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Ginger Marie Kimble
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REACTIONS OF IODINE AND IODATE WITH SPHAGNUM
PEAT:AN EXAMINATION OF KINETICS
AND pH DEPENDENCE

by

Ginger Marie Kimble

Bachelor of Science in Multidisciplinary Science
Texas Tech University
1997

A thesis submitted in partial fulfillment
of the requirements for the

Master of Science Degree in Chemistry
Department of Chemistry
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Graduate College
University of Nevada, Las Vegas
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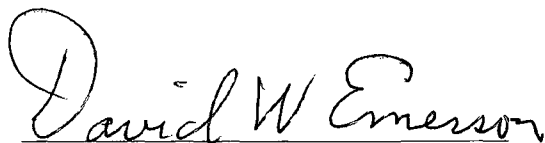
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Examination of Kinetics and pH Dependence

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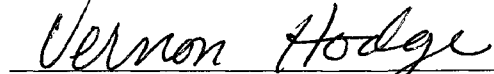
Master of Science in Chemistry


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ABSTRACT

Reactions of Iodine and Iodate with Sphagnum Peat: An Examination of Kinetics and pH Dependence

by

Ginger Marie Kimble

Dr. Spencer Steinberg Examination Committee Chair
Professor of Chemistry
University of Nevada, Las Vegas

Storage of spent nuclear waste is an environmental and industrial concern that must be addressed. Iodine -129, a by-product of nuclear waste reprocessing, has a strong environmental presence with a half live of 15.7 million years. Radioactive iodine is currently immobilized by carbon-containing materials and silver impregnated materials. In this research, sphagnum peat was examined as a material to sequester iodine. Several analytical methods were used to determine the ability of sphagnum peat to sequester iodine. The kinetics of the reaction between sphagnum peat and iodine were also examined.

Solid phase microextraction was used to determine the peat's ability to retain volatile and slightly volatile iodinated compounds. A carboxen/PDMS fiber was a more suitable fiber for the analysis compared to a PDMS and Carbowax-DVB fiber. Diiodomethane, methyl iodide, iodoethene, chloriodimethane, triiodomethane were detected in trace quantities for a sample that had a 15 hour carboxen/PDMS fiber equilibration time in a $\text{Ca}(\text{OH})_2$ matrix.

The reaction of iodine with sphagnum peat was dependent on pH. At pH 4.7, 100% of the iodine was substituted on the phenolic ring compounds in the peat. At pH 5.8 the 66% of the iodine underwent ring substitution, and 60% at pH 8. At pH 10, the reaction kinetics was too fast to examine by the method used.

The reaction of iodate with peat was also controlled by pH. The rate constant k , for the reaction decreased as pH increased.

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I was surrounded by a great group of people and I thank all of them with the utmost sincerity.

CHAPTER 1

INTRODUCTION

Background

Nuclear waste disposal has been an issue of concern for the nuclear industry. Waste reprocessing is difficult, expensive, and time consuming. Long term storage also involves careful design of containment so there is minimal chance of leakage into the environment. The fission products of uranium have very long half-lives and can remain in a radioactive form for millions of years.

Radioactive iodine was discovered by Glen T Seaborg and John Livingood in the late 1930s. Two radioactive isotopes associated with spent nuclear fuel and emissions released during weapons testing are Iodine-129 and Iodine-131. Iodine-131 has a short half life of just eight days, while Iodine-129 has a much longer half life of 15.7 million years (www.epa.gov/rpdweb00/radionuclides/iodine).

Iodine is a biologically important element to the mammalian body and ensures proper functioning of the thyroid gland. Radioactive isotopes of iodine behave similar to the stable form of iodine. Iodine, in both a non-radioactive and radioactive form, can be metabolized by the thyroid gland. In Belarus, Russia, and the Ukraine, areas where the radioactive fallout was greatest from the Chernobyl accident, increased cases of thyroid cancer were linked to the exposure of I-131. Large doses of radioactive iodine have been linked to possible cases of thyroid cancer (Zvonova, 2004).

Iodine-129 is of concern to the Environmental Protection Agency (EPA), and was considered when standards for exposure were developed for the nuclear waste repository at Yucca Mountain (www.epa.gov/rpdweb00/radionuclides/iodine).

Although a small portion of iodine-129 was released into the environment from detonation of nuclear weapons, the greatest quantity of the iodine-129 was and continues to be released from nuclear fuel reprocessing plants in Europe.

Radioactive iodine can be released in both the dissolved and gaseous form. It, along with other radionuclides, can be released from defective or aged fuel rods into the surrounding cooling water. A large majority of iodine -129 is still contained in spent nuclear fuel. (Michel et al 2003). A study done of the West Valley reprocessing facility in New York indicated a strong presence of iodine-129 in a drainage creek twenty years after closure (Usha et al). If not properly contained, this radioactive isotope will eventually migrate into the environment where it will impact food crops, ground water, and animal populations.

Radioactive iodine is also released when the spent fuel rods are reprocessed using the UREX and PUREX processes (Choppin & Morgenstern , 2000). These processes involve the extraction of radioactive uranium (UREX) or plutonium/uranium (PUREX) into an organic solvent tributylphosphate. During this process I-129 is mostly released as HI and I₂. The radioactive iodine is released in the dissolver off gas. If not trapped at this stage, the iodine can become a fugitive emission.

Ideally, the radioactive iodine should be trapped in a stable matrix, where it can be immobilized until it can be transmuted into non-radioactive form. Many matrixes where

investigated for the sequestration of radioactive iodine. The ability of silver to react with iodine makes it a popular material for removal of radioiodine from the dissolver off gas. Mineo et al., (2002) examined the use of silica gel impregnated with silver nitrate. This involves a reaction of iodine with silver nitrate. They also developed a mathematical model to predict the amount of iodine that could be adsorbed by the material. The silver nitrate impregnated silica gel is currently being used for the dissolver off gas in Karlsruhe reprocessing plant. Takeshita and Nakano (2001) examined the use of silver impregnated styrene-co-divinylbenzene and developed a breakthrough curve for that material.

Carbonaceous materials are also used for the removal of radioiodine. Ampelogova et al., (2002) examined the use of a carbon fiber busofite type material. They compared this type of carbon fiber material to SKT-3 activated carbon. This approach also considered the sequestration of organic iodine, in the form of methyl iodide, as well as elemental iodine. The efficiency of adsorption was increased when the carbon fiber busofite material was impregnated with potassium iodide, triethylene diamine, or silver nitrate.

Hoskins et al., (2002) examined silver impregnated activated carbon for the sequestration of iodide. They determined that the amount of iodide removed from solution was dependent upon the silver loading on the carbon, the iodide concentration and also pH.

Molecular sieves have also been used to adsorb radioactive iodine. The company C*Chem manufactures an Ionex-type silver exchanged molecular sieve. These materials have a longer life when compared to activated silver impregnated carbon and they can be reused. The molecular sieves are silver loaded zeolites that react with airborne iodine to produce silver iodide. The solid is trapped in the matrix of the zeolite. These molecular

sieves can become less efficient by contaminants that can affect the structure of the zeolite and hinder the efficiency of iodine absorption.

(www.cchem.com/zeolite/techdata.htm)

Sphagnum Peat

Sphagnum peat is relatively inexpensive and available at any local hardware store or nursery. Sphagnum peat is rich in organic compounds that can react with iodine. Sphagnum peat can be compared to peaty soils and humic material, which also contain large amounts of phenolic organic compounds that can react with iodine by way of aromatic substitution.

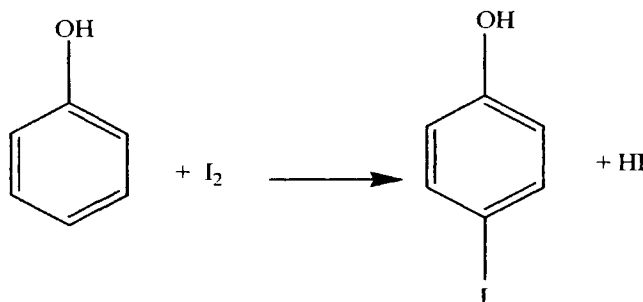


Figure 1: Reaction of phenolic ring with iodine.

Iodine substitution is pH dependent. In this study, several kinetic experiments were done to determine the rate of reaction for iodine and peat at several different pHs. Model compounds including vanillin and acetovanillone were also examined. These have phenolic functional groups similar to those found in natural organic matter.

Substances found in peaty soils impact iodine retention. Bostock et. al., (2003) demonstrated that the sorption of iodine to humic substances in coniferous and grassland

soils reduced the partitioning of the iodine into the atmosphere. A link to microbes was also suggested due to the results of a freezing experiment, which retarded the sorption of iodine in the soil.

In a study of Chernobyl soil by Hou et al.,(2003) it was determined that 70% of all the detected I-129 was bound to oxides and organic matter with the highest content of I-129 being in a peat type soil, which is rich in organic components. In a study of two Chilean peat bogs by Biester et al.,(2004) it was determined that iodine had the highest retention on peaty soil when compared to other halogens. Iodine formed a stable organoiodine compound in the soils through the interaction with the humic substances.

Keppler et al., (2004) did a study on the organoiodide formation in peatlands. They stated that once bound within the peat, organoiodide can be stable for years and that the peatlands are a major reservoir for iodine. In particular, the humic substance plays an important role in iodine fixation onto soils (Keppler et al., 2004).

A study by Whitehead et al., (1973) indicated that the sorption of iodine in soils depended on the organic content as well as the metal oxide content. Whitehead also showed that at a higher pH the organic matter is mainly responsible for the sorption while at a lower pH the oxides played a larger role. He tested soils at temperature ranges of 10-35 °C, and discovered that the temperature change made only a small difference.

I-129 has chemical properties that are similar to the stable I-127. Iodine exists primarily in the oxidation states of -1 and 5 (I^- and IO_3^-).

Purpose of the Study

The sorption and reaction of iodine on sphagnum peat is dependent on factors such as pH and temperature. The purpose of this research is to examine several factors, such as temperature and pH, which influence the sorption of iodine onto sphagnum peat.

This research investigates the use of natural organic matter in the form of sphagnum peat, as a material for use of sequestration of radioactive iodine. It was done to examine a possible alternative to impregnated carbonaceous and impregnated silica gel material that are currently being used to sequester iodine.

CHAPTER 2

MATERIALS AND METHODS

Instrumentation

Measurements for Organic Iodinated Compounds

A Varian Saturn III 3400 GC/MS equipped with DB5 Supelco column was used to measure organic iodinated compounds. This will be referred to in later test as GC/MS system 1. The solid peat samples were analyzed on a Varian Saturn III 3400 GC/MS equipped with an Equity 5 column that was interfaced with a Pyroprobe 2000 from CDS Analytical. The pyroprobe was connected to the GC/MS using a CDS 1500 valved interface. This will be referred to in later text as GC/MS system 2.

Iodide and Iodate Measurements

Iodide and Iodate measurements were performed on a Dionex Ion Chromatograph consisting of an Alltech Novosep A-1 anion exchange resin column, a Milton Roy Conducto Monitor II set to a range of 1.0 and a response of 5 μ s, and a Dionex gradient pump. The flow was set to 1.0 mL/minute and the pressure was approximately 1500 psi. The carrier solvent was 0.05 M Na_2CO_3 . A Dionex ASRS ultra 4mm suppressor and Dionex SRS controller were also used for electrochemical solvent conductivity suppression. The sample acquisition rate was set to 1 Hz. The data was acquired with SRI Peak II software running on an IBM PC.

Iodide Measurements

A Cole-Parmer iodide selective electrode model 27504-18 LL2 was connected to a Lamotte DHA 3000 digital mV meter to measure iodide concentration.

Iodine Measurements

A Lamotte Smart Colorimeter was used to determine iodine concentration of saturated iodine stock solutions. A blank was prepared with 0.100 mL of saturated iodine solution and 9.900 mL of water. The blank was placed in the colorimeter and read as a blank. The sample was prepared by adding 0.100 mL of iodine solution, 9.900 mL of water, and a Lamotte DPD-1 tablet provided by the manufacturer. The tablet was crushed, and the solution was agitated for 20 seconds until the tablet dissolved. The solution was placed in the colorimeter. To obtain the reported value in ppm, the actual instrument value was multiplied by 100 to correct for sample dilution.

Calibration of Iodide

To achieve an iodide concentration of 0.1000 M, 1.6519 ± 0.0001 g of KI was added to a 100 mL volumetric flask and then filled to volume with nanopure water. Calibration solutions of the following concentrations were prepared in 100 mL volumetric flasks by dilution of the stock solution: 1.000×10^{-3} M, 1.000×10^{-4} M, 5.000×10^{-5} M, 1.000×10^{-5} M. Each calibration standard, as well as a blank, was run on the ion chromatograph. The peak area was integrated using Peak II Simple software. The area was plotted against the concentration to obtain a calibration curve. A linear regression of 0.95 or higher was deemed acceptable.

Calibration of Iodate

A stock solution of 5.710×10^{-3} M iodate was prepared by adding 1.2228 ± 0.00001 g of KIO_3 in a 1000 mL volumetric flask. The flask was filled to volume with nanopure water. Solutions of 2.857×10^{-3} M, 1.429×10^{-3} M, and 5.710×10^{-4} M were prepared as calibration solutions from the stock solution in 10 mL flasks. The calibration standards, as well as a blank of nanopure water, were run on the ion chromatograph. The peak area was integrated using Peak II Simple software. The area was plotted against the concentration to obtain a calibration curve. A linear regression of 0.95 or higher was deemed acceptable.

