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Gas chromatographic method for quantification of gasoline and BTEX in water samples

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Abstract

This study was conducted with the aim to determine concentration of benzene, toluene, ethyl benzene, xylene and gasoline in different water samples (drinking water, drain water and canal water) of dry port and surrounding residential area as Presence of excess these compounds in water pose many health problems like cancer, gastroenteritis, dysentery, diarrhea and viral hepatitis. Firstly, physical parameters (pH, turbidity, TSS and TDS) were analyzed as the analysis of these parameters is keen important to get an idea of any organic contamination in water and then in second step selective an sensitive approach of gas chromatography was used for the qualitative and quantitative determination of these compounds. Gasoline was detected in about all samples except one waste water sample. The detected concentrations of gasoline were 8503.2, 568.19, 11546.51, 345.29, 4042.82, 2835.67 and 182.96 ppm. Benzene was detected in all samples in concentrations of 1, 0.007, 391.11, 485.16,121.73,421.23, 183.88, 38.14, 138.12 and 306.87 ppm. Toluene was detected in all samples except one waste water sample and two canal water samples. Detected concentrations of Toluene were 20.45, 160.82, 64.47, 7.34 and 15.5 ppm. Moreover, xylene was not detected in any of the sample. BTEX and gasoline were detected in water samples in concentration exceeding the limits set by WHO and NEQS standards thus posing significant effects towards environment and health.

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Introduction

Benzene, toluene, ethyl benzene and xylene is a group of structurally similar volatile organic compounds. Due to the persistent nature and high toxicity they are considered to be very important environmental contaminants. They are widely used in industries as a solvent and as a fuel. They are mostly found in environmentally matrices near petroleum production, its storage and transport sites. These compounds are the major water soluble constituents of petroleum derivative i.e., gasoline. Benzene, toluene and ethyl benzene are designated priority pollutant. It is difficult to determine BTEX in different environmental matrices because of the loss during sampling and handling (Michael *et al.,* 2010). Due to petroleum spillage and discharge from petroleum related industries and factories surface water is contaminated mostly with BTEX and gasoline .Volatile organic compounds are persistent in the environment so it is very important to control its emissions. BTEX is the group of VOCs compounds. This group of VOCs is mainly found in petroleum derived products like gasoline and diesel fuel. They enter into the environment through variety of sources like engine emissions, cigarette smoke or industrial emissions (Assadi *et al.,*2014). Gasoline is not present in the environment. It is a complex mixture produced during petroleum refining. It contains 150 types of chemicals including BTEX.It comes into the water through accidental spillage or through the discharge waste water of industries and factories into the sea or river .Effects of gasoline includes death ,respiratory effects mostly pneumonia, emphysema, pulmonary edema ,focal alveolar hemorrhage, cardiovascular effects, gastrointestinal effects mostly damage to digestive tract, gastric erythema, gastric mucosa, ulceration of the epithelium , hematological effects like hemolysis, hepatic effects, renal effects like oliguria and renal failure (U.S Department of Health and service. 1994).BTEX is the abbreviation of Benzene, Toluene, Ethyl Benzene and Xylene. They are the mono aromatic hydrocarbons. Their boiling point ranges from 80°C-150 °C (Assadi *et al.,*2014). Due to the increased use and improper disposal of gasoline and other oil fuel in the environment their detection is very important. In gasoline and diesel BTEX is naturally present. BTEX are the major part of gasoline. They are hazardous to the environment and to the human health that's why they are categorized as priority pollutants. It is very important to reduce the effects of BTEX in the environment (Chong *et al.,*1991). BTEX compounds are the most hazardous component of gasoline. They have many health effects like they effect kidney, heart, liver, lungs etc. some of them also causes certain types of cancer (Agapovaand Winkler, 2010). Isolation and pre concentration steps are very important before analysis if we want to determine the BTEX traces in water (Assadi *et al.,* 2014). Due to their increased use and improper petroleum disposal causes them to enter the environment and after entering they damage the environment so the need to monitor BTEX is increasing day by day. Different technologies are used for this purpose some of which are High pressure liquid chromatography, Gas Chromatography-Mass Spectrometer, liquid-liquid extraction, solid phase extraction, solid phase micro extraction, crop trapping couples with solid phase micro extraction, head space solid phase micro extraction, directly suspended droplet micro extraction and purge and trap extraction but from the studies Gas Chromatography was found to be the most appropriate method for the qualitative and quantitative validation of these compounds.

Thus the present study was designed with the aim of qualitative and quantitative determination of BTEX and gasoline in different water samples and further to compare the detected concentrations with the limits set by WHO and NEQs to get idea about their possible impacts and hazards.

