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# Analysis of Kyrock for Leaching of Impurities in Synthetic Rainwater

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ANALYSIS OF KYROCK FOR LEACHING OF IMPURITIES IN SYNTHETIC  
RAINWATER

A Thesis  
Presented to  
The Faculty of the Department of Chemistry  
Western Kentucky University  
Bowling Green, Kentucky

In Partial Fulfillment  
Of the Requirements for the Degree  
Master of Science

By  
Santhosh Kumar Kasulavada

May 2013

ANALYSIS OF KYROCK FOR LEACHING OF IMPURITIES IN SYNTHETIC  
RAINWATER

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I dedicate this thesis to my family for their love and support during my challenging times here at Western Kentucky University. Also, I dedicate this thesis to my research advisor, Dr. Cathleen Webb, for her help and support throughout my research.

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## ANALYSIS OF KYROCK FOR LEACHING OF IMPURITIES IN SYNTHETIC RAINWATER

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May 2013

46 Pages

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Kyrock is a coarse grained sandstone with a complex mixture of organic and inorganic compounds. Mining of Kyrock is for use in road construction and roofing. Kyrock samples were analyzed using scanning electron microscopy to obtain elemental analysis. High levels of carbon indicate the presence of organic compounds. Analysis of an acid digestion of the samples using inductively coupled plasma spectroscopy showed inorganic compounds such as titanium oxide, vanadium oxide along with traces of arsenic. Elemental analysis of samples indicates a percent of carbon, and sulfur with no notable traces of nitrogen. Pyrolysis of the samples was done using gas chromatography mass spectroscopy with a gradual increase in temperature to 160° C resulted in the release of inorganic and organic compounds. Synthetic rainwater was prepared to examine the leaching of compounds and the leachate was analyzed using liquid chromatography mass spectroscopy and gas chromatography mass spectroscopy.

## INTRODUCTION

Kyrocks or Kentucky rock is a name assigned to a form of natural asphalt in Kentucky. A thick, sticky, dark-brown mixture of petroleum tars used in paving, roofing, and waterproofing. Asphalt is produced as a byproduct in refining petroleum or natural beds. The main advantage of using this asphalt mineral is that it does not require any addition of binders. According to the Asphalt Institute at the University of Kentucky, Kyrocks has been considered as a class A prized asphalt rock, non polishing material and an ideal top-coating material in road construction (Crump, 1913).

Natural asphalt was first discovered in 1810 while drilling for a salt water well. The material was not recognized until 1840, in Alabama by European settlers in Lawrence County, Alabama (Crump, 1913). Kyrocks or natural asphalt was studied and documented by geologists from the Kentucky Geological Society in the 1850s. Logan County had a first rock asphalt mining operation for paving purposes but Grayson County provided the first asphalt recovery in 1891 and Edmonson County became one of the important sources in the early 19<sup>th</sup> century. Serious asphalt mining has been started in the early 1900's but really gained importance in 1920, when a report was published in the New York Times on November 28, 1920, that asphalt has been mined in Kentucky like coal in large quantities (© copyright by The New York Times).

Rock asphalt has been found in the southern and eastern outcrop of the Western Coalfield of Kentucky. Figure 1 indicates the presence of rock asphalt in Kentucky (Redfield, R.A. 1930). Historical mining of asphalt has been widely done in the Edmonson, Warren, Logan, Breckinridge, and Grayson Counties in Kentucky. Asphalt content in Kentucky was estimated to be around 5-6 billion barrels, which was developed

by the United States interests (J. Horne, 2009). Historical mining of asphalt has given rise to various mining towns like Black Gold, Sweeden and Kyrock, which has given a large quantity of rock asphalt.

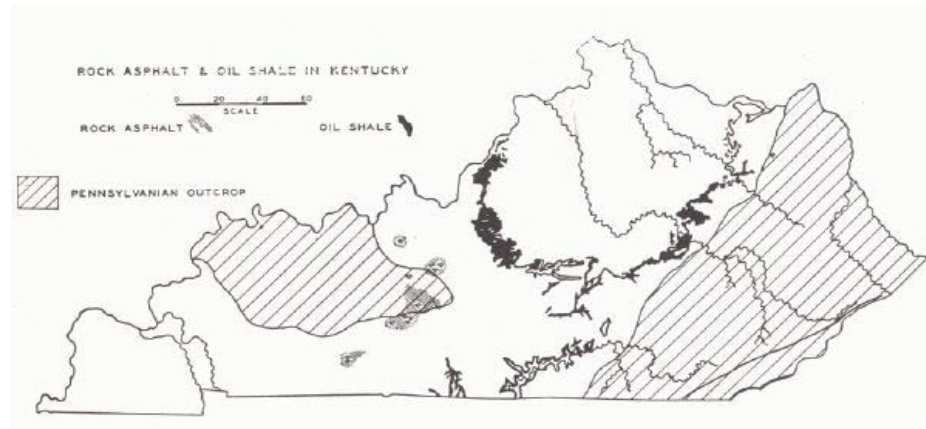


Figure 1: Rock asphalt in Kentucky

Every year about 100,000 tons of asphalt was being mined in Kentucky. An estimated 344,000 tons of rock asphalt was mined in 1927 and was used all over the United States for paving of highways due to its highly skid resistant surface nature (Jerry G. Rose, 1992). Rock asphalt is found from about 3 to 30 feet underground. It is mined by using hand drills or blasted with explosives and again transferred to jaw crushers using tramcars to break them into walnut sized pieces. These are passed through three pairs of rolls to reduce them into sand sized particles, which can be left over and easily used for pavements and other uses.

Paving of asphalt has a series of steps that are required to for a proper layer of roads. The first use of natural asphalt was done in the Pike cemetery at Bowling Green, Kentucky in 1907. No other material was added or modified. It was frequently tested and found to be as good as if the road was paved new, even for years, and has been classified

as the best rock asphalt in the Kentucky. The cost was also very cheap, at about \$5 a ton for this high quality rock asphalt.

### **Asphalt:**

Asphalt is a black or dark brown solid or viscous liquid at room temperature; insoluble in water at 20°C; partially soluble in aliphatic organic solvents; and soluble in carbon disulfide, chloroform, ether, and acetone (Sax & Lewis, 1987). This asphalt is mixed with silicates to form rock asphalt (Kyrock). This rocky asphalt is formed due to the seeping of asphalt into the sand stones in the earth. The chemical components of asphalt can be classified as aliphatic compounds, cyclic alkanes, aromatic hydrocarbons; polycyclic aromatic compounds (PAC's) along with various metals e.g., iron, nickel, vanadium, chromium, asphalt also contains sulfur and nitrogen.

Asphalts are classified into different types:

***Paving Asphalt:*** these are the asphalts that are obtained in the nature. These are formed due to the seeping of asphalt into the rocky stone in nature.

***Asphalt cement:*** this is specifically used for paving industrial use and roofing. It is mostly used as a binder.

***Emulsified asphalt:*** it is simply a suspension of small asphalt in water along with an emulsifying agent (Robert, et al, 1996).

***Cutback Asphalt:*** it is a combination of asphalt and petroleum solvent.

***Foamed Asphalt:*** it is a combination of hot asphalt in cold water. When combined, the water evaporates and asphalt is formed as a layer.

***Oxidized asphalt:*** it is normal asphalt, which is formed by blowing air for oxidation and then forms a layer.

## Physical properties of Asphalt:

**Softening point:** softening point is defined as the temperature at which a asphalt sample can no longer support a weight of a 3.5g steel ball (AASHTO, 2000).

### **Viscosity:**

**Absolute (dynamic) viscosity:** it measures the time taken for a fixed volume of asphalt to be drawn through a capillary tube by means of vacuum under controlled conditions of vacuum and temperature (ASTM, 2001).

**Kinematic Viscosity:** it measures the time taken for a fixed volume of asphalt to flow through capillary viscometer under closely controlled conditions of head and temperature (ASTM, 2001).

**Ductility:** it measures the capacity of asphalt to elongate or stretch an indication of the material to flow. A small quantity of asphalt is taken and is pulled apart at a specified temperature and pressure before it is ruptured (ASTM D113)

**Penetration:** it measures with a penetrometer by which a standard needle is applied to the sample. It is the distance in tenths of a millimeter that a needle penetrates vertically into the sample under fixed conditions of temperature, load and time (ASTM D5).

Table 1: Physical properties of asphalt

Physical Properties	
Solubility in water	Insoluble in water at 25°C
Solubility in organic solvents	Completely soluble in carbon disulfide, chloroform, ether and acetone
Softening point	46.5°C
Viscosity	0.275 at 135°C Pa.s
Penetration	90 dmm
Specific gravity	1.03

### **Chemical properties of Asphalt:**

Asphalt is a very complex mixture of high molecular weight nitrogen, sulfur, and oxygen containing aliphatic compounds, cyclic alkanes, aromatic hydrocarbons; polycyclic aromatic compounds (PAC's) along with various metals (e.g., iron, nickel, vanadium, chromium). Later they were also considered to be intermediate compounds between kerogen and oil.



Table 2: Chemical composition of Asphalt by GC-MS Analysis

Compound class	Compounds
Hydrocarbons	Alkanes, C9–C27 Alkenes/cycloalkanes Benzenes, C2–C8 Indanes/Indenes, C0–C3 Naphthalenes, C0–C5 Biphenyls, C0–C2 Fluorenes, C0–C3 Anthracenes/phenanthrenes, C0–C4 Pyrenes/fluoranthenes, C0–C2 Chrysenes/benz[ <b>a</b> ]anthracenes, C0–C2
Sulfur-containing compounds	Benzothiophenes, C0–C9 Dibenzothiophenes/naphthothiophenes, C0–C4 Tricarbocyclic fused-ring thiophenes, C0–C1
Oxygen-containing compounds	Benzofurans/Dibenzofurans, C0–C2 Acetophenones, C0–C3 Fluorenones, C0–C3 Dihydroindenones, C0–C4 Dihydrofuranones Isobenzofuranones, C0–C3 Phenols/Naphthols, C0–C2 Furanones, C1–C3 Alkanones/Alkanoic acids, C5–C14 Benzoic acids, C0–C4
Nitrogen-containing compounds	Carbazoles, C0–C4
Oxygen and sulfur containing compounds	Hydroxybenzenethiols, C0 –C4

**Purpose of the study:**

It has been understood that the chemical composition of asphalt is very complex and varies with the seeping of asphalt into the rock. Leaching of these organic molecules is very much possible. Leaching can be formed due to the rainwater flowing through this Kyrock material and may cause adverse reactions in the environment. The main object of this thesis is to identify the physical and chemical nature of the asphalt present in the Kyrock obtained from the nearby region of Mammoth Cave National Park and identify the compounds that can be leached into the water by using various pH solutions of synthetic rainwater.

