LICENCE TO McMASTER UNIVERSITY

This Thesis has been written
[Thesis, Project Report, etc.]

by Michelle Margaret-Mary Hendriks for
[Full Name(s)]
Undergraduate course number 4K06 at McMaster University under the supervision/direction of Professor J. R. Kramer.

In the interest of furthering teaching and research, I/we hereby grant to McMaster University:

1. The ownership of 5 copy(ies) of this work;
2. A non-exclusive licence to make copies of this work, (or any part thereof) the copyright of which is vested in me/us, for the full term of the copyright, or for so long as may be legally permitted. Such copies shall only be made in response to a written request from the Library or any University or similar institution.

I/we further acknowledge that this work (or a surrogate copy thereof) may be consulted without restriction by any interested person.

Jan R Kramer
Signature of Witness, Supervisor

M Hendriks
Signature of Student

June 4th, 1991
date

(This Licence to be bound with the work)

Analytical Procedures In Field Sampling For Aqueous Organic Volatile Sulfides

Analytical Procedures In Field Sampling For Aqueous Organic Volatile Sulfides

by

Michelle Margaret-Mary Hendriks

A Thesis

Submitted to the Department of Geology

In Partial Fullfillment of the Requirements for the

Degree Bachelor of Science

McMaster University

April, 1991

BACHELOR OF SCIENCE (1991) McMASTER UNIVERSITY

(GEOLOGY) HAMILTON, ONTARIO

TITLE: Analytical Procedures in Field Sampling For Aqueous Organic Volatile Sulfides

AUTHOR: Michelle Margaret-Mary Hendriks

SUPERVISOR: Dr. James R. Kramer

NUMBER OF PAGES: i-x; 1-57

ABSTRACT

The sulfur cycle is perhaps one of earth's most important cycles. Biologically sulfur is the main constituent needed to form building blocks such as amino acids. Ecologically, it can devastate forests, lakes and ecosystems in one of it's many forms. Industrially (and perhaps naturally) it is the source of our acid rain problem.

An estimation of sulfide fluxes emitted into the atmosphere is extremely variant due to the lack of efficient means of measuring these fluxes. Several simplistic measuring devices have been employed to estimate the oceanic, continental and atmospheric fluxes. Problems have arisen due to the non-uniform distribution of sulfur sources such as industries, volcanoes and marshlands.

In the specific case of organic volatile sulfides, estimates of fluxes have been deduced and not actually measured to any great extent. The fundamental reason for this being the lack of an efficient means of recording data in the field to support the flux estimates.

This study has attempted to secure the efficiency of adsorption tubes used to sample in situ freshwater sulfide fluxes. Optimal preparation involved using Molecular Sieve 5A (60/80 mesh) contained and activated in pyrex glass tubing (6mm. o.d.). Proper activation occurred at 300C for 8 hours under a constant helium flow.

Adsorption of sulfides was by helium induced release of gases at room/atmospheric temperatures. After 15 minutes, the adsorption tube was recapped and stored at (-8C) for no more than 7 days. At this time, the tubes were analyzed.

Analysis was by GC/HECD in the laboratory. A custom made heat desorber (at 270C), in conjunction with liquid nitrogen and hot water sufficiently trapped the released sulfides from the adsorption tube. Calibrated data obtained in the laboratory provided for proper analytical interpretations of the flux of sulfides emitted from the sample.

ACKNOWLEDGEMENTS

This thesis was the result of the combination of a summer NSERC research position obtained by Dr.James R. Kramer and his coincidental supervision. I would especially like to thank Dr. Kramer for providing myself with the opportunity to present my work at the 16th Annual Environmental Science and Engineering Research Seminar in Ganonoque, Ontario January 27-29, 1991 and for his constant encouragement.

I would also like to gratefully(!) acknowledge Dr. Tracey Bryar and Dr. Francois Caron for their consistent help both in the laboratory and in the field. (I'm not sure whether I should thank Francois for running me over with the canoe or not). Special mention of Jasmin Patry for his help on the computer and to both he and Paula Takats for their help in Sudbury.

Finally, I am always grateful for the constant support of my Mom and Dad whose examples have given all of their children much to look up to. To my "little" brothers and sisters: Rick(y)-for his advise, Tim(my)-good luck you engineering geek!, Judy-don't worry, one day we'll stop teasing you and especially Kristy-your drawings made my room much brighter. To my tri-training partner and very close friend Francois Brissette, who was always there for me.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

INTRODUCTION

Sulfur is perhaps one of the most unique elements active in the earth's many cycles as it is both a key nutrient and pollutant to all living things (Brown, 1982). Anthropogenic sources of atmospheric sulfur, primarily as SO2, include the combustion of fossil fuels (85%), smelting of ores (11%) and petrochemical processing (4%) (Black, 1978 and Brown, 1982).

Contrarily, naturally occurring sulfur originates in sea sprays (as aerosols), during volcanic activity (mainly as H2S and SO2), in "anaerobic microbial activity" (Aneja et.al., 1982), from marine algae and finally during decomposition of organic matter (Aneja et.al., 1981 & 1982). The majority of these natural processes involve the reaction with organics in a moist environment.

Among the naturally occurring sulfurs, biogenically produced sulfur compounds are thought to contribute significantly to the global atmospheric sulfur cycle (Brown, 1982, Adams et.al., 1981 and Moller, 1984). Large varia-tions have arisen in estimates of the amounts of sulfur from biogenic emissions due to a lack in prediction accuracy and experimental determination of these emissions.

Classically, global sulfur emissions have been determined using known values from anthropogenic sources and measurements of the global depositions from the atmosphere (Adams et.al., 1981 and Aneja et.al., 1981). Thus biogenic contributions

have been deduced from the difference between anthropogenic and atmospheric contributions.

BIOGENIC CONTRIBUTIONS:

Biogenic contributions are needed to balance the global sulfur budget. There are, however, extremely large deviations in the expected values, varying from 35-289 TgS/yr (Aneja et.al., 1981 and Brown, 1982). Since both organic and anthropogenic sulfur sources vary in time and space, global models give a somewhat illusive perception of the actual distributions of sulfur cycling. As a solution to this problem, regional sulfur budgets are presently being studied as a reference for the overall budget (Brown, 1982).

The importance of determining exactly what proportions and how much biogenically produced sulfur enters the regional or global cycle is important for several reasons. Our main concern is to attempt to grasp a quantitative knowledge of how abundant the atmospheric extent of biogenic sulfate is and consequently its effects on acid rain (Aneja et.al., 1982).

Organic sulfides released from land and water are made up of reduced volatile sulfur compounds. These are metastable and transform in the atmosphere to sulfates or sulfuric acid. Specific sulfur compounds that are formed and emitted from biogenic sources are shown in Table 1.1 and will be referred to in the form of their acronyms throughout this report.

The fundamental processes by which organic volatile sulfides are produced are by (a) Metabolic activities conse-

Table 1.1: Biogenically released volatile sulfur compounds encounteredin this study.
(Adapted from Caron, 1990-Phd. Thesis)

Name	Formula	Acronym
Carbon disulfide	CS_2	CS_2
Carbonyl sulfide	COS	COS
Diethyl sulfide	$C_2H_5SC_2H_5$	DES
Dimethyl disulfide	CH_3SSCH_3	DMDS
Dimethyl sulfide	CH_3SCH_3	DMS
Hydrogen sulfide	H_2S	H S
Methanethiol	CH_3SH	METH
1-Propanethiol	$CH_3CH_2CH_2SH$	PrSH

quential to sulfur (sulfate) reduction and /or other metabolic activities involving sulfur (bacteria, algae, higher plants) (b) Decomposition of roganic matter releasing small compounds, some of which contain sulfur (Moller, 1984).

PREVIOUS WORK:

Studies to determine organic volatile sulfide (O.V.S.) emissions have incorporated several methods. To determine sulfide fluxes to the atmosphere from soils, a flux chamber is commonly used. This consists of, a small chamber analogous to a mini-greenhouse with a surface measuring approximately 0.25-1 square meter (Aneja et.al., 1982 and Steudler & Peterson, 1985).

In this procedure, the air flow is kept constant to provide proper ventilation by circulating a carrier gas through the chamber. The effluent gases are then pre-concentrated on an adsorbent (Langhorst & Coyne, 1989 and Steudler & Peterson, 1985).

The types of sorbents used to collect sulfides vary. Molecular Sieve(s) 5A/13X, Silica gel, Tenax GC, Poropak Q and Chromosorb 107 are a few of the commercially manufactured sorbents tested and/or used in field measurements (Black et.al., 1978, de Souza, 1988, Steudler and Kijowski, 1984 and Torres et.al., 1983).

Subsequent analysis is conducted by gas chromatograph and flame photometric detector after thermal desorption (Lamb et.al., 1987 and Steudler & Peterson, 1985).

This simple set-up yields reasonable results but as yet is only used to sample air over soils. Aquatic sampling however is somewhat more complicated.

Aqueous samples undergo important changes shortly after sampling (Caron and Kramer, 1989). Analysis of sulfides in water are consequently conducted in situ or immediately following sampling (Andreae and Barnard, 1983 and Nriagu and Holdway, 1989). Samples may be simulated in the laboratory using known quantities of sulfides injected into an aqueous medium or by using algal cultures (Caron, 1991).

The apparatus used for water samples is a modified purge and trap method. In this procedure the sample is heated to release the volatiles which are carried with a stream helium. A subsequent system of water traps and loop/coiled trap(s) in combination with the use of liquid nitrogen and heat allows the gases to be filtered and trapped for analysis (Caron & Kramer, 1989, Newman & Gschwend, 1987 and Richards et.al., 1989). Refer to Figure 1.1.

Comparable to air sampling, a GC is used for analysis. The detectors commonly used are a flame photometric detector, electrolytic conductivity detector (Caron & Kramer, 1989) or mass spectrometer (Headley, 1987).

All previous work has allowed atmospheric analysis or water analysis but few "in situ" designs are present for water.

