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VALIDATED METHODS FOR VOCS DETERMINATION BY GC-MS

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Qualitative and quantitative methods for measuring volatile organic compounds by pre-concentration techniques followed by gas chromatography–mass spectrometry (GC–MS) analysis were developed. The MS was operated in the SIM and scan modes. The compounds of interest eluted at the column temperature of 30 ºC. For the quantitative work, the methods were validated and showed good linearity, precision, accuracy, LOD for the compounds studied. Validation of the methods demonstrated the ability to identify and to measure reliably the yields of BTEX, THM, and other VOCs, by using the proper internal standard.

Introduction

Volatile organic compounds (VOCs) are of concern since many are toxic and they may also be persistent in the environment. The main source in the environment is petrol, vehicle traffic and indoors, cigarette smoke. They are also present in small quantities in drinking water and food, in paints and adhesives. The methods are validated for the investigation of VOCs in drinking water or air by the emissions from different materials, adhesives, combustion sources or tobacco smoke.

Benzene, toluene, ethyl benzene and xylene (BTEX) are widespread pollutants of which the main source in the outside environment is vehicle traffic and indoor the cigarette smoke. They are also present in small quantities in drinking water and food, in painting substances or adhesives. All of these sources contribute to pollution of indoor environments [1-4]. Vehicle movement was confirmed as the dominant influence on benzene and associated VOCs in the atmosphere. The benzene outdoor maximum limit recommended by the European Community is 10 $\mu g \cdot m^{-3}$. Occupational maximum exposure limit is 16 $mg \cdot m^{-3}$. BTEX and VOCs could be find in water, soil, substances of abuse, cigarette smoke, adhesives, in paint and varnish shops, breath or blood. It is calculated that a typical smoker inhales 2 mg benzene daily, compared to 0.2 mg per day for the nonsmoker.

Trihalomethanes (THMs) are volatile disinfection by-products (DBPs) in drinking water or recreation waters [5-7]. Chlorination by-products in drinking water are very toxic, human carcinogenic compounds. The ‘high priority’ DBPs include halomethanes, haloacetonitriles, haloketones, haloacids, and halonitromethanes, chloral hydrates, chloropicrin. The THMs (CHX_3, X=halogen)

are: chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$). The maximum contamination level of 100 μgl^{-1} for total trihalomethanes in drinking water, set by US Environmental Protection Agency (USEPA) in 1979 was lowered to 80 μgl^{-1} and is considered to be lowered to 40 μgl^{-1}. The techniques used for the determination of DBPs in drinking water include water extraction procedure as liquid-liquid extraction (LLE), purge and trap or headspace followed by gas chromatographic (GC) separation and electro capture detection (ECD) or mass spectrometric (MS) detection.

In the last years the number of procedures using extraction of organic compounds from air and water has increased. Trace analyses involve pretreatment: of the samples, extraction and concentration procedure to increase the analyte concentration to within instrument sensitivity. The extraction procedure, internal standard selection and method validation are the steps to follow for quantitative analyses by using gas chromatography-mass spectrometric technique (GC-MS).

The preconcentration step could be: (1) solvent extraction (2) headspace analysis, (3) purge and trap, (4) solid phase extraction (SPE) (column and discs) (5) solid phase microextraction (SPME) and some other modern technique. Gas chromatography-mass spectrometry (GC/MS) and GC are the most used quantitative methods for VOCs levels detection in the indoor air and drinking water.

The aim of the paper is to demonstrate the validation of analytical methods for the determination of some carcinogenic VOCs as THMs or BTEX..

Experimental

Extraction procedure

Liquid-liquid extraction (LLE for THMs determination): The water sample is shaken with an immiscible organic solvent, methyl-*tert*-butyl ether (MTBE).

Purge and trap-GC-MS method

The purge and trap concentrator was active charcoal. Standard solutions or drinking water was extracted with a 12 ml/min He, 30 min and followed by desorbtion at 120ºC for 3 min in a U tube containing 50µl dichlormethane. The organic layer is injected into the chromatograph.

After extraction, a known quantity of internal standard (pyridine for BTEX, benzene for THMs) was added to the supernatant and analyzed.

