AD-A056 115 ALASKA UNIV COLLEGE INST OF MARINE SCIENCE F/G 8/12
GASES IN SEA ICE: A FACTOR BEARING ON THE TRANSMISSION OF SOUND--ETC(U)
SEP 77 T A GOSINK, J J KELLEY N00014-76-C-0331

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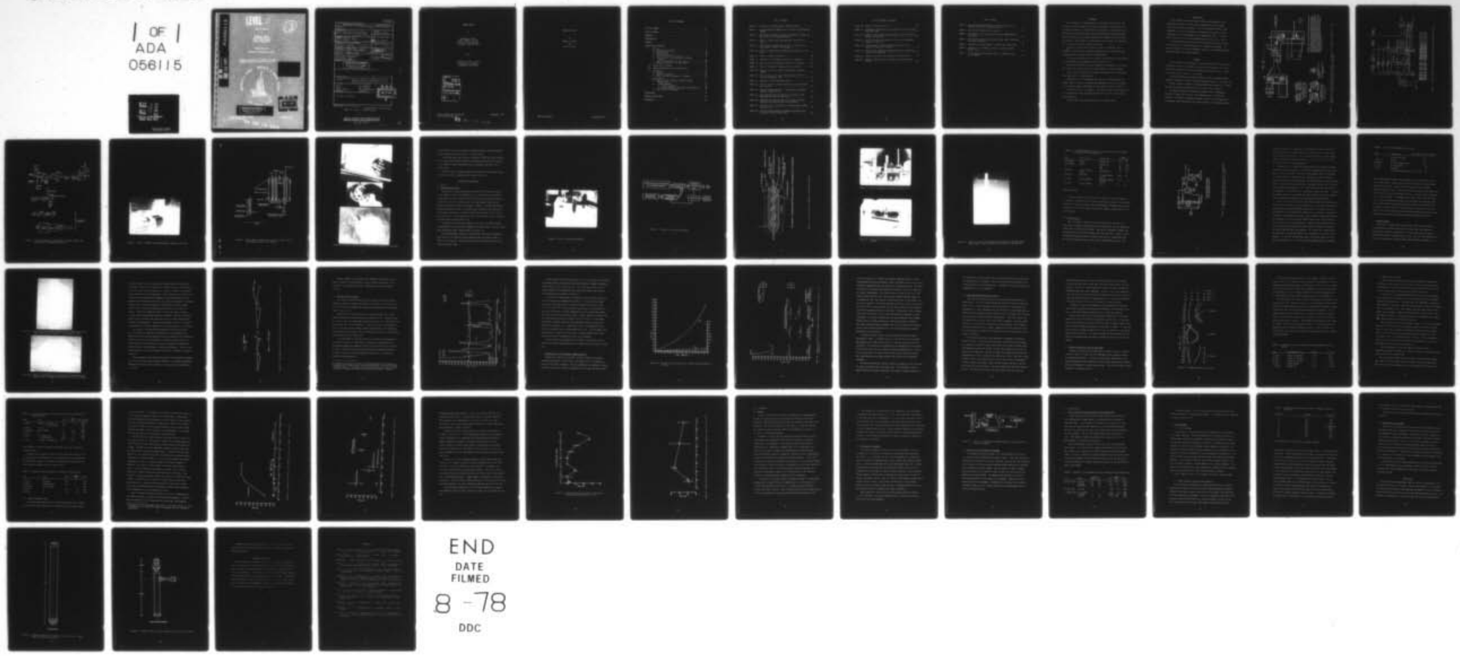

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ANNUAL REPORT

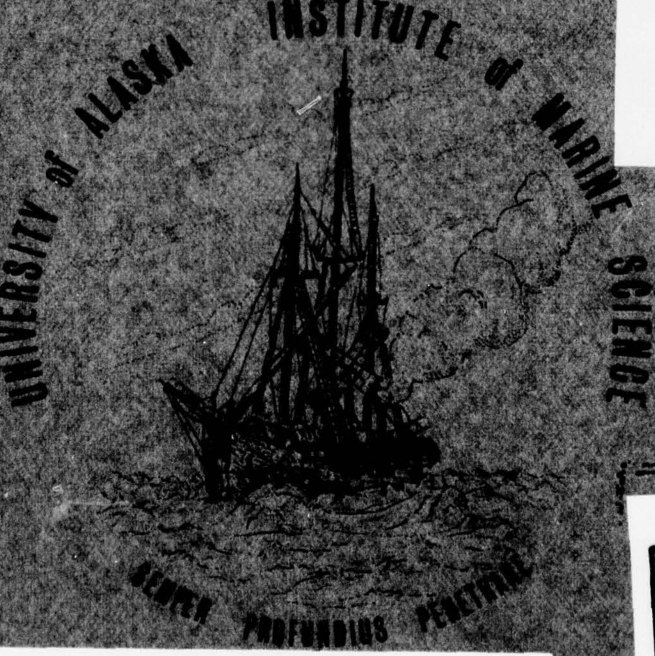
to

Department of Navy
Arctic Branch, Code 461
Office of Naval Research
Arlington, Virginia 22217

GASES IN SEA ICE

Thomas A. Gosink and John J. Kelley

ORIGINAL CONTAINS COLOR PLATES: ALL DDC REPRODUCTIONS WILL BE IN BLACK AND WHITE.



Contract Number N00014-76C-0331
1 Oct. 1976-30 Sept. 1977

September 1977

MIL-STD-847A
31 January 1973

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
A001✓

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
(6) GASES IN SEA ICE: A Factor Bearing on the Transmission of Sound Energy.

5. TYPE OF REPORT & PERIOD COVERED
Annual
10/1/76 - 9/30/77

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)
(10) Thomas A. /Gosink
John J. /Kelley

(9) Annual rept. 1 Oct 76-30 Sep 77

8. CONTRACT OR GRANT NUMBER(s)
N000 14-76C0331

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Institute of Marine Science✓
University of Alaska
Fairbanks, Alaska 99701

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

(15) N00014-76-C-0331

11. CONTROLLING OFFICE NAME AND ADDRESS
Department of Navy, Arctic Branch,
Code 461. Office of Naval Research
Arlington, Virginia 22217

(11)

12. REPORT DATE
September 1977

13. NUMBER OF PAGES
~~50~~

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
ONR Resident Respresentative
University of Washington
3710 Brooklyn Avenue
Seattle, Wn. 98195

15. SECURITY CLASS. (of this report)
Unclassified

(12) 57p.

15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES
To be published in part in Journal of Geophysical Research Letters

ORIGINAL CONTAINS COLOR PLATES: ALL DDC REPRODUCTIONS WILL BE IN BLACK AND WHITE

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Sea ice
Gases
Carbon Dioxide
Hydrogen
Ice atmosphere
Gas exchange
Gas chromatography
Coulometry

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

See page 1 of report

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DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Figure 6. Report Documentation Page.

