

GAS CHROMATOGRAPHY AND METAL ANALYSIS OF PRODUCED WATER  
TREATED WITH A HOUSEHOLD COMMERCIAL FILTER

by

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## Abstract

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Unconventional oil and gas extraction activities, including hydraulic fracturing, are a collection of processes used to liberate significant quantities of natural gas and oil in the United States. Many extraction sites are located in large cities, close to residential areas. In some cases, operational malfunctions can result in spills of thousands of gallons of produced waste water and pose a threat of contaminating underground or surface water resources. Produced water contains a complex mixture of salts, volatile and semi-volatile organic compounds, metals, organic acids, and particulates, as well as additives from the drilling process. In this study, we tested the potential for wastewater treatment using a household grade commercial Brita pitcher filter which uses coconut-based activated carbon with ion exchange resin. In normal usage, a Brita filter can be used with up to 40 gallons of tap water to reduce chlorine taste and odor, zinc, and harmful contaminants copper, mercury and cadmium. A variety of analytical instruments, including GC-FID, GC-MS, TOC, and ICP-OES were used for qualitative and quantitative analysis of water before and after passage through the filter. GC-MS analysis of total petroleum hydrocarbons, based on extraction of the characteristic ion at 57 m/z, showed a decrease in branched hydrocarbon content, in agreement with total organic carbon analysis. Metal analysis with ICP-OES also showed a small reduction in Ba, Be, Ca, Na, and other metals, but not enough to be below safe drinking standards. In general, this work serves to illustrate that drinking water contaminated with waste water from the oil and gas industry may not be reliably treated using this widely-used household product.

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## Chapter 1

### INTRODUCTION AND BACKGROUND

#### 1.1 Produced water from unconventional drilling

Unconventional drilling of oil and natural gas operations produce two primary types of saltwater waste streams, flowback and produced water. Flowback water is the fluid that returns to the surface during and for the weeks following the hydraulic fracturing process. Produced water is naturally occurring water found in hydrocarbon-bearing formations that flows to the surface along with oil and natural gas. A November 2012 presentation by the U.S. Department of Interior Bureau of Reclamation indicates that hydraulic fracturing in the U.S. utilizes 0.5 million to more than ten million gallons of water per well fracturing event. <sup>[1]</sup>

Flowback water consists largely of the water injected into the oil and natural gas wells during the hydraulic fracturing process but also includes clays, fracturing chemical additives, dissolved metal ions and total dissolved solids. At some point, the water recovered from an oil and natural gas well makes a transition from flowback water to produced water for the remaining life of the oil and natural gas well. The transition point can be difficult to discern but is often identified by the chemical composition and weight of the recovered water and the rate of return. Flowback water generally has a higher flow over a matter of weeks while produced water has a lower flow over the lifespan of the well. <sup>[1]</sup>

Produced water is water from underground formations that is brought to the surface during oil or gas production. Because the water has been in contact with hydrocarbon-bearing formations, it contains some of the chemical characteristics of the formations and the hydrocarbons. It may include water from the reservoir, water previously injected into the formation, and any chemicals added during the production processes. The physical and chemical properties of produced water vary considerably depending on the geographic location of the field, the geologic formation, and the type of hydrocarbon product being produced. Produced water properties and volume also vary throughout the lifetime of a reservoir. Produced water is the largest volume by-product or waste stream associated with oil and gas exploration and production. Previous national produced water volume estimates are in the range of 15 to 20 billion barrels (bbl; 1 bbl = 42 U.S. gallons) generated each year in the United States. <sup>[2]</sup>



Per the Argonne study, the majority of this produced water was re-injected for enhanced hydrocarbon recovery (e.g., waterfloods) with virtually all of the remaining produced water (or more than 7.1 billion barrels) injected subsurface for disposal at a solid waste disposal SWD facility. Produced water is typically generated, and saltwater disposal services are required, for the life of an oil and natural gas well, which can span multiple decades. Produced water can represent up to 98.0% of the fluid brought up from U.S. onshore wells nearing the end of their productive lives. [2]

Produced waters typically exhibit significant variations in salinity, sodicity, trace element composition, and organic geochemistry resulting from differences in environmental and geologic conditions. Some of these waters contain relatively high salinity values, sometimes greater than seawater, while others are potable. However, continued concerns over diminishing water resources and expanding needs for next generation energy sources have led to the characterization of produced waters as possible resources. [3]

## 1.2 Potential threat of Produced water on drinking water resources

In April 2015, City of Arlington officials report on a fracking fluid blowout spilled near Lake Arlington Baptist Church. A fracking site 600 feet from a cluster of homes in the state's seventh largest city. In the incident, 42,800 gallons of fracking fluid, boiling up from thousands of feet underground, spewed into the streets and into Arlington storm sewers and streams. Sealing the well took 24 hours and four attempts. [4]

Where does Arlington drinking water come from? Arlington purchases its water for treatment from the Tarrant Regional Water District. The water is taken from four reservoirs. Cedar Creek, Richland-Chambers, Lake Benbrook, and Lake Arlington. Lake Arlington supplies the Pierce-Burch Water Treatment Plant. In City of Arlington most recent 2015 water quality report, it published a list of regulated substances that required to be monitored and were detected in tap water. None of detected substances exceeded the regulated limit. It did mention that salts and metals could be industrial or domestic wastewater discharges; organic chemical substances could be by-products of industrial processes. [5] Railroad Commission of Texas made available on the web a Public GIS Viewer Map that allows users to view oil, gas and pipeline data in a map view. Many drilling sites are located surrounding lake Arlington with hundreds of horizontal drilling lines.[6] Served as one of main drinking water source for a populous

city reported closed to 400,000 residents, it is a legitimate concern for a future gas well spill. We made a rough estimate using reported spilled volume 42,800 gallons over lake Arlington capacity 11.7 billion gallons, that would mean a 3.66 ppm dilution factor contamination.

### 1.3 Household Commercial Water Filter

How Safe Is Public Water? Under the Safe Water Drinking Act, the US Environmental Protection Agency (EPA) is responsible for setting national drinking water standards. The EPA regulates over 80 contaminants—including arsenic, e-coli, cryptosporidia, chlorine, and lead—that may be found in drinking water from public water systems. While the EPA says that 90 percent of US public water systems meet its standards, many people still want to use water filter system to further ensure their water's safety. <sup>[6][7]</sup>

A 2003 study by the nonprofit Natural Resources Defense Council (NRDC) found that due to a combination of pollution and deteriorating equipment and pipes, the public water supplies in 19 of America's largest cities delivered drinking water that contained contaminant levels exceeding EPA limits (either legal limits or unenforceable suggested limits) and may pose health risks to some residents. So even though it may test fine at its source, public water may still pick up contaminants on the way to your house. <sup>[6]</sup>

As more people become suspicious of their tap water, bottled water market has skyrocketed. But come with it is the concern for environmental degradation, landfill waste, and human rights abuses associated with bottled water. Thus, a good alternative option for ensuring that the water you and your family drink is as safe as it can be: a water filter. Putting a water filter in your home is less expensive and far less environmentally damaging than bottled water. And if you choose the right filter, you can minimize or eliminate the contaminants of highest concern in your area. <sup>[6]</sup>

### 1.4 Activated Carbon Treatment

Activated carbon is a material used to filter harmful chemicals from contaminated water and air. It is composed of black granules of coal, wood, nutshells or other carbon-rich materials. As contaminated water or air flows through activated carbon, the contaminants adsorb to the surface of the granules and are removed from the water or air. Granular activated carbon or "GAC" can treat a wide range of contaminant vapors including radon and contaminants dissolved in groundwater, such as fuel oil,

solvents, polychlorinated biphenyls, dioxins, and other industrial chemicals, as well as some radioactive materials. It even removes low levels of some types of metals from groundwater. [8]

Activated carbon treatment generally consists of one or more columns or tanks filled with GAC. As the contaminated water or air flows through the GAC, the contaminants adsorb to the outer and inner surfaces of the granules. The water and air exiting the container will be cleaner. The GAC will need to be replaced when the available surfaces on the granules are taken up by contaminants and additional contaminants can no longer sorb to them. [8]

Activated carbon is highly effective water treatment medium. Due to its high degree of microporosity, just one gram of activated carbon has a surface area in excess of 3,000 m<sup>2</sup> (32,000 sq ft). [9] Coconut shell carbon is becoming popular not only because it is made from a renewable resource but also because it produces very good tasting water and is particularly good at trihalomethane removal.

### 1.5 Total Petroleum Hydrocarbons (TPH)

Total Petroleum Hydrocarbons (TPH) is a term used to describe a broad family of several hundred chemical compounds that originally come from crude oil. In this sense, TPH is really a mixture of chemicals. They are called hydrocarbons because almost all of them are made entirely from hydrogen and carbon. Contamination caused by petroleum products will contain a variety of these hydrocarbons. Because there are so many, it is not usually practical to measure each one individually. However, it is useful to measure the total amount of all hydrocarbons found together in a particular sample of soil, water, or air. [10]

The amount of TPH found in a sample is useful as a general indicator of petroleum contamination at that site. However, this TPH measurement or number tells us little about how the particular petroleum hydrocarbons in the sample may affect people, animals, and plants. By dividing TPH into groups of petroleum hydrocarbons that act alike in the soil or water, scientists can better know what happens to them. These groups are called petroleum hydrocarbon fractions. Each fraction contains many individual compounds. [10]

TPH is released to the environment through accidents, as releases from industries, or as byproducts from commercial or private uses. When TPH is released directly to water through spills or leaks, certain TPH fractions will float in water and form thin surface films. Other heavier fractions will

accumulate in the sediment at the bottom of the water, which may affect bottom-feeding fish and organisms. Some organisms found in the water (primarily bacteria and fungi) may break down some of the TPH fractions. TPH released to the soil may move through the soil to the groundwater. Individual compounds may then separate from the original mixture, depending on the chemical properties of the compound. Some of these compounds will evaporate into the air and others will dissolve into the groundwater and move away from the release area. Other compounds will attach to particles in the soil and may stay in the soil for a long period of time, while others will be broken down by organisms found in the soil. <sup>[10]</sup>

Health effects from exposure to TPH depend on many factors. These include the types of chemical compounds in the TPH, how long the exposure lasts, and the amount of the chemicals contacted. Very little is known about the toxicity of many TPH compounds. Until more information is available, information about health effects of TPH must be based on specific compounds or petroleum products that have been studied. <sup>[10]</sup>

## 1.6 The Analytical Techniques

### 1.6.1 Total Organic Carbon (TOC) analyzers

TOC analyzers adopt the 680°C combustion catalytic oxidation method, which was developed by Shimadzu and is now used worldwide. While providing an ultra-wide range of 4 µg/L to 30,000 mg/L, these analyzers boast a detection limit of 4 µg/L through coordination with NDIR. This is the highest level of detection sensitivity available with the combustion catalytic oxidation method. In addition, the combustion catalytic oxidation method makes it possible to efficiently oxidize not only easily-decomposed, low-molecular-weight organic compounds, but also hard-to-decompose insoluble and macromolecular organic compounds. <sup>[11]</sup>

The 680°C combustion catalytic oxidation method achieves total combustion of samples by heating them to 680°C in an oxygen-rich environment inside TC combustion tubes filled with a platinum catalyst. Since this utilizes the simple principle of oxidation through heating and combustion, pretreatment and post-treatment using oxidizing agents are unnecessary, which enhances operability. The carbon dioxide generated by oxidation is detected using an infrared gas analyzer (NDIR). By adopting a newly-

designed, high-sensitivity NDIR, the TOC-L series achieves high detection sensitivity, with a detection limit of 4µg/L, the highest level for the combustion catalytic oxidation method. [11]

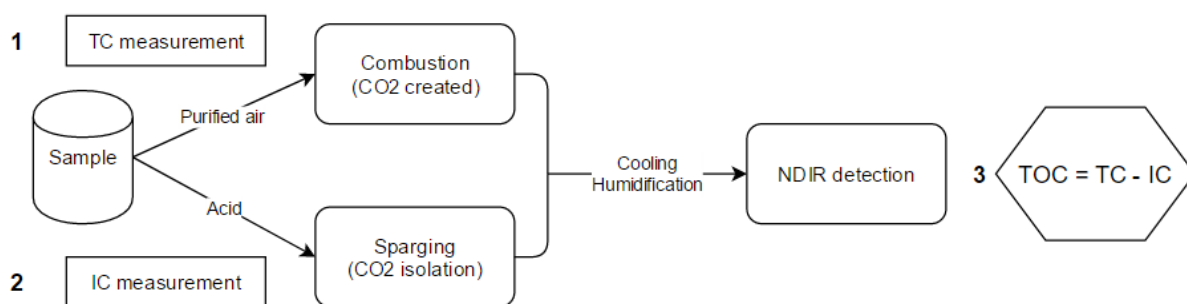


Figure 1-1 Schematic diagram showing TOC measurement.