Quality Assurance of Ion Chromatography Measurements

Once acceptable calibrations were obtained the samples were analyzed. Check standards for both iodide and iodate were run before every set of samples. If the check standard was varied more than 10%, a new calibration was performed before running samples. The peak area for iodide and/or iodate was integrated using Peak Simple II software. The concentration of iodide and/or iodate was determined using a current calibration curve.

Solutions

Saturated Iodine Solution

Approximately 0.5 g of solid iodine crystals were added to 1 L of nanopure water. The solution was sonicated for several hours and allowed to stand overnight. This solution was used and routinely monitored for iodine concentration by the colorimetric method before each use.

Vanillin, Acetovanillone, Tannic Acid, Lignin, and Gallic acid solutions

Phenolic model compound solutions were prepared in nanopure water with reagents purchased from Sigma-Aldrich.

Iodide, Iodate, and Buffer Solutions

Solutions were prepared in nanopure water at appropriate concentrations with reagents purchased from Fisher Scientific.

SPME

Solid phase microextraction (SPME) incorporates a thin fused silica fiber to concentrate volatiles from the headspace or the liquid in a sample vial. The fiber can be inserted into the headspace of a vial or dipped directly into the liquid sample. The fused silica fibers are coated with a polymer that allows the absorption of certain analytes. The fiber can be directly inserted into the GC inlet to desorb the concentrated analyte. This method can be used quantitatively by a calibration with known standard concentrations (Wercinski, 1999). An SPME procedure was employed to examine the release of volatiles when iodine and sphagnum peat were combined. The rationale for this method was to use SPME as a qualitative tool for detecting volatile iodinated compounds in the headspace of a vial containing sphagnum peat and iodine. If the sphagnum peat sufficiently sequesters iodine, then minimal amounts of iodinated volatiles will be detected in the headspace by the SPME fiber.

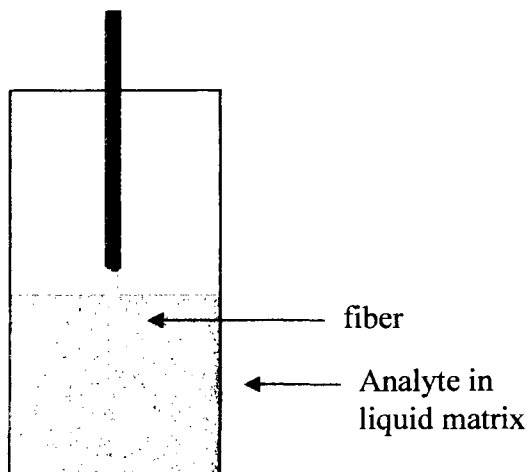


Figure 2: SPME sketch with the fiber in the liquid phase.

The fiber may also be inserted above the liquid to detect volatile compounds that partition into the headspace. In this research, the headspace method was used for the detection of volatile iodinated compounds.

Cancho et al., (1999) used SPME to examine iodinated trihalomethanes in drinking water. They discovered that headspace SPME had several benefits over direct liquid SPME. The fiber had a shorter equilibrium time in the vapor phase as opposed to the liquid phase. The lifetime of the fiber was extended in the vapor phase. Several different fibers were tested and the Carbowax divinylbenzene proved to be the most suitable for their analysis. A polydimethylsiloxane (PDMS) and carboxen-polydimethylsiloxane (CAR-PDMS) fibers were also tested, although these were not as sensitive as the Carbowax divinylbenzene. The detection limit achieved was in the ppb range.

Wuillod et al., (2003) used SPME to detect iodophenol species in water. Three different fibers were tested, CAR-PDMS, PDMS, and polyacrylate(PA). It was determined that the CAR-PDMS had a better extraction efficiency than the other two

fibers. It was also determined that the equilibrium time for the fiber and iodinated phenols was around thirty minutes. The effects of salt were also examined, and a 1M NaCl concentration was optimal. A low detection limit in the ppb range was also achieved in this study. These two studies provided some useful information for developing the method for the detection of any volatile iodinated compounds that may form when peat reacts with iodine.

Fiber selection is important to successfully complete SPME. In general, the fibers have an affinity for either polar or non-polar compounds. Analyte polarity can be used as a guide in fiber selection but other factors also need to be considered when selecting a fiber, such as the analyte volatility and the matrix of the sample (Wercinski, 1999).

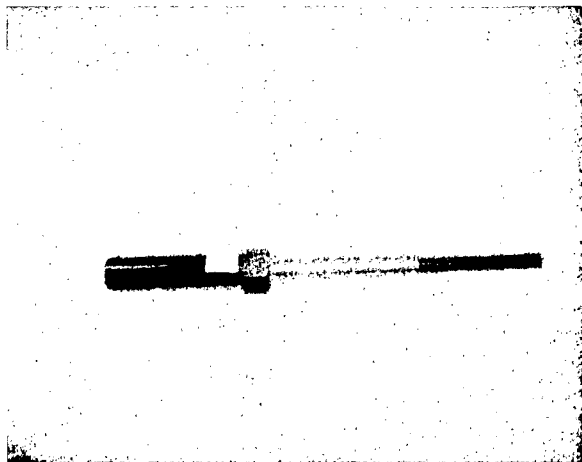


Figure 3: An actual SPME apparatus

For the SPME experiments several different fibers were tested. The carboxen-polydimethylsiloxane (CAR-PDMS) 85 μ M stable flex fiber was the first fiber tested for the detection of iodoform. This compound was chosen because it is an iodinated compound that could be detected in the vapor phase. Iodoform is a product of the

haloform reaction. If there are any methyl ketone groups present in the sphagnum peat, then iodoform could be formed and released into the headspace of the vial. If the iodine is sufficiently trapped in the matrix of the sphagnum peat, no volatile iodinated compounds should be detected.

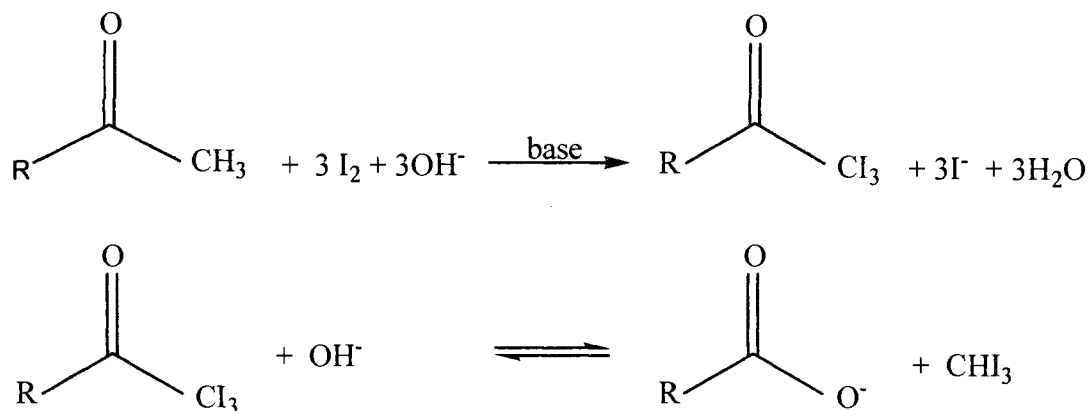


Figure 4: Haloform reaction with iodoform as a product.

Cancho et. al., (1999) also found that iodinated trihalomethanes could be detected in the ppb range. The fiber chosen is suitable for trace level analysis of volatiles. The CAR-PDMS is a polymer coating that is partially bonded to a flexible fused silica core. The structure of carboxen makes it unique. It had a pore structure that has an even distribution of pore sizes and has a high percentage of pores. This makes it suitable for trapping some smaller analytes (Wercinski, 1999). The fiber was conditioned by inserting the fiber into the GC inlet that was held at a constant temperature of 280° C. The fiber was allowed to remain in the inlet for 45 minutes. A 100 µm polydimethylsiloxane (PDMS) fiber was also used. This fiber consists of a fused silica core. It is then coated with the PDMS

polymer which is nonpolar. It contains no crosslinking agents that attach it to the fused silica core and is therefore termed a non-bonded fiber.

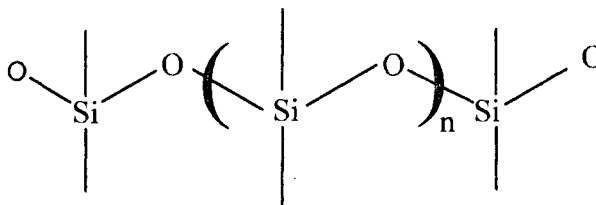


Figure 5: Polydimethylsiloxane polymer.

The PDMS fiber was conditioned before use for 1 hour at 250° C.

Procedure

Iodoform was chosen to monitor for the release of iodinated volatiles.

A calibration was performed with iodoform standard. A stock standard of 1026 ppm was prepared in methanol. This was diluted to 102.6 ppm. A 1.0M NaHCO₃ buffer was prepared by adding 84.009 g of solid NaHCO₃ to 1000 milliliters of nanopure water.

To prepare the standards for the calibration, 12.5 mL of nanopure water and 12.5 mL of bicarbonate were added to a 65 mL headspace vial. Iodoform standard was added to achieve 4.1, 20.5, and 41 ppb. A stir bar was inserted and the vials. They were sealed and crimped and put into a circulating bath which was held at 25° C. The iodoform mixture was stirred at a speed of 300 rpm on a VWR stirrer. The CAR-PDMS fiber was inserted into the headspace of the vial for 10 minutes. Before inserting the fiber into the GC/MS, liquid nitrogen was used to freeze a six cm section of the column to cryofocus analytes.

A 6 cm section of the column taken about 25 cm from the inlet was placed in the styrofoam cup filled with liquid nitrogen. The fiber was then taken out and inserted into the GC/MS injection port. The fiber was allowed to desorb for 5 minutes at 270° C. The GC/MS program was started when the fiber was inserted. The GC oven remained off. At the end of the desorption time, the fiber was removed and the liquid nitrogen was removed from the column. The GC oven was turned on and the temperature program was initiated.

The oven was held at 40° C for 5.40 minutes, then increased to 220° C at 10° C /minute for 18 minutes and held at 220° C for 5 minutes. The MS was set to the EI ion mode with a five minute filament delay and a scan time of 0.500 seconds for the first 10 minutes and then changed to 1.000 second scans for the remaining 18.40 minutes.

The 142 (m/e) ion was integrated using the peak integrator in the Saturn software. The 127 (m/e) ion was also monitored for confirmation.

Once a successful calibration was achieved (linear regression of 0.95 or better) the samples were run. Samples were prepared by adding peat and iodine to a 65 mL headspace vial. Several different matrices were used as well as different desorption times. Two different buffer systems were tested, one with NaHCO₃ and the other with Ca(OH)₂. A previous study done by Schmett, 2004, showed that a 70% peat/ 30% Ca(OH)₂ mixture made an optimal trap for iodine in the vapor phase (Schmett 2004). For the first study sphagnum peat was spiked with a saturated iodine solution. This was done in a buffer solution of Ca(OH)₂ or NaHCO₃. The mixture was then allowed to stir from anywhere from 10 minutes to 2 hours in a circulating bath held at 25° C. An extraction was done with the CAR/PDMS fiber for 10 minutes. The fiber was then desorbed into the GC inlet.

For samples with NaHCO_3 $0.5000 \text{ g} \pm 0.0010 \text{ g}$ of sphagnum peat was added to a 65 mL glass headspace vial. Saturated iodine solution, 1 mL, was added to the peat along with 25 mL of 1.0 M NaHCO_3 solution. A stir bar was inserted and the vial was sealed with a crimp top. This resulted in an initial amount of 270 μg of Iodine and 500 mg of peat in 25 mL of solution or 0.001 % iodine and 2.00 % peat. The mixture was allowed to stir at a speed of 300 rpm in a circulating bath kept at 25° C. Several samples were prepared so that different incubation times could be tested. Incubation times ranged from 0 minutes to 2 hours. After the set amount of stir time, the CAR/PDMS fiber was inserted into the headspace for 10 minute equilibration. After 10 minutes, the fiber was withdrawn in desorbed into the GC inlet for 5 minutes. The GC/MS analysis program was identical to the calibration procedure.

For the samples with the $\text{Ca}(\text{OH})_2$ buffer system, approximately $0.5000 \text{ g} \pm 0.0010 \text{ g}$ of peat were added to a 65 mL headspace vial. $\text{Ca}(\text{OH})_2$, 0.2100g, was added to the peat (a 70 %/ 30 % mixture of peat to $\text{Ca}(\text{OH})_2$). The mixture was swirled to coat the peat with $\text{Ca}(\text{OH})_2$. Saturated iodine solution, 1 mL which ranged from 250-300 ppm, was added to the peat / $\text{Ca}(\text{OH})_2$ mixture. Nanopure water, 25 mL, was added along with a stir bar. This resulted in 270 μg of iodine and 500 mg of peat in 25 mL of solution, or 0.001 % iodine and 2.00 % peat. The samples were analyzed by the same method as the NaHCO_3 samples as described above.

Similar analyses were done varying the following factors: fiber, iodine concentration, peat concentration, and fiber equilibration time. Three fibers were tested PDMS, Carboxen/PDMS and CW-DVB. Peat amounts ranged from about 19-28 mg/mL. The equilibration times tested included 10 min, 30 min, 1 hr, 2 hr, 10 hr, 13 hr, and 15 hr.