## MATERIALS AND METHODS

### Chemicals and Materials:

The below chemicals are used for experiments

Table 3: Chemicals and Manufacturers

Chemical Name	Manufacturer
N-Pentane (HPLC Grade)	Fischer Scientific
Toluene (HPLC Grade)	Fischer Scientific
Sodium Nitrate	Fischer Scientific
Sodium chloride	Fischer Scientific
Potassium chloride	Fischer Scientific
Calcium chloride dehydrate	Fischer Scientific
Magnesium sulfate	Fischer Scientific
Ammonium sulfate	Fischer Scientific
Buffers (pH 4 and pH 7)	Fischer Scientific
Acetonitrile	Fischer Scientific
Methanol	Fischer Scientific
Nitric Acid	Fischer Scientific
Nano pure water	Barnstead Nano Pure II

**Kyrock:** Kyrock for this research was obtained from Mammoth Cave National Park region, from Kyrock tailing piles near Glass Paving Company. The latitude and longitude

for the sample Kyrock R are 86.2556, 37.25323 and Kyrock L are 86.25568, 37.25297.

### **Preparation of Synthetic Rainwater:**

Nano pure water was collected from the Barnstead Nano Pure II generator and the following inorganic compounds were added to a final volume of 1000 ml. A 1:1000 dilution was done to obtain a resulting solution of synthetic rainwater with an ionic strength of 0.3 mM and a pH of 5.3.

Table 4: Composition of synthetic rainwater

Chemical Name	Quantity (g)
Sodium Nitrate	4.07
Sodium chloride	3.24
Potassium chloride	0.35
Calcium chloride dehydrate	1.65
Magnesium sulfate	2.98
Ammonium sulfate	3.41

### **Inductively Coupled Plasma Emission Spectroscopy (ICP-ES)**

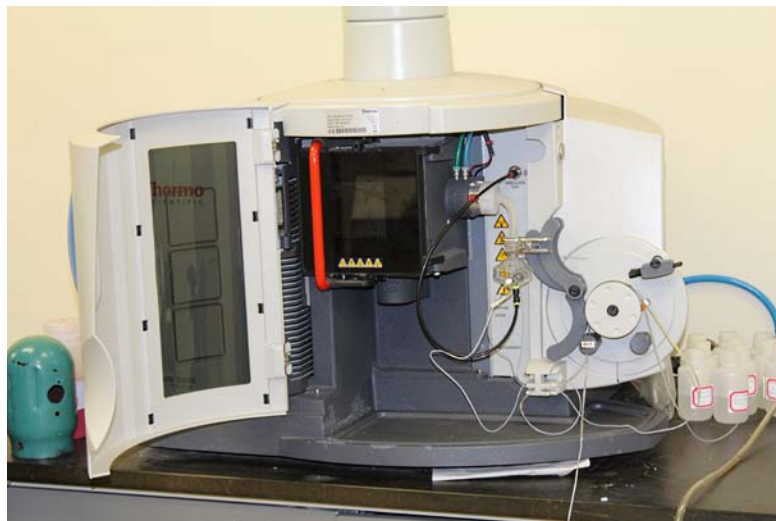
Inductively coupled plasma is used to analyze aqueous or organic liquids quantitatively or qualitatively. Solid samples may also be digested and analyzed using this system. The excited atoms or ions produced by inductively coupled plasma emit electromagnetic radiation at wavelengths characteristic of particular elements. Detection of the specific element is based upon the emission of energy at characteristic wavelengths (Skoog, et al 1998).

#### ***Working Principle***

It is composed of two parts: Inductively coupled plasma (ICP) and an optical spectrometer. Three concentric glass quartz tubes are present in the ICP torch. This quartz torch is surrounded partly by a radiofrequency (RF) generator. Plasma is created by Argon gas. The radiofrequency signal is of high power and flows into the coil. An electromagnetic field is created inside the coil when the torch is turned on. The RF generator is a high power radio transmitter that creates the RF signal and drives the “work coil” like a radio transmitter antenna.

The ionization process is initiated as the argon gas flows through the discharge arc. The Tesla unit ignites argon gas that flows through the torch. As the plasma ignites, the Tesla unit is switched off. The ionization of argon gas occurs in the intense electromagnetic field, which flows to the RF coil magnetic field in a rotational symmetrical pattern. Charged particles collide in-elastically with neutral argon atoms and produce stable high temperature plasma of 7000K. Organic or aqueous samples are delivered into a nebulizer by a peristaltic pump. This is converted into mist and directly delivered to the plasma flame. The sample breaks into ions as it collides with charged ions present in the plasma and with that of electrons. Different molecules break into atoms and atomic ions again combine in plasma repeatedly remitting radiation at the characteristic wavelengths of the elements involved (Skoog, et al 1998).

Figure 2: Inductively coupled plasma Spectrometer



### *ICP Advantages*

- Detection to ppm-ppb levels of numerous trace metals.
- The important feature of ICP is that it is a multi-elemental analysis technique and requires much less time.
- It also requires very low sample volumes.

### *ICP Disadvantages*

- Inert gases and some non-metals such as carbon, nitrogen and oxygen cannot be analyzed by ICP.
- It is an expensive instrument compared to ICP-AAS and is affected by the interferences due to sample preparation and plasma operating conditions.

### *Applications*

- ICP-AES is frequently used for the analysis of trace metals in soil and coal samples.

- It is also used in motor oil analysis and mineral processing.

## **Scanning Electron Microscope (SEM)**

### ***Operation***

The classical method to obtain detailed information about the physical nature of surface is optical microscopy. SEM (Scanning Electron Microscopy) has higher resolution in comparison to a standard light microscope and was used for observing the surface structure of the Kyrock samples. The JEOL JSM-5400 LV SEM was the used to analyze the samples.

### ***Preparation of Samples for SEM***

The samples must be electrically conductive and dry of water and solvents that can vaporize in vacuum. Mounting of the samples for SEM is usually done on metal holders called stubs. The samples are mounted on the stub with the help of a mounting medium. The mounting medium commonly used is glue or tape. The mounting medium should be stable upon production of electrons; should release minimal levels of air or solvents; should not interfere with the image produced in SEM; be mechanically stable; and should also have electrical conductivity (Flegler, 1993).

If any of the samples are nonconductive they are usually coated to make the samples electrically conductive. Mostly the nonconductive materials are coated with very thin layers of gold. Depending on the nature of the sample, other methods like air-drying, drying using solvent, vapor fixation, vapor pre-fixation, freeze drying, and poly-L-lysine procedure may be used.

### ***SEM Advantages***

- Three-dimensional and topographical imaging possible.

- Easy to operate with use of advanced computer technology.
- Analysis time less than 5 minutes.

#### ***SEM Disadvantages***

- Analysis is limited to solids.
- It is a very expensive and large and must be kept in a large area.
- It needs a steady voltage and requires circulation of cool water.

#### ***Applications***

- It is an essential tool in fields of life sciences, gemology and metallurgy.
- It can detect and analyze surface fractures.
- It has applications in topography, morphology and compositional information.

### **Carbon Hydrogen and Nitrogen (CHN) Analyzer**

It consists of a furnace capable of maintaining a temperature in the range to ensure quantitative recovery of carbon, hydrogen and nitrogen and their corresponding gases. The detection system helps in evaluating the gases present accurately.

#### ***Preparation of sample***

The samples are crushed according to procedure in ASTM D 2013 and able to pass through 60 mesh or 250  $\mu\text{m}$ . The sample is weighed in a tin foil boat and introduced into the furnace. A blank analysis is performed to obtain a one percent relative response and the instrument is calibrated with the standard materials and samples are analyzed according to method ASTM 2007. Figure 3 shows the CHN analyzer used for the research.



Figure 3: Carbon Hydrogen Nitrogen analyzer



### ***Applications***

- The amount of carbon, hydrogen and nitrogen are calculated in the coal, soil and fuels.
- Carbon and hydrogen values are used to determine the amount of oxygen required for the combustion process.

### **Sulfur Analyzer**

It is used to determine the amount of sulfur in samples by rapid determination using high temperature tube furnace.

### ***Operation***

The sample is burned in a tube at a minimum operating temperature of 1350°C in

a stream of oxygen to oxidize the sulfur. The moisture in the particles is absorbed using anhydrous magnesium perchlorate and the gas stream is passed through a cell in which sulfur dioxide measured by an infrared absorption detector. This method must be calibrated by the use of reference agent.

### ***Preparation of sample***

The sample is pulverized to pass through mesh 60 (250  $\mu\text{m}$ ) and a portion of the sample must be analyzed for moisture content according to the test method ASTM D 3173 to determine the dry sulfur value in the sample.

### ***Applications***

- Sulfur is converted into sulfur oxide and detected.
- Sulfates and sulfites are detected using sulfur analyzer.

Figure 4: Sulfur Analyzer



## **Gas-Chromatography Mass-Spectroscopy (GC-MS)**

The GC-MS is used to analyze the samples by combining the features of gas-liquid chromatography and mass spectrometry. The gas chromatograph utilizes a

capillary column. The column dimensions like length, diameter and film thickness as well as phase properties determine the specific application. In a mixture of compound, the column differentially retains molecules, which come off from the column at different times (retention time). The mass spectrometer ionizes, and detects ionized molecules by breaking each molecule into ionized fragments and detecting these fragments using the mass to charge ratio. Combining gas chromatography and mass spectrometer gives a much fine degree of molecule identification than using them separately. A solid phase micro extraction (SPME) syringe is used to extract volatile compounds from the samples.

Figure 5: Gas Chromatography Mass Spectroscopy



### ***Applications***

- It is used to analyze blood samples in forensic or crime scenes.
- It is used to detect illegal narcotics.
- It is used to analyze food and beverages to detect aromatic compounds.

### ***Advantages***

- It is very fast and accurate.
- It can be used as a screening technique.
- It requires small amounts of sample.

### ***Disadvantages***

- Not all peaks are calibrated.
- It is limited to volatile compounds.
- Not suitable for thermally labile samples.

## **Liquid Chromatography-Mass Spectroscopy**

It is an experimental technique, which combines liquid chromatography with the mass analysis capabilities of mass spectrometry. It can be used for fast-directed purification of natural products and new molecular entities important to food and agrochemicals. The separation of a mixture of components is based on the elution rate from a mobile phase over a stationary phase. Different molecules have different affinities for the stationary phase and mobile phase leading to the separation of the compounds. Some compounds will be more attracted to the mobile phase and will elute quickly while other compounds elute more slowly and therefore have different retention time. Different column packing materials have different affinities and therefore using columns for specific molecules gives different retention times. Using solutions like methanol or acetonitrile with water to obtain different mobile phase compositions changes retention times. The mass spectrometer is arranged after the gas chromatography to ionize and detect ionized molecules by breaking each molecule into ionized fragments and detecting these fragments using the mass to charge ratio. The molecules are broken into small ions and they are detected using mass spectrometer.

### ***Applications***

- It is used to identify doping agents and drug of abuse in diuretics.
- It is used to study impurity profiling.
- It is used to assay drugs, their intermediates and metabolite studies.

### ***Advantages***

- It has high sensitivity and selectivity.
- It can be used to identify specific compounds in the presence of a mixture.

### ***Disadvantages***

- It fails to distinguish between specific metabolites in the urine samples.
- Detection of some specific drugs is not possible in the LC-MS.

