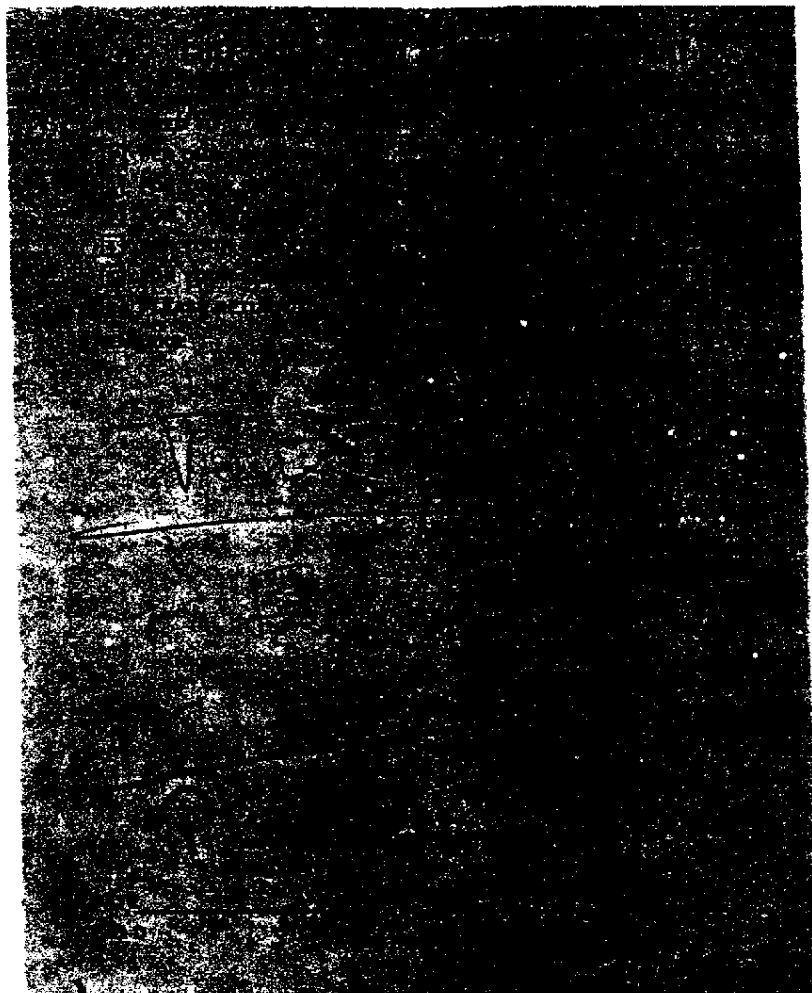




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of about 55 ug/100 ml would seem to provide another physiological basis to support the recent OSHA proposal¹⁰ that "the maximum upper blood lead levels of workers should remain below 60 ug/100 g."

A semi-log plot (Figure 2) converts the arithmetic dose-response curve to a straight line. There is the usual scatter here, characteristic of biological responses, but the correlation coefficient for the direct relationship between log ZP and lead content is quite good (0.8), which suggests that blood ZP might be substituted for blood lead as a preferred biological index of exposure. Several advantages would be offered: (1) ZP more directly reflects the metabolic damage caused by lead and is thus a more useful indicator of the effects of lead absorption; (2) Contamination, an ever-present source of concern and care with lead analyses, is minimal in the determination of ZP; (3) ZP assays are simpler, less costly, and more rapidly performed than blood lead, thereby permitting more effective use of resources and enhancement of any monitoring program.

The foregoing findings, it should be noted, were developed for an industrial population chronically exposed to inorganic lead. Organic lead compounds may follow a somewhat different course through the body, and may not exert their major toxic effects on the hematopoietic system. Hence, a biochemical index such as ZP, may not be appropriate as a monitor for the effects of organic lead absorption. In some other disease states (e.g., erythropoietic protoporphyria or severe iron deficiency anemia), the use of ZP may also not be suitable, since elevated ZP levels can occur in such conditions without concomitant lead absorption.¹¹ Such situations are unusual, however, and likely to be well known to the worker. Hence, the ZP test should be generally applicable to most workers exposed to lead, and should be given serious consideration as the

biochemical test of choice in monitoring such populations.

acknowledgements

Special thanks are extended to Dr. Donald Sherman for providing the blood specimens of the workers used in this study; and to Erodita Empaynado for excellent technical assistance.

