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RESEARCH ARTICLE

# Characterization and Potential Health Effects of Exposing to VOCs in Petrol Filling Stations

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## ABSTRACT

This study aims to characterize and investigate the health effect of exposure to volatile organic compounds (VOCs) in selected petrol filling stations environments. This study was conducted in number of workplaces, in Khartoum state, on the base of their potentiality to produce these compounds, through both field and lab works, where air, blood, and urine samples were collected and analyzed using both modular area monitor and GC-MS instruments. The results indicated that; all the studied petrol filling station environments, contained significant amounts of VOCs. The petrol filling station 2 recorded the highest value of these compounds (192 ppm), followed by petrol filling station 3 (146 ppm), while the least values were recorded in petrol filling stations 1 (91 ppm). Also it revealed that blood and urine samples taken from selected workers contained essential types of VOCs, namely, benzene, toluene, naphthalene, mequenol, phenol, oximes, carbon disulphide, methylene chloride, chloroform as influenced by the type of working activities). The results also confirmed that there is high relationship between worker health problems and presence of VOCs in workplaces.

In conclusion, presence of VOCs in workplace environments, in absence or poor safety applications, leads to accumulation of these compounds in bio-fluids of the exposed workers, and consequently increases the potentiality of health problems.

**Keywords**- VOCs, Petrol Filling Stations, SPME, Biological monitoring

## INTRODUCTION

Airs pollutants are usually characterized as being particulate or gaseous in nature originate from emission of different sources. Among the most important categories of air pollutants, the volatile organic compounds (VOCs) are considered as key components in both polluted and remote regions of the troposphere (Sarigiannis et al., 2011). Volatile organic compounds are known as various groups of volatile hydrocarbons, emitted from different chemical, petrochemical and related activities. These compounds are considered among the most significant pollutants that contribute to the majority of acute and chronic health problems (Khan et al., 2000). Emissions of such compounds, usually release from breathing and vapor losses of petrol storage tanks, venting of chemical process vessels, leaks from piping system of chemical and petrochemical products and equipment, from organic solvents used in printing, publishing and packaging industry, paints industries, automotive refinishing products, as well as waste water streams and heat exchange systems. Some VOCs are considered as toxic air pollutants which have potential to cause serious adverse health effects, vary greatly, ranging from short term (nausea, vomiting) to long terms, including cancer (Nitika Mishra, 2015). Several of these compounds are known carcinogens, while other VOCs may affect the central nervous system, the immune system, liver and kidneys (Fan et al., 2012). Numerous studies have reported that, there are strong relationship between ambient VOCs and adverse health outcomes, such as asthma (Delfino et al., 2003; Wichmann et al., 2009).

Presence of VOCs in the indoor air should be highly considered due to human exposure and health effects. This is because people spend about 80 to 90 % of their time indoors (Schweizer et al., 2006), including the home and workplace. It is well known that, petroleum products are used extensively in petrol filling stations, receiving; storage and dispensing fuel are potential sources to harm human health and environment. These operations usually emit VOCs in workplace environment (Bikbajeva, 2008). As reported in many studies that, the biggest emission of VOC to the environment is usually related to atmospheric pollution (Paliulis et al., 2007). Petrol stations emit vapors ordinary (24 hours/day, 365 days/year). Petrol evaporation may well be one of the sources that lead to extremely high benzene and toluene concentration (Ho et al., 2004). The amount of VOC emissions is depending mainly on the technological processes used in petrol station, which were include loading and breathing of fuel storage tank as well as dispensing fuel (refueling). In general, emission could occur from vehicles operation inside the petrol filling stations and hot-soak as well as spills and leaks from fuel pipe line. Petrol stations distribute the VOCs into their surroundings environments, based on the fact that the ratio of the concentrations of aliphatic and aromatic hydrocarbon pollutants in the air of the petrol stations and their surroundings (basically determined by vapor emissions from unburned gasoline) higher than that found in urban air, which is mainly influenced by traffic emissions. Bearing this in mind, the impact of petrol stations on public should be considered (morales et al., 2010).

However, the most significant VOCs are benzene, toluene, xylene, ethyl-benzene

(BTEX), and halogenated hydrocarbon, such as chloroform, chloromethane, chloroprene, dibromo chloromethane, methylene chloride and carbonyls (Mohamed et al., 2002).

## EXPERIMENTAL METHODS

### 2.1. Analysis of VOCs in workplace environments

The concentration of total volatile organic compounds (TVOCs) in the working environments of the selected petrol filling stations were monitored, to determine whether exposure standards have been exceeded or not. The modular area monitors; GW-3016 instrument was used as a direct reading device. Analysis of VOCs in petrol filling stations was considered as outdoor air analysis. For both type of analysis, breathing zone position (typically a position at 1- 1.5 m above the floor level) was chosen as position of the device to satisfy the requirement of measurements objectives (Yahazata45). Operation of the device was carried out as described by manufacture (GWSS, 2013; UK Environmental technology service, 2013).

### 2.2. Analysis of VOCs in blood

#### 2.2.1. Extraction

VOCs in blood samples were extracted using head space solid phase micro extraction (HS-SPME) method as described by (Laura et al., 2014). In this method blood sample vials were placed in dry block at $45^0$C for 15 min, to allow the analytes to reach the equilibrium between the VOCs concentration in the SPME Fiber and the concentration of the VOCs in the liquid phases. The analytes were sampled from the head space using a manual SPME assembly containing 50/30 µm divinyl benzene–carboxen-polydivinylemethylsiloxan (DVB-CAR/PDMS) purchased from sepleco (pellefonte, PA, USA). The fiber was pre conditioned at 250º C for thirty min prior to sample absorption; the fiber was housed in stainless steel needle, which allowed penetration of the PTFE septa of the vials caps and the septum in the GC injector. The extraction temperature was 40 $^0$C for 1hr. After extraction, the fiber was pushed out and exposed to the head space for 3 min and immediately subjected to gas chromatography- mass spectrometer (GC-MS) analysis.

