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BENZENE IN MOTOR GASOLINE—AN INVESTIGATION INTO POSSIBLE HEALTH HAZARDS IN AND AROUND FILLING STATIONS AND IN NORMAL TRANSPORT OPERATIONS

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INTRODUCTION

BENZENE has been widely used in industry as a feedstock and as a solvent for many years. During this time it has been well known that exposure to high concentrations of benzene vapour could result in acute poisoning, or even death. More recently, however, it has become clear that prolonged exposure to relatively low concentrations of benzene vapour may cause damage to the bone marrow, leading to interference with normal blood-forming processes and consequent aplastic anaemia and, possibly, leukaemia.

The Council of Europe (1966) has proposed that the benzene content of solvents should be limited to 1 per cent. In 1967 the International Labour Office, Geneva, convened a meeting of experts to discuss the safe use of benzene and solvents containing benzene. The meeting recommended (International Labour Office, 1968) that wherever possible benzene should not be used as a solvent; that the amount of benzene contained in other solvent materials should be severely limited, ideally to less than 1 per cent; and that where benzene had to be used, the concentration of airborne vapour should be strictly controlled within the current standards.

All motor gasolines contain benzene; it is unusual for the amount to exceed 5 per cent except when special refining techniques have been used or motor benzole has been added to the gasoline, when the benzene content may be as high as 30 per cent. The normal handling of gasoline minimises the emission of vapour; the liquid is contained within vessels and pipework and only the relatively small volumes of vapour displaced from tanks are vented to atmosphere, usually in open air.

As a consequence of the critical review of the use of solvents containing benzene for industrial purposes, the Atmospheric Pollution Committee of the Institute of Petroleum considered that the possibility of a hazard to health existing in the handling of motor gasoline, particularly at retail filling stations, warranted investigation. A Working Group was convened early in 1968 to plan such an investigation. The members of this Group were G. S. Parkinson (Shell-Mex and B.P., Chairman), D. Blair (Shell Research), Dr. B. W. Duck (BP), K. French (Benzole Producers), J. G. Mitchell (Burmah Oil Trading), G. E. Pamplin (Shell-Mex and B.P.), R. J. Sherwood (Esso Europe) and L. D. Wright (Shell UK). They included representatives from the medical, hygiene, chemical and operational disciplines.

HYGIENE LIMITS FOR BENZENE

Atmospheric

Various standards of acceptability for airborne contaminants in the atmosphere of workplaces have been proposed. The series most widely used in America, Western Europe and the United Kingdom is that published by the American Conference of Governmental Industrial Hygienists. This list of threshold limit values (TLVs) is reviewed annually, and it is published annually by HM Factory Inspectorate as a Technical Data Note. Threshold limit values refer to "airborne concentrations of substances and represent conditions under which it is believed that nearly all workers may be repeatedly exposed, day after day, without adverse effect. Because of wide variation in individual susceptibility, exposure of an occasional individual at or even below the threshold limit may not prevent discomfort, aggravation of a pre-existing condition, or occupational illness". The TLV usually refers to a time-weighted average concentration of contaminant over a 7 or 8 hr working period. However, for certain substances, a time weighted average concentration is not regarded as sufficient, and a ceiling value is recommended which should not be exceeded during the working period.

The TLV for benzene is a ceiling value threshold of 25 ppm (80 mg/m^3). There has been considerable debate on the justification for ascribing a ceiling value to benzene. However, many authorities, including the ILO meeting referred to above, feel that a time weighted average concentration of 25 ppm would be too high. It is of note that the American Standards Institute (1969) advocates three levels of control—a peak exposure value of 50 ppm for not more than 10 min, not more than once per day; a ceiling value of 25 ppm during an 8-hr shift; and a time weighted average concentration of 10 ppm over a similar period. For present purposes the TLV of 25 ppm as a ceiling value has been taken as the standard.

Biological

When benzene vapour is inhaled and absorbed, a certain proportion is subsequently excreted unchanged in the exhaled breath. A further proportion is converted to phenol which is later excreted in the urine, usually in the form of conjugates with sulphuric or glucuronic acid. Determination of benzene in breath or of phenol in urine (after hydrolysis to break down conjugates) are thus possible methods of assessing an individual's exposure to benzene.