The sample is delivered to the combustion furnace, which is supplied with purified air. There, it undergoes combustion through heating to 680°C with a platinum catalyst. It decomposes and is converted to carbon dioxide. The carbon dioxide generated is cooled and dehumidified, and then detected by the NDIR. (Path 1) The concentration of TC (total carbon) in the sample is obtained through comparison with a calibration curve formula. (Path 2) Furthermore, by subjecting the oxidized sample to the sparging process, the IC (inorganic carbon) in the sample is converted to carbon dioxide, and the IC concentration is obtained by detecting this with the NDIR. (Path 3) The TOC concentration is then calculated by subtracting the IC concentration from the obtained TC concentration. [11]

### 1.6.2 Gas Chromatography

#### ❖ Introduction

Gas chromatography (GC) is one of the most versatile and ubiquitous analytical techniques in the laboratory. It is widely used for the determination of organic compounds. There are two types of GC: gas–solid (adsorption) chromatography and gas–liquid (partition) chromatography. The more important of the two is gas–liquid chromatography (GLC), used in the form of a capillary column. In gas chromatography, the sample is converted to the vapor state (if it is not already a gas) by injection into a heated port, and the eluent is a gas (the carrier gas). The stationary phase is generally a nonvolatile liquid or a liquid-like phase supported on or bonded to a capillary wall or inert solid particles such as diatomaceous earth silica. [12]

There are a large number of liquid phases available, and it is by changing the liquid phase, rather than the mobile phase, that different separations are accomplished. The most important factor in gas chromatography is the selection of the proper column (stationary phase) for the particular separation to be attempted. The nature of the liquid or solid phase will determine the exchange equilibrium with the sample components; and this will depend on the solubility or adsorbability of the analytes, the polarity of the stationary phase and sample molecules, the degree of hydrogen bonding, and specific chemical interactions. [12]

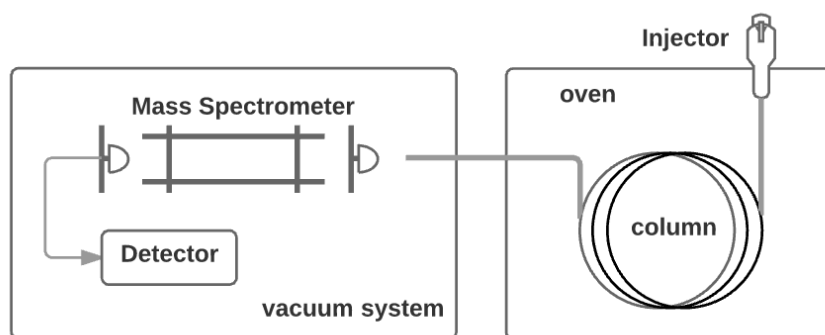


Figure 1-2 Schematic of a Gas chromatography – mass spectrometer.

#### ❖ GC Column & Stationary Phase

The two types of columns used in GC are packed columns and capillary columns. Packed columns came first and were used for many years. Capillary columns are more commonly used today. Open Tubular capillary columns consist of a long narrow tube of silica coated on the inside surface with a very thin 'film' of immobilized polymeric liquid, gum, particulate or zeolite stationary phase. These columns are known as Wall Coated Open tubular columns (WCOT) and provide the highest resolution and efficiency of all gas chromatographic columns. This is mainly due to the length and homogeneously thin stationary phase films that can be achieved with capillary column technology. [12]

Liquid stationary phases are selected based on polarity, determined by the relative polarities of the solutes. For fused silica columns, the majority of separations can be done with fewer than 10 bonded liquid stationary phases of varying polarity. This is because with their very high resolving power; selectivity of the stationary phase is less critical. The stationary phases are high-molecular-weight,

thermally stable polymers that are liquids or gums. The most common phases are polysiloxanes and polyethylene glycols (Carbowax), with the former the most widely used. <sup>[12]</sup>

❖ *Isothermal and Gradient Temperature GC*

In Isothermal GC, the temperature of the GC oven (and hence the column) remains constant during the course of the analysis. This method of analysis is powerful when dealing with groups of compounds whose boiling point does not differ significantly and whose retention characteristics are similar. Where analyte retention characteristics differ – problems can be encountered with long retention times, poor peak shape and poor sensitivity for later eluting peaks; it may also be difficult to achieve a satisfactory separation for early eluting peaks where  $k < 2$ . <sup>[12]</sup>

In temperature programmed GC, the oven starts at a low temperature to assist with the separation of early eluting peaks, is then ramped and usually held for a specified time at an upper temperature. This allows the analytes to elute within a reasonable timeframe and to be sure that all analytes have eluted from the column. In temperature programmed GC, analytes of a homologous series will elute according to a linear scale. A useful benefit of gradient temperature programmed GC is that all peaks elute with approximately the same width. Later eluting peaks therefore do not suffer from dispersion as in isothermal GC and as they are 'sharper', the inherent sensitivity of the method (measured via 'signal to noise ratio'), increases for later eluting analytes. <sup>[12]</sup>

❖ *Flame Ionization Detector (FID)*

The Flame Ionization Detector is the most widely used GC detector and was invented specifically for GC applications. It's high sensitivity and linear range for carbon-containing compounds make it very popular in organic analysis. A typical FID design is shown here:

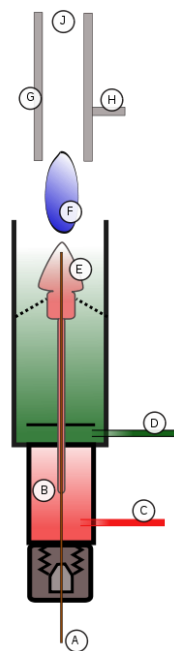


Figure 1-3 Schematic of Flame Ionization Detector (Source: Wikimedia Commons)

A) Capillary tube; B) Platinum jet; C) Hydrogen; D) Air; E) Flame;

F) Ions; G) Collector; H) Coaxial cable to Analog to Digital converter; J) Gas outlet.

The column effluent is mixed with hydrogen and a make-up gas (for capillary systems) before exiting via a small orifice (jet-tip) which is surrounded by a high flow of air. The Hydrogen is combustible in air and can be lit via a remote glow plug. As the column effluent is burned in this flame, ions are created which form a small current when a potential difference is applied. When no analyte (carbon containing compounds) are being burned, a small background current (10-20 picoamperes) arises from impurities in the carrier and detector gases. Conventionally the jet forms the anode and a cylindrical electrode held just above the flame is the cathode. A voltage of between 200 and 300V across these components is usually optimal but depends on detector design. The flame ionization detector produces a proportional response to the number of carbon atoms in a molecule. One suggested reason for this constant response factor is the conversion of all solute carbon molecules to methane in the combustion process. When heteroatoms are present within the analyte molecule the sensitivity of the detector is much reduced. A calibration curve should be constructed for each analyte prior to quantitative analysis to take into account response variations due to detector settings.



❖ Mass Spectrometer (MS) Detector

The detector is maintained under vacuum. Compounds eluting from the GC column are bombarded with electrons (EI) or reagent gas ions (CI) in order to ionize them. Compounds fragment into characteristic charged ions or fragments and the resulting charged species are focused and accelerated into a mass analyzing device –typically a Quadrupole mass analyzer or Ion Trap mass analyzer. The mass analyzer selectively allows ions of a selected mass to charge ratio to pass through the analyzer to the electron multiplier where a signal due to that specific mass to charge ratio ion is generated. The mass filter can be adjusted to allow specified ions to pass (selected ion monitoring SIM mode) or to quickly scan over a range of mass to charge values (scanning mode). The abundance (total ion count) versus time is plotted to form the chromatogram. A mass spectrum can be obtained for each ‘scan’ which plots the number of ions at each different mass to charge ratio in the range selected.

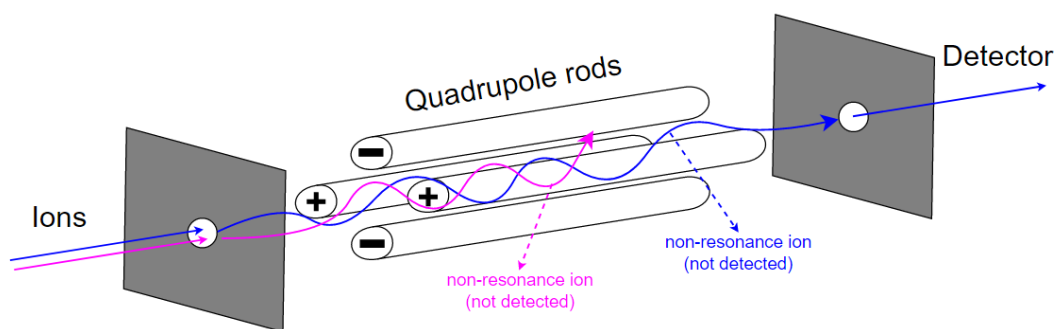


Figure 1-4 Schematic of Quadrupole Mass analyzer.

1.6.3 Inductively Coupled Plasma – Optical Emission Spectrometry ICP-OES

❖ Principle of Emission Spectrometry

Inductively Coupled Plasma (ICP) based analytical techniques can provide quantitative bulk elemental composition of a wide variety of sample types, including powders, solids, liquids, and suspensions. Solid samples are generally dissolved or digested using a combination of acids in a closed microwave system, thus retaining potentially volatile analyte species. The resulting sample solution is then nebulized into the core of an inductively coupled argon plasma, where temperatures of approximately 9000 K are attained. At such high temperatures, the nebulized solution is vaporized, and the analyte species are atomized, ionized and thermally excited. The analyte species can then be

detected and quantitated with an optical emission spectrometer (OES), which measures the intensity of radiation emitted at the element-specific, characteristic wavelength from thermally excited analyte atoms or ions. Intensity measurements are converted to elemental concentration by comparison with calibration standards. This technique is especially powerful for quantitative chemical analysis when standards are not available.

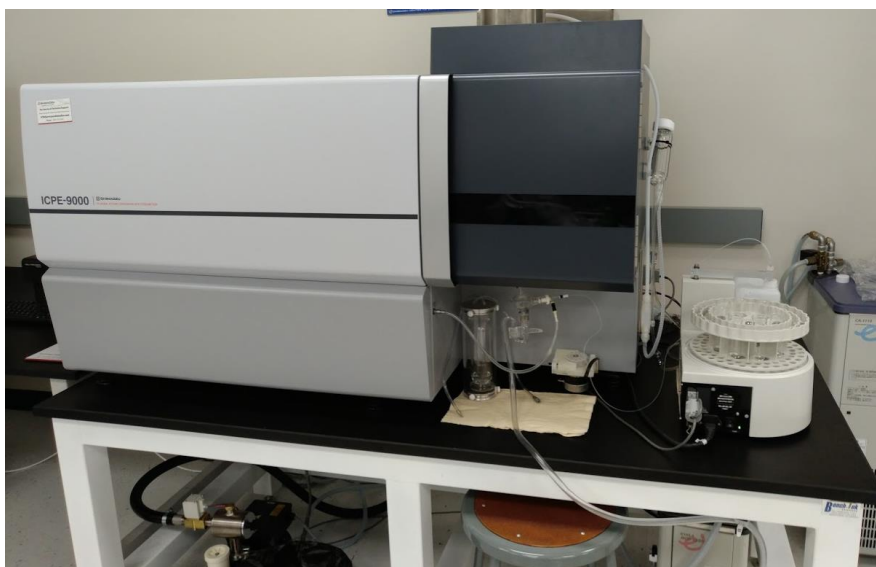


Figure 1-5 Shimadzu ICPE-9000 instrument (picture taken in Geoscience Lab)

❖ Advantages

A range of elements can be measured in a single analysis cycle. The useful linear dynamic range is over several orders of magnitude. The analysis can be automated, enhancing accuracy, precision and sample throughput. The combination of ICP-OES and ICP-MS is very powerful for determining a wide range of elemental concentrations, from major components to trace level components (typically sub ppb) with high accuracy and precision.

❖ Limitations

The sample portion to be analyzed must be completely digested or dissolved prior to analysis. Emission spectra can be complex and spectral interferences are possible if the wavelength of the element of interest is very close to, or overlaps that of another element. Matrix related effects can create challenges in quantitation. Carbon, Nitrogen, Hydrogen, Oxygen and halogens cannot be determined using this technique.

## Chapter 2

### GAS CHROMATOGRAPHY AND METAL ANALYSIS OF PRODUCED WATER TREATED WITH A HOUSEHOLD COMMERCIAL FILTER

#### 2.1 Aim of study

This study is thought of as a hypothetical question: What if my drinking water source or lake water where I go camping is contaminated by spilled fluid from gas and oil drilling activity, is it practical to use a household commercial filter which been known to be effective for tap water to further clean the water. How safe and effective would that be?

Just as water filter and public water facility often rely on their analytical testing on water going through their filtering system, we attempted to perform similar analytical test using university lab instrument such as TOC, GC-FID, GC-MS, ICP-OES to qualitatively and quantitatively analyze the chemical composition of a collected produced water sample before and after treatment with a common household commercial water filter made by Brita.

We plan to look for trend of filtering effect through bulk characteristic with TOC analysis, more detail organic composition and quantitation with GC-FID and GC-MS. Lastly, metal analysis with ICP-OES. We will also attempt to compare some contaminant level with regulated value available.

#### 2.2 Materials

##### 2.2.1 Produced water

The produced water (PW) samples were obtained from Saltwater Disposal Well (SWD) in Midland County of west Texas, a community site for disposing of produced water from nearby oil wells. The Wolfcamp shale in the Midland Basin portion of Texas' Permian Basin province contains an estimated mean of 20 billion barrels of oil, 16 trillion cubic feet of associated natural gas, and 1.6 billion barrels of natural gas liquids, according to an assessment by the U.S. Geological Survey. <sup>[13]</sup>

The average specific gravity of PW coming into the SWD site: 9.1-9.3 lbs per gallon (1.09-1.114 g/ml) Most of the oil and water separation is completed at the well itself. Only 1/10 of 1 percent oil content remains by the time it reaches the SWD site. Homogenization of the PW delivered (produced and flow back put together).

Produced water 6 (PW6) was collected in March of 2016. PW6 had a conductivity of approximately 113.0 mS/cm, equivalent in conductivity to 8.5 % NaCl(aq). Solids and some oil were removed from the sample with vacuum filtration similar to previous samples. The sample had a prominent layer of oil, even after vacuum filtration.