#### 2.2.2. GC-MS analysis

Immediately, after extraction, the SPME fiber was transferred into the GC injection port fitted with a glass liner with an i.d. of 1 to 2 mm and held at 250 ± 0.5 ºC. The sample was introduced into an Agilent DB-1 column (30 m x 0.25 mm x 0.25µm film thickness) via pulsed split less injection set at 50 psi. After 1.0 min, but no more than 2 min, the injection port pressure was then dropped to maintain a constant flow of 1.1 ± 0.1 ml / min of helium. The GC oven temperature was programmed to ramp from 40$^o$C to 140$^o$C at 3$^o$C/min, then 5$^o$C / min to 220$^o$C. Identification of unknowns was established by comparison of GC mass spectra with that of a known standard mass spectral data of NIST 14, Using Agilent U.S.A.7890 gas chromatography equipped with 5977A quad pole mass spectrometer with electron ionization system . The SPME fiber assembly can entrap VOCs and was evaluated before use. Typically, a conditioned SPME fiber is baked out in the GC inlet at 250°C for a minimum of 1 hour before the VOC contaminants fully partition out of the fiber assembly. A fiber blank, prepared by sampling an empty headspace vial, were evaluated using the

same analytical GC/MS method as an unknown to confirm that all VOC concentrations are below instrument background levels. During the analytical run, the SPME fiber remains in the GC injection port until ready to collect the next sample and is not exposed to the laboratory air for more than 1 min so as to reduce the influence of ambient contamination (CDC, 2008).

### 2.3. Analysis of VOCs in urine

#### 2.3.1. Extraction

Extraction of VOCs in urine samples was carried out following head space solid phase micro extraction (HS-SPME) method as described by (Laura et al., 2014). In this method urine sample vials were placed in dry blok at 45$^0$C for 15 min, to allow the analytes to reach the equilibrium between the VOCs concentration in the SPME Fiber and the concentration of the VOCs in the liquid phases. The analytes were sampled from the head space using a manual SPME assembly containing 50/30 µm divinyl benzene-carboxen-polydivinylemethylsiloxan (DVB-CAR/PDMS) purchased from sepleco (pellefonte, PA, USA). The fiber was pre conditioned at 250º C for thirty min prior to sample absorption, the fiber was housed in stainless steel needle, which allowed penetration of the PTFE septa of the vials caps and the septum in the GC injector. The extraction temperature was 40 $^0$C for 1hr. After extraction, the fiber was pushed out and exposed to the head space for 3 min and immediately subjected to gas chromatography- mass spectrometer (GC-MS) analysis.

#### 2.3.2. GC-MS analysis

Gas chromatography- mass spectrometer (GC-MS), (Agilent 7890A, U.S.A) Gas Chromatography coupled to Mass Spectrometer Agilent U.S.A 5977A quad pole. Equipped with DB-1 Fussed silica capillary Colum (30 m, 0.25mm I'd, 0.25 µm film thicknesses) was used for analysis of extracted samples. Helium gas is applied as carrier, at flow rate 1.2 ml\min. The injector and MS transfer line temperatures were 200 and 280 $^0$C, respectively. The ion source temperature was 200 $^0$C. The GC oven was held at35 $^0$C for 3 min and then ramped at 3$^0$C /min to final 240 $^0$C, at total time 66 min. Late eluting compound were removed by raising the oven temperature to 250 $^0$C. The Mass Spectrometer was operated in electron impact (EI) mode with electron energy set at 70 ev. After the extraction, the fiber was pulled in the stainless steel needle and inserted into the injector inlet.

## 3. Results and discussion:

### 3.1 Volatile organic compounds apportionment in selected workplace environments

Table 3.1 summarizes the results of the concentrations of total volatile organic compounds (VOCs) recorded in the environments of selected petrol filling stations, in Khartoum state. Concerning the maximum readings out of the 65 readings of the pollutant detector, the results indicated that, petrol filling station (2) recorded the highest value (190 ppm), flowed by petrol filling station number (3) which was recorded(146 ppm), while the lowest values (91 ppm) was recorded by petrol filling station number (1). The same situation was also observed in results of average readings. However, regarding the results of minimum readings, petrol filling station number (1) and (2) recorded the lowest values (33 ppm), while the petrol

filling station number (3) recorded the highest value (48ppm). In spite of the high chance of petrol filling station to emit VOCs, however the low values of VOCs could be attributed to the fact that the petrol filling station usually located in open areas, and consequently considered as outdoor source of VOCs (USEPA, 2015a). Guo et al, (2003) stated that in most cases, the concentration of specific air pollutant is usually higher in indoor environment than outdoor, regardless of the sort of emission and its sources.

**Table 3.1: Total volatile organic compounds apportionment in selected petrol filling stations environments**

| Workplace environments | Reading Limits | Concentration of TVOCs (ppm) | Temp (°C) | RH % | Reading time |
|---|---|---|---|---|---|
| Petrol filling Station (1) | Max | 91.0 | 33.9 | 20.9 | 11.50 |
| | Avg | 54.7 | 31.48 | 16.47 | |
| | Min | 33 | 29.0 | 15.2 | |
| Petrol filling Station (2) | Max | 192 | 30.8 | 17.9 | 12.23 |
| | Avg | 92.8 | 29.93 | 17.10 | |
| | Min | 33 | 29.2 | 16.9 | |
| Petrol filling station (3) | Max | 146 | 32.3 | 18.4 | 12.54 |
| | Avg | 74.8 | 30.12 | 17.20 | |
| | Min | 48 | 29.83 | 16.85 | |

It is well known that, the TVOC is a very complex value, and it doesn't mean it is just the summation of the values of volatile organic compounds detected in workplace environment. In most cases, a low TVOCs usually indicates that the concentration of each separately VOC is low and then there is no VOC problem (definitely, unless, the TVOC value is resulted to only a small number of compounds); while, a high TVOCs value usually resulted from a high level of one single compound or it may be a vast collection of low compound levels from a chemical, or it may be anything in between (ADLD, 2012). Currently specific standards for the permissible exposure level (PEL) for these total volatile organic compounds are not completely reached. However, some international organization lay down constant values for exposure limit standard to VOCs and TVOCs based on the VOCSs concentrations of individual substances. According to current knowledge and information, standard limits are defined as values which could not cause adverse health problems nor cause discomfort to nearly all workers (SWA, 2012a). As these values are based on duration time and exposure frequency, the standard guide was estimated in the workplace during 8 hours work-day and a 40 hours' work-week. The Occupational Safety and Health Administration (OSHA) established permissible exposure limit (PEL), American Conference Government Industrial Hygiene (ACGIH) state threshold limit value (TLV) and the National Institute of Occupational Health and Safety (NIOSH) set recommended exposure limit (REL). All these organizations set standards for each single VOC, for example, the PEL and TLV for

benzene is 0.5ppm, and while REL is 0.1 ppm in addition toluene PEL, TLV and REL was 200ppm, 50ppm and 100respectively. Moreover, 100ppm was set as xylene standard limit for the three standards (OSHA, 2011). Furthermore, OSHA stated that, the summation of many results of TVOCs during short time in the work place should not exceed 1ppm, consequently detection of any results of this air pollutants into the work environment above 1ppm are seriously danger to the workers (OSHA, 2011). Also, It was reported that, TVOCs less than 500 µg/$m^3$ (0.5 ppm) seems to represents an acceptable TVOC level and that more than 3000 µg/$m^3$(0.3ppm) represents a hazardous TVOC level; and could cause many health problems including drowsiness, eye and respiratory irritation, general malaise, headache, nausea, and exacerbation symptoms of respiratory ailments (LEED, 2012).

