Removal of Hydrogen Sulfide from Landfill Gas Using a Solar Regenerable Adsorbent

by

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ABSTRACT:

Landfill gas is a complex mix of gases, containing methane, carbon dioxide, nitrogen and hydrogen sulfide (H_2S), created by the action of microorganisms within the landfill. The gas can be collected and flared off or used to produce electricity. However, the H_2S content, which may vary from 10's to 1000's of ppm, can cause irreversible damage to equipment, and when combusted creates SO_2, a precursor of acid rain. It is also a toxic eye and lung irritant, so that prolonged exposure must be kept below a few ppm. Therefore, H_2S must be removed before landfill gas can be utilized. Our approach is to scrub H_2S into aqueous media and then use an adsorbent to sequester it. The adsorbent is then regenerated in a photocatalytic reaction potentially using sunlight. The adsorbents are metal sulfides such as CuS, MoS_2, WS_2, and Ag_2S. The expected reaction is the oxidation of sulfide in H_2S to elemental sulfur, and the reduction of water to hydrogen gas, H_2. The volume of H_2 obtained during photoreaction and the potentiometric shift of a sulfide ion-selective electrode were taken as measures of the extent of sulfide uptake and subsequent oxidation. Of the various sulfides examined, MoS_2 with platinum co-catalyst displayed the optimum in terms of toxicity, stability and photocatalytic activity. Using a xenon arc lamp as illumination source and adding a surfactant or low surface energy material such as Teflon® to promote bubble formation, gas evolution rates on the order of 5 mL/g-hour were achieved.

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INTRODUCTION

Hydrogen sulfide is a chemical compound with formula H_2S. It is heavier than air, very poisonous, corrosive, flammable and explosive. H_2S is a major contaminant in drinking water and can be identified by its foul rotten egg smell. It occurs naturally in the environment produced from the bacterial breakdown of organic matter in the absence of oxygen, this process is commonly known as anaerobic digestion. Sulfate-reducing bacteria generate usable energy under low-oxygen conditions by using sulfates as electron acceptors in the oxidation of organic compounds or hydrogen; this produces hydrogen sulfide as a waste product. Small amounts of hydrogen sulfide occur in crude petroleum, but natural gas can contain up to 90%. Volcanoes and some hot springs emit H_2S, where it arises via the hydrolysis of sulfide minerals. Hydrogen sulfide can be present naturally in well water, often as a result of the action of sulfate-reducing bacteria. The human body produces small amounts of H_2S and uses it as a signaling molecule. By far the largest industrial route to H_2S occurs in petroleum refineries. The hydrodesulfurization process liberates sulfur from petroleum by the action of hydrogen. Hydrogen sulfide is primarily released as a gas into the air and so it enters human body through inhalation. It is readily absorbed into the lungs, causing difficulty in breathing and other respiratory problems. H_2S is considered as one of the most common toxic pollutants, causing serious health effects in both children and adults. People working in industries such as mining, and oil and natural gas drilling and refining are more prone to H_2S contamination.

1.1 Structure of H_2S:

H_2S has molecular weight of 34.08 g. mol^{-1}. The molecular shape of H_2S is bent because of two non-bonding pairs of electrons on each side of the sulfur molecule. These electrons pull the H_2S

compound into a bent configuration. As shown in Figure 1.1, H_2S has H-S-H bond angle of 92.1° and S-H bond length of 133.6 pm.

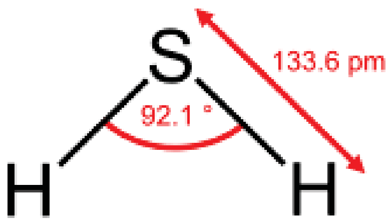


Figure 1.1. Structure of hydrogen sulfide molecule[1]

1.2 Effects of H_2S:

Even at low concentration it causes irreversible damage to downstream equipment. This is because of the acidic nature of H_2S; it dissolves in water to make a weakly acidic solution. In solid oxide fuel cells, H_2S can contaminate the anode cermet, substantially reducing power output in fuel cells. It also poses an environmental issue, as combustion of H_2S produces SO_2, which then reacts with more oxygen and produces SO_3 gas. This SO_3 gas spontaneously reacts with water vapor in the atmosphere, making acid rain:

$$2\ H_2S\ (g) + 3\ O_2\ (g) \longrightarrow 2\ SO_2\ (g) + 2\ H_2O\ (g)$$

$$2SO_2\ (g) + O_2 \longrightarrow 2SO_3\ (g)$$

$$SO_3\ (g) + H_2O\ (g) \longrightarrow H_2SO_4\ (aq)$$

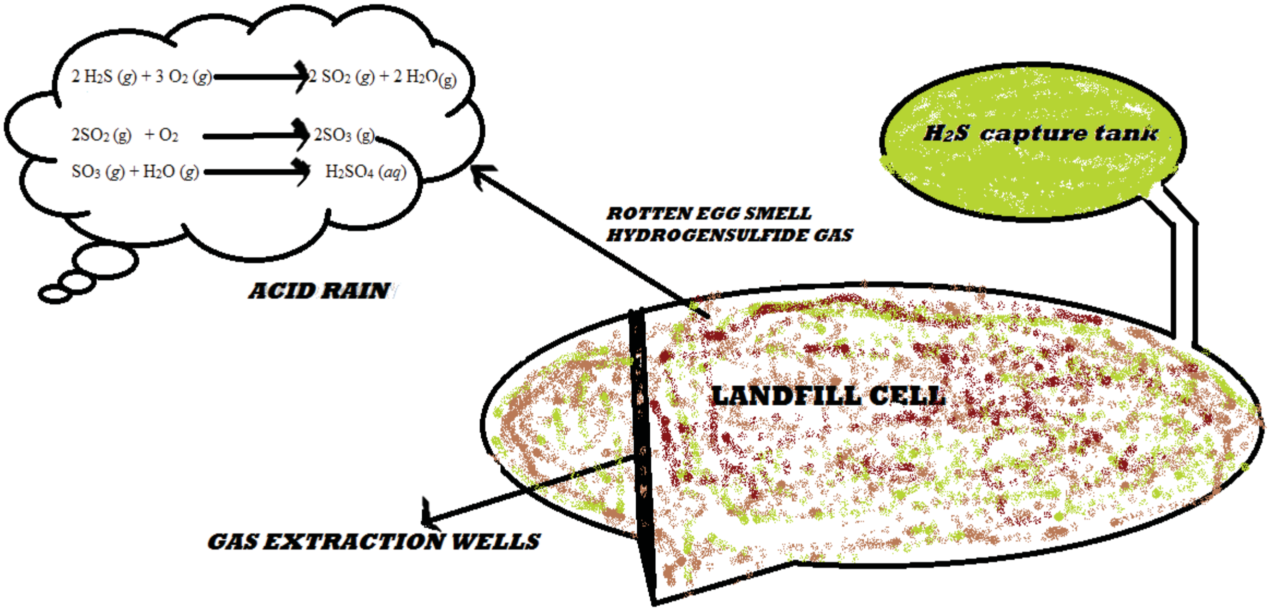


Figure 1.2. Schematic of hydrogen sulfide system in a landfill

H_2S gas has different effects at different concentration on human system. Effects were mentioned in table 1.1

Table 1.1. Effect of H_2S gas on human system over a range of concentrations[2]

Concentration (ppm)	**Symptoms/effects**
0.01-1.5	Odor threshold (when rotten egg smell is first noticeable to some). Odor becomes more offensive at 3-5 ppm. Above 30 ppm, odor described as sweet or sickeningly sweet.
2-5	Prolonged exposure may cause nausea, tearing of the eyes, headaches or loss of sleep. Airway problems (bronchial constriction) in some asthma patients.
20	Possible fatigue, loss of appetite, headache, irritability, poor memory, dizziness.
50-100	Slight conjunctivitis ("gas eye") and respiratory tract irritation after 1 hour. May cause digestive upset and loss of appetite.

100	Coughing, eye irritation, loss of smell after 2-15 minutes (olfactory fatigue). Altered breathing, drowsiness after 15-30 minutes. Throat irritation after 1 hour. Gradual increase in severity of symptoms over several hours. Death may occur after 48 hours.
100-150	Loss of smell (olfactory fatigue or paralysis)
200-300	Marked conjunctivitis and respiratory tract irritation after 1 hour. Pulmonary edema may occur from prolonged exposure
500-700	Staggering, collapse in 5 minutes. Serious damage to the eyes in 30 minutes. Death after 30-60 minutes.
700-1000	Rapid unconsciousness, "knockdown" or immediate collapse within 1 to 2 breaths, breathing stops, death within minutes.
1000-2000	Nearly instant death

1.3 pH dependence of H_2S:

Sulfides exist in three forms in aqueous systems, hydrogen sulfide (H_2S), bisulfide ion (HS^-), and sulfide ion (S^{2-}). These three together are referred to as total sulfide. At pH below 5 only hydrogen sulfide exist in the system, at a pH range of 6 to 8 there is both hydrogen sulfide and bisulfide; at pH range of 9 to 12 all the sulfide is in the form of bisulfide; and above pH 12 there is only sulfide ion, as shown in Figure 1.3

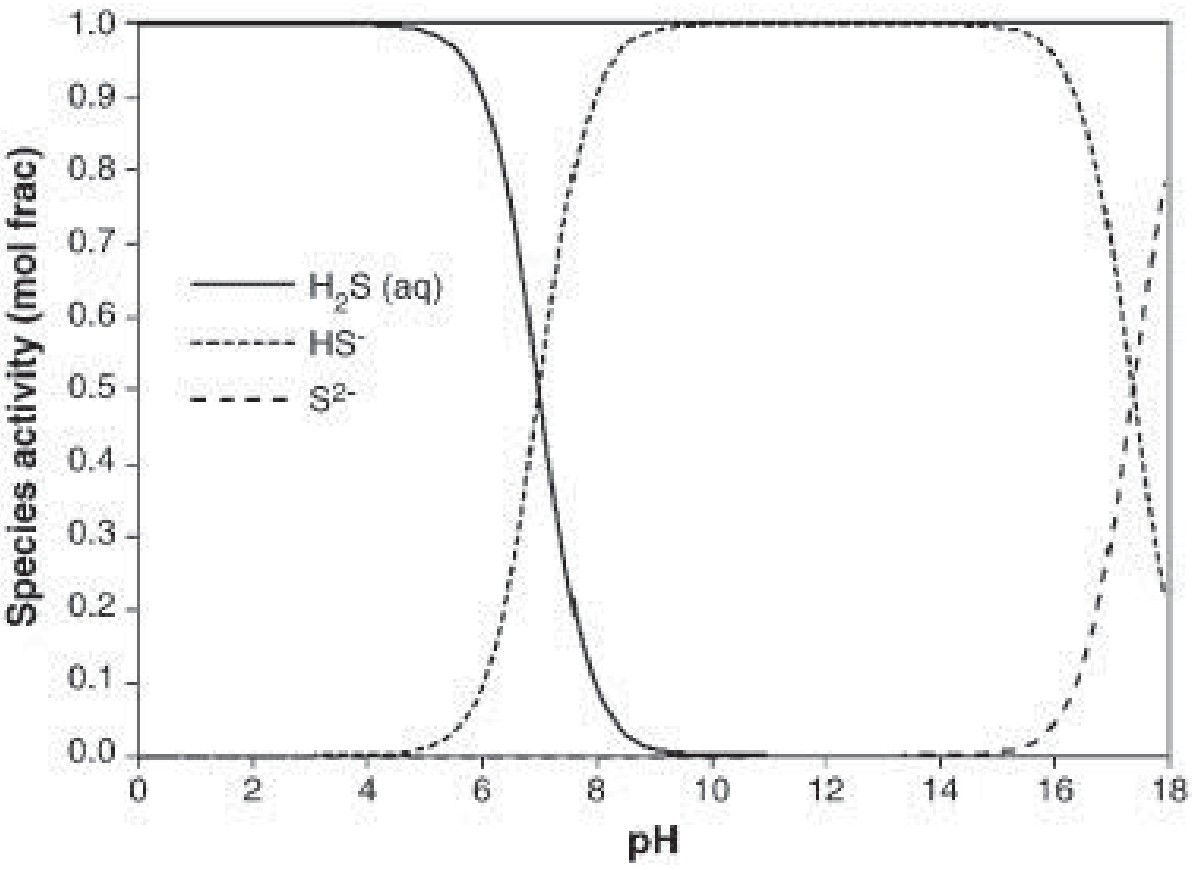
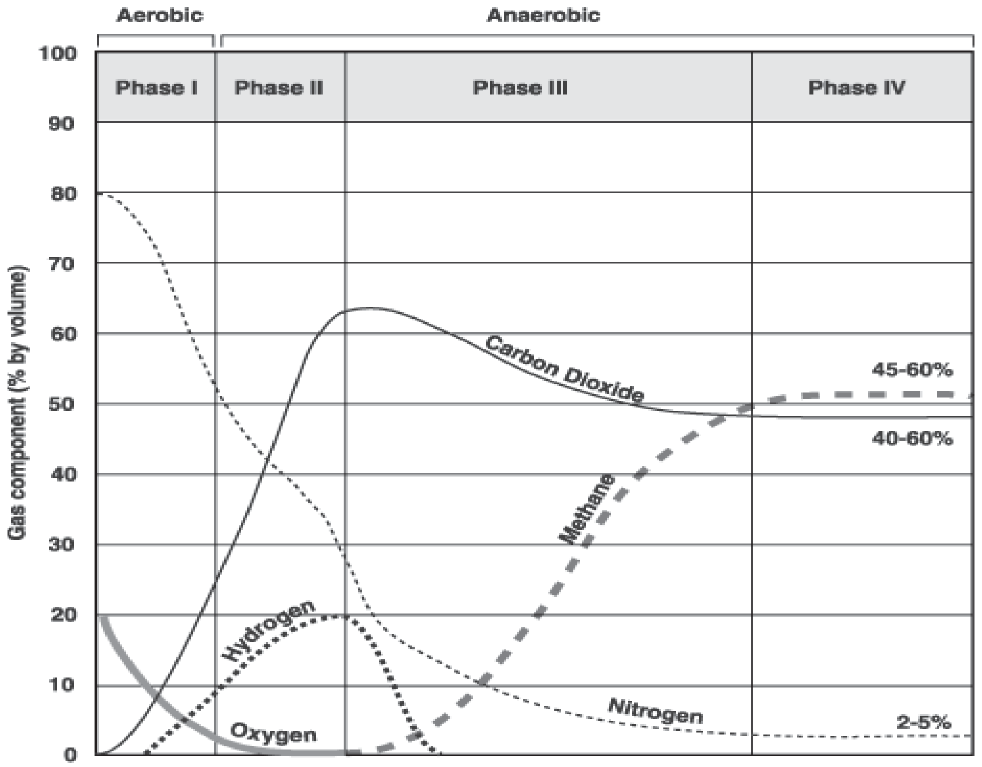


Figure 1.3.pH dependence of H_2S [3]

1.4 H_2S in landfill gas:

United States has 3,091 active landfills and over 10,000 old municipal landfills, according to the Environmental Protection Agency. Landfill gas is produced in four phases in landfills as shown in Figure 1.4.



Note: Phase duration time varies with landfill conditions

Source: EPA 1997

Figure 1.4. Production phases of typical landfill gas[4]

1.5 Composition of landfill gas:

Methane - 50-75%

Carbon dioxide - 25-50%

Nitrogen - 0-10%

Hydrogen - 0-1%

Hydrogen sulfide - 0-3%

Oxygen - 0-2%

Landfill gas has a high concentration of methane, which can be collected and flared off or used to produce electricity as shown in Figure 1.5. It is a growing alternative energy resource.

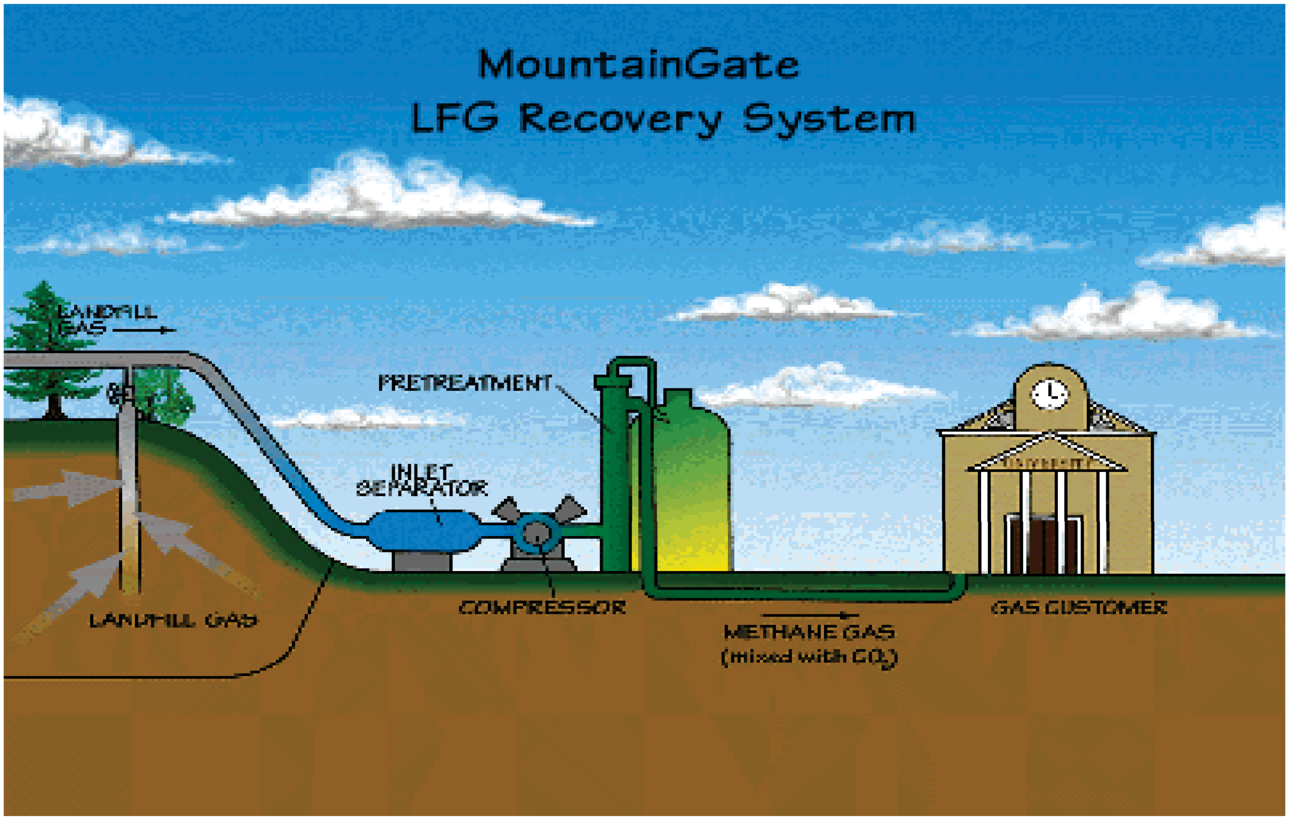


Figure 1.5. Landfill gas collection and utilization system[5]

1.6 Why is it important to remove H_2S from landfill gas?

Methane is a major gas which constitutes about 50-75% of biogas from landfills. If all the biogas were pure methane, it would be an excellent choice for a fuel. Methane has high ease of storage and handling because of its simple structure and high stability. It is a good engine fuel because of the advantages like complete combustion, no dilution of lubricants, better exhaustion performance, and good anti-knock properties. When real biogas is burned as a fuel engines tend to wear out quickly.

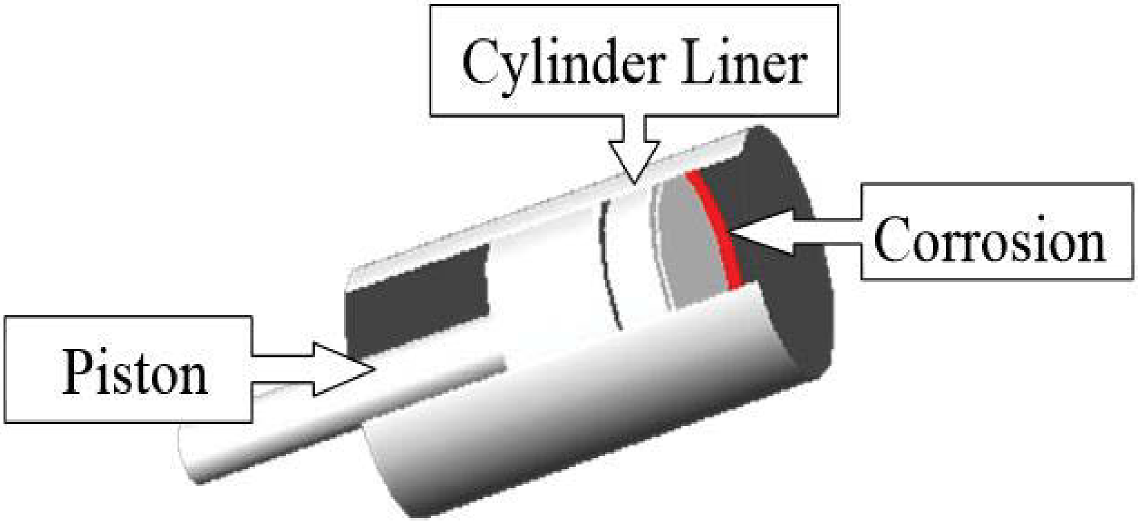


Figure 1.6. Location in cylinder liner where corrosion forms[6]

Corrosion occurs during normal methane combustion. Location of corrosion in the cylinder liner is mentioned in Figure 1.6. Under normal conditions, methane combustion produces water and carbon dioxide. The water produced is an electrolyte and the oxygen is the oxidizing agent needed for corrosion. The carbon dioxide speeds up the corrosion by making the electrolytic solution more acidic, which, in turn, speeds up the dissolution of the metal into ions. Hydrogen sulfide is oxidized into sulfur dioxide, which dissolves as sulfuric acid. Sulfuric acid, even in trace amounts, can make a solution extremely acidic. Extremely acidic electrolytes dissolve metals rapidly and speed up the corrosion process. This is particularly true at high temperatures.

1.7 H_2S in Black Sea[7]:

The Black Sea is the world's largest body of water containing hydrogen sulfide. This is because it has an inflow of salty Mediterranean Sea water in the deep layers and an inflow of river water on the top - so the sea is stratified and cannot even be mixed by wind. This leads to oxygen depletion in the lower layers. The rare forms of life that live in the depths of the sea, extremophile bacteria, metabolize sulfate in the water to survive. Sulfate fulfils a similar biochemical role to oxygen in respiration for these microbes, allowing them to release the energy they need to live and grow from the nutrients they absorb from the water. With organic matter and waste pouring into the Black Sea from waterways running off 17 countries, the Black Sea has a serious environmental contamination problem. The Black Sea has a layer of about 50 meters thick that lies between the anaerobic and aerobic water at a depth of about 200 meters along its axis. The total hydrogen sulfide production in the sediments of the sea is estimated at about 10,000 tons per day and this figure is continually rising. This makes the water in Black Sea not useful for any purpose. H_2S concentration in Black sea is about 0.5 mM.

1.8 Conventional ways of treating sulfides:

There are many methods available to remove sulfides from water. Sulfide removal technologies typically are based on sulfide equilibria. Some of the conventional methods of removing sulfides are mentioned in Table 1.2

Table 1.2. Conventional methods of treating sulfides[7]

Treatment method	**Advantage**	**Disadvantage**
1. Aeration		
Cascade or Tray	Inexpensive	Insufficient removals; not effective; turbidity formation

Volatilization	Inexpensive	Control is difficult; not effective; sulfide bacteria regrowth
Forced-Draft	Effective treatment method and simple operation is attractive; documented experience	Increased capital costs; acid pretreatments must be employed; odor generation requires use of expensive scrubber systems; scrubbate impact to POTW (Publicly Operated Treatment Work) operations;
Fine Bubble	Moderate costs and amenable to GST retrofits	aerated water can contain undesired microbiological constituents Insufficient removals at neutral pH levels; odor generator not easily treated; not typical in drinking water treatment
2. Oxidation		
Oxygen	Minimal capital costs; simple process	Incomplete oxidation can create colloidal sulfur and polysulfides; design and control difficult; turbidity
Chlorine	Minimal capital costs; controllable process	Incomplete oxidation; may increase DBPs; high dosages required, safety concerns, turbidity formation

Ozone	Controllable process; produces high quality finished water	Reaction chambers required; high operating and capital costs; may not be cost effective for small systems having greater than 2 mg/L total sulfide in raw water, turbidity formation
Potassium permanganate	Controllable process; inexpensive capital	Requires filters for residual MnO_2; requires large chemical dose; expensive chemical; turbidity formation
Hydrogen peroxide	Controllable process; inexpensive capital	Requires optimum mixing and long detection/contact times; incomplete oxidation; large dosages needed; turbidity
Ferrate	Powerful oxidant; inexpensive capital	Process has not been demonstrated at a large scale for drinking water treatment
3. **Oxidation filtration:** In this treatment oxidation is followed by membrane filtration	Controllable process; effective; affordable	Typically used for iron and manganese control; sulfide is secondary benefit; discharge of waste streams; discoloration of basin equipment, breakthrough of permanganate if used can cause discoloration (pink)
4. **Membrane filtration**	Controllable process;	Expensive; requires colloidal

	effective if controlled at optimum conditions	sulfur formation to be complete prior to filtration step; irreversible fouling of membranes may occur
5. Microbiological filtration	Natural process; chemical free method; safe to operate	Detachment and clogging are issues; design and control difficult; not proven process for drinking water
6. Anion exchange	Controllable; moderate cost compared to others	Biological fouling can foul resin; salt regeneration impacts discharge permits.