Materials and methods

This research work was designed for the qualitative and quantitative analysis of gasoline and BTEX in various samples (drinking water, canal water, industrial waste water) collected from dry port and surrounding residential area.

Study area

Area selected for the study was dry port and the surrounding residential area .This was the first dry port established in Pakistan. It was Constructed and managed by Pakistan Railways since 1973.

Data collection

Secondary data was gathered by questionnaire and from the previous studies**.** while surveying the concerned area following points were kept in mind i.e. type of container in which gasoline is transported to the port, source of these compounds in drinking water, frequency of water contamination, handling of gasoline, workers health conditions, where they discharge their waste water, is any factory or industry discharges their wastewater in the dry port and if yes what is the composition of the water. For primary data collection following steps were adopted.

Collection of samples

Samples of canal, drinking and industrial water were collected in autoclaved glass by grab sampling. All collected samples were transported immediately to lab for further analysis.

Chemicals

The analytical/HPLC grade chemicals i.e.benzene, toluene, ethyl benzene, xylene and gasoline were used in study.

Determination of physical parameters

The analysis of physical parameters of water samples was done by different tests like turbidity, pH, total suspended solids (TSS), total dissolved solids (TDS) and turbidity. Determination of these parameters was very important to check the water quality. Standard methods (table 1) were used for physical parameter analysis. Procedures that were adopted for conducting tests of physical parameters were as follows:

pH

pH of water samples was analyzed in the environmental lab after sample collection from different sources. The instrument that was used for pH analysis was pH meter. Firstly the small amount (10 ml) of water was taken from the collected bottled water sample. It was filtered with the help of filter paper. After filtration, the pH test was conducted by dipping probe of pH meter in water. For proper measurement the probe was rinsed with deionized water (which removes impurities) before each test.

Turbidity

Turbidity of water samples was determined in the environmental lab. 10 ml of water was taken from different sources of water samples. It was filtered with the help of filter paper. After filtration, turbidity of water was determined with a turbid meter and the readings were noted down.

Total suspended solids (TSS)

Total suspended solids were analyzed in all water samples that were collected from different areas. 30 ml of water was taken from different sources of water samples. It was filtered through pre-weighed filter paper. The wet filters were then placed in lab aluminum trays inside a drying oven at temperature between 103 to 105°C for one hour. The filters were allowed to cool at room temperature without the risk of being exposed to moisture in the air. When the filters cooled to room temperature, they were weighed again. For quality control purposes, the process was repeated.

Total dissolved solids (TDS)

Total dissolved solids were analyzed in all water samples that were collected from different areas. For this purpose 30 ml of water was taken out from the collected bottles of water. It was filtered through filter paper. Then a pre-weighed china dish was taken to heat the sample. Water was evaporated due to heat. Again the weight of china dish was taken. The difference between weights of china dish showed the total dissolved solids in water samples.

Qualitative and Quantitative determination of BTEX and Gasoline

For GC analysis standards/stocks were prepared by dissolving each BTEX compound (Benzene, Toluene, Ethyl Benzene, and Xylene) and gasoline in methanol (10ml) solution to make 100 µg/mL concentrations. These samples were than filtered via micro filter for GC analysis (Michael *and* Frederic L, 2010).

Preparation of Samples for GC

After collection samples were transferred in to 20 ml hand space vials and about 6 gm of salt and 30ul of ISTD solution was added in it in order to avoid any loss of volatile organic molecules. Vials were than caped and shake vigorously for 1 min and labeled for further analysis. These samples were than filtered via micro filter for GC analysis.

Methods for determining Gasoline and BTEX in water samples

Many methods are available for the determination of gasoline and BTEX but the best ones are gas chromatography for determination of BTEX and UV for determination of Gasoline. Conditions used for GC are given in table 2.

Qualitative Analysis

Qualitative analysis was done to determine the presence of gasoline and BTEX in the prepared water samples. Peak that show the maximum height was selected from the chromatogram of standards and then this selected peak was found in sample chromatogram. Peak, retention time (min) for each standard was noted. The noted retention time (min) of the peak in the chromatogram of standard solution was then being taken to make comparison with the retention time (min) of the peaks in the sample chromatogram.

Quantitative Analysis

By calculating response and relative response factor (RRF) quantitative analysis of results will be done. Peak area and concentration will be taken from results of analytes to calculate response factor. Following equations (A) and (B) will be used to calculate response factor.

