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CHRONIC EXPOSURE TO BENZENE (BENZOL). I. TEE INDUSTRIAL ASPECTS*

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FOREWORD

In the three papers comprising this series, a common system of **key** lettering has been adopted to designate the several industrial plants considered, and a common system of key numbering identifies the individual workers whose cases were investigated. The fact that the industrial and medical studies were not in all details co-extensive will explain the omission in one paper of a **key** letter or number which may appear in another.

OF THE 89 benzene workers discussed by Hunter in the second paper of this series, **40** were employed in plants where careful appraisal of the benzene exposure had been made, while **45** worked under conditions which had been inspected but not subjected to detailed study. It is therefore possible to estimate the average concentrations of benzene **vapors** to which these workers were exposed, although in the case of the latter group approximate data **only** will be obtained.

Plant **A** was an artificial leather plant employing about 30 persons.

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The two principal processes involving benzene exposure were the **mixing** of a nitrocellulose dope, carried out in the compounding room, and the coating of fabric therewith, this being done **in** the coating room.

This plant was visited in June, **1936**, and the following December. Several determinations of atmospheric benzene vapor concentrations were made at both times. **In** the compounding room the average concentrations found in June and December were, respectively, **190** and **160** p.p.m., while **in** the coating room, near the coating ends of the machines, the corresponding values were **240** and **420** p.p.m.

Industrial
Type
Data

It is believed that the average coating room concentrations were somewhat lower than those listed, as samples were taken only during actual coating processes. The compounding room values, however, are believed to be representative of those to which most of the workers in that room were exposed regularly. In addition, workers 1 and 2 were partially engaged in cleaning out barrels and cans with a solvent containing 25 to 50% benzene. During such work they would inhale concentrations appreciably higher (possibly twice as high) than those indicated in the previous paragraph.

The coating machines in this plant were enclosed and exhausted. The general ventilation in the compounding room was fairly good, but the room was of relatively small area with a resulting congestion of small mixers and other open or partly open containers, each a source of benzene vapor. The use of a benzene mixture for cleaning purposes and the presence of a large open container of this cleaning solvent were the only conditions not ordinarily present in plants of this type.

Plant C was also an artificial leather manufacturing establishment, employing about 50 men. In this plant the basic solution of nitrocellulose was prepared in a separate building termed the pyro room. The process of filling this dope into drums, which were then sent to the compounding room, was carried out by worker 34.

This plant was visited in March, 1937, and air analyses were made in three departments. A single benzene vapor determination in the pyro room showed a concentration of 270 p.p.m. during the actual dope filling process.

This work was said to consume less than half the worker's time and his total average exposure was therefore estimated as about 100 p.p.m. As only a single determination was made, this cannot be definitely stated to be this worker's exposure.

The average of nine vapor determinations in the compounding room of this plant was 200 p.p.m. The average exposure of a worker while transferring dope from one container to another, adjusting the color of the dope in the open mixer, etc., was found to be 380 p.p.m. This is believed to represent the maximum benzene exposure of such a worker during his regular routine. Workers 79 and 88, who were found to have symptoms of benzene poisoning some time after their exposure ceased, were employed in this room.

A wash solvent containing no benzene was used in this plant, but analysis showed that this solvent gradually picked up benzene from the dope remaining in the cans, so that cleaning processes involved a definite benzene exposure.

In the coating room, an average benzene vapor concentration of 210 p.p.m. was found near the coating ends of the machines. The drying ovens of these machines were well constructed and exhausted, but the general ventilation of the room was not especially good.

Plant G was another artificial leather factory. Only compounding room workers were examined and this department alone will be discussed. Tests made in this room on a cold day in February, 1938, showed concentrations of benzene vapor in the vicinity of the mixers ranging from 200 to 350

p.p.m., the average exposure being 265 p.p.m. Some improvements in the general ventilation were promptly made and a test made in April showed that benzene vapor concentration had been largely reduced. An average exposure of 110 p.p.m. was found in an area previously studied, with somewhat lower values in other parts of the room. At the same time sulfate ratios were determined for workers in this room, varying from 37 to 70% being obtained.