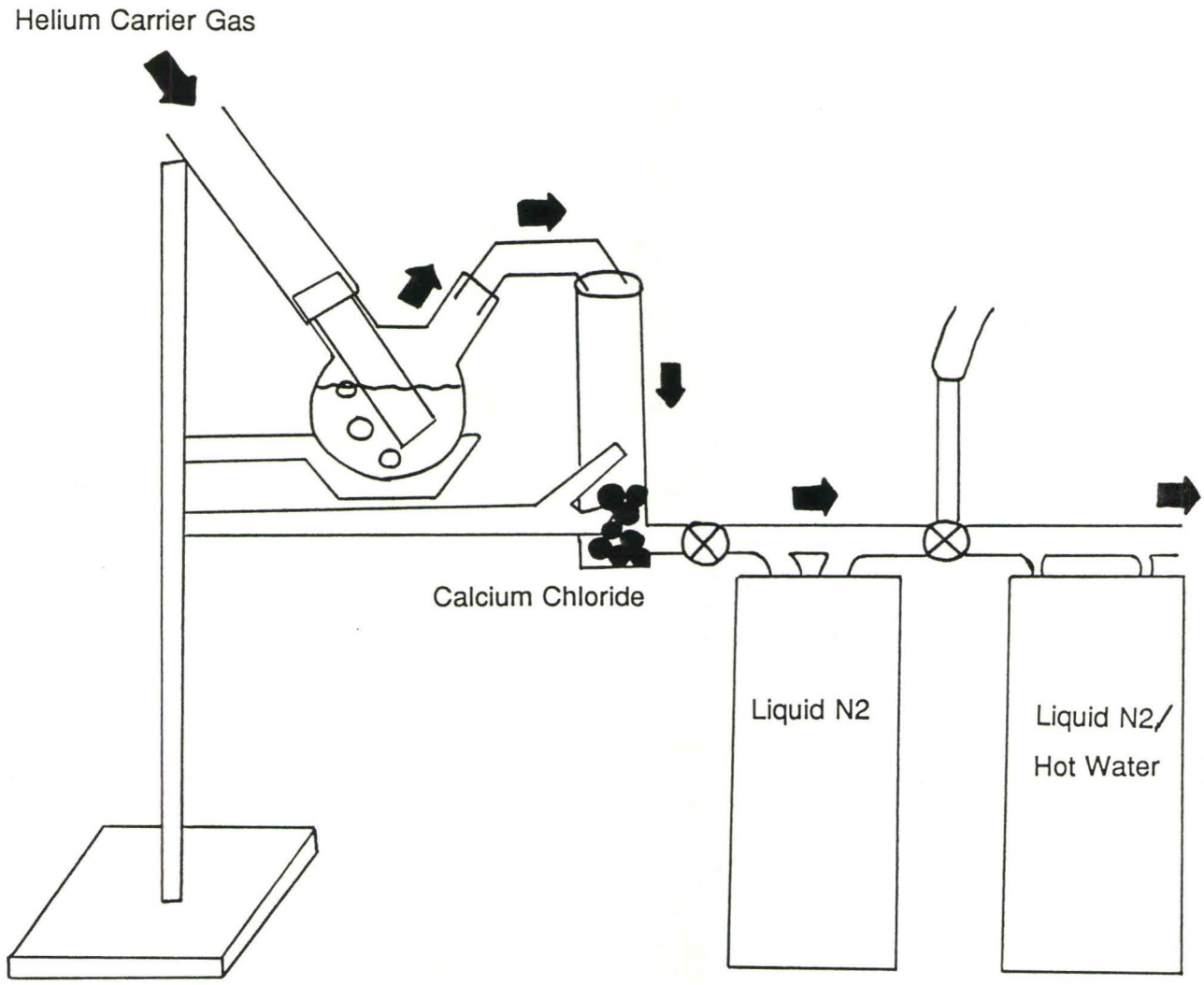


Figure 1.1: Distillation Line For Non-Preconcentrated Aqueous Samples (adapted from Caron, 1990)

PURPOSE AND SCOPE:

Aqueous organic volatile sampling has been restricted to those areas where sampling has permitted moving the gas chromatograph and all pertinent equipment into the field or to areas in close proximity to the laboratory. Evidence suggests that changes occur between sampling (especially in aqueous samples) and laboratory analysis, altering the integrity of the sample.

To obtain significantly meaningful results of the O.V.S. emissions from such remote areas such as the Hudson Bay Lowlands, portable laboratories would have to be developed. The feasibilities of such an undertaking are not too probable. Alternately, a new method of utilizing previously tested sampling methods by compacting their required capacities (ie: eliminating helium gas, a heat source and liquid nitrogen) or adapting them to be suitable for water is a desirable option.

The primary purpose of this study is to test this option. By using previously tested sorbents as a basis for the analytical procedure, the optimization of adsorption tubes in conjunction with a portable field apparatus and stationary laboratory will be examined.

Of specific interest is maintaining the integrity of the sample, maximizing storage time before analysis, and determining the storage and desorption temperatures of the samples. In order to facilitate a large scale sampling such as the Hudson Bay Lowlands, an attempt will be made to optimize all

of the above mentioned parameters.

METHOD OF STUDY:

Initial laboratory analyses were conducted in the Spring of 1990. A first attempt at gathering field data from the Sudbury region was undertaken in July of that same year. Of special interest was the feasibility of the portable apparatus in the field and more importantly to gather some tangible results from the natural environment.

Further laboratory refinements were conducted to try and (a) refine storage time and temperature of the tubes before and after sampling and analysis, (b) eliminate problems with the internal standard and (c) determine the desorption specifications. (Glassware preparation, sorbent types, adsorbing and desorbing apparatus' were tested before initial tests began).

Complete specifications for glassware preparation, calibration, collection of data, storage of adsorption tubes, and analysis by desorption and gas chromatography are given in this study.

CHAPTER II

MATERIALS PREPARATION

GAS CHROMATOGRAPH:

The gas chromatograph is the most extensively used apparatus in analyzing for volatile sulfides in the environment. The GC used in this study was a Hewlett Packard 5890 connected to a brand Hall Electrolytic Conductivity Detector (HECD).

Commonly, the GC is used in conjunction with a flame ionization detector (de Souza, 1988) or a mass spectrometer (Headley, 1987) however recent studies in our laboratory have proven the HECD to be more efficient.

i] DETECTOR

The Hall electrolytic conductivity detector (HECD) was shown to be the detector of choice for low level sulfur detection (Caron & Kramer, 1989). Where the flame ionization detector could not detect precise levels of sulfur at consistent calibrations, the HECD could. Levels down to "picograms" of sulfur were attainable and the calibration curves were reproducible where the detector was held constant at 950° C. Under proper maintenance, the HECD is very reliable for this study. (For further references see Gluck, 1982).

ii] SPECIFICATIONS

The column used was Chromosil 330 (treated silica gel), the recorder an HP 3390A peak integrator. The carrier gas

used in operating the GC was ultra pure Helium (Canadian Liquid Air) while the detector gas was Air Ultra Zero grade (also Canadian Liquid Air). The detector solvent (total 1000 ml) was methanol HPLC grade diluted in Millipore deionized water at a ratio of 1000ml:200ml methanol:water.

Analysis after injection (injection temperature was 200° C, detector temperature 135°C(base) and 900°C(reactor)) was 6 minutes at 40°C, 30°C/min increase for one minute followed by 9 minutes at 70°C. (This standard procedure has been verified in Caron, 1990-Phd. Thesis).

iii] 6-WAY VALVE SYSTEM

In order to minimize human error and sample losses when transferring the sulfide sample from the distillation line (discussed in detail further on) sample loop to the GC, a Hamilton No. 6-way valve system was incorporated. Figure 2.1 shows the complete recovery system. This system is an improvement on the original method of analysis described by Caron & Kramer (1989). The sample loop itself is FEP teflon tubing (1/8" o.d.) and connected the distillation line directly to the GC. The loop fits tightly into the valve system preventing leakage. The addition of the new injection system did not seem to create an appreciable bias on the calibration curves of the 6 major sulfides (Caron-personal communication, 1991)

iv] RETENTION TIMES

The identity of the sulfides was determined by their

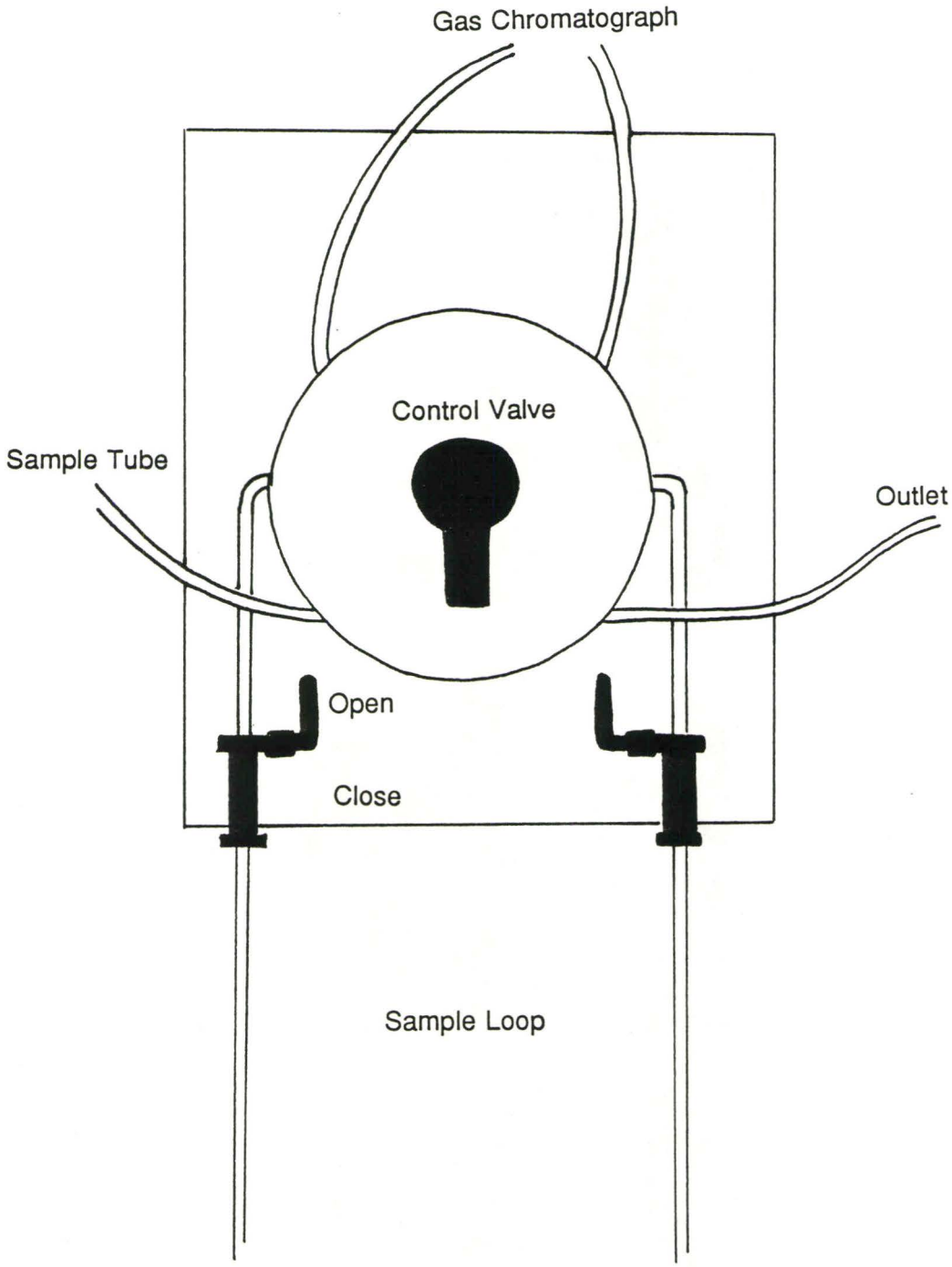


Figure 2.1: 6-Way Valve Laboratory Operating Set-Up

retention times in the GC as compared to standards. Each sulfide has a characteristic retention time which was cross-checked using commercially prepared permeation tubes obtained from Vici Metronics. Figure 2.2 shows a typical chromatogram with each peak identified according to the sulfide type. Problems were encountered in separating the H2S and COS peaks for identification. To facilitate this, a second column was inserted into the GC.

GLASSWARE:

i] BIOLOGICAL USE

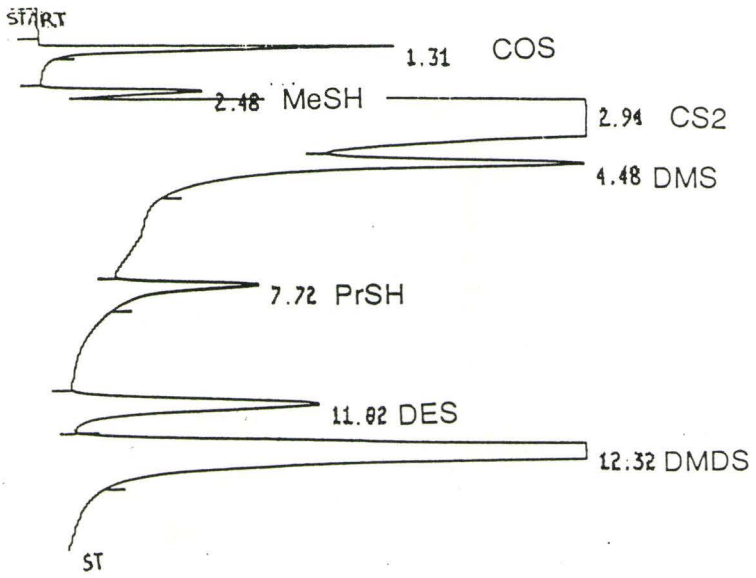
Any glassware that was used to culture algae was properly cleaned and sterilized. Cleaning was by the method in Wong & Couture (1986). Initially the glassware was washed in nonphosphate (liquid) detergent and rinsed 3-5x in tap water. This was followed by soaking in 10%(v/v) HCl for an hour, rinsed 3x in tap water and 5x in deionized water.

