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## DETERMINATION OF 1,2-DIBROMOETHANE, 1,2-DICHLOROETHANE AND BENZENE IN AMBIENT AIR USING POROUS POLYMER TRAPS AND GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC ANALYSIS WITH SELECTED ION MONITORING

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### SUMMARY

A method for the simultaneous determination of benzene and trace concentrations of 1,2-dibromoethane and 1,2-dichloroethane in ambient air was developed, with the use of gas chromatography-mass spectrometry and selected ion monitoring. Samples were collected at ambient temperature on a solid adsorbent followed by thermal desorption into the gas chromatograph-mass spectrometer. The chromatographic column was made of glass (2 m × 1.8 mm I.D.) and packed with 6% poly-*m*-phenyl ether on Tenax GC (60-80 mesh). Four different adsorbents including porous polymers and a carbonaceous material were evaluated for the extraction efficiency of the compounds in air. Sampling periods can be extended from 10 min to several hours and the use of personal sampling equipment is feasible. Samples were taken at different locations in the Stockholm area including streets, parking garages, car repair shops, inside cars and in a private house with a garage on the ground floor.

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### INTRODUCTION

In recent years there has been much concern about the health hazards posed by individual biologically active substances in the polluted atmosphere of cities and in the working environment. Much interest has been focused on the problems associated with automotive emission of volatile organic substances. The development of high resolution gas chromatographic techniques has made it possible to rapidly determine complex mixtures of organic substances such as benzene and several of its alkyl derivatives, cyclic, paraffinic and olefinic hydrocarbons using flame ionization detection or mass spectrometry. However, trace contaminants of special interest such as halogenated hydrocarbons are usually obscured by the more abundant hydrocarbons and do require a more selective technique.

Mass fragmentography is one technique of high sensitivity and selectivity which permits quantitative determination of trace components such as 1,2-dibromoethane (EDB) and 1,2-dichloroethane (EDC) even in the presence of high levels of

hydrocarbons. The dynamics of the system also permits simultaneous determination of a major contaminant such as benzene. Benzene was frequently analyzed by other authors and can therefore be used as a reference.

The toxic properties of benzene are well documented and it is suspected that long-time exposure to even very small quantities may have harmful effects. Concern for these effects has led to a recent OSHA emergency exposure limit for benzene in air<sup>1</sup>. It is well known that the dominating sources of benzene and other non-methane hydrocarbons in the open air of cities are automotive exhaust and gasoline<sup>2-5</sup>. Benzene is also widely used in industrial processes and as a constituent in commercial solvents.

Methods of analysis for benzene and other hydrocarbons in ambient air have been reviewed by several authors<sup>6-9</sup>. The overwhelming majority of the methods are based on gas chromatography (GC) with either flame ionization detection (FID)<sup>10,11</sup> or mass spectrometry (MS)<sup>12,13</sup>. Ambient air samples were enriched on solid adsorbents such as activated charcoal<sup>11,12</sup> or porous polymers<sup>12,13</sup>, or by using cryogenic traps<sup>10</sup>. In a recent application, the photoionization detector (PID) has been used for the direct analysis of benzene and alkylbenzenes in city air without prior sample enrichment<sup>14</sup>.

EDB and EDC are added to leaded gasoline as scavengers of inorganic lead oxides. The amount of EDB and EDC varies but is on a molar basis equal to the amount of alkyllead. It has been suggested<sup>15</sup> that EDB would not survive the combustion process in motor vehicles, however, dynamometer studies<sup>16</sup> have proven this assumption to be invalid. Thus, considering the higher thermal stability of EDC, both compounds may be emitted to the atmosphere by the auto exhaust emissions and by evaporative losses from gasoline.