In January, 1939, a few more tests were made in this plant and benzene vapor concentrations were averaging 100 p.p.m. Urine sulfate ratios ranging from 40% were found in the most heavily exposed workers. Changes in solvent composition and other set of tests, made in March, showed a slight decrease in benzene vapor concentration, the average value being 85 p.p.m. Sulfate ratios ranged between 52%.

The average exposure of workers examined in this plant was found to be just under 100 p.p.m. in cold weather. The large size of the room was such that conditions probably be greatly affected by weather, as natural ventilation was relied upon to keep the concentrations at a low level. Tests made by the plant in warm weather indicated lower benzene exposures were found in winter.

A fourth artificial leather plant was also studied. A worker as a coater in this factory was examined in the summer of 1937 from

p.p.m., the average concentration being 265 p.p.m. Some improvements in the general ventilation of this room were promptly made and further tests made in April showed that the benzene vapor concentration had been materially reduced. An average concentration of 110 p.p.m. was found in the area previously studied, with somewhat lower values in other parts of the room. At the same time urine sulfate ratios were determined for 6 workers in this room, values ranging from 37 to 70% being obtained.

In January, 1939, a further series of tests were made in this same room and benzene vapor concentrations averaging 100 p.p.m. were obtained. Urine sulfate ratios ranging from 19 to 40% were found in the workers most heavily exposed. After minor changes in solvent composition, another set of tests, made the following March, showed a slightly reduced benzene vapor concentration, the average value being 85 p.p.m. Urine sulfate ratios ranged between 13 and 52%.

The average exposure of the workers examined in this plant was estimated to be just under 100 p.p.m. during cold weather. The layout of this room was such that conditions would probably be greatly affected by weather, as natural ventilation was relied upon to keep the vapor concentrations at a low level. Urine sulfate tests made by the plant chemist in warm weather indicated a much lower benzene exposure than was found in winter.

A fourth artificial leather plant, I, was also studied. A worker employed as a coater in this factory died in the summer of 1937 from the effects of

benzene poisoning. Tests made in the coating room of this plant indicated average benzene vapor concentrations of 200 p.p.m. in March, 1936, 130 p.p.m. and 160 p.p.m. on two different days in March, 1937, and 120 p.p.m. in July, 1937.

From the statistical standpoint there have been 8 known recent cases of benzene poisoning terminating fatally in three artificial leather plants. In these plants there were, in all, about 60 workers exposed to benzene vapor in concentrations ranging from 100 to over 200 p.p.m. With the exception of one worker who was a millwright and whose exposure could not be estimated, all the fatalities occurred among men who had had these heavy exposures. As table I indicates, the compounding room is their chief source. In the three plants of this type where the maximum average exposure was judged to be 100 p.p.m. or below, there have been no fatalities. These plants employ at least 50 workers exposed to benzene.

Plants D and E used benzene rubber cements in the manufacture of crepe rubber soles for shoes. No direct measurements of benzene exposure were made, but tests in plant E on the operations performed by worker 78 (which were the same as operations performed in plant D by worker 35), after benzene had been replaced by naphtha, showed naphtha vapor concentrations of from 300 to 1300 p.p.m. It might be pointed out that the poisoning cases in these plants, both involving females, occurred after relatively short exposures to apparently high concentrations of benzene vapor. In the artificial leather establishments, on the other hand, the exposures have in

all cases been longer and, as a rule, less severe.