Fractionation of Iodine Reacted Peat

Saturated iodine solution was added directly to a suspension of sphagnum peat. The reaction of iodine with peat was studied at several different pH values. The iodine, in the form of iodine, iodide, and organic iodides, was recovered from the peat in several different steps. The purpose of this fractionation procedure was to elucidate the fate of iodine in peat and to ascertain the capacity of the peat to retain the iodine during several different types of leaching processes.

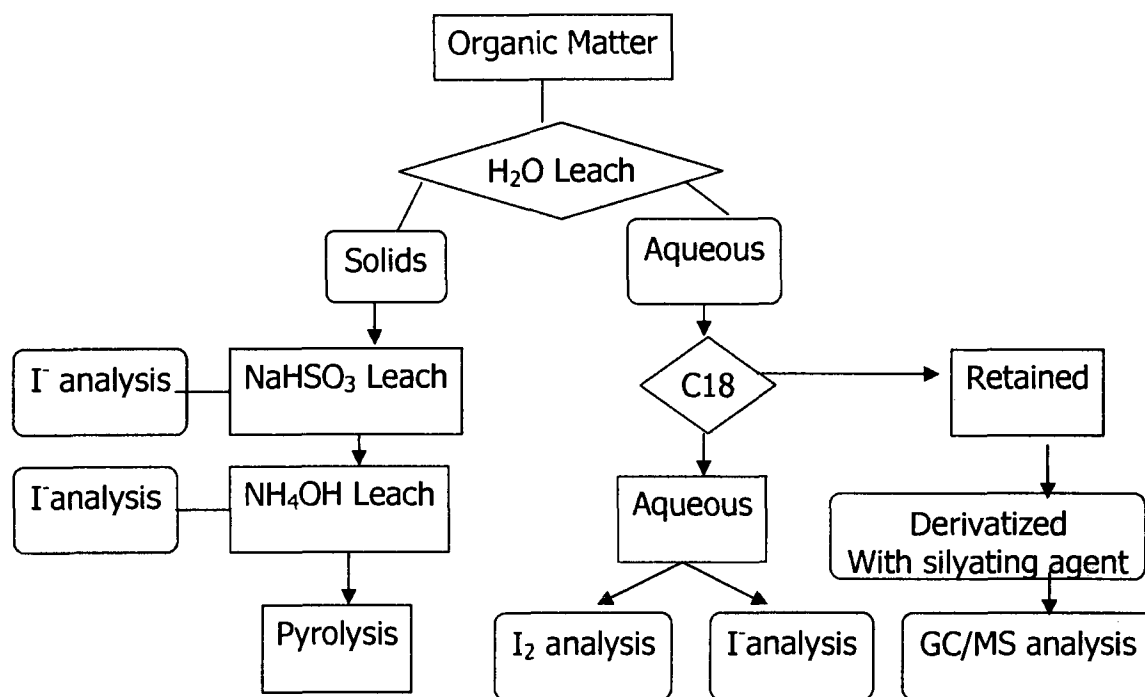


Figure 6: Flow chart of Fractionation Procedure

Sphagnum peat, $0.7000 \text{ g} \pm 0.0015 \text{ g}$, was placed in a 125 mL Erlenmeyer flask. Buffer, 6 mL of KH_2PO_4 adjusted to pH 6 or KH_2PO_4 buffer, was then added to the peat. For the sample at approximately pH 10, 0.3 g of solid $\text{Ca}(\text{OH})_2$ was added to

0.7000 g \pm 0.0015 g of sphagnum peat. The 70 % peat/ 30 % buffer mixture was chosen based on the results from Schmett, 2004. His results showed that this mixture optimal for trapping iodine vapor. Saturated iodine solution (6 mL of 250 ± 50 ppm) was prepared with nanopure water and then added to the peat mixtures. The mixtures were swirled and covered with parafilm for 48 hours. The liquid was filtered off by vacuum filtration and was tested for iodine and iodide by the colorimetric method and the ion selective electrode respectively. The solid peat was then placed in a test tube and covered with 15 mL of water. The pH 10 sample was neutralized to pH 7 with 466 μ L of glacial acetic acid. The water leached peat sat overnight. The water was filtered off of the peat samples by vacuum filtration and an additional 10 mL of water was added to rinse the peat from the test tube. The water samples were stored in the freezer until the solid phase extraction could be done with a C18 cartridge.

The peat sample was again placed in a test and covered with 10 mL 0.1 M sodium bisulfite. It was leached overnight. The sodium bisulfite was removed from the peat by vacuum filtration. An additional 10 mL of water was added to aid in the transfer. The iodide concentration of the filtrate was measured.

The peat was again placed in a test tube and this time covered with 10 mL of 0.1 M NH_4OH and left to leach overnight. The NH_4OH was filtered off by vacuum filtration and an additional 10 mL of water was added to aid in the filtration. The iodide concentration of the filtrate was tested with the ion selective electrode. The peat was left to dry in the vacuum desiccator.

Once the peat was dried, pyrolysis was performed in order to measure the amount of methyl iodide produced by the sample. Dilution with glass beads was not required. The pyrolysis method is described in chapter 5.

The original aqueous samples that were stored in the freezer were taken out of the freezer and thawed to room temperature. A J.T. Baker Bakerbond C18 cartridge was set up with a vacuum apparatus. The cartridge was rinsed with 2 mL of methanol followed by 2 mL of nanopure water. The water samples were run then run through the cartridge. The aqueous portion, a total of 25 mL, was tested for iodide using the ion selective electrode method. The retained fraction on the cartridge was eluted with 10 mL of methanol. It was evaporated using a rotary evaporator and blown dry with nitrogen. 25 μ L of BSTFA, N,O-bis-(trimethylsilyl)trifluoroacetamide, was added to the dry organic portion and left to sit for 1 hour. Dichloromethane was then added to the samples which were then analyzed by GC/MS to detect any organic iodinated compounds.

Fractionation GC/MS Method

GC/MS 2 was used to perform analysis on the C18 fractionated samples of iodine spiked peat. The GC oven was held at 40 degree for 6.00 minutes, and then ramped to 250 ° C at 10 degrees / minute for 21.00 minutes; it was again ramped to a final temperature of 280 at 20 degrees/minute and held for the 15.00 minutes. The injection port was set at a temperature of 240° C. The MS was set to the EI ion mode with a 10 minute filament delay and a scan time of 1.000seconds.

The peaks for 127 (m/e) and 142 (m/e) were integrated using the peak integrator on the Saturn software. The 127 (m/e) was used as a qualifier for organo iodide compounds.

The 142 (m/e) was also looked at for the presence of methyl iodide. Other peaks were examined and their spectrum matched to those found in the NIST 2002 library software.

Model Compounds: Reaction with Iodine

The reaction of iodine with several phenolic compounds was studied to gain additional insight into the mechanism of the reaction of iodine with lignin. These phenols are similar to those produced by destructive analysis of sphagnum peat. Vanillin and acetovanillone were used for the experiments. The reaction of vanillin and iodine is illustrated by the reaction shown below

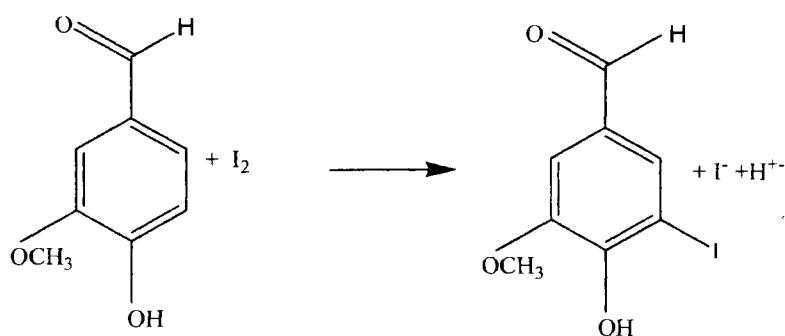


Figure 7: Reaction of vanillin with iodine

Iodine was added to solutions of buffered model compounds. Sodium bisulfite was added to the system after a measured reaction time to terminate the reaction. This reduced any unreacted iodine to iodide.

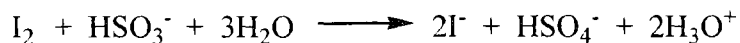


Figure 8: Reaction of iodine with sodium bisulfite. Iodine is converted to iodide.

GC/MS 2 was used to perform analysis of the extracted compounds. The GC oven was held at 40 degree for 6.00 minutes, and then ramped to 250° C at 10° C / minute for 21.00 minutes. The oven was again ramped to a final temperature of 280° C at 20° C / minute and held for the 15.00 minutes. The injection port was set at a temperature of 240° C. The MS was set to the Electron Impact ion mode with a 10 minute filament delay, to allow elution of excess derivatizing agent. The scan time was set at 1.000 seconds.

For the vanillin and acetovanillone samples several different compounds were monitored. These compounds included the vanillin, acetovanillone, 5-iodovanillin, 5-iodoacetovanillone, vanillic acid, and iodovanillic acid. The total ion chromatographs, TIC, were integrated using the peak integrator on the Saturn software. The TIC were examined and their spectrum matched to those found in the NIST library software.

Vanillin with Excess Iodine

A similar study was done with vanillin using an excess of iodine at pH 4.5 and pH 6. Excess iodine was added to ensure that all the vanillin was being iodinated, and to have excess iodine in the reaction mixture that can be converted to iodide by the bisulfite. To a 25 mL test tube 5 mL of 300 ± 50 ppm, 5.90×10^{-6} moles, of saturated iodine solution and 5 mL of 0.1M KH_2PO_4 solution (\sim pH 4.4) were combined. Vanillin solution, 19.2 μL of 3902 ppm or 4.90×10^{-7} moles, was added, and the timer was started. The tube was inverted to mix. After a set amount of time, 1 min, 3 min, 5 min, 10 min, 30 min, 1 hr, and 2 hr, 300 μL of 0.1M NaHSO_3 was added to terminate the reaction. The experiment was repeated with 5 mL of 0.1 M KH_2PO_4 adjusted to pH \sim 6 instead of KH_2PO_4 . The sample analysis was performed the same as above.

Lignin, Gallic Acid, and Tannic Acid

Limited tests were run with Aldrich alkali lignin, gallic acid, and tannic acid.

Measurement of Organic Iodinated Compounds

NNDMA Method

Iodine and sphagnum peat were combined in a 40 mL capped glass test tube, and allowed to react for a certain timed interval. The peat contains phenolic functional groups similar to those in vanillin and acetovanillone.

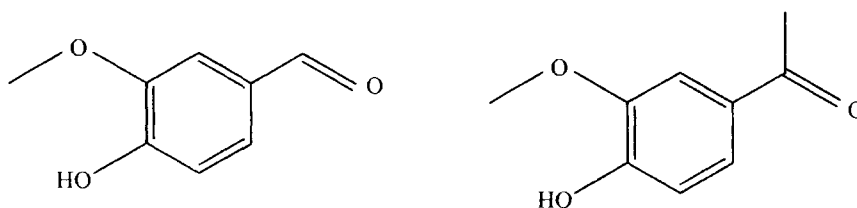


Figure 9: Vanillin and acetovanillone structures

The reaction that occurs is most likely ring substitution of iodine on to the phenolic ring.

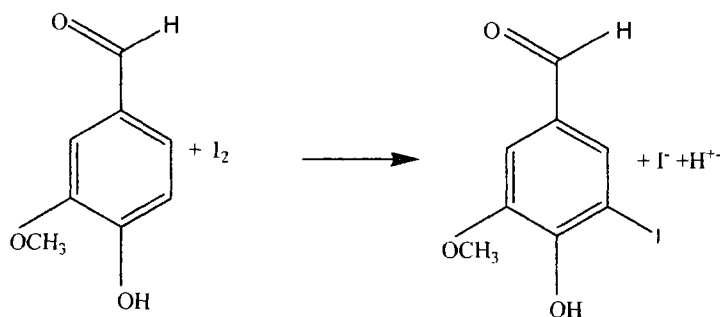


Figure 10: An example of how iodine reacts with vanillin.

Excess iodine remaining at the end of the timed interval, can be reacts rapidly with N-N-dimethylaniline(NNDMA). This acts as a scavenger for any unreacted iodine.

NNDMA is an aromatic amine that undergoes rapid iodination. Mishra et al.,2000, utilized NNDMA for iodine analysis in order to determine a real time concentration of iodide, iodine, and iodate in the presences of one another. They also determined that the reaction is complete in less than one minute. NNDMA also undergoes iodination in only the para position Therefore there is only one isomer to detect on the GC/MS.

After the reaction, iodine occurs in several species that can be quantified. These include iodinated NNDMA, the iodide insolution, and the iodinated peat (quantified by the methyl iodide released during pyrolysis). The iodinated NNDMA can be extracted with hexane and analyzed on the GC/MS. Unreacted NNDMA is also detected. The ratio of unreacted NNDMA to iodinated NNDMA, along with the iodide concentration, can be used to determine the amount of iodine left unreacted with the peat at each reaction time interval.

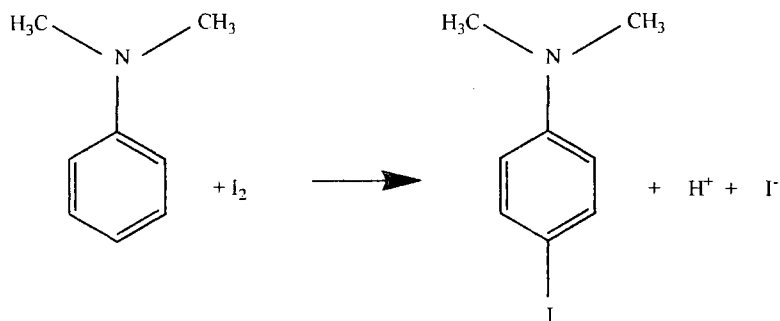


Figure 11: The reaction of NNDMA with iodine. This illustrates the source of iodide produced in the reaction.