Once the growing medium (see Appendix A, Bold's Basic Medium) was placed in the flask the entire contents were autoclaved. Autoclaving was at 248°F and 15-20psi for 15 minutes to sterilize and prevent bacterial contamination.

ii] DIRECT SULFIDE USE

All glassware used in direct contact with sulfides in the sampling lines, was silanized. Silanization prevents sulfides from accumulating on the surfaces of the glassware (Farwell and Gluck, 1980).

The procedure for silanizing is adapted from Caron &



RUN # 149 JUN/25/90 10:57:17

AREA%

RT	AREA	TYPE	AR/HT	AREA%
1.31	298170	PB	0.123	0.873
2.48	148480	PP	0.152	0.435
2.94	2.8447E+07	PB	0.258	83.274
4.48	503640	BB	0.242	1.474
7.72	293660	BB	0.289	0.860
11.02	636320	PB	0.371	1.863
12.32	3833500	BB	0.493	11.222

TOTAL AREA= 3.4161E+07
MUL FACTOR= 1.0000E+00

Figure 2.2: Characteristic Sulfide Retention Times On A Chromatogram

Kramer (1989). The glassware is soaked in Chromerge for about 15 minutes and rinsed in Millipore water. Subsequently, the glassware is soaked for one hour in 10%(v/v) HCl, rinsed in with Milli Q water and dried with acetone. Once completely dry, the silanizing agent is applied. Sylon CT (Supelco, Bellafonte, CA) can be obtained or dimethyl dichlorosilane 5%(v/v) in toluene may be used. The glassware is then rinsed 2x in toluene and 3x in methanol and allowed to dry.

ADSORPTION TUBES:

i] SORBENT CHARACTERISTICS

The adsorption tubes used in this study consisted of the sorbent Molecular Sieve 5A (60/80 mesh) (Chromatographic Specialties Inc., Brockville Ontario). Molecular Sieve 5A is an alkali metal aluminosilicate analogous to naturally occurring clays and feldspars. Table 2.1.

Unique to the Molecular Sieve is the fact that its crystal structure does not collapse when the waters of hydration are driven off (during activation). This characteristic allows a complex network of pore spaces and cavities to form in about 50% of the total volume that the crystals occupy. The cavities permit molecules of up to 13 angstroms to enter the network. (Chromatographic Specialities Inc. Bulletin and Molecular Sieves, 1977).

ii] ASSEMBLY

The adsorption tubes consisted of 26cm long, 6mm(o.d.) silanyzed glass pyrex tubing housing 1.2g of Molecular Sieve

Table 2.1: Adsorption Tube and Sorbent Characteristics	
Sorbent	Molecular Sieve 5A-60/80 mesh
Quantity Used	1.2 grams
Surface Area	700-800 m/g
Container/Housing	26cm./6mm. o.d. silanized glass pyrex tube
Activation	8 hours at 300 C with a helium input flow
Pre-Use Storage	Maximum 48 hours after activation

Table 2.1: Sorbent Characteristics

5A (60/80 mesh). (1.2g makes up approximately 16cm when inside the tubes). While inserting the sorbent into the tube, one end was stoppered with 3mm of packed silanized glass wool (Supelco). A syringe attached to 4mm(o.d.) tubing was used to filter the sorbent into the pyrex tubing. It is best to center the Molecular Sieve 5A (60/80 mesh) in the tube for easier manipulation during the adsorption and desorption procedures. Both ends were capped with GC end column capillary caps (1/4" diameter-Supelco). See Figure 2.3

iii] ACTIVATION AND STORAGE

Molecular Sieve 5A must be heat activated to drive off the waters of hydration in the mesh to provide the necessary pore space for adsorbing (see above). Since this study incorporated the use of more than one tube at a time, a "multiple-activator" was developed.

In this system, up to 14 tubes could be activated at once (Figure 2.4). The heating plate containing the tubes was placed on a heating element at a temperature of 300°C for 8 hours. Helium high purity gas (Canadian Liquid Air) was connected to the pyrex tubes by silicone tubing with a flow of 15 ml/min.

The adsorption tubes may be stored for no more than 48 hours before use. Optimally, temperatures of storage should be (-4°C) to (-8°C) (ie: a fridge freezer's temperature). Dry ice and a large storage freezer allow water to accumulate in the adsorption tubes. Alternately, room temperature defeats

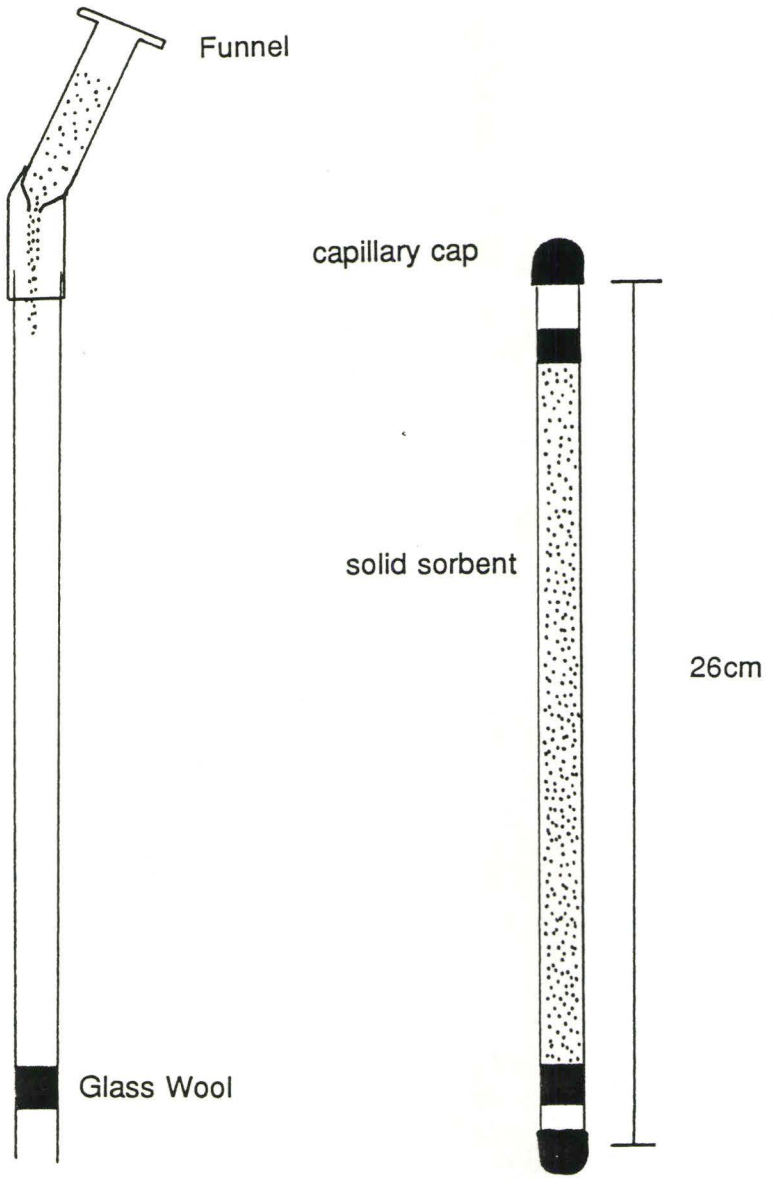


Figure 2.3: Assembly of Adsorption Tubes

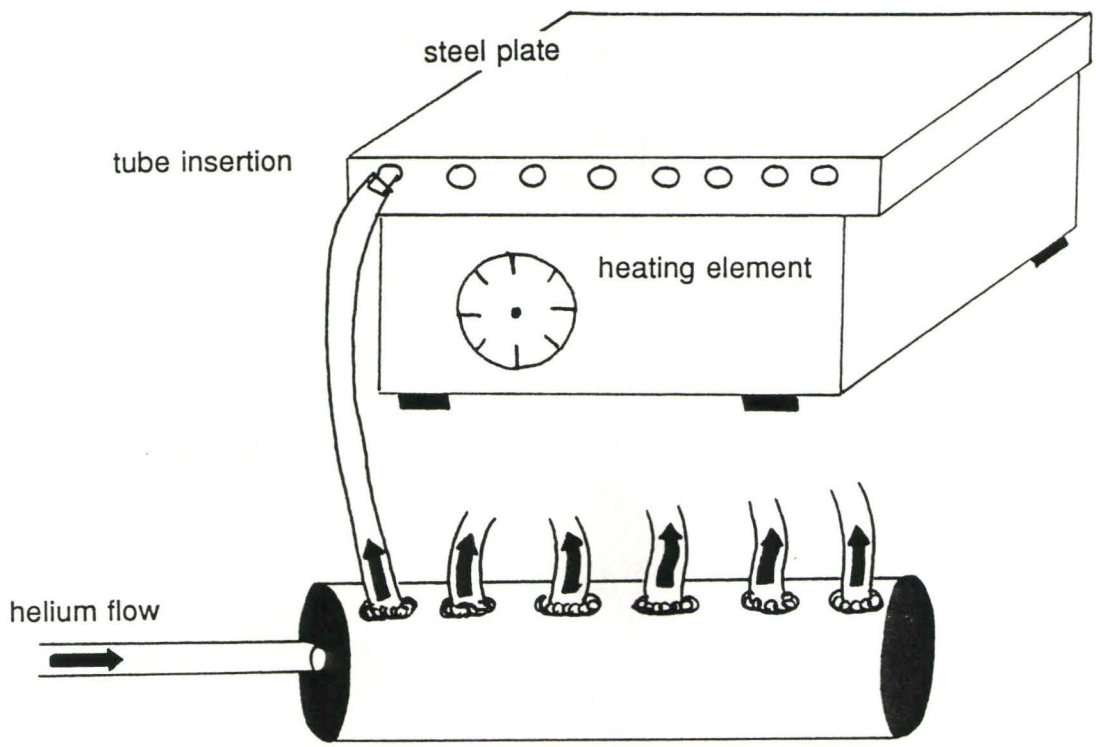


Figure 2.4: Activator For Adsorption Tubes

the activation process by degrading the cavity structures (discussed in Chapter V).

CHAPTER III

ANALYTICAL PROCEDURES

CALIBRATION LINE:

Permeation tubes of CS^2, DMS, PrSH, DES, DMDS were gravimetrically calibrated to determine their permeation rates.

Previous work in the laboratory by Caron (1990), used home-made permeation tubes for the CS_2, DMS, PrSH, DES and DMDS, however it was found that this were not stable over time (Bryar,1991-personal communication). For this reason, all calibrations used commercially prepared synthetic samples.

The method of calibration is as defined by O'Keefe and Ortman (1966) and was also used by Caron & Kramer (1989). Measurements of the weight of the permeation tubes over a known amount of time were recorded. This analysis gives a permeation rate in mass/time.