Photocatalysis: A new method for treating sulfides using semiconductor photocatalysts like CuS, CdS, MoS_2, WS_2, Ag_2S etc	Economical and biofriendly	Some photocatalysts like CdS are toxic. Sun is out less than 12 hours per day, so should use an expensive light source. Photo-corrosion of metals

1.9 Semiconductors:

Atoms are made of orbitals filled by electrons or left empty. In the solid state, based on whether a valence orbital is empty or filled, there are conduction bands (made of lowest energy empty orbitals) and valence bands (made of highest energy filled orbitals).The gap between these two bands is called band gap energy. In conductors, valence band and conduction band are overlapped, requiring negligible energy to promote an electron into the empty band. If the band gap is very high, the materials are called insulators. A semiconductor is a material which has electrical conductivity between that of a conductor and an insulator. The conductivity of a semiconductor increases with increasing temperature. Current conduction in a semiconductor occurs through free electrons and holes which are known as charge carriers. The conductivity of a semiconductor is strongly dependent on the band gap. The optical band gap determines what portion of the solar spectrum a photovoltaic cell absorbs. Relative band gap energies of conductor, semiconductor and insulator are shown in Figure 1.7

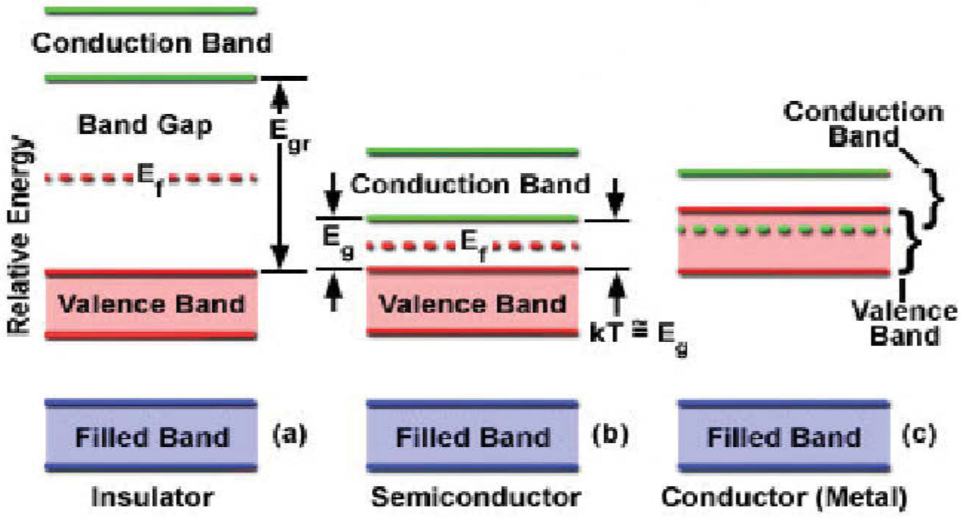


Figure 1.7.Energy band gaps in materials[8]

Band gap energies of the semiconductors used in this research are

cadmium sulfide – 2.3 eV

molybdenum sulfide – 1.9 eV

copper sulfide – 1.7 eV

tungsten sulfide – 1.4 eV

silver sulfide – 1.3 eV

EXPERIMENTAL

CHEMICALS:

Different chemicals used in the research are shown in Table 2.1

Table 2.1. Chemicals used in the research

S.No	**Chemical name**	**Form**	**Brand**	**Assay %**
1	Sodium sulfide nanohydride	crystalline		
2	Sodium sulfite	powder	J.T.Baker	98.0%
3	Hydrochloric acid	Aqueous solution		
4	Sodium chloride	crystalline	Fischer scientific	100.5%
5	Sodium hydroxide	pellets	BDH	97.0%
6	Potassium phosphate, monobasic	crystalline	Baker	99.6%
7	Ortho phosphoric acid	Aqueous solution	Fischer scientific	85%
8	Glacial acetic acid	Aqueous solution	Pharmko-Aaper	99.7%
9	Sodium borohydrate	crystalline	Sigma-Aldrich	≥98.5%
10	Sulfur powder	powder	Damon	
11	Iodine	Aqueous solution		
12	Thiosulfate	crystalline		

13	Starch	Aqueous solution		
14	Triton X-100 surfactant	Aqueous solution	Sigma-Aldrich	
15	Potassium nitrate	crystalline	Fischer scientific	99.3%
16	Poly(tetra fluoroethylene)	1 µm size powder	Sigma-Aldrich	
17	Teflon strip			
18	Chloroplatinic acid hexahydrate	powder	Sigma-Aldrich	≥37.50% platinum base
19	Carbon black (Vulcan XC-72)	powder	Cabot	
20	Activated carbon	powder	Fischer scientific	
21	Cadmium sulfide	powder	Morton Thiokol Inc.	
22	Copper(II) sulfide	powder	Alfa Aesar	99.8%
23	Molybdenum (IV) sulfide	powder	Alfa Aesar	99%
24	Tungsten (IV) sulfide	2 µm size powder	Sigma-Aldrich	99%
25	Silver sulfide	powder	Sigma-Aldrich	99.9%

INSTRUMENTATION

Materials and experimental methods: The main objective of this research is to select an adsorbent which is able to adsorb H_2S from landfill gas and also from water. The adsorbent chosen should be economic, ecofriendly and also should be regenerated in the presence of sunlight. Instruments used during the research are:

2.1 pH meter:

A pH meter is an electronic device used for measuring the acidity or alkalinity of a liquid. A typical pH meter consists of a special measuring probe, usually a glass electrode, connected to an electronic meter that measures and displays the pH reading. This was used to measure the pH of solutions continuously during sulfide ion titrations**.** Schematic of pH meter is shown in Figure 2.1.

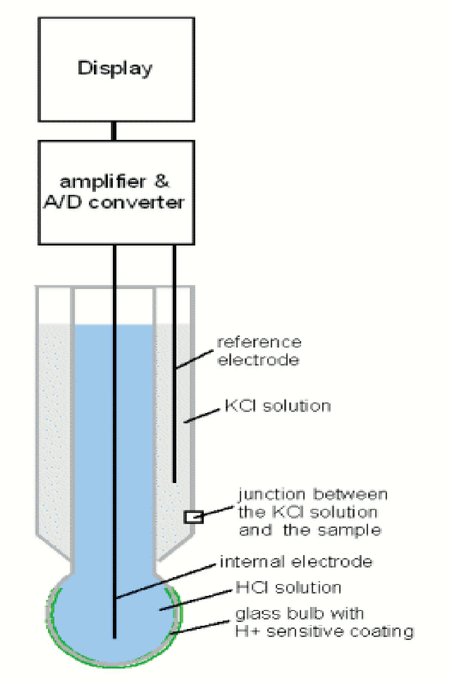


Figure 2.1. Schematic of pH meter[10]

2.2 Xenon-arc lamp:

A xenon arc lamp was used in this research as a source of simulated sunlight to regenerate the adsorbent. It is a specialized type of gas discharge lamp, an electric light that produces light by passing electricity through ionized xenon gas at high pressure. It produces a bright white light that closely mimics natural sunlight. Newport 500 W and 1000 W xenon arc lamps were used in this work. Model of the lamps were shown in Figure 2.2.

(a) (b)

Figure 2.2. Xenon arc lamps (a) A 500 W horizontal light source (b) A 1000 W vertical light source

2.3 Ion Selective Electrode (ISE):

The concentration of H_2S present in an aqueous system can be determined using an ion selective electrode (Ag/Ag_2S). It is a transducer or sensor that converts the activity of a specific ion dissolved in a solution into an electrical potential, which can then be measured by a voltmeter or pH meter. The voltage is theoretically dependent on the logarithm of the ionic activity, according to the Nernst equation. The sensing part of the electrode is usually made as an ion-specific membrane, along with a reference electrode. Schematic of Ag/ Ag_2S combination Ion selective electrode is shown in Figure 2.3.

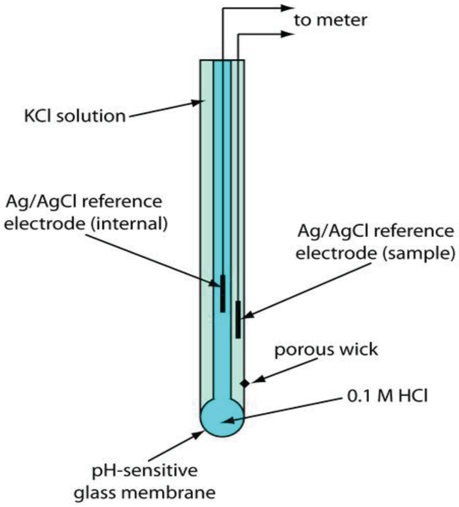


Figure: 2.3 Schematic of Ag/ Ag_2S combination Ion selective electrode[11]

2.4 Infrared spectroscopy:

We used infrared spectroscopy to detect the oxidation products of H_2S. Infrared spectroscopy covers a range of techniques, mostly based on absorption spectroscopy. A Fourier transform infrared (FTIR) spectrometer is a commonly used instrument. The term Fourier transform infrared spectroscopy originates from the fact that a Fourier transform (a mathematical process) is required to convert the raw data into the actual spectrum Infrared spectroscopy exploits the fact that molecules absorb electromagnetic radiation at specific vibrational frequencies that are characteristic of their structure. These absorptions are resonant frequencies, i.e. the frequency of the absorbed radiation matches the transition energy of the bond or group that vibrates. The energies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms, and the associated vibronic coupling. Instrumentation for infra-red spectroscopy is shown in Figure 2.4.

Figure 2.4. Instrumentation for infrared spectroscopy[12]

2.5 Ultraviolet - Visible spectroscopy:

Ultraviolet–visible spectroscopy refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. It uses light in the visible and adjacent ranges, namely the near IR and near UV regions. In the visible region of the electromagnetic spectrum, molecules undergo electronic transitions, where the absorption measures transitions from the ground state to the excited state.

Different molecules absorb light at different wavelengths. Based on this, UV-VIS spectroscopy was used to determine the oxidation products of H_2S based on the maximum absorption. The HP 8452A Diode-Array Spectrophotometer in Figure 2.5 is a single-beam, microprocessor-controlled spectrophotometer. The system has 512 detectors which are all integrated on a single silicon chip called a photodiode array. This model's visible/UV - range of 190 to 820 nm with 2 nm resolution is used when speed of measurement is essential. The photo diode-array detection system found in the HP 8452A makes each unit faster, more sensitive and more precise than conventional spectrometers[13]

Figure 2.5. 2 Diode Array Spectrometer - HP8452A UV/VIS[14]

2.6. Powder X-Ray diffraction:

Powder X-ray diffraction is a technique used for the study of crystal structures and atomic spacing. It is based on constructive interference of monochromatic X-rays which were generated by an X-ray tube, filtered to produce monochromatic radiation, collimated to align the beam, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference when conditions satisfy Bragg's Law:

$$n\lambda=2d\sin\theta$$

This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings.

Typically, this is achieved by comparison of d-spacings with standard reference patterns. This technique was used to identify sulfur adsorption on the photocatalysts and also to identify polysulfides. Powdered samples are piled into a hollow plastic sample holder and then leveled flush with the upper edge of the holder, as shown in Figure 2.6.

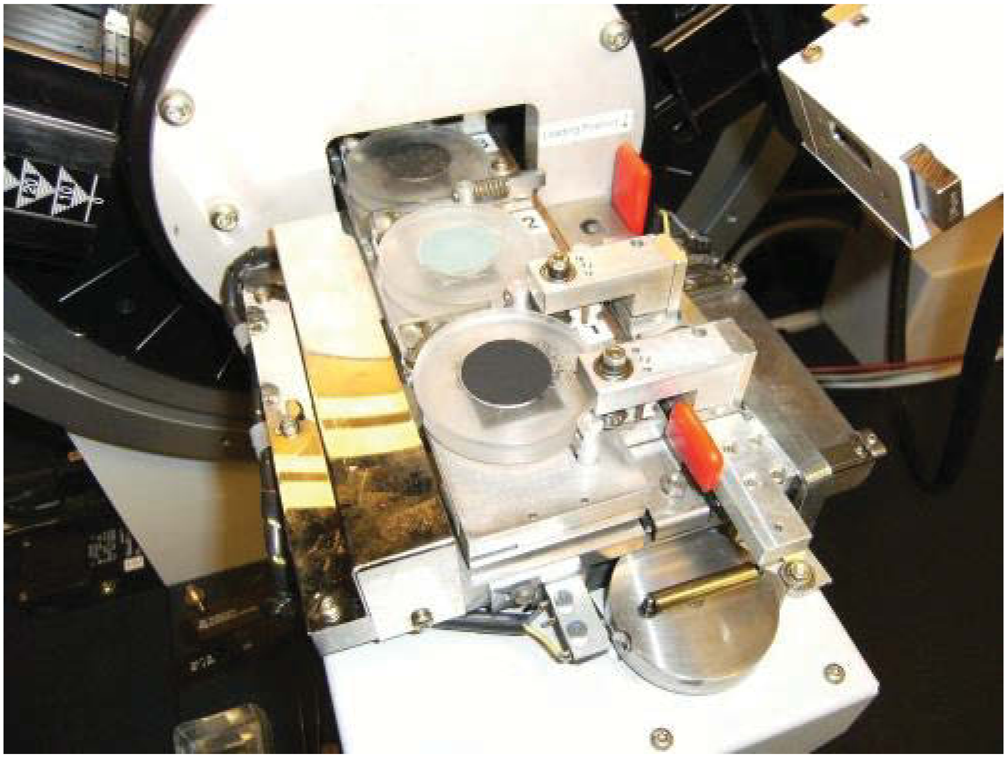


Figure 2.6. Powder XRD sample holder[15]

2.7 Scanning electron microscopy (SEM):

A scanning electron microscope is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing secondary electron signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. An SEM with sufficient beam voltage and sample conductivity can achieve resolution better than 1 nm. A schematic of a scanning electron microscope is shown in Figure 2.7. SEM images were obtained for the platinized semiconductors to evaluate the platinum morphology on the semiconductor photocatalysts.

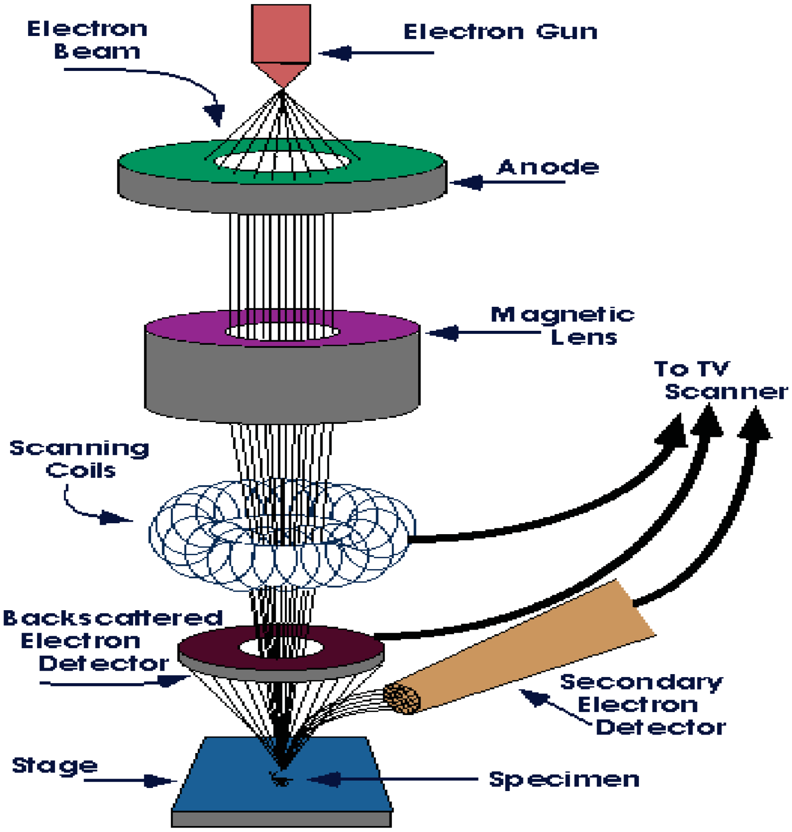


Figure 2.7. Schematic of scanning electron microscope[16]

2.8 Inductively coupled plasma optical emission spectroscopy (ICP-OES) :

ICP/OES is one of the most popular analytical tools for trace element determination in a sample. The technique is based upon the spontaneous emission of photons from atoms and ions that have been excited in an RF discharge. Liquid and gas samples are injected directly into the instrument, Extraction or acid digestion is required for solid samples. The sample injected is converted to an aerosol and directed into the plasma. Inductively coupled plasma (ICP) sustains a temperature of approximately 10000 K which vaporizes the sample. Elements in the sample were liberated as free atoms in the gaseous state. Collisional excitation within the plasma gives additional energy to the atoms, promoting them to excited states. Both the atomic and ionic excited state species then emit photons and come to the ground state. The wavelength of the photons can be used to identify the elements. The total number of photons is directly proportional to the concentration of the originating element in the sample. Schematic of ICP-OES is mentioned in the Figure 2.8. This technique was used in this research in order to determine the trace elements in a liquid sample resulting from photocorrosion.

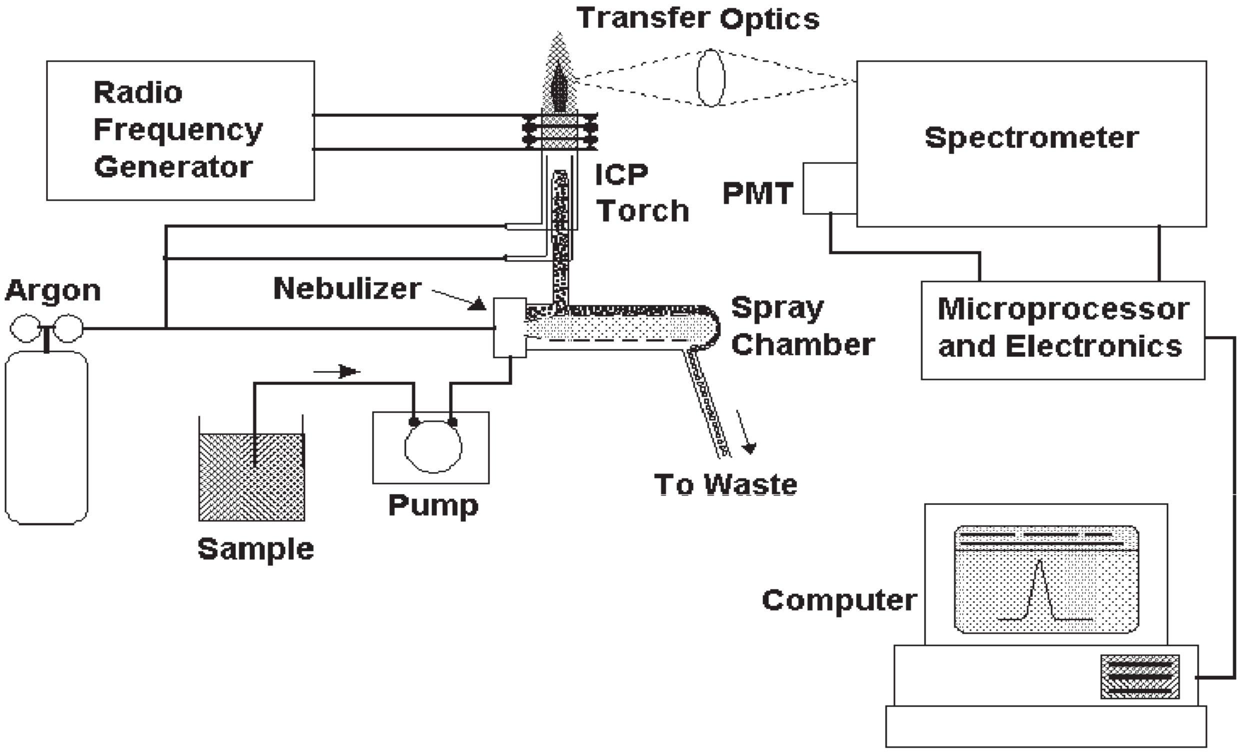


Figure 2.8. Schematic of ICP-OES[17]

2.9 Gas chromatography:

Gas chromatography (GC) is used in for separating and analyzing compounds that can be vaporized without decomposition**.** Uses of gas chromatography include testing the purity of a particular substance, or separating the different components of a mixture. In GC mobile phase is a carrier gas, usually an inert gas and the stationery phase is a microscopic layer of inert liquid or solid support. Instrumental components of GC were mentioned in Figure 2.9. Gas chromatography was used in the research to detect the gas evolved in the photo experiments.

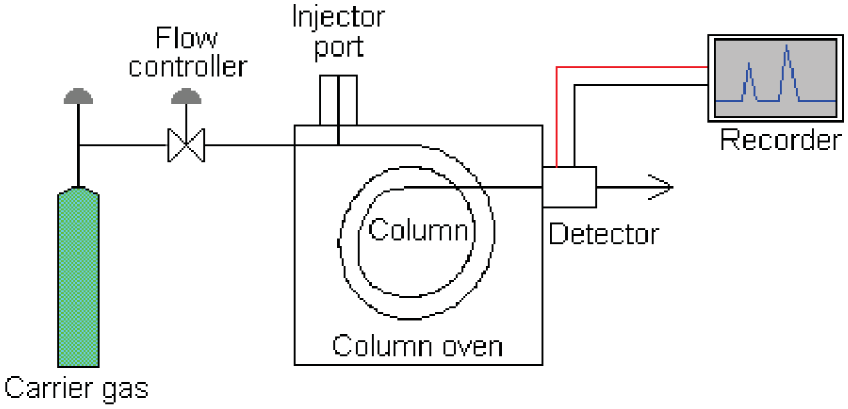


Figure 2.9. Instrumental components of gas chromatography[18]

2.10 RAE system gas-detection tubes:

Rae system gas detection tubes shown in Figure 2.10 enabled to analyze H_2S concentration in landfill. Colorimetric gas detection tubes are an economical solution to gas detection. These tubes are easy to read because of the clear color change and accuracy with no need for calibration.

Figure 2.10 RAE system gas-detection tubes kit

METHODS

2.11 **Adsorbents evaluation setup**:

Adsorbents like carbon black, activated carbon and photocatalyst adsorbents like copper sulfide, silver sulfide, tungsten sulfide and molybdenum sulfide were tested for the hydrogen sulfide removing capacity. Approximately 1 g of the adsorbent was weighed and added to 50 ml of 0.1 M Na_2S solution in a 3-neck round-bottomed flask. Nitrogen was allowed into the system to maintain inert atmosphere. ISE and pH readings were recorded simultaneously. ISE (Ion selective electrode) readings were noted at regular intervals. ISE readings correspond to the sulfide removed from the system. From the calibration curve, the amount of sulfide removed was determined.

2.12 Measuring ISE (Ion Selective Electrode) readings:

A solution of 0.01M Na_2S was prepared which is used as a source of scrubbed H_2S. Electro-potential and pH of this solution were measured and the pH was adjusted to 5 with 0.1 M HCl. With the decrease in pH we observed an increase in the potential.

2.13 Photosystem set-up:

1. ***Platinization of sulfides:***
   a. To increase the efficiency the photocatalyst, adsorbents were platinized. Two different methods were followed for platinization. In the first method, 0.00116 moles of chloroplatinic acid (H_2PtCl_6) was added to 75 ml of 0.25 M acetic acid. To this solution 0.06921 moles of the photocatalyst was added and ultrasonic stirring was carried out for about a minute. The solution was de-aerated with argon gas for 30

min. This was irradiated with a 500 W xenon arc lamp until the color change (yellow-dark green) was observed.

b. Second is the borohydride reduction method. A 0.1 g quantity of adsorbent was added to 550 ml of 0.05 M $NaBH_4$ and stirred. To this solution 0.673 g of chloroplatinic acid was added. Precipitate (platinized photocatalyst) formed was filtered and used.

2. ***Photosystem:***
About 0.069 moles of photocatalyst was weighed and added to a test tube which has 25 ml of 0.24 M sodium sulfide and 25 ml of 0.35 M sodium sulfite. This was then exposed to simulated sunlight (1000 W xenon arc lamp) for two hours. The quantity of gas evolved was measured using an inverted graduated cylinder.

2.14 Preparation of polysulfides:
Polysulfides were prepared as new photocatalyst semiconductor materials, where the following reactions are expected. Sulfide in the system gives free sulfur and 4 electrons; metal sulfide reacts with the free sulfur to form polysulfides and this polysulfide in the presence of light gives metal sulfide and free sulfur.

$$2S^{2-} \longrightarrow 2S^{\circ} + 4e^{-}$$

$$MS_2 + 2S^{\circ} \longrightarrow MS_4 \qquad \text{(dark)}$$

$$MS_4 \xrightarrow{\text{sunlight}} MS_2 + 2S^{\circ} \qquad \text{(light)}$$

$$4e^{-} + 4H_2O \longrightarrow 4H_2 + 4OH^{-}$$

Polysulfides were prepared using the following two methods:

1. ***Wet method*****:** 0.1 M sodium sulfide solution was prepared and 0.3 moles of sulfur powder was added to it. This solution was heated under nitrogen to provide inert atmosphere. This is further heated and then cooled down to -9°C to -15 °C for crystallization. Orange-red colored crystals were formed. Powder X-ray Diffraction was performed for further results.
2. ***Dry method*****:** 0.01 moles (2.4018 gms) of sodium sulfide and 0.03 moles (0.9618 gms) of sulfur were taken into a round-bottomed flask and heated to about 140 °C overnight under nitrogen to provide inert atmosphere. Orange red crystals were formed. Powder X-ray Diffraction was performed for further results.

2.15 RAE system gas-detection tubes:

Both the ends of the tubes have to be broken by using tip breaker in the hand pump. The tube is then inserted into the pump inlet with arrow on the tube facing towards the pump. A sample of 100 ml of Landfill gas was then pulled into the tube by using the pump from a gas tight environment. 2 min trail was performed. The test tubes are based on the reaction of hydrogen sulfide with mercuric chloride. The tubes used for analyzing mercaptans contain lead sulfate.

2.16 Gas chromatography:

Gas evolved from the photo-experiments was tested by manually injecting samples into the gas chromatograph. Temperature of injector, column and detector were 43 °C, 63 °C and 32 °C respectively. Type of column used was a Poropak Q adsorbent packed in stainless steel tube that was 8 feet long and 0.125 inch in diameter. The particle size of the adsorbent was 80/100 mesh. Detector temperature was maintained at 50 mA. Argon was used as a carrier gas so as to increase the difference in thermal conductivity between mobile phase and analyte. This greatly improved the detector sensitivity for H_2 over conventional He gas.

