Investigation of Oil inside the Wells in REY Area in Tehran Oil Refining Company in Iran

Mohammad Ali Hosseinpour, Hossein Ghoreishi, Saeid Gitipour, and Mona Jafarnejad

Abstract**—**REY area has been located in Tehran Province and several archaeological ruins of this area indicate that the settlement in this area has been started since several thousand years ago. In this paper, the main investigation items consist of analysis of oil components and groundwater quality inside the wells. By finding the contents of oil in the well, it is possible to find out the pollution source by comparing the oil contents of well with other oil products that are used inside and outside of the oil farm. Investigation items consist of analysis of BTEX (Benzene, Toluene, Ethyl-benzene, Xylene), Gas chromatographic distillation characteristics, Water content, Density, Sulfur content, Lead content, Atmospheric distillation, MTBE(Methyl tertiary butyl ether). Analysis of polluting oil components showed that except MW(Monitoring Well)10 and MW 15 that oil with slightly heavy components was detected in them; with a high possibility the polluting oil is light oil.

Keywords**—**BTEX ; Oil Component; REY Area; Tehran Oil Refining Company (T.O.R.C) .

I. INTRODUCTION

PRESENT-DAY industrial activities release substantial amounts of crude oil and refined products into the natural environment as a result of events such as storage tank leakage or oil spills during with routine transporting and shipping operations. The contaminant load of soil and water is growing steadily each year in parallel with increasing industrialization and energy demand [1].The release of hydrocarbons into the environment, whether accidental or due to human activities, is the main cause of water and soil pollution and increases the risk of groundwater pollution. Many of these components are toxic, mutagenic and carcinogenic [2]. As petroleum contains hazardous chemicals such as benzene, toluene, ethylbenzene, xylenes, and naphthalene, this contamination can be hazardous to the health of plants, animals, and humans [3]-[4]-[5]- [6].

Oil consists of a great amount of hydrocarbons and high-molecular tar and asphaltene substances. Its main components are carbon (83–87%), hydrogen (12–14%) and oxygen (1–2%), as well as nitrogen, sulfur, various microelements [7]. In pollution, the presence of a great amount of paraffin, tars and asphaltenes in oil renders a considerable negative influence on physical and chemical properties of soil and the condition of the environment [8].

The pollution of soil and groundwater by oil had been actualized around the REY Industrial Area in 1970's, and it has begun to influence the local populace's life directly in 1980's. Tehran Oil Refining Company (T.O.R.C) which is located in the core of REY Industrial Area had conducted some measures in this regard, as much as possible, such as collection of the groundwater samples at the Qanat and water wells inside its site, monitoring of the fluctuation of groundwater level, pumping out of the groundwater and so on. However, spread of the pollution had been started earlier than the expectation, and despite of these activities, there was no effective method due to the shortage of machinery or similar problems. Consequently, the groundwater pollution in the REY Industrial Area has been expanding every year, and this pollution has compelled the resident in the area to live under suffering from a serious health hazard, particularly in recent years.

Obviously, these circumstances indicate that due to the flow of groundwater in T.O.R.C area the circumference of this company is under the risk of pollution, too. Therefore, another investigation on the pollution of soil and groundwater in REY Industrial Area that consists of 7 different companies (Research Institute of Petroleum Industry, Oil Exploration Operations Company, Commercial Storage, Iranol Company, Distribution Product Oil Company, Iranian Pipeline & Telecommunication Company, Persigas Company) has been started.

This paper represents the investigation items consist of analysis of BTEX, Gas chromatographic distillation characteristics, Water content, Density, Sulfur content, Lead content, Atmospheric distillation, MTBE in the soil and groundwater of REY Industrial Area including 7 companies.

II. MATERIALS AND METHODS

A. Investigation items and methods

Investigation items and verified test standards are shown in Table 1.

B. Measurement instruments

Gas chromatography apparatus, gas chromatography mass spectroscopy, fluorescence X-ray analyzer, atomic light absorption apparatus, Karl Fisher coulometric titration apparatus, distillation curve apparatus and other accessory apparatuses are needed.

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C. Methods of site investigation

1) Confirming the presence of oil layer in the wells and boring holes in Distribution Product Oil Company.

2) Sampling the free oil from oil layer.

3) Density, sulfur content, lead content and atmospheric distillation tests were performed in the laboratory of T.O.R.C (hereafter called as T.O.R.C Laboratory.), and BTEX, gas chromatographic distillation characteristics, water content and MTBE tests were conducted in the Research Institute of Petroleum Industry (hereafter called as RIPI).