Once this has been determined, the permeation tubes were placed in a calibration line (Figure 3.1) with a known quantity of helium flowed through the system. (This gives a flow in volume/time). The quantity of helium is altered to obtain values at several limits thus allowing a more precise calibration. Following this, a known volume of the sulfide gas is injected into the GC (ie: 1 ml). The peak area shown on the chromatogram can be related to a mass of sulfide

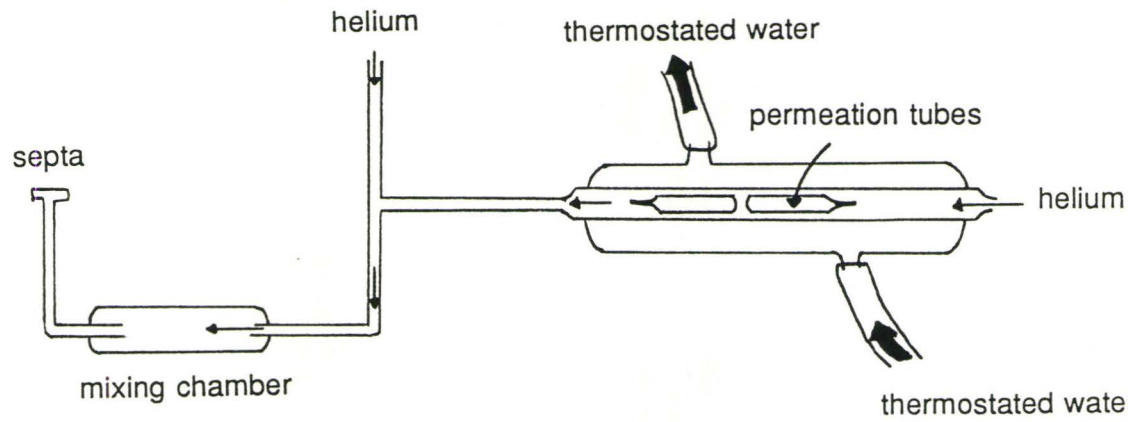


Figure 3.1: Calibration Line (adapted from Caron, 1990)

emitted from the permeation tube.

Figure 3.2 shows the calibration curves of the seven sulfides. Due to the differences in atmospheric concentrations of the different sulfides, COS (and to a lesser extent, MeSH, PrSH and CS_2) are notably on different scales than the remaining sulfides.

INTERNAL STANDARDS:

The use of an internal standard is a common procedure in chromatography. A compound, not present in the sample, is added to a sample to correct for irregularities in preparative work. Diethyl sulfide (DES) was incorporated since it is not found in natural waters. In primary studies the DES was dissolved in ethylene glycol to a dilution of approximately 0.05 µg/ml (Caron, 1990-PhD. thesis). In that case ethylene glycol was chosen due to it's "low vapour pressure at the boiling point of water" (Caron, 1990).

DISTILLATION/ADSORPTION:

i] SET-UP

Because the principal purpose of this study was to devise a simple and compact method of obtaining field samples, the actual adsorbing apparatus developed is very transportable and suitable. Figure 3.3 shows the portable field adsorption line.

With the exception of the stand and clamps, all of the materials consist of silanized pyrex glass. Where connections involve two different glass pieces being fitted to-gether, a

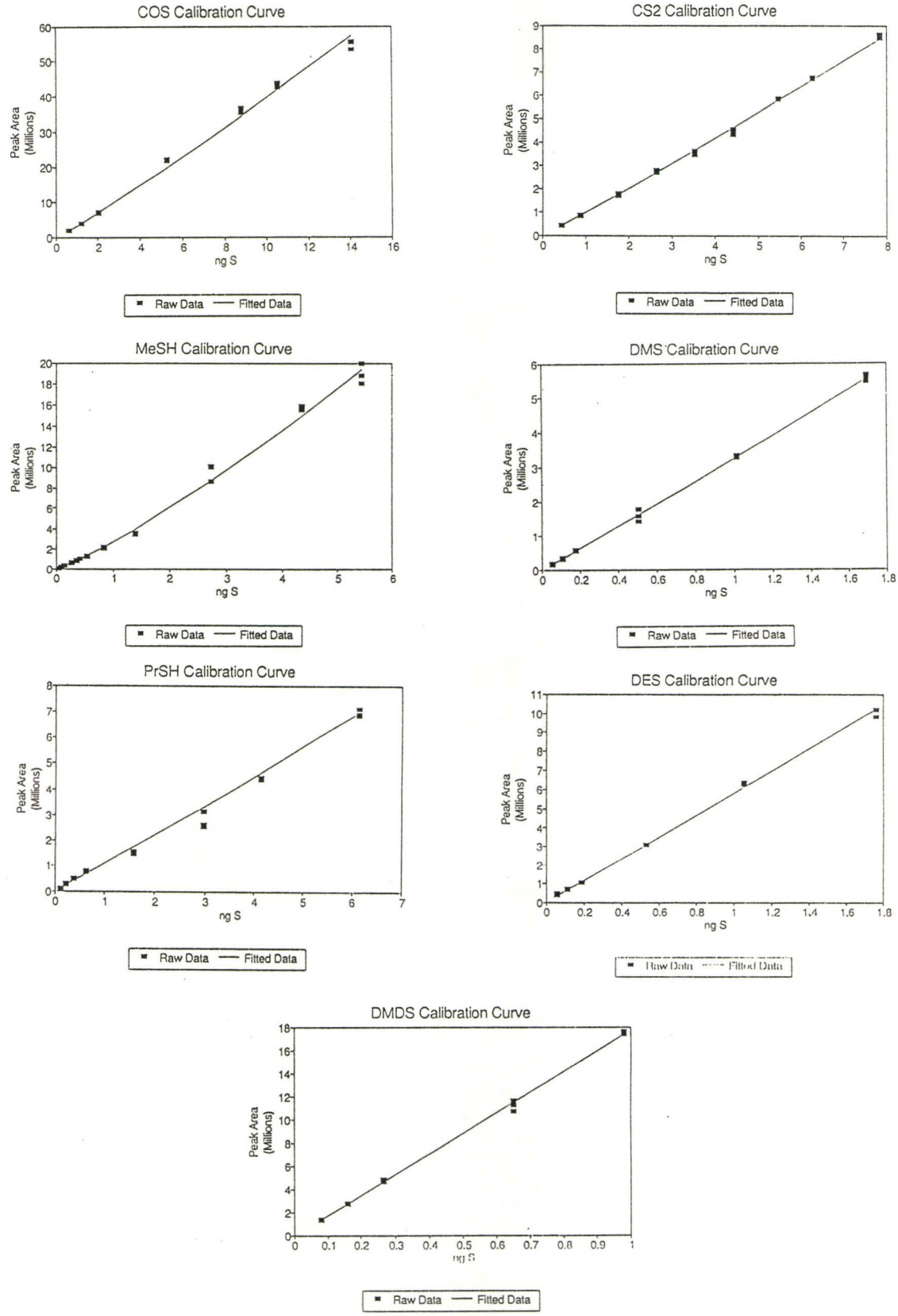


Figure 3.2: Calibration Curves of The Seven Sulfides

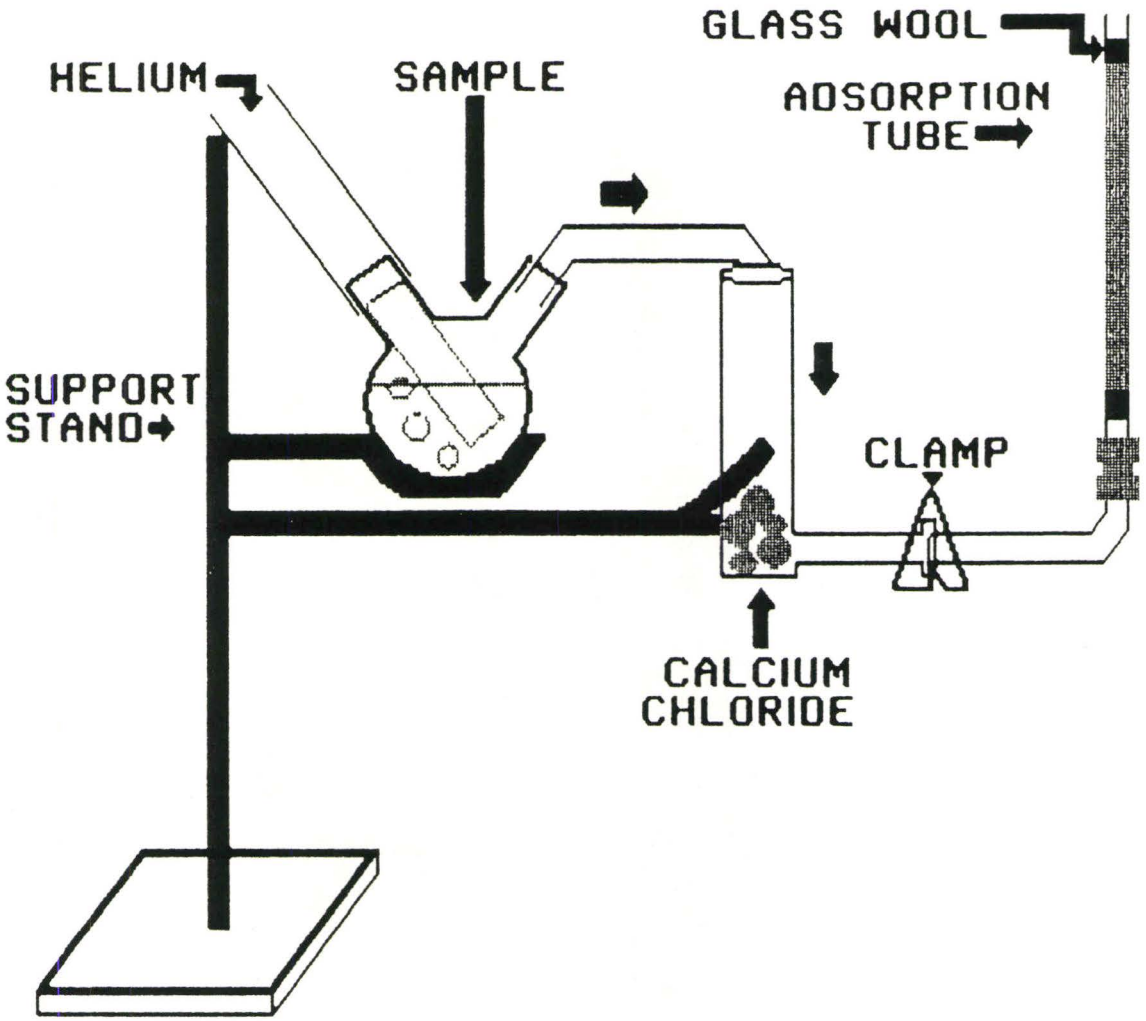


Figure 3.3: Portable Field Adsorption Line

small quantity of silicone grease (Dow) is used to allay the possibility of leaking. Teflon connections and ferrules were used to minimize the chances that the sulfides would accumulate in areas that could not be directly inserted together due to size incompatibilities (ie: where the adsorption tube attaches to the line).

In order to prevent water vapour from accumulating on the adsorption tube, calcium chloride was originally used as a drying trap. Problems began to arise when water continued to accumulate in the adsorption tube. To negate this effect, the volume in the drying trap was reduced to provide minimal space for water to move through the pore spaces of the drying pellets. New dehydrating sorbents are being tested (see Future Considerations-Conclusions).

ii] METHOD

Before taking a sample, the entire apparatus was assembled and the adsorption tube attached to its base. For convenience, the only parts that ever need be removed or replaced during sampling were the adsorption tubes (a new one for every sample) and the sample flask (for cleaning).

The adsorption tube was attached by tightening the teflon connection that joins the tube to the adsorption line. Hand tightening is sufficient. Removal of the sample flask involved loosening the connecting arm and lifting the flask out of the support mantle.

Once the flask and the adsorption tube were in place, a

water sample of approximately 50ml was poured into the flask. 10 µL of ISTD was added and the helium source was inserted into the flask to cap it. (The helium source was a portable tank, smallest in volume, with copper tubing attached to teflon tubing which in turn connected to a pyrex glass frit inserted into the sample flask).