There are two sources of iodide produced in the reaction. There is iodide produced when the excess iodine reacts with NNDMA. Also, some of the original iodine in solution can be reduced to by reaction with peat. The iodide produced during the NNDMA reaction was subtracted from the total iodine detected in the reaction mixture. This was a simple correction since the amount of NNDMA added was quantified and the stoichiometry of the reaction is 1:1. This procedure allowed the amount of iodine that reacted with the peat at different pH's, times, and temperatures to be quantified.

Preparation of NNDMA

NNDMA, 100 μ L of neat, was placed in a 50 mL volumetric flask and diluted to volume with methanol to achieve a concentration of 1.6×10^{-5} mol / mL.

Calibration

A 100 mL volumetric flask was partially filled with nanopure water. 0.5 mL of saturated iodine solution was added to the flask and it was then filled to volume with nanopure water. The flask was inverted to mix. 0.5 mL of NNDMA solution was then added to the flask and it was inverted to mix three times. 5 mL of hexane was added to extract the organic compounds, namely NNDMA and I-NNDMA. The hexane was mixed thoroughly with the aqueous layer and was left to settle. The hexane layer was then pipetted into a test tube. This procedure was repeated using 1.0 mL and 2.0 mL of saturated iodine.

The samples were analyzed on the GC/MS system 1. The hexane layer, 2 μ L, was injected into the inlet which was held at 240° C. The GC oven was held at 40° C for 6 minutes. It was then increased at 10° C/min until it reached 250° C. It was then ramped at 20° C/min until it reached a final holding temperature of 280° C. The MS program was

carried out in EI mode scanning mass ranges of 50-650 m/z at a scan rate of 1.000 seconds. There was a five minute filament delay.

After the sample was analyzed by GC/MS, the response of 121(m/e) and 247 (m/e) were integrated using the peak integrator in the Saturn software. A ratio of NNDMA to I-NNDMA was obtained by dividing ion 247 by the sum of ion 121 and ion 247. This ratio was plotted against the total moles of iodine present in the calibration flask to obtain a calibration. A linear regression of 0.98 or greater was deemed acceptable.

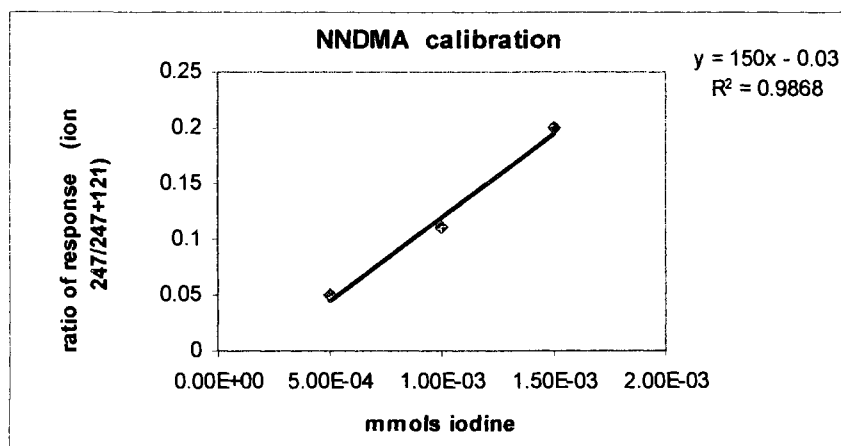


Figure 12: An example of NNDMA calibration

Pyrolysis GC/MS for the Measurement of Methyl Iodide

A solid sphagnum peat sample was ground with a mortar and pestle. If the sample required dilution, it was diluted with a 10:1 mass ratio of crushed 100/120 mesh Alltech glass beads. Quartz wool was inserted into a CDS analytical economy quartz tube for ¼" probe. The tube was heated to 1000° C in the probe to clean the tube. The tube weight was tared, then, 1-10 mg of sample was loaded into the tube. The tube was reweighed and

additional quartz wool was inserted to retain the sample. On the GC, the oven program was turned off, and liquid nitrogen was used to cool a 6 cm portion of the front part of the column to cryofocus volatile pyrolysis products. The tube was then inserted into the pyrolyzer probe. The probe was then inserted into the interface. The interface was turned to the run position and the GC and pyrolyzer program was started.

The pyrolyzer probe was started at an initial temperature of 40° C for 5 s, and then ramped at 0.50° C / mS to a final temperature of 500° C. It was held at 500° C for 10 seconds. The pyrolysis interface program was held at an initial temperature of 90° C then ramped at 50° C / min to a final temperature of 300° C.

After 4 minutes the liquid nitrogen was taken off the column and the GC oven program was turned back on. The interface was changed back to the off position and the pyrolyzer was removed from the interface. The GC/MS program continued as described below.

The GC oven was held at 40° C for 6 minutes. It was then increased at 10° C / min until it reached 250° C and then ramped at 20° C / min until it reached a final temperature of 280° C. The MS program was carried out in EI mode scanning mass ranges of 50-400 m / z at a scan rate of 1.000 seconds. There was a five minute filament delay. Ion 142 was used to quantify the methyl iodide produced by the sample.

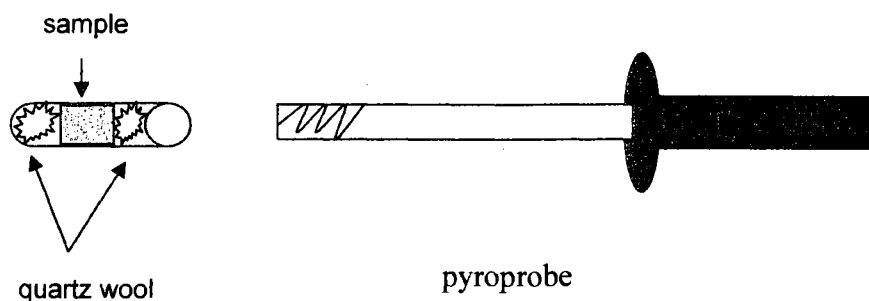


Figure 13: Diagram of pyroprobe and quartz tube (not to scale)

Calibration for Pyrolysis GC/MS

Three gas sampling bottles of 0.125 L, 0.250 L and 0.500 L were flushed with nitrogen gas for 5 minutes to remove any contaminants. A $\frac{1}{2}$ " x $\frac{1}{8}$ " stir bar was placed inside of each vessel. After 5 minutes, the vessels were taken off of the nitrogen flush and sealed. 5 μ L aliquot of reagent grade methyl iodide was delivered into each vessel. The vessels were stirred slowly on a magnetic stir plate for 5 minutes to ensure all the methyl iodide evaporated. A quartz pyrolysis tube was filled with Supelco Carbotrap 20 / 40 mesh, a carbon bases adsorbent. It was held in the quartz sampling tube by quartz wool. A 25 μ L syringe was used to remove 10 μ L of gas containing methyl iodide from the calibration vessel. The 10 μ L was then delivered through the glass wool into the Carbotrap packed quartz pyrolysis tube.

The GC/MS pyrolyzer program was run as stated above in the pyrolysis GC/MS procedure, including the use of liquid nitrogen for cryoconcentration purposes.

Ion 142 was monitored and the peak area was integrated using the Saturn software. Area vs. standard amount was plotted and a linear regression was obtained from the three calibration points. A linear regression of 0.995 or above was deemed acceptable.

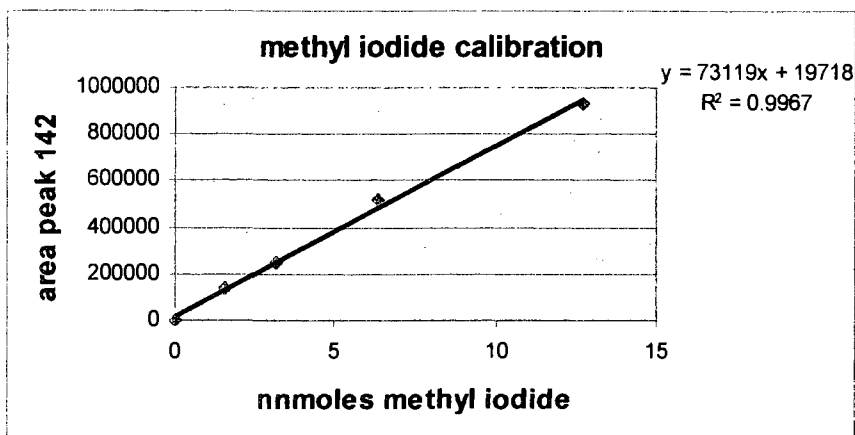


Figure 13: A sample pyrolysis calibration.

Iodine and Peat with NNDMA

Procedure

Peat was added in the amount of $0.0250 \text{ g} \pm 0.0010 \text{ mg}$ to 25 mL of buffer solution in a 40 mL test tube and capped. This test was performed at pH 1.8, pH 6, pH 8, and pH 10. The pH was adjusted using the various buffers described in the solutions section. Saturated iodine solution (2 mL) was added to the tube. The tube was placed in a lab Quake rotisserie mixer. At timed intervals ranging from 30 seconds to 2 hours, 0.5 mL of NNDMA solution was added to the mixture. The tube was inverted to mix. A 5 mL aliquot of hexane was then added to the mixture to extract the NNDMA and the iodinated NNDMA. The hexane layer was pipetted off into a separate test tube. The remaining mixture was filtered through vacuum filtration using Whatman #1 filter paper to remove the solids. The filtrate was tested for iodide using the ion chromatography method. The hexane layer was analyzed on the GC/MS for NNDMA and iodinated NNDMA using the same GC/MS program as the calibration. The solid peat was dried in the vacuum desiccator and then analyzed for methyl iodide using the pyrolysis GC/MS method.

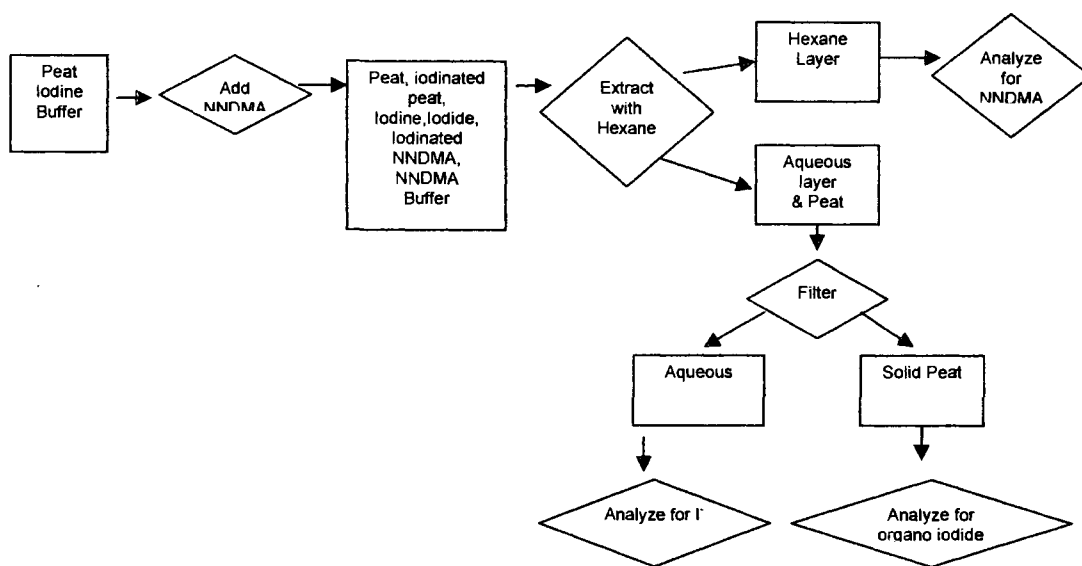


Figure 15: Schematic of the NNDMA procedure.

Iodate and Peat

Iodine can be oxidized to iodate in the presence of nitric acid and nitrogen dioxide, both of which are used in abundance in fuel rod dissolution reprocessing. We examined if iodate can react with phenolic compounds in sphagnum peat. Experiments with iodate and peat were also conducted in order to examine possible reactions. When experiments were conducted with iodate and peat, iodide and organo iodide were detected as by products. This indicates that iodine, as iodate, could react with peat and bind to the phenolic compounds in sphagnum peat.

One of the preliminary experiments done was with a mixture of iodate and peat versus a solution of iodate only. This experiment was conducted in nanopure water and resulted in a pH of 5.5. Iodate, 25 mL of 1000 ppm, was mixed with 0.3498 g of crushed peat and mixed overnight. The peat solution was vacuum filtered. Iodide and iodate were

measured in the solution using the ion chromatography method. A blank sample of iodate, 25 mL of 1000 ppm, was also placed in a sealed tube and mixed overnight. This tube contained no peat. For the tube with iodate and peat, iodide was detected. Also the iodate concentration decreased. This shows that iodate may react with sphagnum peat, be reduced to iodide, and to some extent be incorporated into the peat.