III. Results and Discussion

A. BTEX

Gasoline commonly contains 13 chemicals (9 hydrocarbons and 4 additives) that are regulated as hazardous substances under The Comprehensive Environmental Response, Compensation, and Liability Act (C.E.R.C.L.A). The BTEX compounds are included in these chemicals [17]. The majority of organic wastes generated are comprised of aromatic organics[18]. BTEX is a generic name used for 6 compounds of benzene and its other derivatives, toluene, ethyl benzene and *o*- (ortho), *m*- (meta), *p*- (para) xylene. These hydrocarbons have a single aromatic ring and chemical characteristics of these compounds are similar. They can be found in crude oil and petroleum products. They are miscible in oil and other organic compounds and immiscible in water.

For comparing an oil sample with the other one, it is possible to analyze their BTEX contents and by plotting their compound densities in a hex diagram, they can be compared by considering the ratio of these 6 compounds to distinguish the similarity of samples. This method is the same as comparing the water samples by considering the content ratios of sodium, potassium, calcium, magnesium, chloride, sulfuric acid, nitric acid and carbonic acid. Comparison of water samples by considering these factors may lead to distinguish the water source.

The BTEX analysis result is shown in Table 2.

The following points are concluded by considering these results:

(a) Content of *p*-xylene in all samples is 0.

(b) Except MW12, total content of BTEX in the samples is low. Specially, in MW13 the possibility of designating a petroleum product in which BTEX has been decreased artificially as a base, is high.

(c) In MW12, the total amount of BTEX is higher than the others and among the relating components; content of toluene and *m*-xylene is high. Comparing with o- and p-xylene, the amount of m-xylene as organic ingredient is low. On the other hand, toluene and xylene are added to the unleaded gasoline as antiknock for cars. Therefore, in MW12 the possibility of designating a petroleum product in which toluene and *m*-xylene has been added artificially as a base, is high.

B. Gas chromatographic distillation characteristics

In gas chromatographic distillation by providing the distillation curve applied in gas chromatograph, it is possible to obtain the distribution of n-paraffin from C_5 to C_{44}, simultaneously. Accordingly, it will become a clue for understanding of oil type, whether it is heavy or light, or whether the amount of normal components is high or low (whether it is a product of cracking or not) .

Gas chromatographic distillation curve is shown in Fig. 1. and normal components ratio is shown in Table 3.

TABLE I
INVESTIGATION ITEMS AND TEST STANDARDS

Test items	Applied test standards
BTEX	ASTM D6563-05 (American Society for Testing and Materials)[9]
Gas chromatographic distillation characteristics	ASTM D2887-04a [10]
Water content	ASTM D1533-00 [11]
Density	ASTM D4052-96(2002)e1 [12]
Sulfur content	ASTM D4294-03 [13]
Lead content	ASTM D3237-02 [14]
Atmospheric distillation	ASTM D86-04b [15]
MTBE	ASTM D4815-04 [16]

Among the required tests, PAH analysis was not performed due to some technical problems in Iran. Therefore, it was decided not to execute this test.

TABLEII
BTEX ANALYSIS RESULTS

	Benzene (wt %)	Toluene (wt %)	Ethyl benzene (wt %)	*o*-Xylene (wt %)	*m*- Xylene (wt %)	*p*- Xylene (wt %)	Total BTEX (wt %)
MW10	1.1	0.5	0.5	1.2	0.6	0.0	3.9
MW11	1.0	0.5	2.5	0.4	0.3	0.0	4.7
MW12	2.0	5.8	1.2	3.5	8.1	0.0	20.6
MW13	0.1	0.1	0.5	0.4	0.3	0.0	1.4
MW14	2.6	0.7	2.9	0.4	1.5	0.0	8.1
MW15	0.2	0.5	0.7	0.5	0.1	0.0	2.0