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On the job benzene vapor exposures of less than 5 ppm were measured concurrent with the 24 hour collection of urine from 52 employees. Urinary phenol levels of the collective study group, measured as either concentration or weight, showed a positive statistically significant correlation with benzene exposure. However, due to variances in individual baseline phenol levels, determination of benzene exposure at these low concentrations is relatively weak. Since baseline phenol concentrations exist over a range of values, adjustment for a single value of each individual's baseline did not improve correlation for the collective study group.

A study of benzene exposure versus urinary phenol levels

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introduction

The 1974 NIOSH proposed standard for benzene¹ requires the monitoring of urinary phenol levels of employees with time-weighted average (TWA) exposures exceeding 5 parts per million (v/v air). The correlation between benzene exposure and increased urinary phenol levels has been reported previously.² A level of 75 mg phenol/liter of urine (mg/l) is proposed as a signal of unacceptable benzene absorption requiring close medical surveillance. This study was designed to evaluate the proposed technique of "biological monitoring" in an industrial environment. It was also intended to determine if concentrations in the area of 75 mg phenol/liter of urine are indicative of unacceptable benzene exposure.

benzene vapor sampling procedure

Benzene is widely used as a raw material and solvent by The Dow Chemical Company. Five benzene-consuming production facilities were selected to represent industrial environments where benzene is handled along with other chemicals. Over a six month period, benzene exposures were studied for 52 employees from 25 job classifications, including laboratory technician, production operator, plant

mechanic, and material transfer operator. Usually, samples were obtained from two employees in each job. Participation was voluntary since the collection of urine depended on each person's willingness to cooperate. Urine samples and breathing zone air samples were collected on the same day. Increases in urinary phenol levels were expected to correlate directly with inhalation of benzene vapors. Skin adsorption was assumed to be negligible since most jobs required the wearing of rubber gloves when handling benzene. Potential exposure to other chemicals should not have affected urinary phenol levels since none were known to interfere with, or contribute to the metabolism of benzene to phenol.

Actual TWA exposure to benzene was determined via personal samplers worn on each employee's collar throughout the course of his workday. Workdays varied from 8 to 12 hours in length. A small battery powered vacuum pump provided a low air flow rate, 100 to 250 milliliters per minute (ml/min), through charcoal packed stainless steel tubes. A few "extra large" commercially available sample tubes were used, but most of the sample collection tubes were custom-packed with Pittsburgh coconut base

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activated charcoal, 12-30 mesh. Charcoal was used because of its suitability for collection of a wide range of aromatic compounds which were likely to be encountered. The custom packed tubes were approximately .47 cm (3/16 in.) in diameter by 12.7 cm (5 in.) in length and contained approximately one gram of charcoal. Efficiency of the total sampling system, including error of analysis, was determined by spiking sample tubes and submitting them for analysis with tubes used in monitoring. "Spiking" of the sample tubes was accomplished by preparing in a 100 liter Saran[®] bag a known concentration of benzene, both by itself and with a mixture of other chemicals found in the work place. Air from the bag was drawn through a sample tube at the same flow rate used in the plant studies.

Collection of urine began when the employee started work, and continued for 24 hours. The "day" sample was collected in a hospital specimen container while the employee was at work. A second container for the "night" sample was taken home and used until he returned to work the following day. Thus, the two "combined" urine samples represented approximately 24 hours of urine. A baseline urine sample was collected by each employee after being away from work for a minimum of 48 hours. No other restrictions were placed on the collection of the baseline urine sample. Information concerning consumption, within the last 24 hours, of any medication, tobacco, or alcohol was recorded by each employee for each urine sample. Any known chemical exposure was also noted. Information concerning previous or present health problems, particularly of the liver, kidney, or heart, was requested for each volunteer.

analysis of samples

air samples

The charcoal absorbent used in air monitoring was desorbed with cold carbon disulfide and analyzed by gas chromatography using a flame ionization detector. Specific chromatographic conditions varied over the several months of personnel sampling. Column packings included:

20-30% Carbowax
20,000

10% SP 1000
5% FAPP
5% QF 1:8% SF 30
10% UCW 98
10-20% Carbowax 20,000
5% SP 1200: 1.75%
Bentone 34
10% LAC 2R446
15% Carbowax 4000
10% DC 200
Durapak (OPN) Poracil C
80/100