The knowledge of ambient levels of EDB and EDC is scarce although EDB has been determined in city air in the U.S.A.<sup>15,17</sup> and in London<sup>16</sup>. Grimsrud and Rasmussen<sup>18</sup> have reported that tropospheric levels of EDC in rural air do not exceed 5 ppt (1 ppt =  $10^{-12}$  by volume) which was their detection limit using GC-MS with selected ion monitoring (SIM). Other authors using GC-MS with the SIM technique<sup>19</sup> or GC with electron capture detection<sup>20-22</sup> have determined trace levels of C<sub>1</sub>-C<sub>2</sub> halogenated compounds in the troposphere and stratosphere over Europe and the U.S.A.; there are however no reports on ambient levels of EDB or EDC. It seems that EDC do not have the "ubiquitous nature" of many other light halogenated hydrocarbons. However, it has been shown that EDC is readily photooxidized<sup>23</sup> and it is likely that this reaction plays an important role in the tropospheric breakdown of EDC.

This paper describes a GC-MS method for the rapid and simultaneous determination of EDB, EDC and benzene in ambient air using enrichment on a porous polymer and SIM for detection.

## EXPERIMENTAL

### *Sample tubes*

Sample tubes were made of glass (200 × 1.8 mm I.D.). The tubes were bent to a U-shape, silanized and filled to a length of 150 mm with solid adsorbent. The adsorbent was held in place with two small plugs of silanized glass wool.

Four different adsorbents were initially considered, namely: Porapak Q, 80–100 mesh (Waters Assoc., Milford, Mass., U.S.A.); Chromosorb 105, 80–100 mesh (Johns-Manville, Denver, Colo., U.S.A.), Tenax GC, 60–80 mesh (Alltech, Arlington Heights, Ill., U.S.A.) and Carbosieve B, 60–80 mesh (Supelco, Bellefonte, Pa., U.S.A.). The adsorbents were packed into the tubes and conditioned overnight under a stream of helium. Conditioning temperatures were 200° for Porapak Q, Chromosorb 105 and Tenax GC, and 300° for Carbosieve B. Before use the sample tubes were reconditioned for 2 h. The sample tubes were sealed with plugs of PTFE.

#### *Sampling and sampling locations*

Most samples were taken with stationary equipment. In this case the sampling train consisted of two traps, a 12-V battery-operated diaphragm pump (NV 75 E; KNF Neuberger, Freiburg-Munzingen, G.F.R.) and a flow meter (bubble meter) coupled in series. The second trap in the sampling train was used as a control of sample loss (breakthrough) in the first trap when sampling large volumes of air, and for calibration in the field by injecting standard solutions into the trap just before sampling. Here, only 1 l of air was sampled as it was found that no breakthrough would occur when sampling this volume.

The connections between the traps and the pump consisted of PTFE tubing (3 mm I.D.). The flow was determined by the restriction in the two traps and varied between 50 and 100 ml/min. Thus, a typical sample volume of 1 l was sampled within 10–20 min. Only slight variations of the air flow were observed during sampling, and the sampled volume was calculated from the initial flow-rate and the sampling time. After sampling the traps were sealed and stored in the dark under dry ice until analysis.

Samples were also taken with personal sampling equipment. In this case only one trap and a Sipin SP-15 (Anatole J. Sipin Co., N.Y., U.S.A.) personal sampler pump was used. The flow-rate was set to 3 ml/min. The exact flow through each trap was measured with a bubble meter before and after use. With this method 4–5 h time-weighted average concentrations were measured.

Sampling locations were chosen to measure the effects of both exhaust emissions and evaporative losses. Thus, measurements were conducted at sites of highly and a moderately dense traffic in Stockholm, in the vicinity of gasoline stations, inside parking garages, car repair shops and inside vehicles in traffic. Measurements were also conducted in a private house with a garage on the ground floor. When sampling with the stationary equipment the sample tubes were placed at a height of 1.5 m.

#### *Analysis*

Mass fragmentographic analysis was performed on an LKB 9000 mass spectrometer equipped with a two-stage jet separator and a temperature-programmed gas chromatograph. An electron impact ion source was used. The ionizing potential was 70 eV and the temperature of the jet separator and the ion source was 190°. The GC column was made of glass (2 m × 1.8 mm I.D.), silanized and packed with 6% poly-m-phenyl ether (six-ring) on Tenax GC (60–80 mesh).