Figure 6: Liquid chromatography mass spectroscopy



### **Wrist shaker**

The Burrell Wrist action shaker, model 75 is used to perform batch tests and to

coat the base material. The shaker is constructed in such a way that it may hold conical flasks of 100mL to 1000mL. Flasks are mounted on a spindle and oscillate through small amplitude shaking. An electronic regulator controls the action of shaking speed.

## **X-ray diffractometer**

X-ray diffraction studies determine the arrangement and the spacing of atoms in a crystalline material. Both qualitative and quantitative information about the compounds present in a solid sample can be provided by x-ray powder diffraction. It is a nondestructive analytical technique that gives information about the chemical composition, crystalline structure and physical properties of materials and thin films. The scattered intensity of an x-ray beam hitting a sample is measured as a function of incident and scattered angle, polarization and wavelength. Each crystalline substance has a unique X-ray diffraction pattern. By comparing the pattern of the unknown with known compounds, the chemical identity of the material is obtained (Skoog, 1998).

Figure 7: ARL Thermo X-ray diffractometer



## RESULTS

### Scanning Electron Microscopy Results

Figure 8 shows the scanning electron microscopy of Kyrock R at 100 X and figures 9 and 10 shows the analysis report for Kyrock R at position 1 and 2, respectively. Table 5 shows the concentration of the various elements like carbon, oxygen aluminum, silicon, potassium and sulfur in different locations on the sample.

Figure 8: SEM image of Kyrock R at 100X magnification

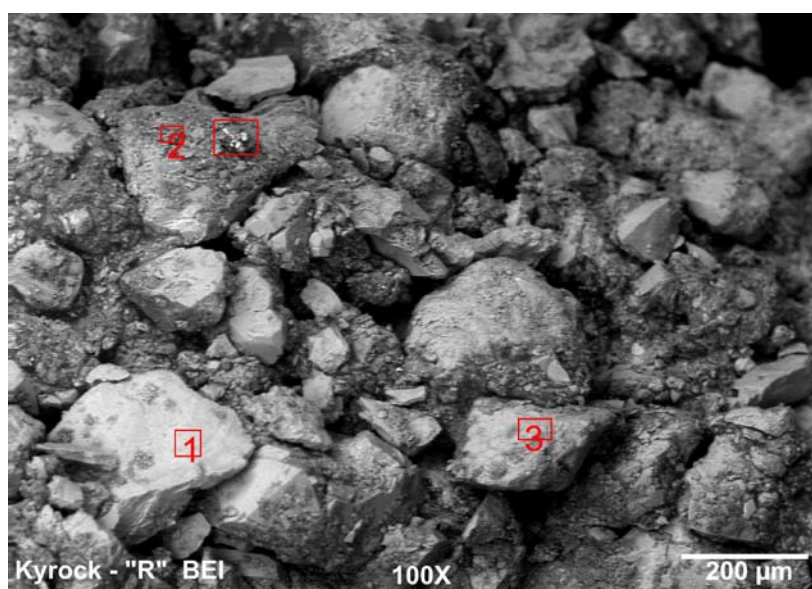


Figure 9: Analysis report for SEM image obtained for Kyrock R at location 1

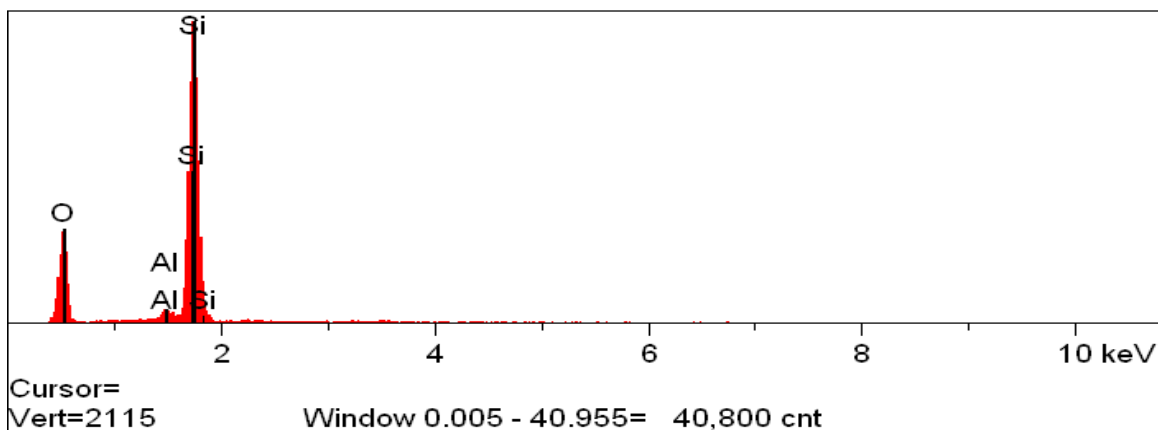


Figure 10: Analysis report for SEM image obtained for Kyrock R at location 2

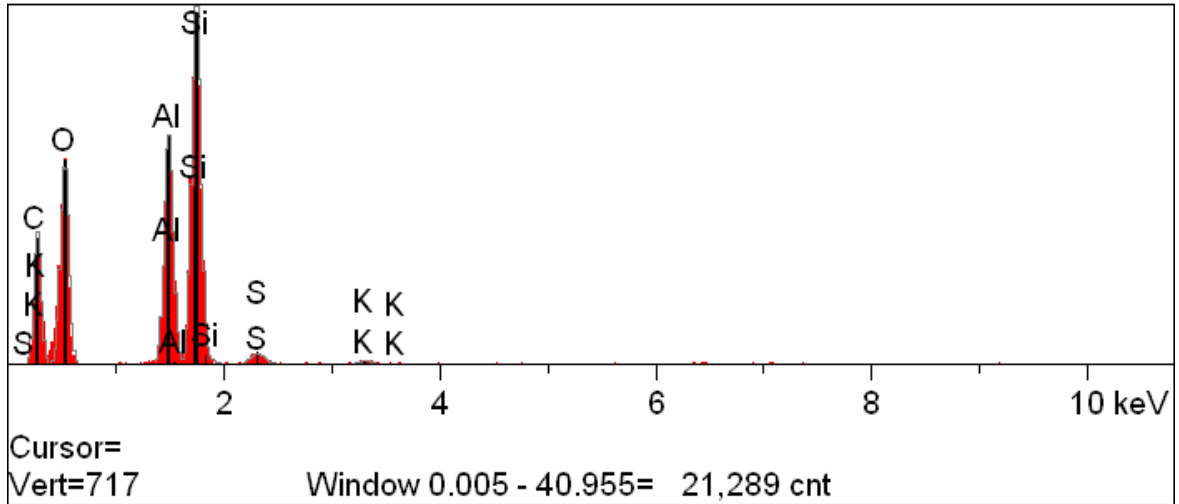


Table 5: Analysis data for SEM image obtained for Kyrock R

Element Name	Location 1		Location 2	
	Atomic percentage	Concentration (wt %)	Atomic percentage	Concentration (wt %)
Carbon			45.15	34.67
Oxygen	67.38	54.10	42.69	43.67
Aluminum	1.49	2.02	4.74	8.18
Silicon	31.13	43.88	7.03	12.63
Sulfur			0.30	0.62
Potassium			0.09	0.23
Total	100.00	100.00	100.00	100.00

The result at 100X magnification clearly shows that the Kyrock R is primarily composed of aluminum silica and oxygen clearly indicating that it is sandstone. It also has an uneven distribution of organic content in the sandstone stating that the seeping of



asphalt is not evenly distributed throughout the sample. Figure 11 illustrating the scanning electron microscopy of Kyrock R at 2000 X and figures 12 and 13 shows the analysis report for Kyrock R at position 1 and 2, respectively. Table 6 shows the concentration of the various elements like carbon, oxygen aluminum silicon potassium and sulfur in different locations in the image.