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ANNUAL REPORT

to

Department of Navy
Arctic Branch, Code 461
Office of Naval Research
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from

Institute of Marine Science
University of Alaska
Fairbanks, Alaska 99701

Contract Number NOOO 14-76C-0331
1 Oct. 1976-31 Sept. 1977

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GASES IN SEA ICE

by

Thomas A. Gosink

and

John J. Kelley

NOOO 14-76C-0331

September 1977

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ABSTRACT

This research is a continuation of the previous year's work on the migration of gases through sea ice and the transport of gases across the ice-snow-air boundary. Carbon dioxide, and possibly carbon monoxide, were observed to be replenished faster than other non-water interacting gases such as nitrogen, oxygen, neon, and methane in flushed probe holes and at the surface. Large pulses of carbon dioxide were observed and suspected as the result of internal stresses in sea ice.

sq cm microliter

microliter sq cm

The flux of gases in probe holes was near 2-4 $\mu l/cm^2/hr$, and 1-2 $\mu l/cm^2/hr$ at the surface, relatively insignificant for oxygen, but very significant for trace gases such as carbon dioxide.

The ocean was observed to be a source of carbon dioxide, carbon monoxide and methane to the atmosphere by way of the sea ice.

Brine content in the ice varies strongly with temperature, and may be the cause of the large variations in the transport of carbon dioxide.

A late spring observation of bubbles from rotting sea ice disclosed very high levels of carbon monoxide.

deg

Observations of the atmosphere over sea ice (to 78°N) through the summer tends to confirm a continued high atmospheric level of CO_2 beyond the time period when it diminishes at Point Barrow, Alaska (71.4°N).

deg

Coulometric work is in progress. The detector alows for the detection of all combustible gases including hydrogen at the 10^{-5} ml level without preconcentration

Several other miscellaneous topics are also entertained.

INTRODUCTION

This research has been directed toward an understanding of the composition of gases in sea ice and the dynamics of their transfer across the sea-ice-air interface. Sea ice is markedly different from freshwater ice in that it permits the movement of gas easily, whereas freshwater ices are impermeable to gas (Hemmingsen, 1959). The movement of gas in sea ice has been demonstrated by Gosink *et al.* (1976).

This year we have more details on the quantity and nature of gases in and over sea ice and some insight as to transport mechanisms. We have also begun to work with coulometric detectors for hydrogen analysis, light hydrocarbon, and carbon monoxide.

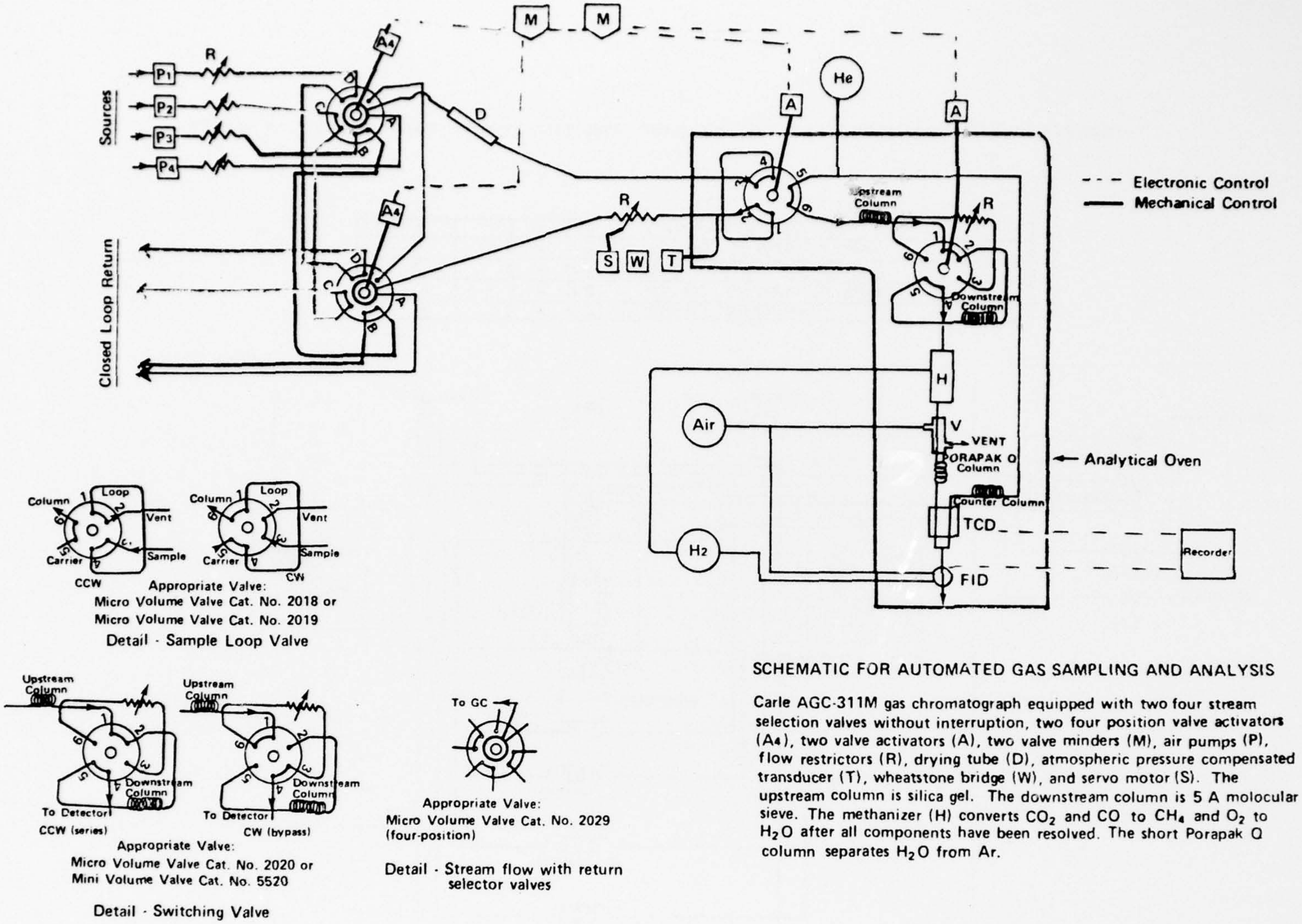
METHODS

The techniques for the analysis of gases associated with sea ice were essentially the same as reported last year with the exception of a Carle 311 M system which was used for the simultaneous analysis of N_2, O_2 with Ar, CO, CH_4 and CO_2, (Figs. 1, 2, 3 and 4).

A prototype sample loop pressure regulator using a UniMeasure ®/80 pressure transducer for the GC system was developed (Figs. 1, 3; section IF).

Packer assemblies similar to those described by Oeschger *et al.* (1976) were used to assure gas-tight seals in ice holes (Figs. 5a and b).