The traps were connected to the gas chromatograph via a four-way valve (dead volume 10  $\mu$ l). Thermal desorption was accomplished by heating the traps at 175° for 3 min with an oven. The carrier gas was then allowed to sweep the content of the trap onto the column, by switching the valve, for 60 sec. The column was kept

at 40° during sample transfer and was then temperature programmed. For detailed chromatographic conditions see legend of Fig. 2.

The ions being monitored were as follows:  $[\text{C}_2\text{H}_5^{35}\text{Cl}]^+$ ,  $m/e = 62$ ;  $[\text{C}_6\text{H}_2]^+$ ,  $m/e = 62$  and  $[\text{C}_2\text{H}_4^{81}\text{Br}]^+$ ,  $m/e = 109$ . The mass spectrometer was initially set to monitor  $m/e = 62$ . After the EDC and benzene peaks had been eluted the magnetic field was changed to monitor  $m/e = 109$  for the detection of EDB. In order to gain highest possible sensitivity, both slits were fully opened during mass fragmentographic runs.

#### *Preparation of standards and calibration*

1,2-Dibromoethane and 1,2-dichloroethane of 99% purity (Merck, Darmstadt, G.F.R.) and analytical grade benzene (Merck) were used for calibration purposes without further purification. Standards were prepared by successive dilution of the compounds with analytical grade carbon disulphide (Merck).

The GC-MS system was calibrated for pico- and nanogram amounts of EDB and EDC, and nano- and microgram amounts of benzene by injecting  $\mu\text{l}$  aliquots of the  $\text{CS}_2$  solutions into empty sampling tubes and analyzing the tubes as above.

## RESULTS AND DISCUSSION

#### *Evaluation of adsorbents*

On the basis of the measurements of others<sup>2,11-13,15-17,24,25</sup> it was expected that the EDB and benzene concentration in Stockholm air would range from 0.01 to 0.5  $\mu\text{g}/\text{m}^3$  for EDB and 0.004 to 0.19  $\text{mg}/\text{m}^3$  for benzene. EDC was expected to be present in the same molar concentration as EDB or higher since it is more volatile and more stable towards hydrolysis and thermal decomposition. The detection limit (peak height equal to 2.5 times the noise width) is *ca.* 30 pg for EDB and EDC, and 1.5 ng for benzene. Thus, taking the above expected ambient levels into consideration it was found that a sampling volume of 3 l would be necessary for the detection of the lower concentrations.

In order to evaluate the retention properties for EDB and EDC at room temperature on the four different adsorbents the following simple experiment was set up. The sampling train was set up in the laboratory as above. Pure nitrogen at atmospheric pressure was supplied to the traps from a gas sampling bag. A restriction between the pump and the second trap in the sampling train kept the gas flow through the traps at *ca.* 50 ml/min. The first trap contained the adsorbent to be tested and the second contained Porapak Q for which preliminary experiments had shown good adsorption and desorption properties for EDB and EDC. A standard of EDB and EDC in  $\text{CS}_2$  was injected into the stream of nitrogen before the first trap. After every 10 min the second trap was disconnected from the sampling train and another trap packed with Porapak Q was inserted. The disconnected trap was analyzed for EDB and EDC and the procedure was repeated until traces of the compounds could be detected. The sampled volume for which traces of a substance could be detected in the second trap was defined according to others<sup>26</sup> as the breakthrough volume. Table I shows the results obtained.

Of the tested adsorbents only Tenax GC did not give the required minimum breakthrough volume of 3 l for both compounds. However, in these experiments

Carbosieve B was found to "irreversibly" adsorb both substances, and thermal desorption could only be performed with considerable losses due to inefficient desorption at low temperatures and thermal breakdown at higher temperatures. Of the remaining two adsorbents Porapak Q was the one selected for further experiments since Chromosorb 105 sometimes showed high background interferences after field sampling.