VOCs emissions from solvent handling, storage and cleaning operations may also be considered (Caselli et al., 2009).

Usually, PEL does not mean that all workplace under standards of TVOCs are safe, due to the fact that, there is no accurate clear line between a healthy and unhealthy work environment. Natural biological variation and the range of individual ability mean that a small number of people might be suffered from many health diseases bellow the exposure standard (SWA, 2012). Furthermore, there is quite tolerable and acceptable relation between concentration of VOCs in the work environment and many health problems (Vilckova et al., 2015).

**3.2 Characterization of volatile organic compounds in blood of workers from selected petrol filling stations**

Table: 3.2, 3.3 and 3.4 illustrate the results of area percentage of different volatile organic compounds and their metabolites detected in blood samples taken from selected workers of different petrol filling stations in Khartoum state. The results indicated that more than (26) compounds were detected in blood samples. These compounds include benzene, ethyle benzene, toluene and xylene (BTEX). Since most of these compounds were known to be constituents of the air environment of these workplaces, the presence of these pollutants supports the fact of exposure of the worker during their work. It was reported that the presence of airborne volatile organic compounds, such as benzene, toluene, ethyl-benzene, xylenes (BTEX), methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), and naphthalene (NAP) in outdoor and indoor air environments are mainly associated with petroleum- based products such as fuels, vehicular exhaust fumes and vapors, products used extensively in vehicle repair industry and printing and photocopy activities (Khan and Goshal, 2000).

Regarding the results of BTEX compounds, as shown in table 4.2, it was observed that the highest percentages and most dominated compounds in blood of petrol filling station workers was toluene 44% (Fig 3.1), followed by p - cresol 42%, while

**Table 3.2: Peak areas and concentration percentages of BTEX compounds in blood of workers from selected workplace environments**

| Compound | Petrol stations | |
|---|---|---|
| | Peak area | % |
| Benzene | 1.32 | 2.1 |
| Toluene | 27.11 | 44.00 |
| Benzenamine,4 –methyl thiobenzylydene) - (naphthalene) | 1.625 | 2.6 |
| Benzene, 1-methoxy-4-methyl- | 0.872 | 1.4 |
| Benzaldehyde | 0.594 | 1.00 |
| 3-Hydroxymandelic acid (benzene acetic acid) | 0.470 | 0.8 |
| Mequinol | 0 | 0 |
| p-Cresol | 25.980 | 42.00 |
| 3,4-Dimethylbenzoic acid | 1.216 | 2,00 |
| Methyl eugenol (benzene methoxy) | 0.164 | 0.3 |
| 5H-dibenzo [a,d] cyclohepten-5- amine | 1.179 | 1.9 |
| D - Carvone | 0 | 0 |
| Indole | 1.462 | 2.4 |
| p-Xylene (dimethyl benzene ) (p-methyl toluene) | 0 | 0 |
| Benzonitrile | 1.208 | 1.95 |
| Acetic acid pentyl ester | 0.266 | 0.43 |

**Table 3.3: Peak areas and concentration percentages of Phenolic compounds in blood of workers from selected workplace environments**

| Compound | Petrol stations | |
|---|---|---|
| | Peak area | % |
| 1,2,4-Oxadiazole,3-(4-nitrophenyl)-5-phenyl- | 2.379 | 55.3 |
| Phenol | 0 | 0 |
| Oxime-, methoxy-phenyl | 1.209 | 28.12 |
| Phenol, 4-ethyl- | 0.469 | 10.91 |
| 2,6-Bis(1,1-dimethylethyl)-4-(1-oxopropyl)phenol | 0.237 | 5.5 |

**Table 3.4: Peak areas and concentration percentages of aliphatic compounds in blood of workers from selected workplace environments**

| Compound | Petrol stations | |
|---|---|---|
| | Peak area | % |
| 4- Cyanocyclohexenone | 1.126 | 57.2 |
| Acetic acid pentyl ester | 0.266 | 13.5 |
| N- Chlorosuccinimide | 0.214 | 10.9 |
| 2-Ethylacridine | 0.368 | 18.7 |
| Tri chloro methane | 0 | 0 |