Further experiments were run with iodate and peat. A set of experiments were conducted with different incubation times at a temperature of 60° C at various pH's. For these experiments, approximately 0.35 g of peat were added to a 40 mL test tube with 10 mL of 1000 ppm iodate solution and 10 mL of buffer. This resulted in an iodate concentration of 500 ppm. The buffers that were used were 0.1 M H_3PO_4 for pH 1.9, 0.1 M NaH_2PO_4 for pH 4, 0.1 M KH_2PO_4 for pH 6, 0.1 M NaH_2CO_3 for pH 8, and 0.1 M Na_2CO_3 for pH 9.4. The solution was inverted and then allowed to incubate at 60° C with times ranging from 10 minutes to up to thirteen hours. After the samples were taken out of the oven, they were filtered using a vacuum filtration system. The filtrate was collected in a glass test tube. Iodate and iodide were measured in the solution by the ion chromatography method. The solid peat samples were dried and tested for methyl iodide using the pyrolysis GC/MS technique.

This experiment was repeated in an oxygen free environment. A similar procedure as above was employed with a few modifications. The iodate and buffer solutions were added to a 40 mL test tube. Nitrogen was bubbled in the solution for three minutes into the solution and two minutes above the solution. The peat was added and the tube was quickly capped. The mixture was placed in the incubator over at 60° C.

CHAPTER 3

RESULTS

Solid Phase Microextraction

The results of the solid phase microextraction indicated no detectable concentration of volatile iodinated compounds were released at temperatures lower than 60° C. The iodine appears to be primarily bound to the NOM, or reduced to a non volatile form of iodine. The area of peak 142 for peat samples were similar to the peak area of 142 in the blank samples. These peaks were not able to be quantified, but were identified qualitatively using the Saturn NIST library software. No iodinated compounds were detected with the PDMS fiber, even after an equilibration time of thirteen hours.

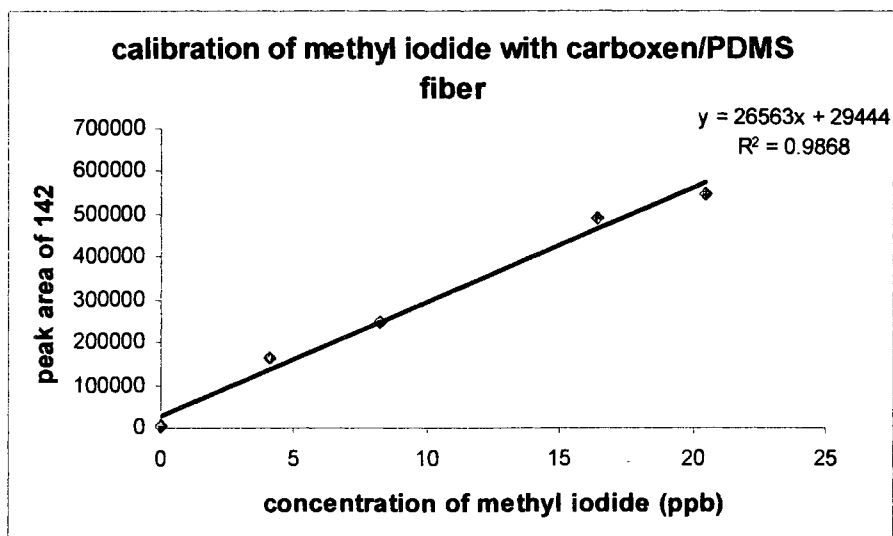


Figure 16: Calibration done with carboxen/ PDMS fiber at 25° C.

Extraction Conditions	Fiber	Peat conc. mg/mL	Iodine Conc. ppm	Peak 142 area
25mL NaHCO ₃ 25° C 10min equilibration	CAR/PDMS	19.24	10.4	3597
25mL NaHCO ₃ 25° C 1 hour equilibration	CAR/PDMS	19.35	10.4	2207
25mL NaHCO ₃ 25° C 2 hour equilibration	CAR/PDMS	19.24	10.4	3166
Ca(OH) ₂ in 25mL H ₂ O 25° C 10 min equilibration	CAR/PDMS	19.98	10.9	5367
Ca(OH) ₂ in 25mL H ₂ O 25° C 1 hr equilibration	CAR/PDMS	19.88	10.9	6342
Ca(OH) ₂ in 25mL H ₂ O 25° C 2 hr equilibration	CAR/PDMS	19.88	10.9	5650
NaHCO ₃ blank 10 min equilibration	CAR/PDMS	0.00	0.00	8465

Table 1: Table of Results for SPME experiments . The retention time for peak 142 was 6.6 minutes.

The blank was prepared with a 25 mL of NaHCO₃ buffer only. The peak area of 142 (m/e) was 8465. This peak area was higher than the peak area of 142 for some of the samples. This could be an indication of carryover from the previous extraction. From the

information obtained from running a blank sample, it was determined that no meaningful levels of iodinated compounds could be reported with confidence for most of the samples that were run. When the iodine concentration was increased to 66.0 ppm and the equilibration time was increased to fifteen hours, some volatile iodinated compound were detected with the CAR/PDMS fiber

Chromatograms

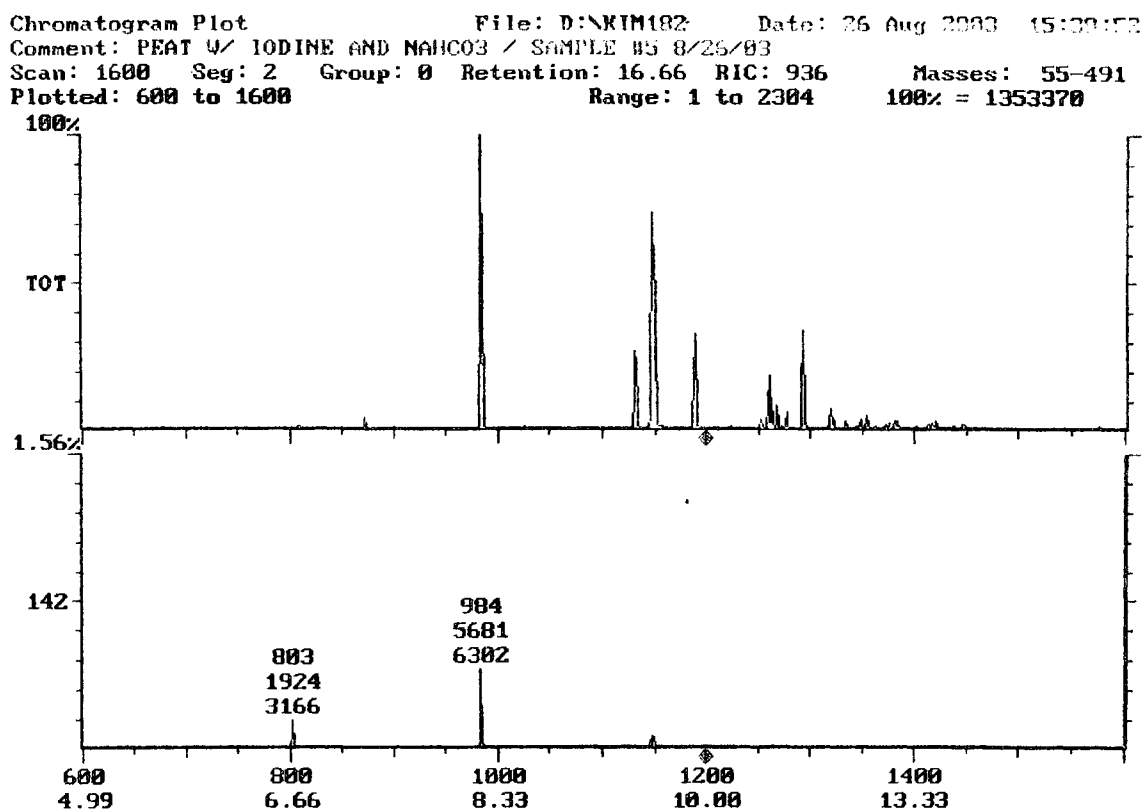


Figure 17: The chromatogram shows that the area of 142 (m/e) is below that of the blank, indicating no detectable volatile iodinated compounds. The conditions for the sample can be found in the third entry in table 1 above.

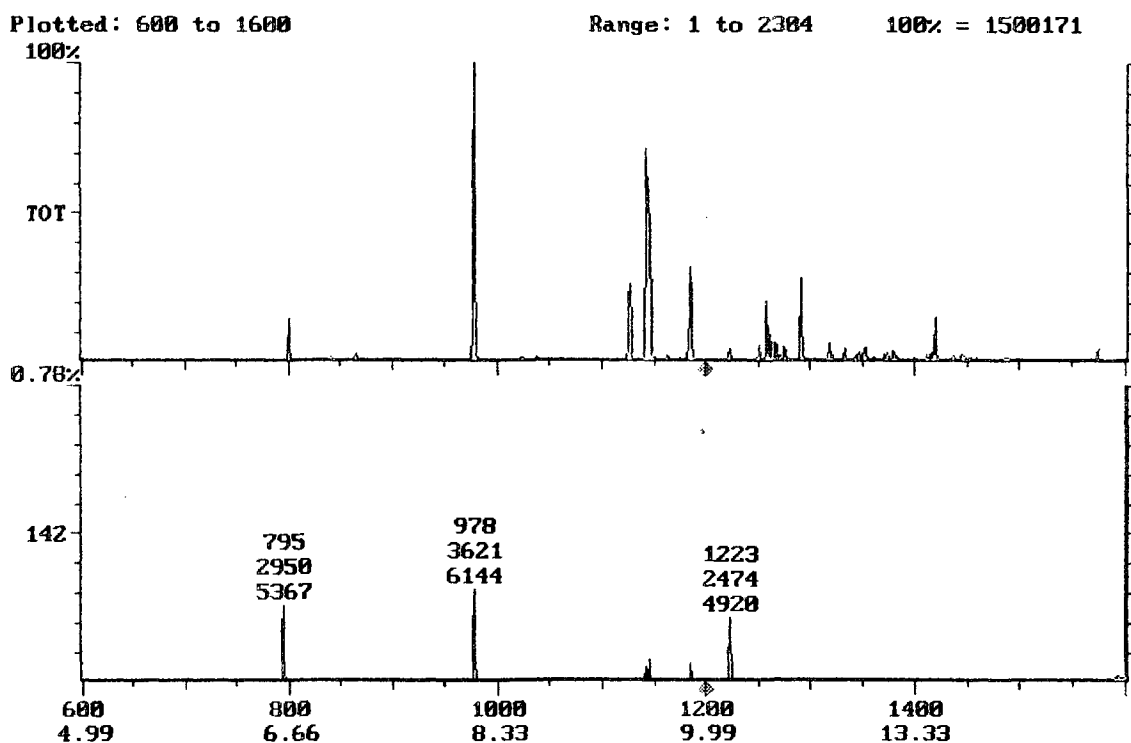


Figure 18: The chromatogram shows that the area of 142 (m/e) is below that of the blank, indicating no detectable volatile iodinated compounds. The conditions for the sample can be found in the fourth entry in Table 1 above.

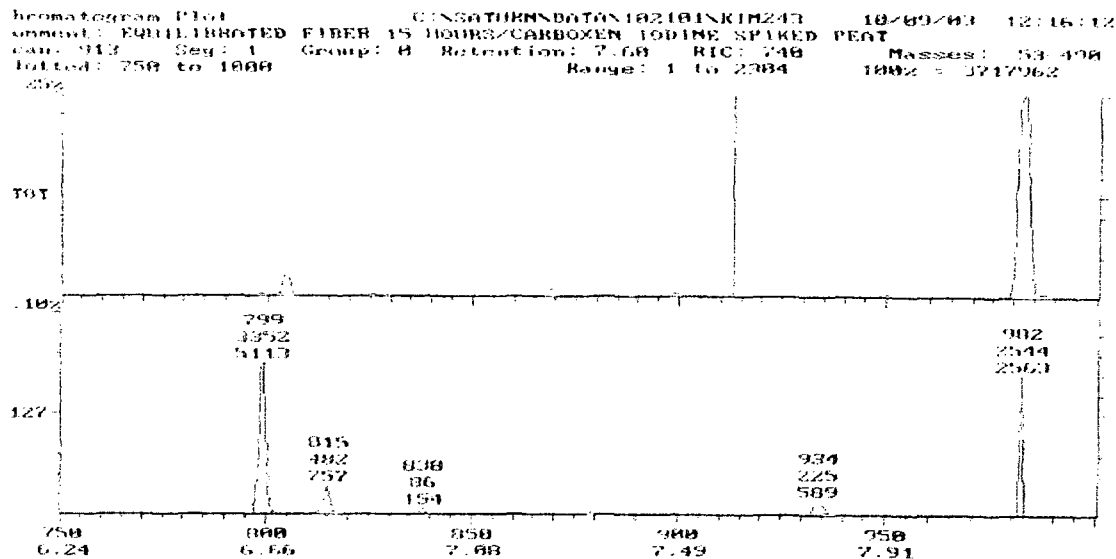


Figure 19: Although below the detection limit, volatile iodinated compounds were detected in this sample. The conditions are described in the text below.

Methyl iodide was detected under the following conditions : a fifteen hour equilibration time with 66.0 ppm iodine with a peat concentration of 28.02 mg/mL, $\text{Ca}(\text{OH})_2$ buffer, with a CAR/PDMS fiber. Although peak 142 (m/e) at retention time of 6.66 minutes was below the method detection limit, there were also some other iodinated compounds that were identified in this sample that were not in a blank sample. These compounds were identified using the NIST library ,diiodomethane, methyl iodide, iodoethene, chloriodomethane, triiodomethane, in a sample run with a 15 hour equilibration with the $\text{Ca}(\text{OH})_2$. These compounds had small peak areas and instrumental response was not calibrated with the fiber. There was not a significant amount of iodinated compounds released during these SPME experiments. From this, the conclusion

can be drawn that most of the iodine remains bound to the peat and was not released in the headspace of the vial. Several fibers and extraction conditions were tested. The following describes the results of the individual fibers that were tested.