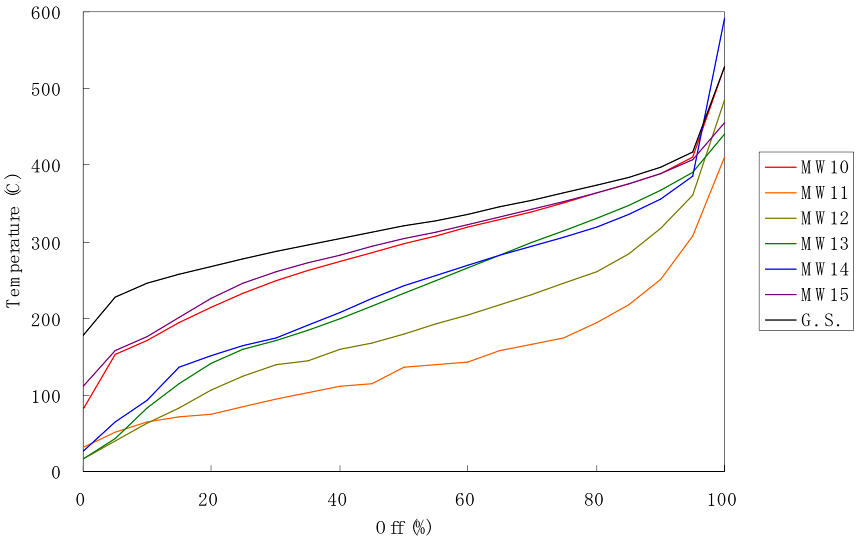

Fig. 1 Gas chromatographic distillation curve

TABLE III
NORMAL COMPONENTS RATIO

	Normal component ratio (%)
MW10	32.2
MW11	24.1
MW12	27.0
MW13	42.9
MW14	29.8
MW15	51.6

The following points can be understood from the analysis results:

(a) Boiling point distribution shows a pattern in which materials with higher boiling points contains higher ratios of big normal paraffin components.

(b) Considering the normal components ratio, the components of MW13 and MW15 are relatively big and it is possible to classify the other ones in a group.

C. Water content

The information of water content in the oil samples provides a clue for understanding whether there is hydrophilic components, other than hydrocarbons, in the samples or not. The results of analysis are shown in Table4.

According to these results, content of water in each sample is low and it can be concluded that almost all samples do not contain hydrophilic components.

TABLE IV
WATER CONTENT

	Water content (wt %)
MW10	0.006
MW11	0.007
MW12	0.004
MW13	0.008
MW14	0.008
MW15	0.006

D. Density

Density of oil (hydrocarbon) is related to the size its molecules. Generally, materials with low density consist of higher amount of small molecules and the boiling point, flash point and ignition point are low. In the case of high density materials, it is vice versa. Considering the petroleum products, density increases in the order of gasoline, jet fuel, kerosene, gas oil, heavy oil A, heavy oil B, heavy oil C and asphalt. The result of this analysis is shown in Table 5.

TABLE V
DENSITY ANALYSIS RESULTS

	Density at 15.56℃ (g/cm^3)
MW10	0.85540
MW11	0.77940
MW12	0.80195
MW13	0.81275
MW14	0.81906
MW15	0.84150

E..Sulfur content

Sulfur content in the crude oil is in the order of percent, and for producing petroleum products it is removed during oil refining in some extend by desulfurization process. Therefore, if the source of oil pollution is the crude oil tanks where it is stored temporarily, or if it is caused from intermediate or final products, comparison of sulfur contact can provide a clue for determining whether the source is something before desulfurization process or the pollution is caused by the products after this stage. Results of this analysis are shown in Table 6.

According to these analysis results, it can be said that higher sulfur concentration indicates that the sample belongs to the sections before desulfurization part and lower sulfur content is an indication of product after desulfurization process.

TABLE VI
SULFUR CONTENT

	Sulfur content (wt%)
MW10	0.871
MW11	0.155
MW12	0.331
MW13	0.488
MW14	0.565
MW15	0.810

F. Lead content

Addition of tetra alkyl lead or etc. as antiknock additives into the intermediate or final products stored in Distribution Product Oil Company or in the storage tanks of refinery was conducted previously; however, this addition of lead chemicals was stopped after 2001. Therefore, detection of lead can provide an important clue for determining the source of pollution whether the source of oil pollution is the crude oil tanks that are stored temporarily, or it is caused from intermediate or final products. Results of this analysis are shown in Table 7.

TABLE VII
LEAD CONTENT

	Lead content (ppm)
MW10	68.0
MW11	54.0
MW12	96.6
MW13	39.0
MW14	36.0
MW15	27.0

Accordingly, if the taken oil sample had been originated from the previous products produced before the stopping of lead chemicals addition in 2001, then it will contain gasoline with lead. In case of addition of lead chemicals into gasoline, tetraethyl lead $(C2H5)_4Pb$ with a molecular weight of 323.43~323.45, and specific gravity of 1.65~1.66, specific volume will increase 0.03%. In the case of addition of tetraethyl lead into gasoline that increases the specific volume 0.03%, lead content of gasoline will be equal to 500 ppm (weight fraction). Also, it is supposed that lead chemicals have not been added to kerosene and gas oil that are heavier products than gasoline.

