

RAPID DETERMINATION OF INDOOR AIR CONTAMINANTS IN SHOE SHOPS USING PHOTOIONIZATION DETECTORS

VICTOR BOCOȘ-BINȚINȚAN^a, ALINA SMOLENSCHI^a,
ILEANA-ANDREEA RAȚIU^{a*}

ABSTRACT. Recently, indoor air quality (IAQ) has become a serious concern. More and more people are facing health problems due to the poor air quality at the workplace; most of them are exposed to pollutants without even realizing it. Therefore, it is important to monitor the indoor air quality to prevent an unsafe environment. In the shoe making process, various volatile compounds – like toluene, found especially in adhesives – are used. These chemicals tend to slowly desorb from the final products and to accumulate ultimately inside the shoe shops. We report here the total volatile organic compounds (tVOCs) that are prone to be ionized by the UV radiation; measurements were performed over eight weeks inside six shoe shops located in Cluj-Napoca, Romania, with a ppbRAE Plus instrument manufactured by RAE Systems Inc. USA. We found with this ultra-sensitive photoionization detector (PID) maximum concentrations up to 7 ppmv of tVOCs (isobutene units) in air for each shoe shop investigated. The obtained results demonstrate that people working in the selected shoe stores may be exposed to significant tVOCs concentrations during a working day. Thus, PID devices are useful tools for quickly surveying the indoor air quality.

Keywords: *photoionization detection PID, indoor air quality IAQ, volatile organic compounds VOCs, toluene.*

INTRODUCTION

People spend most of their life (80-90%) in indoor spaces, such as houses, cars, office buildings and other public spaces. If we assume that people inhale more than 22 m³ of air per day, the contaminants present in the air can constitute a serious threat to their health. The most common indoor air quality problems in buildings were already considered, such as insufficient ventilation rate, too high particle concentration, poor filtration effectiveness and hygienic conditions [1].

^a Babeș-Bolyai University, Faculty of Environmental Science & Engineering, Str. Fântânele nr. 30, 400294 Cluj-Napoca, Romania

* Corresponding author: andreea_ratiu84@yahoo.com

The World Health Organization (WHO) estimates that more than 30% of all buildings where commercial activities are running have problems with indoor air quality. Indoor air pollution in homes, public buildings and offices is produced mostly by activities of the occupants of these spaces and by using various devices, chemicals, clothing, by releasing gas phase compounds from structural or decorative materials, and also by intrusion of outdoor pollutants [1].

Pollutants from the indoor environment may pose an important stress on human health and welfare. When they reach high concentrations, following acute or chronic exposure they can cause discomfort, irritation and illness [2]. One of the most dangerous category of VOCs, the BTEX group (benzene, toluene, ethylbenzene and xylenes), receives special attention, due to their toxicity. Exposure at work can take place for instance in the industry – such as printing, furniture and footwear. The most dangerous of these is benzene, a carcinogenic compound; therefore, its use was banned in several applications [3]. Toluene is used in adhesives, the dilution of the dyes, paint industry, as an additive for gasoline, etc. Acceptable concentration of volatile organic compounds in indoor air is between 0.2-0.5 mg m⁻³ [4]. Toluene is an aromatic hydrocarbon widely used in footwear industry; it is also found sometimes as a metabolic product by some bacteria [5]. Toluene C₇H₈ (CAS No. 108-88-3, MW 92.14 g mol⁻¹) is a colorless, flammable and water insoluble liquid (m.p. -93°C; b.p. 110-111°C; density 0.865 g cm⁻³ at 25°C); it is volatile (vapor pressure of 22 mm Hg at 20°C) and its vapors are heavier than air (vapor density: 3.2 vs. air). Odor threshold for toluene is about 3 ppm_v [6]. The first effects of toluene exposure can be observed at a concentration of ca. 50 ppm_v. Exposure to 100-200 ppm_v (375-750 mg m⁻³) is associated with headache, respiratory irritation; at concentrations of 400 ppm_v one may experience eye irritation, vomiting, ataxia, and dizziness. Chronic exposure of personnel at toluene concentrations of 30-130 ppm_v (113-488 mg m⁻³) can have adverse effects on hearing and visual system (color differentiation) [7]. In the U.S.A., the Occupational Health and Safety Administration (OSHA) indicates an Immediately Dangerous To Life or Health concentration (IDLH value) of 500 ppm_v, and a permissible exposure limit (TWA value) of only 10 ppm_v (37.5 mg m⁻³) [8]. In order to limit human exposure to BTEX group and to toluene especially, it is imperative that their sources can be detected, identified and removed/diminished.