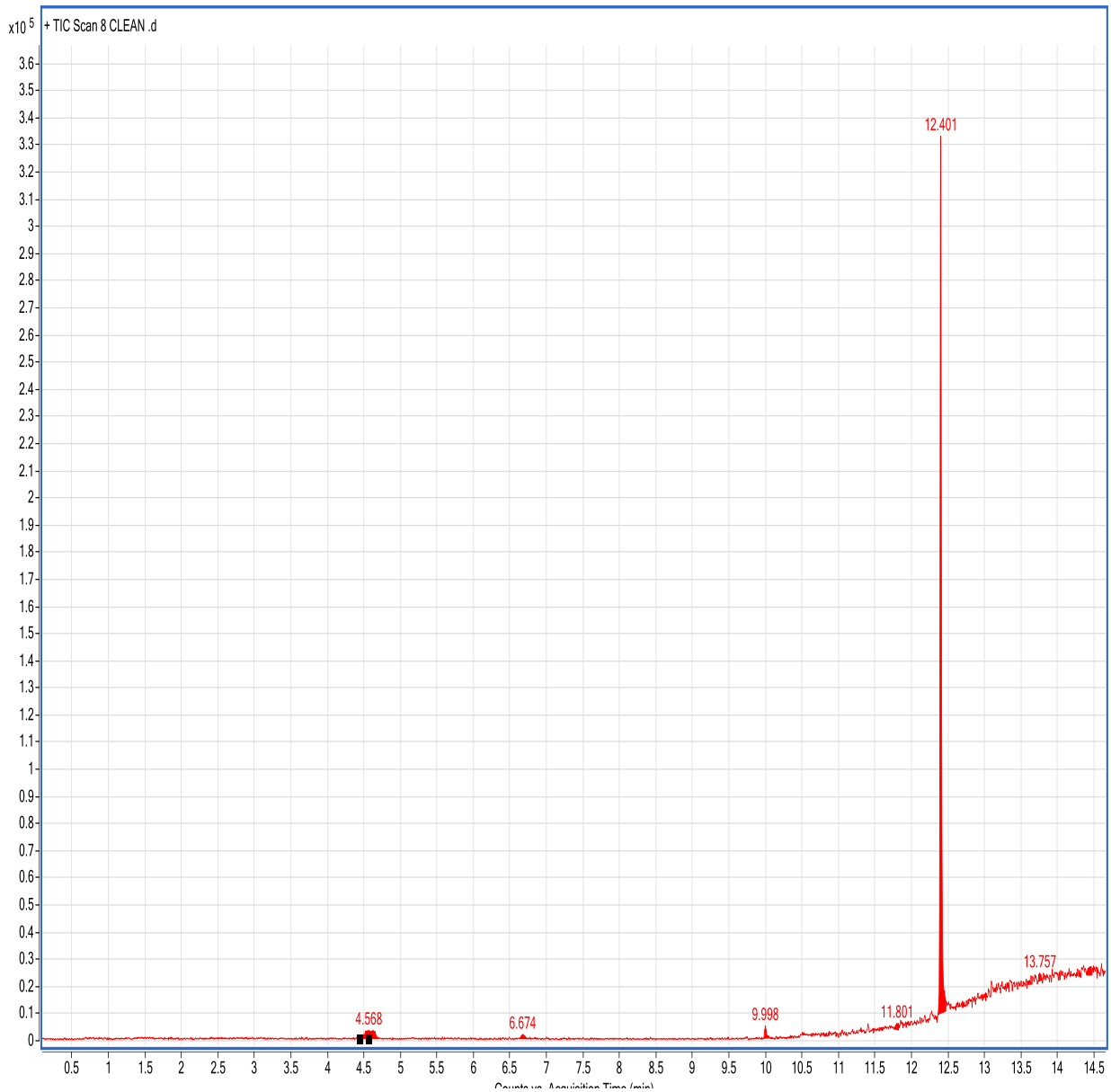


**Fig. 3.1: Chromatogram of toluene (butylated hydroxyl toluene) abundance in blood of the workers of petrol filling stations**

Benzene 2.1%, and naphthalene was 2.6%. Domination of toluene compound in petrol filling environment, was reported by many other findings. Majumdar et al, (2008), reported that among the mono-aromatics, toluene was the most abundant (49.3-236.8 lgm_3) followed by benzene in air samples taken from the environment of fuel pump stations representing different geographical areas in Kolkata.

Presence of toluene as an abundant compounds in blood samples taken from petrol filling workers, may be attributed to the fact that, toluene is considered as main constituent of fuel. in addition, in petrol filling stations VOCs emissions arise from

many sources , which were include the vapor expelled from a vehicle's petrol tank as the tank is filled; drips from the filling nozzle; leaks from hoses and gaskets; and vapors expelled from underground storage tanks as they are refilled by road tankers (DECC, 2009). It was also reported that concentration of toluene compound in cars washing varies from 13 to 145 µg m−3, and it may reach up to 1000 times higher when it is at a petrol station during refueling (Esteve –Turillas et al., 2007).

Although presence of benzene in abundance lower than other BTEX compounds such as toluene, however, presence of its compound and metabolites is a very clear indicator for human health problems, since it is considered as the main known active of cancer, particularly leukemia and other blood cancers. The fact that benzene exposure could result in leukemia was more difficult to establish than the demonstration that benzene could induce a plastic anemia and decreases in blood cells due to benzene exposure could be observed within few months after exposure w initiation. However, there is a lag time (perhaps years) between initial benzene exposure and the development of leukemia (Snyder, 2012). He also reported that high exposure to benzene has been known to damage the bone marrow due to in decreases in the numbers of circulating blood cells, and consequently causes plastic anemia. Furthermore, more recent findings benzene exposure is related for one or more types of leukemia. On the other hands, toluene is classified as probable carcinogen as reported by United State Environmental Agency (USEPA, 2015b). This compound may cause mild neurotoxicity, if the body exposed to it at low doses during long period of time, however, exposed high dose may cause kidney and liver damage. Moreover, toluene is also considered to be a possible reproductive toxin (PHE, 2015). As shown in table 4.2, it was clear that the phenol compound was not detected o in blood samples, while 2,6-Bis (1,1-dimethylethyl) - 4-(1-oxopropyl) phenol compound was detected in all samples of petrol filling stations workers( Fig 3.2 was showed the phenol compounds recorded in blood samples). The results also revealed that the abundant compounds of phenol family in blood of petrol filling station workers was 1,2,4-oxadiazole,3-(4-nitrophenyl)-5-phenyl- (55.3%), followed by oxime-, methoxy-phenyl (28.12%) and Phenol, 4-ethyl- (10.91%). However, oxime-, methoxy- phenyl was recorded as the dominant compound followed by 1, 2,4-Oxadiazole,3-(4-nitrophenyl)-5-phenyl- (26.5 %) and phenol, 4-ethyl- (8.2 %). On the other hand, 2,6-Bis(1,1-dimethylethyl) – 4 - (1-oxopropyl) phenol compounds concentration represents more than 90% of phenolic compounds detected in blood samples of printing presses workers. It is well known that chronic exposure of workers to phenol vapors causes anorexia, lost of body weight, weakness, headache, muscles pain and icterus, and it is mainly accumulated in brain, kidneys, liver and muscles (Perez, 2009). Clinical data concerning phenol and its metabolites in human body tissues, indicate that people exposed to derivatives of phenol influence fall ill with of tumours, sarcoma and lung cancer. Also According to literature data, it was reported that the mixture of chloro phenols or sodium salts of these compounds is probably carcinogenic for animals (Michałowicz et al., 2007).

### 3.3 Characterization of volatile organic compounds in urine of workers from selected petrol station environments

Table 4.5, 4.6 and 4.7, demonstrates the results of different volatile organic Compounds were classified into three categories namely; BTEX and their metabolites, phenolic compounds and aliphatic compounds, presence of these compounds prove that the workers were exposed to such compounds resulting from long time in bulky VOCs workplace work operations. It was reported that the presence of the significant group of airborne volatile organic compounds, such as benzene (the most hazardous), toluene, xylenes and naphthalene have toxicities and classified as carcinogenic (ACGIH, 2009).

compounds and its metabolites detected in urine samples taken from selected workers of different petrol filling stations in Khartoum state. About 32 compounds were detected in urine samples. These

