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Identification of Polycyclic Aromatic Hydrocarbon Anthracene in Beach Sand Extracted from Matagorda Island

Lawrence E. Monte

ABSTRACT

Using spectrophotometry, the presence of anthracene was detected in 10924.45 g of sand extracted from the beach on Matagorda Island, TX in March of 2001. The concentrations ranged from lowest to highest, 0.156 ug/L to 5.295 ug/L. The concentrations were calculated with a standard of anthracene ranging in concentration from 5 ppm, 2.5 ppm, 1.25 ppm, 0.625 ppm and 0.3125 ppm. The sand samples were separated into nine equal amounts into separate jars. Sodium sulfate was added, to remove excess water, and the samples were washed in dichloromethane for 24 hours on shaker at 3,000 rpm. They were filtered through a glass fritz after which the extraction was roto-vaped. The extraction was the redissolved in 100 mL of 75% methanol and 25% deionized water. To add the samples to the cuvette fro analysis, a syringe was used to avoid contamination from any large organic particles. A wavelength of 251 nm was used(100% absorption rate for anthracene). The absorption readings were then compared to the standard curve to determine concentration.

Keywords: *polycyclic aromatic hydrocarbons, anthracene*

INTRODUCTION

Originally inhabited by the Karankawa Indian tribe, Matagorda Island is a former United States Air Force Base used during World War II. The island now serves primarily as a tourist destination and nature preserve. Attractions and evidence of the historical significance of the island include trenches left over from the Civil War, a lighthouse and a now submerged Fort Esperanza (TPW). Unfortunately the island has fallen victim to modern pollution. To the general public, oil pollution in the Texas Gulf Coast Region has been a minor yet frequent problem. Coastal residents and tourists have witnessed the number of offshore oil-rigs increase and with them the amount of petroleum waste washing ashore.

Matagorda Island is a barrier island on the coast of Texas; it collects waste in the form of trash, much of which originates from offshore oil-rigs. Waste in the form of everyday trash, like light bulbs, hard hats, life vests, rope, and even miscellaneous buckets containing unknown chemicals. Most notably however, are the small frequent amounts of crude oil washing ashore as a result of leakage during transfer from rig to transport vessel.

The main objective of this research study is to bring awareness to the impact this is having on the environment. Illustrating this impact is detecting oil pollution in the beach sand. In order to accomplish this, an accurate method of the abstraction of crude oil was developed and tested for a common hydrocarbon, anthracene.

The target hydrocarbon, anthracene, Fig. 1, is a known carcinogen (Agency for Toxic Substances and Disease registry, 1999) and known to be present in crude oil (Heath, Kobli, Shawn). Anthracene was chosen because it is a three ringed hydrocarbon with a molecular weight of 188 (Wang, Yu and Bartha, pg. 2). A large mass makes it less susceptible to bioremediation. Also, anthracene is readily available and the price falls within budget restraints. This made it more convenient to make a standard, or control.

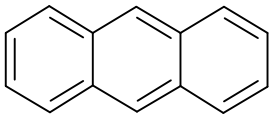

Figure 1. Anthracene

Detecting the presence of anthracene requires the employment of an extraction method as well as a method to determine if anthracene is present in the extracted contaminants. In order to extract the contaminants, a shaking method was done. Also, information on the shaking method was provided by Dr. Karrie Rathbone. The extraction requires a solvent, dichloromethane. This solvent was chosen from the research of Wang, Yu and Bartha (Wang, Yu, Bartha, pg. 2). To detect the presence of anthracene in the extracted contaminants I used a UV variable wavelength spectrophotometer.

MATERIALS AND METHODS

The first step was to extract samples of sand from the beach on Matagorda Island. This was done on March 29th of 2001. A grid was set up overlapping the high tide and low tide mark. The grid measured 20m x 20m and had a marker every 5m around the perimeter and at each corresponding axis on the inside of the grid. A sample of approximately 35g was taken from the surface at each 5m marker and stored in quorpak glass

jar with a foil lined lid. The samples were packed in ice and transported back to McPherson College three days later and stored in a freezer.

A procedure for shaking soil was used as an outline for the extraction of the sand. The procedure was obtained from work conducted at Kansas State University by Dr. Karrie Rathbone. (Karrie Rathbone, Ph.D.) Modifications were made to the shaking procedure to target the sand. Ten grams of sodium sulfate was added to each jar to remove the excessive water in the sand and all jars were shaken for the same amount of time, 24 hours. Dichloromethane was used as a solvent because it is a known solvent for hydrocarbons (Wang, Yu, Bartha). Each sample was divided into nine equal samples and added to a Qorpak jar. Five grams of sodium sulfate was added to each to remove extra water that might impede the hydrophobic shaking extraction. Each jar was topped with a foil lined lid and labeled 1-9. The jars were on the shaker for 24 hours at 3000 rpm, for maximum swirling motion. At the end of the 24 hour period the samples were filtered through a glass fritz to avoid sand contamination.