To test for leaks, a commercial leak-detector (Snoop) was used. Where sealing was not found to be secure, springs held by frits joined connections together. Helium was bubbled through the sample at a rate of 80ml/min for approximately 15 minutes. In sampling using water, samples it is common to use heat to release the volatiles into the distillation line. This would mean finding some source of readily available heat that could potentially be used in remote areas.

To avoid this complication, the samples are adsorbed without heat. Once the sampling period ended, the top end or the tube was recapped, the base unscrewed, sealed and the tube placed in a cooler at approximately (-4°C) to (-8°C).

iii] STORAGE

Storage of the tubes involved no longer than 7 days at optimal temperatures (see Chapter V).

DESORPTION:

i] SET-UP

Since the desorption set-up is meant primarily for the laboratory, it uses electricity as a source of heat. The desorption apparatus is shown in Figure 3.4. The heat

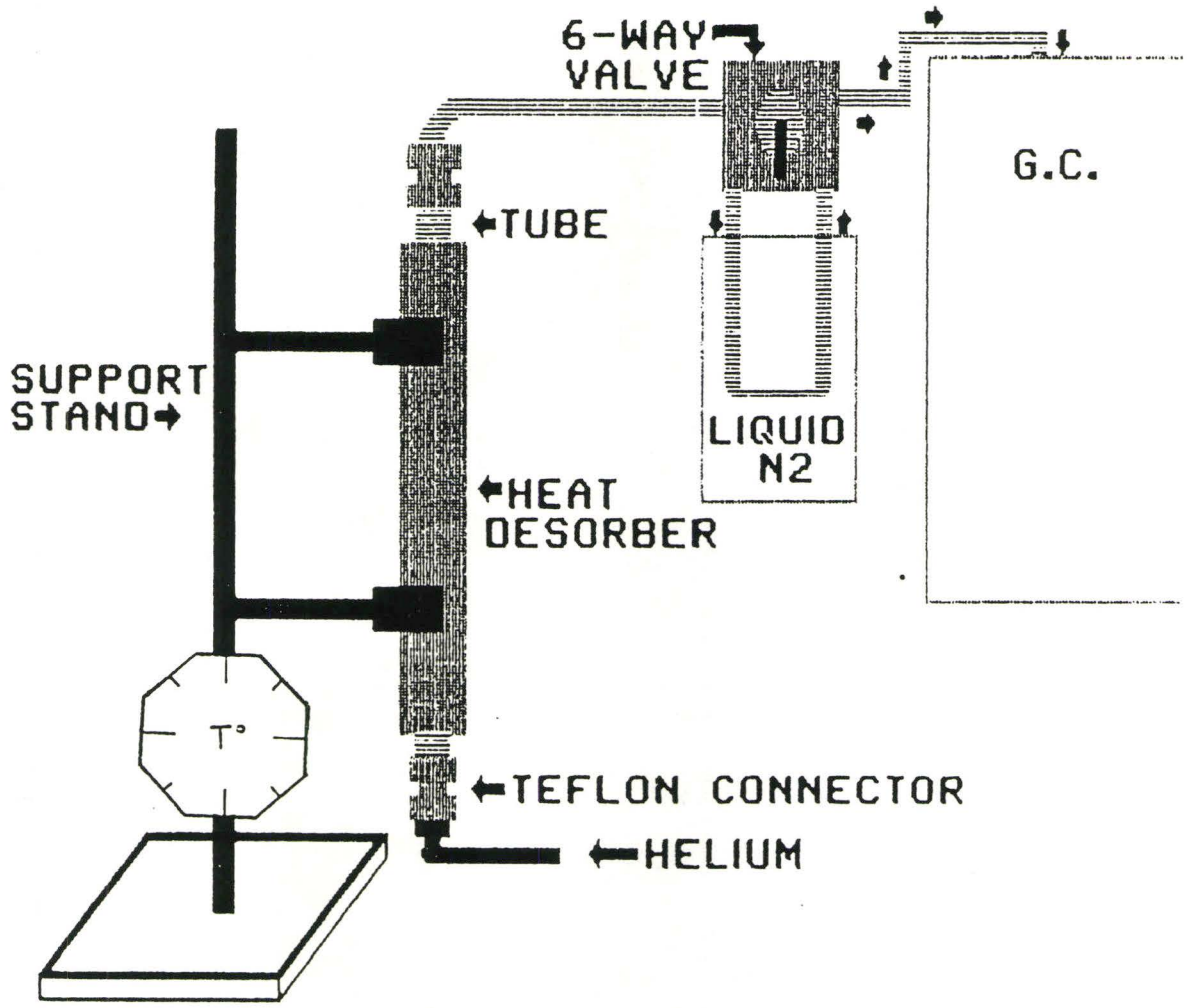


Figure 3.4: Laboratory Desorption Line

desorber consisted of a pyrex glass (8mm o.d.) tube surrounded by approximately 6 meters of tightly coiled conducting wire. The wire was insulated by zirconian oxide cement wrapped in asbestos tape.

The internal temperature of the heat desorber was monitored by a thermocouple. Optimal temperature of desorption was determined to be 270°C. Liquid nitrogen was used to trap the sulfides in the sample loop. The six-way valve system permitted easy and accurate manipulation of the loop containing the sample for GC injection. GC parameters are those described in chapter II.

ii] METHOD

Initially the 6-way valve control knob is kept closed (pointed downward) to segregate the sample loop from the GC. Both of the stopcocks were also closed to segregate the loop from the desorption line (both pointed down). The sample loop was then immersed in a flask of liquid nitrogen.

The adsorption tube was attached to teflon tubing extending from the 6-way valve by a teflon connector. Once the heat desorber reached the optimum desorption temperature of 270°C, the adsorption tube was placed into the desorber. The end extending out of the top of the desorber was in effect sealed and was also the same end that was the base during adsorption. Assuming that the majority of the sulfides adsorb in the first centimetre of the tube, most of the desorption will also be from this same position.

The base of the tube extended out of the bottom of the heat desorber with all of the sorbent contained within the bounds of the desorber. A teflon connector was used to attach the adsorption tube to the copper tubing transmitting the helium flow.

The helium was turned on to 10-12 ml/minute. The first stopcock was opened by moving it to point up. After a few moments, the second stopcock was also opened. 15 minutes time were allowed to elapse before the sample loop was again isolated by closing the stopcocks. The adsorption tube was removed from the heater by disconnecting the helium and lifting it out of the top of the desorber. Immediately, the liquid nitrogen was replaced by hot water for approximately 30 seconds.

The 6-way valve control knob was turned to the right to open it up to the GC. The stopcocks were opened and the GC activated. At least 5 minutes was allowed before the sample loop was segregated from the GC. Another sample could theoretically be started should time optimization or bulk samples need to be processed.

CHAPTER IV

FIELD APPLICATIONS

BACKGROUND ON PROCEDURE:

The procedure for field analysis was that developed and refined in the laboratory (as outlined in Chapter III). The procedure for field analysis was tested in two regions. In Sudbury, a reconnaissance sampling protocol was tested while in Cootes Paradise, the conventions for in situ vertical analysis of organic volatile sulfides were tested.

The adsorption apparatus was highly portable and easy to manipulate while moving from site to site. Since the helium tank was the only synthetic source needed to operate the system, it was obtained in its smallest form to reduce any excessive weight.

The use of an internal standard (ISTD) enabled the results obtained to be monitored for recovery efficiency. A small cooler with ice provided a sufficiently cool storage place for the ISTD in between usage. Calibration data obtained in the laboratory (as mentioned in Chapter III) was again used in interpreting the chromatogram results. All results were obtained from work completed in the laboratory.

RECONNAISSANCE SAMPLING PROTOCOL:

The sampling protocol described below was tested in the Sudbury region. Unfortunately, analytical problems gave highly distorted results for the actual quantities of sulfides present in the lakes sampled (see Chapter V). Nonetheless,

the actual procedural arrangements were efficient for reconnaissance sampling.

i] Equipment

Equipment was assembled beforehand for transport to a base and consequently into the field. The complete list is shown in Table 4.1. The adsorption tubes had to be acti-vated at the maximum 48 hours before use. For areas where tubes would be needed for several days to weeks, the activator would have to be taken to the field base site.

ii] Preparation

The morning of the sampling day, the cooler must be equipped with ice to store both the ISTD and the tubes used in the field (where ice is not readily available, a propane refrigerator would be needed to make ice). The cooler was kept in the vehicle (and could potentially be kept in a helicopter for remote sampling). If chlorophyll is being sampled the fluorometer must be turned on at the base site to equilibrate enough for readings to be taken at night on the samples taken that same day.

iii] Field Steps

A sampling sheet was prepared to record the data obtained in the field and is shown in Figure 4.1. Since the organic volatile sulfide sample took the longest to obtain, it was started immediately upon arrival at the site.

The adsorption line was operated from the back of the truck but could also be operated on flat ground. Initially,

Table 4.1: Reconnaissance Sampling List

adsorption line---sample flask, connectors, CaCl, stand, clamps, springs
adsorption tubes with caps

cooler with ice
filter paper

flow meter-to monitor line
fluorometer
helium tank with connections

internal standard
maps
peristaltic pump

sample bottles-for pH readings
thermometer

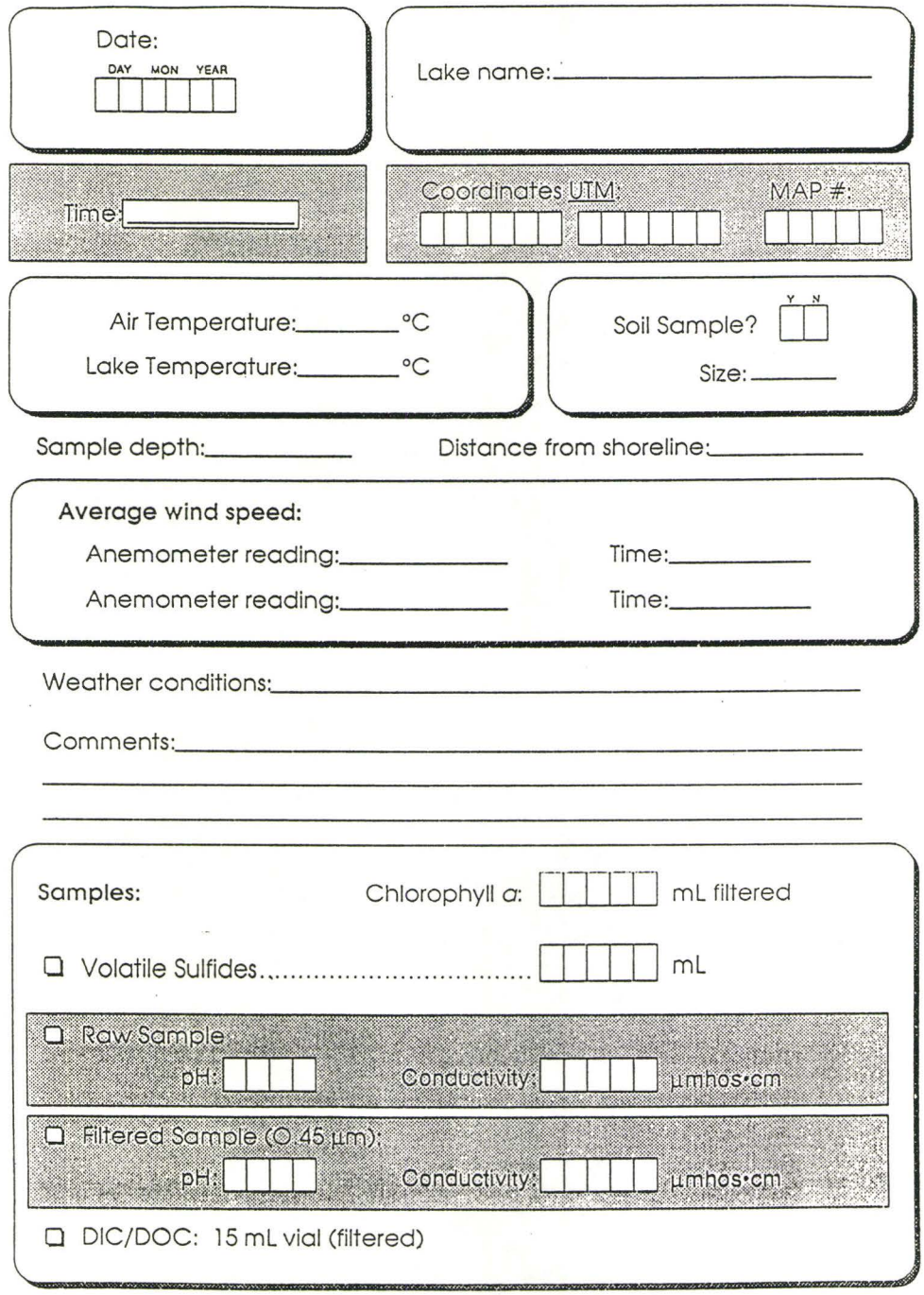


Figure 4.1: Sampling Recording Sheet

the adsorption tube was affixed to the adsorption line and the helium tank readied to attach to the sample flask.

