Evaluation of the Presence of Volatile Organic Compounds in the Outdoor Air in Tîrgu Mureș

Croitoru MD, Țepeș Veronica, Kincses Ajtay Mária, Fülöp Ibolya

Department of Toxicology and Biopharmacy, Faculty of Pharmacy, University of Medicine and Pharmacy, Tîrgu Mureș, Romania

Objectives: Many toxic compounds are present in automobiles exhaust gases. Concentration of these compounds is markedly increased when a defective engine is running. Presence of exhaust gases was linked with asthma, neurotoxicity, cancer and other serious health hazards. The goal of this work was to measure the concentration of volatile organic compounds that are present in the atmosphere when a defective vehicle passes by.

Methods: A head space gas chromatographic technique coupled with flame ionization detection was used to measure total concentration of volatile organic compounds into the air.

Results: Unexpectedly high concentrations of volatile organic compounds, up to 1.04 mg C/L of air, were measured in outdoor air. Every day high number of children is passing through these tested areas when they go to school or back home from school being exposed to such high concentrations of pollutants.

Conclusions: Faulty cars are the major source of volatile organic compounds and children can be affected by exposure to peak concentrations of such substances.

Keywords: gas chromatograph, volatile organic compound, VOC, concentration, outdoor air

Introduction

Volatile organic compounds (VOC) are known pollutants of both indoor and outdoor air. Indoor presence of these compounds is due to evaporation from furniture, building materials and is causing the "sick building syndrome" [1].

Outdoor presence of these compounds is mainly due to incomplete burning of hydrocarbons in internal combustion engines. A broad range of VOCs have been identified in both diesel and gasoline engines. Health effects of exposure to the entire mixture have not been characterized but the toxicity of many individual components is well understood. Some of the compounds present in exhaust gases are: 1,3-butadiene (irritating, cardiovascular disease risk, human carcinogen), benzene (leukemia, cancer, neurotoxicity), toluene (neurotoxicity), formaldehyde (irritant, sensitizer, probable human carcinogen), benzo(a)pyrene (immunosuppressant, anemia, human carcinogen), aliphatic hydrocarbons (hepatotoxicity, neurotoxicity) [2–6].

Asthma incidence in young population is correlated with the exposure to exhaust gases [7,8].

There are no regulations regarding the maximum amounts of VOC that can be present in urban regions. Sometimes individual compounds concentrations are restricted.

Strict regulations that restrict automobiles emissions are employed since Romania joined European Union. However, on a daily basis one can see cars that emit high amounts of smoke into the air. The smoke can be organoleptically detected sometimes for minutes after the car passes. Further more, passengers of the cars that follow such a polluting vehicle can be exposed to high amounts of pollutants.

Correspondence to Mircea Dumitru Croitoru
Email: croitorumircea@yahoo.com

Gas chromatography (GC) with flame ionization detection (FID) or mass spectrometry detection (MS) are used to quantify these compound into the air [9,10].

The goal of this paper was to measure the amounts of VOCs present in:

- outdoor after an intense polluting vehicle pass by. (Polluting vehicle was considered any vehicle that emits large amounts of smoke. Sample collection was made on the sidewalk.)
- inside a car that follows such a polluting vehicle. In order to do that authors followed a car that emitted visible amounts of smoke.

GC-FID was selected as apparatus suitable for this analysis.

Methods

Head space GC system with FID: THERMO SCIENTIFIC TRACE GC ULTRA Thermo-Finnigan. DB-624 30 m column.

Reagents

- GC purity tholuene, Merck KgaA Germany
- N-heptane p.a., Merck KgaA Germany.