RESULTS

3.1 Polysulfide formation:

Color change was observed for the solution in a round bottomed flask as shown in Figure 3.1. At the end of the experiment, crystals were formed. Assuming that the crystals formed were sodium tetrasulfide, different experiments were done to analyze the precipitate through powder X-ray diffraction.

a. Copper sulfate solution was prepared and few drops were added to the crystals. The solution was filtered and the precipitate was dried. This was then subjected to powder XRD. The expected result was CuS_4; instead, the observed results were sulfur powder as shown in Figure 3.2

b. A solution of silver nitrate solution was prepared and added to the crystals (NaS_4) formed from the experiment. A precipitate was formed which was then collected and dried. The powder precipitate was then processed for powder X-ray diffraction to confirm their structures. The result expected was AgS_4; instead, silver sulfide sulfate and sulfur was obtained as shown in Figures 3.3 and 3.4

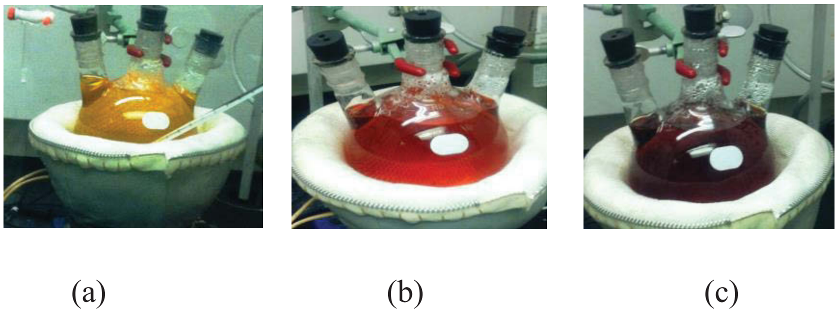

(a) (b) (c)

Figure 3.1. Color change of the solution during the experiment (a) Initial color of the solution (b) color of solution as the experiment progressed (c) Final color of the solution

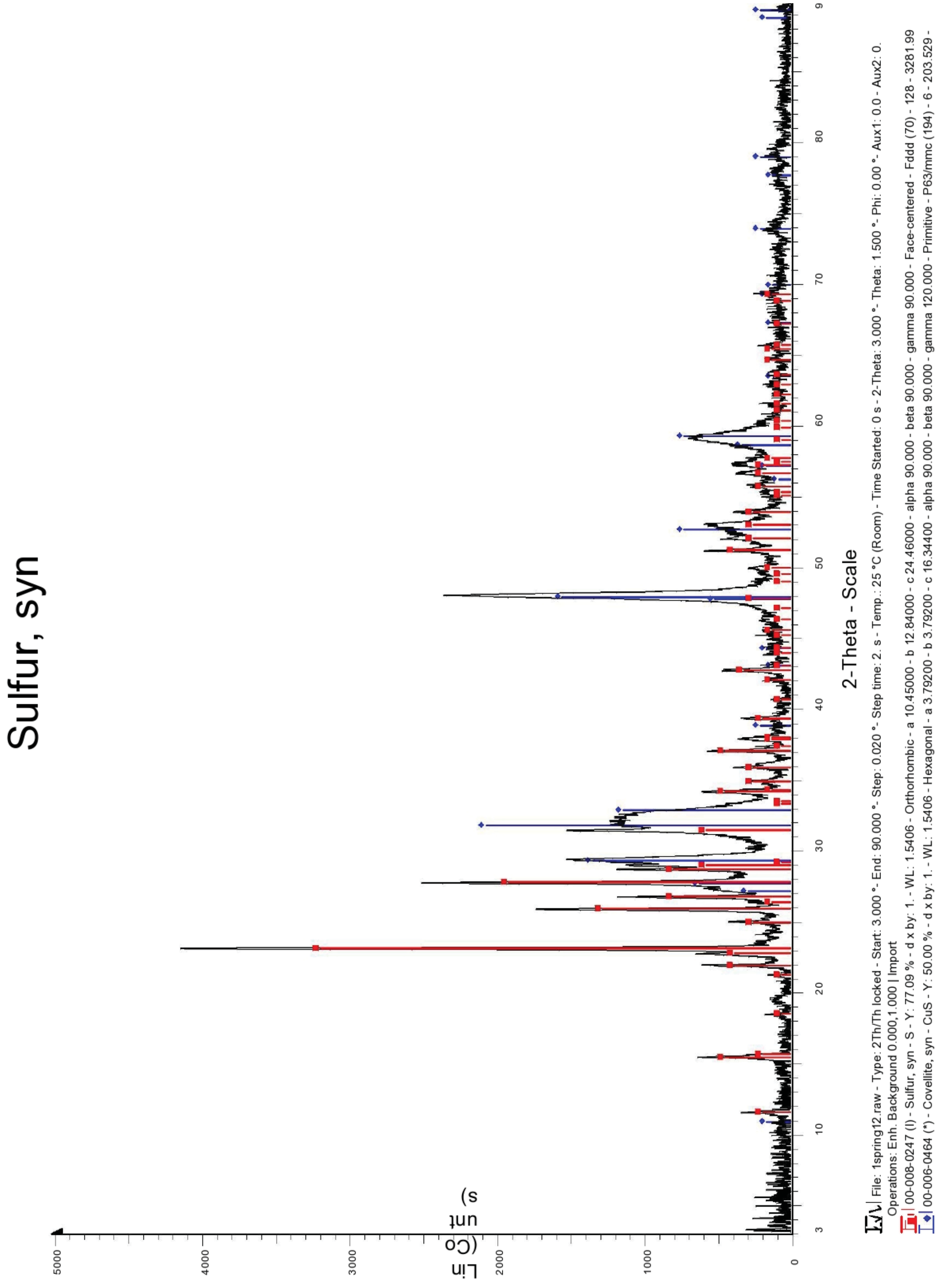


Figure 3.2. XRD results of precipitate formed by adding polysulfide to copper sulfate solution from method-1

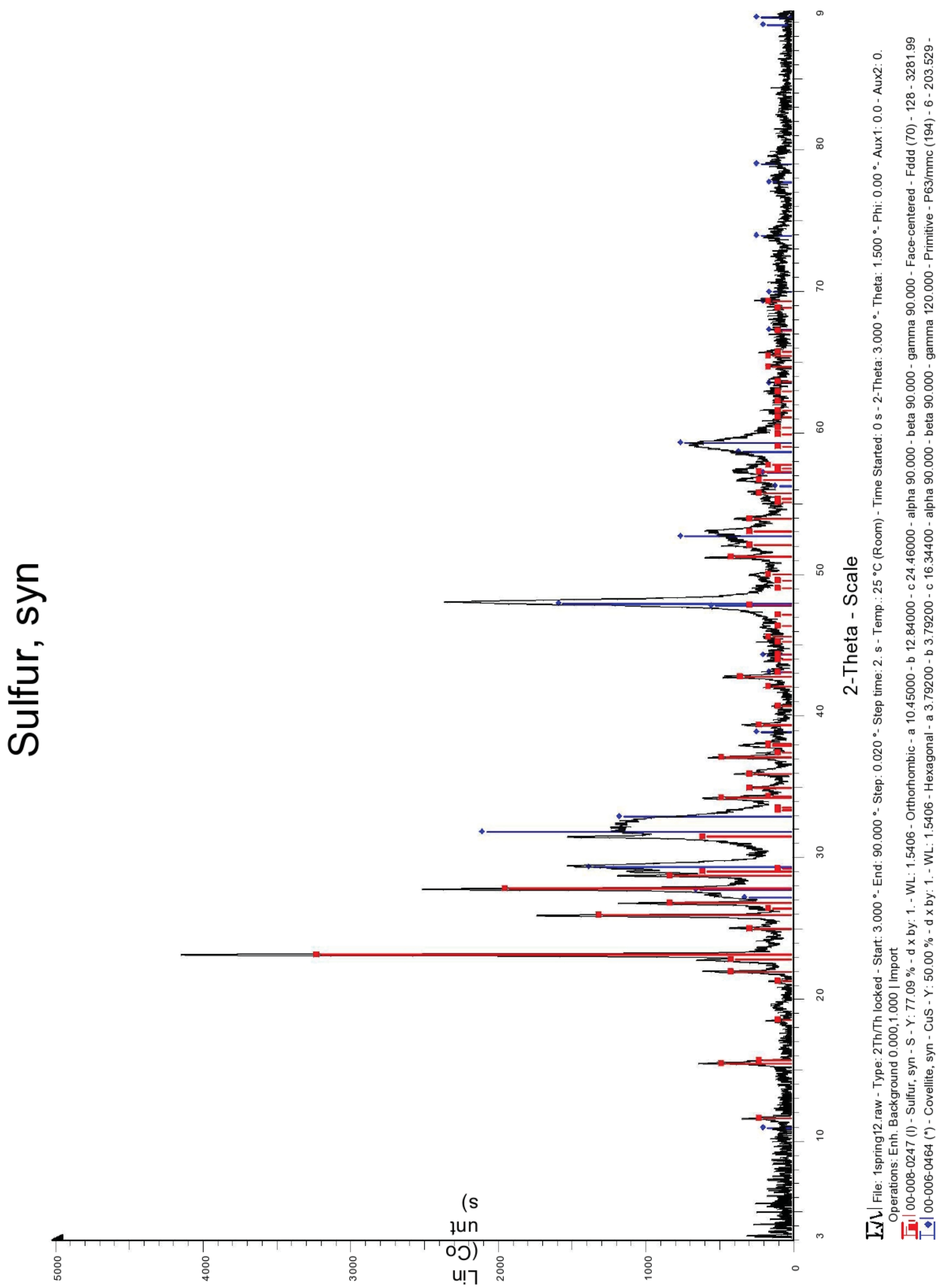


Figure 3.3. XRD results of precipitate formed by adding polysulfide to silver nitrate solution from method-1

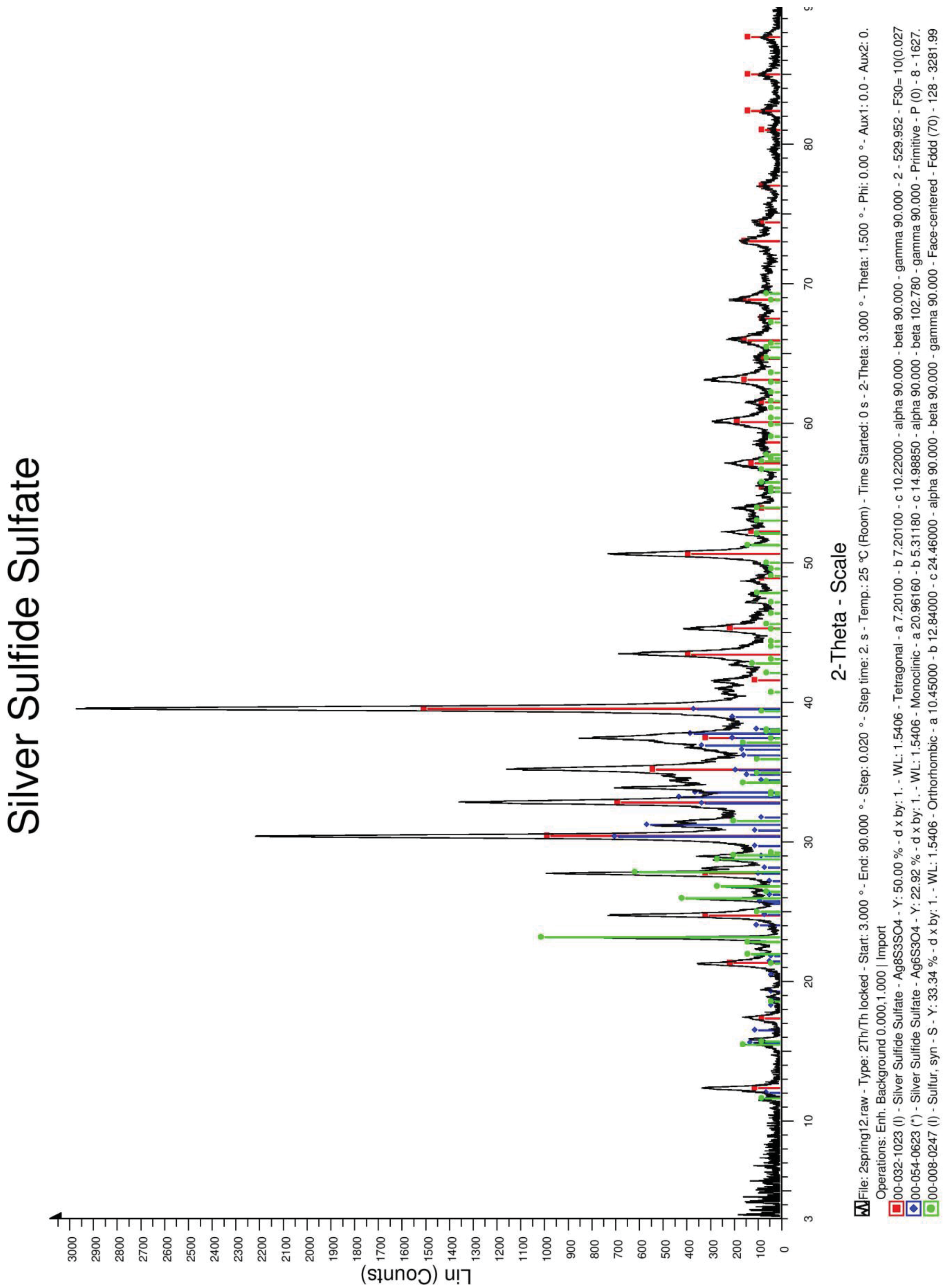


Figure 3.4 XRD results of precipitate formed by adding polysulfide to silver nitrate solution from method-1

Results showed that there is no polysulfide formation, so we tried a solid state reaction in which 0.01 moles of Na_2S and 0.03 moles of sulfur were mixed and heated overnight to 140°C under nitrogen. Orange-red crystals were formed. Powdered X-ray diffraction was done. Results were consistent with the previous experiment. Silver sulfide sulfate and sulfur was formed as shown in Figure 3.5 and 3.6 respectively

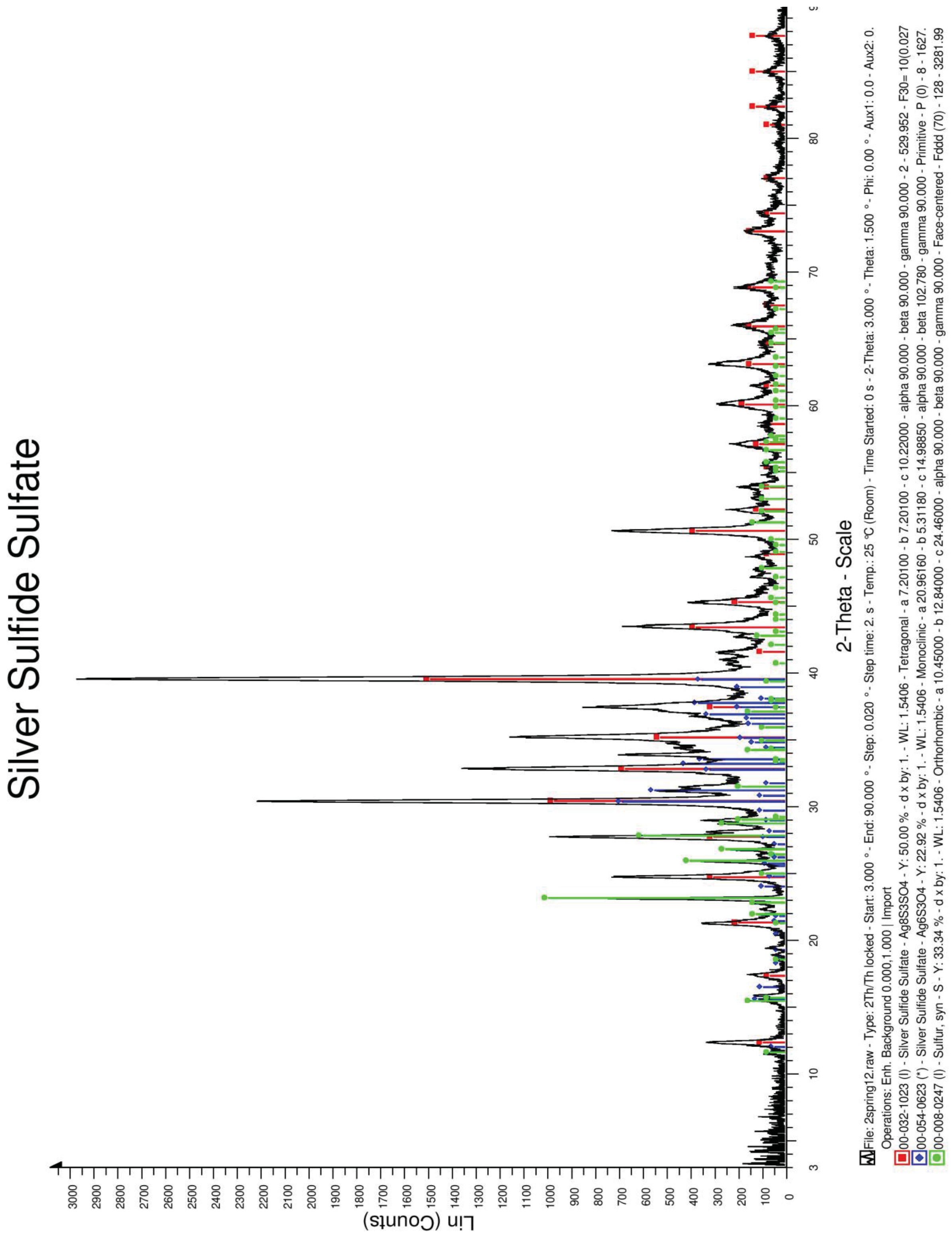


Figure 3.5. XRD results of precipitate formed by adding polysulfide to silver nitrate solution from method-2

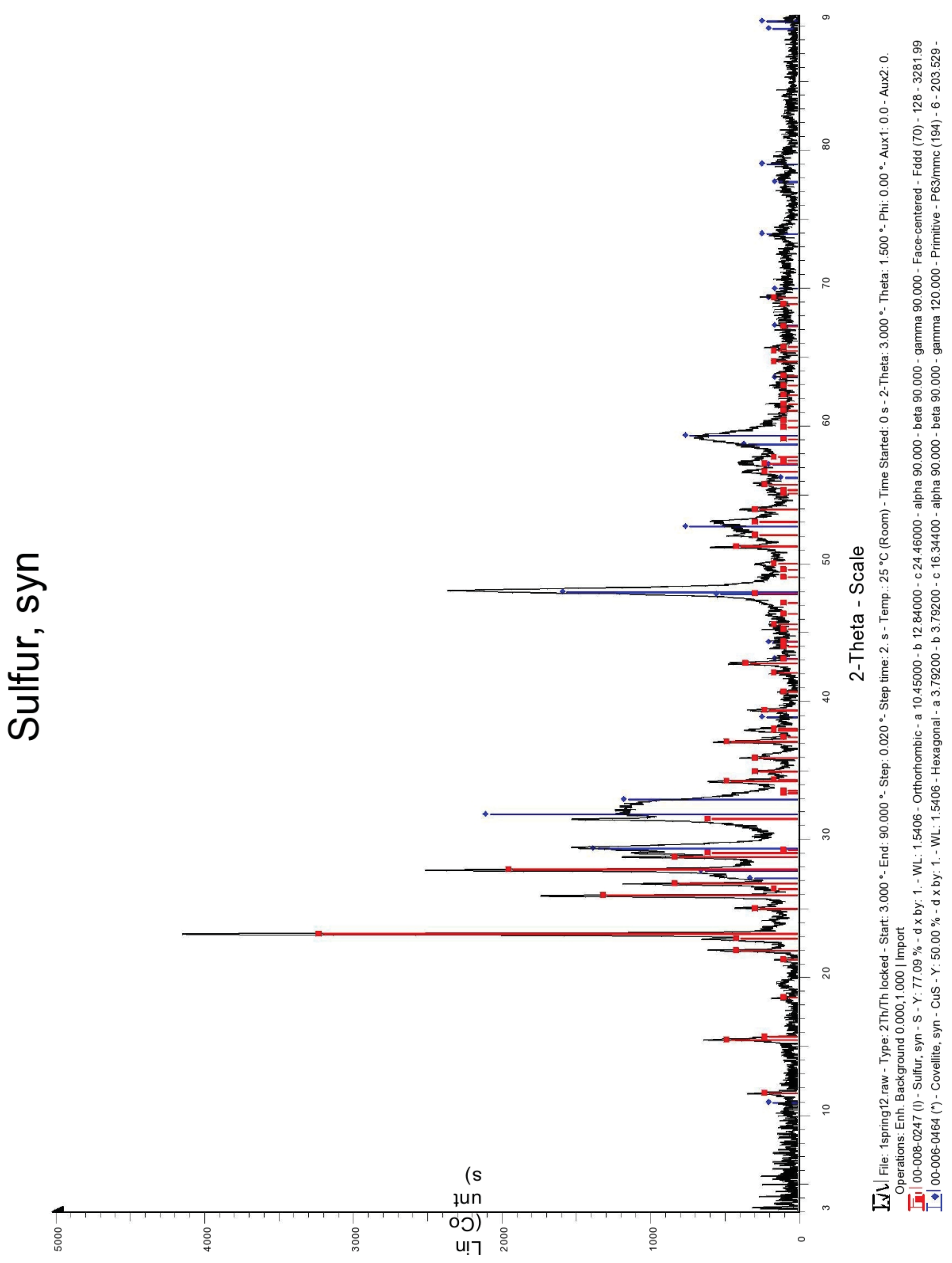


Figure 3.6. XRD results of precipitate formed by adding polysulfide to copper sulfate solution from method-2

XRD results from Figures 3.2, 3.3 and 3.6 shows that either sulfur is formed in both the cases or there is unreacted sulfur in the system. From all the XRD results it is evident that there is no polysulfide formation and the results were same in both processes.

3.2 ISE Calibration curve:

0.01 M Na_2S stock solution was prepared and then a serial dilution was done to prepare 5×10^{-3} M, 2×10^{-3} M, 1×10^{-3} M, 5×10^{-4} M, 2×10^{-4} M sulfide solutions and the ISE readings were measured. A calibration plot was prepared as shown in Figure 3.7 at a constant pH of 8

X-axis: Concentration of sulfide species

Y-axis: Potential

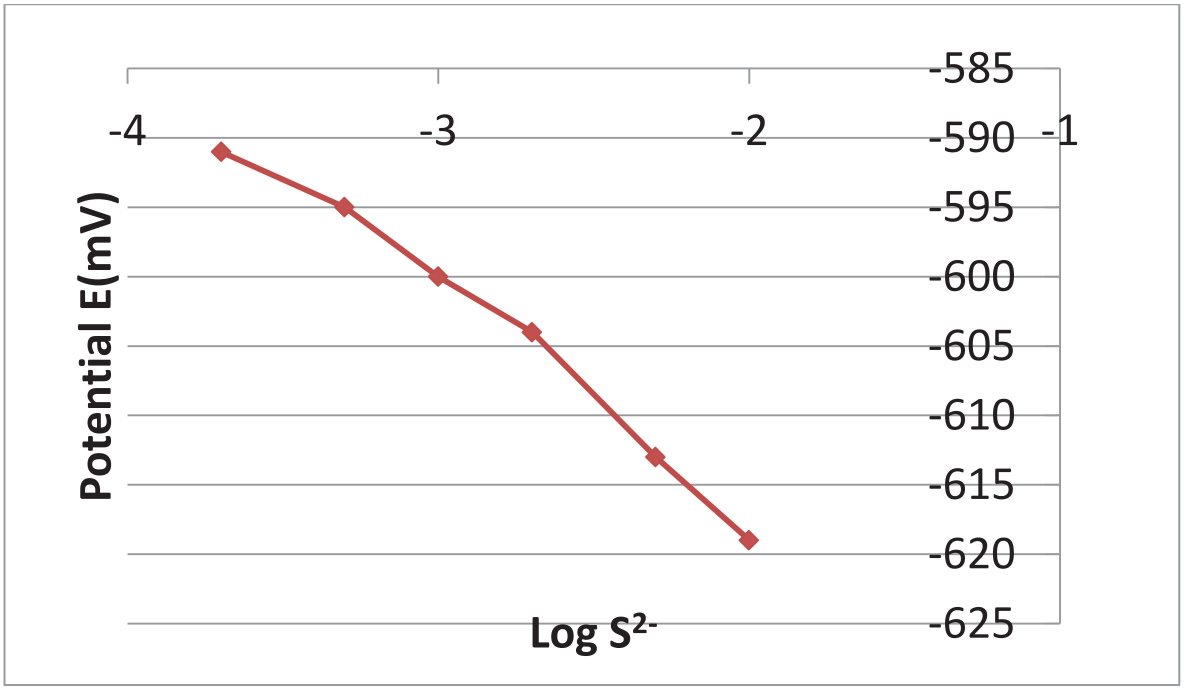


Figure 3.7. Calibration curve for sulfide ion selective electrode at pH 8

3.3 pH dependence of ISE:

A potential shift of 30 mV/unit pH is observed at constant sulfide concentration (10^{-2} M) when there is a drop in pH from 12 to 8. Further decrease in pH showed that there is a potential shift of about 60 mV/unit pH. This is explained using the Nernst equation.

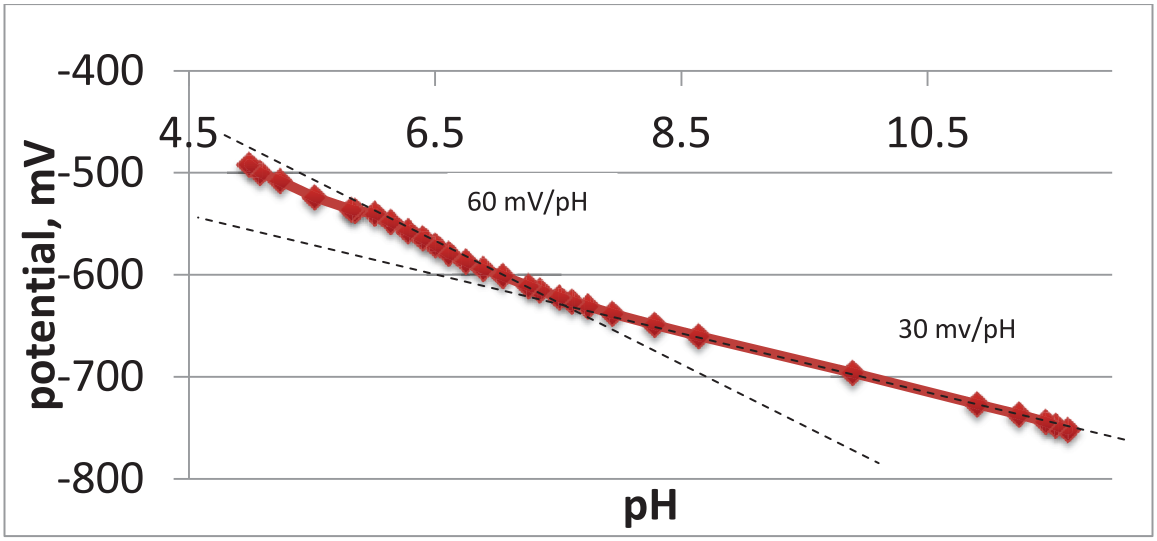


Figure: 3.8 pH dependence of ISE

Nernst Equation: In electrochemistry, the Nernst equation relates the equilibrium reduction potential of a half-cell in an electrochemical cell to the standard electrode potential, temperature, activity and reaction quotient of the underlying reactions and species used

$$E_{\text{cell}} = E^{\ominus}_{\text{cell}} - \frac{RT}{zF} \ln Q$$ (Total cell potential)

Where

- E_{cell} is the cell potential
- E^{o}_{cell} is the standard cell potential at the temperature of interest
- R is the universal gas constant
- T is the absolute temperature

- F is the Faraday constant, the number of coulombs per mole of electrons

  $F = 9.648\ (24)\times10^4\ C\ mol^{-1}$

- z is the number of moles of electrons transferred in the cell reaction or half-reaction
- Q is the reaction quotient

  At room temperature (25 °C), RT/F may be treated like a constant and replaced by 25.693 mV for cells. Changing from natural logarithm to base 10, this factor is multiplied by 2.303 to become 59.16 mV

So the equation can be written as

$$E = E^0 - \frac{0.05916\ \mathrm{V}}{z} \log_{10} \frac{a_{\mathrm{Red}}}{a_{\mathrm{Ox}}}.$$

$$S^{2-} \longrightarrow S^o + 2e^- \qquad (1)$$

$$HS^- \longrightarrow S^o + H^+ + 2e^- \qquad (2)$$

$$H_2S \longrightarrow S^o + 2H^+ + 2e^- \qquad (3)$$

$$E_{\mathrm{cell}} = E^{\ominus}_{\mathrm{cell}} - \frac{RT}{zF} \ln Q$$

Z = 2 in all equations

From equation 1:

$E=E^o - RT/2F \ln S^o/ [S^{2-}]$

$E=E^o + RT/2F \ln S^{2-}$ (as activity of solid is equal to 1)

$E=E^o + 0.059/2 \log S^{2-}$ (as RT/F at room temperature is 0.059 V)

$E=E^o + 0.029 \log S^{2-}$

$dE/ d[H^+] = 0$ for S^{2-}

From equation 2: At pH 8 – 12

$E=E^o - RT/2F \ln S^o \cdot [H^+] / [HS^-]$

$E=E^o + RT/2F \ln [HS^-] / [H^+]$

$E=E^o + 0.059/2 [\log [HS^-] - \log [H^+]]$

$E=E^o + 0.029 [\log [HS^-] – \log [H^+]]$

$dE/ d[H^+] = 29$ mV for HS^-

From equation 3: At pH 5 - 8

$E=E^o - RT/2F \ln S^o \cdot [H^+]^2 / [H_2S]$

$E=E^o + RT/2F \ln [H_2S]/ [H^+]^2$

$E=E^o + 0.059/2 [\log [H_2S] – 2 \log [H^+]]$

$E=E^o + 0.029 [\log [H_2S] – 2 \log [H^+]]$

$dE/ d[H^+] = 59$ mV for H_2S

From equations 1, 2 and 3 it is shown that a difference of 30 mV/pH potential should be obtained for pH between 8 and 12 and a difference of 60 mV/pH potential should be had for pH between 5 and 8, in good agreement with our observations.