Figure 11: SEM image of Kyrock R at 2000X magnification

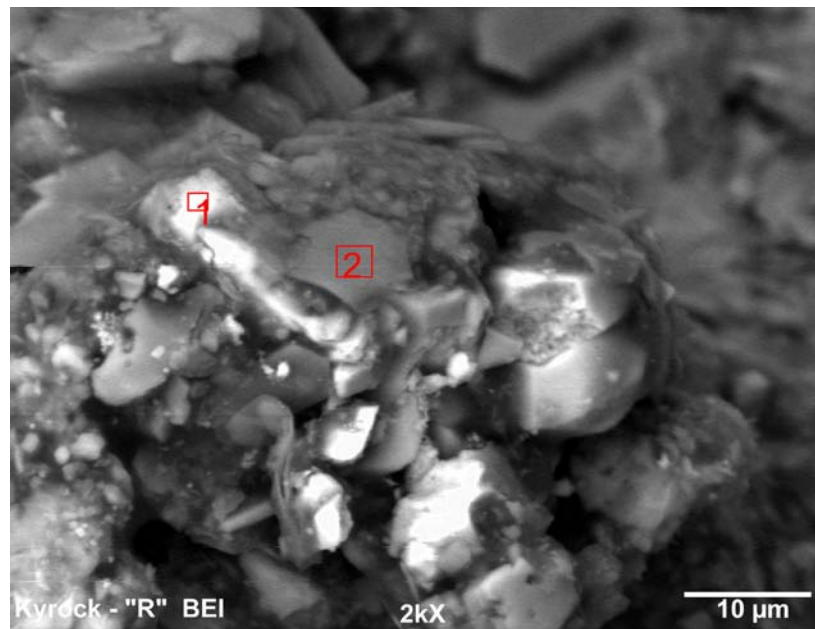


Figure 12: Analysis report for SEM image obtained for Kyrock R at location 1

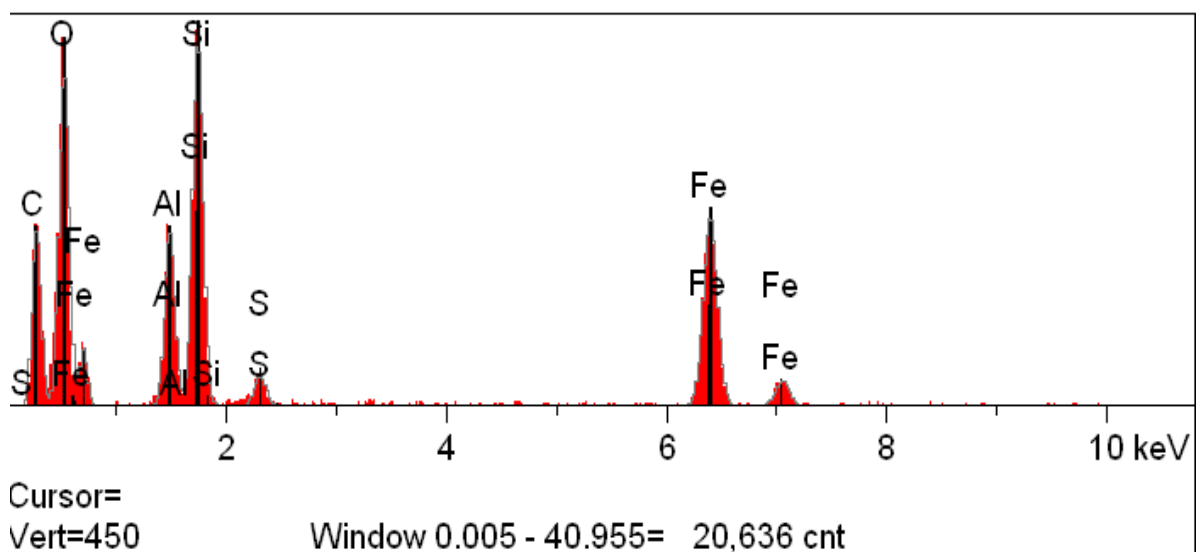


Figure 13: Analysis report for SEM image obtained for Kyrock R at location 2

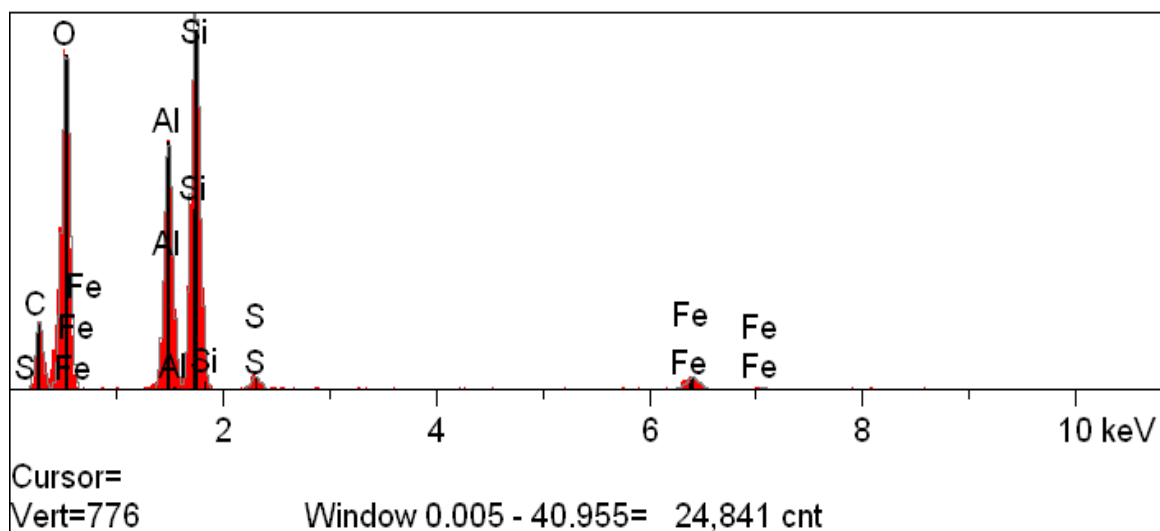


Table 6: Analysis data for SEM image obtained for Kyrock R

Element Name	Location 1		Location 2	
	Atomic percentage	Concentration (wt %)	Atomic percentage	Concentration (wt %)
Carbon	42.54	30.38	29.76	21.51
Oxygen	44.75	42.58	55.83	53.76
Aluminum	3.06	4.91	5.58	9.05
Silicon	5.64	9.42	8.13	13.75
Sulfur	0.44	0.83	0.28	0.55
Iron	3.57	11.87	0.41	1.39
Total	100.00	100.00	100.00	100.00

While the analysis is done under higher magnification of 2000 X in the organic rich area the carbon content is unevenly distributed along with various elements along

with aluminum silicate like sulfur and iron at varied concentrations in different locations.

Figure 14 shows the scanning electron microscopy of Kyrock L at 100 X and figures 15 and 16 shows the analysis report for Kyrock R at position 1 and 2, respectively. Table 7 shows the concentration of the various elements like carbon, oxygen aluminum silicon potassium and sulfur in different places.

Figure 14: SEM image of Kyrock L at 100X magnification

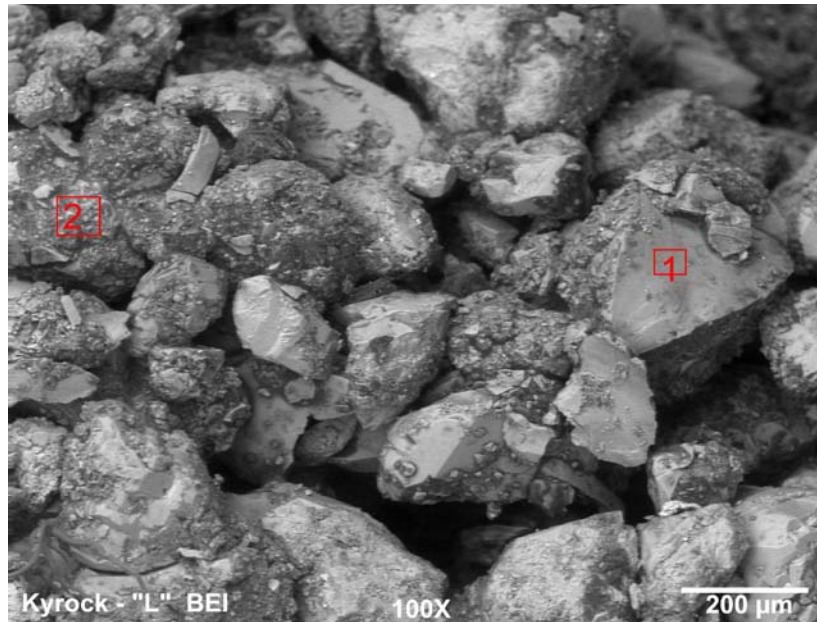


Figure 15: Analysis report for SEM image obtained for Kyrock R at location 1

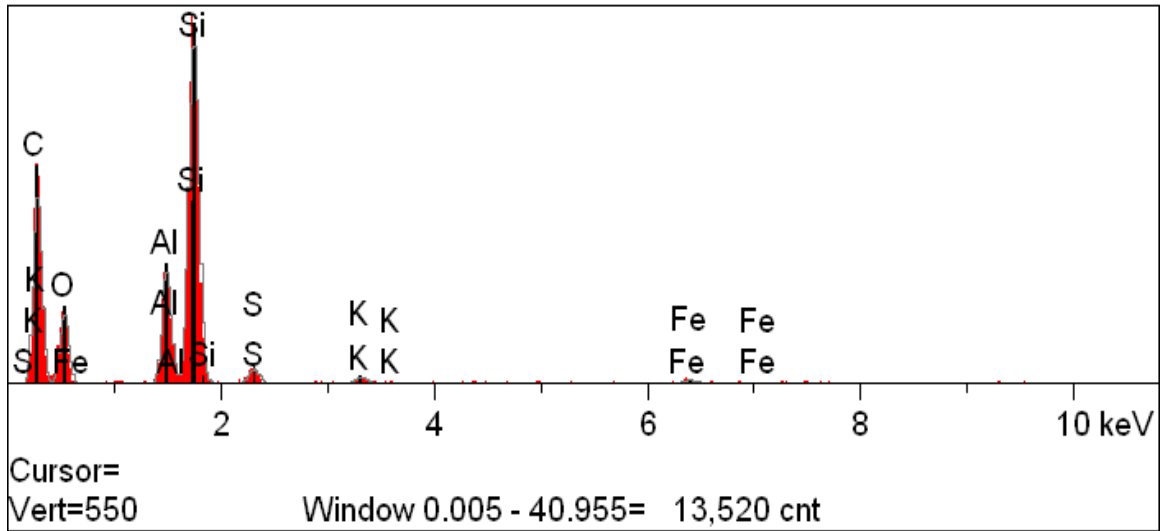


Table 7: Analysis data for SEM image obtained for Kyrock L

Element Name	Atomic %	Concentration (wt %)
Carbon	66.42	54.82
Oxygen	23.90	26.28
Aluminum	2.27	4.20
Silicon	6.85	13.23
Sulfur	0.30	0.66
Potassium	0.14	0.38
Iron	0.12	0.44
Total	100.00	100.00

Figure 16 shows the scanning electron microscopy of Kyrock L at 2000 X and figures 17, 18, and 19 shows the analysis report for Kyrock L at position 1, 2 and 3, respectively. Table 8 shows the concentration of the various elements like carbon, oxygen, aluminum, silicon, potassium, sulfur, and iron.