Some rapid instrumental techniques suitable for detecting pollutants in indoor air are cationic sensors („hot bead”), colorimetric techniques, electrochemical sensors, or photoionization detectors. A hybrid, portable sensor which combines two orthogonal sensing principles (a selective molecular binding with a microfabricated quartz tuning fork detector, and then separation of analytes with a column), was developed for monitoring vapors of BTEX in air in the presence of interferents, at ppb_v levels [9].

The PID utilizes ultraviolet light to ionize gas molecules, and is commonly employed for quick, real-time detection of volatile organic compounds (VOCs). Preliminary studies for the analysis of total VOCs were undertaken, to evaluate the

performance characteristics of a portable analyzer equipped with a PID; they successfully demonstrated the possibility of using PID application for indoor environments that can be made fairly effectively under certain environments such as a newly built apartment [10]. In another study, three ppbRAE PGM-7240 PIDs were employed to concurrently measure the spatial and temporal distributions of ethanol concentration from a gas-pollutant leaking source with the aims to examine the pollutant dispersion flow field in a clean room [11].

The PID technique may be used in stand-alone instruments, but PID devices are also used in tandem with other analytical instruments, such as gas chromatographs (GCs). Cost-effective indoor air quality surveys and making on-site decisions to control VOC emissions were studied [12]; one determined concentrations of five target VOCs (BTEX and hexane) in several buildings in Waterloo, Canada, using solid-phase microextraction technique. Fast separation and speciation of common indoor air pollutants was possible with the use of a modified portable GC instrument, equipped with a PID, a FID, and a dry electrolytic conductivity detector in series. The detection limits for the target compounds in air were between 1 and 9 ppb_v [12]. Using the same instrumentation and technique described in [12], monitoring and analysis of VOCs, formaldehyde, and particulate matter in air were done by Koziel et al.; concentrations measured were as low as 700 parts-per-trillion and the authors considered their work as being a simple approach for fast, cost-effective sampling and analysis of common VOCs in indoor air [13].

PID devices in tandem with gas chromatography/mass spectrometry (GC/MS) were often used in the analysis of environmental pollutants. Volatile coal tar and petroleum hydrocarbons, and an integrated system for detecting pollutants on-line, in real-time by photoionization detection and quantitation by GC/MS was described [14]. Ghira et al. detected very low levels of pyridine vapors in controlled atmospheres from indoor air [15], using both PID and IMS (Ion Mobility Spectrometry), sensitive and powerful analytical techniques with multiple applications in trace detection.

Talking about the occupational exposure to organic solvents, dust, chromium, degradation products of synthetic materials, in particular about people working in shoe & clothes, electronics, food, or cosmetics shops Several studies have shown the presence of chemicals (such as toluene, benzene, or n-hexane) in urine and/or blood samples [16-18]. Studies have been undertaken on the toxicity of shoe soles [16], the exposure of persons who work in indoor environments such as the shoe stalls at dust, portable gas ranges, organic solvents, adhesives and shoe polish [17]. Neurophysiological and psychological disorders caused by occupational exposure to organic solvents were also addressed [18].