An oxygen coulometer from Reaction Coulometers Ltd. (Maidenhead, England) is being used for some of the beginning work on coulometric (absolute - no external standards required) detection of trace gases such as hydrogen, light hydrocarbons and carbon monoxide. The detection limits



SCHEMATIC FOR AUTOMATED GAS SAMPLING AND ANALYSIS

Carle AGC-311M gas chromatograph equipped with two four stream selection valves without interruption, two four position valve activators (A_4), two valve activators (A), two valve minders (M), air pumps (P), flow restrictors (R), drying tube (D), atmospheric pressure compensated transducer (T), wheatstone bridge (W), and servo motor (S). The upstream column is silica gel. The downstream column is 5 A molocular sieve. The methanizer (H) converts CO_2 and CO to CH_4 and O_2 to H_2O after all components have been resolved. The short Porapak Q column separates H_2O from Ar.

Appropriate Valve:
Micro Volume Valve Cat. No. 2018 or
Micro Volume Valve Cat. No. 2019

Detail - Sample Loop Valve

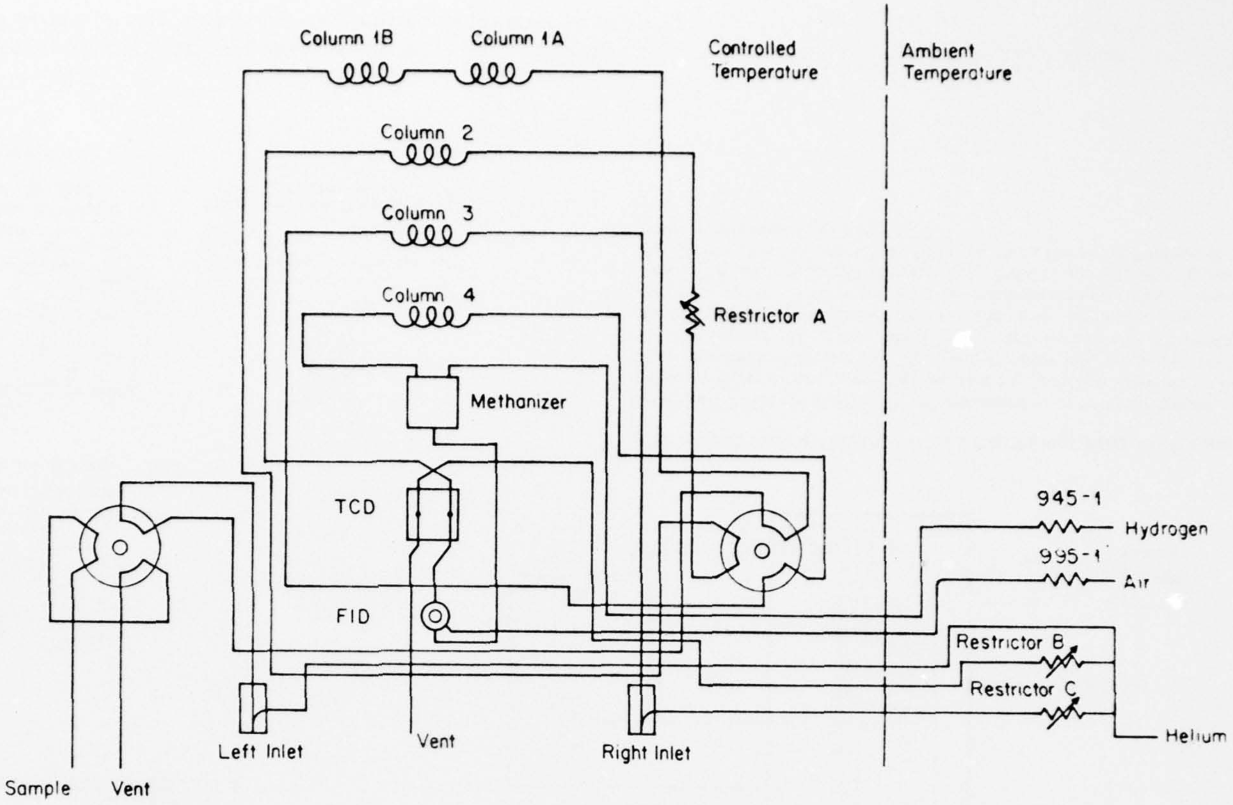
Appropriate Valve:
Micro Volume Valve Cat. No. 2020 or
Mini Volume Valve Cat. No. 5520

Detail - Switching Valve

Appropriate Valve:
Micro Volume Valve Cat. No. 2029
(four-position)

Detail - Stream flow with return selector valves

Figure 1. Intended gas chromatographic plumbing scheme. See Figure 2 for changes in analytical column portion. See Figure 3 for details of pressure transducer.



Col 1A	5' × 1/8	60-80 Silica Gel
Col 1B	4' × 1/8	45-60 5A Molecular Sieve
Col 2	6" × 1/8	Carbosieve-B 60-80
Col 3	1.5' × 1/8	45-60 5A Molecular Sieve
Col 4	4' × 1/8	Carbosieve-B 60-80

Figure 2. Actual analytical columns used in the gas chromatographic system.