Figure 16: SEM image of Kyrock L at 100X magnification

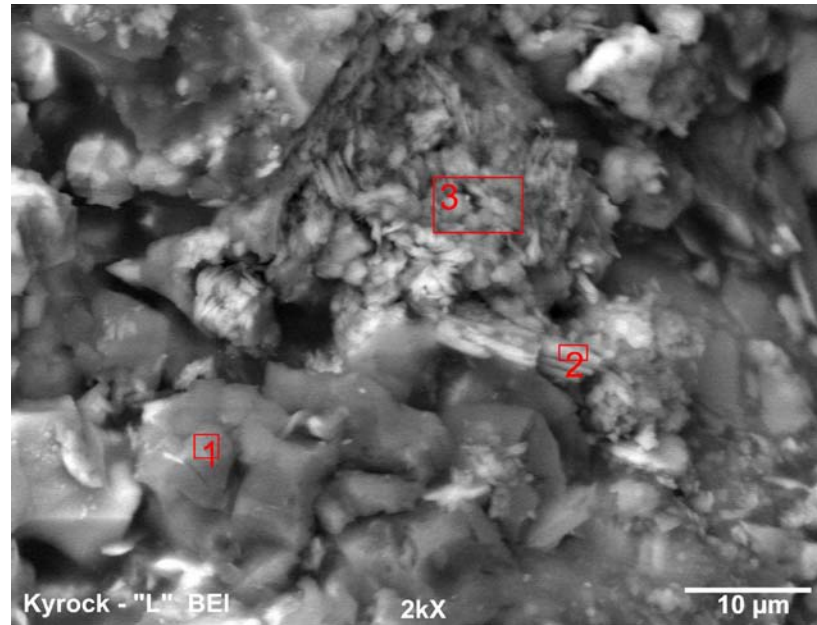


Figure 17: Analysis report for SEM image obtained for Kyrock L at location 1

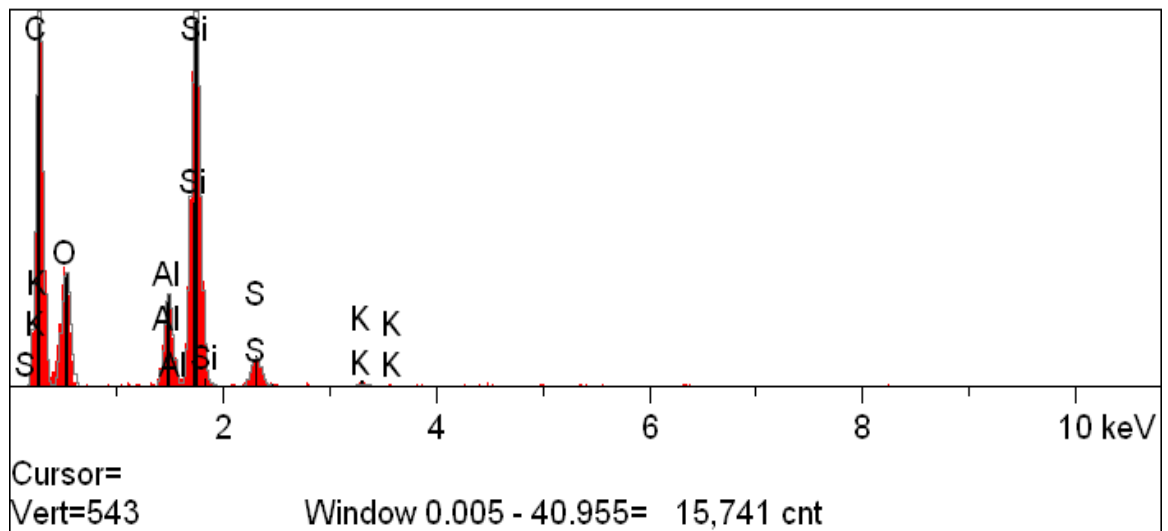


Figure 18: Analysis report for SEM image obtained for Kyrock L at location 2

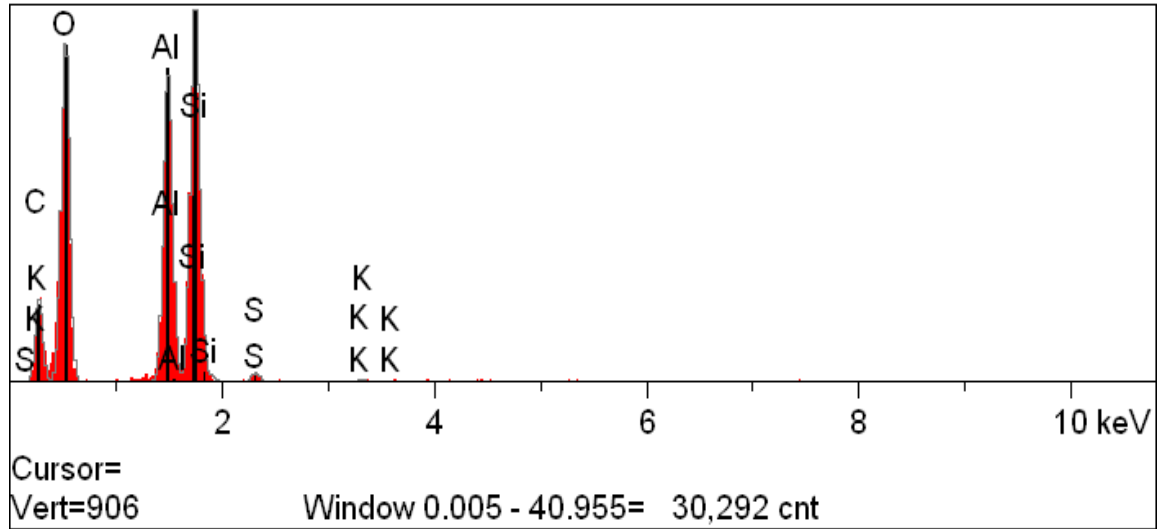
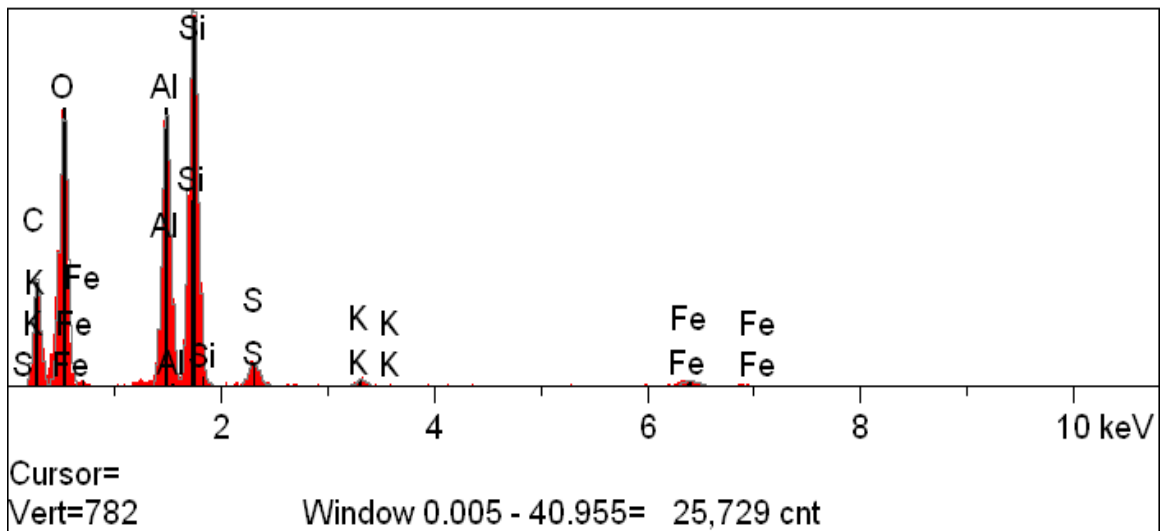


Figure 19: Analysis report for SEM image obtained for Kyrock L at location 3



The concentration of all the elements like carbon, aluminum, silicon, sulfur, potassium, and iron clearly show that there is a wide range of inorganic compounds present in Kyrock with a significant probability of finding trace metal elements in varied concentrations.

Table 8: Analysis data for SEM image obtained for Kyrock L

Element Name	Location 1		Location 2		Location 3	
	Atomic Percentage	Concentration (wt %)	Atomic Percentage	Concentration (wt %)	Atomic Percentage	Concentration (wt %)
Carbon	65.28	55.17	32.02	23.51	38.32	28.58
Oxygen	28.03	31.55	53.93	52.74	48.43	48.11
Aluminum	1.34	2.54	6.37	10.51	5.32	8.92
Silicon	4.93	9.73	7.49	12.85	7.15	12.47
Sulfur	0.39	0.88	0.15	0.29	0.46	0.91
Potassium	0.05	0.13	0.04	0.10	0.11	0.28
Iron					0.21	0.74
Total	100.00	100.00	100.00	100.00	100.00	100.00

The difference in the concentrations of the elements in different locations of the sample indicates the diversity in the formation of asphalt seeping in the Kyrock.

#### **Powder X-ray Diffraction results**

Figure 20 shows the powder X-ray diffraction results of Kyrock R. The compound in Kyrock is identified as aluminum silicate signifying the presence of sand stone.

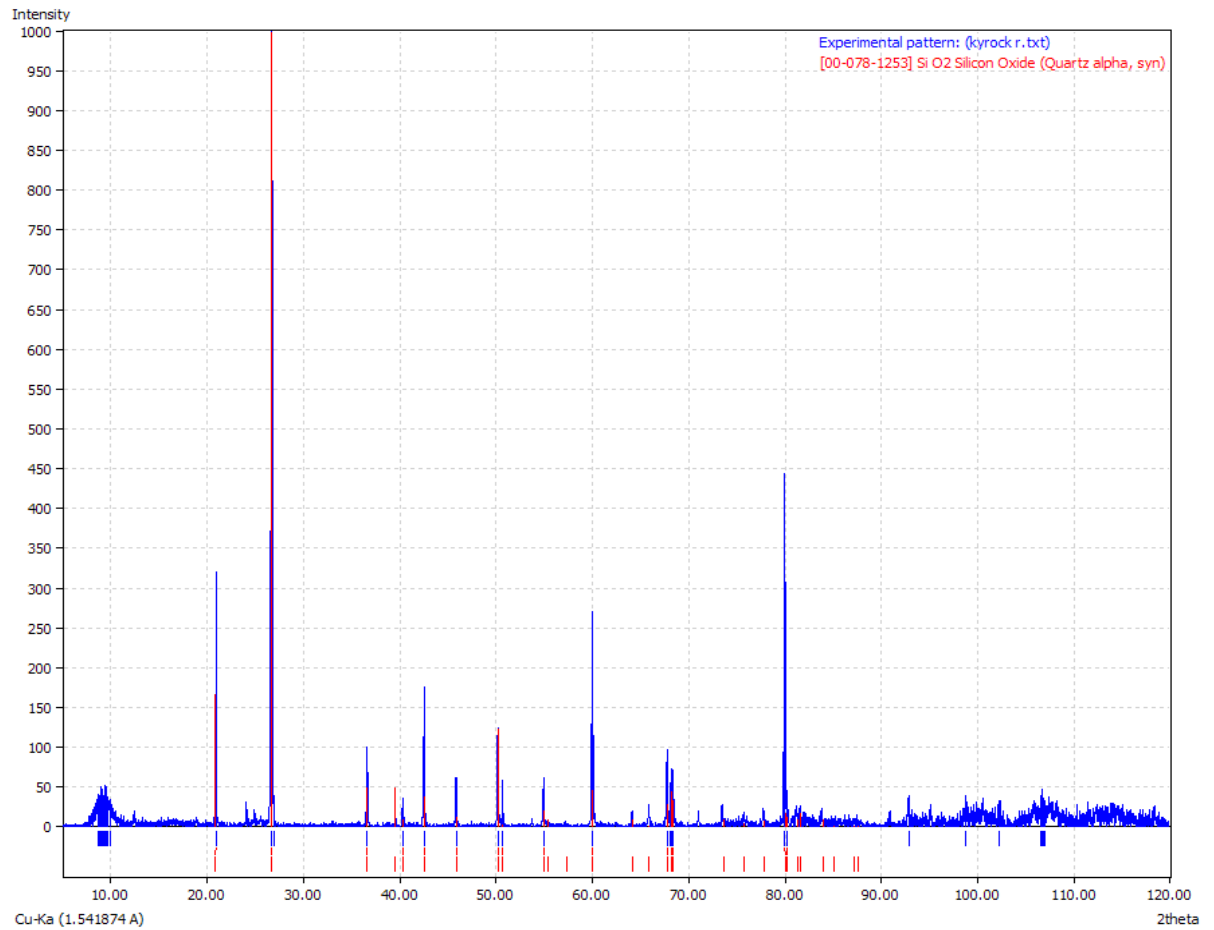


Figure 20: X-Ray Diffraction of Kyrock R

Figure 21 shows the powder X-ray diffraction results of Kyrock L which also shows aluminum silicate confirming the presence of sandstone.