The microenvironments of a multi-store shopping mall in Guangzhou, China, were analyzed using a thermal desorption system and a GC-MS system in order to verify the VOCs produced by indoor emission sources. The fast-food court and a leather products department store have had the highest concentrations

of benzene, toluene, ethylbenzene, xylenes and chlorinated hydrocarbons. The authors considered that the emission sources of monocyclic aromatic hydrocarbons might include cooking, while chlorinated hydrocarbons were possibly connected with their use as cleaning agents or deodorizers. [19]

However, there is no doubt that leather and several other materials (textile, rubber and plastic) from which the shoes are made, plus the adhesives used, embed a wide range of different chemicals; consequently, there are health risks associated with the use of products and with the exposure of personal employed in shoe shops, as well. Unfortunately the most often there is insufficient knowledge about which chemical substances these products contain; also, the properties of these substances are in many cases not known in sufficient detail. This lack of knowledge can potentially affect the human health and the environment.

Because nowadays the effects of harmful substances on human health and well-being represent a major topic of interest to scientists, in the present study we aimed to investigate in real time the indoor air quality of six shoe shops from Cluj-Napoca, Romania. For this purpose we measured total volatile organic compounds prone to be ionized by the UV radiation (tVOCs) inside the shoe stores located in different points of Cluj-Napoca, over eight weeks, using a ultra-sensitive PID detector Model *ppbRAE Plus* manufactured by RAE Systems Inc., USA. We have done 15 sets of measurements in all six shops, starting April until the end of May. The obtained results have shown that people working in the selected shoe stores may have been exposed to significant VOCs concentrations during a work day. Because each group of air contaminants carries its own particular danger, and the higher concentrations of constituents fundamentally affect the quality of indoor air and peoples' health, we strongly suggest the use of portable, autonomous PID devices for monitoring the indoor air quality during a working day. The PIDs are simple, rugged, hand-held, lightweight devices, with high availability on the market and with a relatively low cost (up to 1,000 USD per unit). We are also convinced that PID will be a useful tool for improving the indoor air quality and the global environment in the next future.

RESULTS AND DISCUSSIONS

Through data collection and analysis we found relatively high concentrations of photoionizable chemical compounds in indoor air. We suppose that the largest amount is from toluene, widely used in the manufacture of adhesives for the footwear industry.

Because the purpose of this study was to observe and analyze the variation profile of total VOCs over 15 days in six shoe stores, in order to assess the trend of concentration evolution over time, as summarized in **Table 1** and displayed in **Figures 1** and **2**. The average and maximum values for each data set / day, together with the surface of each shop and the ambient temperature in

commercial spaces were also displayed in **Table 1**. Temperature variation was between 13 and 32°C during the experimental time period. As expected, we have noticed that tVOCs concentrations were higher during a day with a higher temperature.

Table 1. The average values and maximum values (expressed in isobutene units) of total photoionizable compounds concentrations found in each shop

T [°C]	Shop #1 S = 18m ² [ppb _v]		Shop #2 S = 28m ² [ppb _v]		Shop #3 S = 35m ² [ppb _v]		Shop #4 S = 15m ² [ppb _v]		Shop #5 S = 24m ² [ppb _v]		Shop #6 S = 21m ² [ppb _v]	
	Ave- rage	Maxi- mum	Ave- rage	Maxi- mum	Ave- rage	Maxi- mum	Ave- rage	Maxi- mum	Ave- rage	Maxi- mum	Ave- rage	Maxi- mum
19	351	1564	631	1473	536	2515	568	3388	708	939	595	3095
20	305	1295	545	2429	460	2924	1053	5208	676	1084	563	1621
19	583	881	1743	2823	798	1106	1052	1959	565	1902	861	2004
13	859	1063	942	1571	944	1255	756	1930	326	730	689	1997
20	1208	1976	411	625	849	1003	746	1721	208	257	320	1071
21	954	1812	910	4229	2144	3216	1291	3993	534	1784	829	3725
23	415	815	699	1658	1211	1395	625	1187	1184	3272	686	1664
24	540	1848	976	1284	1316	1761	785	1501	1216	3316	538	2738
25	967	2296	1401	7224	623	766	304	1023	969	3106	888	3479
22	1204	2011	1043	2994	313	1233	1145	2416	812	2208	1126	3280
23	653	2325	351	636	1144	1846	908	2426	517	2632	314	2020
21	378	944	1777	2452	783	1237	567	1288	791	3497	570	2506
22	756	889	1045	2706	2230	3612	2138	4639	643	3269	1661	1967
32	405	649	2806	4418	1530	2835	1482	2264	696	3570	1038	3807
28	1996	2203	972	4442	2292	2788	1073	2853	861	3876	1079	2628