A sample of lake water measuring 50ml was directed into the flask and 10µl of ISTD was added. Without delay, the flask was sealed with the helium input valve and the top cap of the adsorption tube removed (if not already done).

While the volatile sulfides were collecting, atmospheric and water temperatures were recorded. 300ml of water was also filtered for use in the fluorometer. A second 250ml sample was filtered for pH, an additional 250ml was collected in a separate container for raw pH readings. As well, both of the pH water samples were used in the laboratory for conductivity measurements. Depth, time and position of sample were recorded and weather conditions were noted.

After the allotted 15 minutes for sample adsorption was complete, the adsorption tube was removed from the line, sealed and stored on ice in the cooler. Further tests were completed in the laboratory to avoid taking the GC, liquid nitrogen, air etc. into the field.

IN SITU VERTICAL DEPTH SAMPLING:

This method was tested in Cootes Paradise due to its close proximity to our laboratories. The actual collection of sulfides also occurred in our laboratory as the sample was not thought to degrade during the half kilometre drive!

i] Equipment

A custom made vertical integrating depth sampler (for

stabilizing the water column) and temperature reader were assembled. Figure 4.2 depicts the water column stabilizer and varying depth "temperature-taker". An equipment list is shown in Table 4.2.

ii] Preparation

The column stabilizer and bottomless bottle were put into place two days before the samples were actually taken to give sufficient time for stabilization. Once again, the adsorption tubes had to be activated the day before usage and stored.

iii] Steps

The site of sampling was chosen at a depth of one meter and a channel width of 3-4 meters. The canoe was equipped with sampling bottles, thermometer and a bucket of ice to store the samples.

Once at the site, the canoe was manipulated adjacent to the column stabilizer. Water samples and temperatures were taken at the bottom and surface both inside and outside the column stabilizer. The bottomless bottle sample was preserved by placing a shovel under the mud bottom and removing the bottle, mud and water surface completely intact. This method worked surprisingly well.

Adsorption and desorption procedures were those described in Chapter III but were both accomplished in the laboratory rather than in the field. This was mainly for convenience.

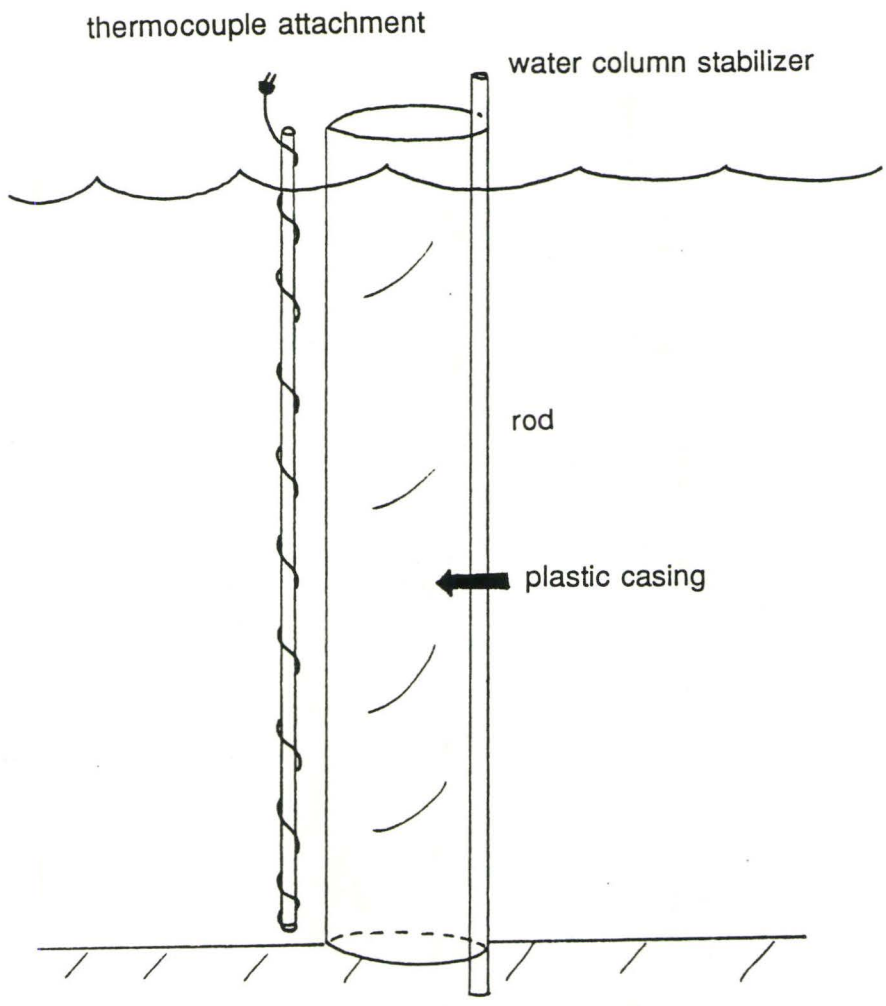


Figure 4.2: Depth Sampler and Temperature Recorder

Table 4.2: In Situ Depth Sampling List

bottomless bottle
canoe
cooler/pail with ice

depth sampler
sample bottles

shovel
thermocouple depth temperature reader

CHAPTER V

RESULTS AND DISCUSSION

LABORATORY STUDIES:

Laboratory studies consisted of the use of pure dry gases to avoid matrix effects induced by water from aqueous samples.

TUBES

i] Dimensions

The length of the tubes was selected purely for practical reasons. One centimetre long tubes would have been sufficient. In order to build a heat desorber, tubes at least 26cm long were made so that the desorber could be manipulated easily.

ii] Sorbent

Two types of sorbents were tested; Silica Gel 60/80 and Molecular Sieve 5A 60/80 mesh. Each was tested separately with results showing that Silica Gel was more efficient than Molecular Sieve at lower flowrates. Molecular Sieve however was more competent both overall and at higher flowrates (Figure 5.1).

COLLECTION

i] Flowrate

Flowrates for collection of samples were determined keeping the desorption parameters constant. 100ml of Milli-Q water, 200 µL ISTD and 200 µL of a CS2, DMS, DMDS synthetic mix were collected for 20 minutes, no heating, onto 100% Molecular Sieve tubes. Flowrates tested were 40, 80 and

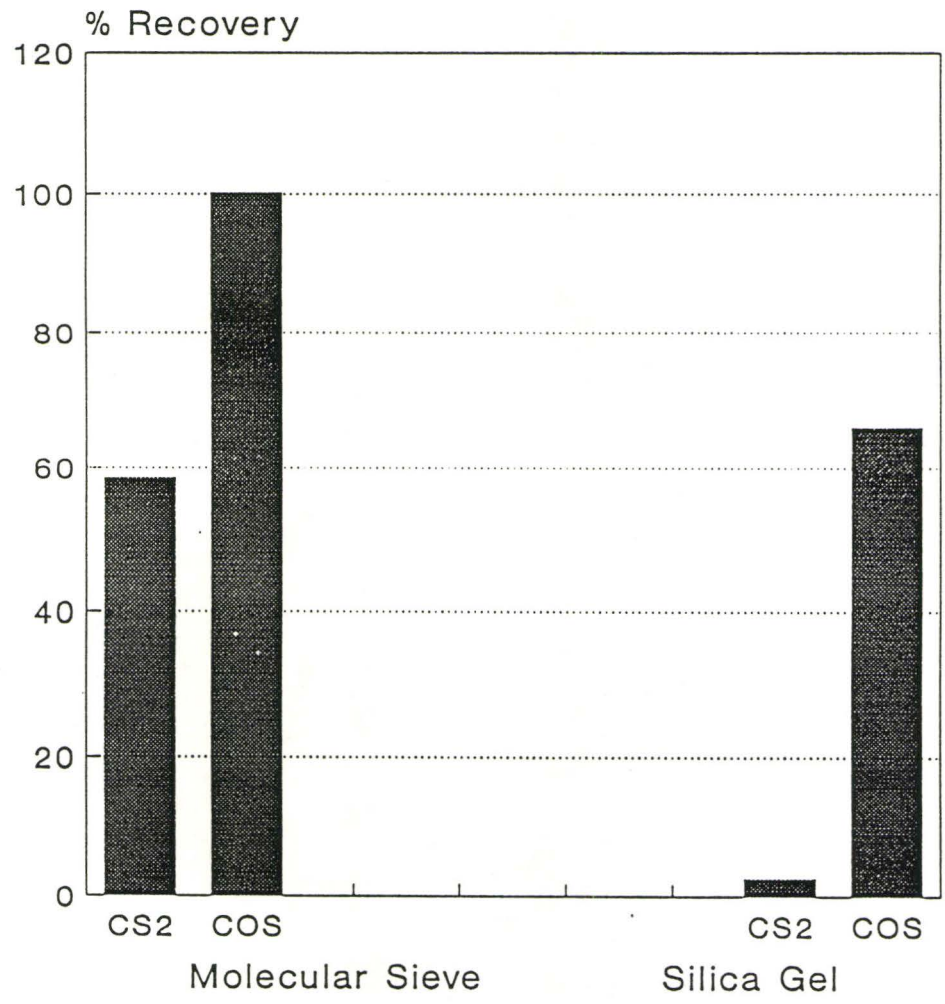


Figure 5.1: Comparative Analysis of Sorbent Retention

120ml/min. The desorption temperature was 295C and flowrate 12ml/min.

Appendix B shows the peak values obtained at each flowrate for each sulfide. With reference to Figure 5.2, 80ml/min was found to be the optimum adsorption flow rate.

ii] Heating

Heating water samples is a standard procedure when operating a purge and trap system. This method was not evaluated in the laboratory however, algae analysis provided some results (see ALGAE SAMPLES, page 45).

STORAGE

i] Method

Four types of storage were tested; dry ice, deep freezer (-18°C), fridge freezer (-4°C) and fridge. Tubes were loaded with pure dry gases (the standard seven) and stored overnight in each of the sites. Desorption was at 295°C for 15 minutes.