Phenol is a natural constituent of urine, normally present in amounts up to 10 mg/l., although occasionally concentrations up to 30–40 mg/l. are found. Significant exposure to benzene results in an increase above this level. DOCTER and ZIELHUIS (1967) report that exposure of several hours to 25 ppm benzene in atmosphere increases the phenol in urine concentration to 150–200 mg/l., although recent experience indicates that lower levels may be produced. A knowledge of the phenol concentration in urine before and after a possible benzene exposure gives an indication of the extent of any absorption.

Benzene is not a natural constituent of the exhaled breath and hence its presence in breath after a possible exposure to benzene is a specific indication of absorption. The amounts of such benzene present in breath are small, and precise collection and analysis are necessary for their accurate determination. Laboratory and field studies

using this technique have been made by some members of the Working Group (SHERWOOD and CARTER, 1970), but as yet criteria for assessing exposure from the results are less well substantiated than those for phenol in urine.

LOCATIONS INVESTIGATED

The prime objective of the investigation was to study working conditions at typical retail filling stations, but the Working Group decided to collect data also at some oil company bulk loading installations where the volume and rate of transfer of gasoline would be much greater, and any potential hazard thereby increased. Subsequently it was possible to arrange that at some bulk installations the gasoline handled was deliberately enriched in benzene content by the addition of motor benzole, in one instance to such an extent as to produce a final benzene in gasoline content of 33 per cent, by volume.

Members of the group arranged for surveys to be conducted in various parts of the country. The monitoring programme was carried out at locations in both the South and North of the country in August and September 1969, mostly during warm weather, and while the demand for gasoline was relatively high.

Filling stations

In order to take account of the influence of the location and design of a site, and of throughput of gasoline, on the atmospheric benzene concentration, three types of site were defined and members of the group ensured that sites of each type were included in the survey. Type A sites were large and open in aspect, built in accordance with oil company recommendations, and of large annual throughput. Type B sites were much more the "typical filling station", medium sized, somewhat enclosed and of average annual throughput. Type C sites were representative of some sites in dense urban areas, very enclosed and with relatively high annual throughput.

Bulk loading installations

Both rail and road car loading was studied at a variety of locations. Tank filling is carried out in gantry installations, with several filling arms, which may be operated singly or concurrently. The installation is usually covered by a light sheet roof, and often has partiallyenclosed sides. Operators filling tank cars conduct much of the operation from a platform beside the tank manhole and are thus exposed to the vapours vented from the tank. Typical filling rates are 1000 gallons/min for railcars and 200 gallons/min for road vehicles. At most locations the loading was done by operators who spent a whole shift loading tank cars at the installation, but not necessarily loading gasoline. At the locations where benzene-rich gasoline was loaded, tanker drivers loaded their own vehicle prior to delivering the gasoline.

METHODS

The assessment of the extent of an individual's exposure to an airborne contaminant while at work, particularly when exposure is intermittent and variable as in retail filling station operation, is best made by continuously sampling the air in his

breathing zone. Ideally, in order to judge the results of monitoring against a ceiling value TLV, a constant recording of the atmospheric concentration of benzene should be obtained. However, this was considered not to be feasible under field conditions and it was agreed to take a series of samples each of some 30 min duration.

The Working Party reviewed various methods available for taking such samples and decided to adopt the technique developed by SHERWOOD and CARTER (1970), based on the use of a personal sampler (SHERWOOD and GREENHALGH, 1960) which could be worn without inconvenience or interference with normal working routine. A series of 30-min samples were taken from each individual using the Casella Mark III Personal Sampler. This comprises an intrinsically safe battery powered pump, housed in a stainless steel case, which can be easily worn on a belt. The pump draws air, at a rate of 1 l./min, through silica gel packed in a cartridge. This cartridge is carried in a holder, clipped to the lapel, and is connected to the inlet of the pump by plastic tubing. Thus a continuous sample of the air in the operative's breathing zone is collected. Benzene and other hydrocarbons are adsorbed on the silica gel. Subsequent elution with a suitable solvent in the laboratory enables the benzene to be determined analytically. Details of the analytical procedure used are given in Appendix II.

Samples were obtained from filling station operators during their entire period on duty, from bulk installation operators over the entire period of motor gasoline loading, and from road car drivers during those periods when they were loading or discharging gasoline, but not when they were driving the vehicle. The tanker drivers were accompanied throughout the working shift by an observer who noted the times during which they handled gasoline, operated the sampling equipment over appropriate periods and "shadowed" the driver during pumping operations in an attempt to duplicate his exposure.

Note was taken of the activity of individuals during each sampling period. Urine samples were collected from most operators, drivers and observers, at the beginning and end of the working period for analysis for phenol content.