However, considering all the cases, we cannot conclude that the temperature is always the decisive factor influencing the concentration of the detected compounds. Also, from data in the Table 1 one can notice that the surface area of stores varies between 15 m² (Shop #4) and 35 m² (Shop #3). By comparing the values recorded in Shop #3 (the smallest space) and Shop #4 (the largest space) for each day, and the graphic representation in **Figure 1**, we observe that in Shop #3 no higher values of total photoionizable compounds were recorded than in Shop #4. From this standpoint, taking in account the values recorded in all 15 days, we still cannot conclude that in small areas the concentrations are always higher than in large spaces. Probably, the ventilation plays the most important role here.

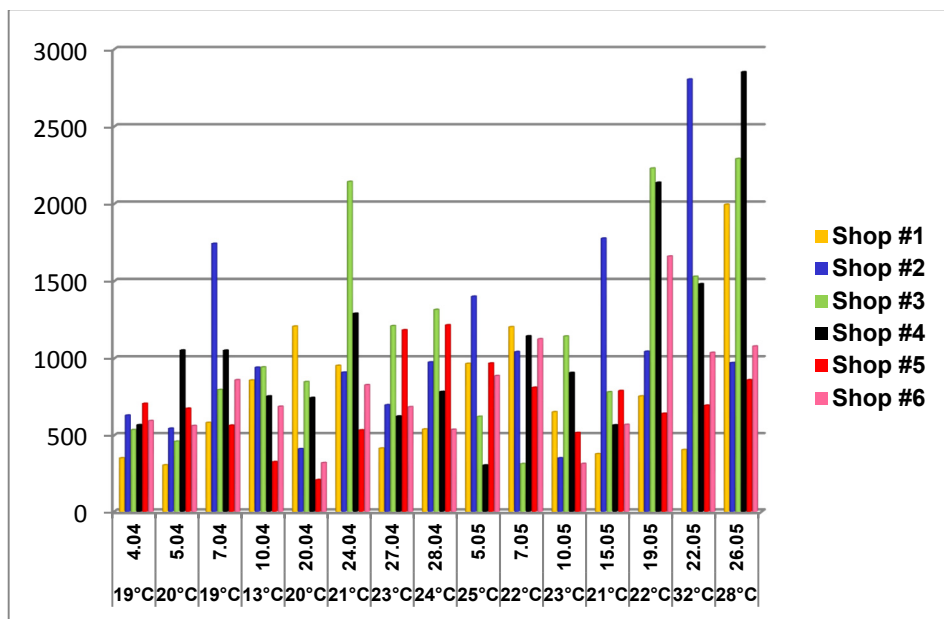


Figure 1. Average concentrations of tVOCs recorded (expressed in isobutene units) for 15 days in the six stores

In conclusion, the differences between compounds concentrations measured daily may be influenced by differences in temperature or store space, but are not caused by temperature fluctuations and surface area of the store. Factors such as the presence or absence of ventilation, organization, placement of goods in store, quantity of goods, customer turnover and movement (which indirectly determines the ventilation space) certainly affect contaminant concentrations inside the store.

For better understanding and interpreting our experimental results we divided the data in two categories: (1) the maximum concentration values (when the instrument was near by the shoes) recorded by PID, represented in **Figure 2** and (2) the average concentration values, which represents the arithmetic average of total recorded values for a distinct shop in each day (**Figure 1**). For each shop a measurement session took about 5 min.

Observing **Figure 1**, we can see that the smallest concentrations of average values were recorded in Shop #5, where only in two days the value of 1000 ppb_v (isobutene units) was exceeded. Followed by shop #5, the smallest concentrations recorded were in Shop #1 and then in Shop #6. The highest values of average concentrations were found in Shop #3, where in three days the average concentration values were more than 2000 ppb_v isobutene units, followed by Shop # 2 and #4.