In another shoe factory where a crepe sole cement containing benzene was used, and where the cementing was done in or near an exhausted hood, urine samples from the two workers

worker. When visited, the only benzene found in the shop was a special product used in small quantities, not over a pint a month. The rubber cement used most freely, about a gallon a month, was at that time a naphtha cement, but it was shown

TABLE 1

WORKER	OCCUPATION	INDUSTRY	BENZENE EXPOSURE		OUTCOME
			Years	Conc. p.p.m.	
0	Coater	Artificial leather	Several	150	Fatal
1	Compounding room	" "	12	180+	"
2	" "	" "	1	180+	"
12	Coating, compounding and finishing	" "	11	Varied	"
32	Mechanic	" "	—	<100 (est.)	"
34	Pyro room—compounding	" "	12	100+	"
79	Compounding room	" "	3	200	"
87	{ Coater Executive	" "	{ 6 4	{ 200+ Slight }	"
88	Compounding room	" "	—	200	Recovering
35	Crepe sole cementing	Rubber goods	$\frac{1}{2}$	500 (est.)	Fatal
78	" "	Shoe mfg.	$\frac{1}{2}$	500	Recovering
80	Rubber cementing	Shoe repairing	Several	<25	Fatal
81	Paint removing	Telephone exchange	5	<10	"

TABLE 2

PLANT	DEPARTMENT	BENZENE EXPOSURE (P.P.M.)	WORKERS EXAMINED	BENZENE CASES	%
A Artificial leather.....	Compounding room	180+	5	4	80
A " "	Coating room	250—	5	3	60
G " "	Compounding room	100—	6	3	50
D Rubber goods.....	Rubber cementing	500 (est.)	44	21	48

exposed were examined and sulfate ratios of 31 and 37% were found. The benzene exposure was almost certainly less in this case than in plants D and E.

Cases 80 and 81 have also been investigated. Worker 80, a cobbler, was found to work in a reasonably well ventilated shop employing one other

conclusively that benzene cement had formerly been used.

A survey of 68 cobbler shops in greater Boston disclosed that the majority of cobblers did not use benzene cements in any quantity, but three establishments using $\frac{1}{2}$ to 1 gallon of cement a week were selected and the urine sulfate ratios of the 4

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cementers exposed. All four samples were ratios of over 80% negligible exposure to

Worker 81 appeared quantity of a paint re benzene for a few m. The exposure to s processes carried o phone exchanges w ceedingly slight. Un additional contact v uncovered by our must be concluded th absorbed much less quantity usually harmful.

The serious cases c ing on which we hav summarized in table on which we have d cases of poisoning are

From these data w to consider the thres allowable concentra vapor in workroom : this, however, it will the technic employ such concentrations. methods of evaluat hazard.

METHODS OF VAPOR

Benzene vapor de made chiefly by the v developed by S samples were taken, fritted glass petri tub of nitric acid (c nitric and concentra

* A large portion c work described in th paper was carried ou Project No. 465-14-2 Progress Administrat

cementers exposed were determined. All four samples were found to have ratios of over 80%, indicating a negligible exposure to benzene.

Worker 81 apparently used a small quantity of a paint remover containing benzene for a few minutes every day. The exposure to solvent in similar processes carried out at other telephone exchanges was obviously exceedingly slight. Unless there was an additional contact with benzene not uncovered by our investigation, it must be concluded that this individual absorbed much less benzene than the quantity usually believed to be harmful.

The serious cases of benzene poisoning on which we have information are summarized in table 1, and the plants on which we have data as to incipient cases of poisoning are shown in table 2.

From these data we are in a position to consider the threshold or maximum allowable concentration for benzene vapor in workroom air. Before doing this, however, it will be well to discuss the technic employed in measuring such concentrations, as well as other methods of evaluating the benzene hazard.

METHODS OF VAPOR DETERMINATION*

Benzene vapor determinations were made chiefly by the volumetric method developed by Smyth. (2). The samples were taken in a special semi-fritted glass petri tube containing 5 ml. of nitrating acid (equal parts fuming nitric and concentrated sulfuric acid).

* A large portion of the experimental work described in the remainder of this paper was carried out as part of Official Project No. 465-14-3-386 of the Works Progress Administration.