The columns ranged in length from 1.83m (6 ft.) to 4.57m (15 ft.) and were prepared from .95cm (1/8 in.) inside diameter stainless steel tubing. Column temperatures ranged from 18.3 to 68.3°C (65° to 155°F). Selection of a column depends on the combination of chemicals absorbed on the charcoal. A column packed with SP 1000, Durapak or SP 1200/Bentone would be suitable for benzene alone.

urine samples

Urine phenol analysis was based on the NIOSH proposed standard for benzene.¹ The urine samples were hydrolyzed with perchloric acid at 95°C for two hours, saturated with sodium chloride, and extracted with isopropyl ether. The ether extract was analyzed for total phenol using a flame ionization gas chromatograph. The only modification of the NIOSH method was the saturation of the hydrolyzed urine with sodium chloride. This step increased the extraction efficiency of the isopropyl ether. The chromatograph column consisted of a tube .95 cm (1/8 in.) in diameter, 1.83m (6 ft.) long and filled with 2% EGA CG-AW-DMCS (980-100 mesh) packing. The following temperatures were utilized: column at 160°C, injection port at 230-250°C, and detector temperature at 290-300°C. Maximum sensitivity under these conditions was about 2 mg phenol/liter urine.

results

data

Table I lists data collected from air and urine sample analysis. TWA benzene vapor exposure concentrations are given as ppm (v/v) and they are grouped according to the length of the workday. Concentrations of phenol in urine are

¹Registered trademark of The Dow Chemical Company advised

TABLE I
Results of Air Sampling (ppm) and Urine Analysis (mg/l)

Benzene TWA Range	Number of People	Hours Worked	Concentration Range of Phenol in Urine, mg/l						
			Baseline	Unadjusted			NIOSH Adjusted		
				Day	Night	Combined	Day	Night	Combined
4.0	1	12	7	51	26	39	51	23	37
2.5	1	12	3	28	14	23	37	18	30
2.0	1	12	5	14	6	11	26	13	21
1.5	1	12	8	17	2	6	14	13	14
1.3	1	12	9	18	17	17	18	26	22
1.2	1	12	58	67	30	38	73	60	66
1.1	2	12	1.6	4.6	2.20	3.10	7.11	4.18	6.15
1.0-0.6	7	12	2.36	2.65	2.83	2.73	4.68	5.80	5.77
≤0.5	15	12	1.32	2.39	2.18	2.20	2.36	3.16	3.16
4.4	1	8	6	27	51	35	27	51	35
3.9	1	8	2	41	22	25	55	29	34
3.8	1	8	4	49	22	32	51	22	33
3.6	1	8	2	3	9	8	7	17	13
3.5	1	8	37	46	45	45	61	64	63
3.0	1	8	4	24	21	22	36	28	32
2.6	1	8	3	14	12	13	22	17	19
2.5	1	8	6	10	6	7	10	5	6
2.1	2	8	4.5	11.23	9.10	9.15	18.20	11.15	15.16
2.0	1	8	75	40	64	57	34	55	49
1.3	1	8	2	6	2	5	7	4	6
1.2	1	8	11	46	25	30	37	18	21
1.0-0.6	4	8	2.6	3.21	4.24	4.23	4.18	4.19	4.18
≤0.5	5	8	3.80	2.16	4.12	4.13	6.15	6.11	6.12

expressed as milligrams of phenol per liter of urine (mg/l). The concentrations are listed as measured, and as adjusted according to the NIOSH proposed benzene criteria. The following equation was used to calculate the adjusted values.

$$\text{Adjusted Concentration} = \frac{\text{Measured Concentration} \times \text{Last 2 digits of NIOSH average specific gravity}}{\text{Last 2 digits of measured specific gravity}}$$

TABLE II
Results of Air Sampling (ppm) and Urine Analysis (mg)