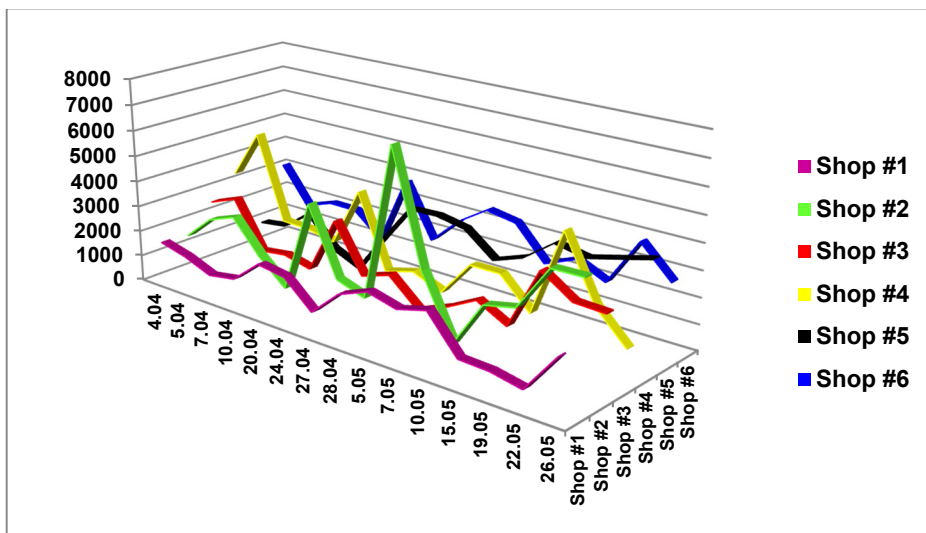


Figure 2. Maximum concentration of tVOCs (expressed in isobutene units) for 15 days in the six stores

In **Figure 2** maximum concentration values of total photoionizable chemical compounds recorded over 15 days were displayed. The smallest values for maximums were recorded in Shop #1, followed by Shop #5 and Shop #6. This can be explained by the continuous ventilation and by location of the store in the basement, with direct access from outside. We could also notice during the experimental sessions that these shops are selling leather shoes only, and not shoes made of synthetic materials.

Higher concentrations of maximum values were identified in Shop #2 and Shop #4. Shop #2 has direct access from outside and ventilation systems, nonetheless, it operates in a very busy area, and the shoes are made from leatherette (synthetic materials). We believe that these are the possible reasons that can account for the high maximum concentration of chemical compounds released in the stores.

Given that a concentration of over 500 ppb_v (isobutene units) in indoor air indicates the existence of a relatively high air contamination [20], we can infer with some worry that in those stores where we performed measurements there is a permanent exposure to volatile organic compounds. Among the tVOCs, the most common in footwear industry is toluene. Toluene has a PID correction factor CF of 0.5 (for a 10.6 eV lamp) and is very easily detected by PID devices; therefore, the PID instrument is more sensitive to toluene than to isobutene, which is used as calibration standard. Assuming that the majority of vapor amounts in shoe shops is represented by toluene, the toluene concentration is equal to the displayed PID concentration (in isobutene units) multiplied by the CF.

CONCLUSIONS

Our research, performed over 15 days and over a total period of 8 weeks, aimed to determine whether there is a chronic exposure of the staff working in shoe shops to volatile organic compounds coming especially from adhesives and leatherette. Our investigation encompassed six different shoe shops from Cluj-Napoca, Romania. Results confirmed the presence in the air of photoionizable compounds at ppm levels, thus approaching the admitted TWA limits for toluene. After a detailed analysis of the collected data, we concluded that one should address urgently the occupational exposure to compounds from the category of dangerous volatile organic compounds; we consider that the principal indoor air contaminant is toluene.