RESULTS

Filling stations

Nine filling stations were visited during the late summer and autumn. Table 1 gives details of the type and location of the stations, of the weather conditions during the period of the test, and summarises the analytical results obtained from the air and urine samples collected. Urine samples were collected before and after work from an operator at each of five stations.

Road car loading—normal blends

The loading of normal motor gasoline, not containing deliberately added benzene, into road cars was studied on two days at one location; details of the location, weather conditions and the analytical results are summarised in Table 2.

Rail car loading—normal blends

The loading of normal motor gasoline into rail cars was studied on 6 days at two locations. Details of the locations and analytical findings are given in Table 2.

TABLE 1. NORMAL OPERATIONS AT TYPICAL RETAIL FILLING STATIONS

Site type*	Weather			Gasoline			Benzene in air concentration			Total phenol in urine	
	General	Temp. (°C)	Wind (miles/hr)	Maximum benzene content (% v/v)	Throughput during test gallons	Duration of test (hr)	No. of tests	Mean (ppm)	Range (ppm)	Before work (mg/l.)	After work (mg/l.)
A	Changeable	15–17	8–12	3·7	850	14	28	2·3	1·3–2·9	—	—
A	Changeable	14–22	4–24	3·7	730	12	27	2·1	1·5–3·2	—	—
A	Sunny	15	1–16	2·8	360	5	16	0·3	0·3–0·4	1	5
A	Sunny	8	1	5·8	600	6	10	0·7	0·2–1·2	3	18
B	Changeable	18–20	19–24	3·7	28	4	4	2·4	2·0–2·8	—	—
B	Changeable	21	4–12	3·7	140	4	6	1·6	0·8–2·4	—	—
B	Sunny	16	1	3·1	155	3·5	8	0·5	0·3–0·9	5	9
B	—	—	—	5·5	150	6	12	0·3	—	1	5
C	Bright	16	1	3.4	500	6	10	0·8	0·4–1·1	4	12

*See text for definitions of types.

TABLE 2. NORMAL OPERATIONS AT OIL COMPANY BULK FILLING FACILITIES HANDLING NORMAL MOTOR GASOLINE

Site type	Test period		Weather			Gasoline		Benzene in air concentration			Total phenol in urine		Benzene in breath
	Day	Time	General	Temp. (°C)	Wind (miles/hr)	Maximum Benzene (% v/v)	Operator	No. of tests	Mean ppm	Range ppm	Before (mg/l.)	After (mg/l.)	After (ppm)
Rail	1	1020–1105	Bright	18–21	3–4	0·4	1	2	0·3	0·1–0·5	4	3	0·1
							2				4	4	0·2
	2	1410–1445	Dull	16	3–4	0·4	1	2	1·6	0·3–2·8	—	4	0·3
							2				—	5	0·4
	3	1050–1130	Bright	18	1	0·5	1	2	0·3	0·1–0·4	—	4	0·3
							2				—	7	0·2
		1420–1455	Bright	21	3–4	0·4	1	2	0·6	0·4–0·7	—	3	0·3
							2				—	9	0·7
	4	1025–1115	Damp	16	5–6	0·7	1	2	4·4	4·1–4·7	—	8	0·9
							2				—	8	0·7
Rail	1	0630–0900	Misty	13	5	3·1	1	4	6·7	0·5–19·5	1	10	
							2	4	2·9	1·7–4·8	1	7	
		1000–1100	Bright	14	5	3·1	1	2	1·8	1·0–2·5	—	—	
							2	2	1·8	1·4–2·1	—	—	
	2	0630–0900	Fine	13	5	1·3	1	4	3·1	0·6–7·7	—	4	
							2	4	3·2	1·7–4·7	—	5	
Road	1	0730–0930	Fine	13	10–18	6·8	1	4	0·6	0·2–1·1	2	1	
							2	4	2·2	1·5–2·7	6	2	
		1030–1330	Sun	13	14–20	6·8	1	6	2·0	1·7–2·3	1	5	
							2	5	2·3	1·6–2·9	2	6	
	2	0630–0930	Fine	11	5	6·8	1	6	2·8	1·9–3·3	—	1	
							2	4	2·2	1·8–2·8	—	4	
		1045–1330	Bright	11	5	6·8	1	5	1·8	1·3–2·4	1	3	
							2	6	1·9	1·5–2·4	4	3	

Road car loading—benzene rich gasolines

The loading of gasoline with added benzole into road cars was studied on three days at three locations. Loading, and subsequent delivery to filling stations, of the gasoline was carried out by the drivers and not by installation operators. Each driver was accompanied by an observer. Details of the locations and analytical results are given in Table 3.