The effect of high pollution and humidity levels on the breakthrough volume was tested by replacing the pure nitrogen in the gas sampling bag with polluted air from a car-parking garage. Excess of moisture was added and the breakthrough volume for EDB, EDC and benzene was determined (Table I).

TABLE I

**BREAKTHROUGH VOLUME OF 1,2-DIBROMOETHANE, 1,2-DICHLOROETHANE AND BENZENE ON VARIOUS ADSORBENTS AT ROOM TEMPERATURE**

Breakthrough volume was determined by sampling with two traps in series. The second trap was exchanged and analyzed every 10 min until traces of the compound were detected. The corresponding volume was rounded downwards to the nearest whole litre. Sample amount: EDB and EDC, 200 ng; benzene, 20 µg. Sampling rate: ca. 50 ml/min. Sampling temperature: 25°. Atmosphere: dry nitrogen. Figures in parentheses are the breakthrough volumes when sampling polluted air at 90–100% humidity.

Adsorbent	Breakthrough volume (l)		
	EDB	EDC	Benzene
Porapak Q (80–100 mesh)	>10 (>10)	3 (3)	(5)
Chromosorb 105 (80–100 mesh)	>10	3	
Tenax GC (60–80 mesh)	8	1	
Carbosieve B (60–80 mesh)	>10	>10	

*Calibration and sample recovery*

Fig. 1 shows the calibration plots for EDB, EDC and benzene. The open triangles illustrate the peak area for standards injected into an empty sample tube as described above. As shown in the figures the plots are rectilinear over more than two decades from just above the detection limit, with a correlation coefficient of 0.997 for EDB and benzene and 0.998 for EDC.

The sample recovery at various concentrations was evaluated by injecting CS<sub>2</sub> standards into traps and sampling 1 l of purified air. Then, the traps were stored in dry ice for at least 1 h before analysis. The response (peak area) versus amount of substance is plotted in Fig. 1 (solid triangles). Again the plots are rectilinear over more than two decades from just above the detection limit, with a correlation coefficient of 0.9993 for EDB and EDC and 0.9998 for benzene. The recoveries for EDB, EDC and benzene over the concentration range were calculated by comparing the slopes of the two plots for each compound. This was done by dividing the coefficient of regression for the recovery plot by the coefficient of regression for the calibration plot. The results are shown in Table II, together with the results from the recovery studies during field sampling. Here, the peak areas from the standards injected into the second trap before sampling are divided by the peak areas from the corresponding standard injected into empty traps.