We expect that in the near future the PID devices alone and / or coupled with other analytical instrumentation (GC-MS, IMS, etc.) will be a very useful tool for monitoring and improving the indoor air quality and the global environment.

EXPERIMENTAL SECTION

The concentration of volatile photoionizable compounds was measured in six different shoe shops from Cluj-Napoca, Romania, using the sensitive PID instrument *ppbRAE Plus* device model PGM-7620 (made by RAE Systems Inc., USA), during 15 days (in April and May). The measurement time in each shop was about 5 minutes / day. With its highly compact design (size 21.8×7.62×5.0 cm and weighing only 553 g), this VOCs detector is used on a large scale as a fast monitor.

In this study, the PID device was able to detect in real time (2-3 s) very low vapor concentrations of volatile organic compounds, down to 1 ppb_v, while the range is up to 200 ppm_v. The main components of the PID instrument are the photoionization sensor and the UV lamp. Once the vapors of organic compounds are passing through the sensor and are exposed to the UV photons from the lamp, they are photoionized and the electrons and positive ions generate an ion current, which is then amplified and displayed on the device's display directly in concentration units (ppb_v).

The used PID device was equipped with a standard UV lamp with photon energy of 10.6 eV. The lamp consists of a glass body, provided with a window transparent to UV radiation at the end; this body is filled with a noble gas (Kr) at reduced pressure. The PID sensor is positioned above of the UV lamp. PID uses a pump with a flow rate of 450-550 cm³ min⁻¹. The air drawn by the pump is then evacuated through an outlet after passing through the PID sensor [21]. A diagram of the photoionization detector is presented in **Figure 3**.

Prior to measurements, the PID instrument has been calibrated using a standard atmosphere containing 10 ppm_v of isobutene in purified air (from a pressure cylinder). All data stored in the internal memory of the instrument were transferred to a PC computer using a RS-232 interface and the appropriate software.

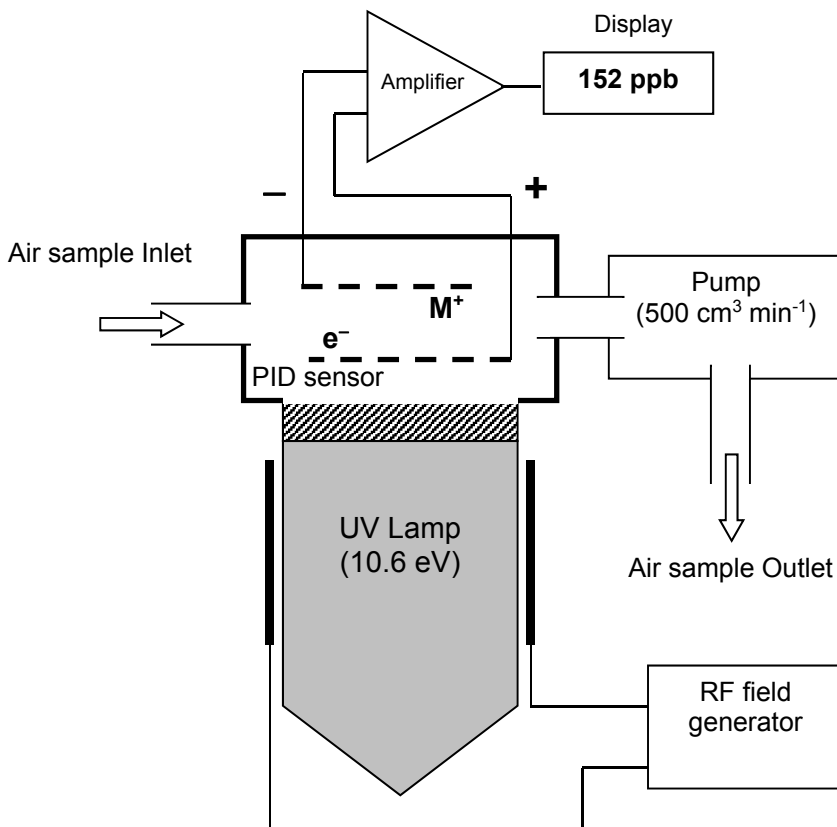


Figure 3. Schematic of the photoionization detector and associated experimental setup. The UV lamp, filled with Kr gas at low pressure, generates photons with the energy of 10.6 eV by using a RF field that induces and sustains a glow discharge when applied onto a set of two opposite metallic plates placed externally to the lamp body. The lamp is a glass body (1/2" o.d. and ca. 4 cm length) with a soldered disc of material transparent to ultraviolet radiation (MgF₂ for 10.6 eV lamps).