3.4 Role of adsorbents: carbon effect/ semiconductors:

Different adsorbents like carbon black (Vulcan XC-72), activated carbon, TiO_2, silica, Dowex® (1X2-20 anion exchange resin), copper II sulfide and Al_2O_3 were tested for the capacity to adsorb H_2S. Results are shown in Figure 3.9.

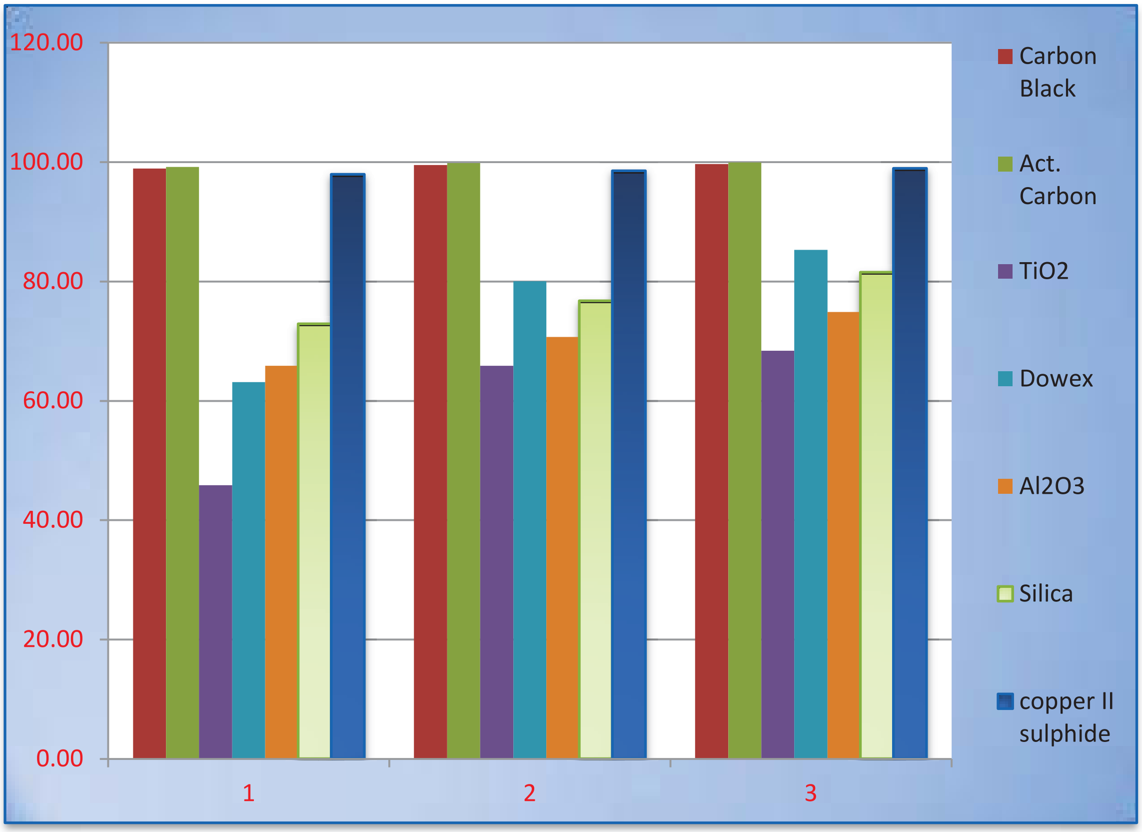


Figure 3.9. Percentage of sulfur removed: Grams of adsorbent used vs. % of sulfur removed for various adsorbents

Semiconductors like CuS, MoS_2, WS_2 and Ag_2S were also tested for adsorption capacity. Results are as shown in Figure 3.10. Almost all the sulfide is removed in each case.

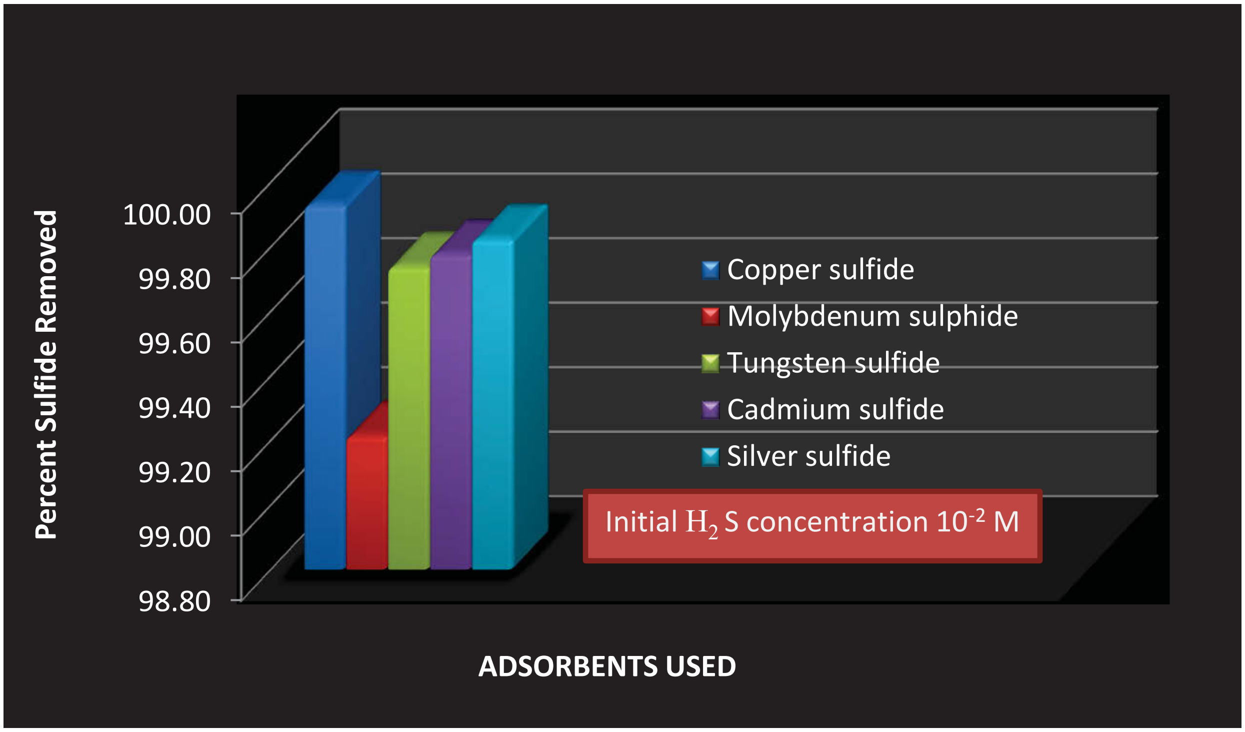


Figure 3.10. Adsorption capacity of various semiconductors

Carbon effect:

Initial adsorbents tested were carbon black and activated carbon. A 50 ml 10^{-2} M solution of Na_2S was taken into a 3-neck round bottomed flask and 1.0 g of adsorbent was added to the system while monitoring pH and ISE. The results are shown in Table 3.1. Almost all the sulfide present in the system seemed to be adsorbed onto the surface of carbon as shown in Figure 3.9

Table 3.1. pH and ISE readings of adsorption of H_2S on carbon

S.No	Adsorbent	pH (Initial)	pH (final)	ISE (initial)	ISE (final)
1	Vulcan XC-72	11.90	7.99	-752 mV	-610 mV
2	Activated carbon	11.83	7.79	-736 mV	-495mV

At this stage it was difficult to conclude whether carbon is an adsorbent or catalyst or a reagent. The filtered solution from testing was studied with UV-Visible spectrometry and IR spectroscopy. Both UV-VIS and IR results showed the presence of sodium sulfate and sodium thiosulfate in the solution as shown in Figures 3.11-3.14.

Figure 3.11 and 3.12 shows the UV-VIS results where the absorption peaks corresponds to sodium sulfate and sodium thiosulfate.

Figures 3.13 and 3.14 shows IR results where the absorption peaks corresponds with sodium sulfate and sodium thiosulfate.

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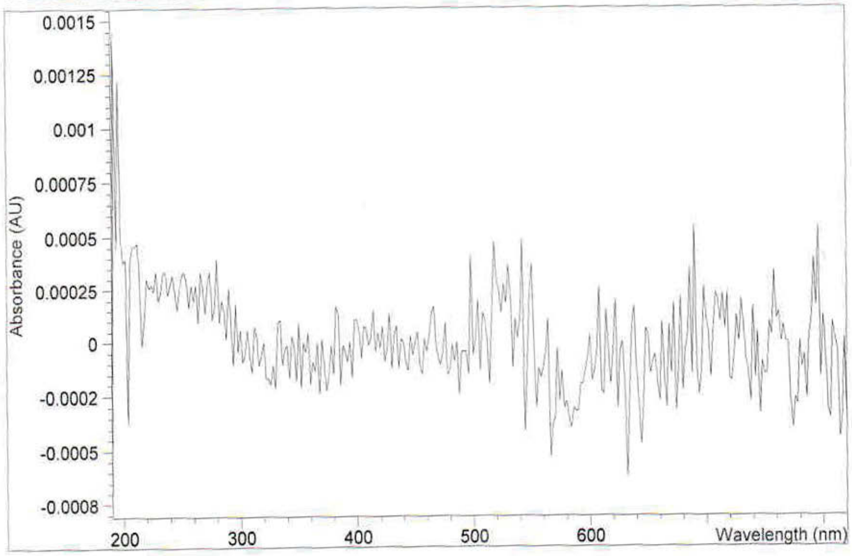
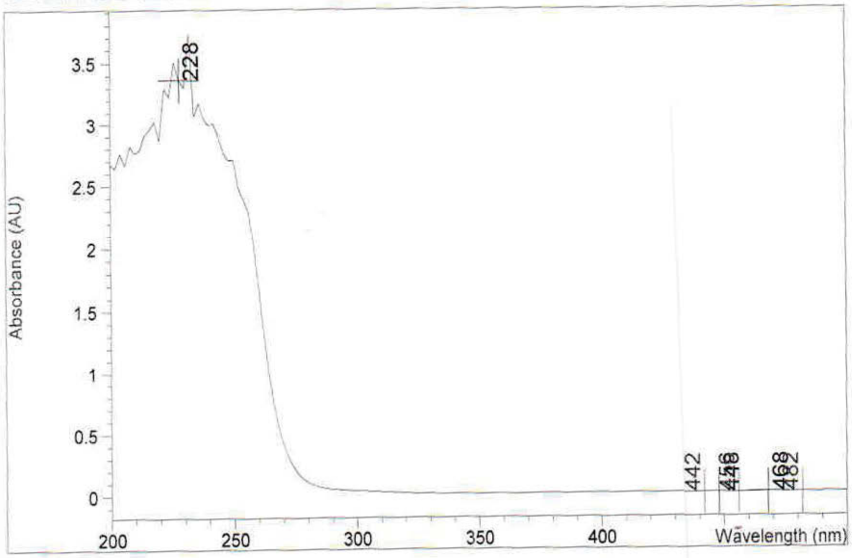


Overlaid Sample Spectra



Sample/Result Table

```
 #  Name                 Peaks(nm)      Abs(AU)  Valleys(nm)     Abs(AU)
---------------------------------------------------------------------------
 1                          228.0       3.36430        442.0  1.0971E-2
 1                          468.0    1.3901E-2         456.0  1.1124E-2
 1                          448.0    1.2070E-2         482.0  1.1734E-2
```

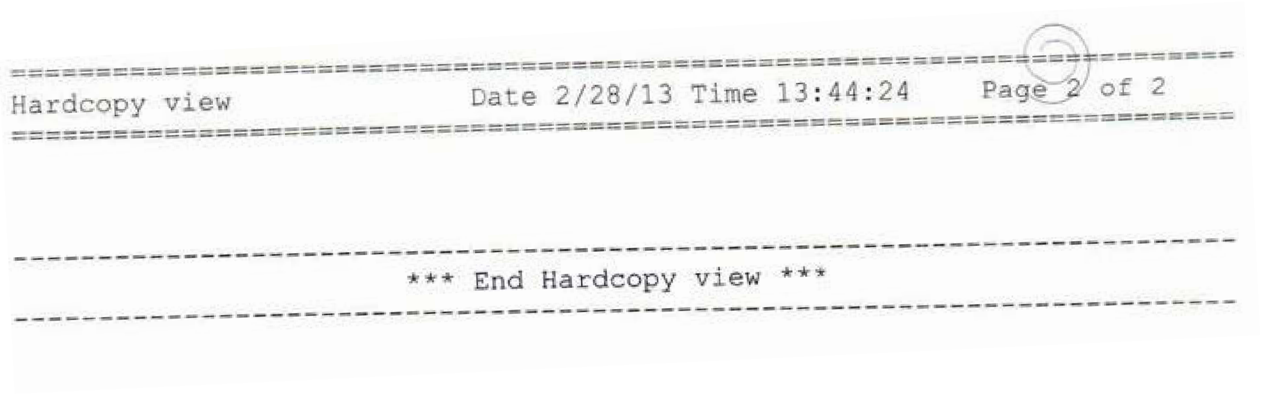


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Figure 3.11 UV-VIS results of a sulfide titration of carbon adsorbent sample from 200-500 nm wavelength

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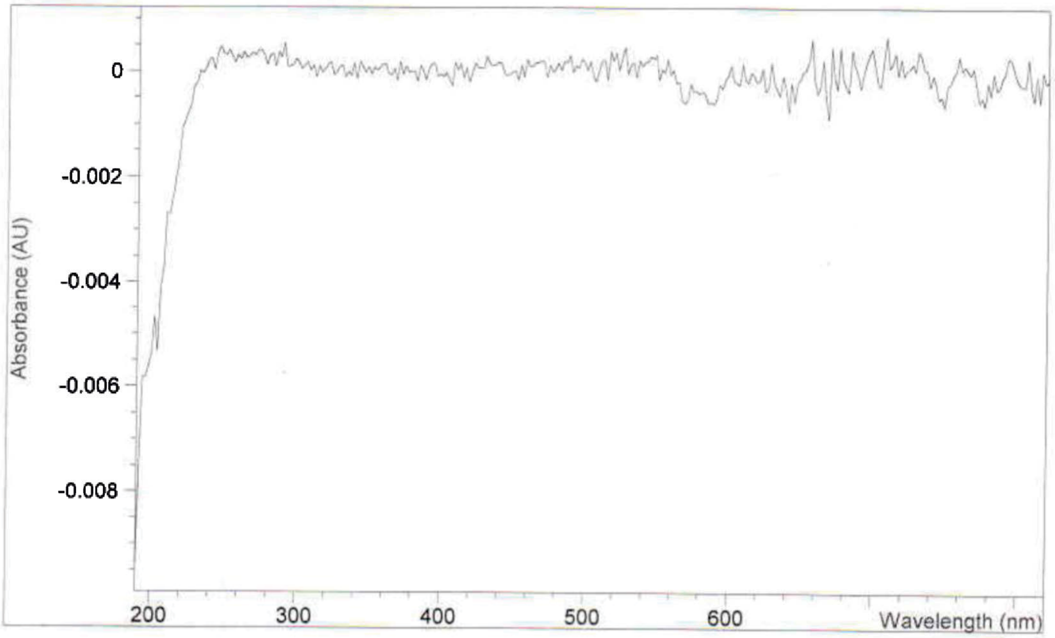

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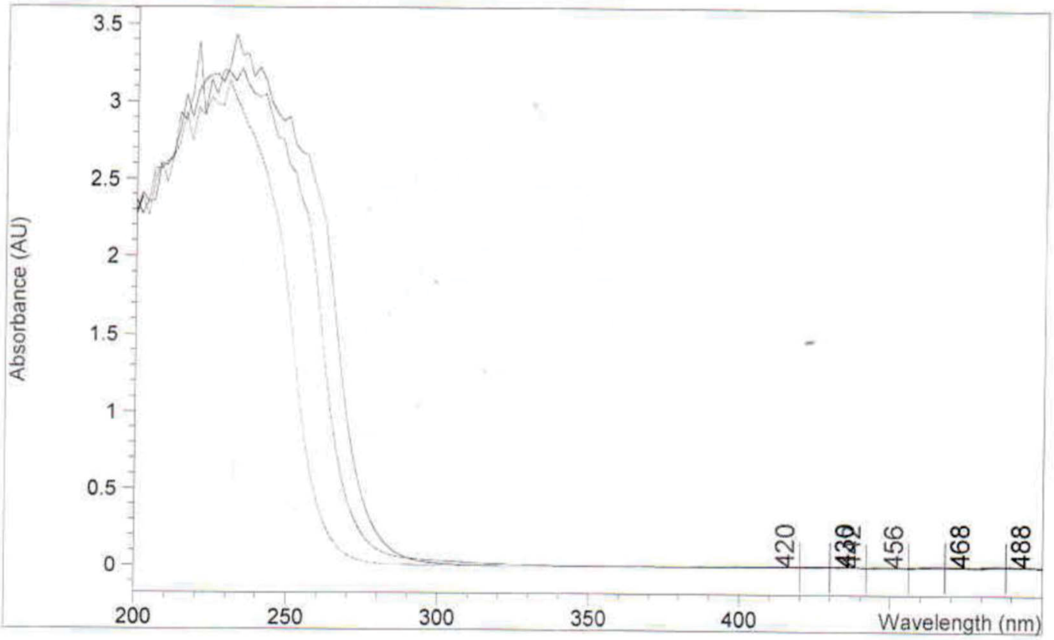
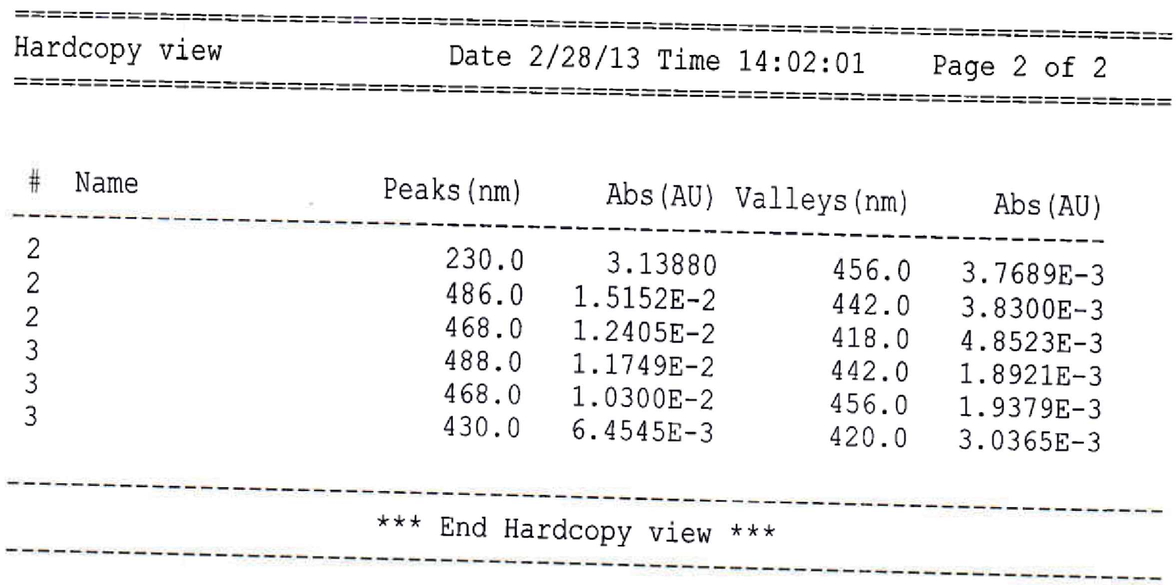


Sample/Result Table

#	Name	Peaks (nm)	Abs (AU)	Valleys (nm)	Abs (AU)
1		232.0	3.43930	442.0	-2.8992E-3
1		488.0	5.9662E-3	456.0	-2.7161E-3
1		468.0	3.9368E-3	418.0	-1.4801E-3



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 #  Name                   Peaks(nm)      Abs(AU) Valleys(nm)     Abs(AU)
-----------------------------------------------------------------------
 2                             230.0      3.13880       456.0  3.7689E-3
 2                             486.0   1.5152E-2       442.0  3.8300E-3
 2                             468.0   1.2405E-2       418.0  4.8523E-3
 3                             488.0   1.1749E-2       442.0  1.8921E-3
 3                             468.0   1.0300E-2       456.0  1.9379E-3
 3                             430.0   6.4545E-3       420.0  3.0365E-3

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Figure 3.12. Overlaid UV-VIS spectra of test solution , sodium sulfate and sodium thiosulfate

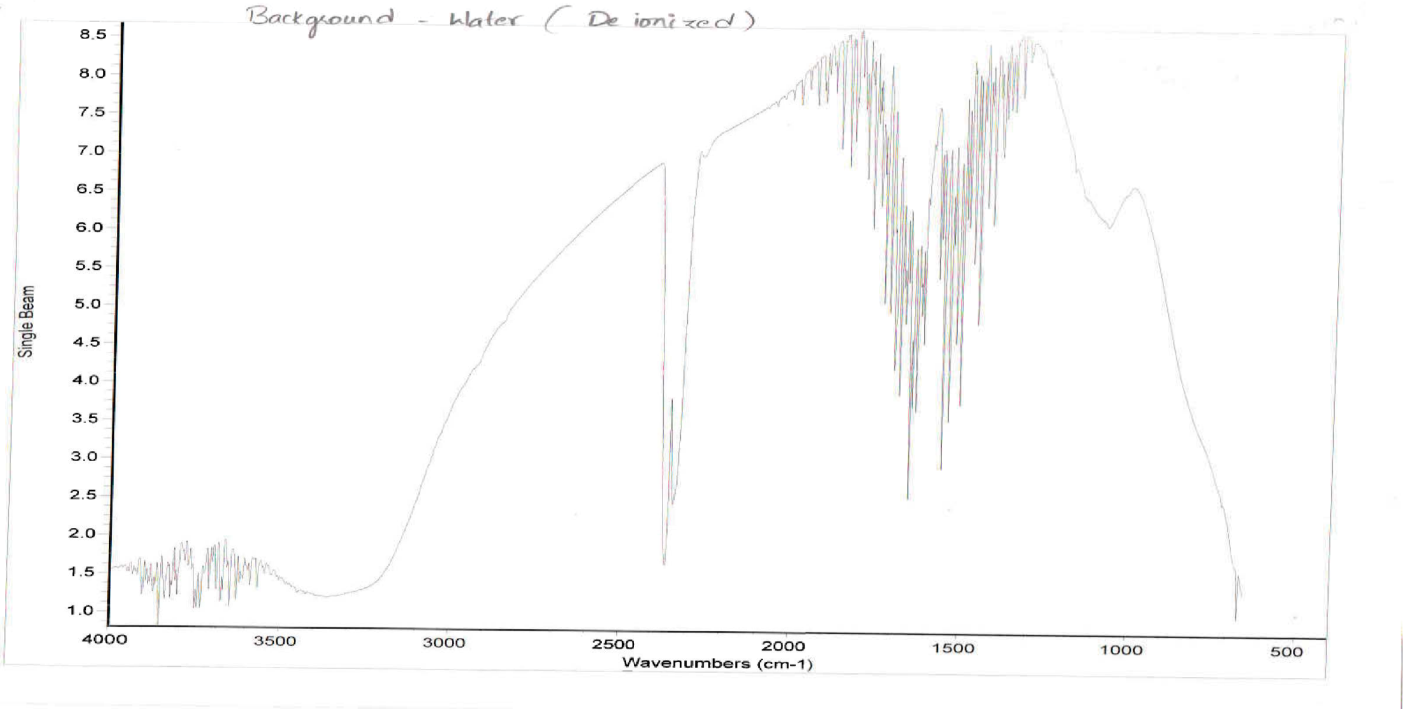


Figure 3.13 IR spectra of de-ionized water vs air

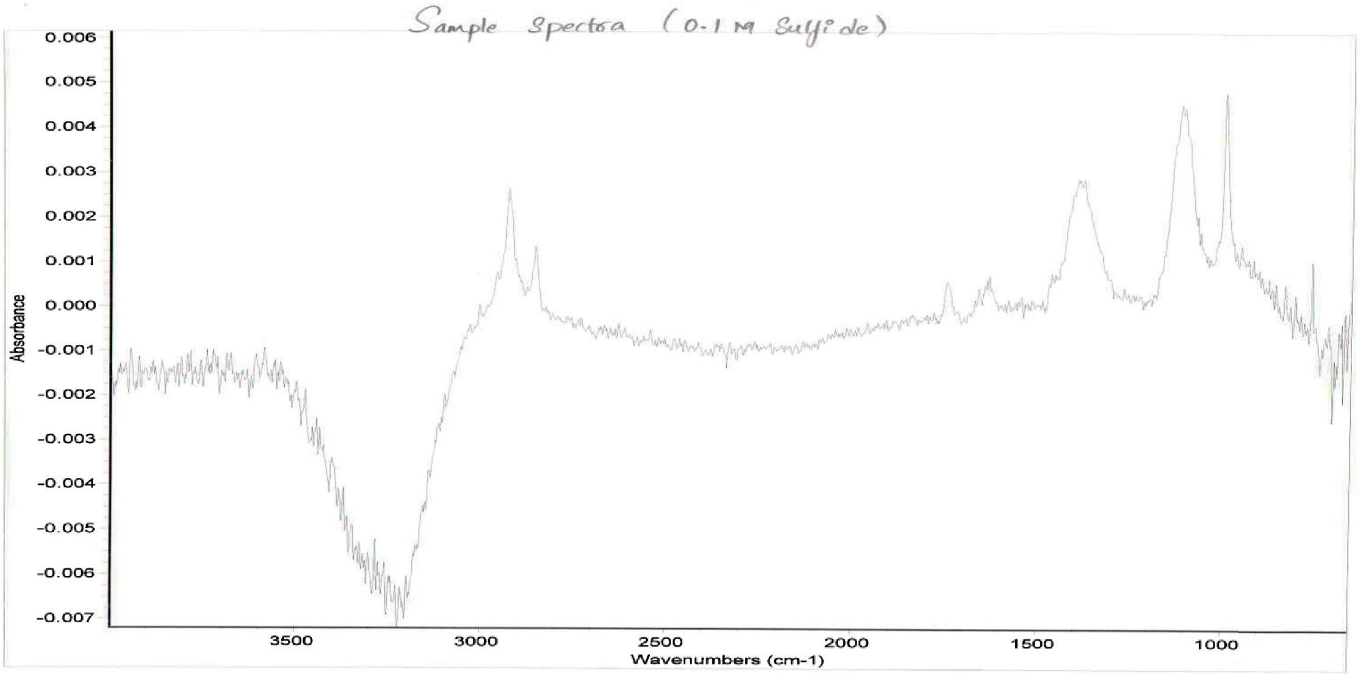


Figure 3.14 IR spectra of the sulfide titration of carbon adsorbent sample

The presence of oxygen in the system might have resulted in the products like sodium sulfate and sodium thiosulfate which are not sensitive to the Ag_2S ISE. Consequently, a four neck 300 ml round bottom flask was designed to maintain an oxygen free atmosphere as shown in Figure 3.15.