2. Standard curve

A standard curve was created by creating a solution containing 75% methanol, 25% deionized water and 5ppm anthracene as a stock solution different concentrations were created as follows. 5 ppm, 2.5 ppm, 1.25 ppm, 0.625 ppm, 0.3125 ppm, 0.0 ppm. Methanol was used because it does not evaporate as quickly as dichloromethane and it is a suitable solvent for spectrophotometry.

Each different concentration was run at the same wavelength, 251 nm as anthracene records a 100% absorption rate at that wavelength. Absorption measurements are recorded in Table 1. The absorption measurements were then used to create a standard curve, Figure 1. Quartz cuvettes were used because of their resillancy to strong organic solvents.

3. Preapring samples

The samples were prepared by roto-evaporation to remove the dichlorolmethane solvent and then resuspended in the same solvent solution as used for the standard; 75% methanol, 25% deionized water. The flask was tared prior to roto-vaping and yeilded different weights each time. 1.48 g, 1.32, and 0.38 thus indicating an extraction of material.

Running the samples under the same conditions as the standard was the next goal. The samples contained organic material. This variable was to be considered as it absorbs at different wavelengths. Thus in order to filter the extractions once more, a syringe with a small bore was used to fill the cuvette with the extraction for the spectrophotometric analysis.

RESULTS

Figure 2 and Table 1 illustrate the standard curve created with the known concentrations of anthracene in dissolved in 75% methanol/ 25% deionized(dei) water. The concentrations are in units of ug/L. The standard curve has a correlation coefficient of 0.9922.

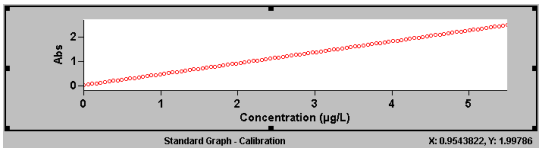

Figure 2. Standard Curve

Table 1. Standard Curve

Standard	Concentration ug/L	Mean	SD	Reading
				0.0002
				0.0003
Std 1	0.0000	0.000	0.0001	0.0004
				0.1457
				0.1458
Std 2	0.3125	0.1457	0.0001	0.1456
				0.2940
				0.2934
Std 3	0.6250	0.2939	0.0005	0.2944
				0.5964
				0.5945
Std 4	1.25	0.5945	0.0002	0.5943
				1.1870
				1.1868
Std 5	2.5	1.1870	0.0002	1.1872
				2.2488
				2.2530
Std 6	5.0	2.2525	0.0034	2.2556

This standard curve served as a comparison for the extractions illustrated in Table 2.

Table 2. Analysis

Collection time 4/7/04 2:39:22 PM

Sample	Concentration µg/L	F	Mean	SD	%RSD	Readings
Sample 1						0.1564
						0.1565
	0.3106		0.1565	0.0001	0.060	0.1566
Sample 2						0.1600
						0.1600
	0.3183		0.1600	0.0001	0.09	0.1598
Sample 3						0.1599
						0.1599
	0.3183		0.1599	0.0001	0.07	0.1601
Sample 4						0.3373
						0.3373
	0.7109		0.3374	0.0001	0.04	0.3375
Sample 5						0.3399
						0.3398
	0.7162		0.3398	0.0001	0.04	0.3396
Sample 6						0.3417
						0.3416
	0.7205		0.3417	0.0001	0.03	0.3418
Sample 7						2.3581
						2.3625
	5.1900		2.3611	0.0026	0.11	2.3628
Sample 8						2.4076
						2.4100
	5.2887		2.4057	0.0056	0.23	2.3993

Sample 9					2.4137
					2.4035
	5.2958	2.4089	0.0052	0.21	2.4096
Sample 10					0.0892
					0.0892
	0.1616	0.0892	0.0000	0.02	0.0892
Sample 11					0.0903
					0.0905
	0.1644	0.0905	0.0001	0.11	0.0905
Sample 12					0.0905
					0.0905
	0.1646	0.0905	0.0000	0.03	0.0906
Sample 13					0.2662
					0.2661
	0.5533	0.2662	0.0001	0.03	0.2662
Sample 14					0.2743
					0.2739
	0.5713	0.2743	0.0003	0.13	0.2746
Sample 15					0.2733
					0.2731
	0.5689	0.2732	0.0001	0.04	0.2731

DISCUSSION

The results of the samples run suggest the presence of anthracene and warrant further investigation. Further research would employ the use of more sophisticated detection equipment while still utilizing the same extraction technique. One goal of this project was to develop an extraction method, displayed by consistent results in the readouts. Also, illustrated is the possible presence of anthracene in the surface layer of the sand. And indicator of the short time that particular sand had been cycled on to the beach. This provides a clue on the bioremediation activity. Once oil is released into the environment it is susceptible photochemical reactions, evaporation, ingestion by marine life, being deposited in the sea bed and biochemical oxidation(Petrakis, Weiss). Further research would also investigate the contamination at different levels in the soil as well as different regions in the tidal zone. This wold provide clues as to the levels of bioremediation as well as the cycling due to the ebb and flow of the tide and surf activity.

Variables that could have possibly impeded the accuracy of the readings was microorganism and other small particles that could have made it throught the filtration proceess. Also, some sand particles may have been small enough to pass through the glass fritz. The presence of this material could possibly affect the abosrbancy readings.

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