

Short communication

# Gas chromatographic–mass spectroscopic determination of benzene in indoor air during the use of biomass fuels in cooking time

Sukesh Narayan Sinha\*, P.K. Kulkarni, N.M. Desai, S.H. Shah, G.M. Patel,  
M.M. Mansuri, D.J. Parikh, H.N. Saiyed

*National Institute of Occupational Health (ICMR), Ahmedabad 380016, Gujarat, India*

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## Abstract

A gas chromatography–mass spectroscopic method in electron ionization (EI) mode with MS/MS ion preparation using helium at flow rate  $1 \text{ ml min}^{-1}$  as carrier gas on DB-5 capillary column ( $30 \text{ m} \times 0.25 \text{ mm i.d.}$  film thickness  $0.25 \text{ }\mu\text{m}$ ) has been developed for the determination of benzene in indoor air. The detection limit for benzene was  $0.002 \text{ }\mu\text{g ml}^{-1}$  with S/N: 4 (S: 66, N: 14). The benzene concentration for cooks during cooking time in indoor kitchen using dung fuel was  $114.1 \text{ }\mu\text{g m}^{-3}$  while it was  $6.6 \text{ }\mu\text{g m}^{-3}$  for open type kitchen. The benzene concentration was significantly higher ( $p < 0.01$ ) in indoor kitchen with respect to open type kitchen using dung fuels. The wood fuel produces  $36.5 \text{ }\mu\text{g m}^{-3}$  of benzene in indoor kitchen. The concentration of benzene in indoor kitchen using wood fuel was significantly ( $p < 0.01$ ) lower in comparison to dung fuel. This method may be helpful for environmental analytical chemist dealing with GC–MS in confirmation and quantification of benzene in environmental samples with health risk exposure assessment.

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**Keywords:** Gas chromatography–mass spectroscopy; Indoor air; Benzene; GC–MS; MS/MS

## 1. Introduction

Benzene is an ubiquitous component in the environment that has been linked to adverse health effects particularly leukemia, plastic anemia, bone-marrow disorders in human and other cancers, even at low dose [1–4]. It is also toxic to the hematopoietic system [5] and causes acute myelogenous leukemia in population with occupational exposure. Combustion of biomass fuels produces a large number of air pollutants including benzene [6–8]. Therefore, it is essential to know the concentration of benzene emitted due to combustion of biomass fuels during cooking time. A number of methods [9–17] are available for analysis of benzene from ambient environment, but the more sensitive procedure of pre-concentration on charcoal followed by GC–MS analysis

is preferred [18]. GC–MS technique is being used in USA for the qualitative and quantitative analysis for methyl tertiary-butyl ether (MTBE) and benzene in gasoline [19–20]. A Carbotrap tube (2 mm) was used to determine volatile organic compounds (VOCs) in ambient air. Such compounds were desorbed and thermally analyzed with GC–MS [21]. With the use of GC–MS technique about 54 toxic hydrocarbons were quantified in the ambient air of Tehran [22]. Recently, Sinha et al. [23] reviewed application of the GC–MS for the analysis of air pollutants. No one reported GC–MS method in MS/MS mode for confirmation and quantification of benzene in indoor air with low detection limit. Therefore, present study aimed to develop suitable analytical technique for confirmation and quantification of benzene in indoor air samples and to assess the exposures to this compound to the rural population. In this paper we report GC–MS method operated in MS/MS mode for determination of benzene in indoor air emitted due to combustion of solid biomass fuels in different type of kitchens in rural village.

\* Corresponding author. Tel.: +91 79 22686351/52;  
fax: +91 79 22686110.

E-mail address: [sukeshnr.sinha@yahoo.com](mailto:sukeshnr.sinha@yahoo.com) (S.N. Sinha).