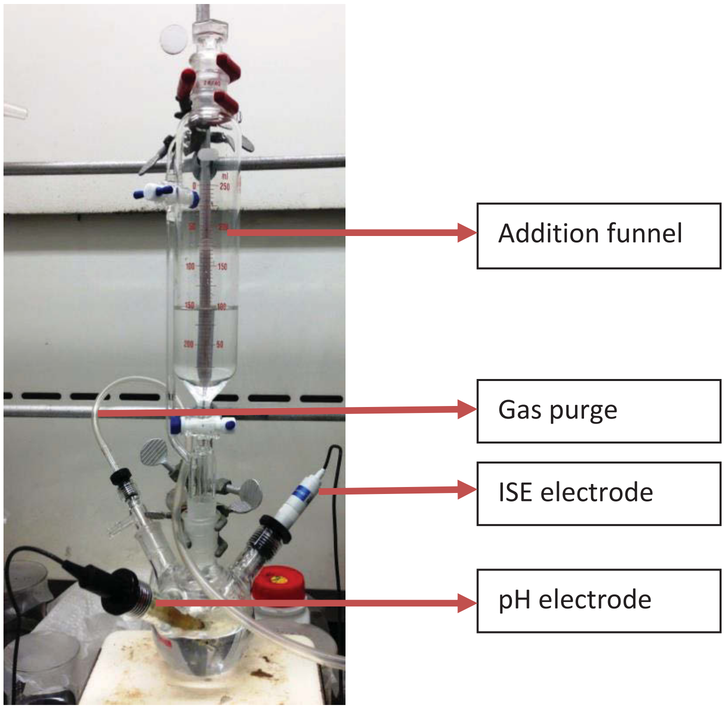


Figure 3.15. Four neck round bottom flask showing pH electrode, ISE electrode, additional funnel and gas purge.

Necks are used for ISE, pH electrode, gas inlet and addition funnel. A volume of 50 ml water was taken into the round bottom flask and 1.0 g of adsorbent was added to it. pH and ISE were monitored continuously in an inert atmosphere (bubbling argon gas). A 5 ml solution of 10^{-2} M Na_2S was added to the system from the addition funnel and pH and ISE readings were recorded. After a certain time interval (about 12 hours) pH and ISE readings were recorded again and another 5 ml of 10^{-2} M Na_2S solution was added. This was repeated again until there was no change in the ISE reading. Results were shown in the Table 3.2

Table 3.2. pH and ISE readings of adsorption of H_2S on Vulcan XC-72 under controlled atmosphere

S. No	Total volume of sulfide	pH (initial)	pH (Final)	ISE (Initial)	ISE (final)	$[S^{2-}]$ M (initial)	$[S^{2-}]$ M (final)
1	0 ml	6.9	6.9	-99 mV	-99 mV		
2	5 ml	11.44	11.46	-704 mV	-691 mV	2.2×10^{-3}	1.4×10^{-3}
3	10 ml	11.71	11.78	-720 mV	-701 mV	4.7×10^{-3}	2×10^{-3}

3.5 Photo-experiments:

About 0.009 moles of photocatalyst was weighed and added to a test tube that had 25 ml of 0.24 M sodium sulfide and 25 ml of 0.35 M sodium sulfite. This was then exposed to simulated sunlight (1000W xenon arc lamp) for 2 h. The quantity of gas evolved was measured using an inverted graduated cylinder. The separation distance between the aperture of the Xe lamp and the cell was approximately 15 cm.

The expected reaction is as follows:

$$H_2S \xrightarrow{\text{sunlight}} S^0 + 2H^+ + 2e^-$$

$$2H^+ + 2e^- \longrightarrow H_2$$

When a photon hits the surface of a platinized photocatalyst, both electrons and holes are generated. In the presence of platinum (co-catalyst), water is reduced to hydrogen using electrons. Hydrogen sulfide is oxidized to sulfur using holes. A schematic of a photocatalyst particle is shown in Figure 3.16.

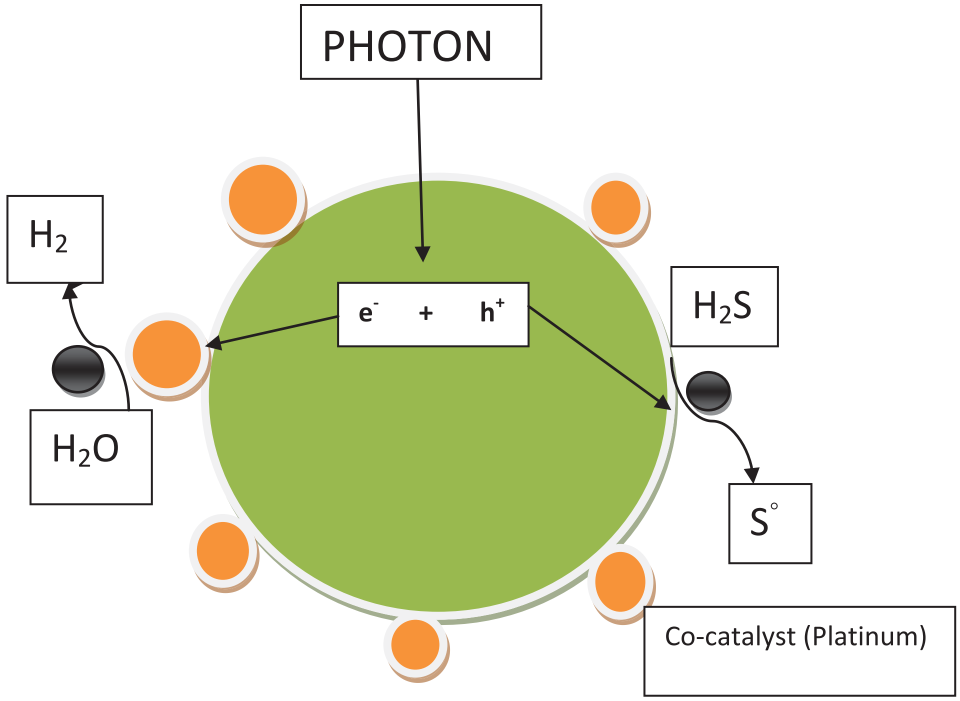


Figure 3.16. Schematic of platinized photo-catalyst particle

Experimental conditions:

Concentration of sulfide: 0.24 M, 25 ml

Concentration of sulfite: 0.35 M, 25 ml

Platinum 1% by weight

1.8 g of photocatalyst

Time: 2 hours

Source: 1000 W Xenon-arc lamp

Photocatalysts tested include cadmium sulfide (CdS), molybdenum disulfide (MoS_2), tungsten disulfide (WS_2), copper sulfide (CuS) and silver sulfide (Ag_2S). Results obtained in each case were tabulated as shown in Tables 3.3-3.7. Gas expansion volume due to heating during the experiment was about 3.5 ml.

Note: Volume of gas evolved mentioned in the Tables below is not corrected for gas expansion.

a. Cadmium sulfide (CdS):

Table 3.3. Gas evolution using CdS at different conditions

CONTENTS IN TEST TUBE	***GAS EVOLVED(ml)***
CdS + H_2O	9
CdS + S^{2-}/SO_3^-	6
Platinized CdS + H_2O	11
Platinized CdS + S^{2-}/SO_3^-	14
CdS + H_2O+ Teflon	10
CdS + S^{2-}/SO_3^- +Teflon	6
Platinized CdS + H_2O+ Teflon	11
Platinized CdS + S^{2-}/SO_3^-+ Teflon	17

b. Copper sulfide (CuS):

Table 3.4. Gas evolution using CuS at different conditions

CONTENTS IN TEST TUBE	***GAS EVOLVED(ml)***
CuS + H_2O	15
CuS + S^{2-}/SO_3^-	9
Platinized CuS + H_2O	8
Platinized CuS + S^{2-}/SO_3^-	10
CuS + H_2O+ Teflon	10

CuS + S^{2-}/SO_3^- +Teflon	5
Platinized CuS + H_2O+ Teflon	8
Platinized CuS + S^{2-}/SO_3^-+ Teflon	7

c. Molybdenum disulfide (MoS_2):

Table 3.5 Gas evolution using MoS_2 at different conditions

CONTENTS IN TEST TUBE	***GAS EVOLVED***
MoS_2 + H_2O	14
MoS_2 + S^{2-}/SO_3^-	5
Platinized MoS_2 + H_2O	12
Platinized MoS_2 + S^{2-}/SO_3^-	11
MoS_2 + H_2O+ Teflon	14
MoS_2 + S^{2-}/SO_3^- +Teflon	9
Platinized MoS_2 + H_2O+ Teflon	13
Platinized MoS_2 + S^{2-}/SO_3^-+ Teflon	12

d. Tungsten disulfide (WS_2):

Table 3.6. Gas evolution using WS_2 at different conditions

CONTENTS IN TEST TUBE	***GAS EVOLVED(ml)***
WS_2 + H_2O	9
WS_2 + S^{2-}/SO_3^-	9

Platinized $WS_2 + H_2O$	10
Platinized $WS_2 + S^{2-}/SO_3^-$	12
$WS_2 + H_2O$+ Teflon	7
$WS_2 + S^{2-}/SO_3^-$ +Teflon	8
Platinized $WS_2 + H_2O$+ Teflon	12
Platinized $WS_2 + S^{2-}/SO_3^-$+ Teflon	14

e. Silver sulfide (Ag_2S):

Table 3.7. Gas evolution using Ag_2S at different conditions

CONTENTS IN TEST TUBE	***GAS EVOLVED(ml)***
$Ag_2S + H_2O$	8
$Ag_2S + S^{2-}/SO_3^-$	9
Platinized $Ag_2S + H_2O$	11
Platinized $Ag_2S + S^{2-}/SO_3^-$	8
$Ag_2S + H_2O$+ Teflon	12
$Ag_2S + S^{2-}/SO_3^-$ +Teflon	8
Platinized $Ag_2S + H_2O$+ Teflon	10
Platinized $Ag_2S + S^{2-}/SO_3^-$+ Teflon	14

Sodium sulfite is used in the system to prevent the following reactions, where sulfide in the system gives free sulfur and electrons and this free sulfur reacts with sulfide in the system to form disulfide which is yellow in color. This yellow colored disulfide blocks the light decreasing the availability of photons

$$S^{2-} \longrightarrow S^{\circ} + 2e^{-}$$

(Yellow solid)

$$S^{\circ} + S^{2-} \longrightarrow S_2^{2-}$$

(Yellow disulfide)

In the presence of sulfite, free sulfur reacts with it to form thiosulfate which is colorless.

$$S^{\circ} + SO_3^{2-} \longrightarrow S_2O_3^{2-}$$

(Sulfite) (Thiosulfate, colorless)

An experiment was conducted with only sulfide in the system using CdS and MoS_2.

Results were shown in the Figure 3.17

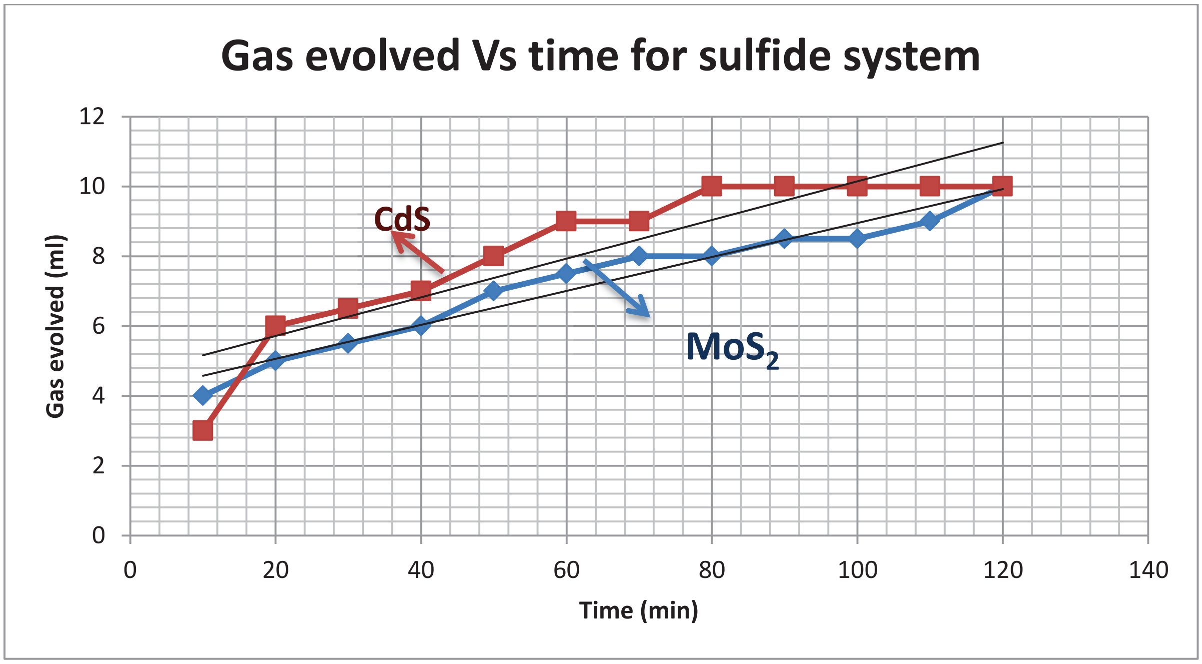


Figure 3.17. Gas evolved Vs Time for sulfide only system

From the Figure 3.17, we can see that gas evolution increased very fast with CdS and then became constant. This might be because of the production of disulfide in the system which has CdS (yellow color) that interfered with photons reaching the photocatalyst. In case of MoS_2 there is gas evolution constantly throughout the experiment. As the MoS_2 is black in color most of the light was absorbed by it.

3.6 Photocorrosion of semiconductors:

All the semiconductor adsorbents were tested for photocorrosion using ICP-OES (Inductive Coupled Plasma-Optical Emission Spectroscope) after running the photo experiments for 2 h in sulfide/sulfite solution. The concentration of free metal in solution was measured and the results were tabulated as shown in Table 3.8.

Table 3.8. ICP-OES data for concentration of dissolved photocatalyst metal in solution after 2 h photolysis in 0.24 M 25 ml of sulfide/ 0.35 M 25 ml of sulfite solution

S.No	Semiconductor	Analysis wavelength	Concentration (ppm)
1	Cadmium sulfide	226.502	0.0852
2	Tungsten sulfide	209.860	342.2
3	Molybdenum sulfide	204.598	2.567
4	Silver sulfide	328.068	0.8149

The photocorrosion reactions are thought to be as follows:

1. CuS:

$$CuS + h\upsilon \longrightarrow S^o + Cu^{2+} + 2e^-$$

$$2e^- + 2H_2O \longrightarrow H_2 + 2OH^-$$

2. CdS:

$CdS + h\upsilon \longrightarrow S^o + Cd^{2+} + 2e^-$

$2e^- + 2H_2O \longrightarrow H_2 + 2OH^-$

3. $Ag_2S + h\upsilon \longrightarrow S^o + 2Ag^+ + 2e^-$

$2e^- + 2H_2O \longrightarrow H_2 + 2OH^-$

4. $MoS_2 + 8OH^- + h\upsilon \longrightarrow 2S^o + MoO_4^{2-} + 4H_2O + 6e^-$

$6e^- + 6H_2O \longrightarrow 3H_2 + 3OH^-$

5. $WS_2 + h\upsilon \longrightarrow S^o + WO_4^{2-} + 4e^-$

$4e^- + 4H_2O \longrightarrow 2H_2 + 2OH^-$

From the ICP-OES data mentioned in Table 3.7 volume of gas that can be evolved from photocorrosion was calculated and the results are shown in Table 3.9. A sample calculation is shown below

For MoS_2:

One mole of MoS_2 gives three moles of hydrogen

1.65×10^{-5} moles of Mo (from ICP-OES data) gives $3\times1.65\times10^{-5}$ moles of hydrogen

Weight of hydrogen = 1.65×10^{-5} mol × 2 g/mol = 3.3×10^{-5} g × 3 moles = 9.9×10^{-5} g

Density= Mass / volume

Volume of hydrogen gas = Mass / density

Volume = 9.9×10^{-5} g / 0.0899 g/L (Density of hydrogen gas = 0.0899 g/L)

V = 110.12×10^{-5} L = 1.10 ml

Table 3.9. Volume of hydrogen gas that can be evolved from photocorrosion

S.No	**Semiconductor**	**Volume of gas (ml)**
1	Cadmium sulfide	4.894×10^{-3} ml
2	Molybdenum sulfide	1.10 ml
3	Tungsten sulfide	39.4 ml
4	Silver sulfide	0.073ml

In case of tungsten sulfide, 39.4 ml of hydrogen gas was expected from photo-corrosion (ICP-OES data), but there is less than 15 ml of gas evolution in all cases. From this we can conclude that corrosion mechanism did not involve hydrogen and was likely simple dissolution of the oxide. Moreover, the hydrogen observed must have resulted from HS^- photo-oxidation.

3.7 Effect of platinization:

As mentioned in Tables 3.3-3.7, the presence of platinum in the system seemed to increase the gas evolution. The platinized site of the photoconductor is believed to reduce water to hydrogen. Platinum helped in almost all cases except for MoS_2 mentioned in Table 3.5. MoS_2 in the presence of water gave only 14 ml of gas while platinized MoS_2 in water gave 12 ml of gas. This might be because of the photo-corrosion of MoS_2 in the absence of platinum.

3.8 Effect of Teflon:

During the photo experiments bubbles were observed rising from the surface of a stirbar which was in contact with the platinized photocatalyst as shown in Figure 3.18.

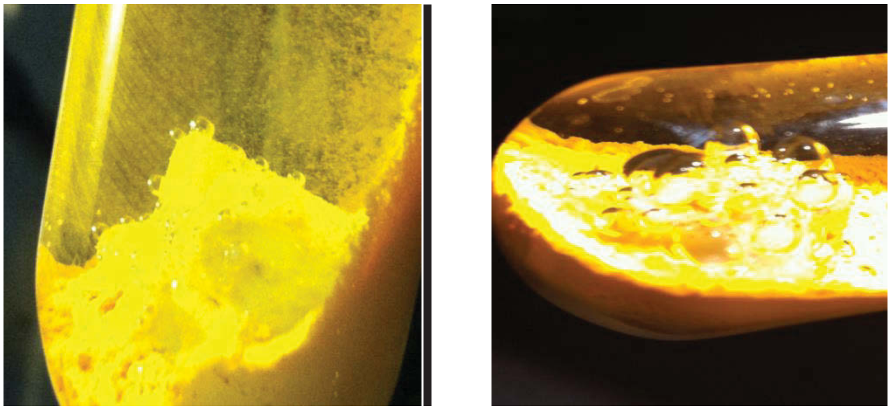


Figure 3.18. Bubbles rising from Teflon stir bar

There was increased gas (hydrogen gas) volume when there was Teflon in the system as compared to platinized photocatalyst alone as shown in Tables 3.2, 3.3, 3.4, 3.5, and 3.6. Different morphologies of Teflon such as Teflon sheet, abraded Teflon sheet and Teflon powder of particle size less than 1 μm were tested to see the effect.

With a Teflon sheet in the 50 ml test tube system there were bubbles on the surface of the strip which is in contact with the platinized photocatalyst as shown in Figure 3.19.

Figure 3.19. Bubbles of hydrogen gas on Teflon strip

With abraded Teflon strip in the system more gas bubbles were formed on the surface than on the smooth, unabraded sheet as shown in Figure 3.20.

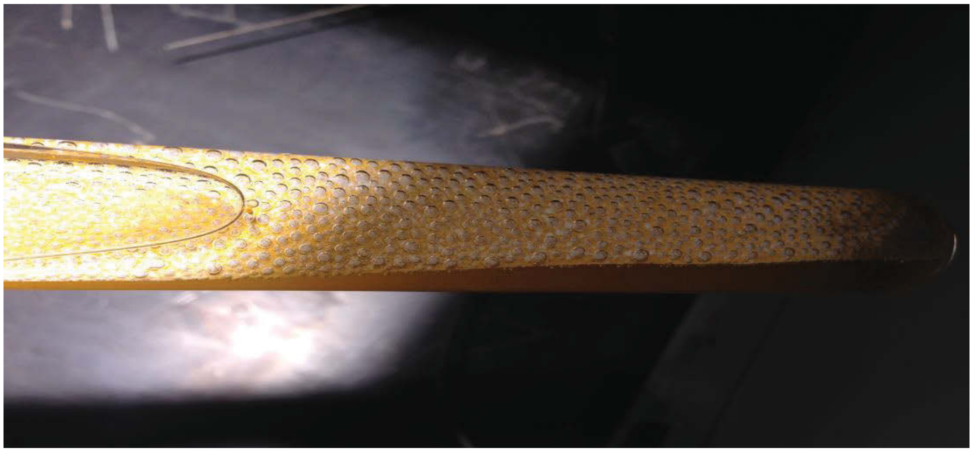


Figure 3.20. Bubbles of hydrogen gas on abraded Teflon strip

When Teflon powder is added to the system during photo experiments, it floated on the surface. There is no contact between the platinized photocatalyst and the Teflon, so platinized photocatalyst (70% by weight) and Teflon powder (30% by weight) were pressed into a pellet and added to the system. More gas evolution was observed from this system than those containing Teflon powder. Bubbles of hydrogen gas rose from the surface of the pellets as shown in Figure 3.21.