Apparatus

A Trace DSQ Thermo Finnigan quadrupole mass spectrometer coupled with a Trace GC was used. A Rtx-5MS capillary column, 15 m or 30 m length x 0.25 mm, 0.25µm film thickness, by using a temperature program from 30ºC kept for some minutes, then increased to 300ºC, in selected ion monitoring (SIM) or scan

mode. The GC/MS interface line and the ion source were maintained to 200^{O}C and 250 ^{O}C. Electron energy was 70eV and electron emission 100μA.

In the SIM mode [Fig.1] the following important ions are used for THMs: m/z 83 and 85 for chloroform, m/z 83, 85, 129 for dichlorobromomethane, m/z 127, 129 for dibromochloromethane, m/z 129, 173, 252 for bromoform and m/z 78 for the internal standard (benzene) [Fig.2].

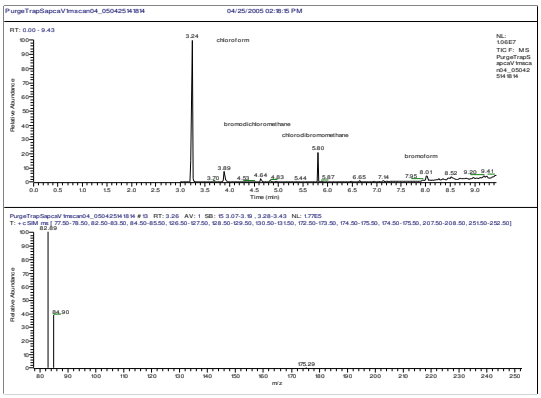

Fig.1. SIM chromatogram of THMs: chloroform, dichlorobromomethane, chlorodibromomethane, bromoform. Selected ions from the mass spectrum of chloroform, 3.26 min.

For BTEX, in the SIM mode, the following important ions from the mass spectra of benzene, toluene, ethyl benzene and xylene [Fig.3] were used: m/z 78 for benzene, m/z 91 and 92 for toluene, m/z 91 and 106 for ethyl benzene and xylenes and m/z 52 and 79 for the internal standard. The method was validated in the range 0 – 100 μg and linearity, precision, accuracy and limit of detection (LOD) parameters were studied.

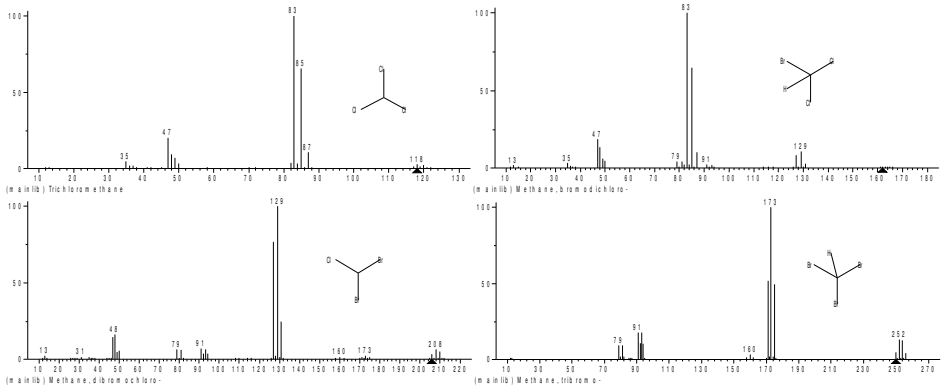

Fig. 2 The mass spectra of THMs chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$).