GC system setup:

- analysis time: 33 minutes
- initial temperature: 50°C
- heating rate: 15°C/min
- column final temperature: 250°C
- injection mode: splitless
- injection volume: 1 ml from the gas phase
- mobile phase: nitrogen 2 ml/min
- hydrogen debit: 35 ml/min
- air debit: 350 ml/min
- detector temperature: 250°C

Table I. Characteristic retention times observed on chromatograms

No	Retention time
1.	8.61
2.	9.59
3.	9.70
4.	10.55
5.	10.98
6.	11.95
7.	12.54

Sample treatment:

- samples were collected from the sidewalk at about 1.7 m from the ground in headspace vials, by removing (with a tube inserted into the vial) gas about 20 times the volume of vial. This way it was ensured that no residual air remains into the vial and composition of gas in the vial is similar to that in the studied air. Samples were taken in comparable meteorological conditions.
- vials were immediately hermetically sealed and transported to the laboratory for the analysis

Standard gases:

- in two 2.8 l flasks, containing aluminium pellets, 20 µl of toluene or 20 µl of heptane were introduced. After shaking the flasks for two minutes a sample was collected in a headspace vial (inserted into the bottom of the flask) that was immediately airtight sealed. Sampling was made in a similar manner as the tested air.

Results

Method performance evaluation

Lacking an MS detector we were not able to identify each peak that appeared on chromatograms. Results were calculated by summing all peaks area and are given as mg of volatile carbon found in each liter of air: mg C/L. Figure 1 shows a typical chromatogram obtained during the study.

Linearity

Since FID detector shows a good linearity over large range of concentrations we decided to not obtain a calibration curve but to use a single point standard.

Table II. Measured VOCs concentrations

Sample source	Concentration mg C/L air	Sample type	Number of samples
1 Dec 1918 Blvd	0.60–1.04	Outdoor	4
22 Dec 1989 Street	0.74–0.83	Outdoor	3
Gh Doja Street	0.37–0.75	Outdoor	8
Gh Doja Street	0.72–1.00	Indoor	5
Revolutiei Street	0.57–0.76	Outdoor	10
1848 Blvd	0.42–0.84	Outdoor	5
City center	0.50–0.64	Outdoor	5
Papiu Ilarian Street	0.50–0.92	Outdoor	5
Gh Marinescu Street	0.52–0.85	Outdoor	5

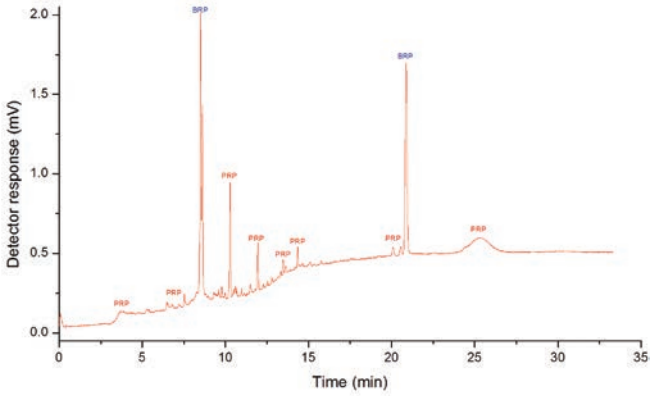

Fig. 1. Typical chromatogram obtained during the study

Response of the FID detector to the amount of carbon present in the samples was evaluated using the two standard gasses (toluene, heptane). Average detector response for a carbon concentration in air of 1 mg/L was 1.95 × 106 µV*s (microvolts × second). Difference between hydrocarbons was insignificant. Repeating the standards analyses 5 times, the coefficients of variation were less than 4%.

Results were calculated using formula: C_{air} = Area air/ADR; where C_{air} is the concentration of VOCs in air expressed as volatile organic carbon, Area air is the sum of all peak areas, ADR is the average detector response.

Specificity

Since FID detector is unable to detect other atoms than carbon a good specificity is ensured for VOCs.

Air samples were collected in areas that were considered not polluted (blanks). Peaks that appeared in the blanks were subtracted from the calculations.

Lower limits of detection and quantification (LOD and LOQ)

LOD and LOQ were not computed since the results are sums of areas of peaks. All peaks taken into calculations were higher than 10 times the height of noise and all samples contained concentrations far beyond the limits of the method.