Carboxen/PDMS Fiber

There was significant carryover between each sample making calibration difficult. Multiple blanks had to be run in order to achieve minimal carryover to the next sample. The fiber also needed to be regenerated by desorbing overnight at 280° C. At the end of a series of five or more samples, the fiber became overloaded and would not show an increase in response with an increase in standard concentration. It was also discovered that there were significant competition effects. For example, the signal for methyl iodide decreased when bromoform was added. However, with this fiber detection down to the ppb level was possible. Sometimes the results for the standards were erratic and unreliable especially after 4 or more runs. This was likely because of carryover. The conditions that worked best for this fiber are as follows: 25 degree extraction temperature, 1.0 M NaHCO₂ matrix, 10 minute headspace extraction, 5 minute desorption at 270 °C. This fiber should not be used to quantitate the methyl iodide but perhaps could be useful as a qualitative tool.

PDMS fiber

Analysis with the PDMS fiber was a lot less sensitive than the CAR/PDMS fiber. The fiber could detect methyl iodide at levels around 500 ppb. However, a calibration was obtained with little difficulty. Analysis with the fiber was reliable and reproducible. There was no significant carryover. The optimal conditions for this fiber were as follows:

25° C headspace extraction for 10 minutes in a 1.0 M NaHCO₃ matrix, 5 minute desorption at 270 °C.

Carbowax/DVB Fiber

This fiber was also used for iodoform analysis. This fiber had sufficient sensitivity but was not durable. After about 10 runs the coating fell off of the fiber. This is not a good choice because of low durability.

Overall

The SPME fibers provided an investigative tool to discover if volatile iodinated compounds were released into the headspace of the vials. Although this method was qualitative, it demonstrated that the iodine spiked peat was not releasing a significant amount of volatile iodinated compounds. This provided a basis for the statement that NOM can sufficiently bind the iodine. The next step was to see if the iodine spiked peat was releasing organic iodinated compounds into a liquid matrix. This led to the design of the fractionation experiment.

Fractionation of Iodine Reacted Peat

There was no iodine, I₂, detected in the aqueous fractions. The aqueous fraction was consistent with blank levels, which were 0.10 ppm. No iodine containing compounds were found in the C-18 fraction. The solid fraction that was tested via pyrolysis GC/MS method showed evidence of methyl iodide. The amount of iodomethane detected from the iodinated peat fraction versus a non-iodine treated peat sample was significantly elevated, almost doubled.

Sample	Iodide detected in first filtrate after C-18 (total μmol)	Iodine detected in first Filtrate (total μmol)	Iodinated Compounds Detected from Silinated Fraction (total μmol)	Methyl Iodide in Solid Peat Fraction (nmol/mg peat)
Blank- 6mL KH_2PO_4 buffer ~pH 6 only +0.7003g peat	Non Detect	Non Detect	Non Detect	1.06
6 mL 221 ppm iodine + 0.3004g $\text{Ca}(\text{OH})_2$ +0.6994 g peat	3.08	Non Detect	Non Detect	2.09
6 mL 221 ppm iodine + 6mL KH_2PO_4 buffer ~pH 6 +0.7009 g peat	12.2	Non Detect	Non Detect	1.88
6 mL 221 ppm iodine + 6 mL KH_2PO_4 buffer ~pH 4 +0.7012g peat	13.8	Non Detect	Non Detect	2.14

Table 2: Table of Fractionation Results. Methyl iodide appears in the last column. The iodine treated samples had almost double the amount of methyl iodide detected. The reported values represent the total number of moles detected. The solid peat fraction was analyzed by pyrolysis GC/MS.

After each leaching with bisulfite and ammonium hydroxide the iodide and iodine levels remained undetectable. This indicates that most of the iodine was converted into iodide almost immediately during the first leaching. Some of the iodine did associate with the peat as indicated by the elevated levels of methyl iodide detected in the solid fraction. There were also no iodinated compounds detected in the filtrate after it was run through the C-18 cartridge. No detectable amounts of organoiodide products were found in the eluted C-18 cartridge. This indicates that there are no iodinated compounds released in

the filtrate. All of the iodine is either converted to iodide or associates with the peat. This supports the data from the SPME which indicated that no iodinated volatile compounds were released into the liquid and detected in the headspace. Since the fractionation results supported the statement that the iodine is binding to the NOM in the peat, an experiment was designed to examine the kinetics of the reaction of iodine and peat. The first experiments were done with model compounds, vanillin and acetovanillone. These model compound were meant to represent the phenolic functional groups that are found in NOM.

Model Compound Experiments

The results of these experiments are that vanillin reacts with iodine at all pHs. The kinetics of the reaction vary with the pH of the test solution. At low pHs, less than 3, the reaction is slower than at pHs 4-12. The reaction was complete in less than thirty seconds. At high pH, the vanillin also reduces I_2 to I^- . Vanillic acid was produced under these high pH conditions. Vanillic acid produced in the reaction can also react with iodine.

Several different model compounds were tested including vanillin, acetovanillone, tannic and gallic acid. The results showed that vanillin was able to undergo aromatic substitution of iodine for hydrogen at a higher percentage at lower pHs. The kinetics of the reaction were very rapid at all the pHs examined. At the pH range of 4-12 the reaction was complete in less than thirty seconds. At a pH lower than 3, the reaction rate was slightly slower. Most of the iodine was reduced to iodide at higher pH tested (greater than 9). There was no iodine added to the aromatic ring at pH greater than 9.

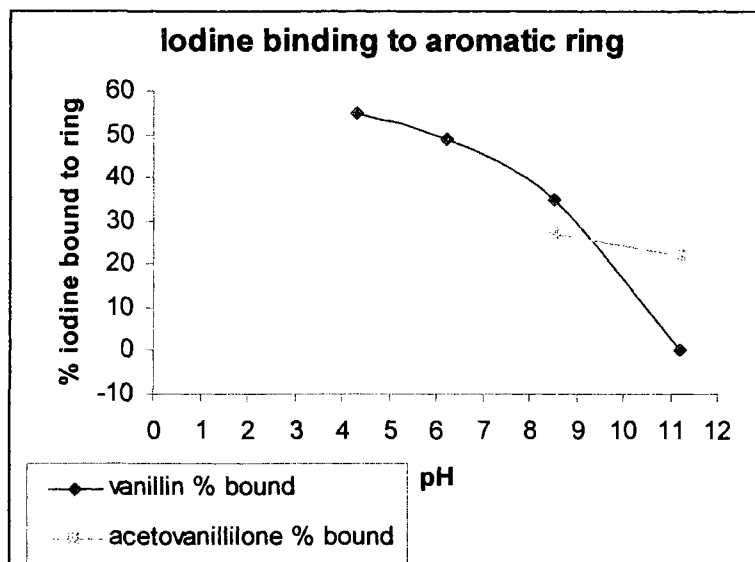


Figure 20: Percentage of iodine bound to the aromatic ring in vanillin and acetovanillone.

The fraction of vanillin iodinated was higher at a lower pH. The graph below illustrates the reaction of vanillin with iodine at pH 2.5. It includes the iodide produced and the iodine left unreacted, which was detected with NNDMA.

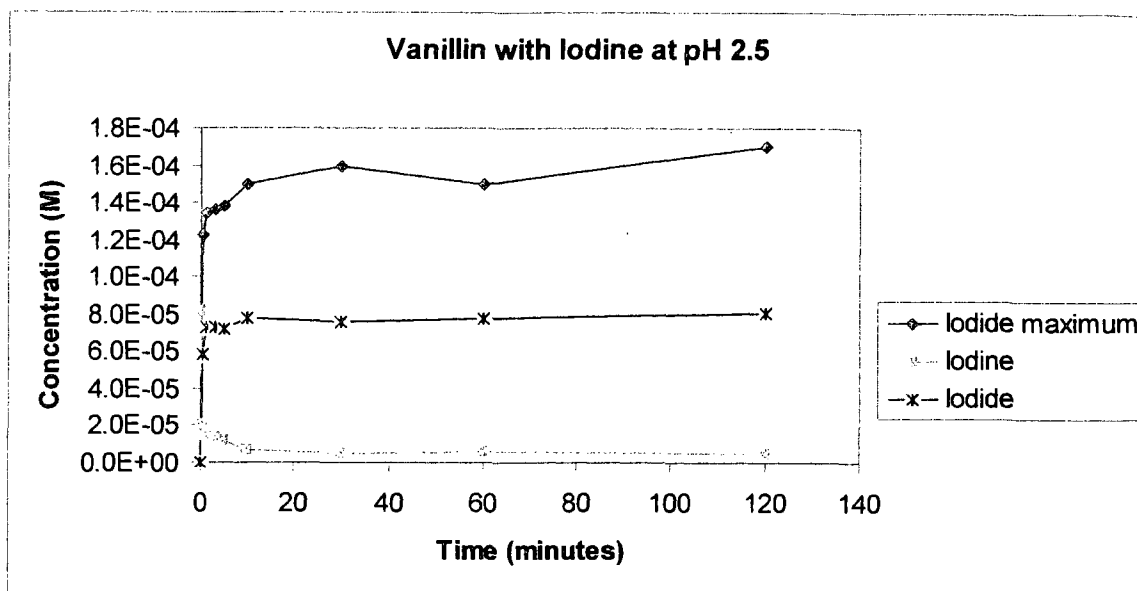


Figure 21: Reaction of Iodine and Vanillin at pH 2.5 at 25° C.

The reaction proceeded at a rapid rate at high pH, however, the iodine concentration never reached zero, but rather reached a final stabilized concentration. This may be due to the O₂ oxidation of iodide to iodine at low pH.

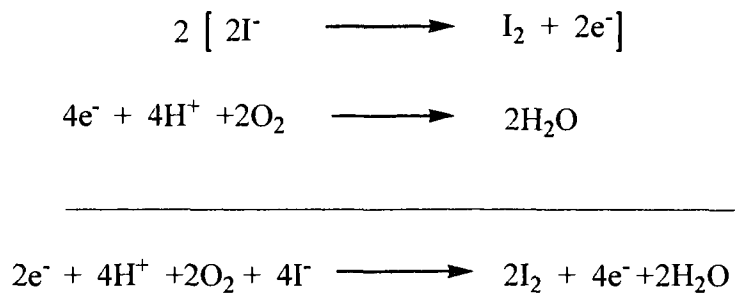


Figure 22: The O₂ oxidation of iodide to iodine.

The reaction at pH 2.5 was controlled by phosphate buffer. Consistent with aromatic substitution, this study showed that half of the iodine available gets reduced to iodide while the other half of the iodine becomes associated with the vanillin aromatic ring.

Gallic acid and tannic acid were also tested. Because of rapid kinetics (complete in less than thirty seconds) this reaction could not be studied using the experimental method for the model compounds.

The model compound studies indicated that some iodine can become bound to the aromatic ring. The extent of the substitution was a function of pH as well as time. This study showed that phenolic compounds in sphagnum peat could react with iodine and that pH is an important control on this reaction.. The model compound studies lead to the experiments with iodine and peat under controlled pH and temperature conditions.

Iodine and Sphagnum Peat

The experiments with peat and iodine that were subsequently quenched with NNDMA were run at pH's 2,6 ,8, and 10. The data below illustrates that the reaction rate increases with pH. From direct iodide measurements, it appears that the iodide produced reaches a maximum at a faster rate for higher pH. The graphs show the direct iodide measurements over time.

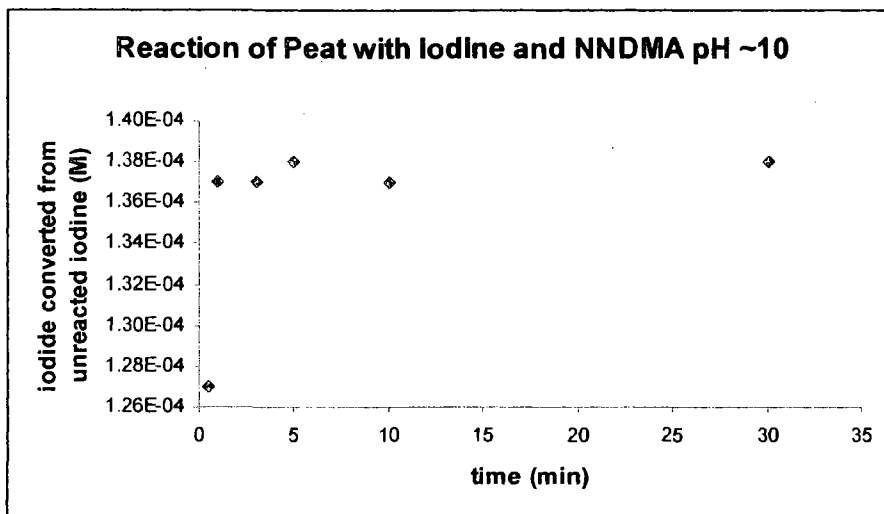


Figure 23: The graph above illustrates a direct iodide measurement over time.