Equation (A)

$$Responce\ factor = \frac{\text{Peak area of Standard}}{\text{Concentration}}$$

Equation (B)

$$\text{Response Factors} = \frac{\text{Peak Area of Sample}}{\text{Concentration}}$$

Equation (C)

Relative Response Factor

The calculated response factor of standard (eq. i) and sample (eq. ii) will then be used to establish relative response factor (RRF) between two analytes. Equation (C) will be used to calculate relative response factor.

$$\text{Relative Response Factor (RRF)} = \frac{\text{Response Factor B}}{\text{Response Factor A}}$$

Equation (D)

RRF will also be used in order to calculate the unknown concentration of analyte (A) in the presence of a known concentration of analyte (B), as shown in following equation (iv) (Mclntyre A and Rome K, 2012).

$$Concentration\ of\ Analyte = \frac{Peak\ Area\ of\ A}{Peak\ area\ of\ B} \times \frac{1}{RRF} \times \text{Concentration of Standard}$$

Results and discussion

The purpose of present study was to analyze BTEX and gasoline concentration in various water samples collected from area near dryport. Detection of these types of compounds in environmental matrices is a prime concern due to their toxicity and persistence in environment. During survey it was found in dry port area, handling and transport of gasoline lubricants, benzene, toluene, ethyl benzene and xylene without adopting proper working conditions and using personal protective equipments are the major activities. The main sources of gasoline and BTEX in water heightened during survey were leakage; spillage from tanks throwing waste into canal, due to the poor handling conditions of these chemicals.

In order to check the quality of water regarding organic contaminants it is important to test the physical parameters of water i.e., (pH, turbidity, TSS and color). Standard methods were used for the determination of physical parameters (table 1).

Table 1. Test methods for physical parameters.

Sr. No.	Physical Parameters	Test Method
1	pH	US EPA 150.1
2	Turbidity	US EPA 180.1
3	TSS	US EPA 160.1
4	TDS	US EPA 160.2
5	Color	Visual Inspection

The results of physical parameters are shown in table 3. Results of analysis were compared with WHO and NEQS standards. pH of all the samples was within the range of WHO standard for drinking water , waste water and for canal water). Results of analysis showed the turbidity of drinking water ranges from 1.47-2.48 which is within the range set by standards. Turbidity of some canal and waste water samples was exceeding the standard values i.e., for water sample labeled as W3 turbidity was 8.76 NTU, for W4 it was 14.7 NTU, 8.6 NTU for C3 is and 6.06 NTU for C4 is. These high values may be attributed to the presence of suspended and dissolved solids and organic contaminants in these samples. Total suspended solids (TSS), an important indicator to ensure water quality, were found within the range except for only one sample (300 mg/l) it was exceeding the limits of standards total dissolved solids in all water samples were present within the range set by national and international standards.

Table 2. Gas chromatography conditions.

Type	Specifications
Detector	Flame Ionization Detector (FID)
Detector Temperature	200° C
Injection Temperature	200° C
Column Temperature	50° C – 100° C
N_2 Flow	40µl/min
H_2 Flow	40µl/min
Air Flow	400µl/min
Run Time	15 min

Table 3. Results of physical parameters.

Sr. No.	Water Sample	pH	Turbidity (NTU)	Amount of TSS (mg/L)	Amount of TDS (mg/l)
Drinking water					
1	D1	7.25	2.12	50	60
2	D2	6.93	2.45	100	50
3	D3	6.45	2.48	100	30
4	D4	7.6	1.47	50	50
5	D5	7.05	1.51	50	100
6	D6	6.90	2.0	50	50
7	D7	6.88	1.82	50	70
8	D8	7.10	1.67	100	60
9	D9	6.58	1.20	100	50
10	D10	7.20	2.01	50	50
	Standard Values	6.5-8.5	5	150	500
Waste water					
11	W1	6.7	2.06	100	1000
12	W2	6.64	2.28	100	1100
13	W3	7.19	8.76	300	800
14	W4	6.79	14.7	50	1400
15	W5	8.0	1.76	150	900
	Standard Values	6-10	5	150	1500
Canal water					
16	C1	6.0	2.54	50	1200
17	C2	6.12	4.21	50	1300
18	C3	6.17	8.60	50	1300
19	C4	5.99	6.06	100	900
	Standard Values	6-10	5	150	1500

BTEX and gasoline are known to have effects on human health including neurological diseases and cancer. (Aurel *et al*, 2014). Presence of BTEX and gasoline in water samples was confirmed by comparing the retention time of standards chromatograms (Benzene, Toluene, ethyl benzene, Xylene and gasoline) with sample's chromatogram. The comparison confirmed the presence of Benzene, gasoline and toluene in many samples while xylene and ethyl benzene was not detected in any sample. Selective and sensitive method of gas chromatography was developed for quick analysis of these compounds. Qualitative and quantitative analysis of water samples showed the presence of benzene in all canal and waste water samples and 2 drinking water samples (Table 4).