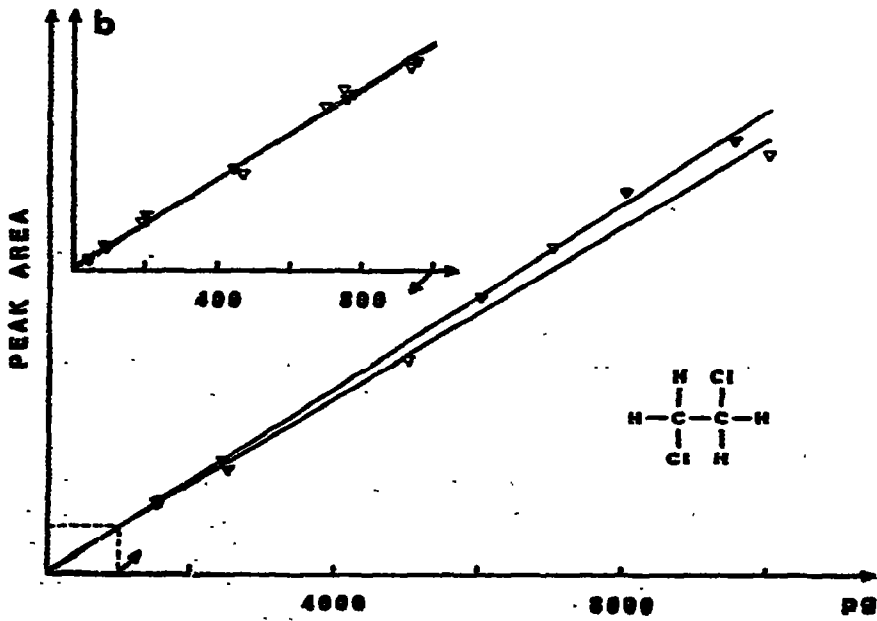
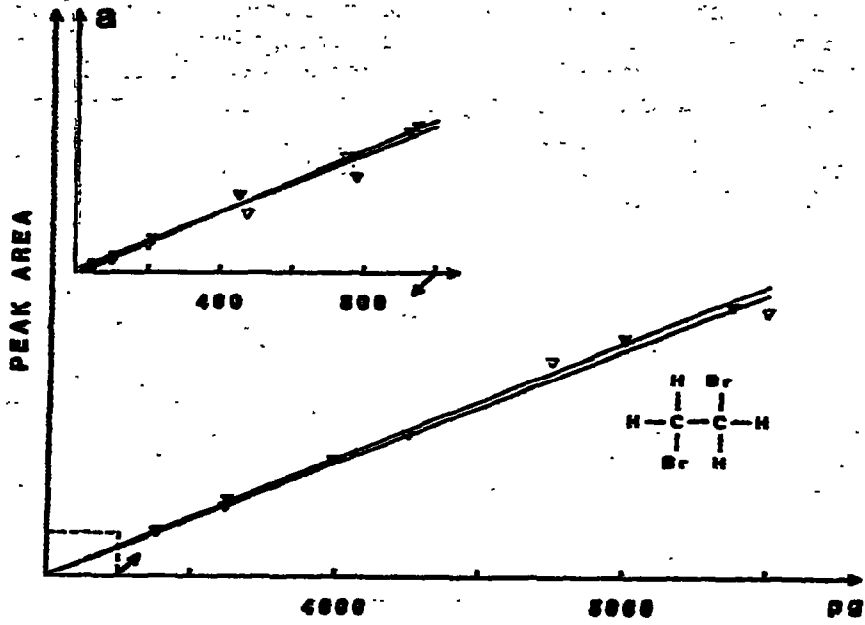


Fig. 1.

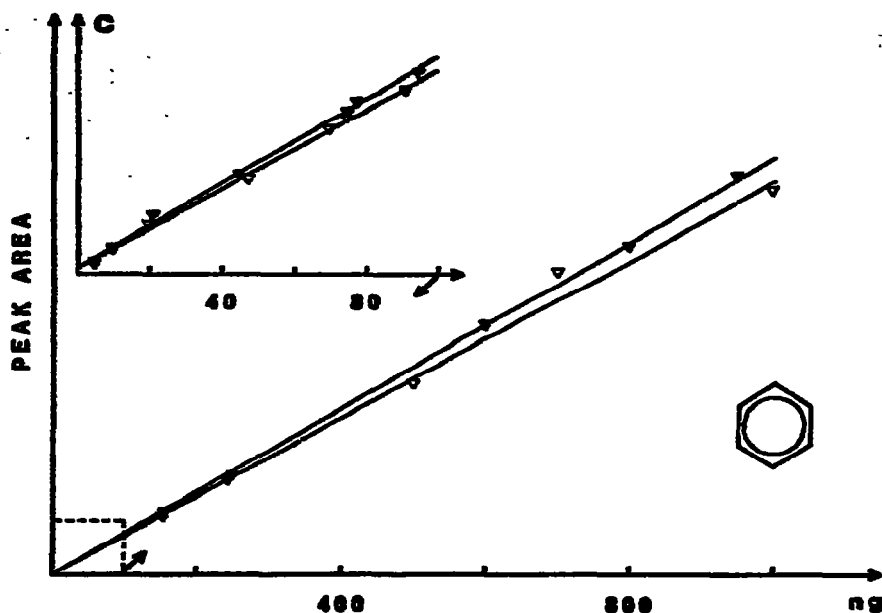


Fig. 1. Calibration graphs for EDB (a), EDC (b) and benzene (c) using direct injection ( $\Delta$ ) or adsorption on Porapak Q followed by storage at  $-79^\circ$  for 1 h and thermal desorption ( $\blacktriangle$ ).