### 2.2.2 Brita Replacement Pitcher Water Filters

A small Brita 6 cup water pitcher with standard replacement filters (model OB03). Brita Replacement Pitcher Water Filters rank #1 on Amazon best seller list of replacement water filter. Brita brand filters are guaranteed to fit in all Brita pitchers and dispensers. The Brita pitcher filter uses technology which combines coconut-based activated carbon with ion exchange resin in a BPA free housing. These materials work together to reduce chlorine taste and odor, zinc, and harmful contaminants copper, mercury and cadmium- often found in tap water. Keep great-tasting filtered water flowing by replacing your filter every 40 gallons or approximately every two months. On the performance data sheet, this filter model is tested and certified against NSF/ANSI Standards 42 (Health Effects) in reducing 3 heavy metals copper, mercury, and cadmium below EPA maximum permissible concentration, as well as Standards 42 (Aesthetic Effects) in lowering Chlorine and Zinc level to improve taste. <sup>[14]</sup>

### 2.3 Preliminary study / screening analysis

This study was performed over two series of instrumental analysis. The first series can be considered as preliminary or screening phase where sample prep procedure and methods for qualitative and quantitative were not fully developed. Its results are valuable in estimating the filter performance and refining the analysis procedure in the second series.

### 2.3.1 PW Filtering Procedure

Produced water 5 (PW5) was used. Water filter is flushed with about 200ml of DI water. Multiple aliquots of PW5 were passed through filter once, each aliquot of eluate was collected to a separate 130ml brown plastic container and stored in the fridge for further analysis.



Figure 2-1a. Visible improvement in water quality can be observed after filtering PW5 with Brita filter.

Vial from left to right: unfiltered PW5 labeled #0, next is 1<sup>st</sup> elution aliquot filtered labeled #1, so on.



Figure 2-1b. Filtering steps performed on PW sample, each consecutive 130ml eluate collected in brown bottle for further analysis.

2.3.2 Salinity, conductivity, pH test

Atago Refractometer PEN-SW(W) was used to measure % Salinity (g/100g), pen was dip onto sample bottle, readings are recorded once number stop fluctuate. Pen tip is cleaned with DI water after each use. Horiba DS-72 pH/Conductivity meters for were used to measure both pH and conductivity.

# Filter Passes	Salinity (g/100g)	Conductivity (mS/cm)	pH
0	13	138.4	6.73
1	9.8	111.0	2.97
2	12.2	134.9	2.46
3	13.2	137.0	2.53
4	13.2	141.9	2.59
5	13.1	139.2	2.60
6	12.9	138.0	2.61

Table 2-1. Salinity, conductivity, and pH.

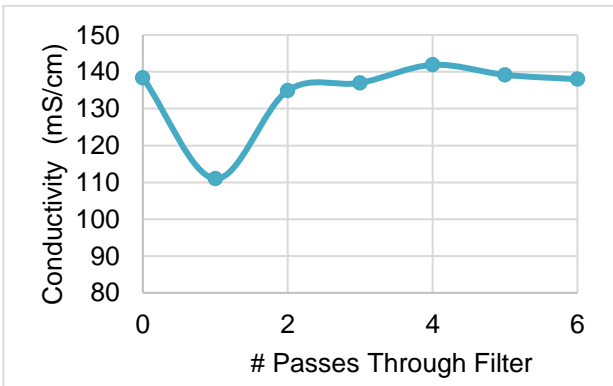
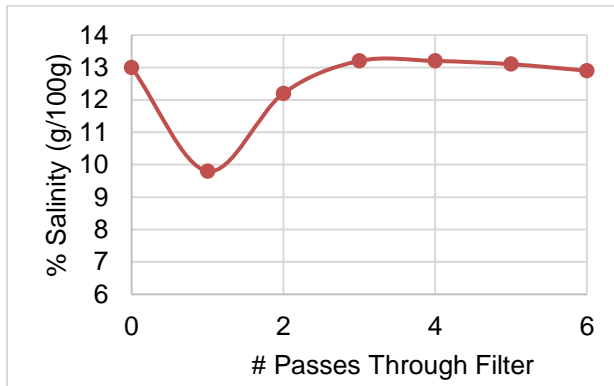
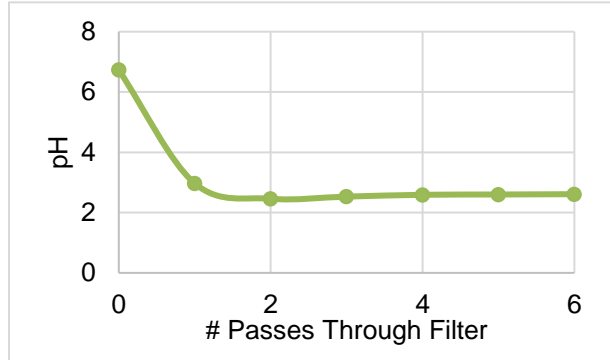


Figure 2-2. Plot of pH, % salinity, conductivity changes as PW5 samples were filtered through.

Very distinctive trends were observed, % salinity and conductivity decrease to a minimum on the 1<sup>st</sup> pass through, return to high level indicate saturation point of filter for removing salts. PW is considerably much higher salty than sea water at around 3.5% salinity. Therefore, it is reasonable for cation to max out the ion exchange resin binding site of the filter. This ion exchange in effect kick out proton and lower the pH of the solution.

2.3.3 TOC analysis

Shimadzu TOC-L equipped with TNM-L module were used to measure total carbon (TC), total organic carbon (TOC), and inorganic carbon (IC) as well as the total nitrogen (TN). The autosampler ASI-L with vial capacity and number of vials: 40 mL vials x 68 allow continuous batch run setup. The more

soiled sample PW5 unfiltered was dilute 5 times before transfer to TOC vial, other samples were diluted 2 times. The purpose is to protect the TOC tubing from concentrated contaminant depositing. Results in table 2-2 are of the undiluted samples after back track calculation.

Filter Passes	TOC (mg/L)	%	TC (mg/L)	%	IC (mg/L)	%	TN (mg/L)	%
0	61.41	100.0%	137.5	100.0%	76.06	100.0%	464.3	100.0%
1	27.01	44.0%	35.99	26.2%	8.976	11.8%	398.8	85.9%
2	20.76	33.8%	26.17	19.0%	5.403	7.1%	446.9	96.3%
3	29.25	47.6%	43.27	31.5%	14.03	18.4%	462.9	99.7%
4	29.02	47.3%	47.73	34.7%	18.71	24.6%	459.5	99.0%
5	34.13	55.6%	53.46	38.9%	19.32	25.4%	464.7	100.1%
6	30.69	50.0%	43.94	32.0%	13.24	17.4%	478.4	103.0%

Table 2-2. TOC, TC, IC, TN results

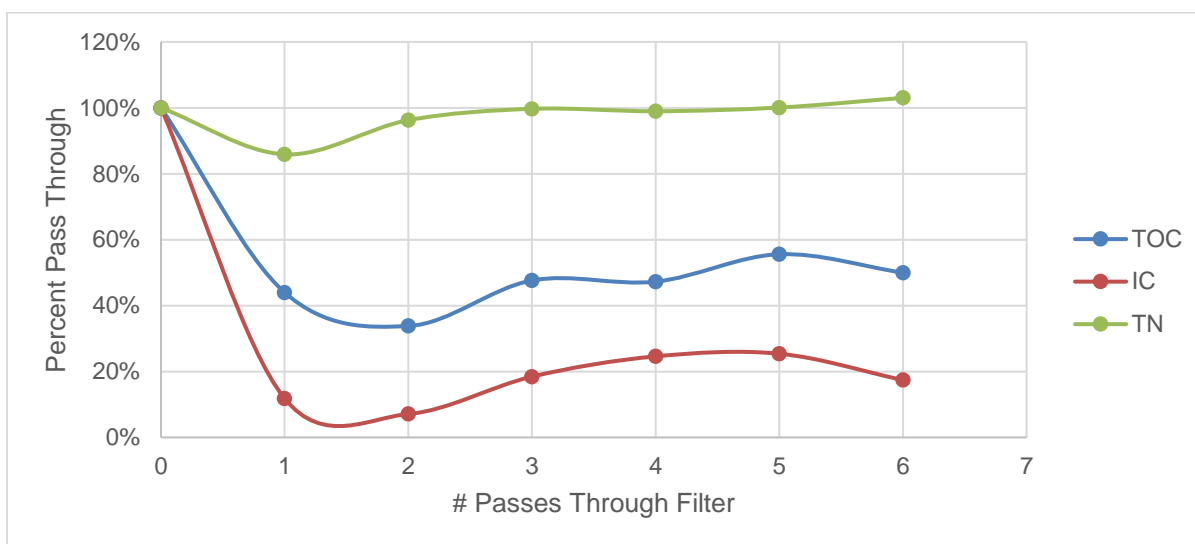


Figure 2-3. Plot of TOC, IC, TN results.

In order to present data on the same graph for easier comparison, Percent pass through is defined as ratio in percentage of the amount of compound unadsorbed in each eluate to total amount found in unfiltered PW. Results show TOC and IC values decrease to minimum on 2<sup>nd</sup> pass and climb back up a little bit, meaning that filter performance is decreasing, but the cartridge is still capable of removing carbon containing compounds and steadily until the 6<sup>th</sup> pass. A possible explanation is that the hydrocarbon adsorbed onto GAC surface acted as nonpolar stationary phase which also capable of binding more nonpolar hydrocarbon.

On the other hand, Total Nitrogen curve behave similar to % salinity curve before. They reached shallow minimum at 1<sup>st</sup> eluate, go back to almost 100% at 2<sup>nd</sup> eluate indicate filter saturation point. When filter is unable to remove a certain type of material, the % pass through would be 100%.

### 2.3.4 HS GC-FID and GC-MS analysis

Headspace mode analysis was performed using Shimadzu GC 2010 gas chromatography flame ionization detector (GC-FID) with an AOC-500 plus sample injection system. In 20ml headspace vial, 5ml of sample is added, heated to 90°C 15 min with agitation at 500 rpm, 5 sec on, 2 sec off. 1ml of headspace vapor is injected to Column: RTX BAC Suite (60 m x 0.32 mm (ID) x 1.20 µm). FID detector temperature set at 225°C.

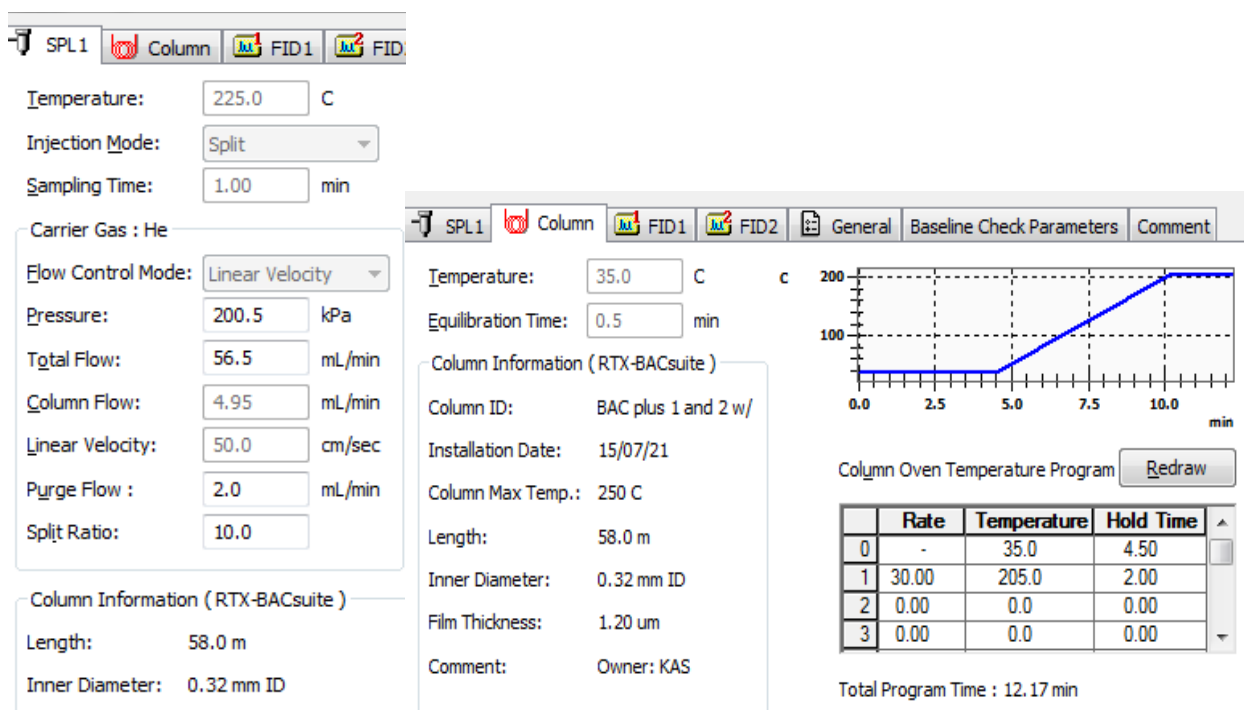


Figure 2-4. GC-FID instrument parameters



GC-MS analysis was performed using a Shimadzu GCMS TQ 8030 with AOC-20i auto sampler. For 5.0 mL of each samples, add 2.0 mL of extracted solvent dichloromethane (DCM), vortex 20s. Then extract the bottom DCM layer for analysis. General-purpose columns for semivolatiles Rxi-5ms (20.0 m x 0.18 mm x 0.18 µm) was used.