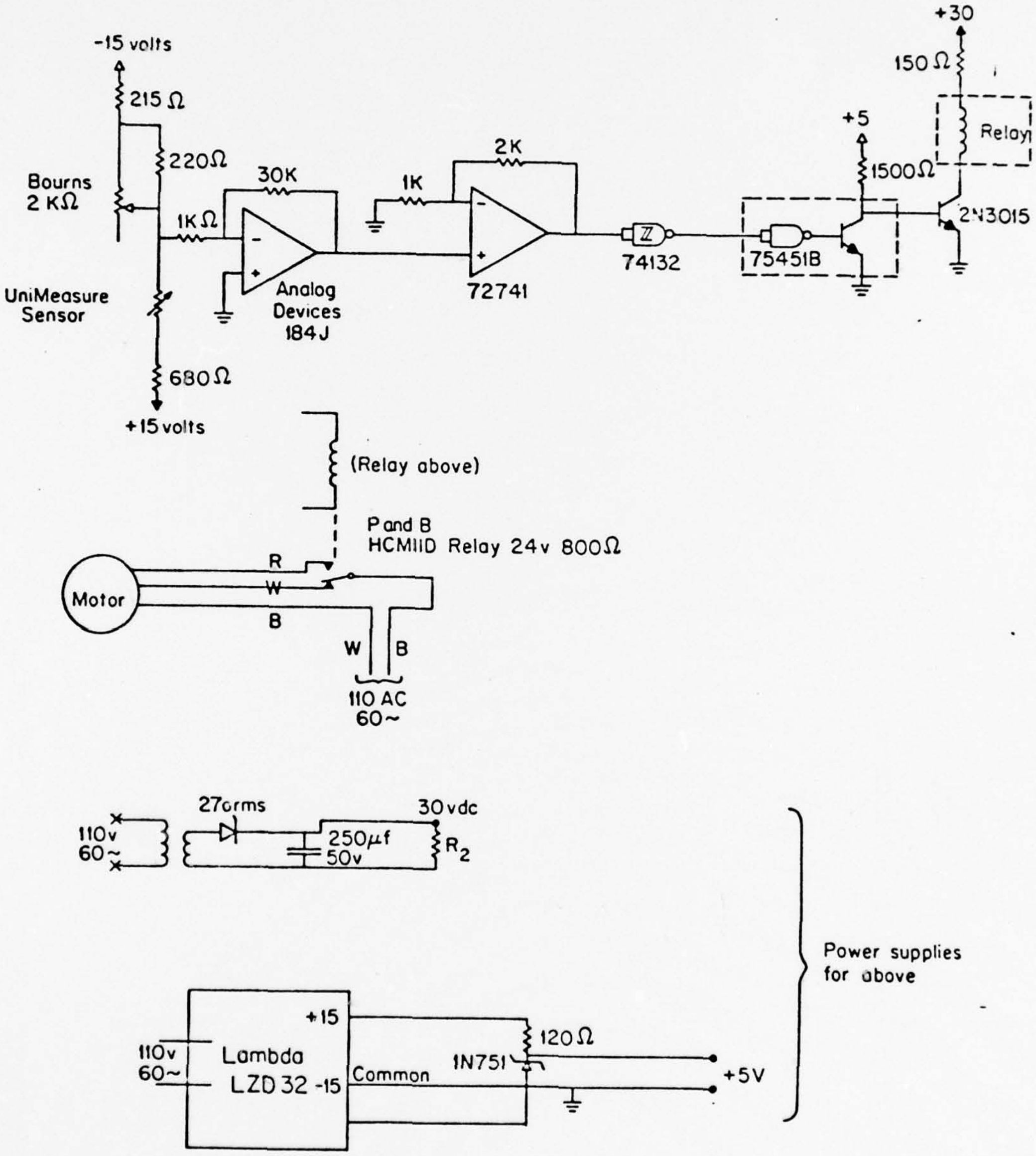


Figure 3. Electronic schematic for pressure transducer readout and motor control of compensating value.

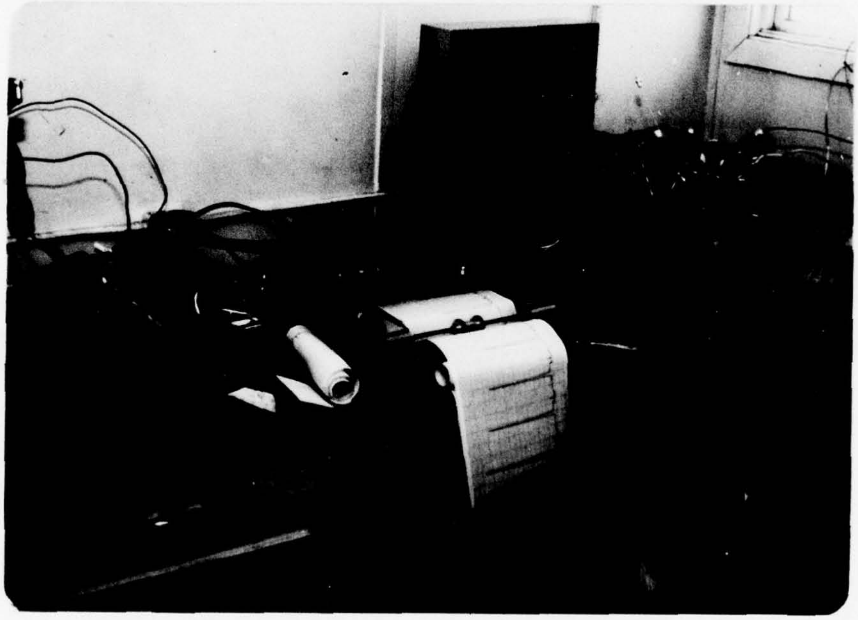


Figure 4. Photo of complete gas chromatographic system in the field.

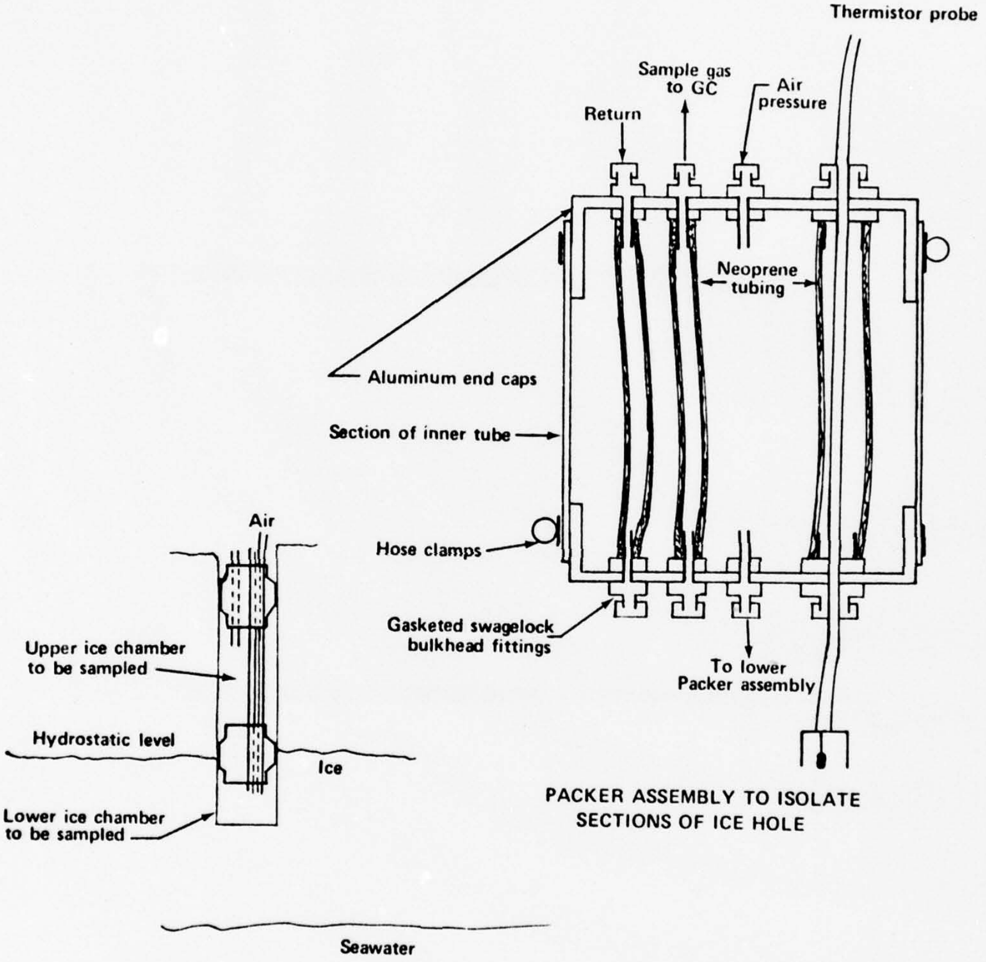


Figure 5a. Rubber packer assembly used to seal ice holes, and to take samples of gas in ice chambers.

Figure 5b. Photos of rubber packer assembly and in position in ice holes.

of this device are up to two orders of magnitude better that the standard flame ionization detector (Figs. 6, 7; section IVB).