Results showed that the dry ice produced an enormous CO2 peak that covered the chromatogram to such an extent that all other peaks were negligible. Both the deep freezer and fridge blocked the ends of the tubes by collecting ice and water (respectively) between the glass wool and sealing caps. Analysis in these two cases was presumed useless. The tubes stored in the fridge freezer allowed for the best desorption results maintaining the best sample integrity.

ii] Time of Storage

Preliminary tests for storage were conducted over the

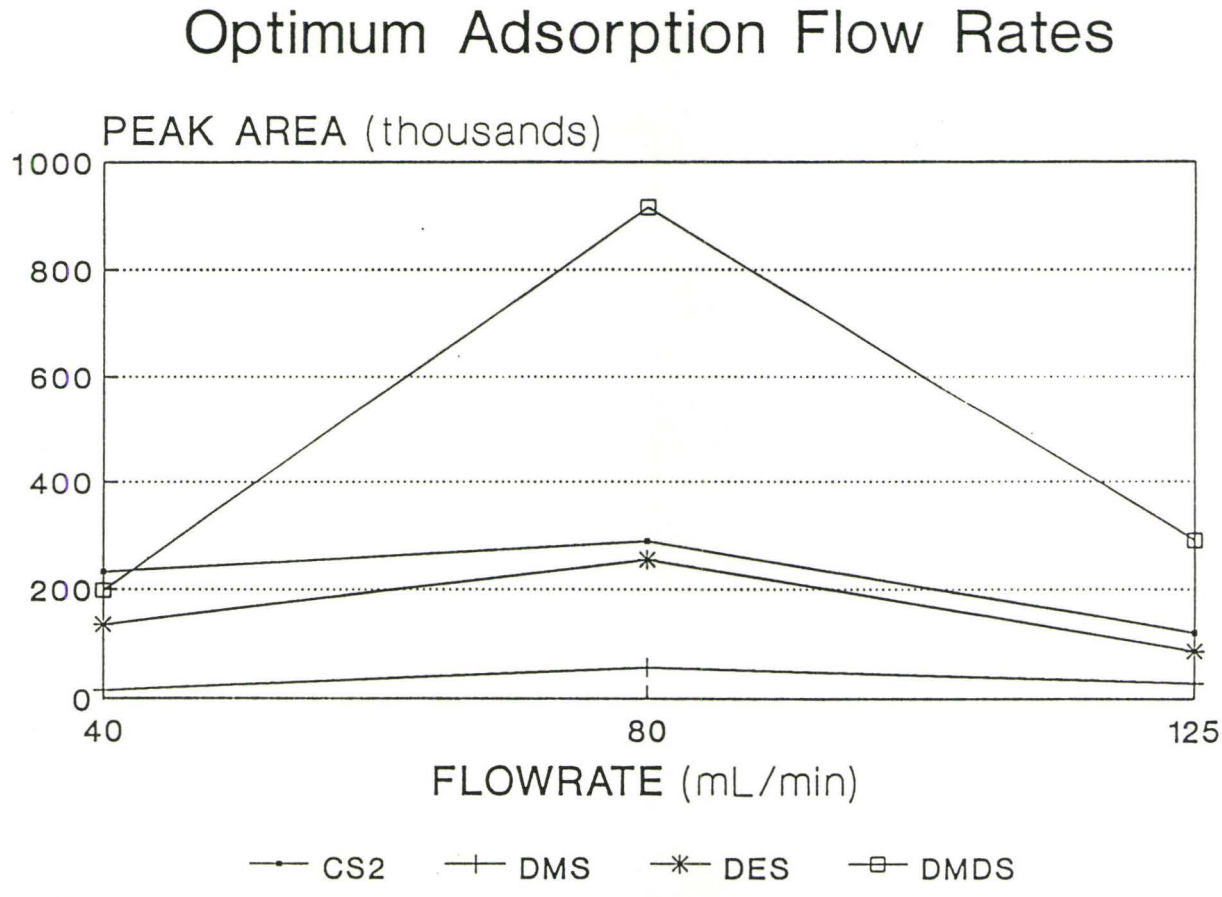


Figure 5.2: Optimum Adsorption Flowrate

period of one week. This reflected the quantity of time that the samples were expected to endure while in transport from the field. Pure gases were adsorbed (one per tube, six tubes per sulfide), stored in the freezer and desorbed 7 days later. Appendix C lists the quantities retained.

Results showed that (a) most of the sulfide is not retained and (b) there is some sort of contamination of the sample. This contamination shows as additional peaks on chromatograms. This may be attributed to poor sealing capabilities of the caps, in which case, sulfides are both released from the tubes and others adsorbed from the atmosphere.

DESORPTION

i] Temperature

To test for the optimum desorption temperature, pure dry gases were adsorbed onto tubes so that there were sets of three tubes for each temperature to be tested. Temperatures were set from 260°C to 290°C at increments of 10 degrees.

Table 5.1 shows complete data sets. Temperatures of 290°C are best for dry gases which is comparable to previous work sited at 295°C (Steudler, 1984). As an aside, the temperature of desorption for water samples is slightly lower at 270°C. Data to support this is limited due to problems originating from the GC.

ii] Flowrate

Flowrates of desorption are taken to be 12ml/min as sited from Steudler (1984). These were tested minimally, in

Table 5.1: Optimum Desorption Temperature Data

Temperature 260	Sample #1	Control
COS	4274300	3318400
MeSH	4893	594760
CS2	628470	2661700
DMS	425280	1240900
PrSH	5062	925720
DES	6514	1006900
DMDS	483990	10731000

Temperature 270	Sample #1	Sample #2	Control
COS	3847800	3830100	3469800
MeSH	2075	6105	619020
CS2	945040	1096000	2516500
DMS	256970	427650	1199300
PrSH	8369	17566	918100
DES	30191	171340	825100
DMDS	533220	515930	8469700

Temperature 280	Sample #1	Sample #2	Control
COS	3358900	351300	3447100
MeSH	3679	4933	632050
CS2	818090	1101800	2434600
DMS	393310	347630	1236900
PrSH	16227	11476	946270
DES	33543	77808	750460
DMDS	320600	585010	7733700

Temperature 290	Sample #1	Control
COS	3595400	3479800
MeSH	1073	639320
CS2	1551300	2668700
DMS	168100	1303300
PrSH	10073	913730
DES	133340	913300
DMDS	814710	9407500

preliminary experiments.

ALGAE SAMPLES:

As mentioned above, water samples are traditionally heated to release the volatiles into the purge and trap system. It should be noted that heating samples produced a greater degree of incompetency on the chromatograms. Several additional peaks were stored other than the standards expected in normal analysis (Figure 5.3).

At temperatures greater than 250°C, sulfide gases react with one another. The integration of sulfides released in desorption is highly distorted and not dependable. For this reason, water samples should not be heated when adsorbing onto a sorbent.

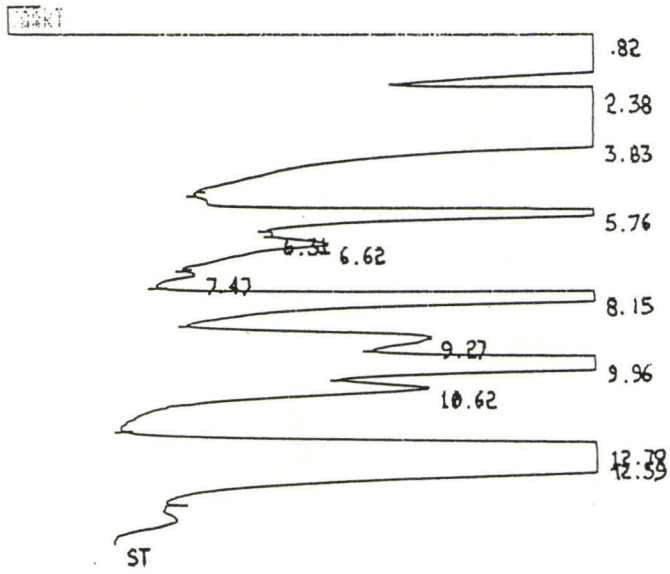
FIELD STUDIES:

i] Lakes

The lakes chosen to sample in the Sudbury field analysis were chosen for their diversity. Five lakes were chosen for reconnaissance sampling (Kelly, Dill, Joe, Crooked and Silver) while two were sampled over the period of 5 hours (Clearwater and McFarlane).

ii] Heating

For practical, and analytical reasons, heating was not opted for in the field adsorption procedure. As previous results showed, this method would have caused additional problems in integrating the sulfides.



RUN # 770 JAN/19/91 15:45:02

AREA%

RT	AREA	TYPE	AR/HT	AREA%
0.82	4.4999E+07	SPB	0.321	39.436
2.38	5.2647E+07	TBV	0.265	46.139
3.83	1335100	TVP	0.424	1.170
5.76	1510600	TPV	0.312	1.324
6.31	94718	TVV	0.142	0.093
6.62	576280	TVV	0.530	0.505
7.47	57953	TVP	0.237	0.051
8.15	2763100	TPV	0.301	2.422
9.27	1060100	TVV	0.523	0.929
9.96	3298600	TVV	0.378	2.891
10.62	986150	TVP	0.472	0.864
12.32	1310600	TPV	0.309	1.149
12.59	3467200	TVB	0.788	3.039

TOTAL AREA= 1.1411E+08
MUL FACTOR= 1.0000E+00

Figure 5.3: Chromatogram From Heated Water Sample

iii] Flow rates

Flow rates were those adapted from laboratory studies. A flow rate of 80 ml/min prevented the sample from bubbling out of the flask. This flow rate allowed for maximization of adsorption in lieu of the fact that heating was not used.

iv] Storage

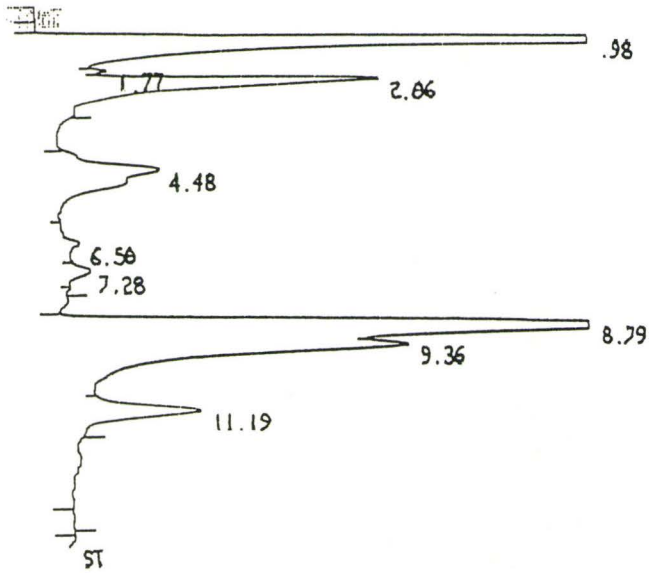
The tubes were stored in a cooler on ice while in the field. The cooler was plugged in at the base to maintain the temperature of the unit (approximately 0°C). The samples were kept in this unit until they were analyzed 8 days later.

v] Results and Interpretation

The results showed that all of the samples lost their integrity by the time they were analyzed. Consistent to all samples were peaks at approximately 2.06, 4.43, 6.5, 8.95 and 11.14 (Figure 5.4).

2.06 may represent a byproduct of COS and MeSH. 4.43 is probably DMS. The peaks at 6.5 and 8.95 are reactions that may have involve PrSH, or are ethanes. 11.14 is the DES. Recoveries were minimal to none for the internal standard.

These results suggest that the tubes have to be completely sealed and segregated from any possible conta-minants. Contamination may be from sulfides escaping from the tubes, other gases entering the tubes or by equilibrium conditions being attained between all of the tubes while they are stored together.



RUN # 198 JUL/17/90 12:08:56

AREA%

RT	AREA	TYPE	AR/HT	AREA%
0.98	1855400	PV	0.330	27.110
1.77	63046	VV	0.165	0.921
2.06	737420	VB	0.328	10.775
4.48	490780	BP	0.695	7.171
6.50	54867	PV	0.398	0.802
7.28	76284	VV	0.398	1.115
8.79	1930900	PV	0.446	28.213
9.36	1243200	VV	0.521	18.166
11.19	392050	VB	0.457	5.728

TOTAL AREA= 6843900
MUL FACTOR= 1.0000E+00

Figure 5.4: One of the Field Sampling Chromatograms

CHAPTER VI

CONCLUSIONS AND FUTURE CONSIDERATIONS

Working with aqueous samples introduces significant problems in the collection of in-situ organic volatile sulfides using a solid sorbent.