Table 4. Results of quantitative analysis of BTEX and gasoline by GC.

Sample ID	Gasoline (ppm)	Benzene (ppm)	Toluene (ppm)	Xylene (ppm)
Drinking water samples				
Standard value	NA	0.005	1	10
D1	×	×	×	×
D2	×	×	×	×
D3	×	0.009	×	×
D4	×	×	×	×
D5	×	×	×	×
D6	×	×	×	×
D7	×	0.007	×	×
D8	×	×	×	×
D9	×	×	×	×
D10	×	×	×	×
Waste water samples				
Standard value	NA	0.01	1	NA
W1	8503.2	391.11	×	×
W2	568.19	485.16	20.45	×
W3	×	121.73	×	×
W4	11546.51	421.23	160.82	×
Canal water samples				
C1	345.29	183.88	64.47	×
C2	4042.83	38.14	7.34	×
C3	2835.67	138.12	×	×
C4	182.96	306.87	15.5	×

*NA:Not Available ; Ethylbenzene was not detected in any sample.

Benzene in two drinking water samples was found in concentration of 0.007 and 0.009ppm which was above the standard value i.e., 0.005ppm. Detected concentration of benzene in waste water and canal water samples ranges from 38.14ppm to 485.16ppm which was above the limit set by standards 0.01ppm. Petroleum handling, storage and transport are the major activities of the dryport area which are responsible for such high concentration of these detected VOCs. People living and working in the area are using this water for drinking and other purposes thus they are at alarming health risk as these can be inhaled or ingested by the people. Previous studies also reported that the exposure to such compounds like benzene pose potential hazards to health people living in these areas like neurological damage, dizziness, headache, vomiting and convulsions, eye and skin irritation, damage of upper respiratory tract and blister formation on skin. Chronic effects include blood disorders, affect bone marrow, anemia, and excessive blood loss and affect the structure of chromosomes (Mclntyreand Rome, 2012). During our field survey also residents of the area reported that they frequently suffered from irritation of skin, eyes, and throat. According to report prepared by Agency for Toxic Substances and Disease registry a very small exposure to a very high level of benzene can result in death toulene was not detected in any drinking water sample while it was found in five waste water and canal water samples in range from 7.34 ppm to 160.82 ppm which was far above the concentration 1ppm set by standards. Presence of toluene in water may is responsible for acute effects include damages central nervous system and causes narcosis, cardiac arrhythmia, Lungs and kidney damage and depression as reported in previous studies and was also mentioned by people living and working in area (Zaikowski, 2008). As our area of concern in this study was dry port and surrounding area the industries located in that area were mostly automobile industries. The waste water from these industries contains large amount of gasoline, Benzene and toluene as it is produced during the cleaning of vehicles and during petroleum refining. Gasoline was detected in seven waste water and drinking water samples in concentration ranges from 182.96 ppm to 11546 ppm which was very high from values set by national and international standards i.e., 10 ppm. Gasoline as detected in many samples was may be due to the activities in area and also due to discharges from industries which contains large amount of gasoline as it is used there during the cleaning of vehicles and during petroleum refining. Studies reveal that the presence of gasoline may pose severe health impacts like respiratory effects mostly pneumonia, emphysema, pulmonary edema, focal alveolar hemorrhage, cardiovascular effects, gastrointestinal effects mostly damage to digestive tract, gastric erythema, gastric mucosa, ulceration of the epithelium, hematological effects like hemolysis, hepatic effects, renal effects like oliguria, renal failure and death (U.S Department of Health and service .1994)

Conclusion

In this research paper analysis of BTEX and gasoline in selected water samples by GC was performed. Sensitive and selective analytical technique of gas chromatography was used for analysis. Benzene was present in all waste and canal water samples and two drinking water samples. Furthermore Toluene was detected in two drain water samples and three canal water samples. Xylene and ethyl benzene was not detected in any of the water sample. The concentration of detected compounds was exceeding the limits set by national and international standards. Presence of these compounds in water bodies may be due to different activities in the catchment area of water is alarming as they are known to poses many health problems like cancer, gastroenteritis, dysentery, diarrhea, nurological disorders and viral hepatitis. Excessive use of these VOCs results in the contamination of ground water sources and drain water. Strict regulations should be imposed to prohibit the use of gasoline and BTEX in the manufacturing of various products to save people from their negative impacts.

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