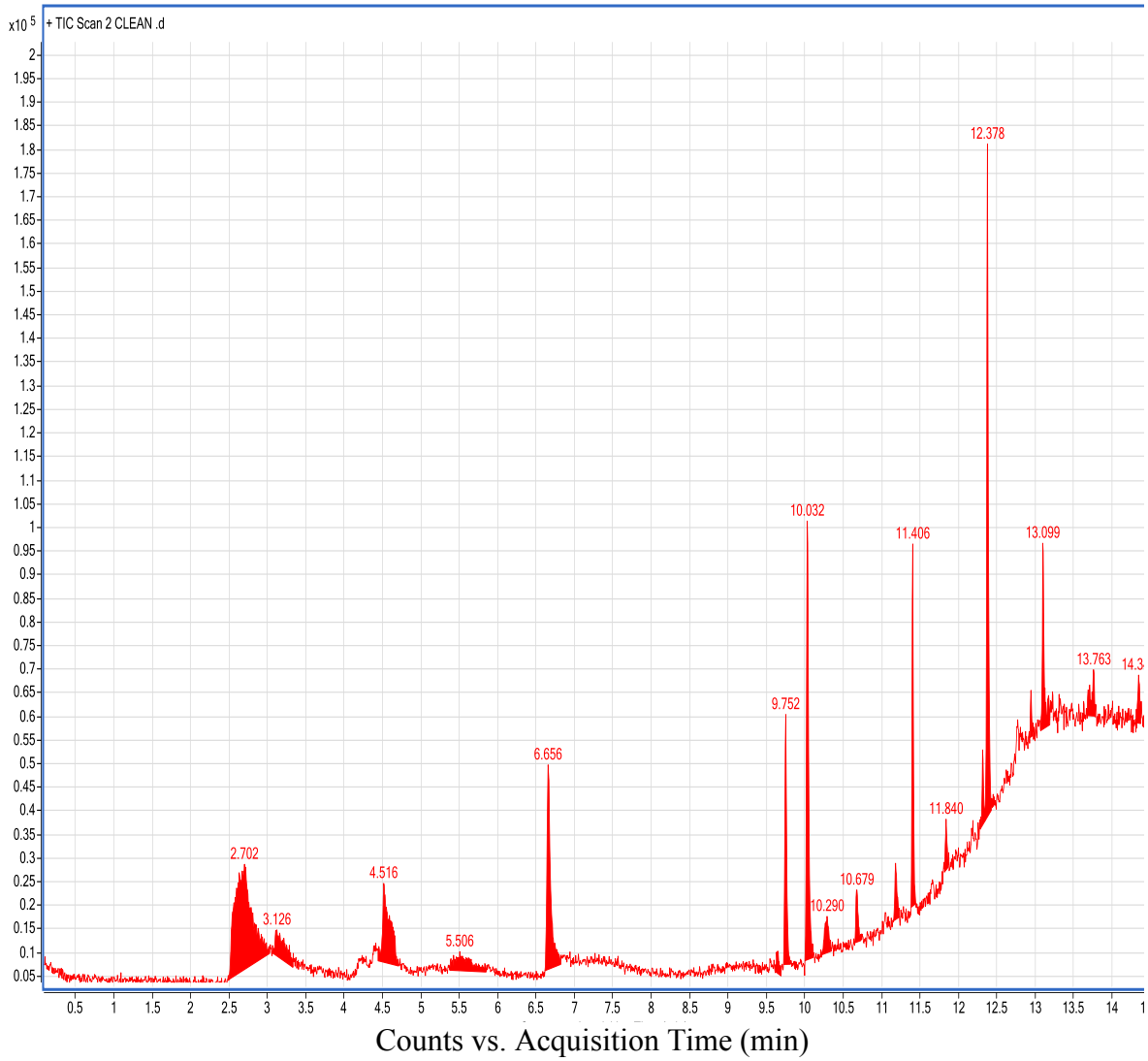


**Fig. 3.2: Chromatogram of phenol abundance in blood of the workers of petrol filling stations**

**Table 3.5: Peak areas and concentration percentages of BETX compounds and their metabolites in urine of workers from selected workplace environments**

| Compound | Petrol stations | |
|---|---|---|
| | Peak area | % |
| Benzene | 0.24 | 2.01 |
| Toluene | 0.69 | 5.70 |
| Naphthalene | 1.7 | 13.90 |
| N- [4-Methoxy-3-methoxy carbonyl) benzoyloxy] succininide | 0.29 | 2.40 |
| Benzene, 1-methoxy-4-methyl- | 0.73 | 6.01 |
| Benzaldehyde | 0.14 | 1.20 |
| 3-Hydroxymandelic acid (benzene acetic acid) | 0.05 | 0.40 |
| Mequinol | 1.30 | 10.70 |
| p-Cresol | 0.54 | 4.50 |
| 3,4-Dimethylbenzoic acid | 0.35 | 2.90 |
| Methyleugenol ((benzene methoxy)) | 0.82 | 6.80 |
| 5H-dibenzo[a,d]cyclohepten-5-amine | 1.72 | 14.20 |
| D-Carvone | 2.59 | 21.40 |

**Table 3.6: Peak areas and concentration percentages of phenolic compounds and their metabolites in urine of workers from selected workplace environments**

| Compound | Petrol stations | |
|---|---|---|
| | Peak area | % |
| 1,2,4-Oxadiazole, 3- 4 nitro phenyl) - 5- phenyl- | 0.94 | 9.41 |
| Phenol | 0.21 | 2.07 |
| Oxime-, methoxy-phenyl | 2.63 | 26.30 |
| Phenol, 4- methyl- | 5.21 | 52.12 |
| 2,6-Bis (1,1-dimethylethyl) -4-(1-oxopropyl) phenol | 1.02 | 10.20 |

**Table 3.7: Peak areas and concentration percentages of aliphatic compounds and their metabolites in urine of workers from selected workplace environments**

| Compound | Petrol stations | |
|---|---|---|
| | Peak area | % |
| Ethyl ether | 0 | 0 |
| Carbon disulfide | 7.70 | 16.70 |
| Methylene chloride | 5.13 | 11.20 |
| Heptane, 3-methyl- | 0 | 0 |
| N-Hexane | 21.17 | 46.00 |
| 4-Cyanocyclohexenone | 0.58 | 1.30 |
| Acetic acid pentyl ester | 3.36 | 7.30 |
| Silane, methylvinyl | 2,40 | 5.20 |
| N-Chlorosuccinimide | 0.49 | 1.10 |
| Tetra ammonium fluoride | 0.56 | 1.20 |
| Tri chloro methane | 4.12 | 9.00 |

Furthermore, workers of fuel (petrol and diesel) filling stations are usually exposed to a mixture of hydrocarbons in fuel vapors during normal operation (Rekhadevi et al., 2010). It was stated that, the outdoor and indoor air environments have been largely associated with petroleum- based products such as fuels, components of both vehicular exhaust fumes and vapors, therefore, workers are highly exposure to organic solvents to a great extent (Schmitz et al., 2000; Khan and Goshal, 2000). It was also reported that, occupationally, volatile organic compounds and benzene exposure occurs in workplaces like petrol filling stations and most of other chemical industries (Chunrong, 2012). the increase of VOCs emission in petrol filling stations, particularly BTEX, raising the cancer risk for both workers and ordinary customers (Karakitsios et al., 2007), It is well known that benzene is a common component of petroleum products, and grouped by USEPA as known human carcinogen, moreover there are many acute and chronic health effects addressed as health problems associated to benzene exposure, therefore, it can be concluded that the biological fluids of workers involved in petrol filling station are known to contain high load of benzene (Talamanca and Salera, 2001).