A rate of flow of 0.25 l.p.m. was ordinarily used. The exact technic has been described elsewhere (3).

In an extensive series of experiments the colorimetric method developed by Schrenk and others (4) was compared with the Smyth method. For this purpose the sample was diluted to 50 ml., and 45 ml. used for the Smyth determinations, portions of the remainder of the colorimetric test. It was found that fair agreement between the methods was usually obtained and that when the agreement was not good, a further check on the colorimetric

TABLE 3
COMPARISON OF SMYTH AND SCHRENK
METHODS FOR BENZENE VAPOR
DETERMINATIONS

AGREEMENT	NUMBER OF DETERMINATIONS		
	Original	Repeat	Final
Good, within 10%.....	12	3	15
Fair, 10-20%.....	10	3	13
Poor, 20-50%.....	7	3	10
Failures, over 50%.....	11	—	2

method usually gave a result closer to that obtained by the Smyth method. A summary of the checks obtained is shown in table 3.

Our conclusions regarding these two methods are as follows:

1. With all the apparatus and reagents available, the two methods are approximately equally laborious.

2. The colorimetric method is more accurate for low concentrations (below 50 p.p.m.), the Smyth method for high concentrations.

3. There is no systematic error in either method. Of 37 determinations, the average result was 104 p.p.m. by the Smyth method, 106.5 by the colorimetric method.

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4. The Smyth method is more reliable. If the colorimetric method is to be used, checks should be run on all samples.

5. The colorimetric method is invaluable when toluene is present.

USE OF GRAB SAMPLE DEVICES

In one plant where rubber cementing was being carried on, samples were taken both by the chemical continuous sampling method and by a sensitive combustible gas indicator. As the cement solvent consisted of a 40 to 60 mixture of benzene and naphtha, the data obtained by a method not specific for benzene could be approximate only. Readings of 100 to 200 p.p.m., indicating 40 to 80 p.p.m. of benzene, were obtained with the indicator, while concentrations of 10 to 20 p.p.m. were found by the chemical method. Normal urine sulfate values confirmed the latter finding.

While the use of grab sample devices should not be condemned on the basis of this single case, it may be said that it is difficult to obtain average values for exposure by such methods. There is always a tendency to obtain the maximum momentary exposure, rather than an integrated sample covering all phases of the worker's routine. Direct-reading instruments such as the combustible gas indicator and interferometer find their chief advantage in obtaining data for use in designing exhaust equipment, rather than in the evaluation of average exposure to solvent vapor.

URINE SULFATE DETERMINATIONS

Schrenk and others have shown that the ratio of inorganic to total sulfates in the urine is lowered if there is ab-

sorption of benzene (5). Several authors have discussed the practical application of the test to benzene workers. In the Bureau of Mines' plant study, 15 vapor determinations were made and compared with 60 urine sulfate ratio tests (6). The correlation obtained was not especially good. Kammer and others found that workers treated with sodium salicylate gave low urine sulfate ratios (7). Jephcott and Bulmer suggest that the daily excretion of organic sulfate, rather than the sulfate ratio, be taken

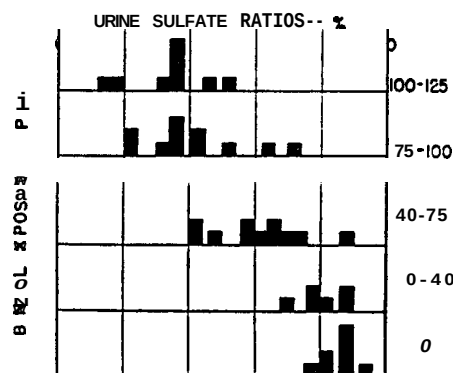


FIG. 1. Correlation of urine sulfate ratios with atmospheric benzene concentrations. Each square represents one urine sulfate determination.

as the criterion of benzene exposure (8). Both of these last papers report that the sulfate ratio of the sample does not change materially on standing, a finding which we have confirmed.