## 2. Materials and method

### 2.1. Chemicals and standards

Methanol (HPLC grade) and VOC standards were procured from Sigma–Aldrich Inc. USA. The purity level of standard and methanol was 99.9%. Ultra pure helium gas was used as carrier gas for GC–MS analysis. Personnel sampler (Airchek 52) and sorbent charcoal sample tubes (Cat. No. 226-01) used in this study were procured from SKC Inc., 863 Valley View Road Eighty Four, PA 15330, USA. A stock solution 10 ppm of VOC's standard was prepared in methanol. The concentration ranges of 0.002–2.0  $\mu\text{g ml}^{-1}$  were used for the standardization of the method.

### 2.2. Isolation of compound

Benzene was extracted from sorbent charcoal tube using methanol (1 ml) with ultrasonication. The methanol extract was analyzed by GC–MS technique. Instead of  $\text{CS}_2$ , the HPLC grade (99.9%) methanol was used for the isolation of sample for avoiding extreme human toxic effect, lower flash point ( $-34.4^\circ\text{C}$ ) and lower ignition point ( $37.7^\circ\text{C}$ ) of carbon disulfide as compare to methanol.

### 2.3. Chemical analysis by gas chromatography—mass spectroscopy

In order to develop more sensitive method for determination of concentration of benzene in indoor air, the MS method first attempted in GC–MS with electron impact auto ionization in scan mode. Interfering peaks from indoor air, poor chromatograms due to peak tailing, matrix effect, peak broadening, and poor sensitivity complicated this method. Therefore, a more sensitive MS/MS method was developed for confirmation and quantification of benzene produced in indoor air due to burning of different types of biomass fuels like wood and cow dung in different type of kitchen.

### 2.4. Gas chromatography

Varian CP-3800 gas chromatography equipped with Saturn 2000 (Varian Pvt. Ltd. USA) mass detector with data system was used for GC–MS analysis. Chromatography separation was carried out using a DB-5 capillary column supplied by Varian Pvt. Ltd. USA (30 m  $\times$  0.25 mm i.d. with the film thickness of 0.25  $\mu\text{m}$ ). The carrier gas was ultra pure helium at a flow rate of 1  $\text{ml min}^{-1}$  and split ratio was 1:10. The injector temperature was  $100^\circ\text{C}$  while the oven initial temperature was  $40^\circ\text{C}$  maintained for 2.50 min after injection, there after raised to  $150^\circ\text{C}$  at a rate of  $17^\circ\text{C/min}$ , maintained at 2.5 min. The total running time was 11.47 min. One microlitre sample was injected for analysis.

### 2.5. Mass spectroscopy (MS/MS)

Mass spectral analysis was carried out with Varian Saturn 2000 system in the EI mode with MS/MS ion preparation by using a mass range 40–200 amu background mass of 40 amu and mass scan rate equal to 1 s/scan. The used operating voltage for EI mass spectra was 1750 V. The transfer line, trap temperature and manifold were set at 270, 170 and  $40^\circ\text{C}$ , respectively. The calibration slope and SD were 6.259 and 0.054 for FC-43 mass calibration. The axial modulation voltage and emission current for MS have been used 4 V and 10 mA. For MS/MS ion preparation the parent ion storage was  $m/z$  78  $\mu$  and used excitation storage level was 35  $m/z$ , while the isolation window for the spectra was three  $m/z$ . The trap function was calibrated in MS/MS using ions at  $m/z$  69 (frequency: 259:900 kHz) and 131 (257:600 kHz). The segment starting time for benzene was 2.56 min and ending time was 3.10 min.

### 2.6. Quality assurance

Capillary gas chromatography with auto electron ionization mode with MS/MS ion preparation has been used to quantitative indoor air concentrations of benzene emitted due to burning of different type of biomass fuels. Five point calibration curves were obtained showing linearity in the used concentration range 0.2–2  $\mu\text{g ml}^{-1}$ . Accuracy was found very good along with standard deviation on response factors within 2%. The percentage recovery of this method was determined using benzene concentration in range of 0.2, 0.5, 1 and 1.5  $\mu\text{g ml}^{-1}$ . To check the quality assurance and carryover affect the blank samples and standards were injected after the analysis of every five-study sample.

