Abstract

Wei Jin. An Evaluation of Employee Exposures to Organic Solvents at a Printing Facility

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Employee exposures to four organic solvents (toluene, methyl ethyl ketone, isopropyl acetate and n-propyl acetate) were sampled at a printing facility in Durham, North Carolina. Workers were divided into four groups by their job title, job function, and the chemical exposure similarities. Each group was sampled twice over 8 hour long shifts. Two strategies were used to compare the employee exposures to the Occupational Exposure Limits (OEL). The first one is the conventional method, commonly used for regulatory compliance verification, which evaluates each individual exposure against the OEL, for each organic solvent and for the solvent mixture. The second strategy is to determine, for a group of workers in any given day, whether the probability of overexposure is acceptable. Here overexposure is defined as the likelihood that a randomly selected worker's true mean exposure exceeds the OEL. Though both strategies indicate that workers' exposures are acceptable, the later statistical method does provide more information with which to evaluate the hazard.

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Λ	an arbitrarily assigned acceptable probability that a randomly selected worker's mean exposure is greater than the OEL
C*	data-driven multipilier used in calculating and assessing the value of T
SD	the standard deviation used to construct error bands involving the expected cumulative distribution function (CDF)
W	wald-type statistic
T	a test statistic recommended in the event of a negative estimate of σ_B^2
X_{ij}	the shift-long exposure received by the i-th worker on the j-th day in an observational group
Y_{ij}	the natural logarithm of X_{ij}
θ	probability that a randomly-selected worker's mean exposure is greater than the OEL
β_i	random deviation of the i-th worker's mean logged exposure from μ_y
μ_x	mean of X_{ij}
μ_y	mean of Y_{ij}
σ_B^2	between-worker component of variance of the logged exposure variable Y_{ij}
σ_W^2	within-worker component of variance of the logged exposure variable Y_{ij}

Note that the '^' symbol above a Greek letter refers to an estimated parameter.

Introduction

Background

Exposures were monitored in a printing facility in Durham, North Carolina. Over several visits, we learned about the rotogravure printing process, the physical layout of the facility and the potential chemical exposures through discussions with the plant engineer, tours of the facility, a review of the history of the facility, a review of the bulk chemical usage and selected material safety data sheets, and interviews with various employees. With this information we were able to form a plan for measuring and evaluating the employee chemical exposures. The samples were collected with two other fellow students as part of a class project.

Determine an appropriate air sampling strategy

The primary goal of the air sampling strategy used at the facility was to provide a quantitative assessment of employee exposures to the organic solvents that are used in the working environment. At the facility, the primary chemicals of interest for exposure monitoring were toluene, methyl ethyl ketone, isopropyl acetate and n-propyl acetate.

These four chemicals were selected based upon their usage and relative toxicity compared to the other organic chemicals used in the printing process. The estimated uses of these solvents are all over 500 gallons/month. All of the chemicals selected for monitoring were volatile organic solvents with similar chemical properties that presented a potential for exposure via inhalation and , in some cases, skin contact.

Workers were selected for monitoring if they were expected to have direct contact with the solvents (i.e. laminators, presses, make ready). Workers who did not have direct contact with the solvents were not included in the sampling strategy because their exposures were expected to be below the detection limits of the analytical procedures.

Additional goals for the air sampling strategy included: testing the effectiveness of the engineering controls, identifying processes or operations that were major contributors to employee exposures, pinpointing groups of employees that had higher/lower relative exposures, highlighting work practices that contributed to higher exposures, and identifying the areas of a facility requiring further engineering controls.

Several topics will be covered in this report. First, the specific health effects, associated with exposure to the four organic solvents, will be discussed, then, two methods of exposure assessment will be used to relate the sampling results to the current OELs. Finally, the two assessment methods will be compared.

Health Effects of Organic Solvents

Effects of Solvent Mixtures

As mentioned in the introduction section, all four of the solvents evaluated (toluene, methyl ethyl ketone (MEK), isopropyl acetate (IPA) and n-propyl acetate (NPA) have similar chemical and biological properties. Because of similar effects upon the target systems within the body, these chemicals are considered to have "additive" effects on target organs when there is an exposure to a mixture of the solvent vapors. In order to assess the combined effects of the solvents, the level of exposure to the "mixture" is compared to a calculated exposure limit (TLV) for the mixture.

Airborne Exposures

There are two short term, reversible health effects associated with airborne exposures to toluene, MEK, IPA and NPA. These effects are eye and respiratory tract irritation at lower concentrations. Table I lists the observed adverse health effects for short term exposures to the individual solvents at various airborne concentrations.

Long term (chronic) exposures to methyl ethyl ketone at levels exceeding 300 ppm may cause peripheral nervous system depression in the form of numbness in the extremities. Long term exposures to toluene that exceed the current occupational exposure limit may cause increased reaction times and memory disturbances. The specific health effects associated with long term exposures to toluene and MEK are listed in Table II.

The health effects listed in Tables I and II are derived from both occupational (i.e. rotogravure printing facilities) and nonoccupational (i.e. chronic solvent abuse through intentional concentration and inhalation) studies of human populations. This information has also been used by the ACGIH and OSHA for establishing the current OELs for each of the solvents. The current OELs for these solvents have been set at levels which prevent both eye and upper respiratory tract irritation and the formation of chronic health effects.

Skin and Eye Contact

Another route of exposure for two of the solvents (methyl ethyl ketone and toluene) is skin absorption through prolonged or repeated skin/solvent contact. Although this is not a primary route of entry into the

body, prolonged skin/solvent contact can contribute to the airborne exposure and increase the likelihood of experiencing the narcotic health effects through an increased body burden of that chemical. IPA and NPA have not been associated with any long term health effects through either inhalation or skin absorption.

All four solvents can cause irritation and tearing if the liquid is splashed into the eyes.