A palladium pump with a Keithly electrometer (Model 604 with differential current shunt) modeled after the hydrogen pump described by Lovelock *et al.* (1970) is being investigated for the hydrogen work (Figs. 8, 9; section IVA).

Gas-tight glass stripping chambers as described in the previous report were used to collect and preserve ice samples (Fig. 10).

RESULTS AND DISCUSSIONS

I. Sea Ice

A. Entrained gas bubbles

The quantity of gases entrained in annual sea ice varied from about 1-5 ml gas/kg of sea ice for subsurface ice, slightly more than observed and reported last year. The top 10 cm of sea ice this year was observed to contain 10+ to 30 ml of gas/kg of sea ice, significantly less than the quantity reported last year (>120 ml/kg). However, it should be noted that the age and history of polar ice should cause significant gas composition and transport differences. Figure 11 shows the hydrostatic level of seawater in sea ice on a pit wall in sea ice. The top light layer is not snow, but bubbly brine drained surface ice.

The sample of multiyear ice appeared to be gassy in content (volume not measured) but fractured like freshwater ice upon coring. The CO_2 content was significantly lower, being similar to glacier ice.

Gas chromatographic analysis of these bubbles (head space analysis of large pieces of ice melted in glass chambers) gave the results shown in Table 1 for CO and CH_4. Carbon dioxide and other dissolved gases are discussed separately below.

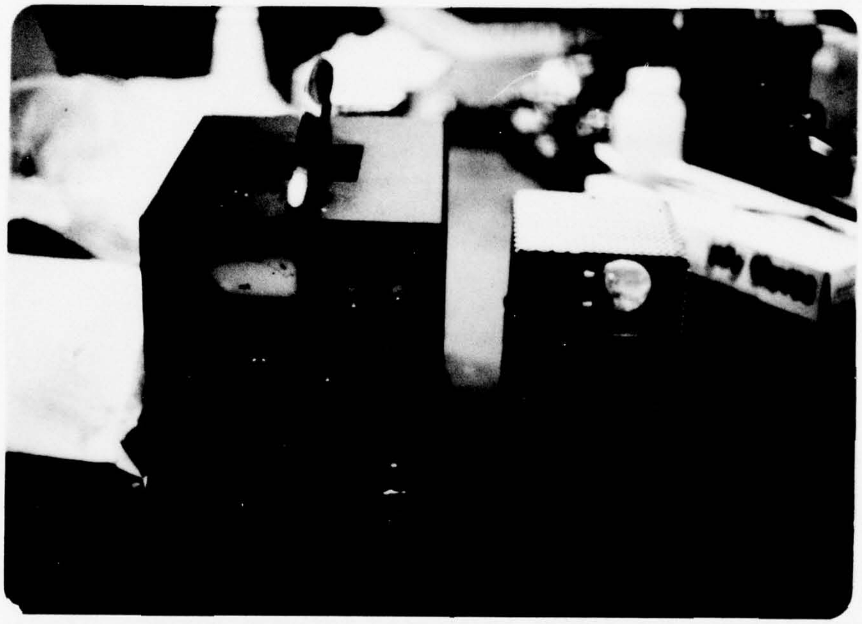


Figure 6. Photo of reaction coulometer.

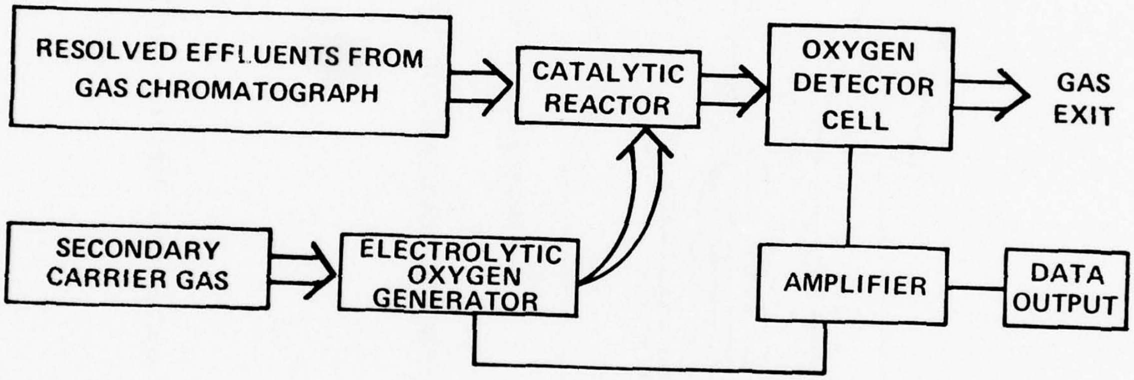
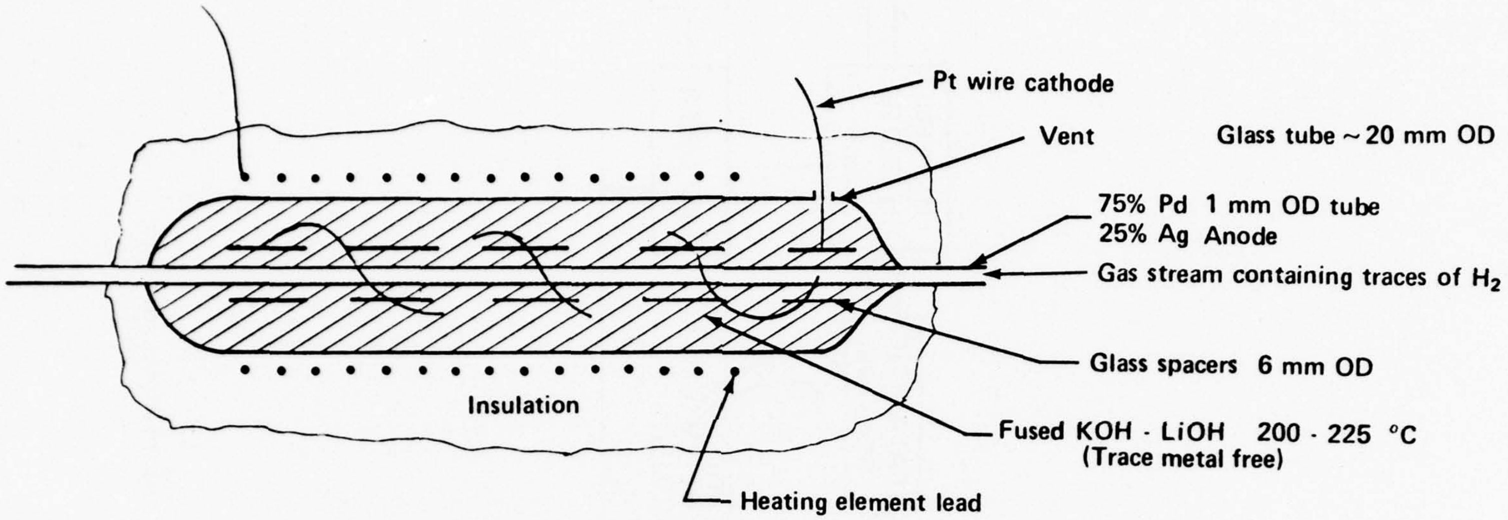


Figure 7. Schematic of reaction coulometer.