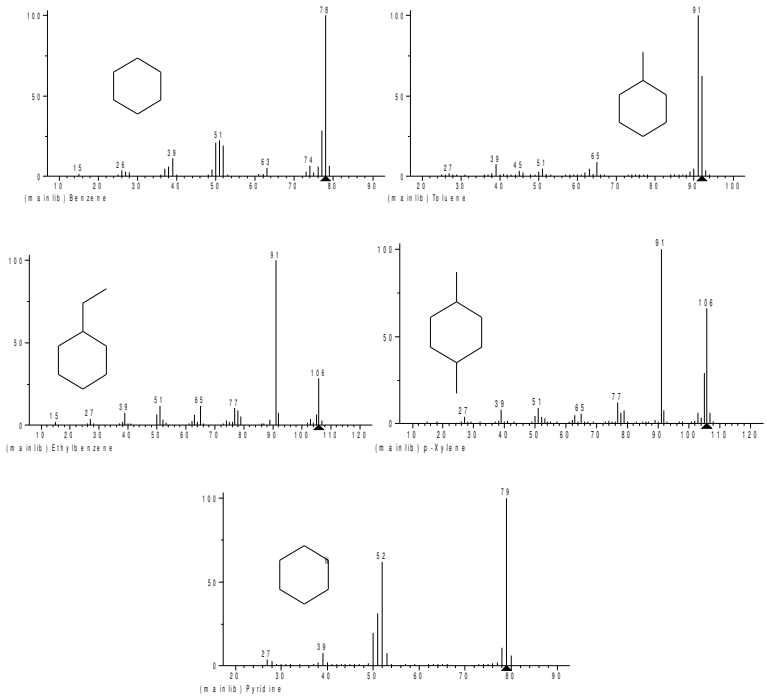

Fig.3 Mass spectra and chemical formula of BTEX and the internal standard (pyridine)

Results

Methods validation

Aliquot samples containing 20, 100, 300 and 600 ng and 20, 40, 60, 80, 100μg BTEX were adsorbed with a pump on 300 mg active coal at a flow rate of 60 $mL \cdot min^{-1}$ and then were extracted in 1ml dichloromethane. 1mg of pyridine as internal standard was added at each sample.

Table 1 presents the linearity parameters obtained in the range 0 - 100μg and 0 - 600 ng for BTEX, by using 1mg pyridine or respectively 20 ng pyridine as internal standards and for chloroform, in the range 0 – 200 μg/l..

Precision studied for the aliquot samples of 40 and 80 μg showed R.S.D. values between 6.5 – 22 % and respectively between 7.5-25.8%. The accuracy R.S.D. calculated were between 7.6-24.4% for the sample of 40μg and between 2.5-24.9% for the sample of 80 μg. Table 2 presents the results obtained for precision and accuracy. A limit of detection of 0.01 μg was obtained for the VOCs studied.

The separation chromatogram for BTEX in the SIM mode is presented in Fig. 4. A 9 minute temperature program was used. Some volatile compounds identified in

the tobacco smoke extract are shown in Fig.5. Table 3 shows the BTEX levels measured in the air contaminated with varnish or adhesive, as well as the indoor pollutants found in a shoe maker workshop. In the last column, the ppm levels for an outdoor air sample were obtained after a short sampling time, 1 L air, in a small parking area, 10 m to a truck with engine running at rest. Table 4 compares some indoor air values for BTEX measured in the mainstream smoke of a Winston cigarette, in the side stream smoke of a Kent cigarette, in the laboratory room (40 m^3) and in a pub. The laboratory room was not ventilated during the experiment and the pub was very poor ventilated.

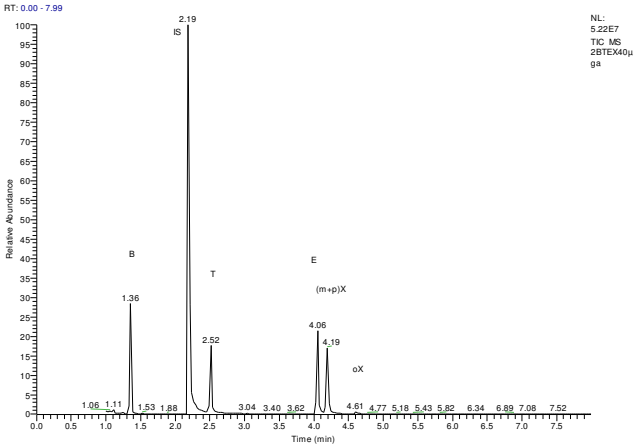

Fig.4 Chromatographic separation of BTEX and the internal standard (IS). 9 min temperature program: 30ºC (2 min), 10ºC/min to 70 ºC then 50ºC/min to 220ºC, SIM mode

Discussion

The SIM-GC/MS methods developed for VOCs determinations in indoor air and drinking water are good and rapid. The validation of the methods gave good values for precision, R.S.D. of 6.5 – 25 % and accuracy, R.S.D. between 2.5-24.9%. The limit of detection was 10 ppb.

The methods tested for applications showed ppm indoor values or µg/cigarette values for tobacco smoke (Table 3 and 4). The precision of the repeated measurements gave R.S.D. lower than 10 %.

The measurement of THMs in our town distribution system showed the following values: $CHCl_3$: 90 µg/l; $CHCl_2Br$:3.9 µg/l; $CHClBr_2$:1.7µg/l.