Table I: Acute Health Effects of the Solvents

Chemical	Airborne Concentration	Health Effect Duration	Adverse Health Effects
toluene	100 ppm	acute	headache, dizziness, fatigue, CNS depression
toluene	100-200 ppm	acute	upper respiratory tract irritation *
toluene	400-600 ppm	acute	mild eye irritation, lacrimation, nausea *
toluene	800 ppm	acute	rapid eye and respiratory tract irritation, nasal discharge, drowsiness, ataxia *
methyl ethyl ketone	100-200 ppm	acute	slight eye and throat irritation
methyl ethyl ketone	<200 ppm	acute	eye and upper respiratory tract irritation
methyl ethyl ketone	300-500 ppm	acute	headaches, irritation, nausea
isopropyl acetate	200 ppm	acute	eye and respiratory tract irritation
n-propyl acetate	approx. 300 ppm	acute	eye and respiratory tract irritation

* includes the health effects listed above

Table II: Chronic Health Effects of the Solvents

Chemical	Airborne Concentration	Health Effect Duration	Adverse Health Effects
toluene	50-200 ppm	subchronic	headache, impaired coordination, transient memory loss, increased reaction time, fatigue
toluene	117 ppm	chronic	memory disturbances, decreased reaction time
methyl ethyl ketone	300-600 ppm	chronic	numbness in upper extremities

Evaluating Solvent Exposures

Each of the four solvents monitored has an individual occupational exposure limit (OEL). These limits are provided by the American Conference of Governmental Industrial Hygienists (ACGIH) and the Occupational Safety and Health Administration in the form of both TWAs (Time Weighted Averages for 8-hour exposures) and STELs (Short Term Exposure Limits for a maximum of 15 minutes, four times per day). The TWAs are established to prevent the occurrence of long term health effects related the chemical exposure over a working lifetime (e.g., CNS effects). The STELs are established to prevent the occurrence of short term health effects that may occur with brief exposures to concentrations above the TWA (e.g., eye and respiratory tract irritation).

Table III summarizes the current occupational exposure limits for the four solvents monitored. This table also contains a listing of the BEIs (Biologic Exposure Indices) for toluene and MEK. BEIs are used for chemicals that have more than one potential route of entry into the body that may contribute to total body burden. For toluene and MEK, the two routes of intake are inhalation and skin absorption. BEIs for these two chemicals are evaluated by comparing either urine, blood or exhaled air concentrations to the BEI limits. Since these tests are invasive and the air concentrations for these two chemicals at this facility were expected to be well below the TLVs, these tests were not performed. However, in the future, if the air concentrations of toluene and/or MEK begin to approach the TLVs and if skin absorption is expected to be a contributor to total exposures, then these tests should be conducted in order to accurately assess a worker's total exposure.

Table III: Occupational Exposure limit Information

Chemical	CAS#	ACGIH TLV (STEL) ppm	OSHA PEL (STEL), ppm	Odor detection threshold, ppm	BEI
Toluene	108-88-3	50 (skin)	100 (150)	2.5	2 mg/l **
MEK	78-93-3	200 (300)	200 (300)	5.4	2.5 g/g ***
IPA	108-21-4	250 (310)	250 (310)	2.7	none listed
NPA	109-60-4	200 (250)	200 (250)	0.67	none listed

** in urine *** creatinine in urine

When exposures to multiple chemicals occur simultaneously, the ACGIH recommends establishing a TLV for the mixture. The "TLV mixture" combines and weights the TLVs of the individual chemicals using the following equation, where "C" is the measured air concentration for the chemical. Any mixture ratio that exceeds "1" is considered to exceed the mixture TLV.

$$C1/TLV1 + C2/TLV2 + \ldots + Cn/TLVn \leq 1$$

Air Sampling Strategy

Sampling Media and Analysis

Personal sampling organic vapor badges were used to assess individual exposures to toluene, MEK, IPA and NPA. Since the badges use a charcoal collection media, they can monitor several volatile organic chemicals simultaneously. Both the badges and the laboratory analysis were purchased from Lab Safety Supply which limited the analysis to four chemicals per badge using gas chromatography. Analysis was conducted by Assay Technology, a certified testing laboratory contracted through Lab Safety Supply. The sampling parameters and limitations specified by Assay Technology for the badges are listed in Table IV. Accuracy of the results meet both OSHA and NIOSH requirements of ±25% or better at the OSHA permissible exposure limit (PEL).

Table IV: Assay Technology Organic Vapor Badge Analysis Parameters

Chemical name	Badge #	Badge Type	Sampling Rate (ml/min)	Detection Limit (ppm/hr)
IPA	541	Hi-Sampling Rate Organic Vapor	5	0.7
NPA	541	Hi-Sampling Rate Organic Vapor	6	0.7
MEK	541	Hi-Sampling Rate Organic Vapor	7	0.7
Toluene	541	Hi-Sampling Rate Organic Vapor	7	0.3

Sensidyne colorimetric sampling tubes were used to assess the contribution of isolated sources (i.e. paint reservoirs or open drums of solvent) to employee exposures. These detector tubes are chemical specific and allow for on-the-spot evaluation of air concentrations.

Sample Groups

All employees working in either the press, laminator, ink or make ready rooms were sampled over three shifts. In addition, a subset of the maintenance workers were also sampled. The monitoring results were then divided into sampling groups based on the chemical exposure similarities within each group. The criteria used for establishing these groups include: the chemicals used, the equipment generating the exposures, physical locations of the processes, exposure duration, and job classification. Table V lists the groups and the number of personal samples collected.

Table V: Actual solvent monitoring groups

Group name	# individuals over 3 shifts	# individuals sampled	# of days of sampling	Total # samples
Presses #9 and #11	13	13	1 or 2	21
Presses #7 and #13	14	14	1 or 2	21
Laminators #1 and #2	15	15	1 or 2	29
Make Ready	3	3	2	6
Ink Room	6	6	2	12
Maintenance	5	4	1 or 2	7
Total	56	55	1 or 2	96

A total of 109 samples were collected over two days. Each sample was analyzed for IPA, MEK, NPA and toluene. Although the sampling strategy called for each employee to be monitored twice, some of the workers were sampled only once due to variations in the work schedules (i.e. some of the presses were not operating on the first day, a few workers were out sick or no vacation). A total of 55 workers were monitored, 14 for one day and 41 over two days. Nine monitors were used as either field or media blanks for quality control and four monitors were used as area monitors to assess potential solvent exposures in the cafeteria and foil slitting rooms.

Data Analysis

Conventional method

The sampling results were evaluated against the OELs using several different comparison techniques. Initially, all of the individual worker measurements were compared to the OELs for each of the four solvents. Then, the individual worker measurements were compared to the TLVs for the solvent mixture. Finally, the results for all of the workers that were monitored for more than one day were averaged and compared to OELs to assess both the individual and group exposures.