PALLADIUM – HYDROGEN PUMP FOR COULOMETRIC DETERMINATION OF HYDROGEN

Figure 8. Cross section of coulometric detector for hydrogen.

Figure 9. Photo of coulometric hydrogen detector system.

Figure 10. Photo of sea ice in helium flushed glass stripping chamber.

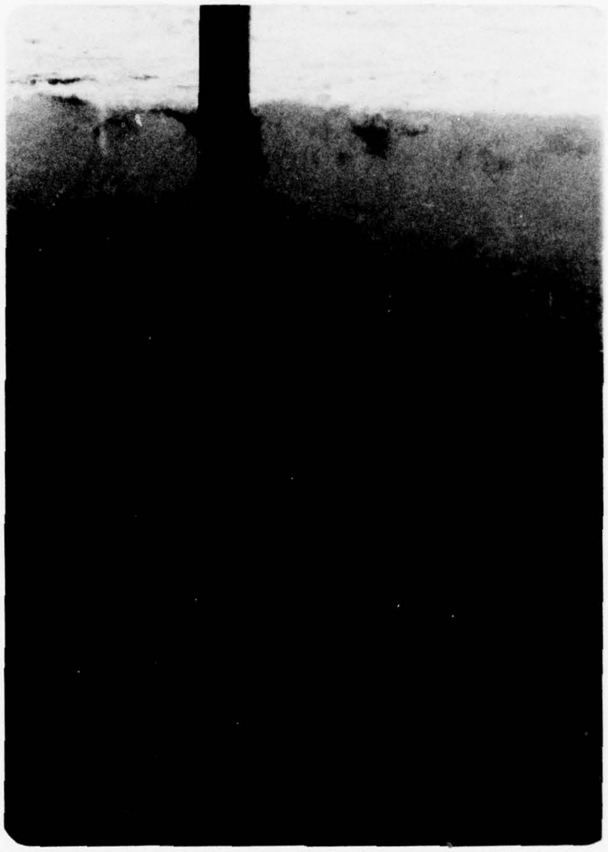


Figure 11. Photo of a sea ice pit showing gassy surface ice and the hydrostatic level. White top layer is not snow, but the gassy ice.

TABLE 1. Gas chromatographic analysis of CO and CH_4 in sea ice bubbles (corrected for helium dilution).

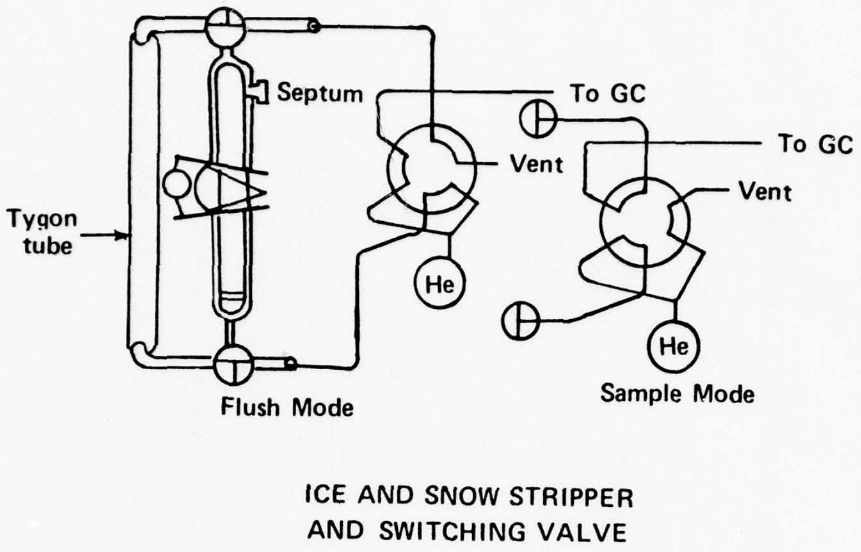
Date	Type of Ice	Depth (cm)	ppm	
			CO	CH_4
23 February	Annual	Surface 10	2.1	11
28 February	Annual	Surface 10	6	6.6
		50	ND	4.6
		100	ND	20
10 March	N. Salt Lagoon Annual	Intermediate	ND	ND
10 April	Multiyear	30 cm excluding top 10	trace	ND
10 June	Rotting Annual	bubbles escaping surface	19.3	7.1
22 June	Rotting Annual	top 30	15	21

ND=not detected

The gas entrained in the sea ice was essentially air with respect to O_2 and N_2. The quantities of O_2 and N_2 were used to correct for the helium dilution to obtain the values above for atmospheric concentrations; the one exception is the 10 June sample which was for bubbles trapped under an inverted beaker.

B. Dissolved gases

Total stripping of smaller ice chips (exclusive of bubbles) was thwarted by equipment operating pressure incompatibility and the unexpected large loads of total carbon dioxide. Time was not available to modify the strippers because of the late funding date this past year. Figure 12 shows the previously employed glass stripping tower which is incompatible with the 50 psi operating pressure of the new gas chromatograph system. Two



ICE AND SNOW STRIPPER
AND SWITCHING VALVE

Figure 12. Schematic of glass stripping tower. Incompatible with new gc system which operates at 50 psi.

new metal systems (see Section V), one for gases in general and one for total CO_2, have been designed and will be available for the next season. The one trusted result for a sea ice sample, not acidified, shows normal values for dissolved gases as follows: $N_2 + O_2 + Ar$, 6; CO, 3×10^{-4}; CH_4 7×10^{-3} and CO_2, 1.6 ml/kg sea ice.

Swinnerton *et al.* (1969, 1970) report that CO is richest in surface waters and is on the order of 4×10^{-4} ml/ℓ, essentially the result above. They also report a diurnal cycle for CO with highest values in daylight. It is interesting to speculate on the significance of the very high CO values in the surface ice and rotting ice with reference to light intensity, which by June was continuous and high. The methane values are on the high end as reported by Swinnerton *et al.* (1969, 1970), but this may be due to the proximity of the NARL site to a productive natural gas field. It should be further noted that gas pockets have been observed in the local thermokarst environment and should be expected along the drowned shelf.

There is a brief note in Riley and Skirrow (1965) that occluded CO_2 in sea ice is on the order of 0.1-0.5 ml/kg sea ice. Our work with the head space gases of unacidified samples shows 0.4-8 ml of CO_2/kg of sea ice. Acidification of the samples with several ml of 3-6 M H_2SO_4 to destroy all carbonates, bicarbonates and carbonic acid, followed by vigorous shaking of the meltwater in the sealed glass chambers shows large values (Table 2). The low value for the rotting annual ice suggests that the major portion of the CO_2 is associated with the brine which is principally located in the grain boundaries and brine channels. On 10 June the rotting sea ice was observed to contain many small holes, estimated to be from 1-5 mm in diameter. It was also observed that water was flowing along the top of sea ice, probably due to a littoral current pushing seawater up through

TABLE 2. Total carbon dioxide load in sea ice.