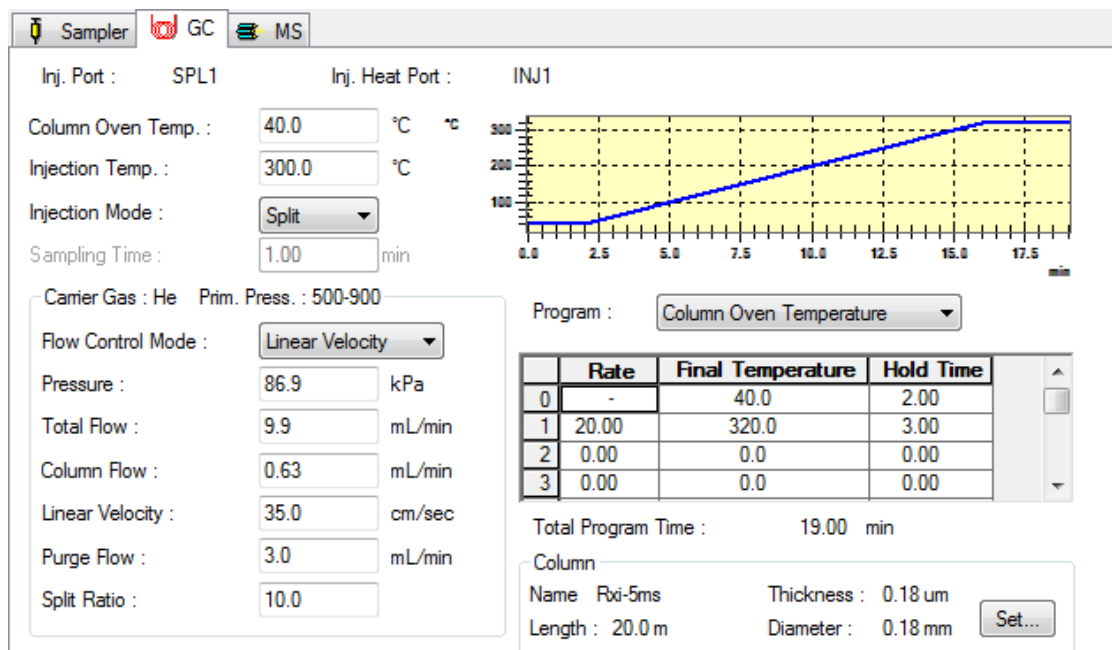


Figure 2-5. GC-MS instrument parameters

### ❖ Results and Discussions

GC-FID and GC-MS chromatograms show good correlation with TOC data above, #2 eluate has the lowest concentration of volatile organic compounds. One would think the eluate #1 should have yield the cleanest filtered water because the filter GAC condition was new, having the most free adsorption surface. One possibility was realized because we did not flush filter well enough prior to use per manufacturer instruction, only 200ml DI water were used instead of flushing for 15 seconds under running cold tap water. The bulk of filter cartridge might not have been completely wet for effective adsorption.

On GC-FID chromatogram, a large number of peaks eluting in relatively even spacing under temperature gradient mode. This suggests sample contain some sort of hydrocarbon series. This is more evident in GC-MS chromatogram where we can view the extracted ion fragment 57.1 m/z chromatogram, which is the most common fragment C<sub>4</sub>H<sub>9</sub><sup>+</sup> of long chain hydrocarbon.

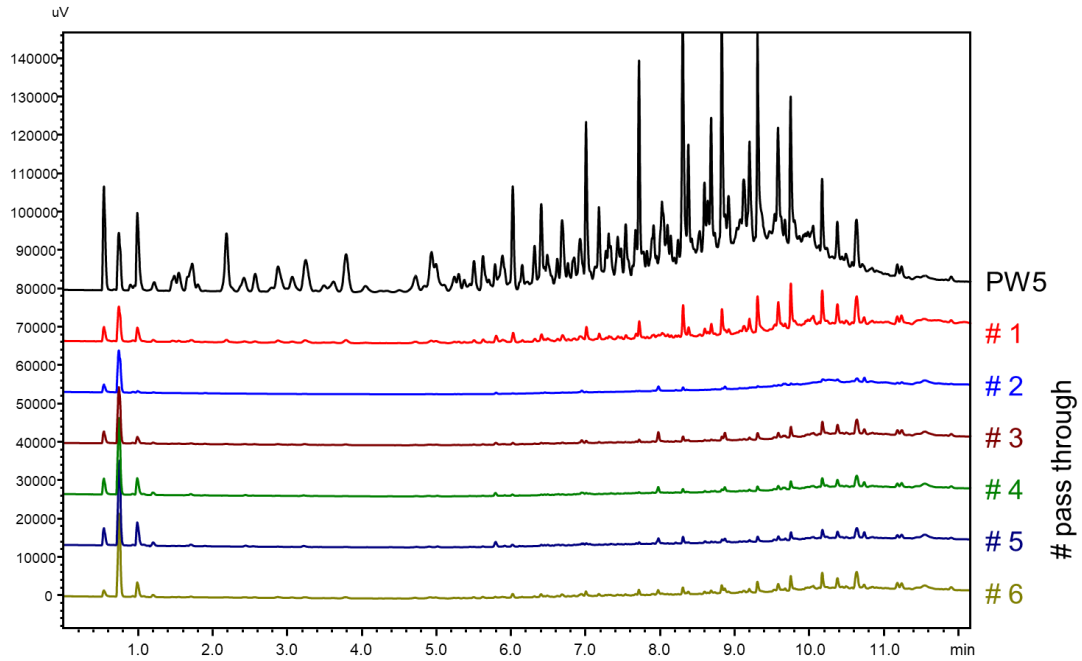


Figure 2-6. HS GC-FID chromatograms of unfiltered PW5 and its filtered eluates.

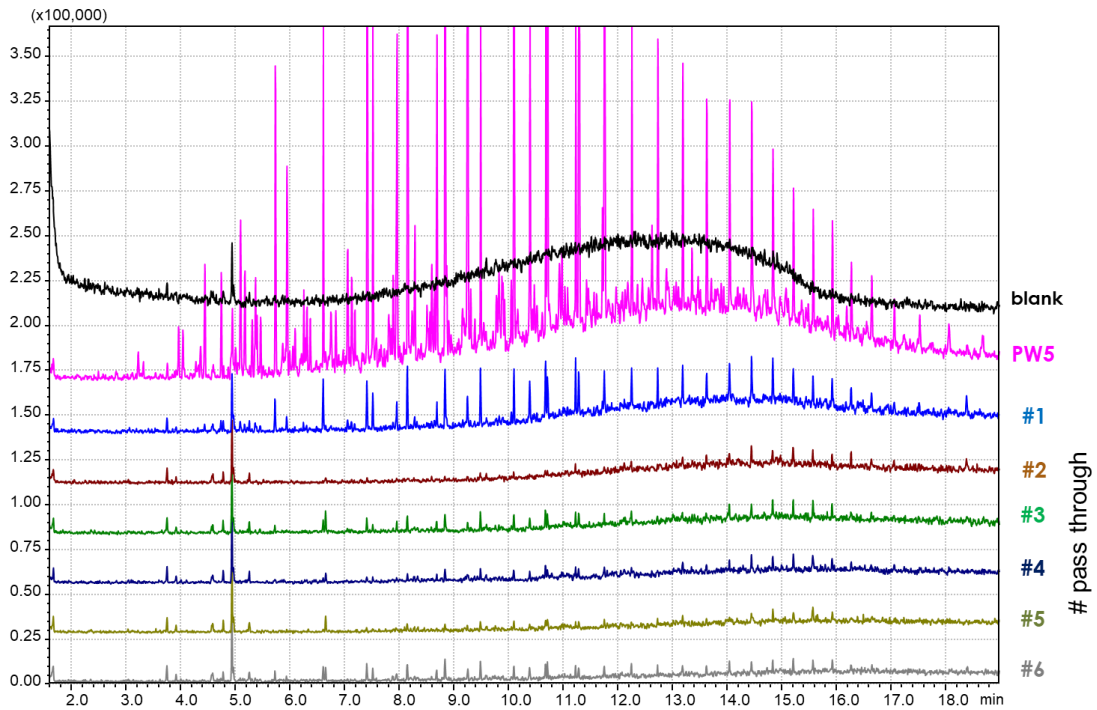


Figure 2-7. GC-MS chromatograms of extracted fragment ion 57.1 m/z of PW5 samples.

Another feature is hydrocarbon “hump” baseline containing unresolved complex mixtures, a characteristic of oil & gas fuel type sample. Our filter does a good job of trapping these compound to a certain level, but not completely.

The intended goal from performing analysis on both type of GCs was to figure out which prominent compounds are there in the produced water source. Then attempt to identify and quantify the filter effect on those compounds. An overlay chromatogram of total ion in Scan mode with its extracted ion chromatogram containing fragment ion 57.1 m/z does confirm most of compounds in PW5 belongs to this group of hydrocarbon series. This finding hence guide our focus on optimizing methods for qualitative and quantitative of these hydrocarbon peaks. According to literature papers from WHO and EPA, total petroleum hydrocarbon (TPH) analysis is a suitable choice.

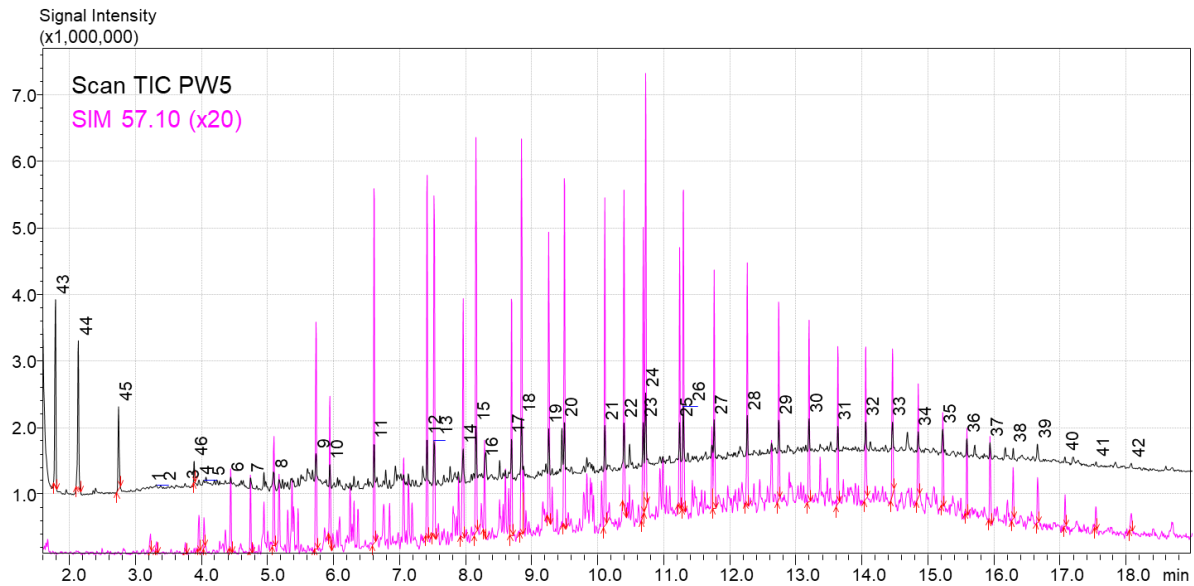


Figure 2-8. GC-MS Scan & SIM 57.1m/z chromatogram overlay. 50 highest peaks are labeled.

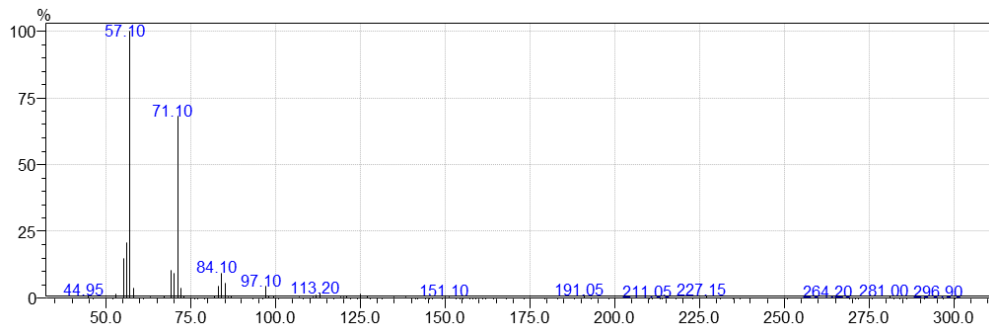


Figure 2-9. Representative mass spectrum of the hydrocarbon peaks from GC-MS scan PW5 showing most intense base peak 57.1m/z  $C_4H_9^+$  ion.

Over the course of the experiments, a few months span, several repeats of PW5 filtering were needed. The original PW5 big bottles kept at room temperature, its content may have undergone biological or chemical changes, giving inconsistent TIC chromatograms.

We observed a different filter adsorption rate for different type of compounds (halogenated, aliphatic, aromatic). Or it could just be the PW5 contain different amount of those compounds to begin with.

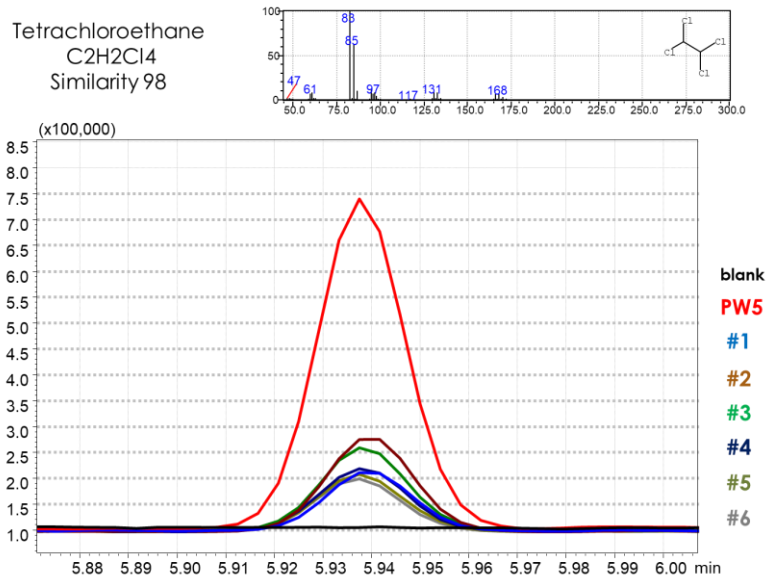


Figure 2-10. Adsorption filter on chlorinated compounds.