DISCUSSION

The initial objective of this investigation was to assess whether any significant hazard to health occurred from exposure to benzene during normal operations at retail filling stations. Nine retail sites of differing types were surveyed during warm or very warm weather and at a time of year when gasoline sales were expected to be above average. It may be seen from Table 2 that, even under conditions which favoured the emission of vapour to the atmosphere, on no occasion was an atmospheric benzene concentration greater than 3·2 ppm recorded, averaged over a half-hour period. The accepted TLV for benzene when it is used industrially is 25 ppm; in this study only 12 out of 121 individual determinations exceeded 2·5 ppm.

Although reservations may be made on the application of industrial TLVs to conditions at retail filling stations, where women, young persons and others not normally engaged in work with industrial products may be employed, the concentrations measured in this study during the normal operation of a variety of filling stations were so much less than the TLV that it is difficult to conceive that any benzene inhalation hazard exists.

This conclusion is supported by the results of phenol in urine analysis on samples obtained from filling station personnel, which showed little evidence of absorption of benzene.

The results obtained in other locations where gasoline was handled in greater quantities, at very much higher flow rates and in certain instances, at considerably higher benzene content, serve to underline the acceptability of current methods of handling gasoline. When road cars were loaded with normal gasoline, at rates of about 200 gallons per min, the average atmospheric benzene concentration increased to 2·5–3 ppm on most occasions; a further increase in flow rate to 1000 gallons per min when rail cars were loaded was accompanied by an increased scatter in the atmospheric concentrations. The average atmospheric concentration increased to 6·7 ppm over one period of 2 hr; this was due to an abnormally high concentration (19·5 ppm) during the first 30 min, a period of still air and early morning mist. During only one other half-hour period was a concentration greater than 5 ppm recorded; this was during a period when a spillage occurred, and the concentration of benzene rose to 7·7 ppm.

The effect of considerably increasing the benzene content of the gasoline is indicated by comparison of the data on road car loading of normal and benzene-rich gasolines. The results from locations where benzene contents of 33% and 20% occurred (Table 3), show that somewhat greater atmospheric levels arose and that the changes in phenol in urine concentration tended to be greater in the personnel concerned.

TABLE 3. LOADING AND DISCHARGING OF ROAD TANKERS WITH MOTOR GASOLINE CONTAINING ADDED BENZOLE

Weather		Gasoline			Benzene in air concentration			Total phenol in urine	
Temp. (°C)	Wind (miles/hr)	Benzene content (% v/v)	Gallons loaded	Driver No.	No. of Tests	Mean (ppm)	Range (ppm)	Before (mg/l.)	After (g/l.)
16–23	1	33	8800	1	3	5·7	2·9–7·8	3	16
				Obs*				6	14
			11,300	2	5	4·5	1·4–9·4	5	9
				Obs				4	9
			10,000	3	4	6·7	1·6–9·4	7	48
				Obs				8	20
10–26	1	20	6200	4	1	3·5	—	18	28
				Obs				3	9
			4300	5	2	6·7	4·3–9·1	11	34
				Obs				5	19
13–20	1	10	7300	6	1	1·6	—	7	4
				Obs				7	4
			10,500	7	3	3·3	1·4–4·0	22	21
				Obs				21	31

*Obs refers to the observer who accompanied the driver.

Here again, however, the values recorded were well within the current limits, even during abnormally warm weather.

In the event, very few samples of expired air were collected and analysed. The results have been given in Table 2. None of the results exceeded 1 ppm.

CONCLUSIONS

Comparison of the results obtained by monitoring the working environment and the operational personnel at various typical filling stations and bulk loading installations, with current limits for acceptable industrial conditions for the handling of benzene, leads to the following conclusions:

Only trivial exposure to airborne benzene vapour occurred when motor gasoline of normal benzene content (up to 5% v/v) was dispensed at typical filling stations.

Atmospheric benzene concentrations during the loading of normal motor gasoline at rates up to 1100 gall/min were much less than the current TLV ceiling value of 25 ppm.

Atmospheric benzene concentrations during the loading of motor gasoline containing up to 33% v/v benzene at rates up to 200 gall/min were much less than the current TLV ceiling value of 25 ppm.

Changes in the excretion of phenol in urine among personnel handling gasoline at filling stations and bulk loading installations did not indicate any significant exposure to benzene.

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