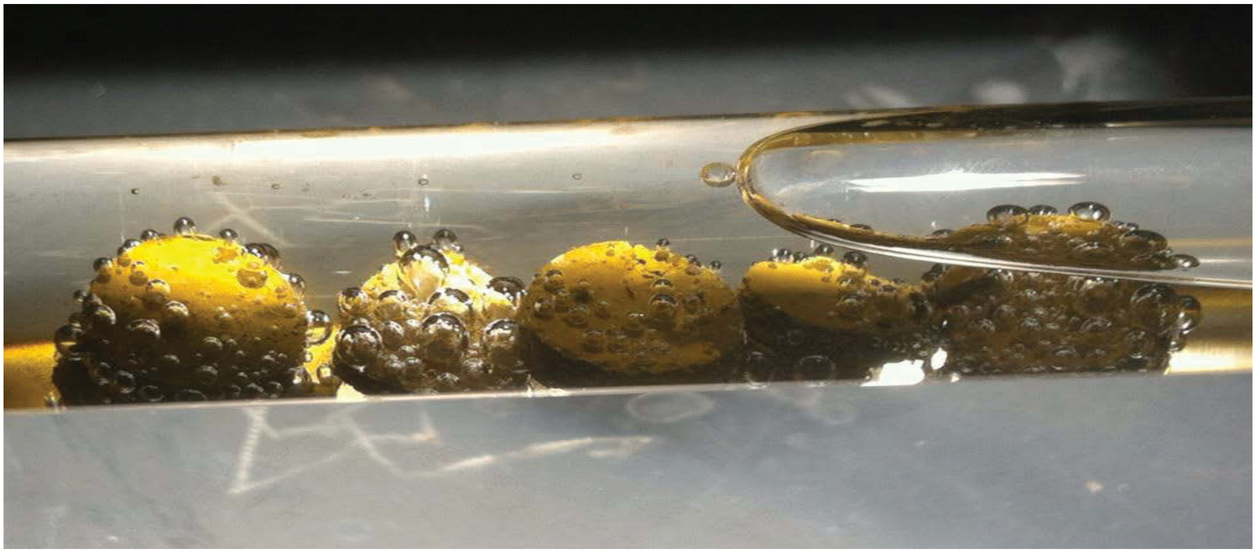


Figure 3.21. Bubbles of hydrogen gas rising from pellets made of Teflon powder and platinized CdS photocatalyst

To test the effect of Teflon in photo experiments various tests were performed, where hydrogen is bubbled vigorously into a test tube containing Abraded Teflon strip in test tube along with the following contents for 10 min as shown in the Table 3.10

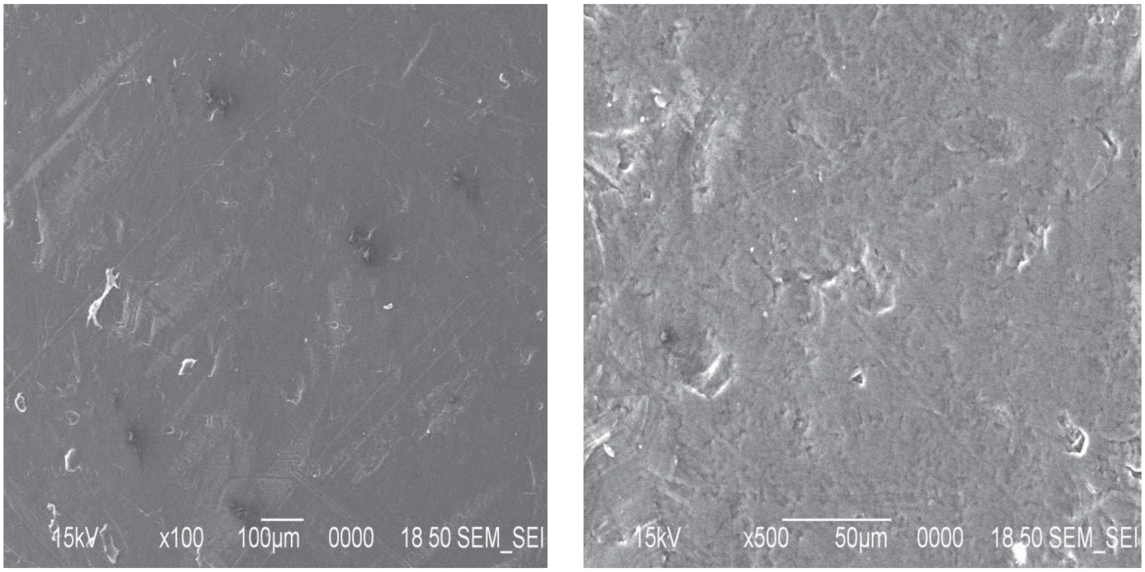
Table 3.10 Testing of abraded Teflon strip at different conditions

S.No	**Contents in the test tube**	**Results**
1	pH12 NaOH	Small bubbles were observed on the surface of Abraded Teflon strip
2	Pt-CdS in water	Large bubbles were observed on the surface of the Abraded Teflon strip
3	Water	Small bubbles were observed on the surface of the Abraded Teflon strip
4	Pt-CdS in pH 12 NaOH	Small bubbles were observed on the surface of the Abraded Teflon strip
5	Teflon + CdS + water	Minute bubbles rising up in solution and on

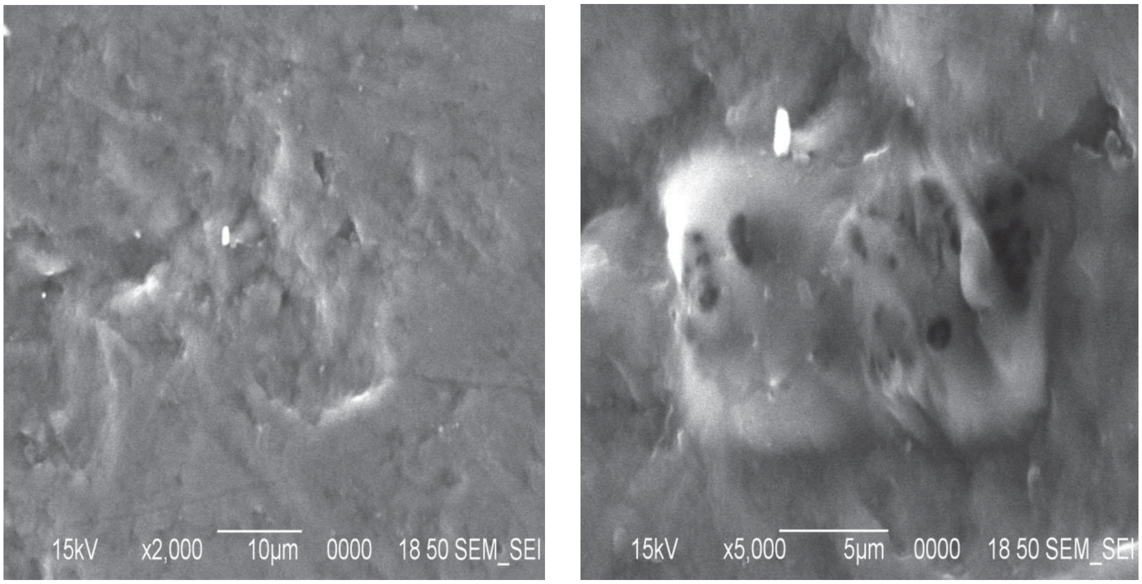
		Abraded Teflon strip
6	Water + Pt-CdS + sand paper	Very small bubbles on the surface of Abraded Teflon strip
7	Pt-CdS + SO_3^{2-}/SO_2^{-}	Medium sized bubbles all over the surface of Abraded Teflon strip

The surface of different types of Teflon was analyzed through electron microscopy. The images of Teflon strip, abraded Teflon strip and Teflon powder are shown in Figure 3.22, 3.23, and 3.24, respectively.

The surface of the Teflon sheet was analyzed at 100 µm, 50 µm, 10 µm and 5 µm scale magnification. The surface appeared to be very smooth. The surface of abraded Teflon strip was analyzed at 100 µm, 50 µm and10 µm. The surface seemed to be rougher because of the abrasion. Teflon powder was analyzed at 100 µm, 50 µm, 10 µm, 5 µm and 1 µm. The particle size of Teflon powder was found to be less than 1 µm from the image in Figure 3.24 (e)

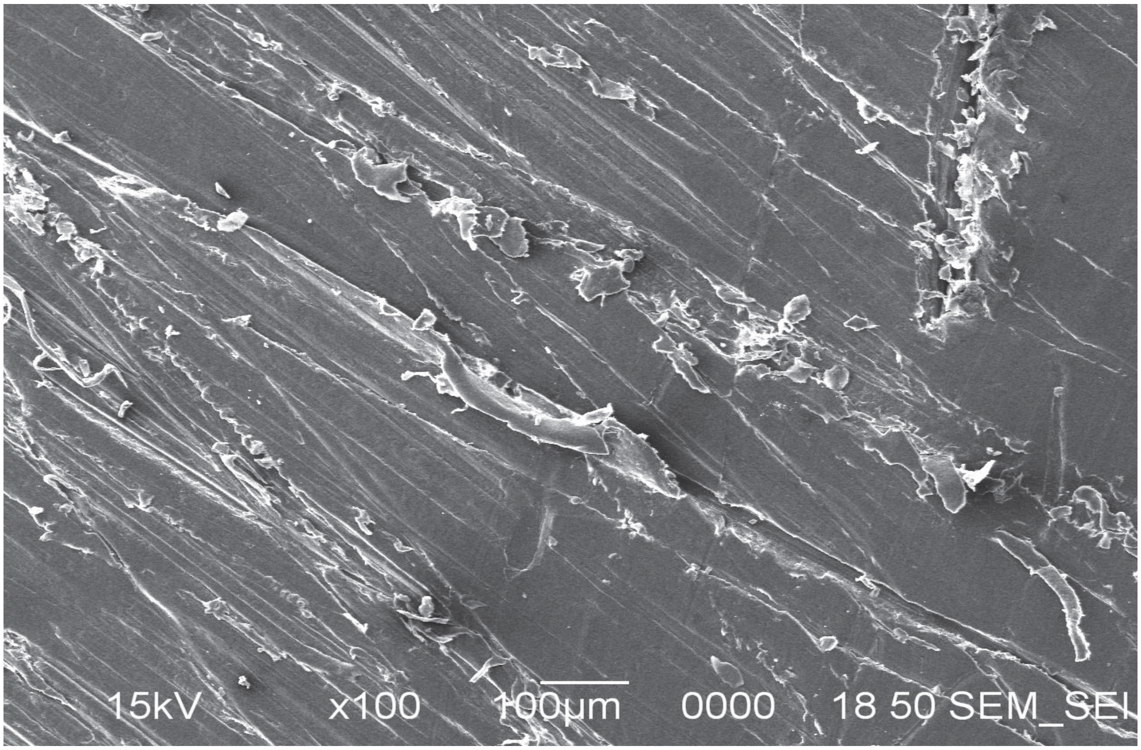


(a) **(b)**

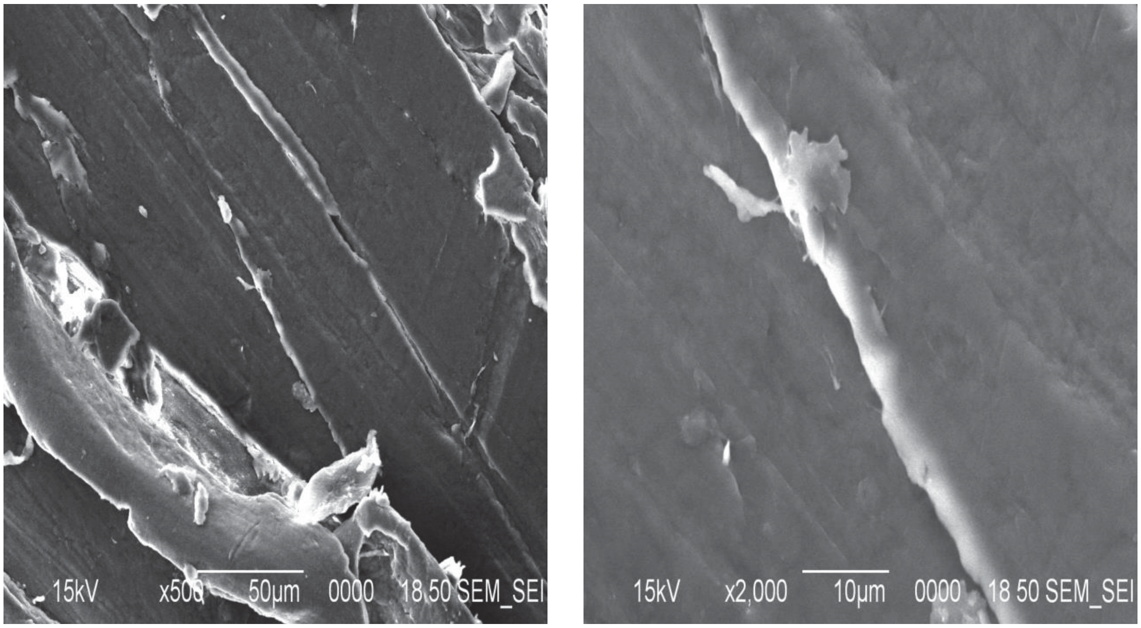


(c) **(d)**

Figure 3.22. SEM images of Teflon strip (a) at 100 µm (b) at 50 µm (c) at 10 µm (d) at 5 µm

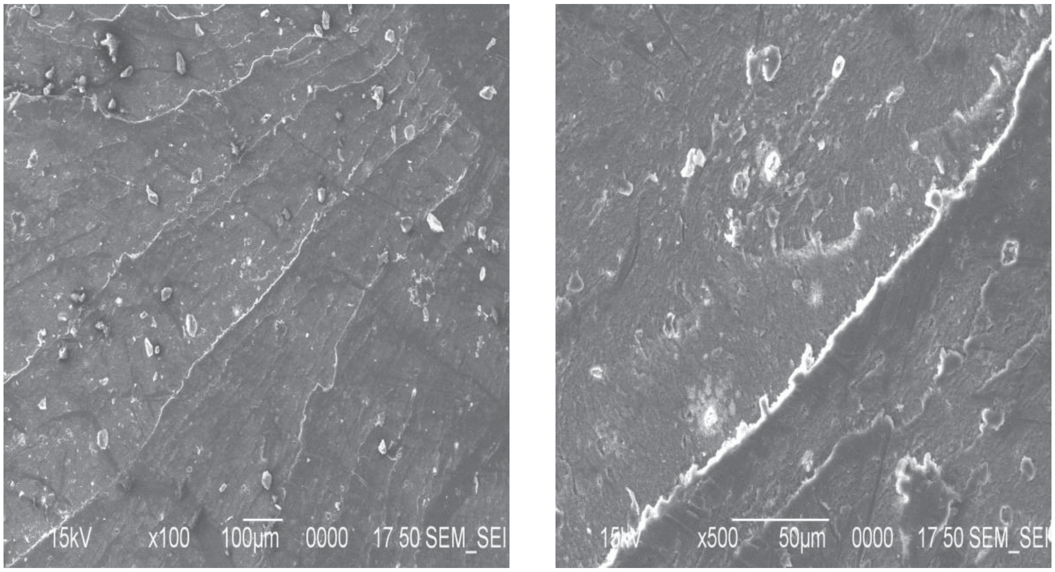


(a)

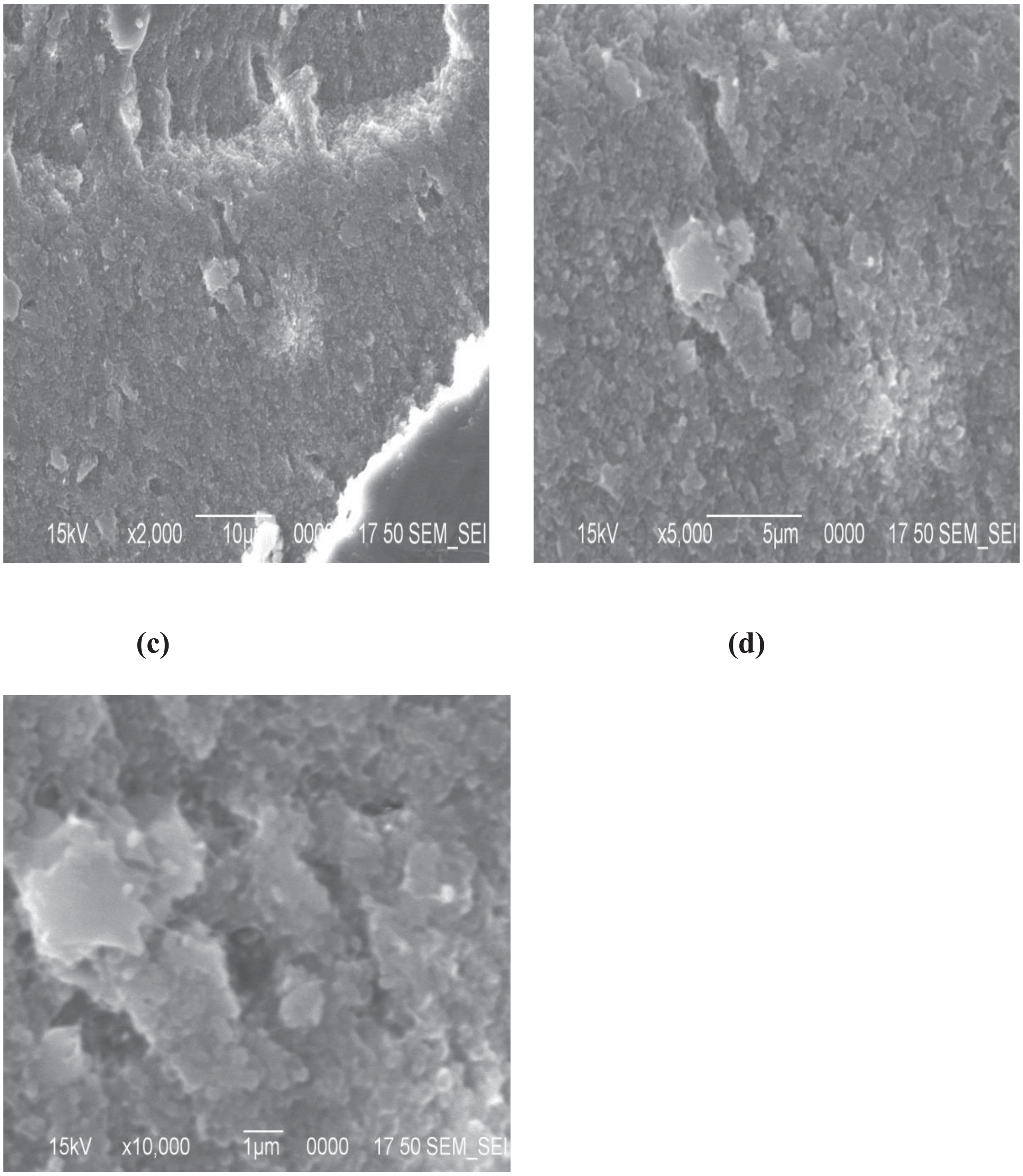


(b) **(c)**

Figure 3.23. SEM images of abraded Teflon strip (a) at 100 µm (b) at 50 µm (c) at 10 µm



(a) **(b)**



(c) **(d)**

(e)

Figure 3.24. SEM images of Teflon powder pressed to a pellet strip (a) at 100 μm (b) at 50 μm (c) at 10 μm (d) at 5μm (e) 1 μm

3.9 Effect of surfactants:

Addition of 2 drops of surfactant (Triton X-100) in the system (25 ml of 0.24 M Na_2S and 25 ml of 0.34 M Na_2SO_3 in a 50 ml test tube containing platinized photocatalyst) showed decreased uniform bubble size and increased hydrogen gas volume. Hydrogen gas evolved is less when compared to abraded Teflon sheet, but together (abraded Teflon sheet and the surfactant) in the system gave more hydrogen gas than both alone as shown in Table 3.11. After letting the solution stand for some time it turned pink showing that the surfactant is not photostable.

Table 3.11. Effect of surfactant on hydrogen gas evolution

S.No	**Contents in the test-tube**	**Gas evolved (ml)**
1	25 ml of 0.24 M Na_2S and 25 ml of 0.35 M Na_2SO_3 , 1 g of platinized CdS and abraded Teflon sheet	15
2	25 ml of 0.24 M Na_2S and 25 ml of 0.35 M Na_2SO_3, 1 g of platinized CdS and 2 drops of Triton X-100 surfactant	13
3	25 ml of 0.24 M Na_2S and 25 ml of 0.35 M Na_2SO_3, 1 g of platinized CdS, abraded Teflon sheet and 2 drops of Triton X-100 surfactant	16

3.10 Kinetics:

To know if the photocatalyst can perform under different conditions the following experiments were performed with 1.8 g of platinized adsorbent (CdS), under simulated sunlight.

Effect of concentration: To know the effect of concentration different solutions of varying sulfide concentration were prepared keeping pH constant at 10.

0.24 M Na_2S, 0.20 M Na_2S, 0.15 M Na_2S, 0.10 M Na_2S, 0.05 M Na_2S, 0.01 M Na_2S

Table 3.12. Effect of concentration on gas evolution at constant pH (10)

S.No	Concentration of solution	Volume of gas evolved (ml)
1	0.24 M Na_2S	8
2	0.20 M Na_2S	7
3	0.15 M Na_2S	6
4	0.10 M Na_2S	6
5	0.05 M Na_2S	5
6	0.01 M Na_2S	5

From Table 3.12 it is evident that as the concentration decreases from 0.24 M to 0.01 M volume of gas evolved also decreased from 8 ml to 5 ml.

Effect of pH: A solution of 0.24 M sodium sulfide was prepared and the pH was varied from 5 to13 keeping the concentration constant. To the prepared solution one gram of adsorbent (platinized MoS_2) was added and this solution was exposed to a 1000 W xenon arc lamp for 2 h. The gas evolved is measured.

Table 3.13. Effect of pH on gas evolution from 0.24 M sodium sulfide solution

Sample number	pH	Volume of gas evolved (ml)
1	5	33
2	6	20
3	7	18
4	8	9
5	9	9
6	10	12
7	11	9
8	12	9
9	13	9

From Table 3.13 at pH 5-7 the volume of gas is the highest, because most of the sulfide at that pH consists of dissolved H_2S gas. From pH 8-13 evolved gas volume remained the same.

3.11 RAE system gas-detection tubes:

From the Figure 3.25 it is clear that the concentration of hydrogen sulfide in landfill gas (New Springfield, OH) is 200 ppm. Color change is observed from white to dark brown.

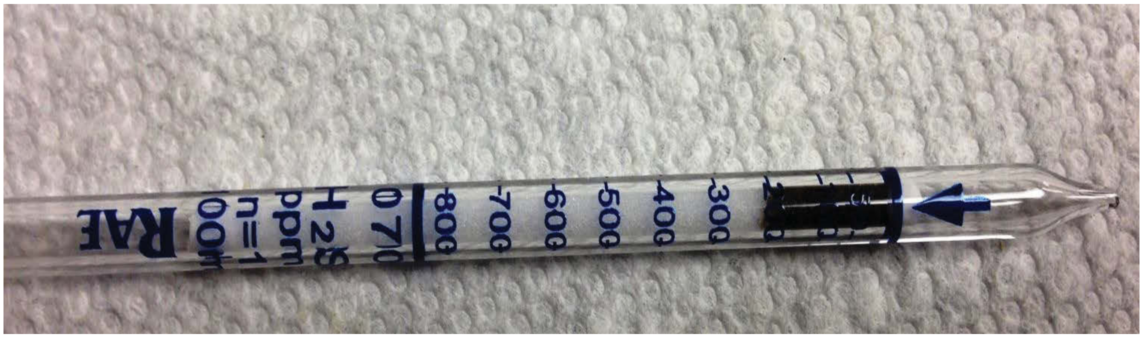


Figure 3.25 H_2S concentration in landfill gas detected by RAE tubes

3.12 Real world applications:

Adsorbents discussed above were tested under the simulated Black Sea conditions (pH - 8, Concentration - 0.5 mM) and simulated landfill gas conditions (pH: 4.2, concentration: 50 ppm). Adsorbent (MoS_2) was painted onto the plastic surface as shown in Figure 3.26. To paint the plastic surface, 1 part of poly (methyl methacrylate) is mixed with 9 parts of solvent (methylene chloride) and 9 parts of solid filler (70% platinized MoS_2 and 30% Teflon by weight). A flat cell shown in Figure 3.27 was designed for these experiments. The separation distance between the aperture of the Xe lamp and the flat cell was approximately 12 cm.

Figure 3.26. Plastic surface painted with a mixture of platinized MoS_2 and Teflon

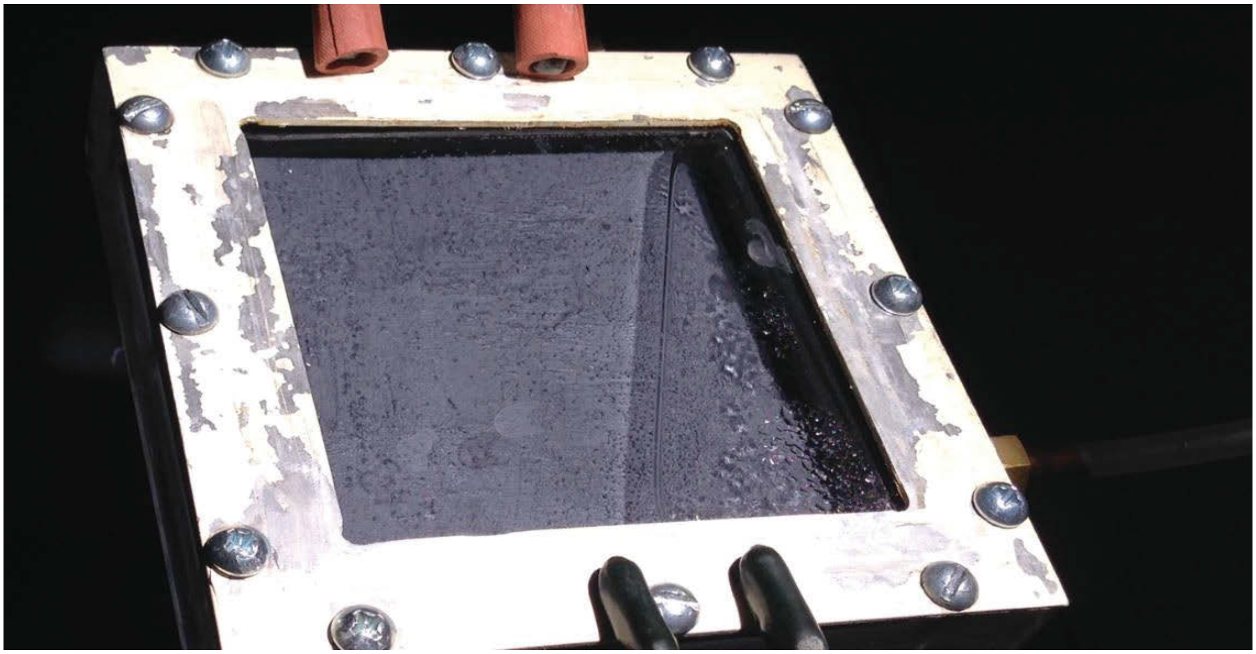


Figure 3.27. Flat cell containing platinized molybdenum sulfide adsorbent painted onto a plastic surface

Black Sea: A flat cell experiment was done at simulated Black Sea conditions (0.5 mM Na_2S solution, pH adjusted to 8 with 0.1 M KH_2PO_4). A 2 h experiment was conducted by pumping 0.5 mM Na_2S solution continuously into the system at a flow rate of 10 ml/min. A total volume of 1200 ml was consumed. Gas evolved during the process was collected using the inverted measuring cylinder method and recorded. Volume of gas evolved is shown in Table 3.14.

Table 3.14 Gas evolved using flat cell in simulated conditions of Black Sea and landfill

S.No	Contents in the flat cell	Gas evolved (ml)
1	Water + platinized MoS_2 and Teflon painted on plastic surface	5
2	50 ml of 0.24 M Na_2S + 50 ml of 0.35 M Na_2SO_3 + platinized MoS_2 and Teflon painted on plastic surface	14
3	0.5 mM Na_2S + platinized MoS_2 and Teflon painted on plastic surface	13
4	Water + plastic substrate only	3

Landfill: As noted in the Introduction, landfill gas consists primarily of methane, carbon dioxide, and nitrogen. Of these, only carbon dioxide would influence the pH of an aqueous scrubber solution. It behaves as an acid gas, undergoing hydrolysis to generate carbonic acid

$$CO_{2\,(g)} + H_2O_{(aq)} \longrightarrow H_2CO_{3\,(aq)} \longrightarrow H^+_{(aq)} + HCO_3^-{}_{(aq)}$$

In order to accurately simulate landfill gas conditions in the laboratory it was decided to confirm the steady state pH of an aqueous solution continuously purged with real landfill gas. An experiment was conducted at the landfill (New Springfield, OH) where landfill gas is pumped continuously into 150 ml of water in a 4-neck round bottom flask. pH and ISE were measured simultaneously with time. The setup of the experiment is shown in Figure 3.28. This was done on a cool day, so the temperature of the solution in the flask was only 10°C. All the readings are shown in Table 3.15

Figure 3.28 Set-up for the landfill gas real world experiment

Table 3.15. pH and ISE readings for landfill gas (bubbled into water) with time

S.No	Time (min)	pH	ISE (mV)
1	0	5.98	35
2	1	4.28	-25
3	2	4.23	-144

4	3	4.22	-266
5	4	4.21	-338
6	5	4.21	-353
7	6	4.21	-356
8	7	4.21	-357
9	8	4.21	-358
10	9	4.21	-358
11	10	4.21	-359
12	11	4.24	-361
13	12	4.24	-361
14	13	4.25	-361
15	14	4.25	-361
16	15	4.25	-362
17	16	4.25	-362
18	17	4.25	-362
19	18	4.25	-363
20	19	4.25	-363
21	20	4.28	-364
22	21	4.29	-364
23	22	4.30	-364

At room temperature (25˚C) back in the laboratory, the final pH was 4.21 and ISE was -252 mV

Results showed that the concentration of H_2S (from ISE reading) and pH decreased with the bubbling of landfill gas into water.