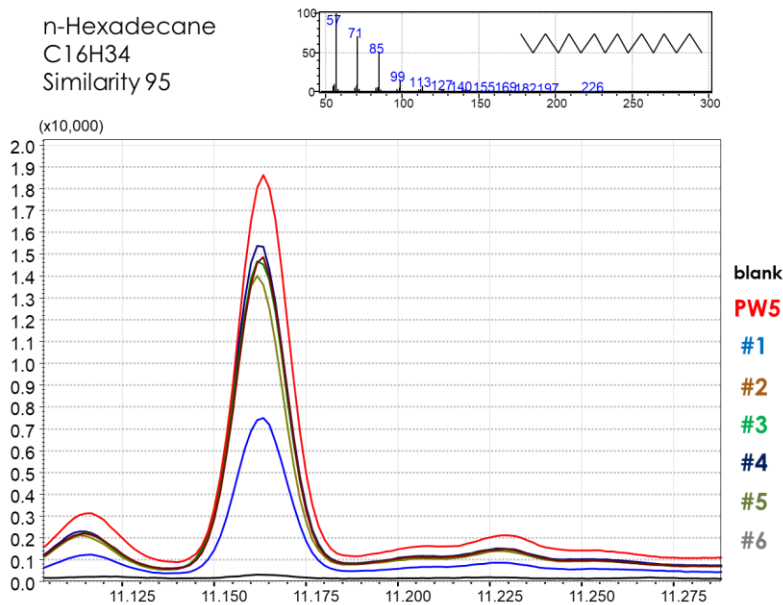


Figure 2-11. Adsorption filter on aliphatic compounds.

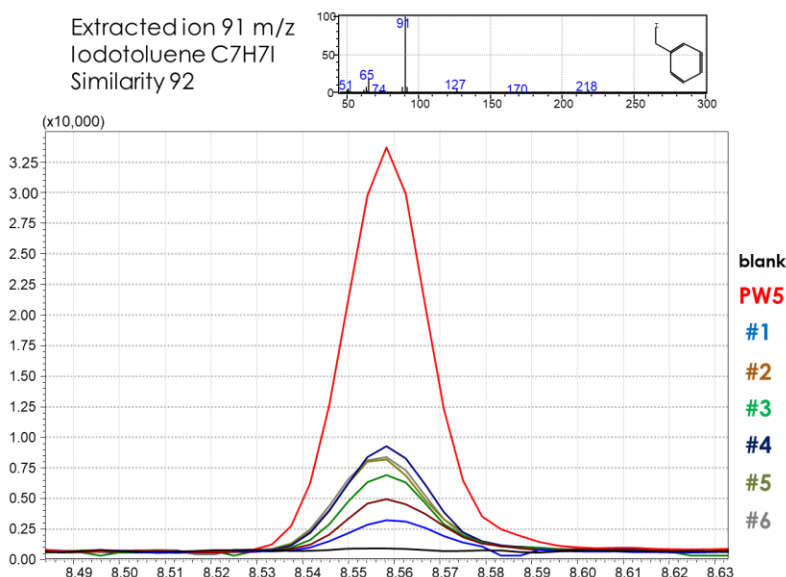


Figure 2-12. Adsorption filter on aromatic compounds.

### 2.3.5 Analytical assessment with low accuracy

A second attempt on PW5 filtering a larger volume to find break-through volume of filter on organic carbon adsorption. Using a new filter, flush filter with tap water as instructed by manufacture to better resemble real life usage. But for fear of clogging filter prematurely, vacuum filter on stock PW5 was done to remove suspended solid before the regular Brita filter procedure. As TOC analysis show, this extra step also greatly reduce TOC content of unfiltered PW5 from ~60mg/L down to ~26mg/L. With almost triple the amount of PW5 filtered, TOC level in the filtered eluates plateau out at ~20mg/L compared to first attempt ~30mg/L.

Filter Passes	TOC (mg/L)	%	TC (mg/L)	%	IC (mg/L)	%	TN (mg/L)	%
0	26.30	100.0%	63.42	100.0%	37.11	100.0%	610.20	100.0%
1	11.63	44.2%	19.34	30.5%	7.71	20.8%	328.60	53.9%
2	15.03	57.1%	28.49	44.9%	13.46	36.3%	541.10	88.7%
3	17.05	64.8%	31.96	50.4%	14.91	40.2%	579.30	94.9%
4	18.19	69.2%	34.70	54.7%	16.51	44.5%	598.10	98.0%
5	18.04	68.6%	35.81	56.5%	17.77	47.9%	600.10	98.3%
6	19.34	73.5%	38.33	60.4%	18.99	51.2%	603.30	98.9%
7	18.40	70.0%	40.20	63.4%	21.80	58.7%	613.40	100.5%
8	19.57	74.4%	41.45	65.4%	21.88	59.0%	615.60	100.9%

9	18.98	72.2%	39.45	62.2%	20.47	55.2%	606.00	99.3%
10	18.20	69.2%	42.45	66.9%	24.24	65.3%	619.00	101.4%
11	18.54	70.5%	40.91	64.5%	22.37	60.3%	623.10	102.1%
12	19.61	74.6%	42.74	67.4%	23.13	62.3%	617.80	101.2%
13	16.43	62.5%	39.58	62.4%	23.15	62.4%	620.80	101.7%
14	18.01	68.5%	40.34	63.6%	22.32	60.1%	630.70	103.4%
15	19.17	72.9%	41.09	64.8%	21.93	59.1%	635.80	104.2%
16	18.40	70.0%	41.01	64.7%	22.60	60.9%	637.30	104.4%

Table 2-3. TOC, TC, IC, TN results for 2<sup>nd</sup> filtering attempt.

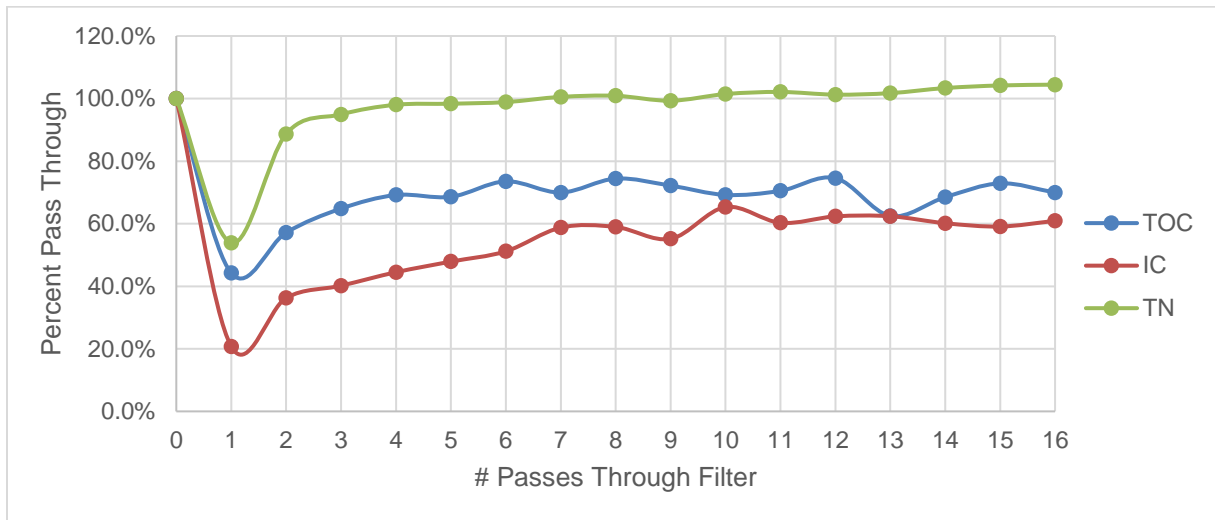


Figure 2-13. TOC, IC, TN results for 2<sup>nd</sup> filtering attempt.

❖ Metal screening with XRF (X-ray fluorescence analyzer)

Due to complex composition of Produced water, a correct calibration method for metal screening with XRF instrument wasn't developed. Thus, this screening result is not to be taken at face value for the actual metal element and its concentration detected, but rather served as an estimation for filter rate of metal uptake. The Ca, Sr, Cu readings are consistent with salinity data above. Maximum adsorption is at first pass, either the ion exchange capacity is low or the amount of metal ions in PW5 is very high. This will be explored further with ICP-OES in the next section.

This take us to a different approach on our final series of test. Perform a 10x dilution of PW6 and attempt to analyze the breakthrough volume of metal uptake by filter.

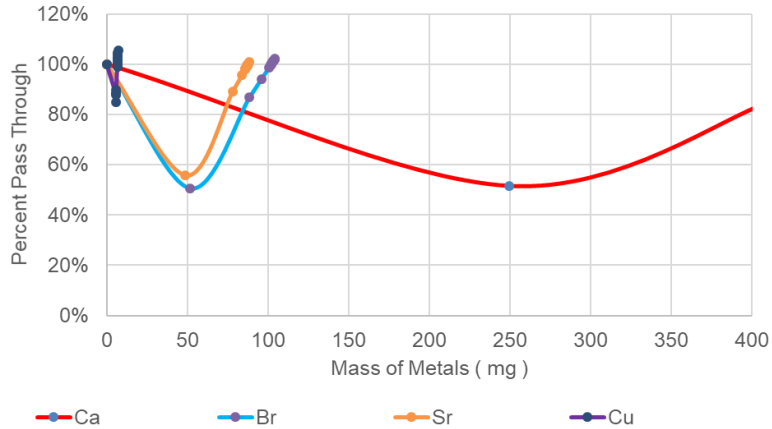


Figure 2-14. XRF metal content measurement of PW5 samples.

## 2.4 Total Petroleum Hydrocarbon (TPH) Quantification

The United States Environmental Protection Agency (US EPA) has published different methods for TPH in water. These include modified EPA 3510C/8015B, which is based on gas chromatography with flame ionization detection. This method is for TPH as gasoline, jet fuel and diesel and allows the quantification of the hydrocarbons EC6 through EC20 aliphatic fraction. (EC is equivalent carbon number) [15]

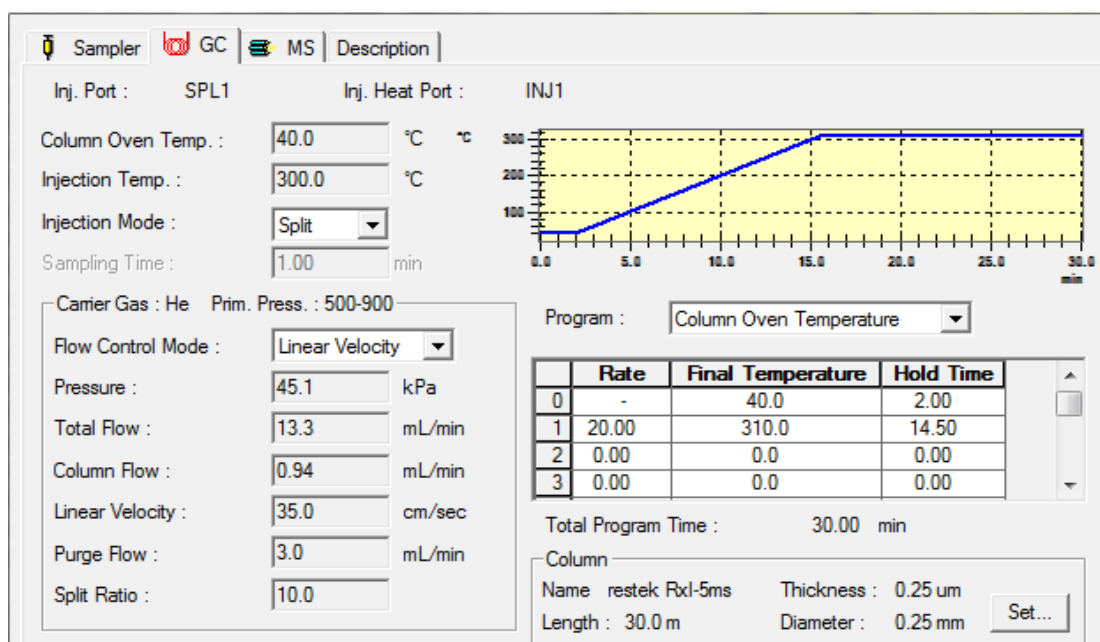
In 2005, World Health Organization released a technical report titled Petroleum products in drinking-water: background document for development of WHO Guidelines for Drinking-Water Quality. In the context of drinking-water, assuming a 60-kg adult drinking 2 liters of water per day and allocating 10% of the reference dose RfD (Use in Health Risk Assessments, equivalent to a tolerable daily intake) of 0.1 mg/kg of body weight per day to drinking water would give a guideline value of 0.3 mg/liter for this fraction of aliphatics. The approach was developed by TPHCWG Total Petroleum Hydrocarbon Criteria Working Group. It has been followed by other national agencies responsible for environmental protection and is used here as the basis for providing guidance as to tolerable levels of hydrocarbon fractions in drinking-water, in the event of spills of petroleum products. [15]

### 2.4.1 Materials and Methods

Shimadzu TOC-L equipped with TNM-L module were used to measure total carbon (TC), total organic carbon (TOC), and inorganic carbon (IC) as well as the total nitrogen (TN). The autosampler ASI-

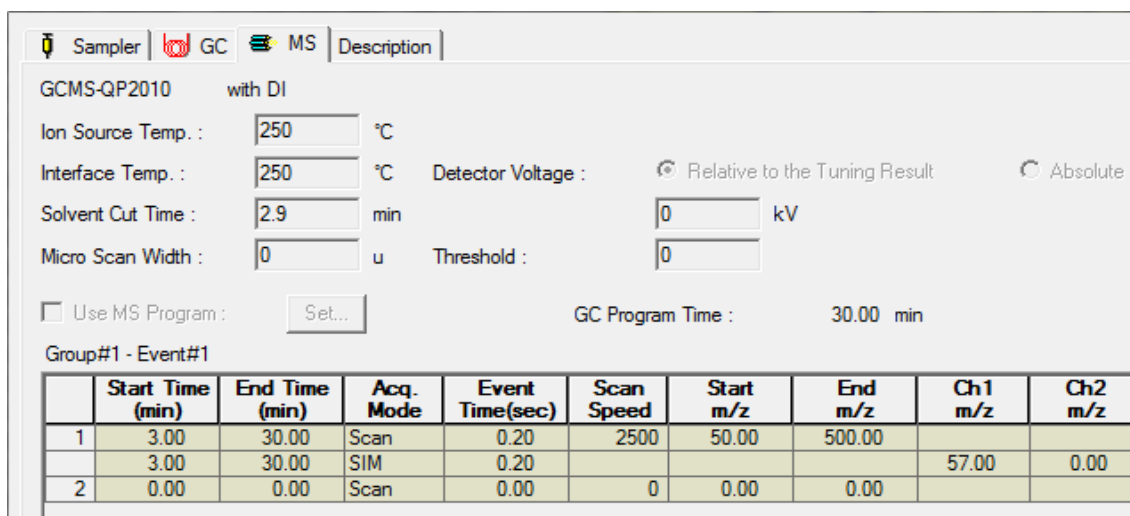
L with vial capacity and number of vials: 40 mL vials × 68 allow continuous batch run setup. The more soiled sample PW6 unfiltered was dilute 5 times before transfer to TOC vial, other samples were diluted 2 times. The purpose is to protect the TOC tubing from concentrated contaminant depositing.