Statistical method

The preceding data analysis is typical for regulatory compliance verification. Another technique evaluates data by assuming that worker exposures are log-normally distributed. If this assumption is correct, then the data can be used to determine group averages and worker variability. This technique requires that a statistical random-effects model be fit to the data. To fit the balanced model, only workers having two exposure measurements were used in the analysis.

A random-effects model can be used to predict the properties of the population using the log normal distribution (Rappaport et al. 1994). Let X_{ij} (for i = 1, 2, ...,k workers and j = 1,2,...,n days) represent the shift-long exposure received by the i-th worker on the j-th day in an observational group. Let $Y_{ij} = \ln(X_{ij})$ represent the natural logarithm of X_{ij}, with mean μ_Y and variance σ_Y^2. The random efects model is specified by the following expression:

$$Y_{ij} = \ln(X_{ij}) = \mu_Y + \beta_i + \varepsilon_{ij},$$

where β_i represents the random deviation of the i-th worker's mean logged exposure from μ_Y, and ε_{ij} represents the random deviation from $\mu_{Y\,i}$ on the jth day for worker i. It is also assumed under the model that both β_i and ε_{ij} are normally distributed, namely, that $\beta_i \sim N(0, \sigma_B^2)$, and $\varepsilon_{ij} \sim N(0, \sigma_W^2)$, and that the β_is and ε_{ij}s are statistically independent of one another. Thus, the parameters σ_B^2 and σ_W^2 represent the components of the total variance of exposure.

The fit of the random effect model can be assessed using a graphical diagnostic procedure similar to that of Dempster et al. (1985). The observed and expected cumulative distribution functions (CDFs) are compared in a p-p plot. To evaluate the fit, error bounds are given by the empirical CDF ± SD, where SD represents the unadjusted standard deviation (Rappaport et al. 1994). If the observed CDF lies 'mostly inside' these approximate error bounds, then the fit of the random effects model is judged to be acceptable. Then, it is reasonable to describe the individual workers' mean exposures by a log-normal distribution for subsequent testing (Rappaport, 1991).

Once the random effects model has been applied to a group of workers, the following estimated parameters can be computed. $\hat{Y}_i$: the mean of the logged exposure measurements for the i-th person, $\hat{\sigma}^2_W$: ANOVA estimate of the within-worker variance component , $\hat{\sigma}^2_B$: ANOVA estimate of the between -workers variance component, and $\hat{\theta}$: the estimated probability that a randomly selected person from the group would be overexposed, i.e. would have a mean exposure greater than the OEL.

$$\hat{\theta} = (\ln(\text{OEL}) - \hat{Y} \cdot \hat{\sigma}^2_W/2) \; / \; \hat{\sigma}_B \quad ,$$

$$\text{where the } \bar{Y} = \sum_{i=1}^{K} Yi \qquad \text{for i = 1,2,...,K workers in the group.}$$

In general, a limit (A) of 10% has been set for θ, in situations where chronic health effects are being evaluated (Rappaport et al., 1994). A Wald-type test can be used to determine whether Ho:$\theta \geq A$ can be rejected in favor of H1:$\theta < A$ at the desired level of significance. If Ho can be rejected, then exposure can be declared acceptable (Rappaport et al., 1994; Lyles et al., 1994).

Occasionally, negative ANOVA estimates of the between worker variance component $\hat{\sigma}^2_B$ can occur, in such case, an approximate 95% confidence bound on $\hat{\sigma}^2_B$ can be used as substitute, i.e., $\hat{\sigma}^2_{B,0.95}$, and the following null hypotheses can be used in place of the original Ho and H1(Lyles et al., 1997).

$$\text{Ho}': \mu_X \geq c^*(\text{OEL}) \quad \text{vs} \quad \text{H1}': \mu_X < c^*(\text{OEL}) \quad ,$$

where μ_X is the overall population mean of shift-long exposure for the group of workers in question. The multiplier c^* is a constant based upon the exposure data, where $c^* = \exp\{\hat{\sigma}^2_{B,0.95}/2 - z_{1-A} \; \hat{\sigma}_{B,0.95}\}$.

In this case, the statistic T is used to test the null hypotheses. T is defined by the following formula:

$$T = \hat{Y} + d^{*}S_{y}$$

Here, $\hat{Y}$ is the sample mean of the total logged exposure measurements, S_y is the sample standard deviation of the total measurements, and d* is a statistically computed constant given the measurements.

$$d^{*} = (S_{y}\sqrt{N-1} / (2\chi_{N-1,\alpha}) + t_{N-1,1-\alpha}/\sqrt{N},$$

where N represents the total number of measurements for the group. $\chi_{N-1,\alpha}$ is the square root of the 100(α)th percentile of the chi-squared distribution with (N-1) degrees of freedom, and $t_{N-1,1-\alpha}$ is the 100(1-α)th percentile of the central t distribution with (N-1) degrees of freedom(Lyles et al., 1997). If T is less than ln (c*OEL), the Ho' would be rejected in favor of H1' (Lyles et al., 1997).

This statistical method provides the following advantages over the conventional method: First, it allows prediction of the exposures of workers not sampled. Second, it allows the probability that an individual's mean exposure would exceed an OEL to be predicted. Third, it allows data variability to be separated into within-worker (the same worker's exposure from one day to the next) and between-worker (different individuals in a group) components to focus on effective exposure controls. Finally, it provides an incentive to conduct thorough monitoring of worker's exposures.

Separating variability into within-worker and between-worker categories is useful for determining the type and extent of workplace controls. A large between-worker variability indicates that most of the exposure differences are due to differences in individual personal environments. In this case, in order to effectively minimize worker exposures, focus should placed on establishing effective and repeatable work practices schedules, tasks, equipment, ventilation, etc. A large within-worker variability coupled with a small between-worker variability indicates that most of the exposure differences arise from changes in the environment and either process or engineering controls are needed.

Results

Conventional method

As shown in table VI and VII, the solvent monitoring results indicate that none of the employee exposures exceeded the 8-hour TLV-TWA for either each solvent or the solvent mixture. In a few cases, the colorimetric tubes indicated that the TLE-STELs for IPA were exceeded. These results are presented in Table XV. While collecting the samples presented in Table XV, there was a noticeable solvent odor in the laminator, press and make ready rooms indicating that the odor detection thresholds for these solvents are well below the TWAs and STELs. While collecting the samples where the air concentrations exceeded the STELs (i.e. IPA concentration > 500 ppm) one of the industrial hygiene group members did experience moderate eye irritation and tearing. We also noted that the workers in these rooms were aware of the areas that have higher solvent concentrations and avoided them whenever possible. Table VI summarizes the average of the individual chemical exposures, the highest individual chemical exposure was 120 ppm for NPA. Table VII shows the average of mixed exposures for each group. The highest mixture exposure was 77% of the OEL.