TABLE II

RECOVERY OF 1,2-DIBROMOETHANE, 1,2-DICHLOROETHANE AND BENZENE FROM PORAPAK Q USING THERMAL DESORPTION

Sampled volume: 1 l. Sampling temperatures: room temperature and  $5-15^\circ$  during field sampling. Desorption time and temperature: 3 min and  $175^\circ$  respectively.

Compound	Recovery (%)		
	Low range <sup>a</sup>	High range <sup>ab</sup>	During field sampling <sup>abc</sup>
EDB	100	104	107
EDC	98	108	107
Benzene	106	105	97

<sup>a</sup> The recovery was determined for 50–1000 pg EDB and EDC, and 5–100 ng benzene.

<sup>ab</sup> The recovery was determined for 50–10,000 pg EDB and EDC, and 5–1000 ng benzene.

<sup>abc</sup> The recovery was determined for 1000 pg EDB and EDC, and 100 ng benzene.

*Quantitative data*

Fig. 2 shows a typical chromatogram of EDB, EDC and benzene in urban air. The concentration ranges of the compounds identified in 35 urban samples were as follows: EDB,  $0.034-1.5 \mu\text{g}/\text{m}^3$  or 4.4–200 ppt; EDC,  $0.079-1.9 \mu\text{g}/\text{m}^3$  or 19.5–470 ppt; benzene,  $0.025-0.60 \text{ mg}/\text{m}^3$  or 7.8–190 ppb. Samples were collected at one site of moderate and one of high traffic density. The mean values from measurements at several different locations are illustrated in Fig. 3. The measured concentrations of EDB and benzene at the site of moderate traffic density are in good agreement with the results obtained by others<sup>2,11-13,15-17,24,25</sup>. Three to six times higher concentrations

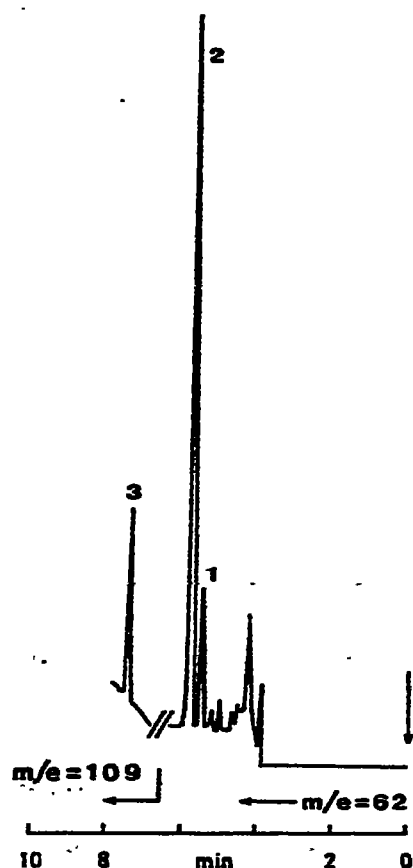


Fig. 2. Typical chromatogram of EDB, EDC and benzene in urban air (Stockholm city) using adsorption on Porapak Q, thermal desorption and selected ion monitoring. Sample taken on October 18th, 1978. Sample volume: 1 l. Column: 6% poly-*m*-phenyl ether on Tenax GC (60-80 mesh), 2 m  $\times$  1.8 mm I.D. Temperature program: held for 1 min at 40°; 30°/min to 110°; 10°/min to 185°; held for 3 min. Carrier gas (helium) flow-rate; 15 ml/min. Peaks: 1 = EDC ( $[C_2H_3^{35}Cl]^+$ ), 175 ppt; 2 = benzene ( $[C_6H_6]^+$ ), 75 ppb; 3 = EDB ( $[C_2H_4^{81}Br]^+$ ), 83 ppt.

were determined at the site of high traffic density. The values are higher than earlier reported concentration levels in city air.