Table 4.5, illustrated the presence of BTEX and their metabolites in urine samples of workers in areas under study. P-cresol was detected as a dominant compound in all urine samples and formed about (72.7%) of compounds that detected in urine samples of printing presses workers (Fig 3.3).The abundance of p-cresol in printing press samples as well as its appearance in all urine samples of workers in areas under could be attributed to the fact that, this compound has been used in petroleum. Acute (short-term) exposure by humans to mixed cresols cause, dryness, nasal constriction, and throat irritation as symptoms of respiratory tract irritation. Mixed cresols are also strong dermal irritants. Now a day, the information about chronic (long-term) effects of mixed cresols in humans is insufficient, while many studies using animal experiments were conducted. These studies prove some effects of cresol on their blood, liver, kidney and central nervous system, and reduced body weight. The most significant information about cresol is that, several studies suggest that all cresol isomers may act as tumor promoters as well as it was classified by USEPA as possible human carcinogens (group C) (USEPA, 2015b). The results also indicated that, benzene was detected in all urine samples; the highest percentage of benzene was recorded in petrol filling stations samples (2.01%), the highest level of benzene in petrol filling stations samples (Fig 3.4) may resulted from excessive use and large bulk of storage of benzene in petrol service stations as well as the direct exposure to benzene vapor through benzene saturated breathing air. In spite of the fact that small amounts of benzene enter the body and bloodstream during contact with benzene or benzene-containing products passing throughout the body, temporarily stored in the bone marrow and fats, and then converted to benzene metabolites in the liver and bone marrow. Some of the health problems of benzene exposure are caused by those metabolites which are usually disposed from the body into the urine (ATSDR, 2015a and CDC, 2000).

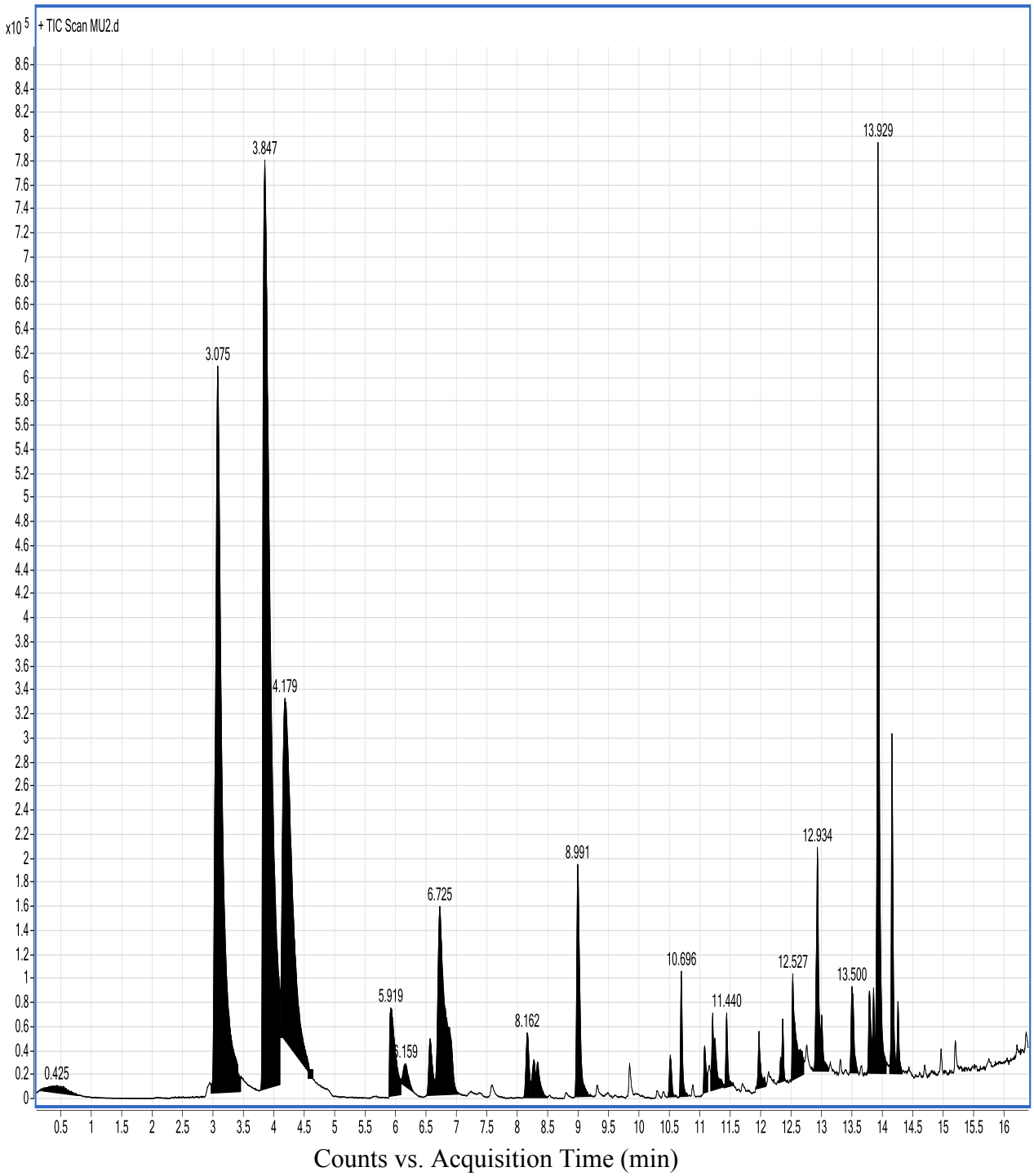


**Fig. 3.3: Chromatogram of p- cresol in urine of the workers of petrol filling stations**

As shown in table 4.5, toluene was detected in all urine samples of the workers of petrol filling stations (5.7 %). Toluene can enter the body through inhalation as well as contact with skin and ingestion; it is taken directly into the blood from lungs after breathing, or can pass through skin into the bloodstream when it is in contact. When it is ingested it is also absorbed and passed into bloodstream. After toluene entering into the body, the majority is removed from the body within a day; but, small amounts may accumulate in fat tissue with the daily exposure. It was reported that breath toluene may excreted outside the body directly unchanged in breathe out air, while dermal absorbed toluene is excreted into the urine (ATSDR, 2015a).