### 2.7. Air sampling of benzene

Present study was executed in Valad village of Ahmedabad district (Gujarat), India, 20 km away from the known anthropogenic sources as well as industrial zone, where villagers used dung and wood as a fuel for the cooking purposes. The personal sampler fitted with activated charcoal sorbent tube with flow rate of 0.5  $\text{L min}^{-1}$  was used for indoor air monitoring in houses during cooking times (45–60 min depending upon the cooking activity of households) as per the reported method [18,24]. Separate samples were taken in indoor kitchen as well as open type kitchen in breathing zone. The sampler was placed in breathing zone, front of nose, and 30 cm away from the cooks near cooking activity to assess the exposure of benzene. A total of 26 samples were analyzed by GC–MS/MS to know the concentration of benzene emitted due to combustion of solid biomass fuels in indoor air.

### 2.8. Statistical analysis

The levels of benzene showed skewed type distribution therefore the logarithmic transformation of data was em-

ployed. Unpaired ‘*t*’ test was used on log transformed benzene levels for all type of comparisons.

### 3. Results and discussion

The GC–MS method in EI with MS/MS ion preparation was developed for the confirmation and quantification of benzene concentration in indoor air, emitted due to incomplete combustion of biomass fuel. Slight modification was made in the method reported by OSHA; 1987 for the estimation as well as environmental monitoring of benzene and these modifications were in flow rate of personnel sampler, solvent selection for extraction and selection of sensitive operational mode, i.e. MS/MS to achieve best measurement of pollutants. The chromatographic separation of volatile organic compound (standard) was best achieved using ultra pure helium at the flow rate of  $1 \text{ ml min}^{-1}$  as a carrier gas on fused silica DB-5 capillary column ( $30 \text{ m} \times 0.25 \text{ mm i.d.}$  coated with the film thickness of  $0.25 \text{ }\mu\text{m}$  film of a non-polar liquid phase). The injector temperature was  $100 \text{ }^\circ\text{C}$  while the oven initial temperature was  $40 \text{ }^\circ\text{C}$  increased to  $150 \text{ }^\circ\text{C}$  at a rate of  $17 \text{ }^\circ\text{C/min}$ . In this experimental condition benzene, toluene and xylene were resolved to base line separation

Table 1  
Benzene concentration ( $\mu\text{g m}^{-3}$ ) of different fuels in indoor and open type kitchen

Fuel type	<i>N</i>	GM	GSD	Minimum	Maximum
Indoor kitchen					
Dung	6	114.1	1.2	98.2	159.0
Wood	14	36.5**	1.3	22.9	49.6
Open type kitchen					
Dung	6	6.6**	1.5	4.0	11.2

GM: geometric mean, GSD: geometrical standard deviation, *N*: number of samples. All comparison were made using logarithm transformation of benzene.

\*\*  $p < 0.01$  when compared with dung indoor.

(Fig. 1). The presence of benzene was confirmed by using NIST library search as well as their retention time. The peak at  $m/z$  78 was assigned to the molecular ion peak of benzene (Fig. 2), which confirms the molecular weight  $78 \mu$ . The retention time (RT) of benzene is 2.967 min. The detection limit was as low as  $0.002 \mu\text{g/ml}$  with a S/N: 4 (S: 66, N: 14) for benzene, and can easily be achieved by confirmation and quantification in this experimental condition. The % recovery for this method was 88–92% using benzene concentration in range of 0.2, 0.5, 1 and  $1.5 \mu\text{g ml}^{-1}$ . The