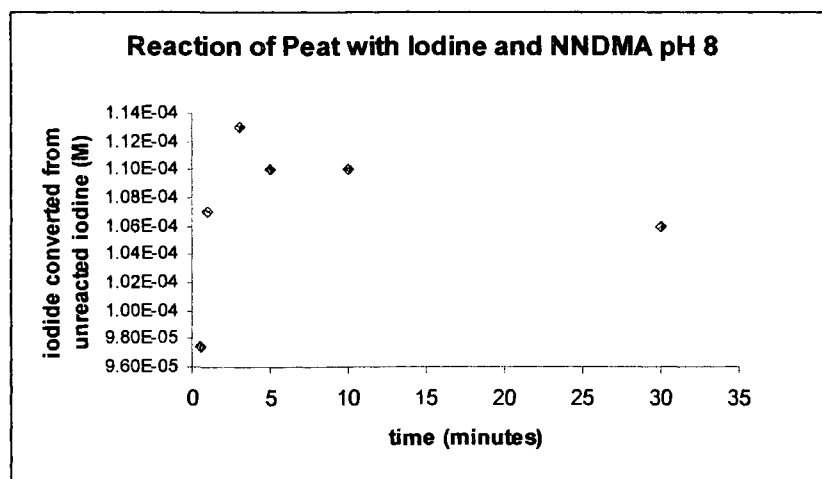


Figure 24: The graph above illustrates a direct iodide measurement over time at pH 8

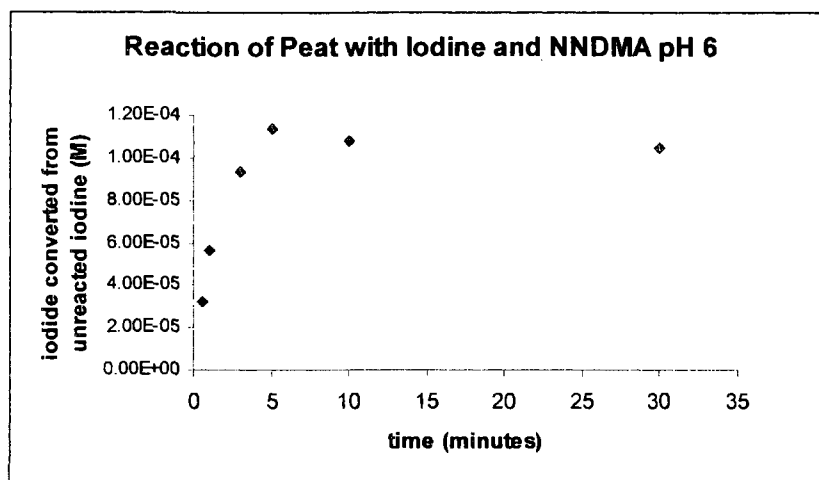


Figure 25: The graph above illustrate a direct iodide measurement over time at pH 6

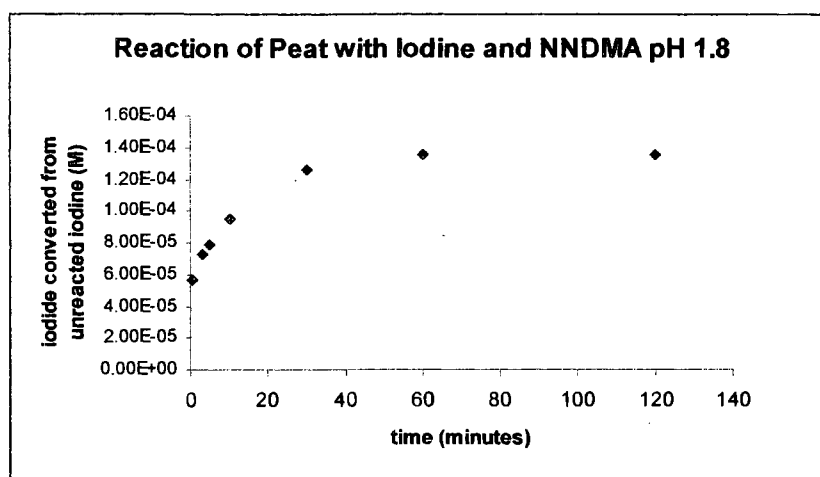


Figure 26: The graph above illustrate a direct iodide measurement over time at pH 1.8

From the four graphs above, the kinetics of the reaction are partially determined by the pH. At pH 1.8, the reaction is much slower and iodide is still being released after 10 minutes. At pH 10, the reaction is completed in one minute or less. At pH 6 and 8, the reaction appears to be complete in less than five minutes. All of these experiments were done at room temperature and were sampled at intervals of 30 seconds, 1 minute, 3,

minutes, 5 minutes, and 30 minutes. Additionally, the sample at pH 1.8 was sampled at 1 hour and 2 hours.

From this data, it was determined that there was a kinetic relationship between the pH of the reaction and the percent of iodine that is bound to the sphagnum peat. There are two sources of iodide produced in the reaction. Since both reduction of iodine to iodide and the addition of iodine to the ring need to be considered, there are two reactions involved.

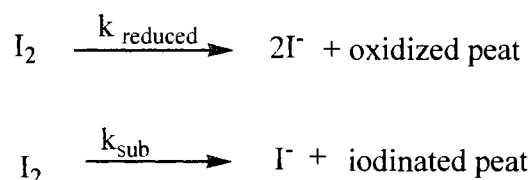


Figure 27: Reaction scheme where iodine is either reduced in the reaction to iodide, or substituted on the phenolic rings in the sphagnum peat matrix.

The two equations above can be combined to model the change of iodine and iodide over time. The two reactions can be modeled as first order equations with respect to iodine.

$$\begin{array}{l} \text{(a)} \quad \frac{d\text{I}_2}{dt} = -k_{\text{reduced}} + k_{\text{substitution}} * \text{I}_2 \\ \text{I}_2 = \text{I}_{20} e^{-(k_{\text{red}} + k_{\text{sub}})t} \end{array}$$

Figure 28: Above equations shows how the iodine concentration changes over time.

$$(b) \quad \frac{dI^-}{dt} = 2 * k_{\text{reduced}} * I_2 + k_{\text{substitution}} * I_2$$

$$\frac{dI^-}{dt} = (2k_{\text{red}} + k_{\text{sub}}) * (I_2)_0 e^{-(k_{\text{red}} + k_{\text{sub}})t}$$

Figure 29: The first equation shows the change in iodide concentration over time. The second equation is a substitution made from the integration of equation (a).

$$(c) \quad dS \, dI^- = (2k_{\text{red}} + k_{\text{sub}}) * (I_2)_0 e^{-(k_{\text{red}} + k_{\text{sub}})t} dt$$

$$I - I_0 = \frac{2k_{\text{red}} + k_{\text{sub}}(I_2)_0}{k_{\text{red}} + k_{\text{sub}}} * (1 - e^{-(k_{\text{red}} + k_{\text{sub}})t})$$

Figure 30: Integration of equation (b) yields an equation that can be used to calculate the iodine and iodine concentration over time.

The rate constants k_{reduced} and $k_{\text{substitution}}$ can be estimated by fitting the data to the two above equations using the Burlirsch-Stoer Integrator. The fitting was done by using a commercial software package (ScientistTM from Micromath). Looking at the data from pH 5.8, it is obvious that the iodide increases as the iodine decreases. Using this data and the software we can show that the equations fit the rate constant. This shows that the reaction of iodine with the sphagnum peat follows a pseudo first order rate law.

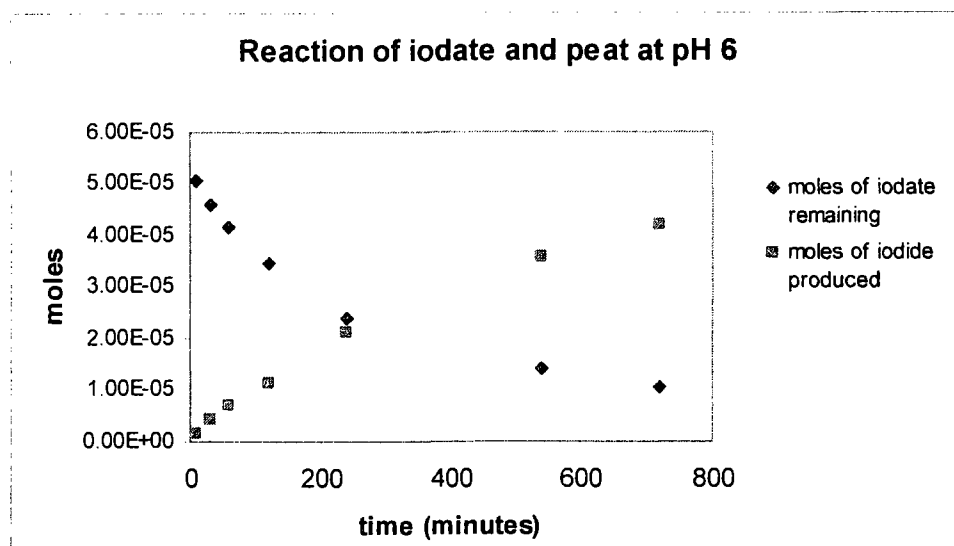


Figure 31: Change in concentration of iodine and iodide over time.

We were able to determine the best fit rate constants for the flowing pH 4.7, 5.8, and 8. We were not able to fit the data for pH 2 because of interference with the ion chromatography analysis. There were peaks that were co-eluting with the iodide peak in the sample. The ion selective electrode was not accurate enough for the fitting purposes in this experiment. Also, pH 10 was not able to be fit to the model. Below is the best fit values for the rate constants that could be determined.

pH	$k_{red} \text{ (min}^{-1}\text{)}$	$k_{sub} \text{ (min}^{-1}\text{)}$	$k_t \text{ (min}^{-1}\text{)}$	% Ring
4.7	~ 0	0.63	0.63	100
5.8	0.25	0.48	0.73	66
8	0.41	0.61	1.02	60

Table3: Best fit values for the rate constants for the reaction sphagnum peat and iodine.

$$k_t = k_{red} + k_{sub}$$

The fraction of iodine that reacts with the sphagnum peat can be calculated from the rate constants.

$$\% \text{Substitution} = \frac{100 * k_{\text{sub}}}{k_{\text{sub}} + k_{\text{red}}}$$

Figure 32: The equation representing the % iodine that undergoes substitution.

Iodate and Peat

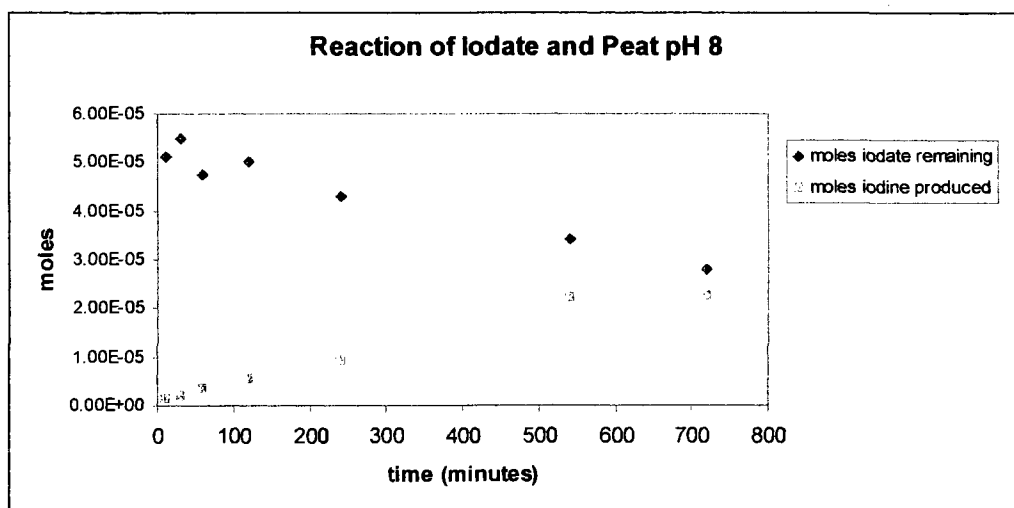


Figure 33: The reaction of iodate and peat at pH 8 show the disappearance of the iodate and the appearance of iodide. These are direct measurements taken from the ion chromatograph.

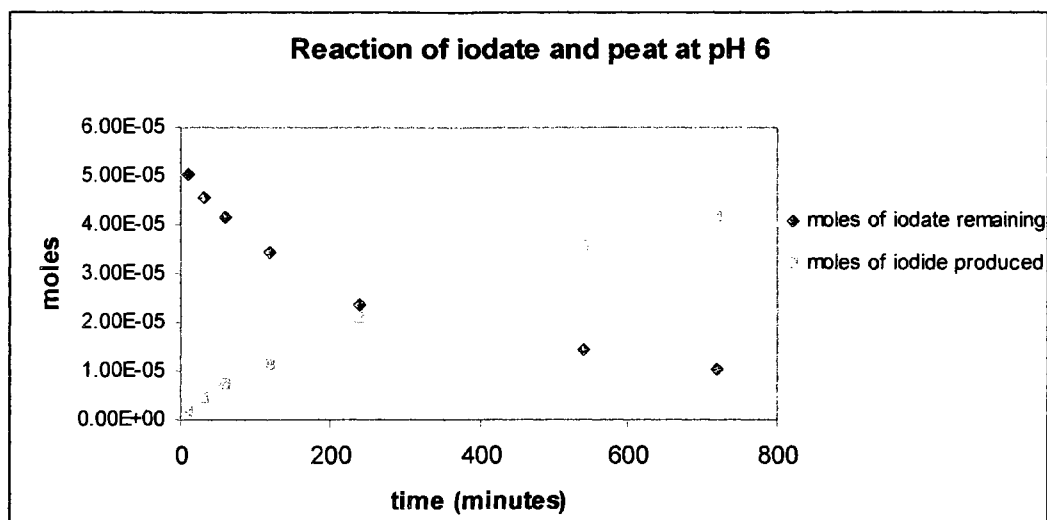


Figure 34: The reaction of iodate and peat at pH 6 show the disappearance of the iodate and the appearance of iodide. These are direct measurements taken from the ion chromatograph.