Shimadzu GC-MS QP2010 Ultra was utilized for semivolatile compounds separation, identification, and quantification of Total Petroleum Hydrocarbon. According to EPA method 8015b recommendation, Rxi-5ms column (5%-Phenyl)-methylpolysiloxane which was chosen as general-purpose columns for semivolatiles & volatile in the preliminary study is still a suitable choice for TPH. Standard Prep: C7 - C40 Saturated Alkane Mixture ( 49452-U SUPELCO 1000 µg/mL each component in hexane) a glass vial of stock 100 ppm in hexane was used. A total of 7 n-alkane standards were prepared by serial dilution in n-pentane from 10 ppb to 1000 ppb. Internal Standard: Chlorobenzene ( 270644-100ML SigmaAldrich 99% for HPLC 1.106 g/ml ) was used to make 5ml of stock 200 ppm in n-pentane. 10 µL aliquot was added to all n-alkane standards (1 ml vial) and PW6 filtered samples (1 ml vial) to account for variation in instrument response. Sample Prep: Pipet 5 ml of each PW6 filtered 130 ml brown bottle samples, add 2 ml of n-pentane, 20s vortex. Liquid-liquid extraction to 1 ml vial for GC-MS analysis. Add 10 ul Internal standard.



(a)





(b)

Figure 2-15 (a) (b). Shimadzu GC-MS QP2010 Ultra instrument parameters for PW6 TPH analysis.

### 2.4.3 Results and Discussions

There were concerns in TPH calculation, specifically regarding peak integration approach of multiple continuous peaks, the high baseline of unresolved complex mixture, and peaks due to column bleed at high temperature range in gradient mode.

Guibo Xie et al. [16] paper, Quantification and Interpretation of TPH in Sediment Samples by GC/MS stated their use of both Internal standard and External standard, separately. Three integration approaches were used to obtain the total area of a total ion chromatogram: (a) manual integration along the lowest-point baseline; (b) sum of resolved individual compounds after integration with the lowest-point baseline held on; (c) sum of resolved individual compounds after integration with the baseline established by MS ChemStation integration. [16]

EPA method 8015B describe the following: Fuels contain many other components that are not chromatographically resolved. This unresolved complex mixture results in the "hump" in the chromatogram that is characteristic of these fuels. In addition, although the resolved peaks are important for the identification of the specific fuel type, the area of the unresolved complex mixture contributes a significant portion of the area of the total response. Also, chromatographic conditions employed for DRO (Diesel range organics) analysis can result in significant column bleed and a resulting rise in the baseline, it is appropriate to perform a subtraction of the column bleed from the area of the DRO chromatogram. [17]

We decided the most suitable approach (c) by having GCsolutions software perform peak integration of 50 highest resolved peaks, its sum would cover the majority of sizable peaks. Column bleed subtraction is not necessary in SIM mode 57.1 m/z, the advantage of having quadrupole mass spec detector in selected ion monitoring mode in obtaining a subset chromatogram with cleaner set of hydrocarbon peaks, and lower unresolved mixture baseline. [18]

GC-MS parameters slightly tweaked compared to screening condition to obtain well resolved alkane series. A couple GC-MS test run was done to estimate suitable concentration of internal standard Chlorobenzene (2ppm) that would yield a comparable signal intensity of alkane standards.

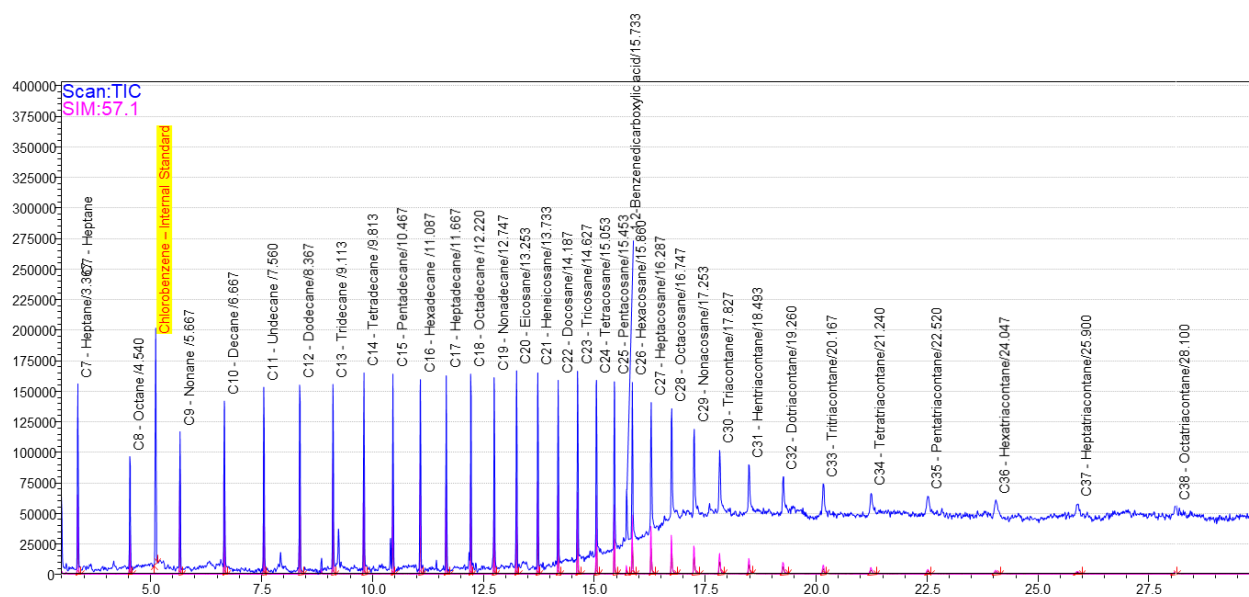


Figure 2-16. GC-MS chromatogram of n-alkane calibration standard and chlorobenzene internal standard.

EPA Method 8015b requires Calibration linearity: The linearity of the calibration must be assessed. This applies to both the single component analytes (which we not doing) and the fuel types (aliphatic hydrocarbons in this case). We validated calibration linearity by performing peak area ratio of total TPH over internal standard chlorobenzene. Linear correlation coefficient  $R^2 = 0.9992$  indicate good linearity.

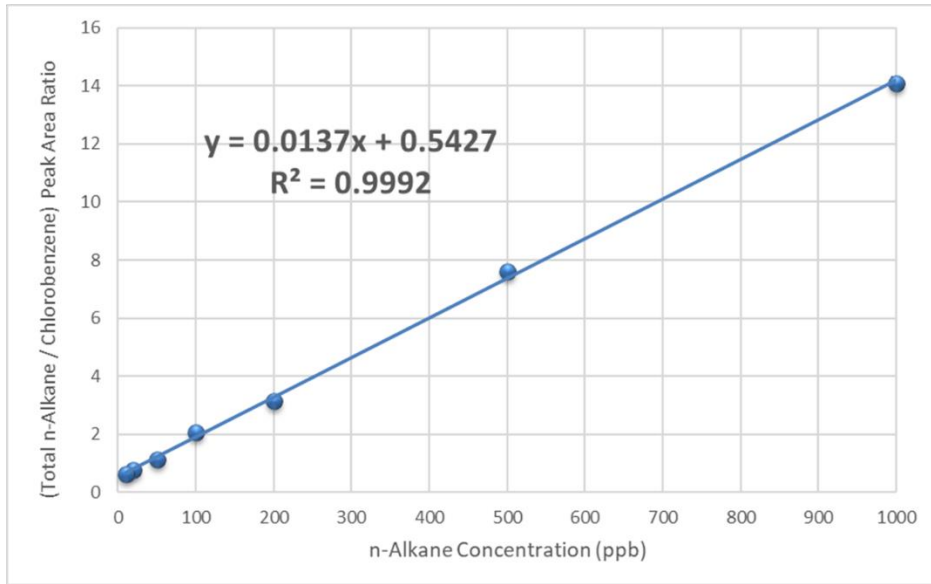


Figure 2-17. 7-points TPH Calibration Curve 10ppb – 1000ppb

The GC-MS analysis on the PW6 samples were run on the same instrument parameters as that of n-alkane standards. Their chromatograms were overlaid below for qualitative assessment.

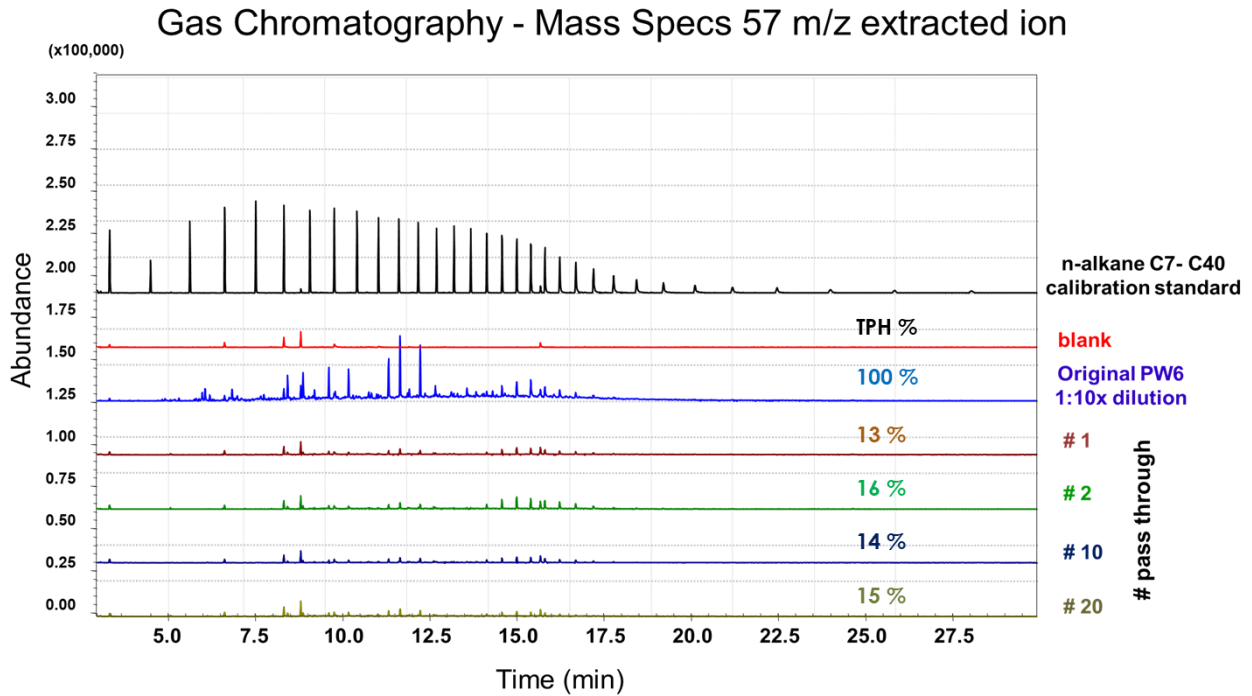


Figure 2-18. Qualitative comparison of PW6 unfiltered vs filtered.

Since we purposely dilute the original PW6 by 10 times, in search of breakthrough volume of metal uptake by filter. However, the reduced TPH concentration of PW6 samples still fell in the range of TPH calibration curve.