Vigliani and Giannini made sulfate ratio determinations on 39 benzene and 22 benzine workers (9). They showed that even short exposures to moderate benzene vapor concentrations affected the sulfate ratio.

We have made 36 urine sulfate ratio determinations where the exposure during the day was measured by air analysis, a total of 84 atmospheric

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samples being taken at these tests are in

These tests were where relatively maintained, no at the average be greatly exceeded whole, there is a between the two age ratios for the groups are shown

The benzene exposure obtained by averaging all vapor determinations given worker's results in a few cases correct

T	
GROUP	BENZENE EXPOSURE
I	0
II	<40
III	40-75
IV	75-100
V	100-1

tracting 10 to 20 that the job involved a greater or less measured. The benzene exposure quite as definitely indicated in this test given room unduplicated the results closely, even though samples varied

These urine sulfate tests at the end of the least 6 hours of exposure. A few tests were obtained in the comparison of more results is shown

It is seen that

samples being taken. The results of these tests are indicated in figure 1.

These tests were made in plants where relatively good control was maintained, no area being found where the average benzene concentration greatly exceeded 100 p.p.m. On the whole, there is a very good correlation between the two methods. The average ratios for the different exposure groups are shown in table 4.

The benzene exposure was as a rule obtained by averaging the results of all vapor determinations made in the given worker's area. This was in a few cases corrected by adding or sub-

tracting 10 to 20% where it was known that the job included operations with a greater or less exposure than that measured. Though the degrees of benzene exposure are probably not quite as definitely known as is indicated in this table, repeat tests in a given room under similar conditions duplicated the average concentrations closely, even though individual air samples varied considerably.

These urine samples were taken near the end of the working day, after at least 6 hours of benzene exposure. A few tests were made on samples obtained in the late forenoon. A comparison of morning and afternoon test results is shown in table 5.

It is seen that the time of day at

which the sample is taken is very important. In every case except that of worker 3, the ratio of the afternoon sample was over 20% lower than that of the forenoon sample. The exposure of worker 3 was highly irregular and might easily have been very high before the first sample was taken and much lower during the latter part of the day.

The remarkable difference in forenoon and afternoon samples caused us to question the effect of the previous day's exposure on the sulfate ratio. Accordingly one of us and an assistant spent nearly a full day in an artificial

TABLE 4

GROUP	BENZENE EXPOSURE, P.P.M.	NUMBER TESTS	AVERAGE RATIO, %
I	0	8	86
II	<40	6	81
III	40-75	11	61
IV	75-100	11	42
V	100-125	9	34

TABLE 5

WORKER	BENZENE EXPOSURE, P.P.M.	URINE SULFATE RATIO, %		
		(1) A.M.	(2) P.M.	(1) - (2)
		88	59	29
	40	77	49	28
c	>80	51	52	-1
d	100	72	37	35
e	100	62	38	24
f	<75	78	56	22
g	70	68	40	28

leather plant taking air samples, and urine samples were collected over a 24-hour period and the sulfate ratios determined. The results of this study are shown in figure 2.

It is seen that subject X, who had an average exposure of about 80 p.p.m. from 7:45 to 12:00, 60 p.p.m. from 1:00 to 2:30 and 80 p.p.m. from 2:30 to 4:00, showed sulfate ratios of 69% at 2:30 and 55% at 7:00 p.m., with 88% at 7:00 a.m. the following day.

Subject Y, whose exposure was slightly less, showed ratios of 79% at 7:00 a.m., 68% at 11:15, 40% at 4:00 p.m., 46% at 6:30 p.m., 79% at 10:45 p.m., and 79% at 8:00 a.m. the next

day. In other words, the sulfate ratio returns to normal shortly after the exposure ceases.