The molar ratio of EDC to EDB at the two different sites varies between two and four with an overall mean of 3.0; the standard deviation is 0.87. Possible reasons for the higher EDC level were discussed above. Virtually the same ratio of EDC to EDB (2.9, standard deviation = 0.69) was found from 56 measurements in car-parking garages, car repair shops, inside vehicles and in a private house. However, the molar ratio of EDC to benzene in city traffic is  $2.5 \times 10^{-3}$  with a standard deviation of  $0.21 \times 10^{-3}$  and increases to  $4.7 \times 10^{-3}$  with a standard deviation of  $1.6 \times 10^{-3}$  at the indoor locations. However, at the indoor locations there is only a minor contribution from exhaust emissions; here the evaporative losses dominate. Thus, the increase in ratio indicates a difference in the emission pattern of EDB and EDC on one hand and benzene on the other.



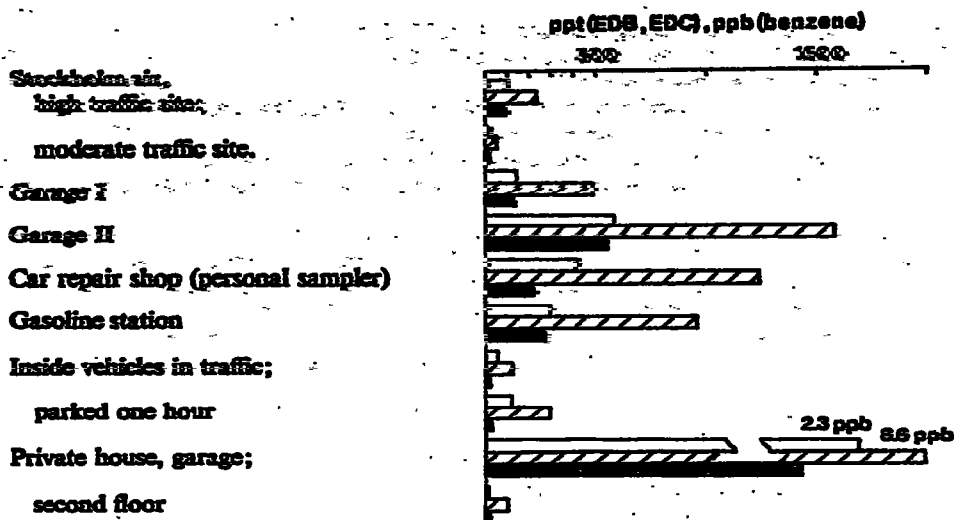


Fig. 3. Concentrations of EDB ( $\square$ ), EDC ( $\text{||||}$ ) and benzene ( $\blacksquare$ ) in ambient air at different locations in the Stockholm area. The outdoor samples were collected in October 1978. The rest of the samples were collected during the early spring or the late autumn of 1978. The concentrations of EDB and EDC (ppt) and benzene (ppb) are mean values from a total of 91 samples.

## CONCLUSION

A method for the simultaneous determination of benzene and trace concentrations of 1,2-dibromoethane and 1,2-dichloroethane in ambient air has been described. The samples were collected at ambient temperature on Porapak Q, a porous polymer. Sampling periods from as short as 10 min up to several hours could be used with reproducible results. Ambient levels of EDB and benzene in the Stockholm air were in reasonable agreement with the reports from other cities. The mean molar ratio of EDC to EDB in ambient air is 3 and is likely due to the higher volatility of the former.

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