VOCs concentrations

Seven peaks were common to almost all chromatograms (Table I, Figure 1). This observation suggests that regardless the vehicle type, there is no significant difference between the compounds released into the atmosphere.

Using the described method we were able to measure high amounts of VOCs into the air of Tîrgu Mureş. Highest concentration measured was 1.04 mg C/L. The results are summarized in Table II.

Discussions

Our results show that malfunctioning vehicles can significantly contaminate air in the major cities. Presence of these kinds of compounds into the air can be a health hazard especially for children, whom can be sensitized. The sensitization induced by VOCs is a risk of developing airways,

hematological and neurological problems [5–8]. VOC concentrations measured during this study are certainly a health risk, and such concentrations can be present for minutes in the air in the absence of wind.

Samples were taken from places where usually children pass by when they walk to school or back home. Results show that they are certainly inhaling on an every day basis these compounds.

When samples of air are taken by monitoring authorities, this is done by passing slowly large volumes of air through an adsorbent. This way only an average concentration can be computed and peak values are lost. Unfortunate those peak values can affect the health of people that pass by.

Toxicologically important concentrations were recorded in cars that follow a polluting car. This means that drivers are as affected by this type of pollution as much as pedestrians.

Unfortunate literature lacks data regarding VOC determination in the cities air; there are available data only for individual compounds measurements. This is probably due to the fact that limits are stated for individual compounds only not for VOC as a mixture. Most of the accepted values are in the ppb range but our results exceed sometimes the ppm levels. This means that measured concentrations are of toxicological importance.

Conclusions

Concentrations of VOCs in the air can be easily monitored by using a GC-FID, and direct gas phase analysis should also be made to observe peak concentrations.

The problem of malfunctioning vehicles is an important issue in Târgu Mureş and probably other major cities in Romania affecting especially young population. Such pollution can be easily reduced if authorities would be interested in maintaining a reasonable air quality.

References

1. Sundell J, Levin H, Nazaroff WW, Cain WS, Fisk WJ, Grimsrud DT, Gyntelberg F, Li Y, Persily AK, Pickering AC, Samet JM, Spengler JD, Taylor ST, Weschler CJ. Ventilation Rates and Health: Multidisciplinary Review of the Scientific Literature, Indoor Air 2011; 21(3):191-204.
2. xxxx State and Federal Standards for Mobile-Source Emissions, The National Academies Press, Washington DC, 2006.
3. Goel SK, Rao GS, Pandya KP. Toxicity of n-hexane and n-heptane: some biochemical changes in liver and serum. Toxicol Lett 1982;14:169-74.
4. Takeuchi Y, Ono Y, Hisanaga N, Kitoh J, Sugiura Y. A comparative study on the neurotoxicity of n-pentane, n-hexane, and n-heptane in the rat. Br J Ind Med 1980;37:241-7.
5. Filley CM, Heaton RK, Rosenberg NL. White matter dementia in chronic toluene abuse. Neurology 1990;40:532-534.
6. Maffei F, Angelini P, Carbone S, Cantelli F, Mattioli G. Effects of environmental benzene:micronucleus frequencies and hematologicl values in traffic police working in an urban area. Mutat Res 2005;7:1-11.
7. Modig L, Forsberg B. Perceived annoyance and asthmatic symptoms in relation to vehicle exhaust levels outside home: a cross-sectional study. Environ Health 2007;6:29.
8. Bonay M, Aubier M. Air pollution and allergic airway diseases. Med Sci (Paris) 2007;23:187-92.
9. Tiwari V, Hanai Y, Masunaga S. Ambient levels of volatile organic compounds in the vicinity of petrochemical industrial area of Yokohama, Japan. Air Qual Atmos Health 2010;3:65-75.
10. Ly-Verdú S, Esteve-Turrillas FA, Pastor A, de la Guardia M. A passive sampling-based analytical strategy for the determination of volatile organic compounds in the air of working areas. Anal Chim Acta 2010;677:131-9.