G. Atmospheric distillation characteristics

By atmospheric distillation characteristics, it is possible to obtain the boiling point distribution of oil sample, directly. Atmospheric distillation characteristics provide a clue for determining roughly whether the oil sample is heavy or light fraction. The result of this analysis is shown in Fig. 2.

H. MTBE

MTBE (methy-ltertiary-butyl ether) as an antiknock additive was applied in the gasoline products instead of lead chemicals; however afterwards, it was stopped due to identification of its carcinogenesis effects. Knowing that MTBE was added into intermediate petroleum products or final products handled in the Distribution Product Oil Company and not in the handled products of refinery or its relating facilities, detecting of MTBE in the polluting oil can provide an important clue to find out whether the source of pollution is located in the Distribution Product Oil Company or not. It is noteworthy that the percent ratio of the weight fraction will be increased by the addition of MTBE to gasoline. Results of analysis are shown in Table 8.

TABLE VIII
MTBE CONTENT

	MTBE content (g/L)
MW10	0
MW11	6.4±0.2
MW12	0
MW13	3.3±0.2
MW14	3.6±0.2
MW15	0

MTBE was detected in each sample of MW11, MW13 and MW14. However, it was not detected in the samples of MW10, MW12 and MW15. In addition, considering the MTBE content of each sample of MW11, MW13 and MW14, the weight fraction of MTBE in these samples was found in the order of 1/100～1/1000 (specific gravity of MTBE is 0.7455). According to these results, there is a possibility that MTBE-added gasoline has been moved to the wells of MW11, MW13 and MW14, but there is no such a possibility for MW10, MW12, and MW15. Table 9 and Fig. 3. show the summary of the above-obtained results.

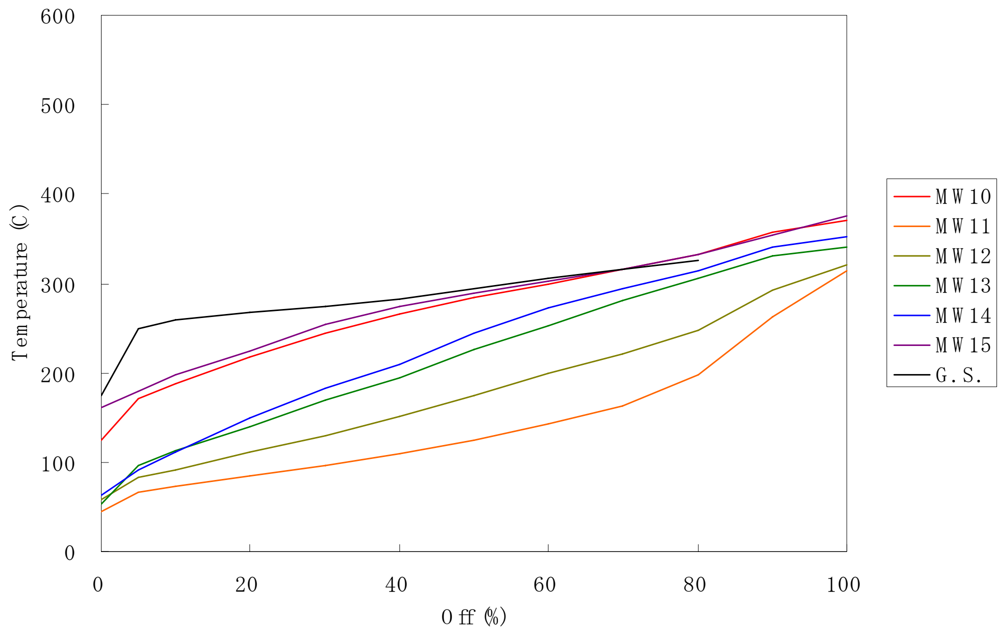

Fig. 2 Atmospheric distillation curve (atmospheric pressure 0.9 bar)