Table 1

Linearity for VOCs

Range: 0-100µg (IS: 1mg pyridine)		
Compound	Regression curve	r
B	y=0.0039x+0.0092	0.932
T	y=0.0039x+0.0123	0.927
E	y=0.0047x+0.0235	0.923

X	y=0.0038x+0.021	0.922
Range: 0-600ng (IS: 20ng pyridine)		
B	y=0.0002x+0.05	0.98
T	y=0.0001x+0.39	0.95
E	y=0.0001x+0.02	0.97
X	y=0.0003x+0.5	0.98
Chloroform	y=0.9121x+0.0313	0.975

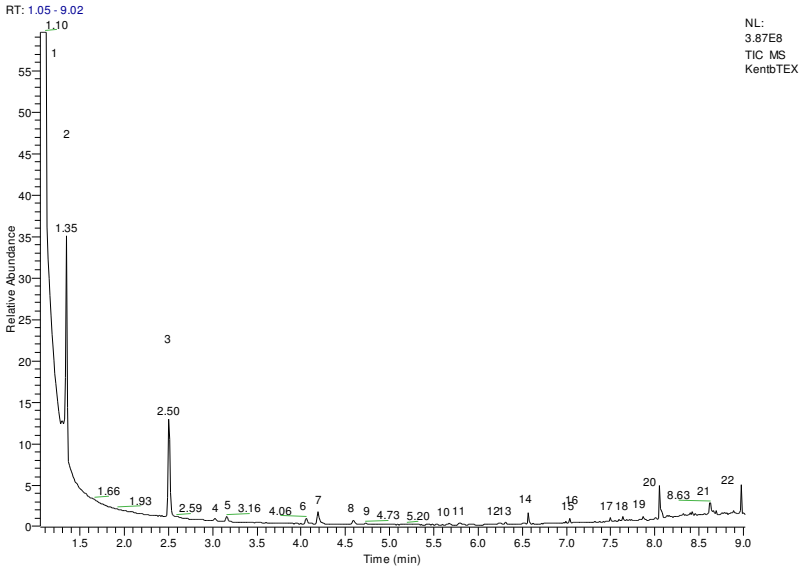

Fig.5 The VOCs identified in a tobacco smoke extract (SCAN mode): 1. chloroform; 2.benzene; 3. toluene; 4.octane; 5.tatrachloroethylene; 6.ethyl benzene; 7. (m+p) xylene; 8 o-xylene; 9. nonane; 10. camphene; 11. 1,3,5 trimethylbenezene; 12. 1,2,3 trimethylbenzene; 13. decane; 14. limonene; 16. undecane; 17. dodecane; 19. cinnamaldehyde; 20. nicotine; 21. dibutylphtalate; 22. nonadecene

Table 2

Precision and accuracy of the method for indoor air BTEX

Compound		Concentration(μg)		Comp/IS		Precision	Accuracy
	n	Added	Measured		SD	RSD(%)	RSD(%)
B	4	40	43.02	0.18	0.04	22.2	7.6
T	4	40	36.75	0.16	0.01	6.5	8.1
E	4	40	30.91	0.17	0.02	11.8	22.7
X	4	40	30.23	0.13	0.02	15.4	24.4
B	3	80	99.9	0.40	0.03	7.5	24.9
T	3	80	75.4	0.31	0.08	25.8	5.8
E	3	80	82.0	0.41	0.05	12.2	2.5
X	3	80	75.2	0.31	0.05	16.1	6.0

Table 3

BTEX (ppm) determination in some indoor and outdoor air measurements (n=2)

Compound	varnish	adhesive	shoe maker		outdoor air
B	38.81	60.15	21.43	0.024	
T	41.31	157.86	95.85	0.001	
E	0.55	-	1.5		
X	1.79	2.56	0.7		

Table 4

BTEX determination in tobacco smoke extracts (n=2)

Compound	Winston µg/cig.	Kent ppm.	lab. ppm	pub ppm
B	14.86	44.6	21.26	5.97
T	229.04	76.36	15.3	37.38
E	0.5	4.88	5.06	0.21
X	37.69	3.99	2.55	-

Conclusions

The methods developed demonstrate that GC-MS technique is the best choice for VOCs quantitation at trace levels.

References

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