Benzene TWA Range	Number of People	Hours Worked	Weight Range of Phenol in Urine, mg			
			Actual		Adjusted for Baseline	
			Day	Night	Day	Night
4.0	1	12	32	16	28	12
2.5	1	12	21	7	19	5
2.0	1	12	22	7	14	1
1.5	1	12	8	3	4	7
1.3	1	12	12	18	5	8
1.2	1	12	16	25	2	23
1.1	2	12	6	2.11	1 to 4	1 to 8
1.0-0.6	7	12	3.85	4.77	5.1 to 39	20 to 52
≤0.5	15	12	2.28	2.9	10 to 23	20 to 5
4.4	1	8	21	20	17	18
3.9	1	8	13	31	12	28
3.8	1	8	7	6	7	4
3.6	1	8	5	17	2	13
3.5	1	8	32	82	6	15
3.0	1	8	17	17	14	14
2.6	1	8	12	18	9	13
2.5	1	8	4	3	2	1
2.1	2	8	5.12	10.11	3 to 10	5 to 6
2.0	1	8	15	52	13	9
1.3	1	8	5	1	4	1
1.2	1	8	8	16	6	8
1.0-0.6	4	8	2.6	2.8	0 to 5	1 to 7
≤0.5	5	8	2.6	5.10	24 to 2	56 to 3

TABLE III
Coefficients from Correlation of Benzene TWA Exposures with Weight of Urinary Phenol and Urinary Phenol Concentrations

	Urine Segment	Phenol Weight Coefficients	Phenol Concentration Coefficients	
			Measured	NIOSH Adjusted
TWA of 8 hour workday (22 men)	Day	0.66	0.65	0.88
	Night	0.46	0.50	0.63
	Combined	0.53	0.52	0.64
TWA of 12 hour workday (30 men)	Day	0.44	0.42	0.51
	Night	0.16	0.18	0.23
	Combined	0.32	0.34	0.41
TWA of combination of 8 and 12 hour workdays	Day	0.38	0.45	0.56
	Night	0.40	0.37	0.42
	Combined	0.42	0.43	0.50
TWA of combination of 8 and 12 hour workdays, 5 cases of "unacceptable" phenol concentrations deleted	Day	0.57	0.56	0.69
	Night	0.69	0.55	0.69
	Combined	0.72	0.61	0.77
TWA of combination of 8 and 12 hour workdays, 5 cases of "unacceptable" phenol concentrations deleted, 12 hour workday data adjusted to an 8 hour workday	Day	0.70		

Note: A perfect correlation is ± 1.0 ; no correlation is 0.0. Each product moment correlation coefficient above was calculated as follows:

$$\text{Coeff} = \frac{\sum X_i Y_i + \sum X_i \bar{Y}_i + \sum \bar{X}_i Y_i - (n \bar{X} \bar{Y})}{(n-1)(\text{Std deviation of } X)(\text{Std deviation of } Y)}$$

Where n = number of observations
 X, Y = parameters being correlated

The average specific gravity of urine used by NIOSH is 1.024. As a comparison, the respective average specific gravities of urine samples included in this report were 1.021, 1.021, and 1.022, for the day samples, night samples and baseline samples. These values are similar to those recently reported¹ for a large work population.

The weight of phenol measured in the urine samples is shown in Table II. Phenol weight was of interest as an alternative to concentration as a means of measuring benzene exposure. Measuring weight instead of concentration would eliminate the problem of low phenol concentration due to the intake of large volumes of liquid. This dilution of urinary phenol levels is handled in the NIOSH criteria by measuring specific gravity, comparing it with a traditionally used average, and adjusting the measured concentration accordingly.

Correlation of data parameters

Two main parameters, urinary phenol concentration and phenol weight, were

correlated with measured employee TWA benzene exposures. The correlation coefficients and the equation used in calculating them are shown in Table III. A correlation coefficient is a measure of the strength of relationship between two variables. In Table III, most of the coefficients exceed 0.3, a value representing the highest correlation which would be expected if random numbers were substituted for the reported sample values. This value assumes a sample size of 52 observations and a confidence level of 95% or $p < 0.05$. Since most of the coefficients exceed 0.3, in most instances a positive significant correlation exists between TWA benzene exposure and the two different measures of urinary phenol levels. Figures 1 and 2 are plots of the strongest relationships for phenol concentration and phenol weight respectively.