Iodide is formed by the reduction of iodate in addition to the organically bound iodine. From the iodide released and the iodate remaining in solution after either addition or reduction, the moles organically bound can be calculated by mass balance.

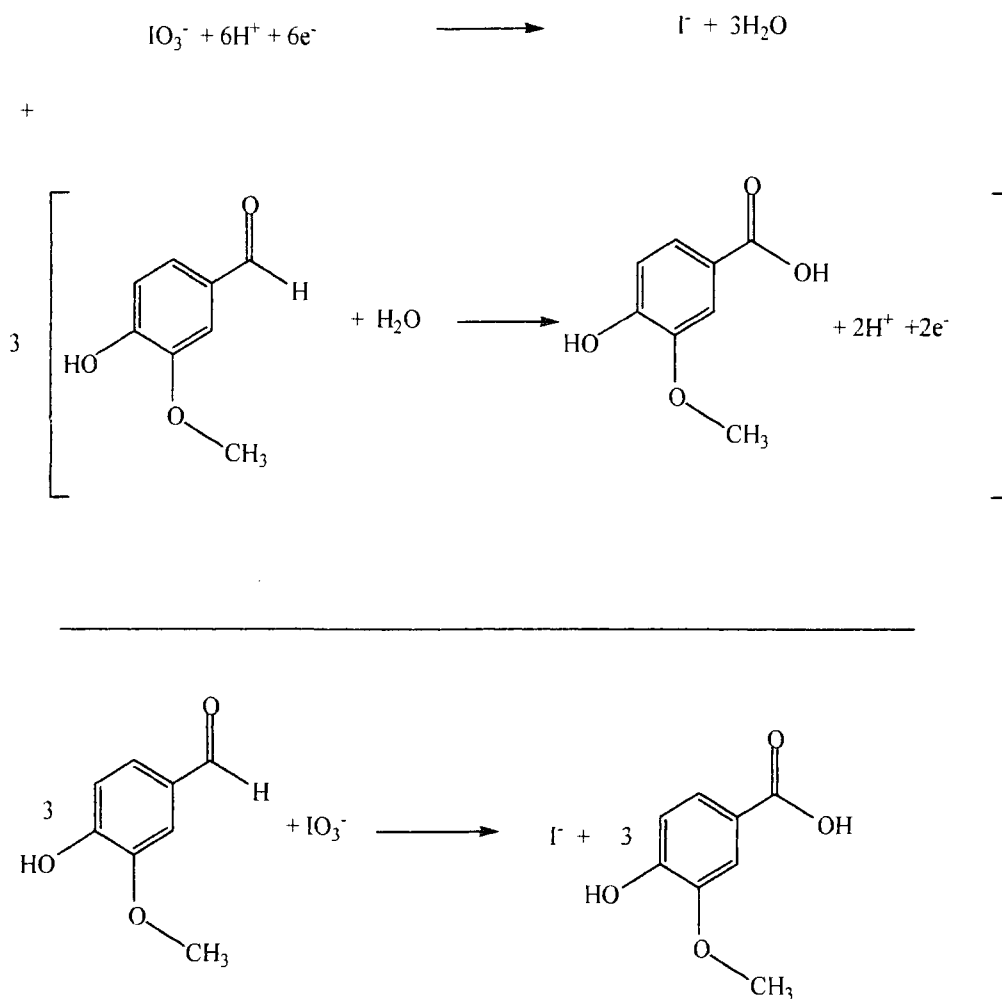


Figure 35: The above redox reaction of iodate and a phenolic compound show one way which iodide could be produced. Iodate may also be reduced to an IOH intermediate.

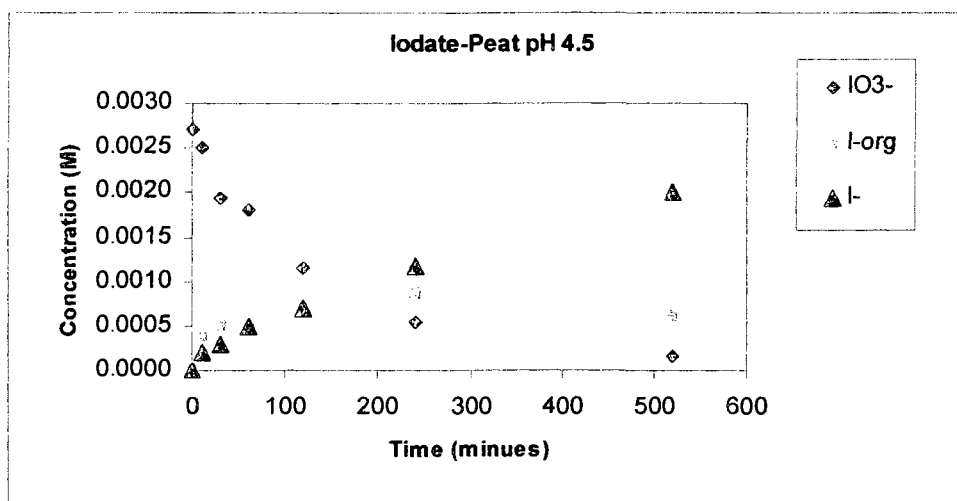


Figure 36: The reaction of iodate and peat at pH 4.5 show the disappearance of the iodate and the appearance of iodide . The iodine bound to the organic matter (I-org) was calculated by mass balance.

The recovered peat was dried and was analyzed for methyl iodide. Generally as incubation time increased the methyl iodide concentration also increased.

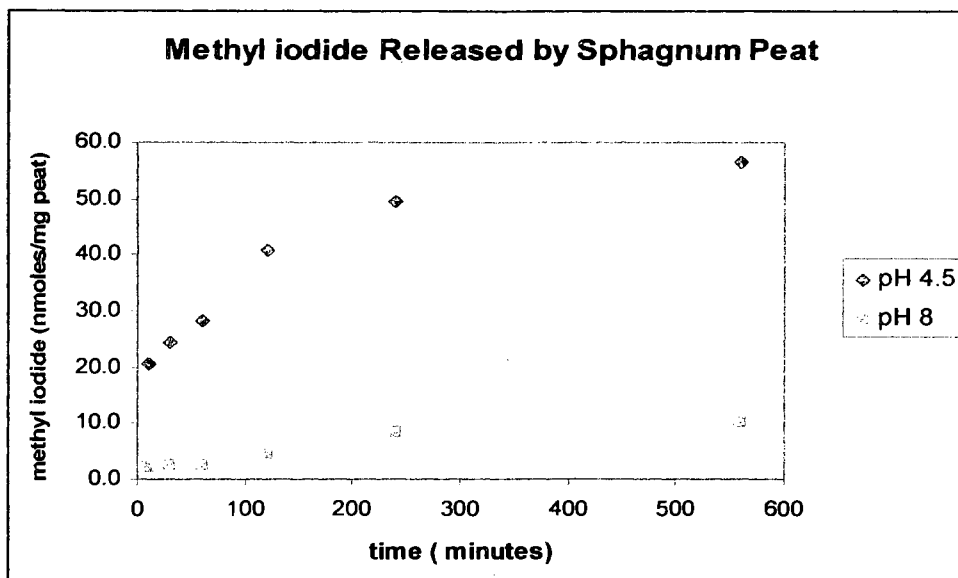


Figure 37: The following graph shows the increase of methyl iodide detected in sphagnum peat over time.

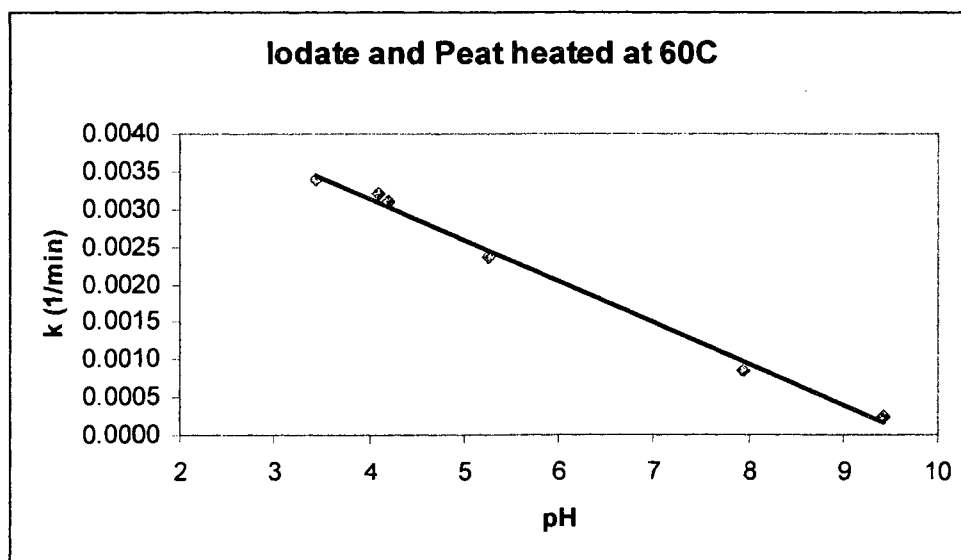


Figure 38: A graph of iodate and peat heated at varying pH's show the dependence of time and pH. The value for k was one that was used from a previous experiment of iodine and peat. The iodide and iodate concentrations were determined by ion chromatography.

The loss of iodate appears to follow pseudo first order kinetics. Using the rate constants that were derived with the iodine and NNDMA data, the iodate data was graphed as a function of pH. This data can be found in table X of the iodine and peat results. The results showed that there was a strong dependence on pH. As shown in figure X above, the rate of the iodate and peat reaction decreases as pH increases. One reason for this could be at a higher pH, there is more of an electrostatic repulsion between the peat matrix and the iodate. As pH increases, there are more negative ions formed from the ionization of carboxylic acid and phenolic functional groups in the Sphagnum peat.

This reaction was also done in an oxygen free environment with no significant change in the results.

CHAPTER 4

CONCLUSION

The experiments performed supported the hypothesis that iodine is trapped by the sphagnum peat. During the SPME experiments, low amounts of volatile iodinated compounds were detected in the headspace of the vial. This indicates that the peat was adequately trapping the iodine in the solid phase.

Fractionation of iodinated sphagnum peat demonstrated that some of the iodine is associating with the organic matter in the peat. The recovered solid peat in the fractionation experiment, which was treated with iodine, showed an increase in methyl iodide production when tested by pyrolysis GC/MS. This is a result of the sphagnum peat successfully trapping the iodine. The aqueous phases of the fractionation experiment were treated with a C-18 cartridge to determine if hydrophobic or non-polar organic iodinated compounds were being released from the peat, once it reacted with the iodine. The results from the C-18 treatment indicated that no significant formation of volatile and semi-volatile iodinated compounds released in the aqueous fraction. Once it was established in our experiments that sphagnum peat was trapping iodine, other conditions such as time, temperature and pH, were also examined.

Using the NNDMA method, we were able to quantify the amount of unreacted iodine remaining in solution after the reaction with sphagnum peat, allowing us to examine the

kinetics of the reaction. The reaction was terminated when the NNDMA was added to the reaction solution. The pH was the most important influence on the rate of the reaction. There was a clear correlation between pH and rate of reaction. At lower pH (2-4), the reaction proceeded at a slower rate than at high pH (>8). Data taken from reactions at different pHs were analyzed and a pseudo-first order rate constant for the reaction of iodine and sphagnum peat was determined.

The reaction of iodate with sphagnum peat was also examined at different incubation times over a pH range. Most of the iodate in these experiments was reduced to iodide. Iodine was also incorporated into the sphagnum peat as a result of iodate treatment. These experiments demonstrated that the iodate can become bound to the organic matrix in the sphagnum peat or reduced to iodide. A pH dependence was also discovered in the reaction of iodate and sphagnum peat. The rate of reaction decreased as the pH increased. The use of an oxygen free environment did not impact the kinetics of the reaction. From the data collected, it is hypothesized that iodate may be first reduced to hypoiodous acid. The HOI can then either be reduced to iodide or reacts with the peat, where it is sequestered in the organic matrix.

Further experiments were reported by Dr. Steinberg et al.(2008) to determine if HOI or iodine is produced as an intermediate when iodate is reduced. These experiment utilized leucocrystal violet, which was selectively oxidized to crystal violet by iodine. The formation of an iodine intermediate is quantified his results by visible spectroscopy at 592nm. This method had some limitations at lower pH due to the limited reactivity of leucocrystal violet. Steinberg et al., (2008) suggested that hydroquinone moieties in humic material were responsible for iodate reduction. Therefore, hydroquinone was

chosen as a natural organic matter surrogate to reduce iodate to iodine (or IOH).

Hydroquinone experiments were utilized to study the influence of temperature on the reaction kinetics, as this reaction could be measured at both high (70° C) and lower temperatures and be monitored by continuous UV/Vis spectroscopy.

From this study it was concluded that NOM, in the form of peat, may be a viable way of collecting radioactive iodine released from nuclear waste reprocessing. Radioactive iodine can be stored in the peat and then held until the iodine can be recovered for transmutation. By examining the kinetics of the reaction of iodine and peat, as well as iodate and peat, we gain a further understanding of how the reaction is dependent on pH and temperature. This data could give insight into optimal conditions for containing or recovering the radioactive iodine that is stored in sphagnum peat.

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Reactions of Iodine and Iodate with Sphagnum Peat: An Examination of Kinetics and
pH Dependence

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