Water, both collecting in the tube and mixing with the sulfides, creates two main problems. First, in storing the adsorption tubes, water from the atmosphere can collect at the ends of the tubes. This causes significant variations in the integrity of the sulfides stored on the tube and also blocks the collection loop in the desorption process. Secondly, the original aqueous nature of the sample itself seems to be enhancing the degradation of sulfides (especially when heated to release the volatiles). Proper sealing of the tubes and avoiding heating would alleviate these two problems.

The sorbent type, Molecular Sieve 5A 60/80 mesh, was chosen over Silica Gel 60/80 mesh. Although this sorbent proved to be more efficient than Silica Gel, its recovery was far from proficient. This suggests that alternatives may be opted for in view of the fact that aqueous sampling introduces a great deal more variation than dry gases.

Leaking and sample degradation were two problems that must be overcome before this method will be dependable enough for field analysis. A valve seal (although more costly) may have to be adapted to ensure that sulfides remain intact and that no foreign gases enter the tubes while in storage.

FUTURE CONSIDERATIONS

i] Sealing

A study should be undertaken to test the use of valves as an alternative to the capillary caps for sealing the tubes. Alternately, the tubes may be cut to a length of 40cm instead of 26cm. This would allow the ends to be heat sealed in the field with a propane torch. They could be stored in the freezer and at the time of desorption, the ends could be broken away cleanly before placing in the heat desorber. Two disadvantages to this method are that the tubes could be used only once before the sorbent had to be replaced in a new tube and propane would have to be carried in the field.

ii] Sorbent

A wider study of sorbent types should be considered. This would ensure that Molecular Sieve 5A 60/80 mesh is suitable for water samples. Some sorbents could be eliminated due to their metallic nature (ie: gold) and others by expense (if this is an issue).

iii] Adsorption

Adsorption with heat introduces some static to the integrity of the sample. Alternatively, heating should enhance the recover percentages of the sample. An in depth study of heating temperatures and flowrate variations may result in an optimum combination of low temperature/high flowrate adsorption parameters.

Alternatively, a different type of drying agent within

the adsorption line may recover more of the water that is reaching the sorbent and storing on the adsorption tube. CaCl may not be sufficient for capturing the waters released in the volatilization of the water sample.

REFERENCES

Adams, D.F., Farwell,S.O., Pack,M.R. and Robinson, E. Biogenic sulfur gas emissions from soils in Eastern and Southeastern United States. J.A.P.C.A. (1981-October) 31(10):1083-1089

Adams, D.F. and Sherry O.Farwell. Biogenic sulfur source strengths. Environmental Science and Technology (1981-December) 15(10):1493-1498

Andreae, M.O. and Barnard, W.R. The marine chemistry of dimethylsulfide. Marine Chemistry (1984) 14:267-279

Andreae, M.O. and Barnard, W.R. Determination of trace quantities of dimethyl sulfide in aqueous solutions. Analytical Chemistry (1983) 55(4):608-612

Aneja, V.P., Aneja, A.P. and Adams, D.F. Biogenic sulfur compounds and the global sulfur cycle. J.A.P.C.A. (1982) 32(8):803-807

Aneja, V.P., Overton, J.H. and Aneja, A.P. Emission survey of biogenic sulfur flux from terrestrial surfaces. Journal of the Air Pollution Control Association 1981(March) 31(3):256-258

Banwart, W.L. and Bremner, J.M. Gas chromatographic identification of sulfur gases in soil atmospheres. Soil Biological Biochemistry (1974) 6:113-115

Black, M.S., Herbst, R.P. and Hitchcock, D.R. Solid adsorbent preconcentration and gas chromatographic analysis of sulfur gases. Analytical Chemistry (1978) 50(7):848-851

Boreal Laboratories: Culture of Freshwater and Marine algae in the Laboratory

Bruner, F., Ciccioli, P., and DiNardo, F. Further developments in the determination of sulfur compounds in air by gas chromatography. Analytical Chemistry (1975) 47(1):141-144

Brown, K.A. Sulphur in the Environment: A Review. Environmental Pollution (Series B) (1982) 47-80.

Caron, F. Production of Volatile Sulfides From Freshwater Algae and Implications to the Environment. PhD Thesis-McMaster University, Hamilton Ontario (1990)

Caron, F. and Kramer, J.R. Gas chromatographic determination of volatile sulfides at trace levels in natural freshwaters. Analytical chemistry (1989) 61(2):114-118

Chromatographic Specialties Inc. Physical properties of Linde Molecular Sieves Types 4A, 5A and 13X. Public Information Bulletin issued from Chromatographic Specialties 1990

Chromatographic Specialties Inc. Physical properties of Chromatographic Silica Gel. Bulk Desiccants and Adsorbents. Public Information Bulletin issued from Chromatographic Specialties, 1990

Deprez, P.P., Franzmann, P.D. and Burton, H.R. Determination of reduced sulfur gases in Antarctic lakes and seawater by gas chromatography after solid adsorbent preconcentration. Journal of Chromatography (1986) 362:9-21

deSouza, T.L.C. Efficient trapping of ambient organic and sulphur gases for gas chromatographic analysis. Pulp and Paper Canada (1988) 89:139-144

deSouza, T.L.C. Dedicated, automatic gas chromatograph for monitoring sulphur gases. Journal of Chromotography (1987) 395:413-422

Gluck, S. Performance of the model 700A Hall Electrolytic Conductivity Detector as a sulfur-selective detector. Journal of Chromatographic Science (1982) 20:103-108

Hall, R.C. A highly sensitive and selective microelectrolytic conductivity detector for gas chromatography. Journal of Chromatographic Science (1974) 12: 152-160

Hartmann, C.H. Gas chromatography detectors. Analytical Chemistry (1971) 43:113-125

Headley, J.V. GC/MS identification of organosulphur compounds in environmental samples. Biomedical and Environmental Mass Spectrometry (1987) 14:275-280

James, D.E. Culturing Algae. Carolina Biological Supply Company 2700 York Road, Burlington, North Carolina 27215

Jenkins, D., Lloyd L. Medsker and Jerome F. Thomas. Odorous compounds in natural waters. Some sulfur compounds associated with blue-green algae. Environmental Science Technology (1967) 1(9):731-735

Kellogg, W.W., R.D. Cadle, E.R. Allen, A.L.Lazrus and E.A. Martell. The sulfur cycle. Science (1972-February) 175(4022): 587-596

Lamb, B., Westberg, G., Allwine, L., Bamessberger, L. and Guenther, A. Measurement of biogenic sulfur emissions from soils and vegetation: Application of dynamic enclosure

methods with Natusch Filter and GC/FPD analysis. Journal of Atmospheric Chemistry (1987) 5:469-491

Langhorst, M.L. and Coyne L.B. Industrial hygiene. Analytical Chemistry (1989) 61(12):128R-142R

Moller, D. On the global natural sulphur emission. Atmospheric Environment (1984) 18(1):29-39

Newman, R.A. and Gschwend, P.M. A method for quantitative determination of volatile organic compounds in marine macroalgae. Limnological Oceanography (1987) 32(3):702-708

Nriagu, J.O. and Holdway, D.A. Production and release of dimethyl sulfide from the Great Lakes. Tellus (1989) 41B:161-169

Nriagu, J.O., Holdway, D.A. and Coker, R.D. Biogenic sulfur and the acidity of rainfall in remote areas of Canada. Science (1987-September) 237:1189-1192

Steudler, P.A. and Peterson, B.J. Annual cycle of gaseous sulfur emissions from a New England Spartina alterniflora marsh. Atmospheric Environment (1985) 19(9):1411-1416

Steudler, P.A. and Kijowski, W. Determination of reduced sulfur gases in air by solid adsorbent preconcentration and gas chromatography. Analytical Chemistry (1984) 56(8): 1432-1436

Torres, L., Frikha, M., Hathieu, J. and Riba, M.L. Preconcentration of volatile sulphur compounds on solid sorbents. International Journal of Environmental and Analytical Chemistry (1983) 13:155-164

Wong, P.T.S and Couture, P. Toxicity screening using phytoplankton. In: Toxicity Testin Using Microorganisms, Volume 2 . Dutka, B.J. and Bitton, G. (Eds.) CRC. Press, Boca Raton, Florida (1986)

APPENDIX

A: Bold's Basic Medium

B: Peak Area of Sulfides Under Varying Adsorption Flowrates

C: Quantities of Individual Sulfides Retained After A One Week Storage Period

APPENDIX A: BOLD'S BASIC MEDIUM

Two sets of concentrated solutions are first prepared:

SALT SOLUTIONS: each one of these salts is dissolved in 400 mL of glass-distilled water or Milli-Q (low organic) water.

Salt	amount/400 mL (g)	Salt	amount/400 mL (g)
$NaNO_3$	10.0	KH_2PO_4	6.0
$MgSO_4 \cdot 7H_2O$	2.0	$CaCl_2 \cdot 2H_2O$	1.0
K_2HPO_4	4.0	NaCl	1.0

TRACE ELEMENT SOLUTIONS: each solution (A, B, C, D) shall contain the following salts (per 100 mL):

Solution	Salt	amount/100 mL (g)
A: EDTA stock	EDTA, disodium salt	5.0
	KOH	3.1
B: Fe stock*	$FeSO_4.7H_2O$	0.5
C: Boron stock	H_3BO_3	1.14
D: H-H5 stock*	$ZnSO_4$	0.88
	$Na_2MoO_4 \cdot 2H_2O$	0.12
	$Co(NO_3)_2 \cdot 6H_2O$	0.05
	$MnCl_2$	0.14
	$CuSO_4 \cdot 5H_2O$	0.16

* Stock solutions B and D are dissolved in 100 mL acidified water (0.1 mL conc. sulfuric acid in 100 mL water).

INSTRUCTIONS: Add 10 mL of each one of the SALT SOLUTIONS, and 1 mL of each of TRACE ELEMENT SOLUTIONS to distilled water. Complete the volume to 1000 mL. Add HCl or NaOH to adjust the pH to the desired value.

APPENDIX B: PEAK AREAS OF SULFIDES UNDER VARYING ADSORPTION FLOW RATES

Flowrate	40ml/min	80ml/min	120ml/min
CS2	233180	290080	120210
DMS	15263	56782	28545
DES(ISTD	134850	255990	86455
DMDS	198090	915620	291510

APPENDIX C: QUANTITIES OF INDIVIDUAL SULFIDES RETAINED AFTER A ONE WEEK STORAGE PERIOD

COS	
Adsorbed	Desorbed
749170	26908
702080	1387900
719170	547360
711870	346610
724170	345940
848030	N/A

MeSH	
Adsorbed	Desorbed
412740	51954
371860	67499
382460	N/A
395050	32917
332020	28801
427720	N/A

CS2	
Adsorbed	Desorbed
3898400	5181100
4043000	7458700
4647300	9481800
5996700	9073400
6627500	2967700
7967100	14894000

DMS	
Adsorbed	Desorbed
1250500	83477
1327100	1382900
1255500	222060
1316900	509330
1358200	211300
1321400	316950

PrSH	
Adsorbed	Desorbed
744300	139830
650320	180980
443110	28163
607570	18679
634840	15486
646410	N/A

DMDS	
Adsorbed	Desorbed
2999900	101320
3560900	175280
3588400	200340
4638000	N/A
4516200	170250
4216800	247860

DES	
Adsorbed	Desorbed
872090	N/A
870950	N/A
816280	35132
858590	N/A
877220	22670

***N/A refers to sulfides that could not be distinguished from surrounding peaks