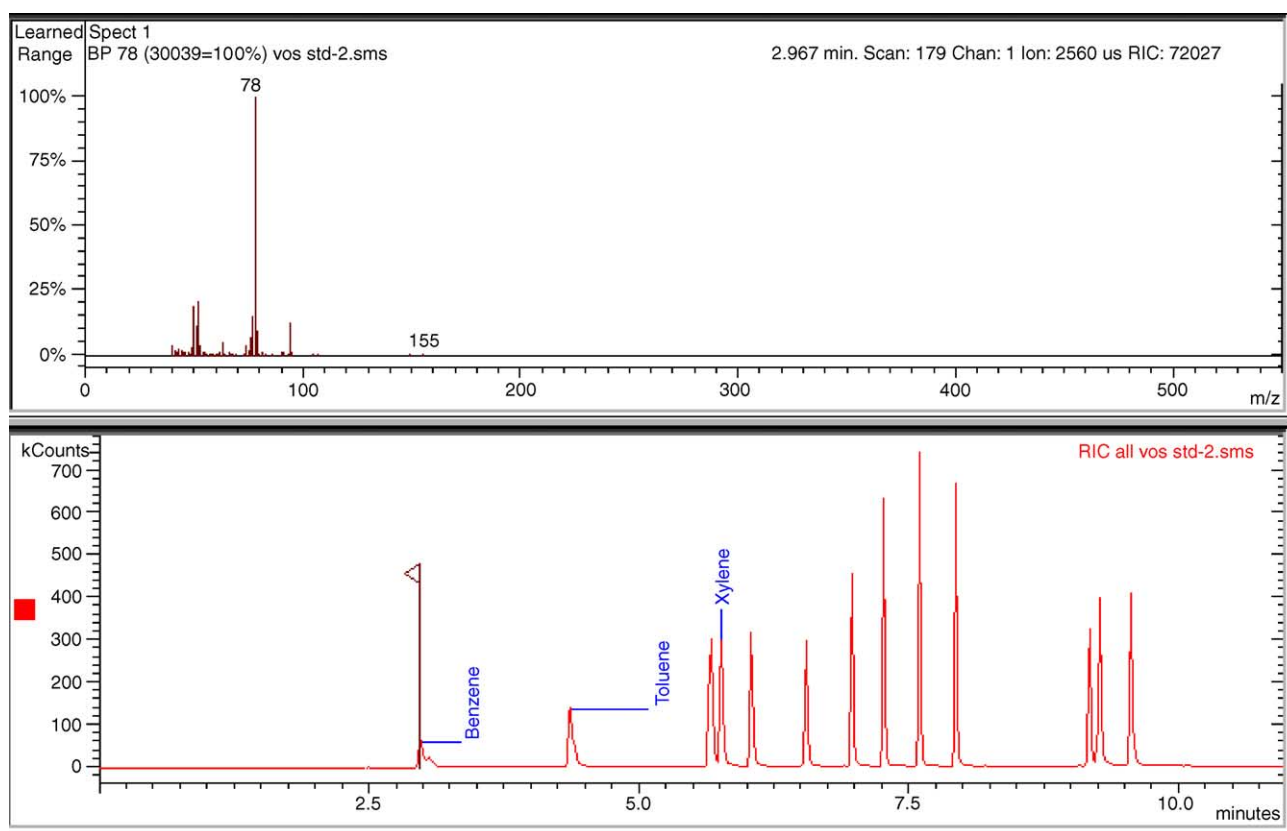


Fig. 1. GC–MS spectrochromatogram of standard of benzene, toluene and xylene on DB-5 capillary column ( $30 \text{ m} \times 0.25 \text{ mm i.d.}$  with the film thickness of  $0.25 \text{ }\mu\text{m}$ ) with carrier gas ultra pure helium at a flow rate of  $1 \text{ ml min}^{-1}$ , injection volume was  $1 \text{ }\mu\text{l}$ , retention time of benzene toluene and xylene were 2.967, 4.383 and 5.768 min, respectively. The molecular ion peak of benzene at  $m/z$   $78 \mu$ .