Table VI: Individual measurements (mean and range for each chemical)

Chemical	Mean	Low	High
IPA	23.4 ppm	0.81 ppm	82 ppm
MEK	6.1 ppm	0.15 ppm	46 ppm
NPA	18.3 ppm	0.55 ppm	120 ppm
Toluene	1.4 ppm	0.04 ppm	8.7 ppm

Table VII: Summary of group exposure mixture results

Groups	# Workers	Mean	Low	High
Presses #9 & #11	13	0.28	0.11	0.77
Presses #7 & #13	13	0.40	0.12	0.65
Laminators #1 &#2	15	0.20	0.04	0.59
Make Ready	6	0.41	0.22	0.54
Ink Room	3	0.15	0.09	0.21
Maintenance	4	0.05	0.01	0.10

Personal sample results were divided into groups and are presented, by group, in Tables VIII - XIII. Individual workers were identified by employee number. The job title, shift, sample day, sample monitor # and sample time are also included. The results for each chemical are provided in ppm and an overall solvent mixture exposure for each sample is listed. If the worker had two samples, a mixture average for that person is also listed.

Tables VIII and IX present the results for both press rooms. Table IX demonstrates that the first day of sampling had consistently higher results, compared to the second day of sampling, for IPA, NPA and toluene. The difference between daily air concentrations is also indicated in the "within-worker" variability discussed in the data analysis section of this report. In addition, when employees were asked to evaluate the day's workload they described the first day as a "heavy" day with several "change overs".

Table XIV includes the area sample results for the foil slitter room and cafeteria. The results show that the background levels were approximately 2 ppm for IPA and for NPA, 1 ppm for MEK, and 0.2 ppm for toluene. These levels indicate that workers not directly using solvents were receiving low level exposures to solvents. These exposures should be preventable by increasing general dilution ventilation in the cafeteria and foil slitting rooms or by creating a negative relative pressure in the rooms using the solvents.

Table VIII: Presses #9 & #11 - Worker results

Worker ID	Job	shift	Sample day	Monitor #	Time (hour)	IPA (ppm)	MEK (ppm)	NPA (ppm)	Toluene (ppm)	Mixture Exposure	Mixture Average
617	AP11	1	1	7688	7.43	11.00	8.20	18.00	0.65	0.19	0.21
			2	6259	7.63	12.00	19.00	15.00	0.48	0.23	
831	P9	1	1	7055	7.38	14.00	16.00	28.00	1.20	0.30	0.28
			2	6089	7.62	7.90	9.20	31.00	1.20	0.26	
321	AP9	1	1	6877	7.38	15.00	21.00	24.00	1.10	0.31	0.25
			2	5907	7.58	8.60	11.00	17.00	1.30	0.20	
113	P9	2	1	6052	7.40	12.00	16.00	120.00	2.10	0.77	0.48
			2	6873	7.35	8.00	15.00	13.00	0.63	0.18	
385	P9	2	1	7095	7.55	6.90	6.80	41.00	1.30	0.29	0.23
			2	7312	7.33	7.30	12.00	11.00	1.00	0.16	
317	P9	3	1	6136	7.77	6.40	1.50	14.00	0.67	0.12	0.20
			2	7831	7.97	14.00	15.00	19.00	2.50	0.28	
332	P11	3	1	7947	7.88	6.30	2.70	20.00	0.24	0.14	0.30
			2	7284	7.72	22.00	30.00	35.00	2.10	0.46	
323	P11	3	1	6865	7.38	5.90	0.91	22.00	0.25	0.14	0.31
			2	6362	7.57	21.00	30.00	41.00	1.90	0.48	
587	P11	1	1	7511	7.42	10.00	7.20	20.00	0.67	0.19	
810	P11	1	2	6149	7.90	5.60	6.50	9.10	0.46	0.11	
828	P11	2	2	7224	7.00	11.00	20.00	12.00	0.05	0.21	
358	P11	2	2	6509	6.28	22.00	46.00	26.00	0.10	0.45	
843	P11	3	2	7363	7.57	19.00	30.00	34.00	5.00	0.50	
Average					7.48	11.71	15.43	27.15	1.19	0.27	

Table IX: Presses #7 & #13 - Worker Results

Worker ID	Job	shift	Sample day	Monitor #	Time	IPA (ppm)	MEK (ppm)	NPA (ppm)	Toluene (ppm)	Mixture Exposure	Mixture Average
962	P7	1	1	6266	7.32	41.00	0.75	31.00	6.80	0.46	0.34
			2	6954	7.58	23.00	1.80	21.00	0.95	0.23	
349	AP13	1	1	6284	7.32	47.00	0.88	31.00	7.70	0.50	0.34
			2	6321	7.50	17.00	3.70	14.00	1.50	0.19	
366	P7	1	1	6088	7.27	43.00	1.10	31.00	8.10	0.49	0.40
			2	7125	7.62	30.00	2.00	29.00	1.40	0.30	
407	P7	2	1	7600	6.87	42.00	0.97	38.00	7.40	0.51	0.49
			2	6709	6.97	38.00	13.00	45.00	0.97	0.46	
386	P7	2	1	5951	7.25	49.00	0.96	55.00	8.70	0.65	0.49
			2	6348	6.65	35.00	3.80	32.00	0.98	0.34	
315	P7	3	1	6978	7.92	35.00	0.34	29.00	4.60	0.38	0.39
			2	6036	7.78	53.00	3.60	29.00	0.92	0.39	
357	P7	3	1	7161	7.85	37.00	0.60	35.00	8.50	0.50	0.47
			2	6511	8.03	57.00	4.00	34.00	0.88	0.44	
985	Ap7	1	2	6171	7.53	49.00	2.60	31.00	1.60	0.40	
949	P7	2	2	5962	7.23	30.00	11.00	28.00	1.10	0.34	
373	P13	2	2	6514	7.05	19.00	5.80	22.00	0.61	0.23	
384	P13	2	2	6768	7.03	20.00	4.50	20.00	0.71	0.22	
392	P7	3	2	7357	7.77	49.00	2.90	32.00	0.98	0.39	
383	P7	3	1	7582	7.78	38.00	1.20	43.00	6.80	0.51	
979	P13	1	2	7142	7.05	11.00	2.90	11.00	0.50	0.12	
Average					7.40	36.33	3.26	30.52	3.41	0.38	