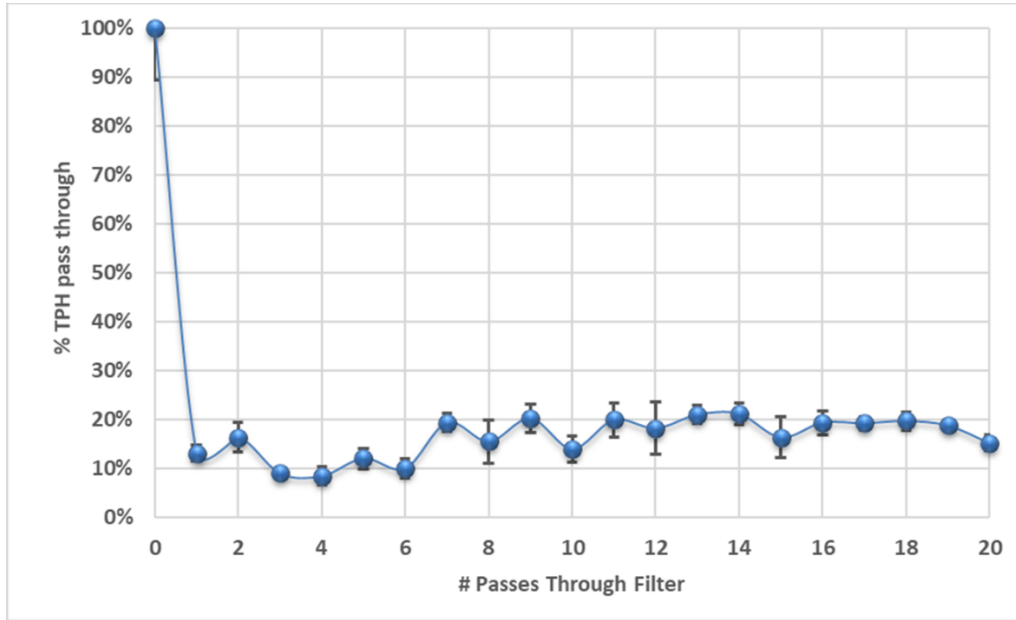


Figure 2-19. Total Petroleum Hydrocarbon (TPH) Reduction of PW6 filtering.

We observed good correlation between TOC and GC data, both graphs show a drop to 20% in organic carbon of filtered vs unfiltered PW sample and the uptake by Brita filter remain flat trend over time.

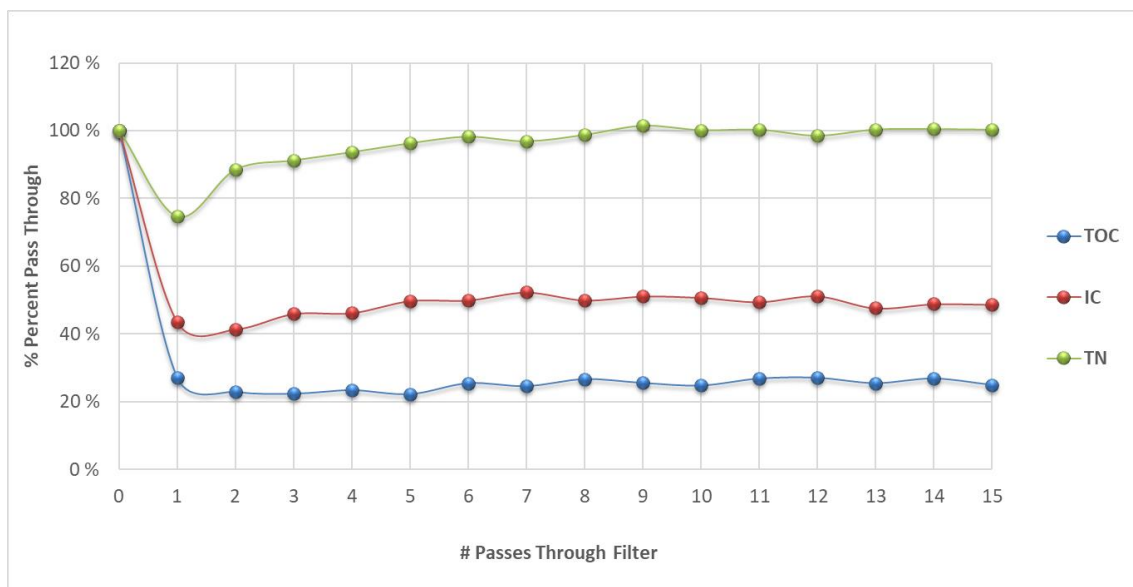


Figure 2-20. Total Organic Carbon (TOC) Inorganic Carbon (IC) Total Nitrogen (TN)

According to WHO guideline, the reference dose RfD tolerable is 0.3 mg/liter for aliphatic fraction of TPH. Our filtered PW6 which was originally diluted 10 times contain a 0.1 mg/liter TPH is safe to drink in theory. But since aliphatic fraction of TPH are not well dissolved in water, and filter performance was not necessarily linear. On the preliminary study, TOC level drop to ~40% on PW5. This time on diluted PW6 (a different batch of PW from the same source), TOC level reduced down to 20%. We can't positively say if original concentration of PW6 were to be filtered, its eluate would fall below the 0.3 ppm RfD or not. But it very likely in term of aliphatic fraction of TPH, a very diluted sample of lake water contaminated with this type of PW when treated with Brita filter would have a reduced TPH content that is in safe range. Whether it is safe to drink still depends on a more thorough analysis of other type of organic compounds in PW. Aliphatic fraction were tested because it was the main signal observed.

Upon identifying the composition of the hydrocarbon peaks in PW6, using NIST database, PW6 peaks elute in vicinity to alkane series, NIST database matches >90 similarity score of branched hydrocarbons.

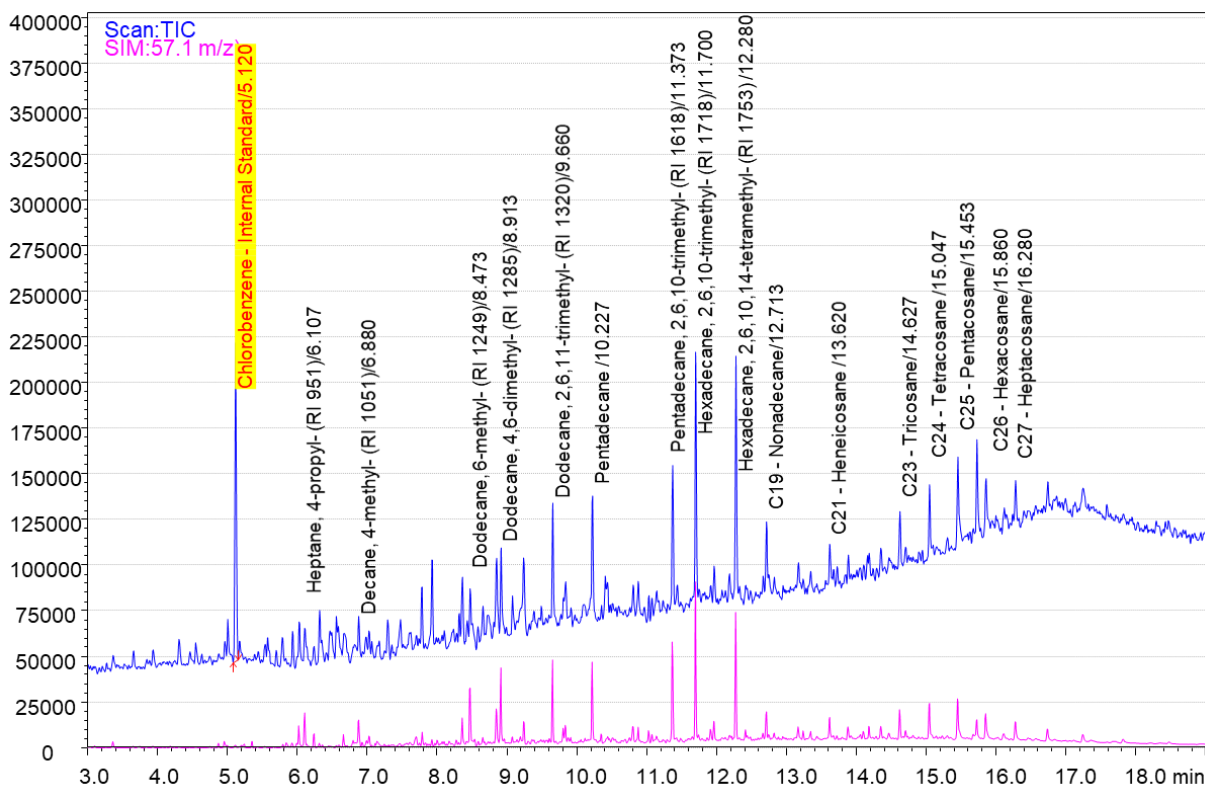


Figure 2-21. NIST database match similarity score above 90, mostly branched hydrocarbon.

The overlay chromatogram of n-alkanes series on top of PW6 series is helpful in justifying the NIST database matching results, technically, each peak spectrum matching result in multiple possible branched hydrocarbons, all have similarity score above 90, some cases, multiple matches with same highest score, only different in 1 carbon count or position of methyl substituent. But from the flat line no peak in blank, the high peak and low peaks in filtered eluates, it is positively sign that activated carbon in Brita filter can reduce aliphatic compounds found in PW.

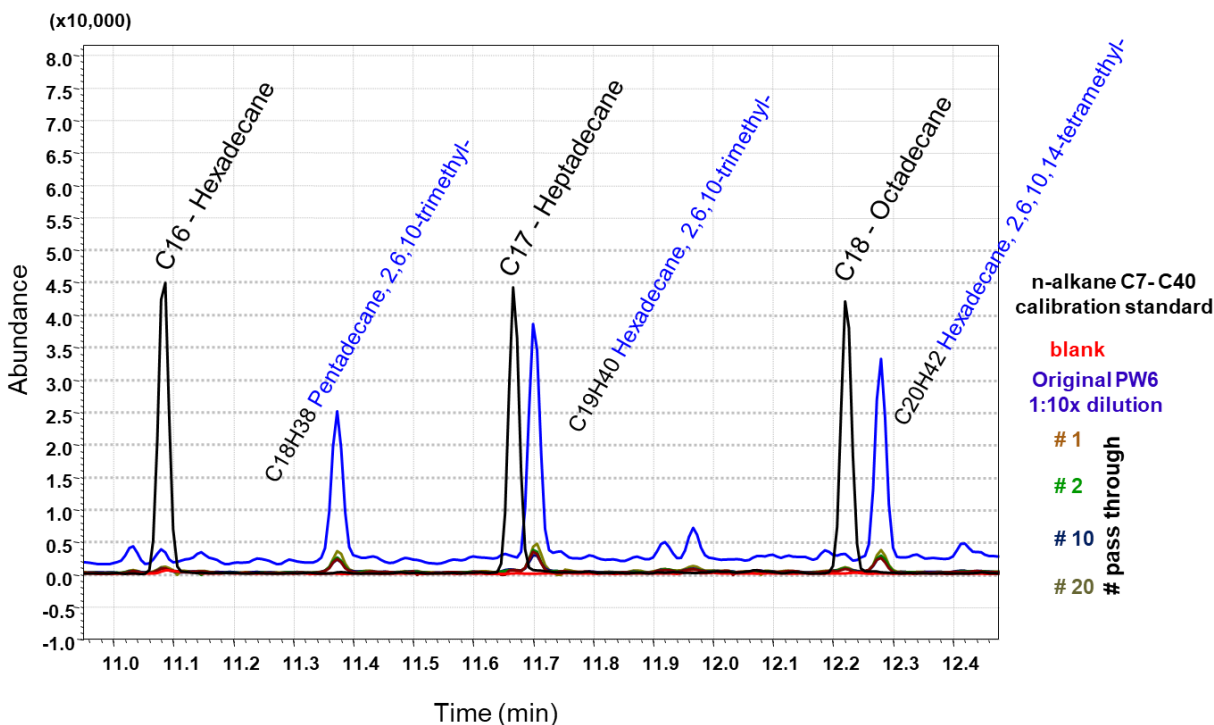


Figure 2-22. Overlay chromatogram of n-alkane calibration standard and PW6 samples.

## 2.5 ICP-OES Metal Analysis

### 2.5.1 Materials and Methods

Shimadzu ICPE-9000 equipped with high-salt torch. High-Purity Standards QCS-26-R ICP 26 Element Quality Control Standard (100 mg/l Ag Al As B Ba Be Ca Co Cr Cu Fe K Mg Mn Mo Na Ni Pb Sb Se Si Ti Tl V Zn) in 5% HNO<sub>3</sub> was used to make calibration curve 7-points range 50 ppb to 3 ppm. PW6 samples also prepared in 2% nitric acid. 10ml each standard and samples were put on ICP plastic tube for analysis. Instrument parameters set at default, Ar gas supply pressure 450 kPa, flow rate 12L/min, axial observation mode for High sensitivity (ppb level).

ICPE-9000 instruction manual recommends the use of Standard addition method, more suited for wastewater sample due to matrix effect. Each PW sample would need its own standard addition calibration curve, this required a large amount of sample prep, consume more standard materials and instrument run time. So we opted for external standard calibration curve for now.

In ICP emission spectrometry, measurement errors can have a number of causes, including physical interference, ionization interference, and spectral interference. The first two interference are due to matrix effect. Since metal standards were prepared in DI water, by analyzing PW6 samples diluted 10x helped reduce matrix effect. As for spectral interference, we made use of ICPE-9000 advanced features in optimizing wavelengths of measurement for each metal. Modern CCD and software allowed measurements can be recorded for all elements and all wavelengths.

