY	498	479
3	TWO WEEKS	465	452
4	TWO WEEKS	481	459
5	TWO WEEKS	475	464
6	FOUR WEEKS	486	461
7	FOUR WEEKS	490	467
8	FOUR WEEKS	470	459
		n = 8	8
		\bar{X} = 481	461
		sd = 10	9

TABLE 8

Samples Subgrouping Due to (A), (T), (R)

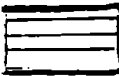
		ATMOSPHERE (A)											
		1. UNCATALYZED						2. CATALYZED					
Temp. (T)		1. Refrigerated			2. Room Temp.			1. Refrigerated			2. Room Temp.		
No. of Sets		1	2	3	1	2	3	1	2	3	1	2	3
	1												
	2												
	3												



Subgroups each dot indicates a sample collected



Subgroups that were impractical to collect



Subgroups with no samples collected due to limitations of experimental conditions.

TABLE 9

<u>Source of variation</u>	<u>SS</u>	<u>MS</u>	<u>DF</u>
Total	144327		47
Among subgroups	140322		13
Error	4005	117.8	34

TABLE 10

SUMMARY OF HIERARCHICAL (NESTED) ANOVA

<u>Source</u>	<u>SS</u>	<u>MS</u>	<u>DF</u>	<u>F</u>
Atmosphere (A)	41360	41360	1	4.09
Storage time (T)	7726.7	3863.3	2	0.38
Storage temp. (R)	228.2	228.2	1	0.02
Sets (A,T,R)	91007	10111.9	9	85.2