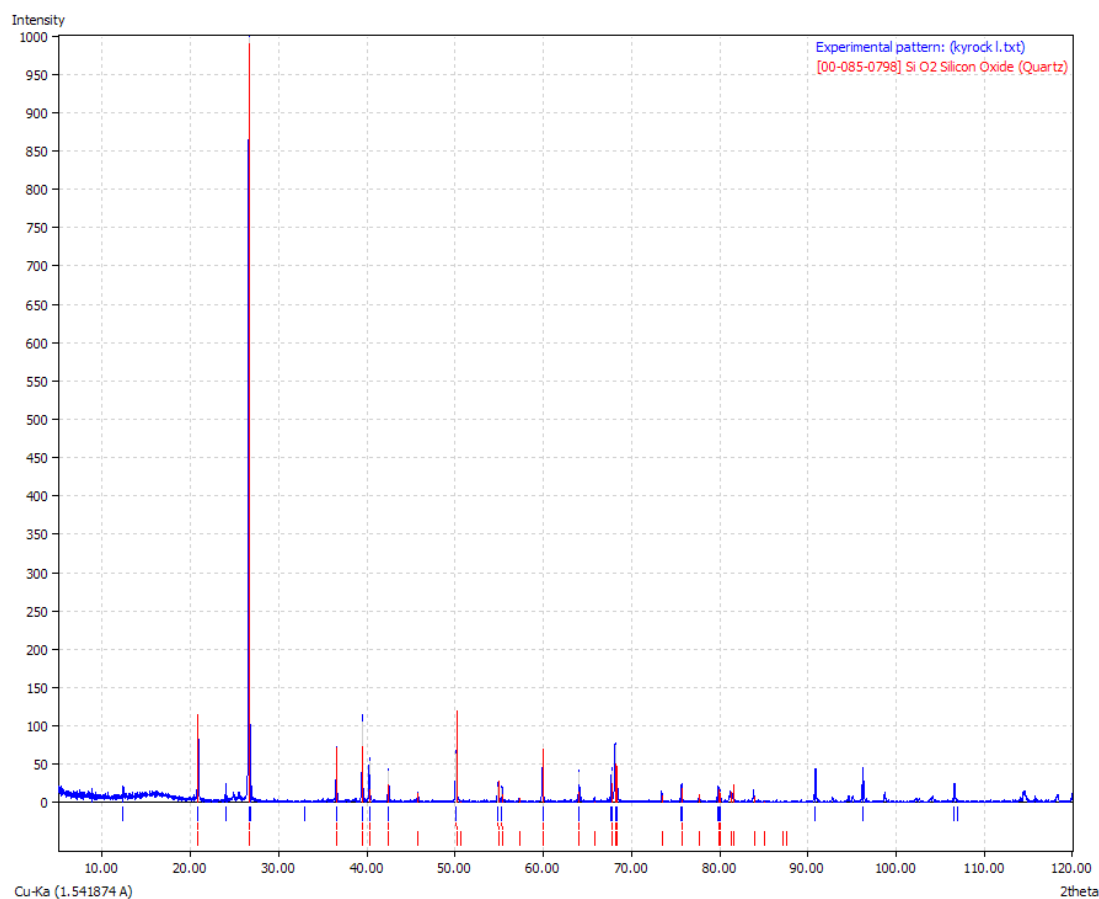


Figure 21: X-ray Diffraction of Kyrock L

Figure 22 is an overlay of both Kyrock L and Kyrock R. the peaks that are overlaying significantly show that they have a common base with similar organic content in them. The figure also illustrates the diversity in the composition of Kyrock.

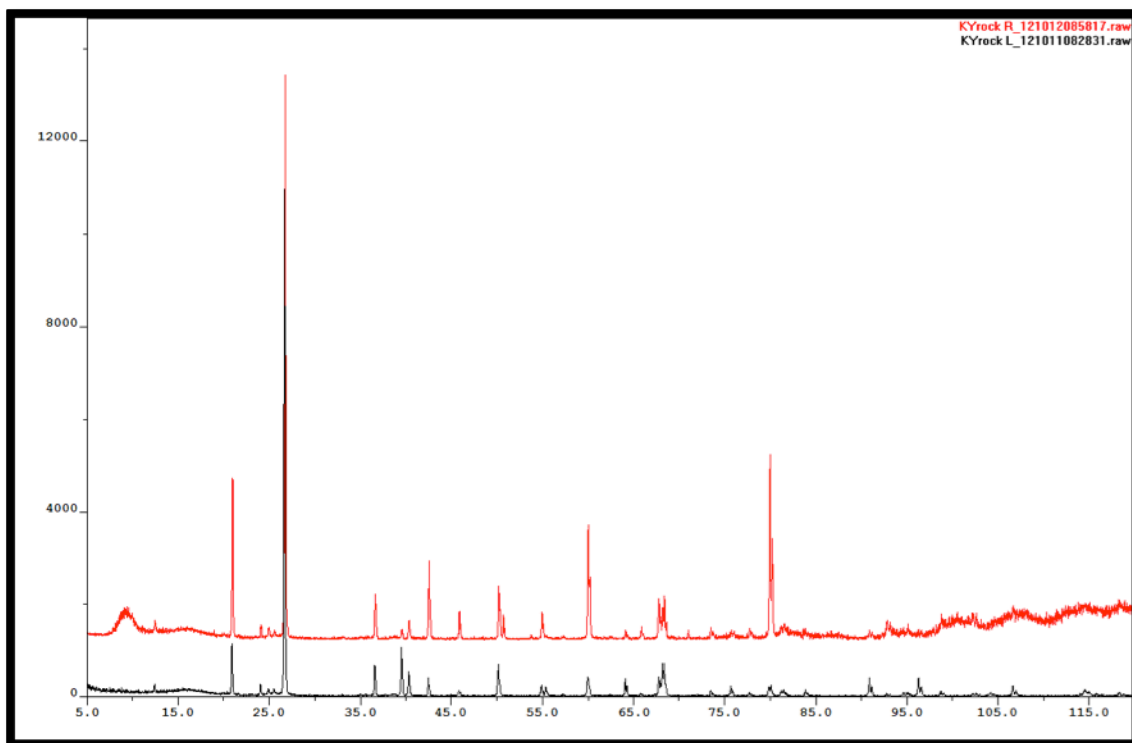


Figure 22: Overlay of Kyrock R and Kyrock L

### Elemental analysis of Kyrock

Figure 23 and 24 shows the calibration curve for carbon and hydrogen, respectively. The elemental analysis of Kyrock R and Kyrock L indicates a difference in the concentration of organic content. Table 9 shows the amount of carbon, hydrogen and sulfur for Kyrock L and Kyrock R. Notable traces of nitrogen was not recognized in the instrument.

Figure 23: Calibration curve for carbon.

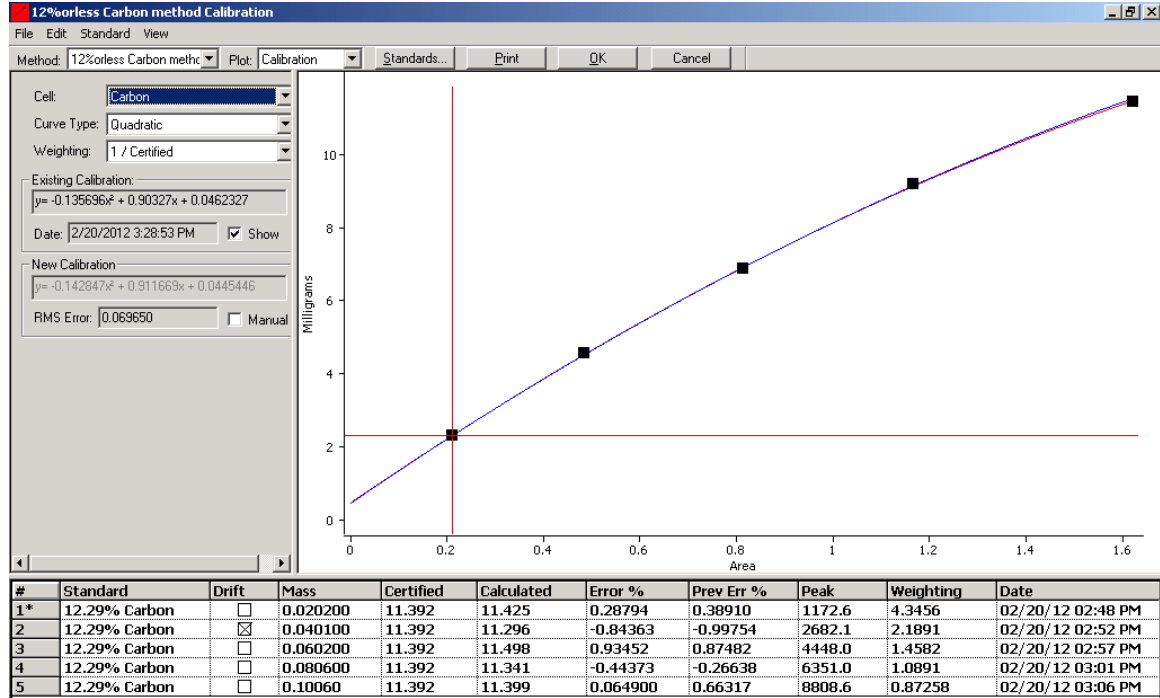


Figure 24: Calibration curve for Hydrogen.

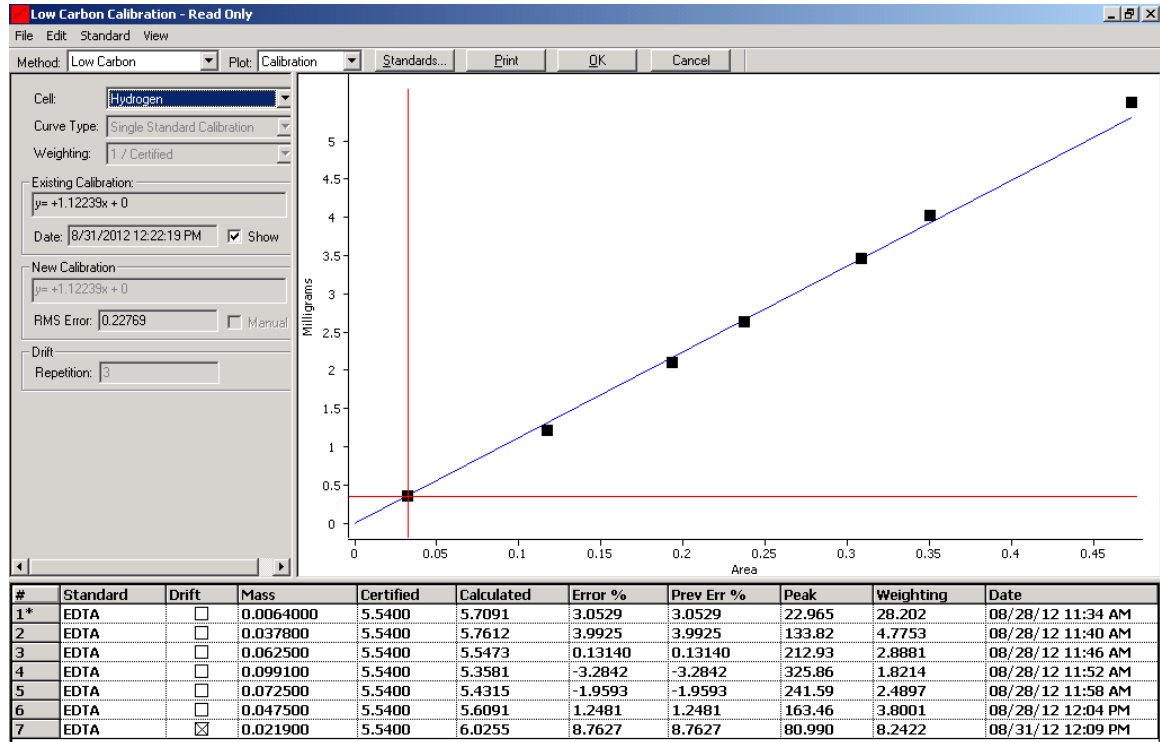


Table 9: Elemental analysis of Kyrock R and Kyrock L

Element Name	Kyrock R	Kyrock L
Carbon	5.71 %	3.48 %
Hydrogen	12.00 %	8.00 %
Sulfur	0.78 %	0.88 %

#### Elemental analysis results-ICP

Table 10 shows the concentration of various minor and major inorganic elements in the oxide form in parts per million (PPM). Kyrock is formed of many inorganic elements like barium, titanium, iron, magnesium sodium and strontium.