Date	Type of Ice	CO_2 Content ml/g ice ($x10^4$)
--	Average sea water	560
3 March	Annual	47
10 March	N. Salt Lagoon Annual	38
22 June	Rotting Annual	8.4
14 April	Multiyear	2.3
--	Average Glacier (Weiss *et al.*, 1972)	2.0

these former brine channels, thus flushing the ice of the winter load of CO_2 laden brine. Figures 13 and 14 show the porosity of these brine channels even at -8°C. The block of ice in Figure 13 was freshly quarried from an ice pit. A small groove was scratched in the surface and ink in brine from the pit was poured onto it. All of the blue coloration is on top and internal. The height of the block in the center was about 30 cm. After approximately one-half hour the block was overturned (Fig. 14) to disclose the blue mark on the bottom internal surface and on the ice below. Further evidence of the porosity of rotting sea ice was observed (June 77) when exhaust gases from divers working below the ice were observed to percolate up through the otherwise apparent solid ice.

C. Subnivean Gases

Kelley *et al.* (1968) and Coyne and Kelley (1974) reported that CO_2 is significantly enriched under the arctic snow pack (the subnivean), particularly towards the spring melt. Our experience this past season clearly shows that the subnivean level of CO_2, over both the tundra and the sea ice, is elevated to a greater extent than previously reported. In

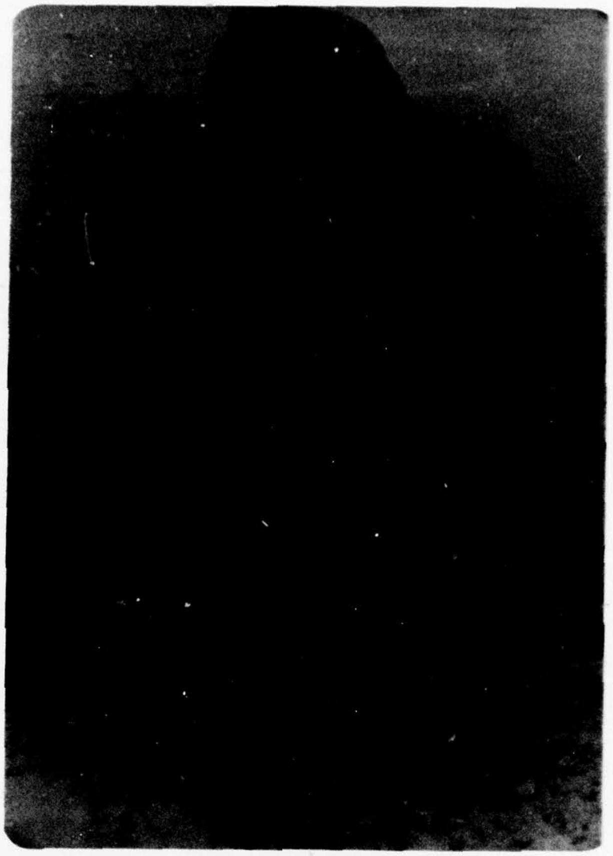


Figure 13. Photo of block of freshly quarried sea ice marked with ink in brine. Blue stain is internal. Air temperature ∿-8°C.

Figure 14. Photo of overturned block of ink marked ice showing internal passage of ink. Distance travelled was ∿30 cm in ∿30 minutes.

the past subnivean air was continuously pumped through the analytical instrument. When such a technique was employed this year, relatively low trace gas levels were also observed as a result of ambient air flushing of the samples area of the subnivean. On the other hand, if small (10 ml) discrete syringe samples were withdrawn, the microenvironment was not disturbed and consistently high trace gas values were observed. Continuous pumping with a return line seemed to alleviate the flushing problem, but there were significant problems with freeze-up of the 1/8" O.D. tubing. Larger bore tubing will help, but the time delay in moving the gas through long lengths should be considered. Addition of Drierite drying tubes is helpful, but inefficient at the already relatively low humidity and temperatures. Magnesium perchlorate is better, but there is some question of possible oxidation of the trace quantities of CO and CH_4.

Over sea ice, the subnivean environment was usually enriched in CO_2, CO, and CH_4 as compared to the ambient air at the sample site. Wind stress across the snow surface is also an important factor (Bernoulli effect) and the trace gas enrichment is inversely proportional to it. Carbon dioxide in the subnivean over sea ice tended to be elevated by about 30 ppm, but varied between 0 and 80 ppm enrichment. There was also some evidence for a cyclic variation of CO_2 in the subnivean as shown in Figure 15.

Carbon monoxide could always be detected in the subnivean environment over sea ice and was usually enriched relative to the ambient atmosphere. Subnivean levels were on the order of ≤ 0.5 ppm, and the atmosphere was ≤ 0.1 ppm.

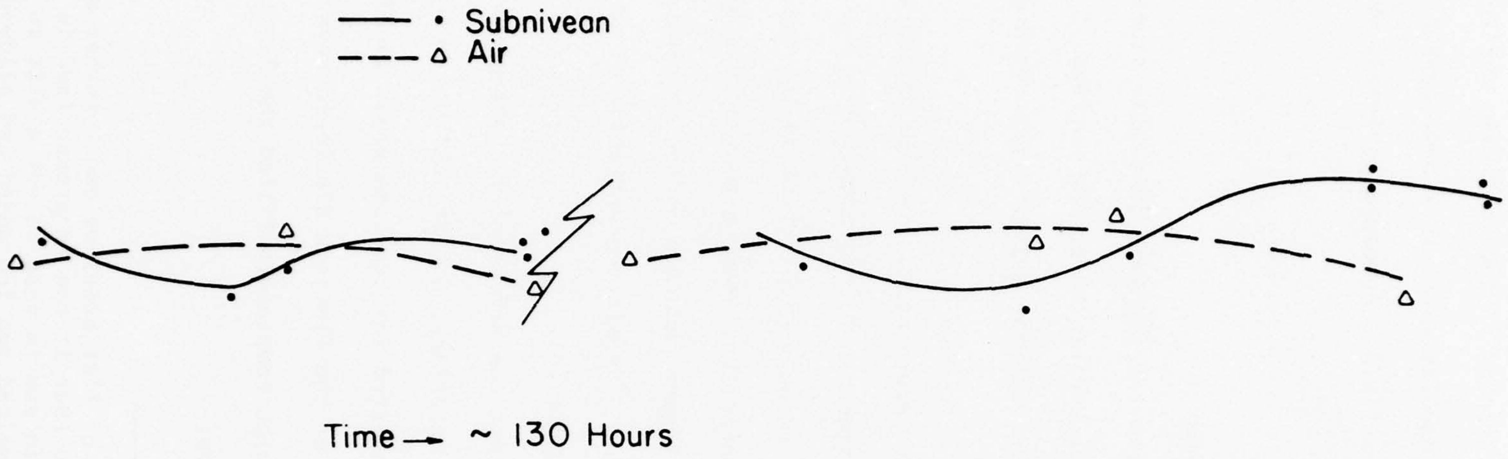


Figure 15. Data showing cyclic variation of CO_2 levels in the subnivean area sea ice. May 1977.