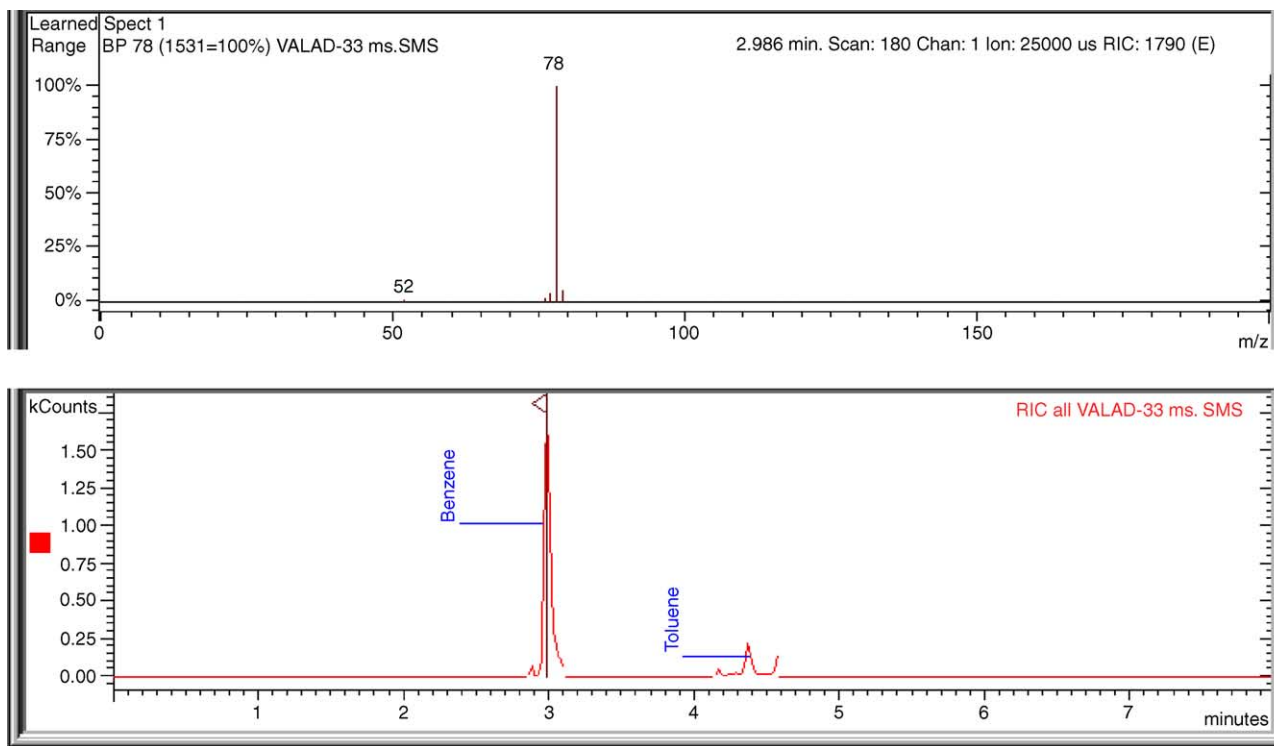


Fig. 2. GC–MS spectrochromatogram of study sample of benzene in MS/MS mode on DB-5 capillary column (30 m  $\times$  0.25 mm i.d. with the film thickness of 0.25  $\mu$ m) with carrier gas ultra pure helium at a flow rate of 1 ml  $\text{min}^{-1}$ , injection volume was 1  $\mu$ l, retention time of benzene and toluene were 2.967 and 4.383 min. Molecular ion peak of benzene at  $m/z$  78  $\mu$  in MS/MS mode.

calibration curve obtained having the correlation coefficient  $r > 0.998$ .