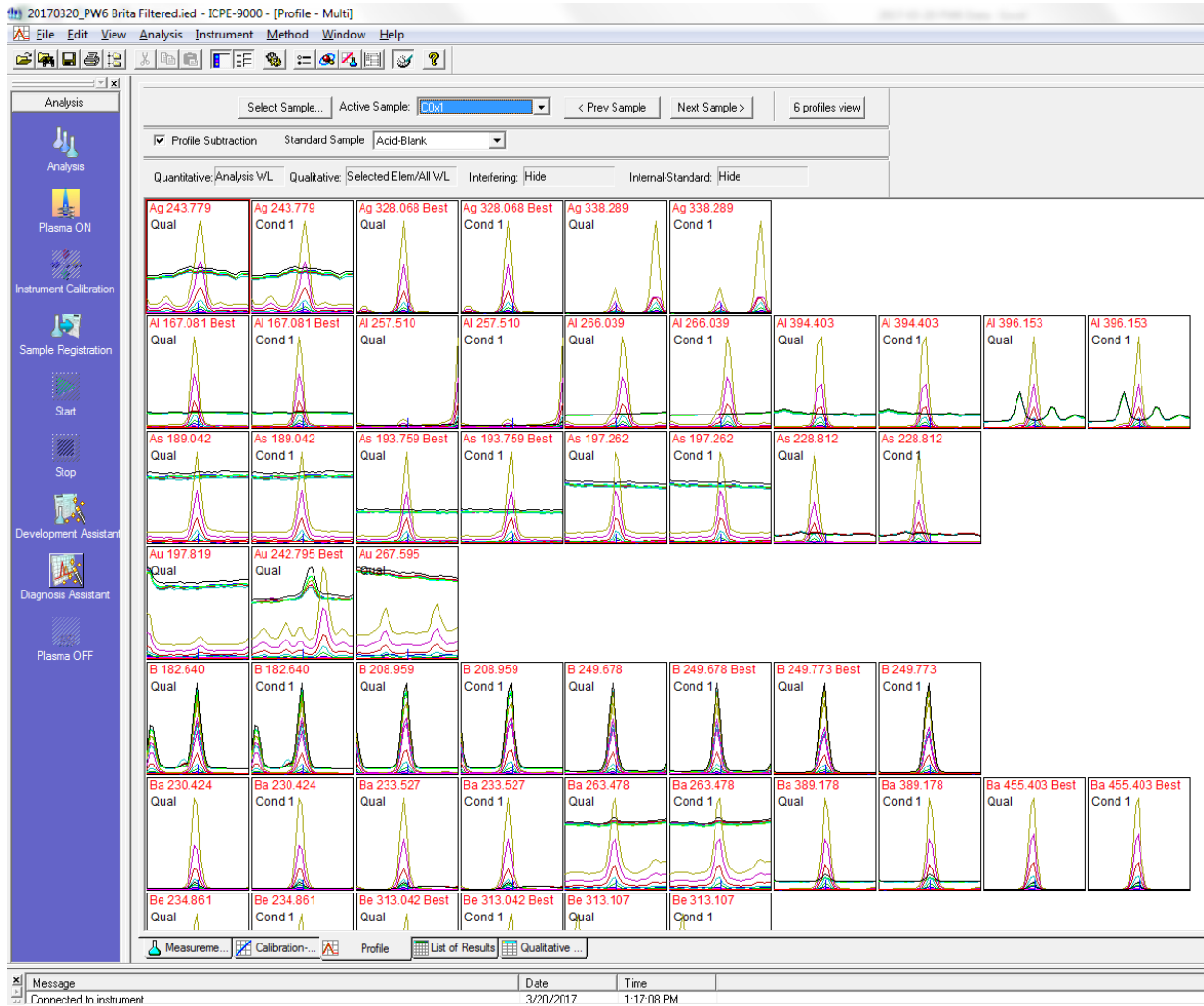
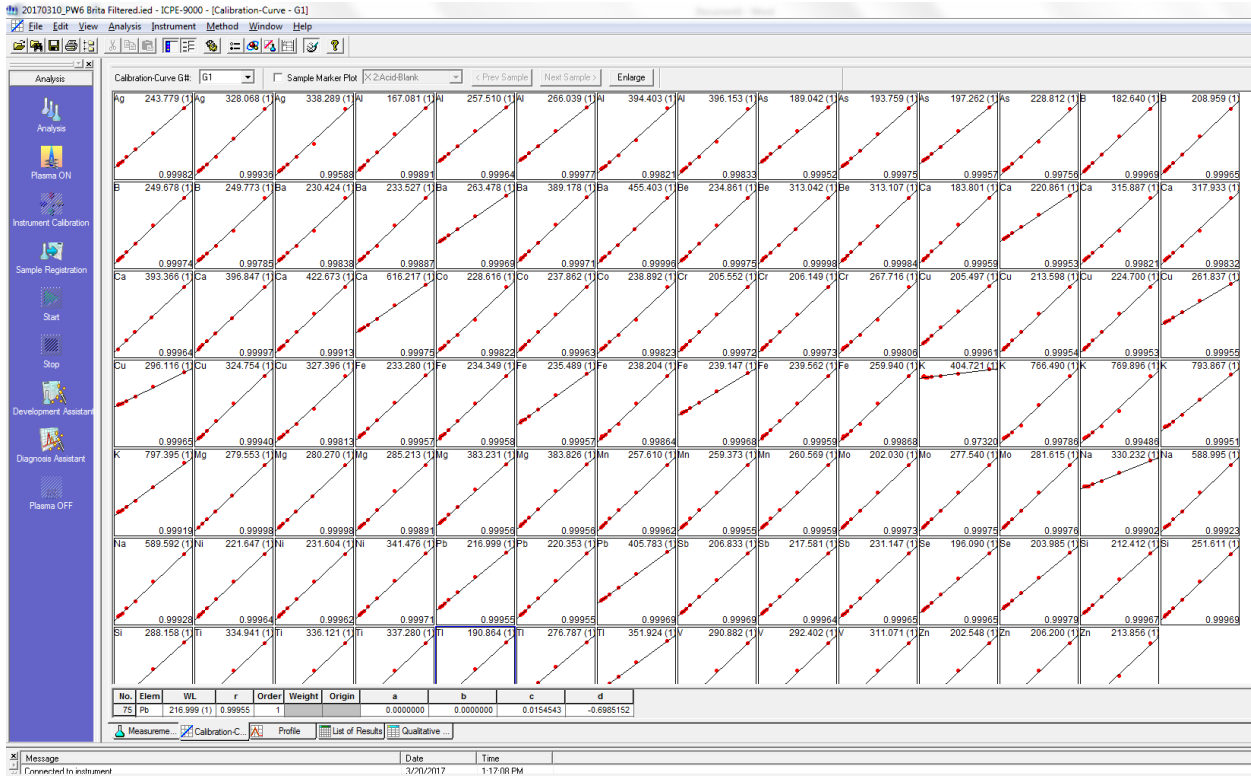
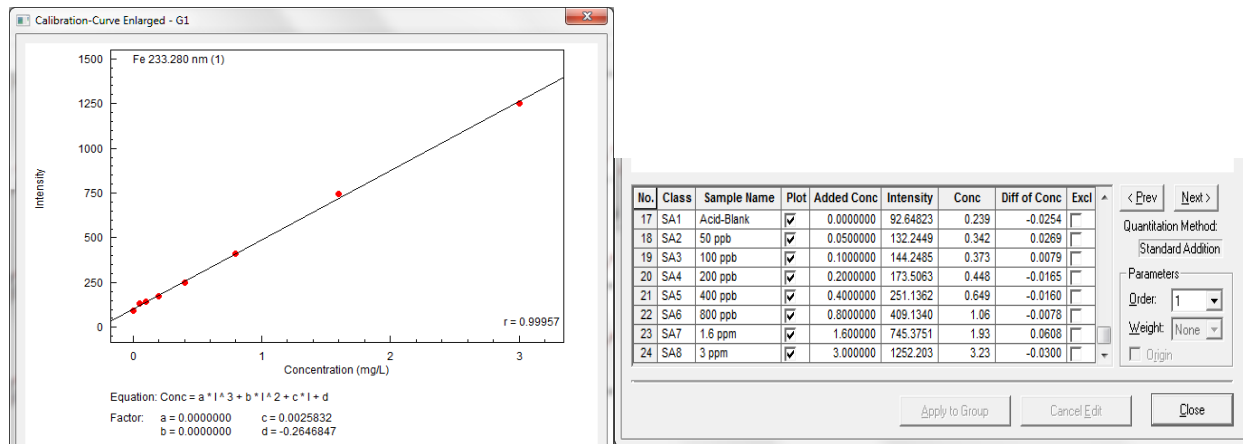


Figure 2-23. Optimizing emission wavelength by ICPE-9000 software.

All possible emission wavelength of each metal analyzed are selected, software picked out the best wavelength that has no overlapping signal from other elements. All calibration curves have good linearity  $R^2 > 0.995$ .



(a)



(b)

Figure 2-24 (a)(b). Calibration curve of all 26 metal standards.

Each metal has multiple emission wavelengths.



### 2.5.2 Results and Discussions

ICPE-9000 report extremely high concentration of Na, which is expected from salinity test. It also detected K, Mg, S, Sr concentration greater than 1mg/L but with relative high RSD above 20%, those elements are omitted in this table. Only Barium and Beryllium are on EPA contaminant Inorganic Chemicals with regulated maximum contaminant level MCL. [20] Beryllium level on PW6 is determined by our method to be above the MCL 0.004 ppm. A further analysis using standard addition method is needed to improve accuracy in determination of metal content in PW6. Activated carbon has minimal filter effect on metal ions, it is mainly done by ion exchange resin. Since it was not disclosed of which specific type of ion exchange resin was used. We speculate resin that similar to polystyrene sulfonate, a commonly used commercial resin is at play. It is the type that would release proton and lower pH when exchange for cation.

# Passes through filter	B (ppm)	Ba (ppm)	Be (ppm)	Ca (ppm)	Fe (ppm)	Na (ppm)
Blank	0.0345	0.0054	0.0035	0.0242	0.0426	0.0743
0	3.44	0.216	0.0043	76.3	0.352	2590
1	1.53	0.113	0.0042	63.7	0.139	1670
2	1.54	0.116	0.0042	67.8	0.135	1960
3	1.71	0.117	0.0042	67.3	0.140	2210
5	2.69	0.131	0.0041	68.5	0.167	2420
10	2.83	0.142	0.0041	71.0	0.202	2490
15	2.86	0.145	0.0041	70.2	0.224	2500
20	2.92	0.148	0.0041	70.5	0.248	2520
EPA MCL		2	0.004			

Table 2-4. Metal contents on PW6 samples analyzed by ICPE-9000.

Na<sup>+</sup> ion quickly consume the ion exchange site, but other stronger binding ions can still compete such as Ba, Be, Ca, Fe which are +2, +3 charged ions. Fe<sup>3+</sup> is has the most binding strength. These effect are seen on figure 2-25 below.

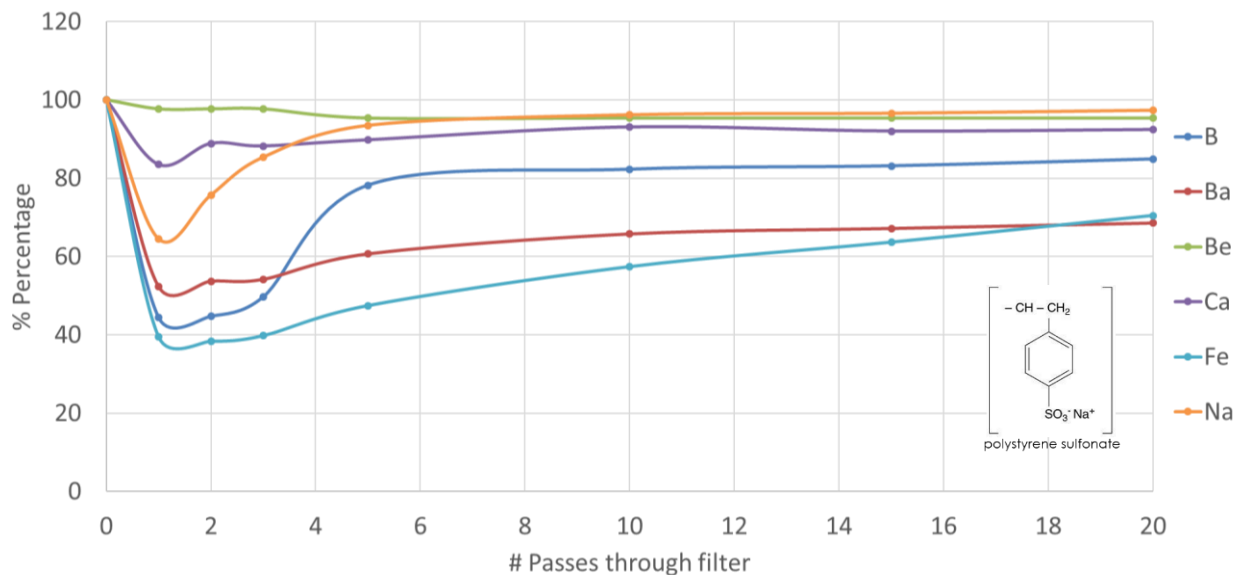


Figure 2-25. Metal contents on PW6 samples analyzed by ICPE-9000.

In conclusion, GC-MS analysis of total petroleum hydrocarbons, based on extraction of the characteristic ion at 57 m/z, showed a decrease in branched hydrocarbon content, in agreement with total organic carbon analysis. Metal analysis with ICP-OES also showed a small reduction in Ba, Be, Ca, Na, and other metals, but not enough to be below safe drinking standards. In general, this work serves to illustrate that drinking water contaminated with waste water from the oil and gas industry may not be reliably treated using this widely-used household product.

## Chapter 3

### FUTURE WORK

The produced water analysis results were informative but still leave many aspects that could be improved to better understanding the capacity of household commercial filter in treatment of diluted produced water. Particularly, standard addition method in ICP-OES analysis would better account for complex matrix effect of produced water.

Once our method of using TOC, GC-MS, ICP-OES has provided adequate qualitative and quantitative analysis of PW. We can expand study on a wider range of commercial household filter beyond the Brita specific model filter.

Further study on the efficiency of filter is to simulate filtering spiked water samples with organics and metals known to be contained in many produced water study, such as BTEX compounds, other harmful heavy metals. Analysis can be done both separately by compound group and as a mixture (simulating PW sample) to evaluate the filter capacity in more interesting scenarios. Additionally, such controlled experiment will provide a more positive confidence in establish the safety range limit of filter when compare with regulated maximum contaminated level.

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