Besides comparing two methods of reporting urinary phenol levels, Table III indicates the different ways in which the experimental data was analyzed. Obvious subgroups exist in the total of 52 observations reported. Examination

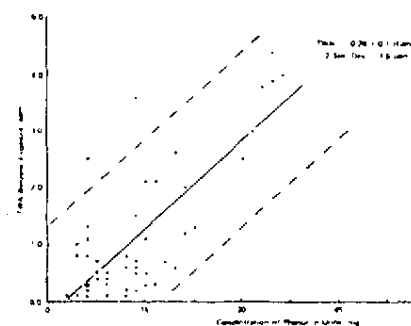


Figure 1—TWA benzene exposure versus adjusted concentration of phenol in urine (5 cases of high baseline concentrations deleted).

of the data included analysis of these subgroups as well as the total group. Two of the sub-groups in Table III resulted from the sampling of employees with two different length, 8 and 12 hour, workdays. A third sub-group with the high baseline urinary phenol levels became evident after the data had been collected. High baseline levels are apparently normal for some individuals and these individuals may exceed the concentration of 75 mg/l, proposed in the NIOSH document as an unacceptable level of "absorption." The five individuals with high background phenol levels will be discussed in more detail later. They were deleted in the last two correlation groups in Table III in order to determine the degree of influence they exerted on the collective group.

The last correlation in Table III was an effort to further examine the relationship between excreted phenol weight and benzene exposure. Since the data had been collected using two different length workdays, it was logical to expect a higher weight of phenol to be excreted in the "day" samples by persons working the longer day. This was assuming vapor exposures were fairly equal throughout the workday. The individual phenol weights collected during the 12 hour workdays were reduced by 1/3 to equalize them with the 8 hour workday. The correlation of this adjusted "day" weight of phenol is reported as the last section of Table III.

This study agrees with previous studies showing a good correlation between benzene

exposure and urinary phenol levels. The highest correlations in Table III occurred when the five persons with high background phenol levels were deleted from the data. These correlations are statistically significant at the critical level, $p \leq 0.005$. If persons with high baselines are included in the data field, the best correlations are significant at $0.0005 < p \leq 0.005$. However Figures 1 and 2 show the unpredictability of this association at relatively low exposure levels. These figures are plots of data, excluding high baseline phenol levels, which generated the highest correlation between phenol concentration/weight and TWA benzene exposure. Plots of data which included persons with high baseline phenol levels showed an even wider and more unpredictable scattering of points. The solid line in Figures 1 and 2 is a least-squares plot, or regression line. The broken lines represent plus or minus two residual standard deviations and should contain between them approximately 95% of the data points. Efforts to use the regression line to predict benzene exposure resulted in the equations shown in Figures 1 and 2. The ppm value for two standard deviations is given below each equation. Two standard deviations for these, the best two correlations, represent an unacceptable 35-40% of the experimental (0-5 ppm benzene) data range. For example, assume an employee's urine was monitored and it contained 25 mg/l of phenol. Based on Figure 1, the best conclusion that can be drawn is that the employee is 95% sure his TWA benzene exposure was between 0.4 and 3.9 ppm. Or, if 100 employees were monitored for one day, and all of the urine

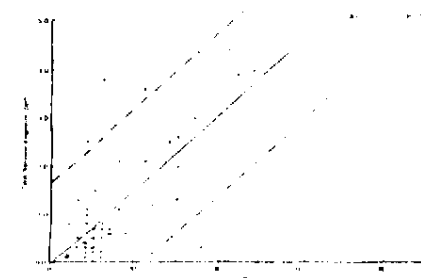


Figure 2—TWA benzene exposure versus weight of phenol in urine (5 cases of high baseline concentrations deleted).

TABLE IV
Correlation Coefficients for TWA Benzene Versus Urinary Phenol Weight,
Adjusted and Unadjusted for Background Phenol Levels

	Urine Segment	Unadjusted for base	Adjusted for base
TWA of 8 hour workday (2 men)	Day	0.66	0.59
	Night	0.46	0.59
	Combined	0.53	0.60
TWA of 12 hour workday (30 men)	Day	0.44	0.38
	Night	0.18	0.15
	Combined	0.32	0.29
TWA of combination of 8 and 12 hour workday	Day	0.38	0.38
	Night	0.40	0.40
	Combined	0.42	0.41
TWA of combined 8 and 12 hour workdays. 5 cases of "unacceptable" phenol concentrations deleted	Day	0.57	0.41
	Night	0.54	0.58
	Combined	0.65	0.53
TWA of combination of 8 and 12 hour workdays. 5 cases of "unacceptable" phenol concentrations deleted. 12 hour workday data adjusted to an 8 hour workday	Day	0.70	0.46

Note: Perfect correlation is 1.0; no correlation is 0.0

samples contained 25 mg/l of phenol, one could assume that approximately 95 out of the 100 had had a TWA benzene exposure between 0.4 and 3.9 ppm. Less than 10% of the time will an employee's actual exposure fall on (within 0.1 ppm of) the regression line. Urinary phenol levels are not an accurate method of predicting

TWA benzene exposures in the range of 5 ppm or less.