Considerations on the acute health effects of toluene regarding to observations in humans experimentally exposed to toluene, it can caused headache, dizziness, feeling of intoxication, irritation and sleepiness. Furthermore, toluene can cause impaired neuropsychological function, damage to liver and kidney, as well as reproductive problems (ECHCP, 2006). Many USA agencies such as USEPA, ACGIH and ATSDR stated that, there are no enough evidences to classified toluene as carcinogenic, and the US National Toxicology Program considered the toluene as non-carcinogenic (ATSDR, 2015a). on the other hand Xylene was not detected in urine samples taken from workers of petrol filling stations.

As shown in table 4.6, it was observed that five phenol family compounds were detected in all urine samples taken from petrol filling stations workers. These compounds are phenol, Phenol, 4 - ethyl, Oxime, methoxy-phenyl, 1, 2, 4-Oxadiazole, 3-(4 - nitrophenyl) - 5 - phenyl and 2,6-Bis (1,1- dimethylethyl) - 4- (1-oxopropyl) phenol. Phenol, 4- methyl was detected as a dominant compound; it was recorded in petrol filling station samples as highest percentage (52.12%). The abundance of phenol, 4- methyl may be resulted from normal presence of methyl phenols in the environment, in considerable concentrations, particularly as phenol, 4-methyl form (Duda et al., 2007). Also the results indicated that, phenol was detected in all urine samples of worker in areas under study. The high percentage of phenol was recorded in petrol filling stations samples is (2.07%). In spite of the bulky presence of phenol in petroleum products usually, the level of phenol detected in urine may not accurately reflect to actual phenol exposure because phenol may also formed as a metabolite of benzene or other drugs (Waechter, 2007). Moreover, Phenolic compounds could be metabolized through conjugation after exposed and entering the human body (USEPA, 2002); conjugated species are readily leaving the body via urine (Liao et al, 2012). Usually, the conjugated phenolic compounds comprise the bulk of the total biomarker concentration in urine (Koch et al., 2012). Many acute effect of phenol on human was reported as human health problems associated with inhalation and dermal exposure to phenol and phenolic compounds such as irritation to the skin, eyes, and mucous membranes in human. The major symptoms of acute toxicity in human are irregular breathing, muscle weakness and tremors, loss of coordination, convulsions, coma, and respiratory arrest at lethal doses. Also the reported chronic exposure to phenol, are anorexia, progressive weight loss, diarrhea, vertigo, salivation, a dark color of the urine, gastrointestinal irritation, blood and liver effects (Ye X, 2007). Moreover, direct contact of phenol to the skin results in dermal inflammation and

necrosis. Based on lack of sufficient information focusing in carcinogenic effects of phenol in human and experimental animal, Phenol was classified in group D, regarding human carcinogenicity (USEPA, 2015b; ATSDR, 2015c).