The area between the curve of sulfate ratio and the line representing the normal ratio is 200 units for X and 230 for Y, a fair check, although Y's exposure was about 10% less than that of X. Y's ratio before and after exposure

ately high benzene vapor concentration showed a high sulfate ratio (97%). This case is not included in figure 1. Another worker in the same plant showed a very low ratio (40%), considering the exposure. Samples taken 4 months later showed that each reacted normally (ratios of 71 and 82%, respectively), indicating that the

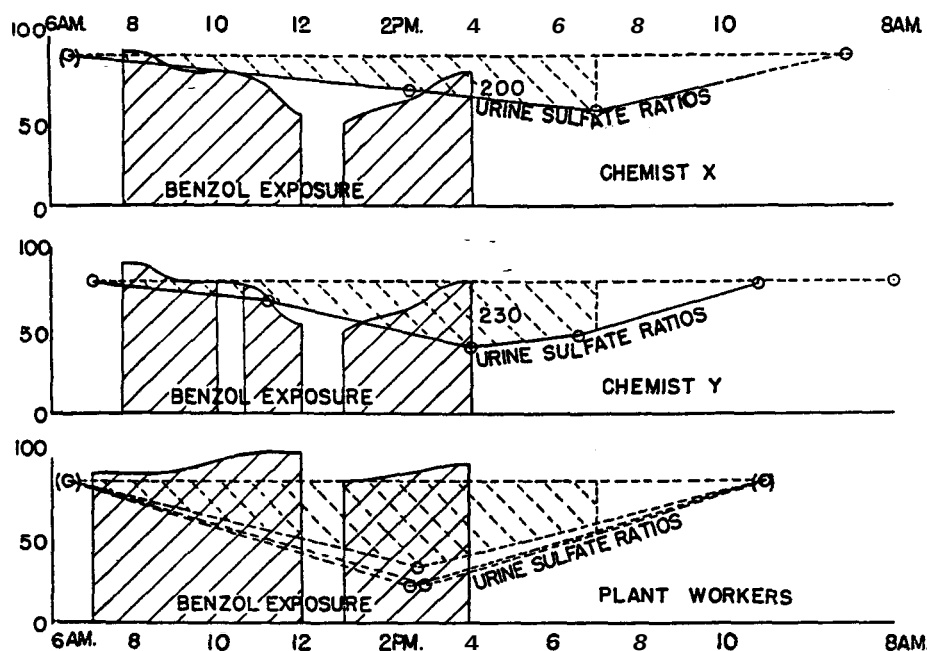


FIG. 2. Variation of urine sulfate ratio with time of day, relative to exposure period

was slightly below the normal value, but it is not believed that this fact affects the results in any material way.

From this evidence we are forced to conclude that the day of the week on which the sample is taken is of little importance, while the time of day, with relation to the benzene exposure, is of great significance.

According to Schrenk (5), persons with liver damage do not react normally to benzene exposure. We found one case where a worker in a moder-

previous physical condition of the worker was a temporary one.

URINE SULFATE RATIO VS. AIR ANALYSIS

Schrenk (5) and Sayers (1) emphasize the advantages of the urine sulfate test over the measurement of atmospheric benzene vapor concentrations, while Kammer (7) goes so far as to say that the latter are practically worthless as a control measure. Our results indicate that the two methods,

when properly results, and successfully hazard. An that the ai determine t process or of and thus in where conti applied, while indicates on the worker c hours, cith of the actua

In the 1 Bureau of M tions, urine determinatio Massachuse medical exa tially nega ratios, 22 between 50 50% (only workers wl was evaluat 22 were exp and 35 to c

From thi that the n cated no ha a slight haz serious haz servations paper) and would be fo conclusion.

It is pre posure whe was mitiga poor busin that time, doubted in the actual during the

when properly carried out, give similar results, and that either can be used successfully to evaluate the benzene hazard. An important difference is that the air analysis method will determine the exposure of a given process or of various steps in a process, and thus indicate directly the points where control measures should be applied, while the urine sulfate method indicates only the average exposure of the worker during a period of several hours, without direct determination of the actual sources of exposure.