Table X: Laminators #1 & #2 - Worker Results

Worker ID	Job	shift	Sample day	Monitor #	Time	IPA (ppm)	MEK (ppm)	NPA (ppm)	Toluene (ppm)	Mixture Exposure	Mixture Average
451	L1	1	1	6335	7.68	61.00	9.30	3.30	4.50	0.40	0.30
			2	7029	7.17	45.00	2.80	0.97	0.04	0.20	
815	L1	1	1	6668	6.78	12.00	0.94	3.40	0.65	0.08	0.11
			2	6166	7.15	34.00	1.30	0.67	0.06	0.15	
656	L2	1	1	6076	7.75	32.00	4.70	3.10	2.30	0.21	0.27
			2	6070	7.15	82.00	0.31	0.90	0.05	0.34	
235	AL2	1	1	5837	6.78	14.00	1.30	3.70	0.93	0.10	0.17
			2	5858	7.13	58.00	0.22	0.65	0.04	0.24	
951	LH	1	1	6062	6.55	14.00	1.90	3.20	1.00	0.10	0.12
			2	5895	7.18	31.00	0.75	0.62	0.12	0.13	
942	L1	2	1	7642	7.40	74.00	9.00	5.40	5.90	0.49	0.40
			2	7315	7.32	65.00	6.90	2.10	0.13	0.31	
346	L2	2	1	7148	7.40	8.30	0.72	3.80	0.84	0.07	0.13
			2	6680	7.32	44.00	0.74	0.66	0.04	0.18	
352	L	2	1	7066	7.32	9.20	0.77	4.10	0.89	0.08	0.16
			2	7037	6.70	60.00	0.63	0.55	0.05	0.25	
406	L	2	1	6103	7.43	57.00	7.00	5.80	4.20	0.38	0.35
			2	7164	7.20	73.00	6.90	0.82	0.04	0.33	
289	L2	3	1	7750	7.75	22.00	0.60	4.40	0.55	0.12	0.11
			2	7386	7.58	19.00	0.86	0.92	0.10	0.09	
372	L	3	1	5887	7.75	7.80	0.59	3.20	0.50	0.06	0.05
			2	7103	7.62	8.30	0.66	0.68	0.16	0.04	
387	L	3	1	7709	7.57	16.00	1.70	3.60	0.61	0.10	0.07
			2	7244	7.73	8.70	0.69	0.72	0.06	0.04	
389	L1	3	1	5925	7.73	53.00	4.20	5.00	0.71	0.27	0.26
			2	7187	7.65	55.00	3.20	1.00	0.68	0.25	
853	L1	3	1	7717	7.72	53.00	7.40	12.00	0.64	0.32	0.28
			2	7450	7.63	48.00	3.80	0.81	0.68	0.23	
398	L	2	1	5875	7.12	16.00	1.90	4.20	1.10	0.12	
Average					7.35	37.25	2.82	2.77	0.95	0.20	

Table XI: Ink room results

Worker ID	Job	shift	Sample day	Monitor #	Time	IPA (ppm)	MEK (ppm)	NPA (ppm)	Toluene (ppm)	Mixture Exposure	Mixture Average
946	IR	1	1	6899	6.85	12.00	9.30	4.50	0.98	0.14	0.13
			2	6169	7.95	9.70	14.00	2.90	0.33	0.13	
351	IR	1	1	7784	6.88	9.80	2.00	3.70	1.10	0.09	0.10
			2	6146	7.55	8.90	9.20	3.20	0.38	0.11	
777	IR	2	1	6989	8.90	27.00	6.40	5.90	1.10	0.19	0.18
			2	7733	6.58	21.00	10.00	4.00	0.68	0.17	
365	IR	2	1	7770	6.95	22.00	12.00	4.50	0.58	0.18	0.16
			2	6829	7.37	17.00	6.80	4.70	0.29	0.13	
184	IR	3	1	6339	7.97	13.00	2.40	7.50	2.00	0.14	0.17
			2	7455	8.00	18.00	14.00	6.60	1.50	0.21	
377	IR	3	1	6846	7.98	16.00	14.00	3.20	0.49	0.16	0.16
			2	7412	8.08	12.00	16.00	6.00	0.51	0.17	
Average					7.59	15.53	9.68	4.73	0.83	0.15	

Table XII: Make ready results

Worker ID	Job	shift	Sample day	Monitor #	Time	IPA (ppm)	MEK (ppm)	NPA (ppm)	Toluene (ppm)	Mixture Exposure	Mixture Average
369	MR	1	1	6728	6.92	4.50	0.86	98.00	0.74	0.53	0.53
			2	7075	7.40	9.20	0.92	96.00	0.90	0.54	
399	MR	2	1	6100	6.43	1.40	0.66	40.00	0.32	0.22	0.28
			2	7133	7.22	5.50	1.00	62.00	0.32	0.34	
345	MR	3	1	7510	7.62	3.70	0.47	61.00	0.85	0.34	0.42
			2	7823	7.70	5.70	1.40	93.00	0.38	0.50	
Average					7.22	5.00	0.89	75.00	0.59	0.41	

Table XIII: Maintenance results

Worker ID	Job	shift	Sample day	Monitor #	Time	IPA (ppm)	MEK (ppm)	NPA (ppm)	Toluene (ppm)	Mixture Exposure	Mixture Average
945	EM	1	1	5960	6.63	3.70	0.39	4.90	0.61	0.05	0.05
			2	5967	7.05	4.30	0.32	2.60	0.32	0.04	
375	EM	1	1	6992	7.47	6.30	4.90	7.30	0.60	0.10	0.05
			2	6111	7.55	0.81	0.15	0.82	0.12	0.01	
972	EM	1	1	6869	7.52	2.40	0.65	3.70	0.29	0.04	0.02
			2	6329	8.08	0.84	0.37	0.77	0.09	0.01	
991	EM	2	2	7472	7.15	7.80	1.40	7.10	0.13	0.08	
Average					7.35	3.74	1.17	3.88	0.31	0.05	