In this study the concentration of benzene was determined in breathing zone using different types of fuel in indoor kitchen as well as open type kitchen. The villager used two types of fuels (dung and wood) in indoor kitchen. Therefore, the separate samples were collected from indoor kitchen as well as open type kitchen to assess the exposure of cooks during cooking time. The personnel sampler was operated at flow rate 0.5 L  $\text{min}^{-1}$ . In almost all reported methods (Table 2),  $\text{CS}_2$  was used for extraction of benzene from activated charcoal tube in indoor samples but in our method first time we used methanol for the extraction of benzene from activated charcoal tube to avoid human toxic side effect of  $\text{CS}_2$ . Carbon disulfide easily explodes in air and also catches fire

readily because the flash point and Ignition point are  $-34.4$  and  $37.7^\circ\text{C}$ . Hence in our study the methanol was selected as extracting solvent instead of  $\text{CS}_2$  to take such type of precautions.

Table 1 shows the GM, GSD and range of benzene concentration of different type of fuels. The benzene ( $114.1 \mu\text{g m}^{-3}$ ) concentration for cooks in indoor kitchen using dung fuel was significantly higher in comparison to ( $6.6 \mu\text{g m}^{-3}$ ) open type kitchen. The level of benzene was  $36.5 \mu\text{g m}^{-3}$  for cooks using wood fuel in indoor kitchen. The test of significance shows that the benzene concentration among the dung and wood fuels in indoor air differ significantly ( $p < 0.01$ ). The benzene concentration of cooks also in open type kitchen differed significantly ( $p < 0.01$ ) for dung fuels. The finding of this study indicated that benzene produced due to burning

Table 2  
Analytical methods for the determination of benzene

Sample	Preparation	Analytical method	Detection limit	Reference no.
Air	Silica gel trap	Indicator tube	4.9 mg/ $\text{m}^3$	[9]
Air	Charcoal trap, $\text{CS}_2$ desorption	GC–FID	3.2 $\mu\text{g}/\text{m}^3$	[10]
Air (ambient)	Tenax GC sorbent, thermal desorption,	Capillary GC–MS computer analysis	NR	[11]
Air	Direct injection	UV spectrometry	800 $\mu\text{g}/\text{m}^3$	[16]
Air	Tenax or cryogenic trap, thermal desorption	GC–FID	NR	[17]
Air	Solid sorbent trap, thermal desorption	GC–MS	NR	[14]
Air (occupational)	Activated charcoal sorbent, $\text{CS}_2$ desorption	GC–FID	0.64 mg/ $\text{m}^3$	[13]
Air (ambient)	Porous polymeric sorbent, thermal desorption	GC–FID	0.96 $\mu\text{g}/\text{m}^3$	[15]

of dung was significantly higher than that of wood used as fuel. The level of benzene exposure was high in dung fuel as compared to wood due to the fact that the structural composition and particle size distribution are different. Thus the present study has provided another most sensitive method for the estimation of benzene in indoor air by GC–MS. The some reported methods for the estimation of benzene is summarized for comparison (Table 2). The table showed that the method reported by different workers has high detection limit with less percent recovery. Very few methods have been used for benzene estimation in indoor air. The reported GC–FID technique is more sensitive than reported GC–MS technique but GC–FID [25] is not confirmatory technique. Our study showed that GC–MS in EI mode with MS/MS ion preparation is the best technique for the confirmation as well as quantification of benzene in indoor air at ppb level.

#### 4. Conclusion

The gas chromatographic mass spectrophotometer system in EI mode with MS/MS ion preparation described here is sensitive and specific for the monitoring of benzene exposure in indoor air and applied to investigate its concentrations during the use of different type of biomass fuels in cooking time. The methanol is the better choice as a solvent for extraction of benzene from indoor air instead of carbon disulfide, which is more toxic and volatile solvent than methanol. The GC–MS analysis in MS/MS ion preparation used in this study may be adapted to most environmental laboratories for analysis of benzene in indoor air with health risk assessment. The most important finding in this study is wood as a fuel produces less benzene than dung as a fuel. The wood may be the better choice as a fuel in rural population as compare to the dung fuel.

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