In the 1933 plant study of the Bureau of Mines (6), medical examinations, urine sulfate tests and vapor determinations were made in three Massachusetts plants (C, G, I). The medical examinations were all essentially negative. Of 60 urine sulfate ratios, 22 were over 80%, 31 were between 50 and 80% and 7 were below 50% (only two below 40%). Of 57 workers whose exposure to benzene was evaluated by means of air analysis, 22 were exposed to less than 50 p.p.m. and 35 to over 120 p.p.m.

From this study we would conclude that the medical examinations indicated no hazard, the urine sulfate ratio a slight hazard and the air analyses a serious hazard. From Hunter's observations on plant C (see following paper) and our own on plant I, we would be forced to agree with the last conclusion.

It is probable that the actual exposure when the 1933 study was made was mitigated by the fact that, due to poor business, production was low at that time, and that, in spite of undoubted improvements in ventilation, the actual hazard increased materially during the years 1935-1937 as produc-

tion was increased. It should be said for the air analysis method that it could have been the means of predicting this situation, showing as it did high concentrations of benzene vapor for definite processes which would become increasingly hazardous as they became more and more nearly continuous.

A further limitation of the urine sulfate test is its inutility in measuring excessively high exposures. In figure 3 the organic sulfate ratio is plotted against benzene exposure in hours

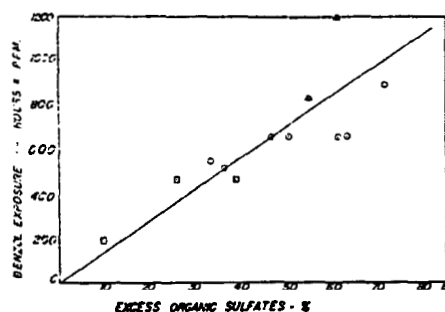


FIG. 3. □ Subjects X and Y. Normal ratio measured. ○ Plant workers. Normal ratio assumed 85%. △ From Vigliani and Giannini. Normal ratio assumed 89%.

times concentration. It is obvious that, with a material increase in concentration, the organic sulfate percentage would become practically 100 and still higher exposures would produce no change. It is also seen that a very low sulfate ratio, e.g. 10%, represents an exposure only 50% greater than does a ratio of 30%, and only twice as great as does a 50% ratio.

The urine sulfate method is, on the other hand, more convenient than that of vapor determinations, and will indicate absorption through the skin and variations in individual absorption due to variations in rate of respiration, etc. This information cannot be ob-

tained through air analysis. In general, more can be learned from the use of both methods in combination than from either alone, and both should be employed in important cases of benzene exposure. Neither method shows benzene poisoning, which can be determined only by medical examinations. The latter, however, should not be relied upon as an index of benzene absorption or of the benzene hazard.

THRESHOLD CONCENTRATIONS

The commonly accepted maximum allowable concentration for benzene vapor is 100 p.p.m., although Greenburg (10) reported a definite hazard in even lower concentrations. On the other hand, 50% has been proposed as the limiting safe value for the urine sulfate ratio. It is obvious from table 4 that these two standards are not correlative. A 50% urine sulfate ratio, based on a single sample taken at the end of the working day, would

probably correspond to an average benzene vapor concentration of slightly below 75 p.p.m. This value has been proposed as the maximum allowable concentration by the Massachusetts Dust and Fume Code Committee and, in the light of our experience, seems not unduly restrictive.

While we have found that benzene vapor concentrations may readily be kept below 75 p.p.m. in the great majority of industrial processes involving its use, this is not true of all such operations. It is our belief that cases 80 and 81 were exposed to average concentrations well below 75 p.p.m., indicating the possibility of occasional cases of benzene poisoning with even the best of control. Close medical supervision of all benzene workers is thus most important and it is to be hoped that adequate substitute materials will be developed for the more hazardous industrial uses of this excellent solvent.

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