Table XIV: Area sample results

Area	shift	sample day	Monitor #	Time	IPA ppm	MEK ppm	NPA ppm	Toluene ppm	Mixture Exposure
CAFE	whole day	1	5848	23.17	1.29	1.40	2.40	0.20	0.03
		2	7936	23.93	0.89	0.54	0.95	0.07	0.01
Foil Cutter	whole day	1	6788	23.58	2.00	0.34	2.30	0.27	0.03
		2	7674	23.48	4.70	0.35	1.40	0.10	0.03
Average				23.54	2.22	0.66	1.76	0.16	0.02

Table XV: Detector tube results

General Area	Location/Operation	Chemical	Concentration (ppm)
Laminator 1	waist height over ink/solvent reservoir	Toluene	30
Laminator 2	waist height at operator station between laminators	Toluene	7
Make Ready	over dip tank	Toluene	2
Make Ready	over dip tank	IPA	ND
Press 11	waist height over ink/solvent reservoir	IPA	ND
Press 11	waist height over ink/solvent reservoir	Toluene	ND
Ink Room	shoulder height over mixing tank	Toluene	32
Press 13	waist height over ink/solvent reservoir	Toluene	5
Press 7	waist height over ink/solvent reservoir, solvent and ink being added	Toluene	80
Press 7	waist height over ink/solvent reservoir, solvent and ink being added	IPA	>500
Press 11	waist height over ink/solvent reservoir	IPA	500
Press 11	waist height over ink/solvent reservoir	IPA	500
Press 9 & 11	waist height sample near solvent inlet valves	IPA	ND

ND = None Detected

To give an indication of the exposure for each chemical, plots for each chemical versus individual worker daily measurements are given in Figures 1-4. Figure 5 is the mixture exposure versus the individual worker daily measurements.

Figure 1: Individual Exposure to IPA
OEL = 250ppm

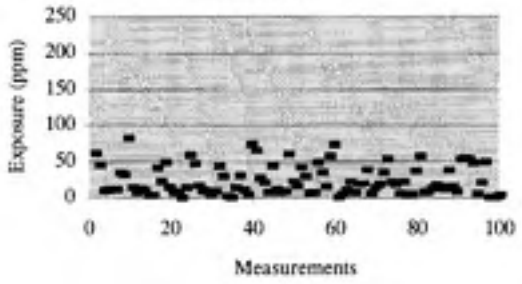


Figure 2: Individual Exposure to MEK
(OEL = 200ppm)

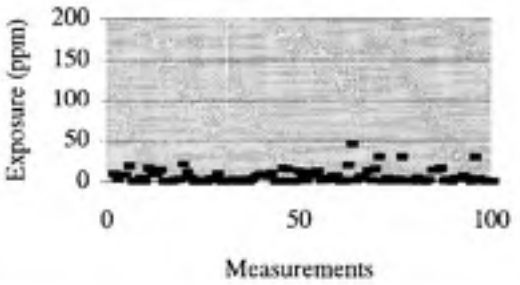


Figure 3. Individual Exposure to NPA
(OEL = 200ppm)

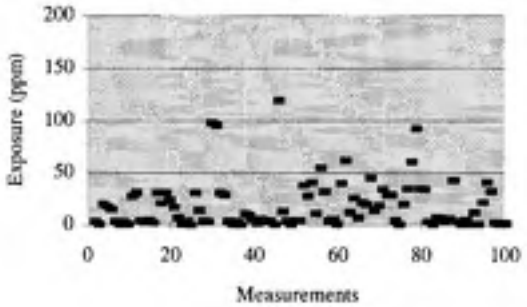


Figure 4. Individual Exposure to Toluene
(OEL = 50ppm)

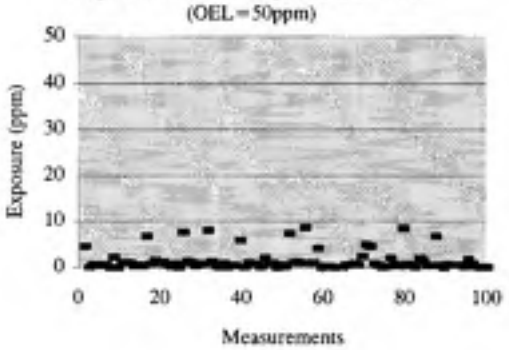


Figure 5. Individual mix exposure (OEL=1)

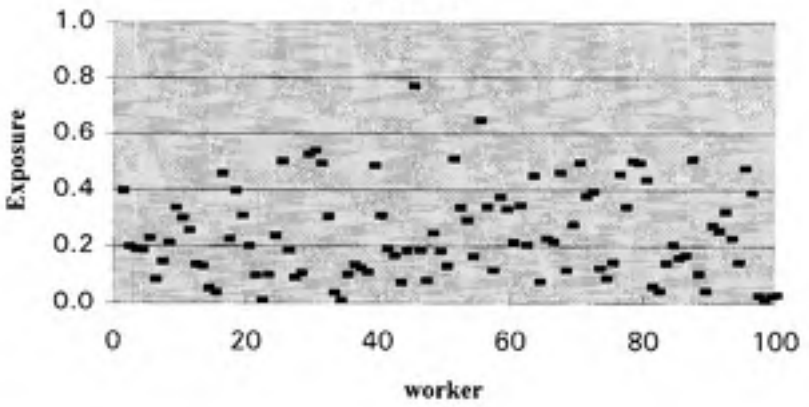


Figure 6 presents the results of the group mean mixture exposures. The make ready and press #7 and #13 groups had the highest combined exposures. Presses #9 and #11 exposures were slightly lower, followed by the laminators , ink room and maintenance. Figure 7 presents the exposure results by individual chemical for each group. Make ready employees received over 90% of their mixture exposure from NPA. Higher NPA exposures relative to the other solvents was expected in these room because the dip tank uses NPA to clean the parts. The laminators received over 74% of their mixture exposure from IPA. The other groups' total mixture exposures were a combination of NPA, IPA and MEK. Toluene was not a significant contributor to anyone's mixture exposure.