Landfill gas was then bubbled into 150 ml of water containing 1 gm of platinized molybdenum sulfide in a 4-neck round bottomed flask. pH and ISE were measured with time at 10 °C. Results are shown in Table 3.16

Table 3.16 pH and ISE of landfill gas (bubbled into water with Pt-MoS_2) with time

S.No	Time (min)	pH	ISE (mV)
1	0	3.77	71
2	1	3.72	-117
3	2	3.71	-229
4	3	3.70	-256
5	4	3.69	-276
6	5	3.69	-285
7	6	3.69	-288
8	7	3.69	-288
9	8	3.69	-288
10	9	3.69	-288
11	10	3.70	-285
12	11	3.70	-283
13	12	3.70	-282

14	13	3.70	-280
15	14	3.70	-279
16	15	3.70	-277
17	16	3.70	-275
18	17	3.70	-274
19	18	3.70	-272
20	19	3.70	-271
21	20	3.71	-271
22	21	3.72	-270
23	22	3.72	-268
24	23	3.72	-268
25	24	3.72	-266
26	25	3.72	-266
27	26	3.73	-266
28	27	3.73	-266
29	28	3.73	-265
30	29	3.73	-265

At room temperature (25˚C) pH was 4.26 and ISE was -196 mV

Results from Table 3.16 showed that, as the land fill gas was bubbled into the system, there was a decrease in pH. ISE readings showed that the concentration of sulfide increased gradually in the beginning and then decreased. This might be due to the presence of platinized molybdenum acting as adsorbent in the system.

Presence of carbon dioxide in the system seemed to decrease the dissolution of H_2S in pure water from the landfill experiment results. So an experiment was conducted to see the effect of CO_2 on H_2S dissolution. By continuously monitoring pH and ISE (Ion Selective Electrode) readings, 100 ppm of H_2S and methane mixture was bubbled into the system for 15 minutes. Then CO_2 was bubbled into the system to decrease the pH to 4.20. From the results mentioned in Table 3.17, it is evident that CO_2 present in the system decreases the dissolution of H_2S.

Table 3.17. Effect of CO_2 on H_2S dissolution

Time (min)	pH Reading	ISE Reading
0	7.22	23
1	7.64	-131
2	7.58	-232
3	7.58	-343
4	7.58	-419
5	7.59	-440
6	7.62	-469
7	7.64	-503
8	7.66	-519
9	7.68	-534
10	7.68	-543

11	7.71	-551
12	7.72	-552
13	7.73	-559
14	7.74	-559
15	7.75	-562
CO_2 bubbled into the system		
16	4.48	-351
17	4.45	-348
18	4.42	-347
19	4.42	-345
20	4.42	-341

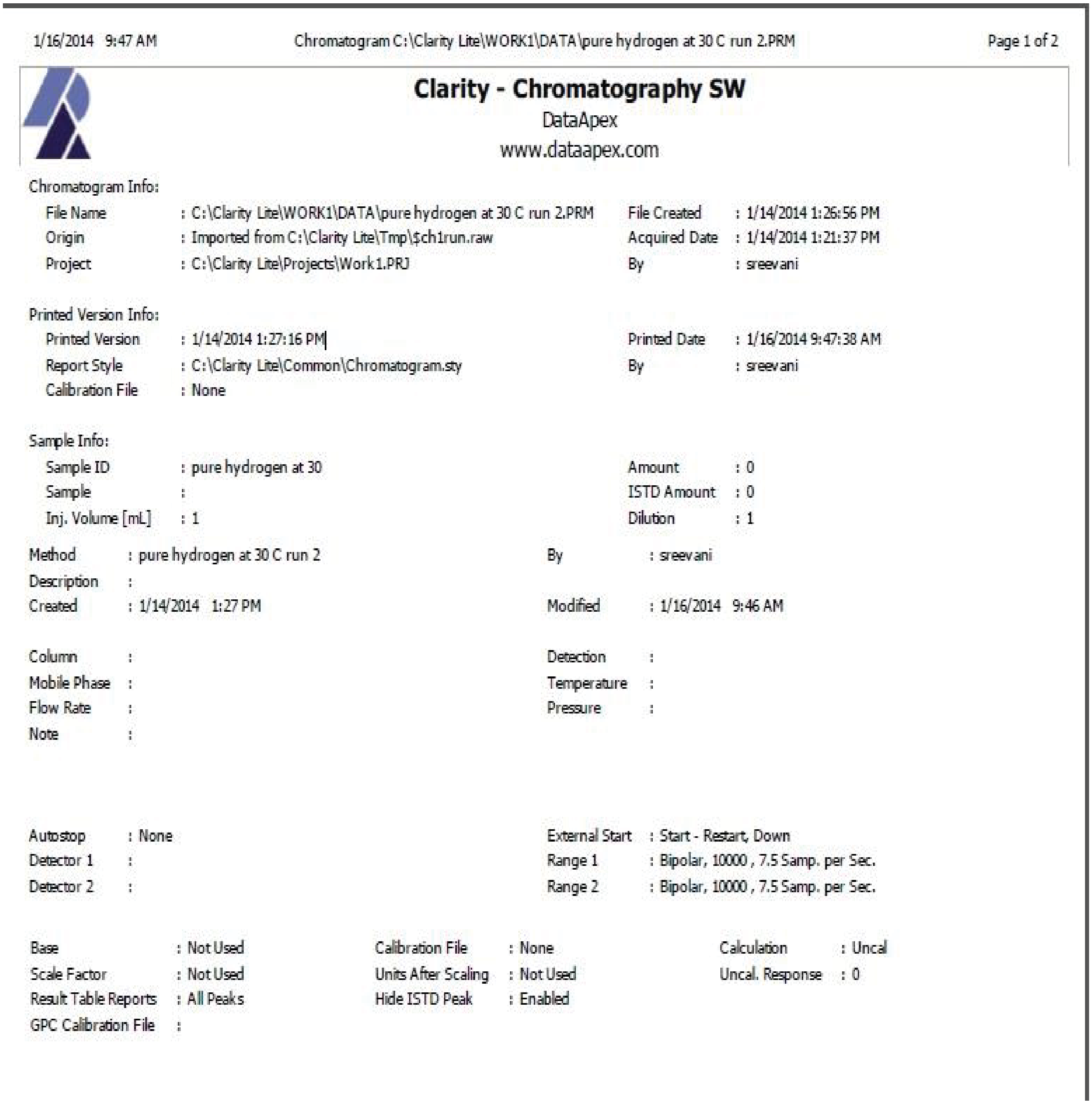
A simulated experiment was conducted with flat cell where a mixture of H_2S, CO_2 and CH_4 were bubbled into water continuously. This water is then pumped into flat cell that contains adsorbent. This experiment was conducted for 2 hours continuously under simulated sunlight (1000 W xenon arc lamp). Gas that is evolved in this time span was collected into inverted measuring cylinder.

About 124 ml of gas was collected into the cylinder which also includes 100 ml of cell volume. The gas collected was tested using a gas chromatograph.

3.13 Gas chromatographic analysis of simulation experiments:

Sample injections of 1.0 ml of the following gas samples were made and the chromatographs collected are shown in Figures 3.29-3.33

1. Pure hydrogen
2. Pure air
3. 1:1 hydrogen to air
4. Gas evolved from landfill simulation experiment
5. Gas evolved from Black Sea simulation experiment



1/16/2014 9:47 AM Chromatogram C:\Clarity Lite\WORK1\DATA\pure hydrogen at 30 C run 2.PRM Page 1 of 2

Clarity - Chromatography SW

DataApex

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Chromatogram Info:

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Printed Version Info:

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Calibration File	: None		

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Sample ID	: pure hydrogen at 30	Amount	: 0
Sample	:	ISTD Amount	: 0
Inj. Volume [mL]	: 1	Dilution	: 1

Method	: pure hydrogen at 30 C run 2	By	: sreevani
Description	:		
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Column	:	Detection	:
Mobile Phase	:	Temperature	:
Flow Rate	:	Pressure	:
Note	:		

Autostop	: None	External Start	: Start - Restart, Down
Detector 1	:	Range 1	: Bipolar, 10000 , 7.5 Samp. per Sec.
Detector 2	:	Range 2	: Bipolar, 10000 , 7.5 Samp. per Sec.

Base	: Not Used	Calibration File	: None	Calculation	: Uncal
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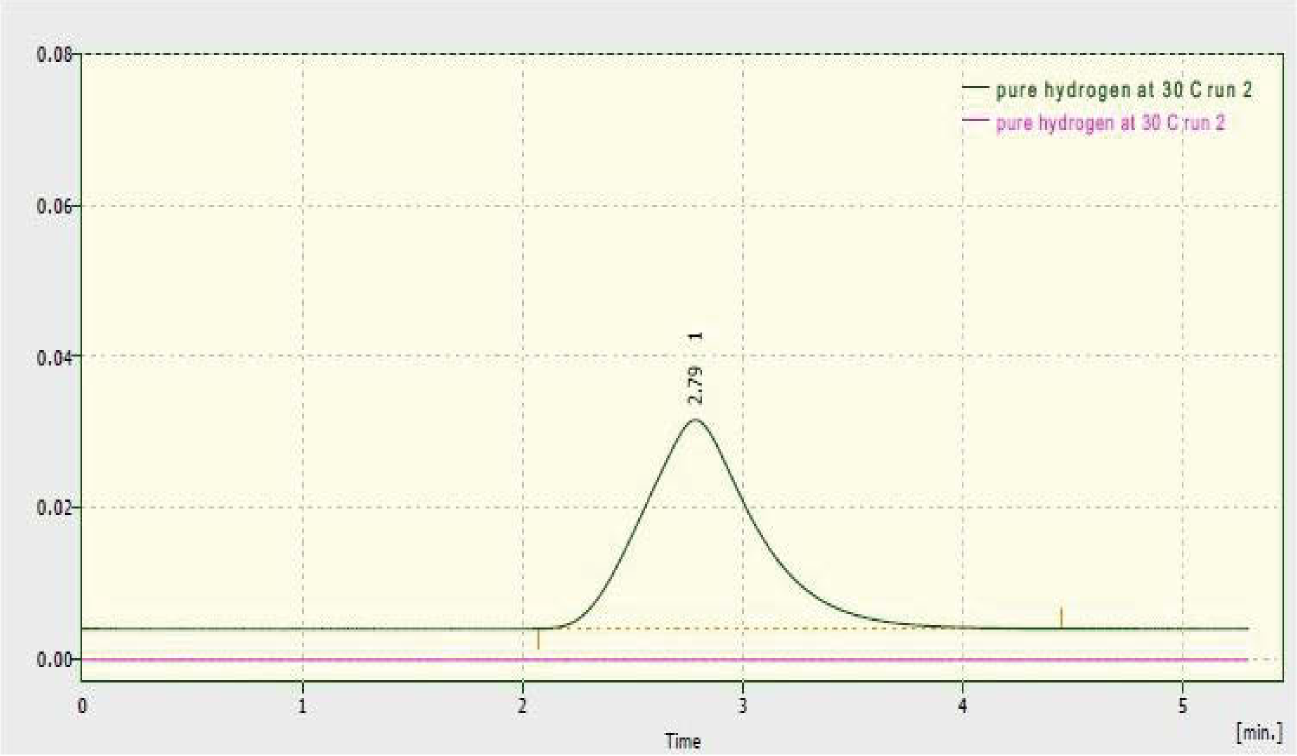
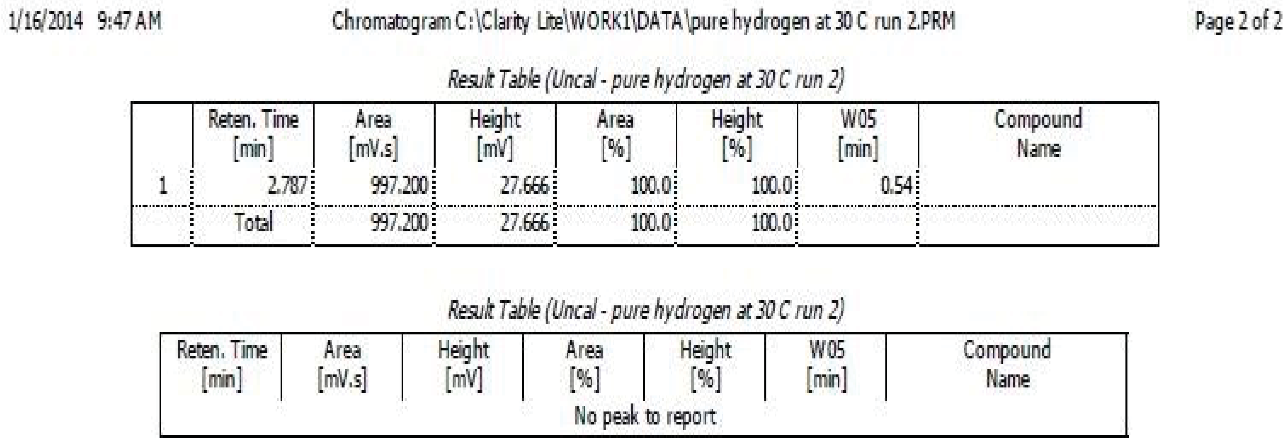



1/16/2014 9:47 AM Chromatogram C:\Clarity Lite\WORK1\DATA\pure hydrogen at 30 C run 2.PRM Page 2 of 2

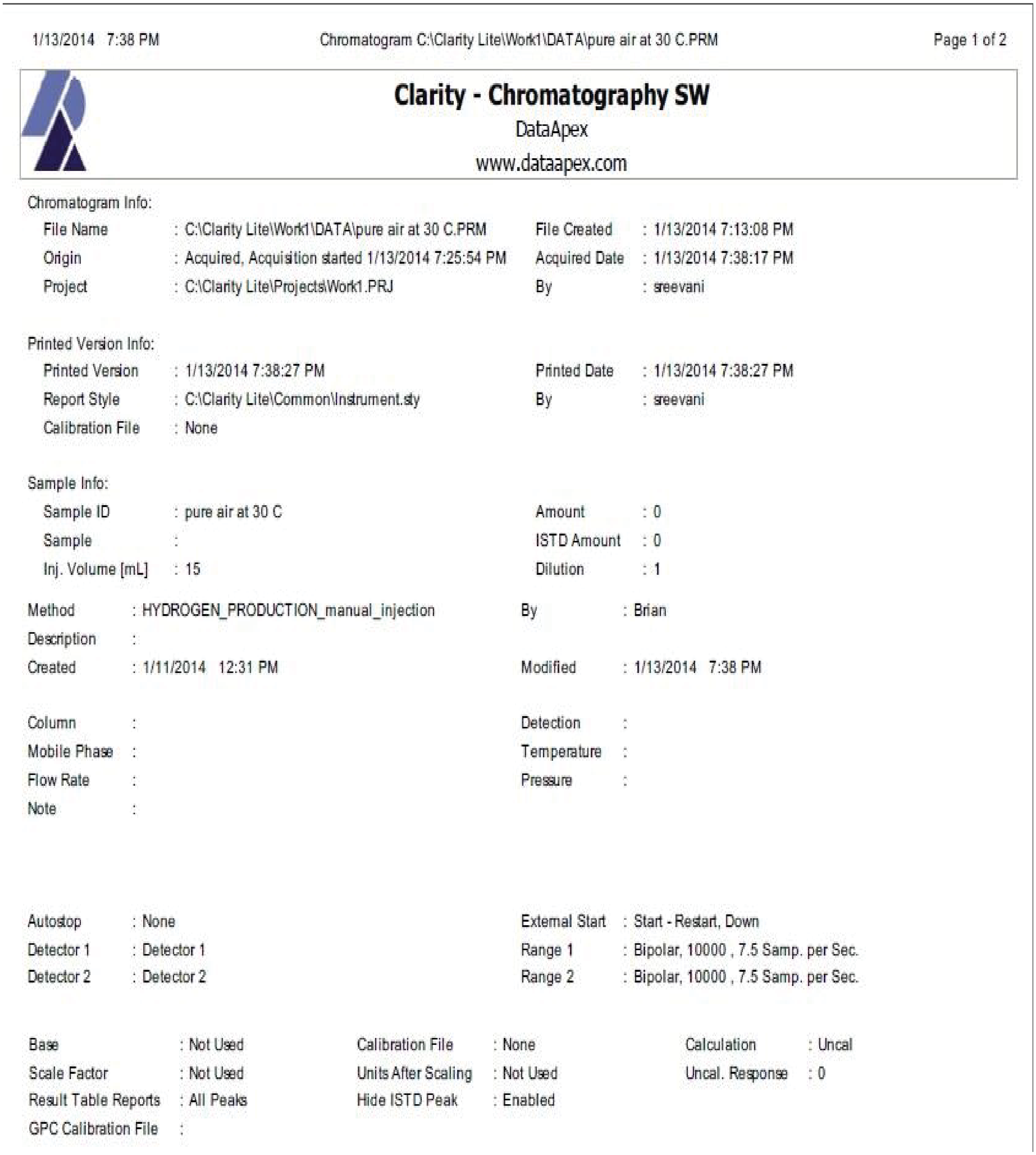
Result Table (Uncal - pure hydrogen at 30 C run 2)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	2.787	997.200	27.666	100.0	100.0	0.54	
	Total	997.200	27.666	100.0	100.0		

Result Table (Uncal - pure hydrogen at 30 C run 2)

Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
No peak to report						

Figure 3.29. Gas chromatograph of pure hydrogen at 32 ˚C



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Clarity - Chromatography SW

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Sample Info:

Sample ID : pure air at 30 C
Sample :
Inj. Volume [mL] : 15

Amount : 0
ISTD Amount : 0
Dilution : 1

Method : HYDROGEN_PRODUCTION_manual_injection
Description :
Created : 1/11/2014 12:31 PM

By : Brian
Modified : 1/13/2014 7:38 PM

Column :
Mobile Phase :
Flow Rate :
Note :

Detection :
Temperature :
Pressure :

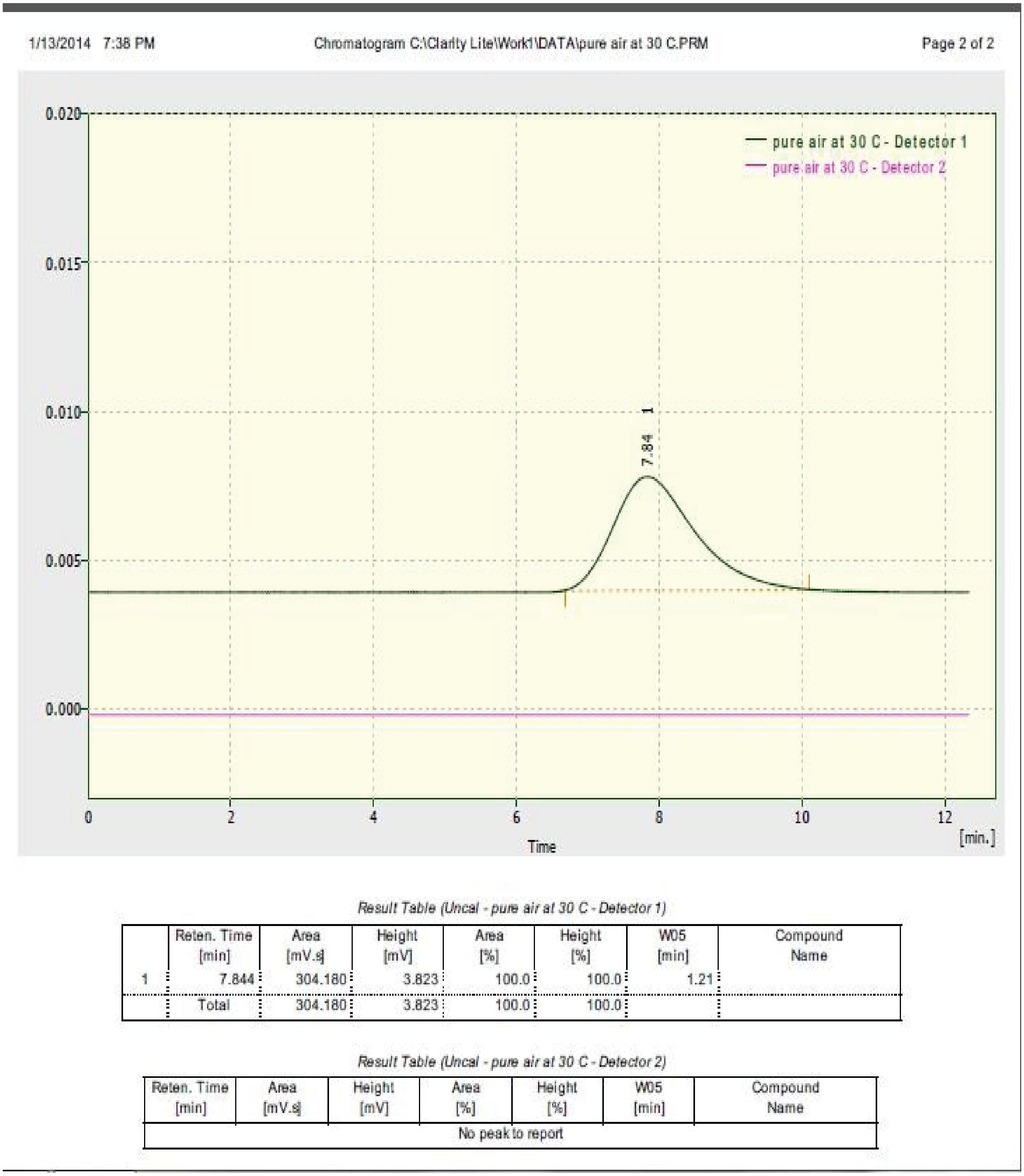
Autostop : None
Detector 1 : Detector 1
Detector 2 : Detector 2

External Start : Start - Restart, Down
Range 1 : Bipolar, 10000 , 7.5 Samp. per Sec.
Range 2 : Bipolar, 10000 , 7.5 Samp. per Sec.

Base : Not Used
Scale Factor : Not Used
Result Table Reports : All Peaks
GPC Calibration File :

Calibration File : None
Units After Scaling : Not Used
Hide ISTD Peak : Enabled

Calculation : Uncal
Uncal. Response : 0



1/13/2014 7:38 PM Chromatogram C:\Clarity Lite\Work1\DATA\pure air at 30 C.PRM Page 2 of 2

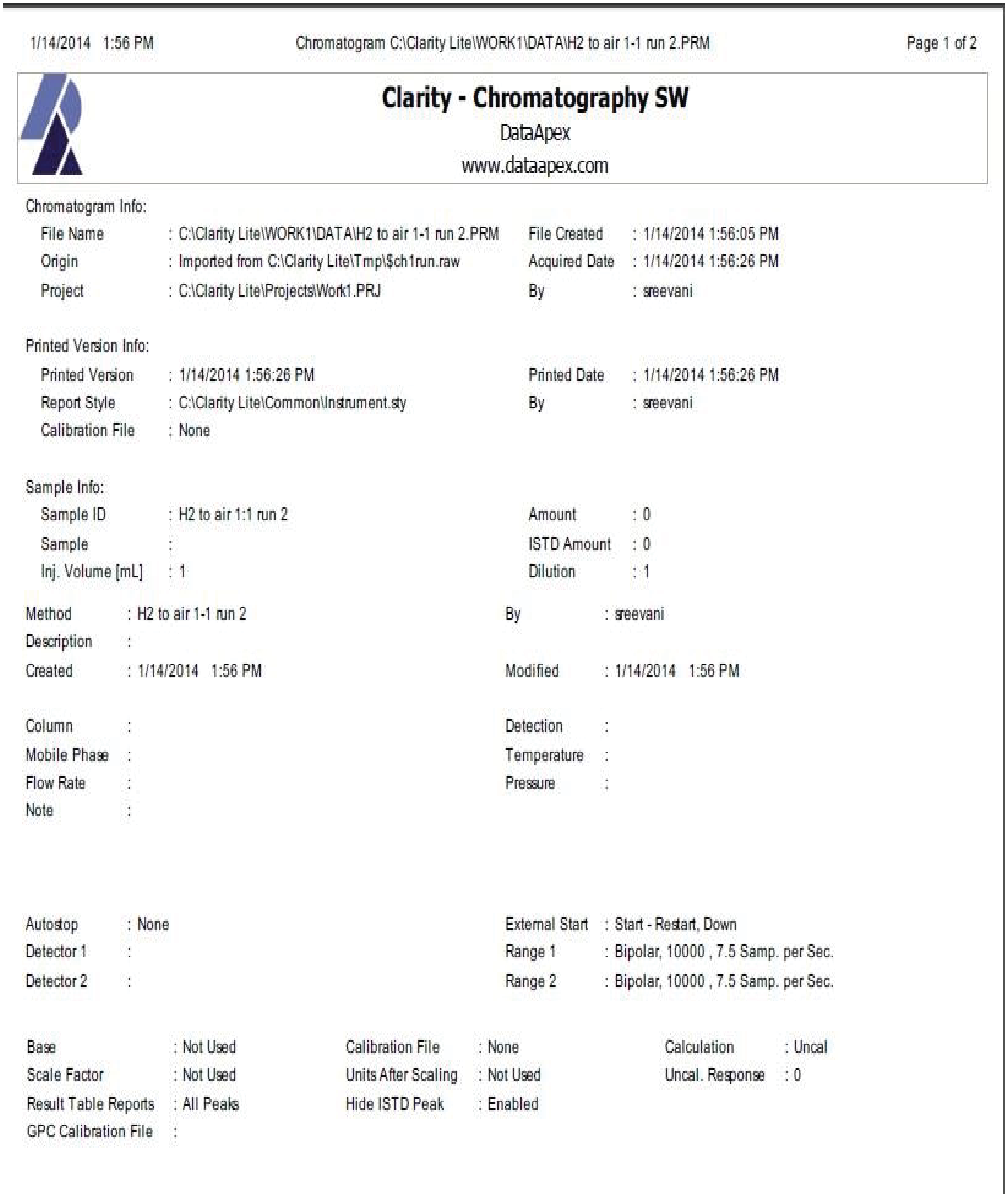
Result Table (Uncal - pure air at 30 C - Detector 1)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	7.844	304.180	3.823	100.0	100.0	1.21	
	Total	304.180	3.823	100.0	100.0		

Result Table (Uncal - pure air at 30 C - Detector 2)

Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
No peak to report						

Figure 3.30. Gas chromatograph of pure air at 32 ˚C



1/14/2014 1:56 PM Chromatogram C:\Clarity Lite\WORK1\DATA\H2 to air 1-1 run 2.PRM Page 1 of 2

Clarity - Chromatography SW

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Chromatogram Info:

File Name : C:\Clarity Lite\WORK1\DATA\H2 to air 1-1 run 2.PRM
File Created : 1/14/2014 1:56:05 PM
Origin : Imported from C:\Clarity Lite\Tmp\$ch1run.raw
Acquired Date : 1/14/2014 1:56:26 PM
Project : C:\Clarity Lite\Projects\Work1.PRJ
By : sreevani

Printed Version Info:

Printed Version : 1/14/2014 1:56:26 PM
Printed Date : 1/14/2014 1:56:26 PM
Report Style : C:\Clarity Lite\Common\Instrument.sty
By : sreevani
Calibration File : None

Sample Info:

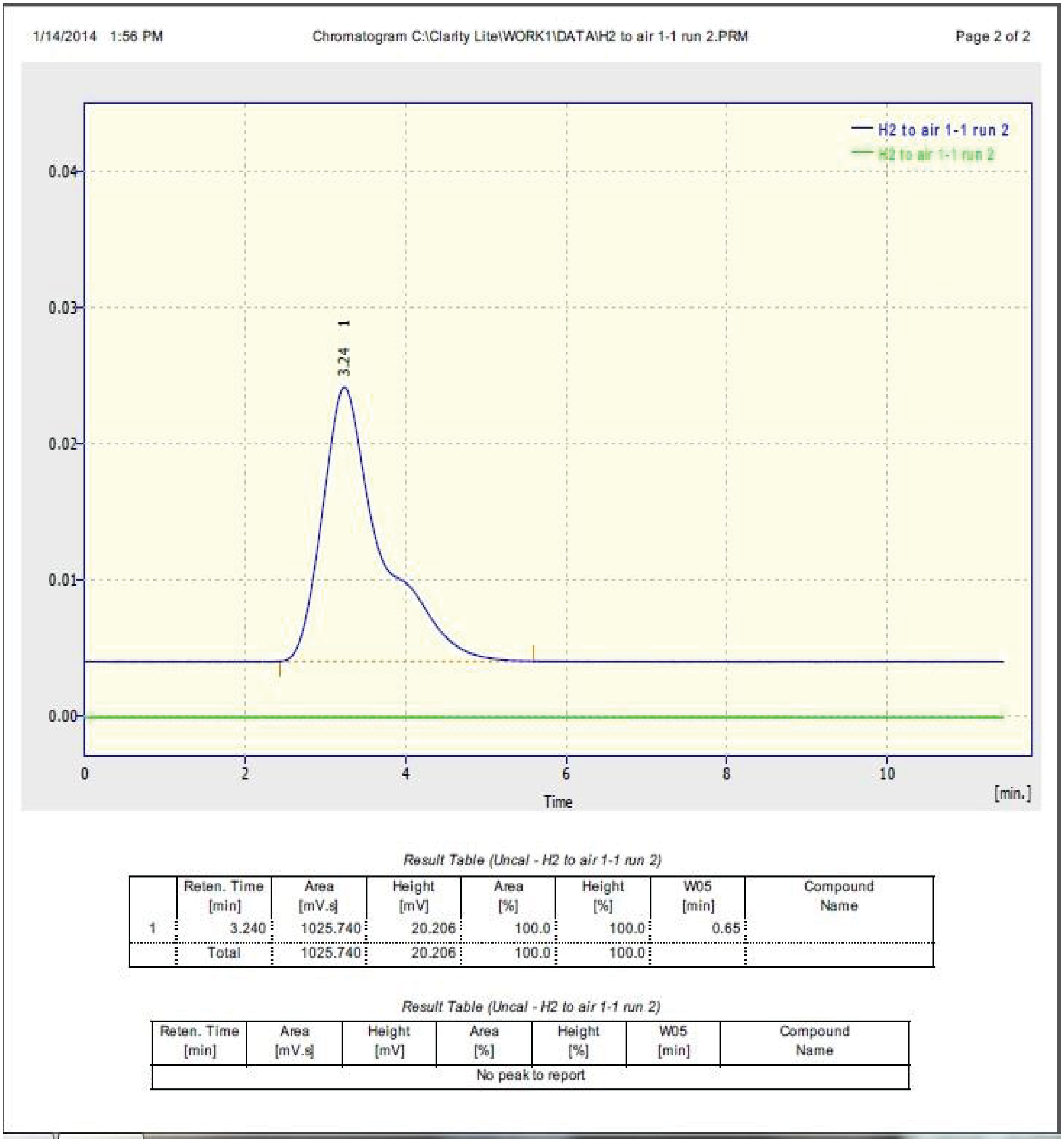
Sample ID : H2 to air 1:1 run 2
Amount : 0
Sample :
ISTD Amount : 0
Inj. Volume [mL] : 1
Dilution : 1

Method : H2 to air 1-1 run 2
By : sreevani
Description :
Created : 1/14/2014 1:56 PM
Modified : 1/14/2014 1:56 PM

Column :
Detection :
Mobile Phase :
Temperature :
Flow Rate :
Pressure :
Note :

Autostop : None
External Start : Start - Restart, Down
Detector 1 :
Range 1 : Bipolar, 10000 , 7.5 Samp. per Sec.
Detector 2 :
Range 2 : Bipolar, 10000 , 7.5 Samp. per Sec.

Base : Not Used
Calibration File : None
Calculation : Uncal
Scale Factor : Not Used
Units After Scaling : Not Used
Uncal. Response : 0
Result Table Reports : All Peaks
Hide ISTD Peak : Enabled
GPC Calibration File :



1/14/2014 1:56 PM Chromatogram C:\Clarity Lite\WORK1\DATA\H2 to air 1-1 run 2.PRM Page 2 of 2

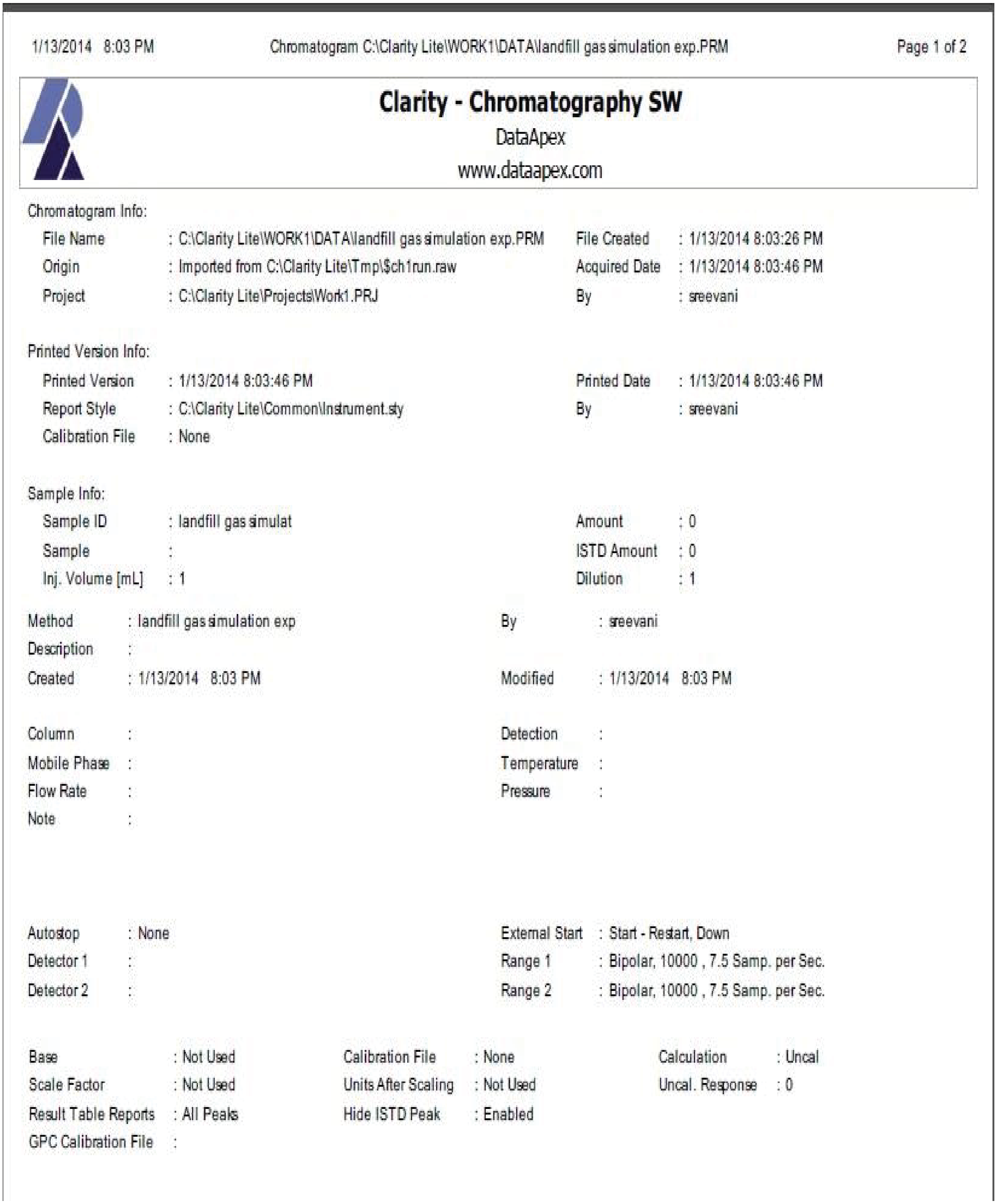
Result Table (Uncal - H2 to air 1-1 run 2)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	3.240	1025.740	20.206	100.0	100.0	0.65	
	Total	1025.740	20.206	100.0	100.0		

Result Table (Uncal - H2 to air 1-1 run 2)

Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
No peak to report						

Figure 3.31. Gas chromatograph of 1:1 ratio of air and hydrogen at 32 °C



1/13/2014 8:03 PM Chromatogram C:\Clarity Lite\WORK1\DATA\landfill gas simulation exp.PRM Page 1 of 2

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Chromatogram Info:
File Name : C:\Clarity Lite\WORK1\DATA\landfill gas simulation exp.PRM File Created : 1/13/2014 8:03:26 PM
Origin : Imported from C:\Clarity Lite\Tmp\$ch1run.raw Acquired Date : 1/13/2014 8:03:46 PM
Project : C:\Clarity Lite\Projects\Work1.PRJ By : sreevani

Printed Version Info:
Printed Version : 1/13/2014 8:03:46 PM Printed Date : 1/13/2014 8:03:46 PM
Report Style : C:\Clarity Lite\Common\Instrument.sty By : sreevani
Calibration File : None

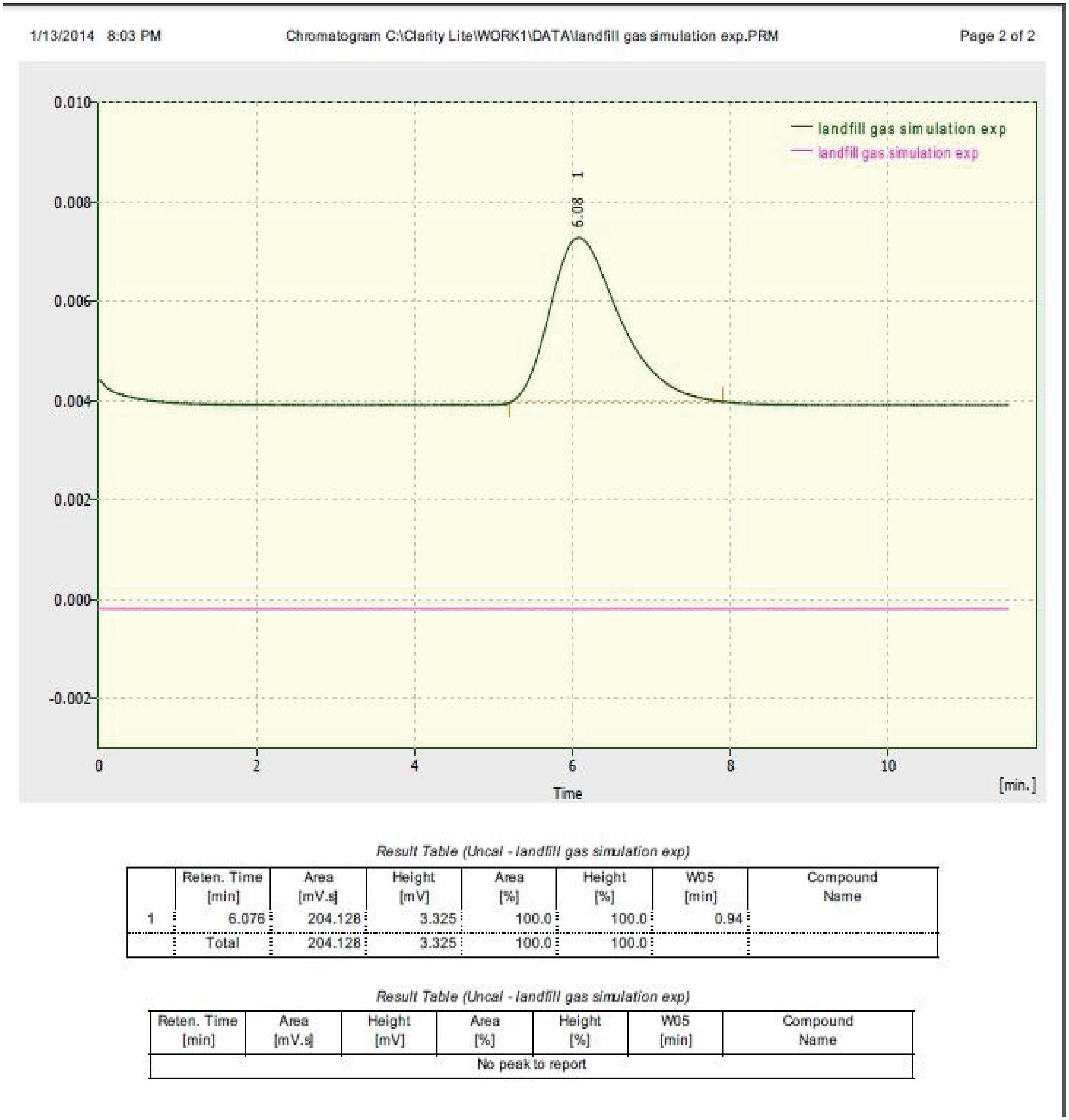
Sample Info:
Sample ID : landfill gas simulat Amount : 0
Sample : ISTD Amount : 0
Inj. Volume [mL] : 1 Dilution : 1

Method : landfill gas simulation exp By : sreevani
Description :
Created : 1/13/2014 8:03 PM Modified : 1/13/2014 8:03 PM

Column : Detection :
Mobile Phase : Temperature :
Flow Rate : Pressure :
Note :

Autostop : None External Start : Start - Restart, Down
Detector 1 : Range 1 : Bipolar, 10000 , 7.5 Samp. per Sec.
Detector 2 : Range 2 : Bipolar, 10000 , 7.5 Samp. per Sec.

Base : Not Used Calibration File : None Calculation : Uncal
Scale Factor : Not Used Units After Scaling : Not Used Uncal. Response : 0
Result Table Reports : All Peaks Hide ISTD Peak : Enabled
GPC Calibration File :



1/13/2014 8:03 PM Chromatogram C:\Clarity Lite\WORK1\DATA\landfill gas simulation exp.PRM Page 2 of 2

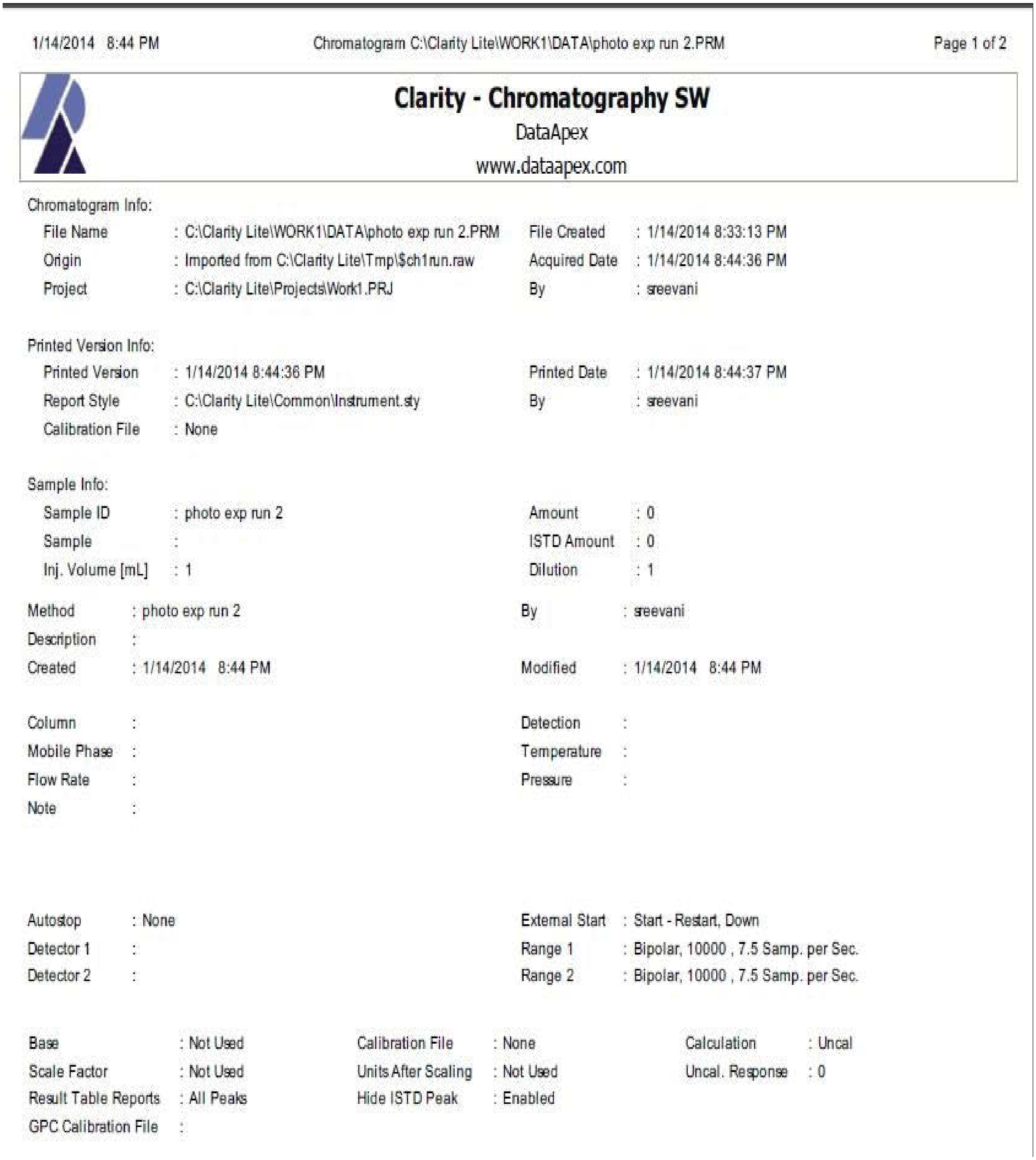
Result Table (Uncal - landfill gas simulation exp)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	6.076	204.128	3.325	100.0	100.0	0.94	
	Total	204.128	3.325	100.0	100.0		

Result Table (Uncal - landfill gas simulation exp)

Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
No peak to report						

Figure 3.32. Gas chromatograph of gas evolved from landfill gas simulation experiment at 32 ˚C



1/14/2014 8:44 PM Chromatogram C:\Clarity Lite\WORK1\DATA\photo exp run 2.PRM Page 1 of 2

Clarity - Chromatography SW

DataApex

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Chromatogram Info:

File Name : C:\Clarity Lite\WORK1\DATA\photo exp run 2.PRM
File Created : 1/14/2014 8:33:13 PM
Origin : Imported from C:\Clarity Lite\Tmp\$ch1run.raw
Acquired Date : 1/14/2014 8:44:36 PM
Project : C:\Clarity Lite\Projects\Work1.PRJ
By : sreevani

Printed Version Info:

Printed Version : 1/14/2014 8:44:36 PM
Printed Date : 1/14/2014 8:44:37 PM
Report Style : C:\Clarity Lite\Common\Instrument.sty
By : sreevani
Calibration File : None

Sample Info:

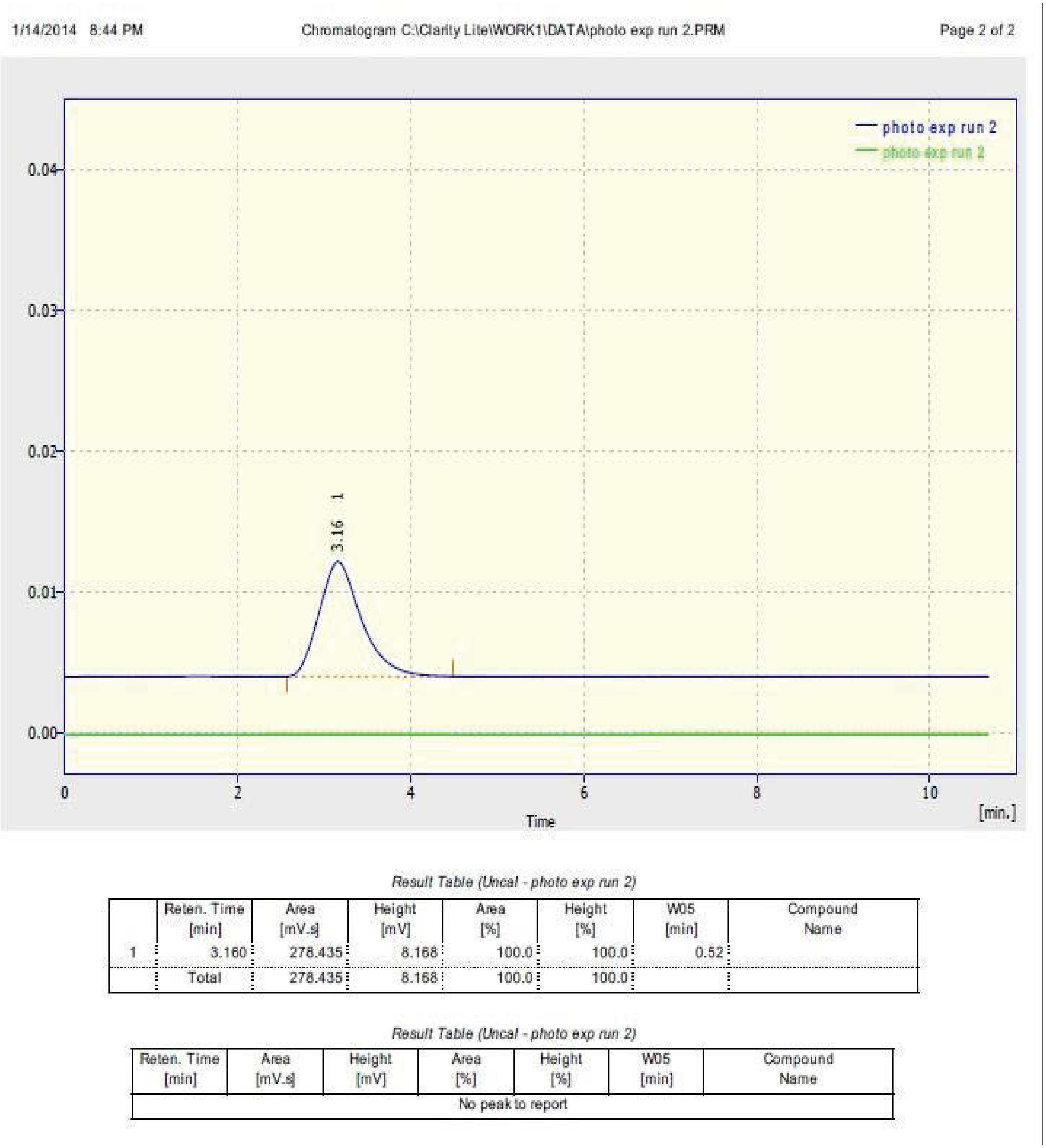
Sample ID : photo exp run 2
Amount : 0
Sample :
ISTD Amount : 0
Inj. Volume [mL] : 1
Dilution : 1

Method : photo exp run 2
By : sreevani
Description :
Created : 1/14/2014 8:44 PM
Modified : 1/14/2014 8:44 PM

Column :
Detection :
Mobile Phase :
Temperature :
Flow Rate :
Pressure :
Note :

Autostop : None
External Start : Start - Restart, Down
Detector 1 :
Range 1 : Bipolar, 10000 , 7.5 Samp. per Sec.
Detector 2 :
Range 2 : Bipolar, 10000 , 7.5 Samp. per Sec.

Base : Not Used
Calibration File : None
Calculation : Uncal
Scale Factor : Not Used
Units After Scaling : Not Used
Uncal. Response : 0
Result Table Reports : All Peaks
Hide ISTD Peak : Enabled
GPC Calibration File :



1/14/2014 8:44 PM Chromatogram C:\Clarity Lite\WORK1\DATA\photo exp run 2.PRM Page 2 of 2

Result Table (Uncal - photo exp run 2)

	Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
1	3.160	278.435	8.168	100.0	100.0	0.52	
	Total	278.435	8.168	100.0	100.0		

Result Table (Uncal - photo exp run 2)

Reten. Time [min]	Area [mV.s]	Height [mV]	Area [%]	Height [%]	W05 [min]	Compound Name
No peak to report						

Figure 3.33. Gas chromatograph of gas evolved from Black Sea simulation experiment at 32 ˚C

From the Figure 3.33, it is observed that we did not make any hydrogen. This might be because of the CO_2 effect on the solubility of H_2S in water making much less sulfide available for the photocatalyst. Any hydrogen that was made might be below the GC detection limits.

Comparing the retention time for H_2 in Figure 3.32 to the single peak obtained in Figure 3.34, it is clear that H_2 was a major gaseous product in the photolysis of simulated Black Sea water.

Conclusion and Future work:

Based on H_2S removing capacity and H_2 gas evolution, copper sulfide was comparable to cadmium sulfide, which is used as a standard in the experiment, but it is prone to photo-decomposition. ICP-OES results showed high concentrations of tungsten free metal in the solution, which shows that WS_2 is also prone to photo-corrosion. Based on the above results further tests were conducted on molybdenum sulfide.

Many tests were conducted on carbon to see whether it acts as a catalyst or a reagent. From the round bottom flask test we can conclude carbon as an adsorbent and a catalyst, which in the presence of oxygen converts hydrogen sulfide to sodium sulfate and sodium thiosulfate.

The photo-experiment results showed that Pt and Teflon in the system increased gas evolution. Platinum aids in catalytic water splitting. Hydrogen sulfide gives free sulfur and hydrogen in the presence of platinum. Teflon aids in bubble formation, acts as nucleation site for dissolved gas. So, in the presence of Teflon more gas evolution was observed.

Ion selective electrode measurements required two electropotential calibration curves, one versus sulfide concentration at constant pH, and one versus pH at constant sulfide concentration, in order to accurately determine the concentration of free sulfide ion in solution.

In the future we need to confirm the stability of the semiconductor photocatalysts with AA, OES, or atomic mass analysis. Gas evolution in the absence of sulfide in the system should be studied, if it is due to photo-corrosion or water-splitting. The fate of sulfide at the end of experiment should be studied, elemental sulfur have many applications compared to SO_4^{2-} . Less expensive substitutes for the co-catalyst platinum should be tested.

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