Table 10: Major and Minor Inorganic elements in Kyrock

<b>Element in oxide form</b>	<b>Kyrock R (µg/g) Oxide in sample</b>	<b>Kyrock L (µg/g) Oxide in sample</b>
Aluminum	1.22	1.23
Barium	0.01	0.02
Titanium	0.06	0.06
Iron	0.11	0.17
Potassium	0.09	0.10
Magnesium	0.02	0.02
Silicon	57.18	65.7
Strontium	0.01	0.01

Table 11 shows the trace metal elements found in the Kyrock R and L. The major trace metal elements that were found were cobalt at almost 50 ppm and sodium at about 60 ppm. Vanadium, phosphorous and chromium have the next higher levels along with traces of arsenic and other trace metal elements.

Table 11: Trace metal elements in Kyrock from ICP

<b>Element</b>	<b>Kyrock R</b> <b>µg/g</b>	<b>Kyrock L</b> <b>µg/g</b>
Beryllium	0.09	0.10
Cadmium	0.07	0.07
Chromium	12.90	15.90
Copper	1.80	2.68
Cobalt	42.10	53.33
Manganese	4.58	4.88
Nickel	6.13	1.34
Lead	6.56	7.14
Vanadium	12.35	12.82
Zinc	8.95	9.53
Phosphorous	13.20	11.30
Sodium	58.75	59.10
Selenium	1.60	1.70
Arsenic	Traces	Traces

## Pyrolysis Results

Table 12 shows the Pyrolysis results of Kyrock L. The compounds were classified into different compound classes.

Table 12: pyrolysis results of Kyrock L

Compound class	Compounds
Hydrocarbons	2-Naphthoic acid, 1-nitro-
	2,2-Bis[4-[4,6-dichloro-1,3,5-triazin-2-yl)oxy]phenyl]-1,1,1,3,3,3-hexafluoropropane
	Benzocycloheptano[2,3,4-I,j]isoquinoline, 4,5,6,6a-tetrahydro-1,9-dihydroxy-2,10-dimethoxy-5-methyl-Octadecanoic acid, 9,10-epoxy-18-(trimethylsiloxy)-, methyl ester, cis-
	[(1H)-Pyrrole-3-propanoic acid, 2-ethoxycarbonyl-4-ethoxycarbonylmethyl], bis-, diethyl ester
	2,4-Bis(indol-3-ylmethyleneamino)toluene
Sulfur-containing compounds	2-Myristynoyl pantetheine
	Sulfabenzamide
Oxygen-containing compounds	N,N'-Bis(Carbobenzyloxy)-lysine methyl(ester)
	Cyclopentane-1,2-dione (2,4-dinitrophenylhydrazone)
	2,4-Imidazolidinedione, 5-[3,4-bis[(trimethylsilyl)oxy]phenyl]-3-methyl-5-phenyl-1-(trimethylsilyl)-
	1,2-benzenedicarboxylic acid, diisooctyl ester
Nitrogen-containing compounds	Phenylhydrazine, 5-chloro-2,4-dinitro-
	Acetamide, N-methyl-N-[4-[4-fluoro-1-hexahydropyridyl]-2-butynyl]
	4,4-Ethylenedioxy-1-pentylamine
Oxygen- and sulfur-containing compounds	N,N'-Pentamethylenebis[s-3-aminopropyl thiosulfuric acid]
	Thiosulfuric acid, S-(2-(cyclopropylamino)-2-iminoethyl) ester

Table 13 shows the pyrolysis results of Kyrock R. The compounds were classified into different compound classes.

Table 13: Pyrolysis results of Kyrock R

Compound class	Compounds
Hydrocarbons	[(1H)-Pyrrole-3-propanoic acid, 2-ethoxycarbonyl-4-ethoxycarbonylmethyl], bis-, diethyl ester
	2,4-Bis(indol-3-ylmehtyleneamino)toluene
	2,2-Bis[4-[4,6-dichloro-1,3,5-triazin-2-yl)oxy]phenyl]-1,1,1,3,3,3-hexafluoropropane
	4-[4-Diethylamino-1-methylbutylamino]-1,2-dimethoxy-6-bromonaphthalene
	2-Naphthoic acid
Sulfur-containing compounds	2-Myristynoyl pantetheine
	Sulfabenzamide
	Arginine, N(2)-p-toluenesulfonyl-, methyl ester
Oxygen-containing compounds	N,N'-Bis(Carbobenzyloxy)-lysine methyl(ester)
	Cyclopentane-1,2-dione (2,4-dinitrophenylhydrazone)
	1,2-benzenedicarboxylic acid, diisooctyl ester
Nitrogen-containing compounds	Phenylhydrazine, 5-chloro-2,4-dinitro-
	Acetamide, N-methyl-N-[4-[4-fluoro-1-hexahydropyridyl]-2-butynyl]
	4,4-Ethylenedioxy-1-pentylamine
Oxygen- and sulfur-containing compounds	N,N'-Pentamethylenebis[s-3-aminopropyl thiosulfuric acid]
	Thiosulfuric acid, S-(2-(cyclopropylamino)-2-iminoethyl) ester
	2,6-Bis[2-[2-S-thiosulfuroethylamino]ethoxy]pyrazine

Table 14 shows the common volatile compounds that were identified in both Kyock L and Kyrock R.

Table 14: Common compounds of Kyrock pyrolysis

Compound class	Compounds
Hydrocarbons	2,2-Bis[4-[4,6-dichloro-1,3,5-triazin-2-yl)oxy]phenyl]-1,1,1,3,3,3-hexafluoropropane
	2-Naphthoic acid, 1-nitro-
	Imidazole-4-carboxylic acid, 2-fluoro-1-methoxymethyl-, ethyl ester
	4,25-Secoobscurinervan-4-one, O-acetyl-22-ethyl-15,16-dimethoxy-, (22.alpha.)-
	4-[4-Diethylamino-1-methylbutylamino]-1,2-dimethoxy-6-bromonaphthalene
	2,3-Dihydroindole-4-ol-2-one, 5,7-dibromo-3,3,-dimethyl-
Oxygen-containing compounds	Pregn-4-ene-3, 11, 20-trione, 6,17,21-tris[(trimethylsilyl)oxy]-, 3,20-bis(O-methyloxime), (6.beta.)-
	Phenylhydrazine, 5-chloro-2,4-dinitro-
Nitrogen-containing compounds	4,4-Ethylenedioxy-1-pentylamine
	4,5-Methylenedioxy-2-bromo-N- [1-methyl-4-diethylaminobutyl]aniline
	.alpha.-D-Glucopyranoside, methyl 2-(acetylamino)-2-deoxy-3-O-(trimethylsilyl)-, cyclic methylboronate
Oxygen- and sulfur-containing compounds	6-Chloro-2-oxo-7-(trifluoromethyl)[1,3]dithiolo[4,5-b]pyridin-5-yl dimethyl-(dithiocarbamate)
	1(H) Benzimidazole, 2-(1,3- benzodioxol-5-yl)-5-(thien-2-ylcarbonyl)-1-hydroxy-3-oxide



The volatile compounds were identified using the Pyrolysis method. The temperature of samples was gradually increased to a temperature of 160 °C and the gas was collected using solid phase micro extraction (SPME) injection and the highest probability of finding the compounds were classified into different classes.

### **Gas Chromatography Mass Spectroscopy results for synthetic rainwater**

Synthetic rainwater was prepared with a pH of 3, 4.5, 5.3, 7, 8, and 9. The samples were kept in a shaker for 24 hours and filtered. The leachate was separated using toluene solution to obtain the organic compounds into the solvent and analyzed using gas chromatography mass spectroscopy.

Figure 25 shows the Chromatogram of volatile compounds in pH 3 synthetic rainwater of Kyrock L. Figure 26, 27 and 28 shows the compounds that may come out in the pH 3.