Figure 6: Actual Arithmetic Mean Exposure (Mixture) for Groups

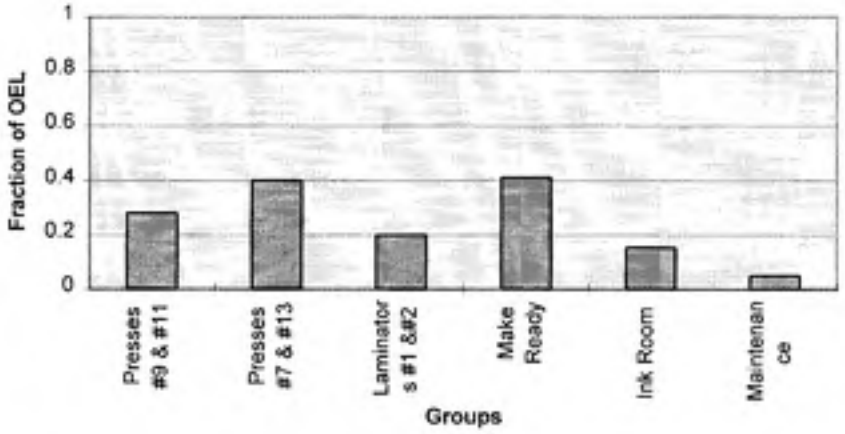
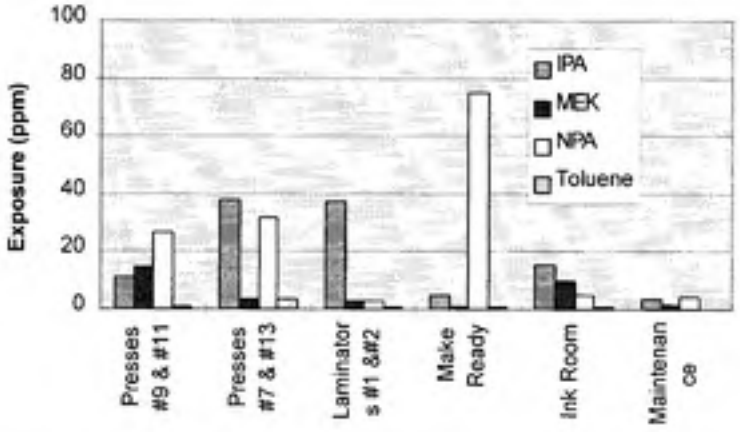


Figure 7: Actual Arithmetic Mean Exposure (each Chemical) for Groups



Statistical method

Four groups were created for implementing the statistical method, and only workers with multiple measurements were included. The groups were laminators, presses #9 and #11, presses #7 and #13, and an additional group was created by merging the remaining workers from make-ready, ink room, and maintenance. This grouping was used because the individual groups were too small to apply the model.

Figure 8-11 are graphical assessments of the fit of 4 subgroups to the random effects model (Rappaport et al.,1994). The solid individual points represent each individual worker in a group, the solid line represents the perfect fit to the model, and the two dashed curves are error bands representing CDF±SD.
As shown in all four charts, the individual points lie 'mostly inside' the respective error bands, indicating that the fit of the random effects model was acceptable in each case (Rappaport et al., 1994).

Figure 8: Graphic assessment of the fit of Pressess 9 & 11

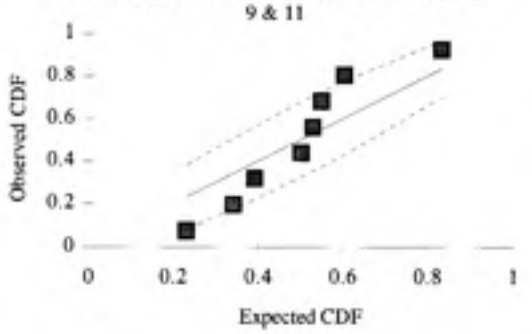


Figure 9: Graphic asssessment of the fit of Pressess 7 & 13

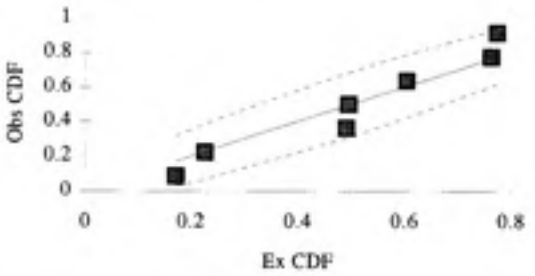


Figure 10: Graphic assessment of the fit of Laminator

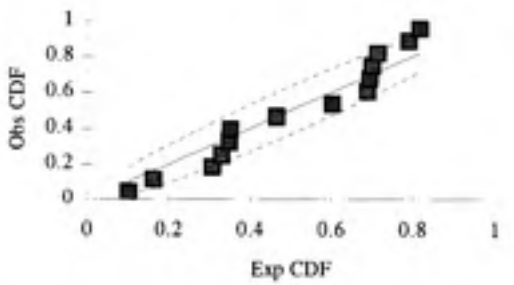


Figure 11: Graphic assessment of the fit of IR, MR, and Maintenance Worker

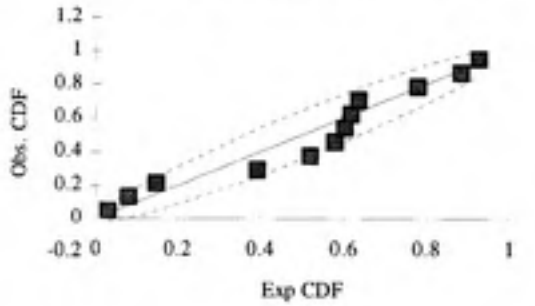


Table XVI summarizes statistical results for each group. The values were determined using the random-effects model listed in the data analysis section. All of the groups tested had acceptable θ's compared to a value of A=0.1. For all groups, the null hypothesis Ho:θ≥A (A=0.1) were rejected at a 5% significant level. Thus, the exposure for these group of workers are considered acceptable.