REFERENCES

- [1]. Care For Your Life: A guide to Indoor Air Quality, **2008**, available on-line at <http://www.epa.gov/iaq/pubs/careforyourair.html>, accessed in 10.05.2016.
- [2]. I. Haiduc, L.D. Boboș, A. Oltean, *Environment & Progress*, **2004**, 2, 153.
- [3]. S.K. Kang, M.Y. Lee, T.K. Kim, J.O. Lee, Y.S. Ahn, *Chemico-Biological Interactions*, **2005**, 153-154, 65.
- [4]. C. Klaassen, Cassarett & Doull's Toxicology - The Basic Science of Poisons (6nd ed.), McGraw-Hill Publishers, **2001**, chapter 24.
- [5]. I.A. Rațiu, V. Bocoș-Bințințan, M. Turner, V.H. Moll, C.L.P. Thomas, *Current Analytical Chemistry*, **2014**, 4, 488.
- [6]. L. Wilkins, *Teratology*, **1997**, 55, 145.
- [7]. Cantox Environmental, Assessment report on toluene for developing ambient air quality objectives, RWDI West Inc., Alberta Environment, **2004**, 12-35.
- [8]. U.S. Department of Labor - Occupational Safety and Health Administration, https://www.osha.gov/SLTC/toluene/exposure_limits.html [accessed in October 2016]
- [9]. C. Chen, F. Tsow, K. Driggs Campbell, R. Iglesias, E. Forzani, N.J. Tao, *IEEE Sensors Journal*, **2013**, 13, 1748.
- [10]. A. Mizukoshi, K. Kumagai, N. Yamamoto, M. Noguchi, K. Yoshiuchi, H. Kumano, Y. Yanagisawa, *International Journal of Environmental Research and Public Health*, **2010**, 7, 4127.
- [11]. Y.C. Shih, A.S. Yang, C.W. Lu, *Building and Environment*, **2011**, 46, 1104.
- [12]. M. Jia, J. Koziel, J. Pawliszyn, *Field Analytical Chemistry and Technology*, **2000**, 4, 73-84.
- [13]. J. Koziel, M.Y. Jia, A. Khaled, J. Noah, J. Pawliszyn, *Analytica Chimica Acta*, **1999**, 400, 153.
- [14]. A. Robbat, Jr., T. Considine, P. M. Antle, *Chemosphere*, **2010**, 80, 1370.
- [15]. G.B. Ghira, I.A. Rațiu, V. Bocoș-Bințințan, *Environmental Engineering & Management Journal*, **2012**, 12, 251.
- [16]. E. Ingre-Khans, C. Rudén, M. Breitholtz, *Ecotoxicology and Environmental Safety*, **2010**, 1633.
- [17]. H. Bae, W. Yang, M. Chung, *Science of the Total Environment*, **2004**, 323, 99.
- [18]. P. Grasso, M. Sharratt, D.M. Davies, D. Irvine, *Food and Chemical Toxicology*, **1984**, 22, 819.
- [19]. J. Tang, C.Y. Chan, X. Wang, L.Y. Chan, G. Sheng, J. Fu, *Atmospheric Environment*, **2005**, 39, 7374.
- [20]. RAE Systems Inc., **2002**, Using PIDs for indoor air quality surveys (Application Note-AP 212).
- [21]. RAE Systems Inc., **2003**, Operation and Maintenance Manual, Parts per Billion VOC monitor PMG-7240, pp. 8-20.