Another observation exists. It is that NIOSH's recommended procedure for adjusting "spot" urine samples to a standard specific gravity slightly improved the correlation of the 24 hour urine samples. NIOSH recommends this

TABLE V
Summary of Employees* with High Baseline Urinary Phenol Levels

Benzene, ppm TWA	Age	Medication used at time of survey	History of medical problems	Work hours per day	Urinary Phenol Levels, mg/l					
					Measured			NIOSH Adjusted		
					Day	Night	Base	Day	Night	Base
0.2	57	Esidrix	Hi blood pressure	8	16	12	80	15	12	68
0.8							12			9
0.8	48	2 Aspirin day of 1st base	No Problems	12	65	83	26	65	91	33
							99			108
							62			64
1.2	23	Diet medication during workday sample. Roloids on 3rd base	No Problems	12	87	30	58	73	60	87
							44			91
							63			58
2.0	33	None	No Problems	8	40	64	76	34	55	64
							59			64
							36			32
3.5	27	2 Aspirin day of 2nd base	No Problems	8	46	45	37	61	64	47
							6			7
							84			77

*All male employees

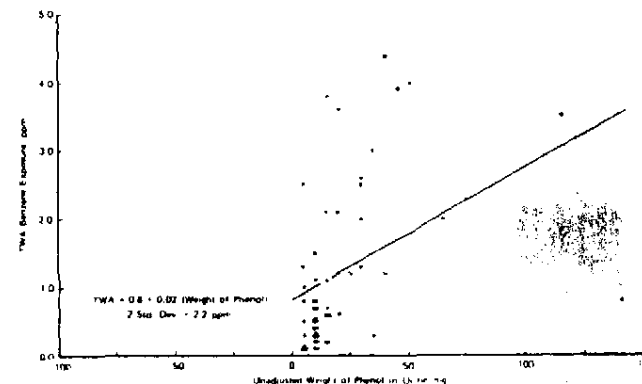


Figure 3-TWA benzene exposure versus unadjusted weight of phenol in urine.

procedure when a single urination is sampled, to allow for dilution of phenol concentrations due to large volumes of liquid intake. When this adjustment was applied to the various urine segments, Table III, the resultant concentration correlated better with TWA benzene exposure.

Background phenol levels

Table IV, and Figures 3 and 4 present the result of adjusting measured urinary phenol levels

according to each individual's normal baseline level. A baseline urine sample was collected after each volunteer had been away from work or any known chemical vapor exposure for 48 hours. Each baseline phenol weight was calculated and subtracted from the total weight of phenol in their "day" and "night" urine segments. Theoretically, this adjustment should have compensated for persons with normally high urinary phenol levels, leaving the adjusted weights of phenol entirely related to benzene absorption. Figure 3 is a plot of unadjusted urinary phenol weight for all 52 observations. Figure 4 illustrates the effect of subtracting the baseline ground weights of these 52 individuals. Table IV compares group correlation coefficients for TWA benzene exposures versus both unadjusted and adjusted weights of urinary phenol. In most cases, the unadjusted measured weights have a higher group correlation than the adjusted weights. This finding indicates the difficulty in using a single value for baseline urinary phenol levels. For any individual, a baseline range should be determined to accurately assess what phenol level is "above" normal. The negative phenol weights in Figure 4 also indicate that unknown factors are causing greater fluctuations in baseline levels than those resulting from low benzene exposures. A study of non-exposed controls is underway and will be reported in a future publication.