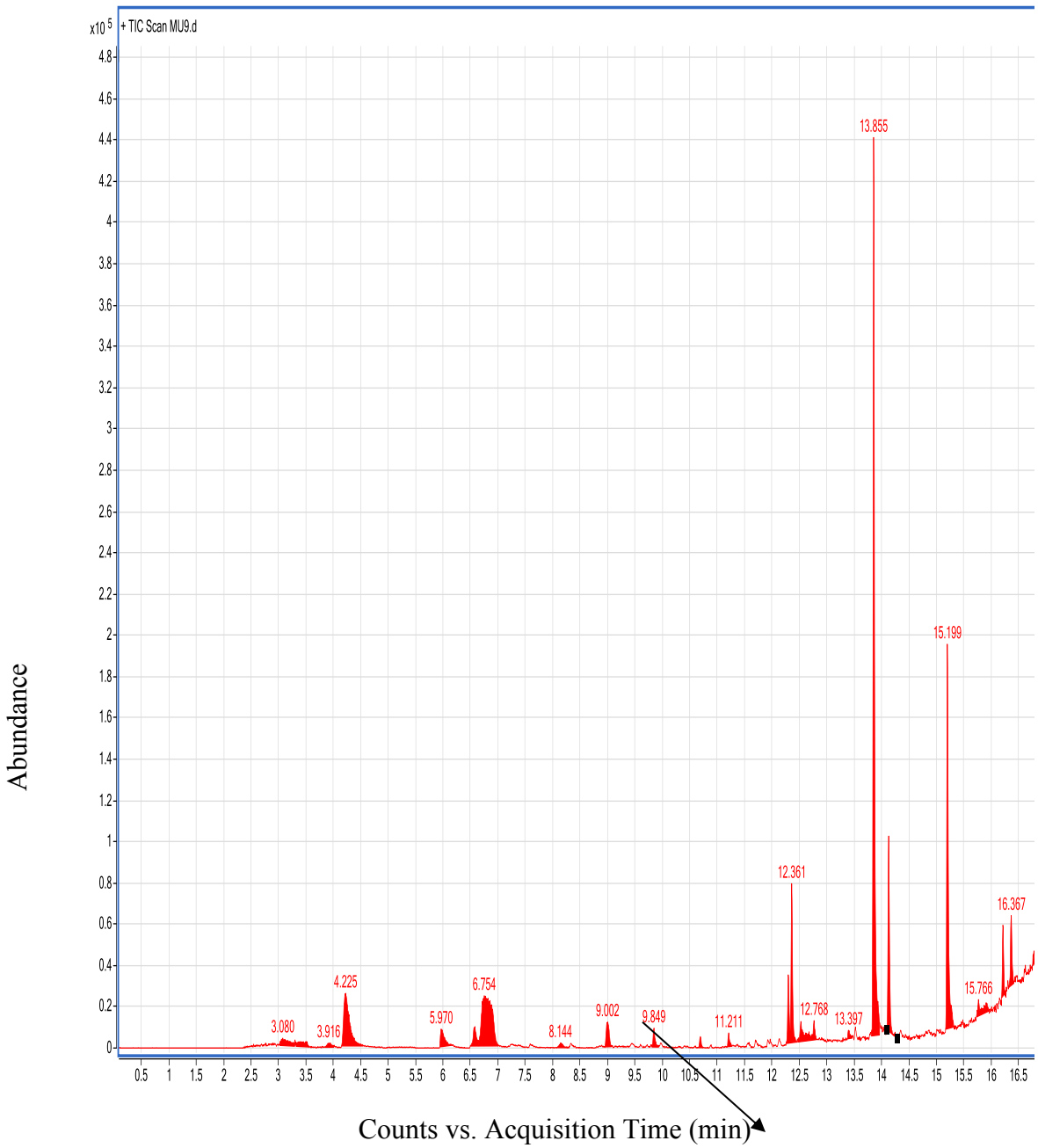


**Fig. 3.4: Chromatogram of benzene compound in urine of the workers of petrol filling stations**

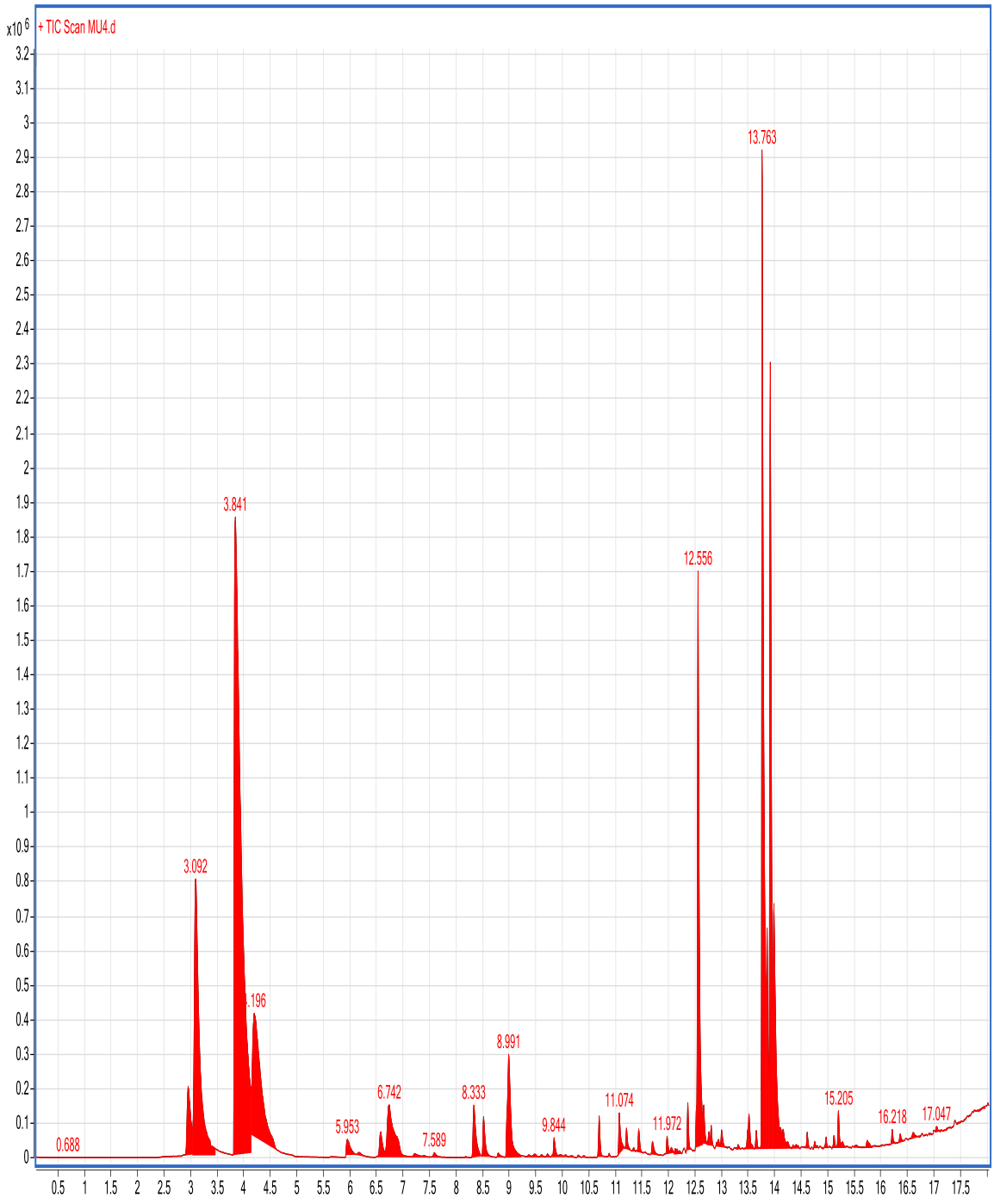


**Fig. 3.5: Chromatogram of carbon disulfite compound in urine of the workers of petrol filling stations**

Table 4.7, illustrates the results of aliphatic compounds and its metabolites in urine samples of workers in the studied areas. N-hexane was the most dominated compound in urine samples of worker of petrol filling stations (46%) followed carbon disulfide (16.7%) Fig3.5. While, methylene chloride was (11.2%) and 4-cyanocyclohexanone was (1.3%). The abundance of n-hexane in fuel stations samples, may be attributed to the fact that, n-hexane is a constituent of the paraffin fraction of crude oil and natural gas as well as its wide use as an industrial solvent in paint thinner and printing ink, because it is cheap, non-polar solvent, non-reactive, easily evaporated and relatively safe (ATSDR, 2015). It was reported that, approximately 10-20 % of n-hexane absorbed by inhalation is excreted unchanged in exhaled air; the remainder is metabolized. Metabolism takes place via mixed-function oxidize reactions in the liver and the n-hexane is metabolized in the body to a number of metabolites. One of these metabolites is 2, 5-hexanedione, the ultimate toxic agent in n-hexane that induced neurotoxicity. These metabolites are excreted from the body in the urine within a few days of exposure. Acute inhalation exposure of humans to high levels of n-hexane lead to mild central nervous system effects, such as dizziness, giddiness, slight nausea, and headache, while chronic exposure to is associated with poly neuropathy in humans, with numbness in the extremities, muscular weakness, blurred vision, headache, and fatigue. Currently no sufficient data is available related to carcinogenic effects of n-hexane in human or animals and therefore, it was classified in group ( D), as not human carcinogenic (USEPA, 2015a).

## CONCLUSIONS

The most significant conclusions, which can be derived from this research work, are the following**:**

- All the three studied workplace environments (petrol filling stations), contained significant amounts of volatile organic compounds (VOCs).
- Petrol filling station 192 ppm recorded the highest values of volatile organic compounds (VOCs), followed by petrol filling station 2 and the least values were recorded in petrol filling stations 1.
- Blood and urine taken from selected workers contained significance types of volatile organic compounds (VOCs), namely (e.g) benzene, toluene, naphthalene, mequenol, phenol, oximes, carbon disulphide, methylene chloride, chloroform as influenced by the type working activities.
- Blood and urine taken from workers of petrol filling station 3 recorded high percentage of the commonly known volatile organic compounds (VOCs) followed by petrol filling stations and petrol filling station 1.
- All studied workplace environments under risk; however, the highest risk was scored in spray painting workshops, followed by petrol filling stations and printing presses.
- High relationship was recorded between worker health problems and VOCs presence.

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