TABLE IX
OIL TYPE PRESUMPTION ACCORDING TO THE RESULT OF EACH TEST

Investigation item	MW10	MW11	MW12	MW13	MW14	MW15
BTEX			Toluene, Xylene added oil product (Gasoline ?)	BTEX reduced oil product	Toluene, Xylene added oil product (Gasoline ?)	
Gas Chrom. Distillation characteristics	A little heavy (gas oil)	(Jet fuel, Kerosene)	(Jet fuel, Kerosene)	(Jet fuel, Kerosene)	(Jet fuel, Kerosene)	A little heavy (gas oil)
Water content	Nil	Nil	Nil	Nil	Nil	Nil
Density	Jet fuel, Kerosene	Jet fuel, Kerosene	Jet fuel, Kerosene	Jet fuel, Kerosene	Jet fuel, Kerosene	Jet fuel, Kerosene
Sulfur content	Nondesulfurized oil	Desulfurized oil product	Desulfurized oil product	Desulfurized oil product	Desulfurized oil product	Nondesulfurized oil
Lead content	Gasoline produced before 2001	Gasoline produced before 2001	Gasoline produced before 2001	Gasoline produced before 2001	Gasoline produced before 2001	Gasoline produced before 2001
Atmospheric distillation	A little heavy (gas oil)	Jet fuel, Kerosene	Jet fuel, Kerosene	Jet fuel, Kerosene	Jet fuel, Kerosene	A little heavy (gas oil)
MTBE	A kind of oil without MTBE	MTBE added gasoline	A kind of oil without MTBE	MTBE added gasoline	MTBE added gasoline	A kind of oil without MTBE

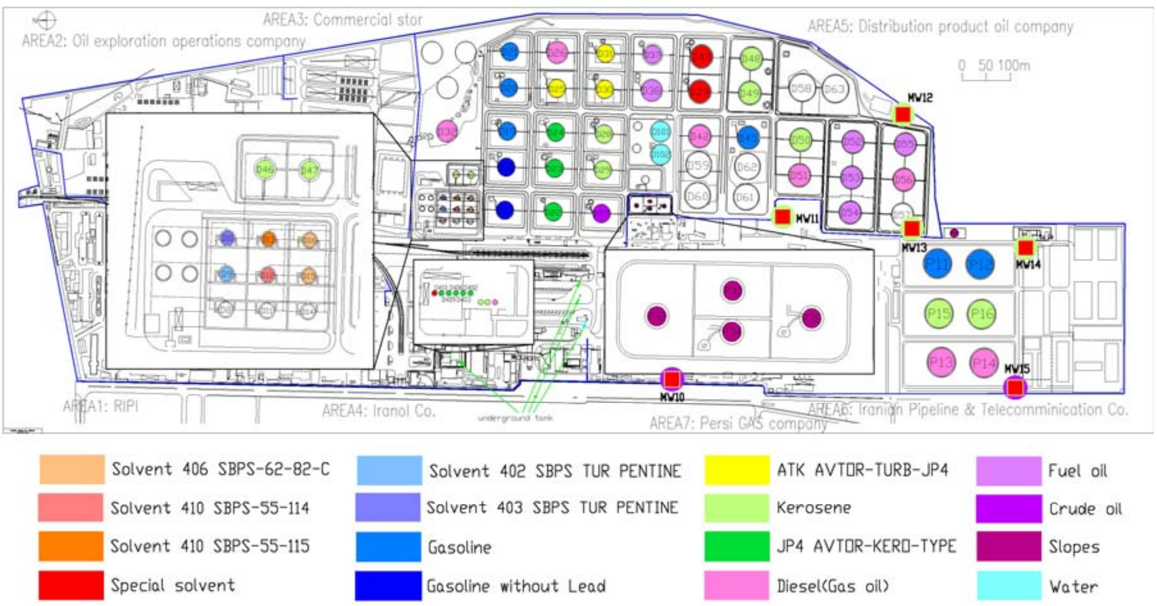

Fig. 3 Presumed oil types and the relating positions

IV. CONCLUSION

There is a wide range of oil pollution in REY industrial area. Ground of REY industrial area consists of a uniform sticky soil. The polluting oil is mainly light oil and it is mixed with groundwater. Oil components are also dissolved in groundwater. Polluting oil consists of lead containing gasoline. It is thought that the oil leaked before 2001 has discharged into wells.

It seems that some cracks exist in the ground of REY industrial area that become bleeding channels. Therefore, the strength of the ground will possibly increase due to a dynamic compression. There are probably several pollution sources such as leakage from bottom plates of tanks, leakage from underground buried pipelines or other facilities and etc. Comparing the pollution circumstances of T.O.R.C and the oil pollution of soil and groundwater in REY industrial area, excluding the existence of drain pits, both cases have the same conditions such as existence of the pollution from before, sticky soil condition of ground, detecting the polluting oil as light oil and so on. Therefore, effective measures used in the oil pollution of soil and groundwater of T.O.R.C can be applied for the oil pollution of soil and groundwater in REY industrial area. It is thought that measures the same as that for T.O.R.C (underground consecutive wall, oil pump up, bioremediation and so on) can be applied for REY Industrial Area.

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