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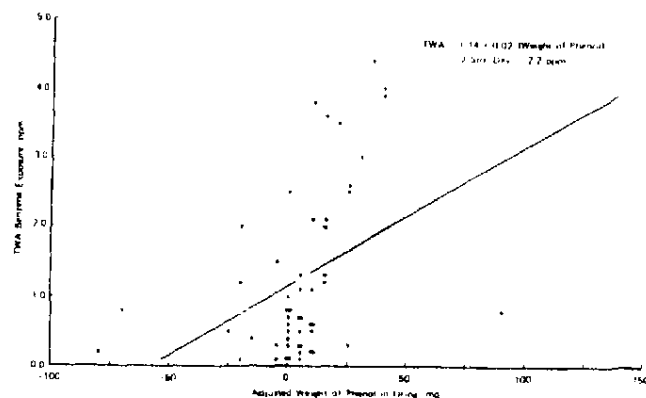


Figure 4—TWA benzene exposure versus adjusted weight of phenol in urine

While consideration of baseline phenol levels for a large group does not improve correlation with benzene exposure, its consideration can very heavily influence correlation for individuals with naturally high baseline phenol levels. Urinary phenol levels approached or exceeded the criteria action level of 75 mg/m³ in one or more urine samples of five different persons, or about 10% of the total number of persons sampled in this study. Several urine sample concentrations of these five persons are shown in Table V, both as measured and adjusted according to NIOSH formula. The baseline concentrations indicate that these five individuals frequently, but not always, have higher than normal (>30 mg/l) phenol concentrations in their urine. Average levels for these individuals varied from 40 to 60 mg/l, but the full range of measured "normal" urinary phenol levels varied from 5 to 100 mg/l. Analysis of the sample data, Table V, did not indicate a one-to-one correspondence of high urinary phenol with any of the known parameters, such as sample volume, specific gravity, medications, medical problems, or age. There is no indication in this study as to why normal urinary phenol levels fluctuate over a relatively broad range, and are characteristically high for certain individuals.

conclusions

1. A positive statistical correlation exists for

urinary phenol levels versus TWA benzene exposures, at exposures of less than 5 ppm. This correlation is statistically significant at the 0.005 level for a large group of people. Both total weight of phenol in the urine, and phenol concentration in urine gave similar results.

2. The correlation between individual benzene exposure and urinary phenol levels is not strong enough to assess past TWA benzene exposures less than 5 ppm. Assessment improves if individuals with normally high background phenol levels can be identified and treated as special cases. Even so, the actual TWA exposure may be $\pm 40\%$ of the exposure determined from urinary phenol levels.
3. Urinary phenol levels, which have been adjusted for baseline values resulting from a single measurement, do not have a higher group correlation with benzene exposure.
4. Baseline phenol levels for a group and an individual can vary over wide range. Approximately 10% of the persons in this study exceeded the "unacceptable" level of 75 mg/l, as expressed in the NIOSH proposed benzene standard, even though they had no known exposure or their TWA benzene exposure was less than 5 ppm.

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Accepted August 7, 1976

ABIH annual certification examinations . . .

Examinations for certification by the American Board of Industrial Hygiene will be held in New Orleans on May 21 and 22, 1977. The following examinations will be conducted.*

CERTIFIED INDUSTRIAL HYGIENIST—This consists of a two day written examination. The first day is the CORE examination in the basic principles of industrial hygiene practice. The second day consists of examinations in the Comprehensive Practice or in an Aspect of industrial hygiene, e.g., Acoustical, Air Pollution, Chemistry, Engineering and Toxicological. Persons who have completed one part of the examination successfully need take only the other part.

INDUSTRIAL HYGIENIST IN TRAINING—This consists of the CORE examination covering the basic principles of industrial hygiene practice. Qualifications for admission to the above examinations include a baccalaureate degree in a science closely related to industrial hygiene and industrial hygiene experience varying from five years for a candidate for Certified Industrial Hygienist to one year for Industrial Hygienist in Training. Up to one year credit may be allowed for a completed graduate degree.

*Examinations will be held at the Fairmont Hotel

INDUSTRIAL HYGIENE TECHNOLOGIST—This consists of a one day written examination covering the principles of various technical aspects of industrial hygiene, e.g., air sampling, laboratory analyses, air monitoring, etc. Qualifications for admission to this examination are a high school diploma and five or more years of experience involving at least 25% of the time in industrial hygiene activities during each year. The Board may accept alternative education—experience requirements for persons having an associate degree or who have completed two years in an accredited college.

application cut-off date

All applications for examination must be received before March 21, 1977. All candidates accepted for examination in New Orleans must have their fees paid at least 30 days before the examination date.

Specific information about eligibility requirements, the examinations and application forms may be obtained from American Board of Industrial Hygiene, 66 S. Miller Rd., Akron, OH 44313 (216) 836-9339.