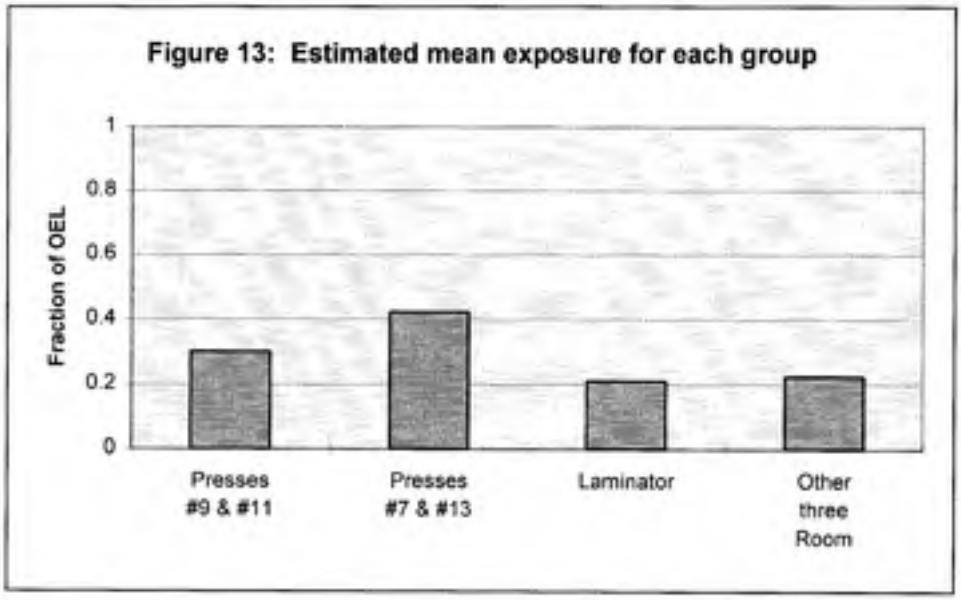
Table XVI: Predicted log-normal group information

Group	# workers	$\hat{\sigma}_B^2$	$\hat{\sigma}_W^2$	$\hat{\mu}_x$	$\hat{\theta}$	W* (Wald-type stat.)	Z α=0.05
Presses #9 & #11	8	negative	0.384	0.300	0.060	N/A	-1.645
Presses #7 & #13	7	negative	0.167	0.422	0.095	N/A	-1.645
Laminator	14	0.325	0.148	0.211	0.001	-4.058	-1.645
Other three Room	12	0.827	0.304	0.223	0.0178	-1.819	-1.645

If W < Z, then Ho is rejected indicating that θ < A (A=0.1).

Figure 13 is the predicted mean exposure for each group from the random effects model.

Figure 13: Estimated mean exposure for each group



Looking at the between-worker and within-worker variances, for the two press rooms the estimated between-worker variance was negative. Table XVII includes predicted upper limits of $\hat{\sigma}_B^2$, the multiplier c*, test statistic T and the value of ln(c*OEL) for two presses groups. Since both values of T are less than the values of ln(c*OEL), Ho' was rejected in favor of H1' (see data analysis section). For Presses #9 &

#11 group, the approximate upper bound of $\hat{\sigma}^2_{B,0.95}$ was negative, so c* value was considered as 1 due to very small between worker variance in the group. Thus, this group exposure was also considered acceptable.

The within-worker variance for the two press rooms was high because of its varying work load. Therefore, the volume of work done each day exerted a stronger influence on worker exposure than the individual personal environment.

Table XVII: Alternative hypotheses evaluation for two presses groups

Group	$\hat{\sigma}^2_{B,0.95}$	c*	μ_x	S_y	T	ln(c*OEL)
Presses #9 & #11	-0.007	1	-1.396	0.505	-1.204	0
Presses #7 & #13	0.028	0.817	-0.946	0.335	-0.857	-0.202

If T < ln(C*OEL), then Ho' is rejected.

Conclusion:

Although both exposure assessment methods came to the same conclusion, the statistical method provided additional information of worker's exposure. The statistical method provided additional insight into causes of worker's exposure variability. For example, a large $\hat{\sigma}_W^2$ and a small $\hat{\sigma}_B^2$ were obtained for the two presses rooms, indicating that most of the exposure differences was taking place in the environment for the whole room, rather than the individual personal environments. Thus, either process or engineering control would be needed to reduce workers' exposure. For group 4 (workers in Ink, Make ready, and Maintenance room), a large between worker variability was found. In order to effectively minimize worker exposure in this case, focus should be placed on the worker's individual personal environments (e.g., individual work practice, schedules, tasks, equipment, ventilation, etc.). Similar information could not be obtained from the conventional method due to lack of the appropriate characterization of the data, and thus inappropriate control methods could be chosen.

In conventional method, exposure was regarded as acceptable only if all measurements were less than the OEL, thus, it would discourage the employers to conduct thorough monitoring because the probability that at least one measurement would exceed the OEL is dependent upon the sample size (Rappaport, 1984). But using the statistical method, incentive is provided to conduct thorough monitoring of worker's exposures with which to assess health risks.

References

ACGIH(1995) *Guide to Occupational Exposure Values*. American Conference of Governmental Industrial hygienists, Cincinnati, Ohio, U.S.A.

Aitio, A., Riihimaki, V., Liesivuori, J., Jarvosalo, J., and Hernberg, S. (1994) Biologic Monitoring *Occupational Medicine*, edited by Carl Zen, Mosbey, St. Louis. pp 149.

Powell, C. (1982) Evaluation of exposures to chemical agents. *Patty's Industrial Hygiene and Toxicology*, 3rd rev. Ed., Volume III, Part A, edited by R.L. Harris, L. Crawley, and L.V. Crawley, John Wiley and Sons, New York. Pp. 349-403.

Krasavage, W.J., O'Donoghue, J.L., and Divincenzo, G.D. Ketones.(1982) *Patty's Industrial Hygiene and Toxicology*, 3rd rev. Ed., Volume II, Part C, Toxicology, edited by G. Clayton and F. Clayton, John Wiley and Sons, New York. Pp. 4728-4733.

Lyles, R. H., Kupper, L. L., and Rappaport, S. M. (1997) A lognormal distribution-based exposure assessment method for unbalanced data. *Ann. occup. Hyg.* **41,** 63-76.

Rappaport, S. M. (1984) The rules of the game: An analysis of OSHA's enforcement strategy. *Am. J. ind. Med.* **6,** 291-303.

Rappaport, S. M. (1991) Assessment of long-term exposures to toxic substances in air. *Ann. occup. Hyg.* **35,** 61-121.

Rappaport, S. M., Lyles, R. H. and Kupper, L. L. (1994) An exposure-assessment strategy accounting for within- and between-worker sources of variability, *Ann. occup. Hyg.* **39,** 469-495.

Sandmeyer, E., and Kirwin, C. Esters. (1982) *Patty's Industrial Hygiene and Toxicology*, 3rd rev. Ed., Volume II, Part C, Toxicology, edited by G. Clayton and F. Clayton, John Wiley and Sons, New York. Pp. 2268-2271.

Von-Burg, R. (1993) Toluene, *Journal of Applied Toxicology,* **13,** 41-46.

World Health Organization (1993) *Environmental Health Criteria 143, Methyl Ethyl Ketone* .