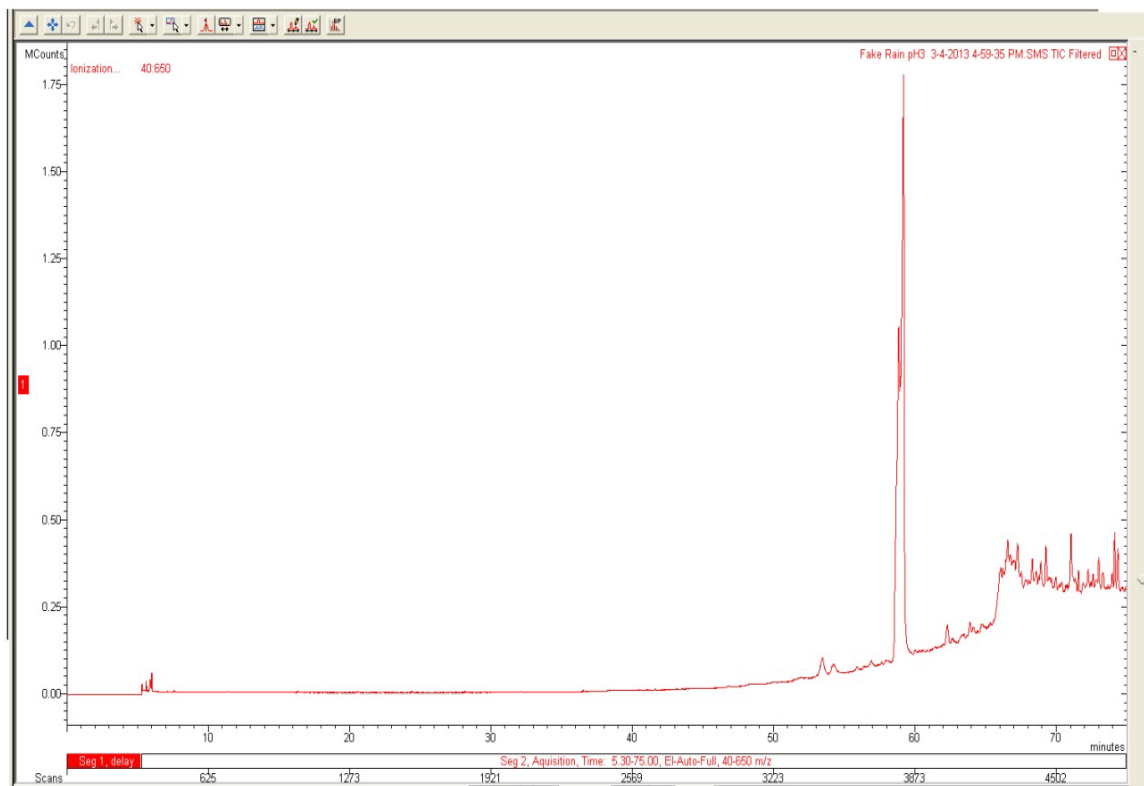


Figure 25: chromatogram of Kyrock L at pH 3

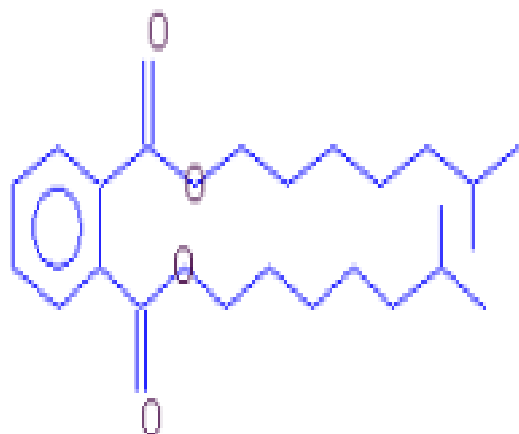


Figure 26: 1,2-benzenedicarboxylic acid, diisooctyl ester

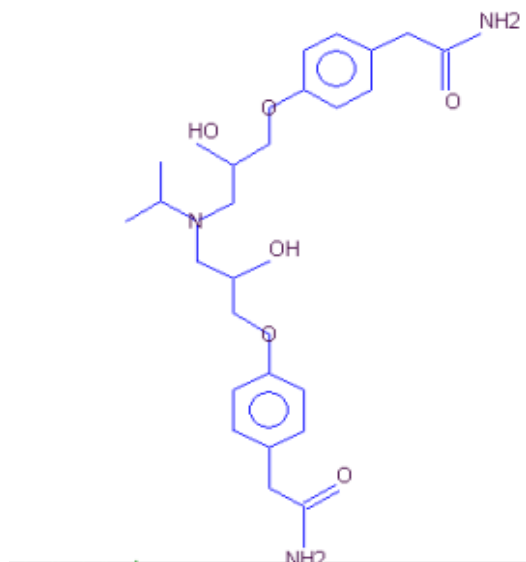


Figure 27: N,N-Di-(3-p-carbamoylmethylphenoxy-2-hydroxypropyl) isopropyl amine

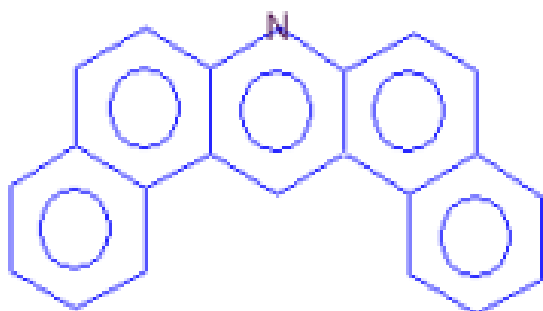


Figure 28: Dibenz[a,j] acridine

Figure 29 shows the chromatogram of volatile compounds in pH 3, synthetic rainwater of Kyrock. Figures 30 and 31 shows the compounds that leached at pH 3. Though various pH levels of synthetic rainwater were created Kyrock L treated for 24 hours, only pH 3 solution of synthetic rainwater was shown to leach volatile components. Kyrock R also only leached organic components at a acidic pH of 3.

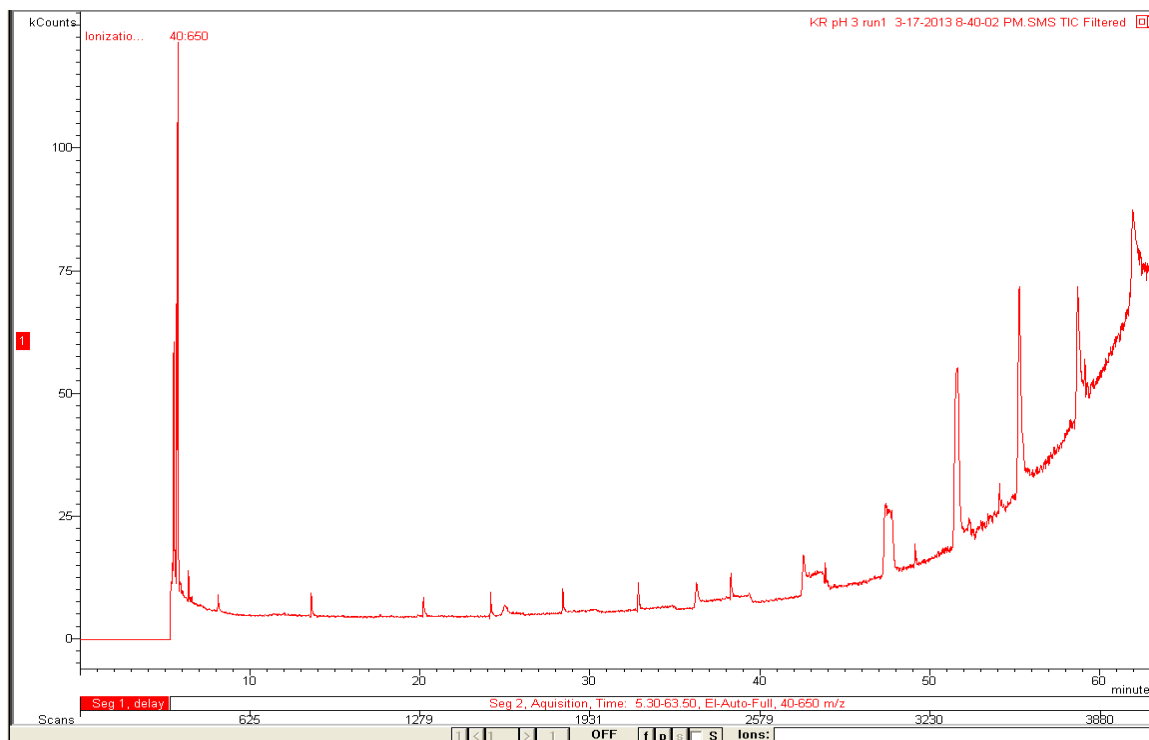


Figure 29: chromatogram of Kyrock R at pH 3

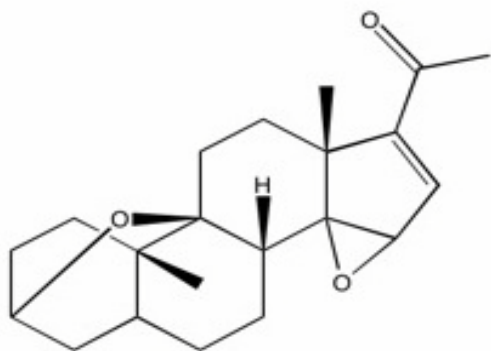


Figure 30: 3,9. Beta. 14,15-diepoxy pregn-16-en-20-one

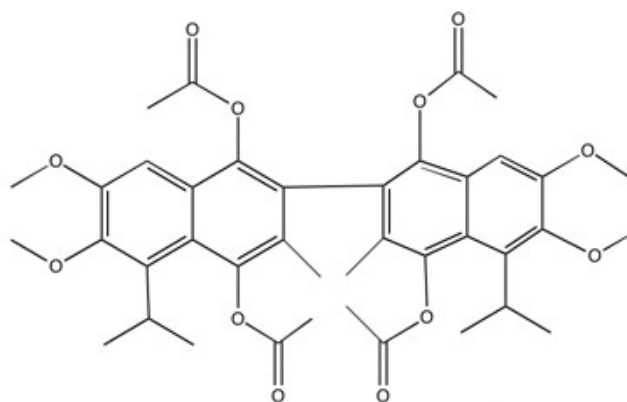


Figure 31: Acetic acid, 1,1', 4'-triaceetoxy-5, 5'-diisopropyl-6, 7,6', 7'-tetramethoxy - 3,3'-dimethyl-(2,2') binaphthaleneyl -4-yl ester

## CONCLUSIONS

Kyrocks or Kentucky rock is a name assigned to a form of natural asphalt in Kentucky. Due to its high non-skid property it is used as a road construction material. The amount of natural asphalt present in Kentucky was found to be 5-6 billion barrels of oil equivalent (BOE) and over one hundred thousand tons of natural asphalt is being mined every year. The asphalt is composed of aliphatic compounds, cyclic alkanes, aromatic hydrocarbons; polycyclic aromatic compounds (PAC's) along with various metals (e.g., iron, nickel, vanadium chromium), sulfur and nitrogen molecules. The leaching of these complex compounds into rainwater may cause adverse affects on the environment.

Kyrocks was characterized to have a thorough understanding of its properties. The surface property of the Kyrocks was evaluated with scanning electron microscope; the diversity in the amount of organic and inorganic content is clearly stated. The sample had diversity in the inorganic and organic content and is not uniform throughout the sample due to the varied concentration of the elements.

An acid digestion of the Kyrocks in concentrated sulfuric acid and hydrofluoric acid was then analyzed by inductively coupled plasma to clearly show the amount of various trace metal elements like cobalt, strontium, barium, titanium, iron, magnesium and sodium, along with traces of arsenic.

Pyrolysis of Kyrocks to a very high temperature produced many volatile compounds. Common volatile compounds were identified in the Kyrocks L and Kyrocks R such as 2,3-Dihydroindole-4-ol-2-one, 5,7-dibromo-3,3,-dimethyl, 2-Naphthoic acid, 1-

nitro Phenylhydrazine, 5-chloro-2,4-dinitro, alpha.-D-Glucopyranoside, methyl 2-(acetylamino)-2-deoxy-3-O-(trimethylsilyl)-, cyclic methylboronate  
6-Chloro-2-oxo-7-(trifluoromethyl)[1,3]dithiolo[4,5-b]pyridin-5-yl dimethyl-(dithiocarbamate).

The pH of runoff water is increased due to the presence of limestone in the soil layers in Kentucky. Kyrock is treated with a pH of 3, 4.5, 5.3, 7, 8, and 9 of synthetic rainwater to study the affect of pH on leaching of compounds. Volatile compounds were identified at a pH of 3 in both the Kyrock samples.

## PERSPECTIVE

Kyrocks is a name assigned to a form of natural asphalt in Kentucky. A thick, sticky, dark-brown mixture of petroleum tars used in paving, roofing, and waterproofing. It is a prized Class A material for road constructions. It is found in very large quantities in the Mammoth Cave region. We would like to characterize the Kyrocks and investigate if there are any chemical compounds that are coming out in synthetic rainwater.

In our proposed research we have successfully characterized the Kyrocks for the presence of organic and inorganic compounds. Synthetic rainwater was prepared and acidity of the solution was changed and the leaching of the compounds was studied. It was found that at very acidic conditions there were compounds leaching into the rainwater. These compounds can have a significant affect on the environment.

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