Methane tended to be enriched in the subnivean environment, but was highly variable (2-12 ppm, usually close to 2 ppm) possibly due to the proximity of a producing gas field. Atmospheric levels were usually 1-2 ppm.

D. Gases in sealed ice holes

The efflux of gases from the ice were initially studied by means of chambers, either as a coffee can sealed to the surface of the sea ice, or as a hole in sea ice plugged with the helium pressurized device described earlier (Fig. 5a, b).

Figure 16 is a 19-hour record of an ice hole during a very active period showing large variations in CO_2 as compared to N_2. During the time of the test there was considerable wind stress on the ice. Nearly all other records show only little variation. A four-hour record of the subnivean level of CO_2 shown in the figure recorded on the morning of 15 March also shows significant variation. The air concentration of CO_2 at that time was about 335 ppm (see also Figure 18).

In an experiment to test the effect of ice stress on the movement of CO_2 across an air and ice interface, a flatjack* was borrowed from an engineering program and inserted into the ice about 25-30 cm away from the ice hole. Pressurization of the flatjack disclosed unexpected mobility of brine in the sea ice which completely filled the 3-ℓ ice hole and flooded the instrumentation.

---

*A flatjack is two pieces of flat steel welded together at the edges and equipped with fittings so that it can be pressurized in the space between the metal sheets. A chain saw is used to cut a slit in the sea ice, the flatjack is dropped in, melted sea ice added and allowed to refreeze.

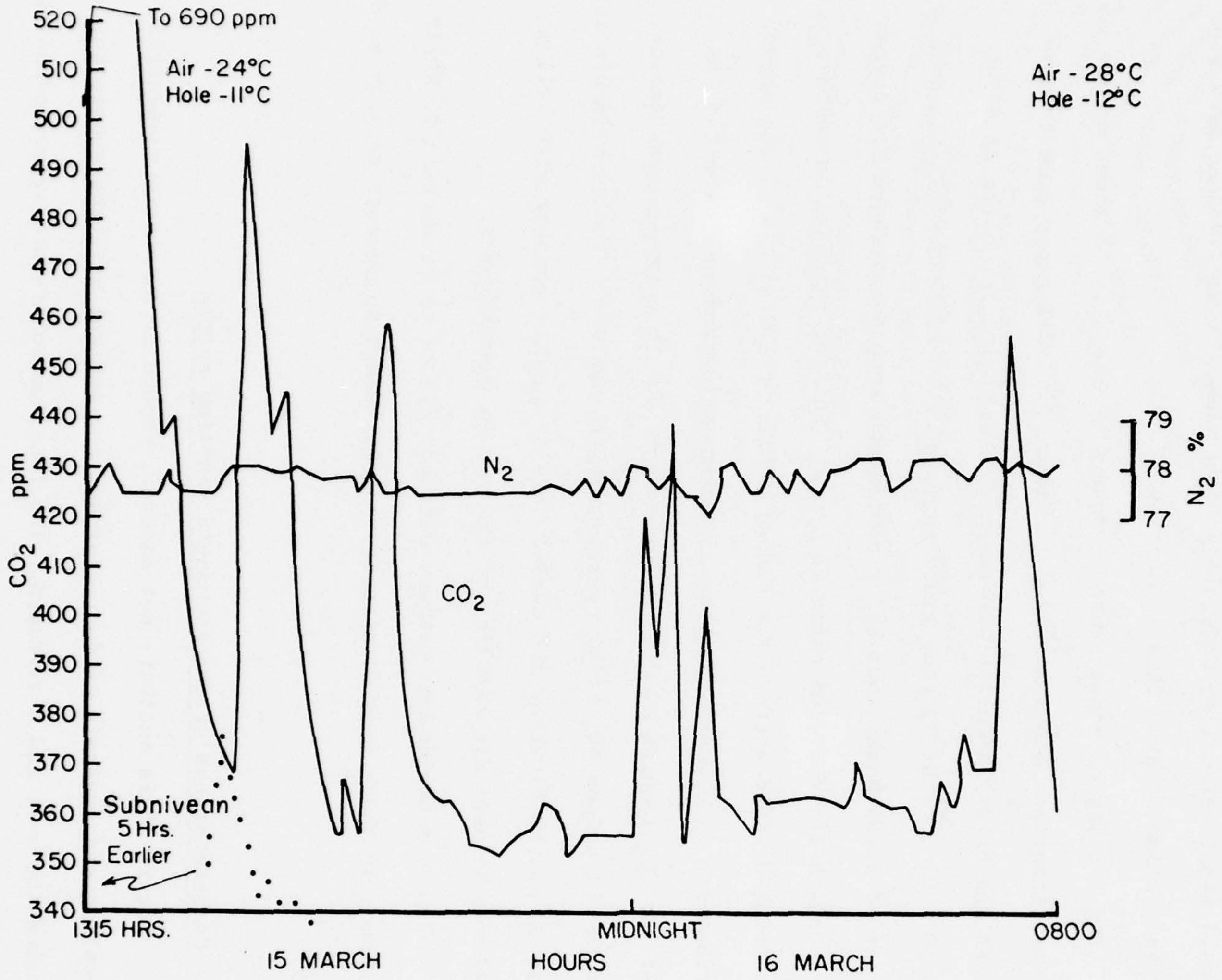


Figure 16. Nineteen hour record of gases in a sealed ice hole during an active period due to wind stress.

Other smaller pressure disturbances to the ice hole such as increasing the helium pressure inside the plugs usually produced a dramatic temporary rise in the CO_2 level in the ice hole. This rise was not due to an increased sample size (compressible gas) because the sample loop pressure was controlled as described in section IE.

The results of experiments to determine the flux of gases across the ice/air interface are summarized in Figure 17. All gases seem to move across the brine laden ice-air interface in sealed ice holes at about 4×10^{-3} ml cm^{-1} hr^{-1}, thus trace gases such as CO_2 are replenished in a matter of a few hours, but major components such as nitrogen and oxygen were only half recovered after 24 hours. Surface chambers in contact with the brine-drained surface ice showed a flux of 1/2 to 1/4 of the above. Furthermore it appears that the high permeation constant reported last year for CO_2 (Gosink *et al.*, 1976) was not due to a temperature factor, but to the unique CO_2-brine relationship in sea ice. The experiments were carried out by flushing the sealed hole or surface chamber with helium followed by periodic sampling of the gas in the chambers.

Carbon monoxide and methane were too dilute to be certain of their presence in these flushed systems, but CO seemed to recover rapidly as did CO_2.

E. Considerations of the automatic sampling system

Figure 18 is another, but shorter, record of automatic sequential sampling and analysis of four sources, the ambient air, the subnivean, a sealed ice hole and a standard. The four components are separated as shown in Figure 18, but were actually accomplished in the same four-hour period.

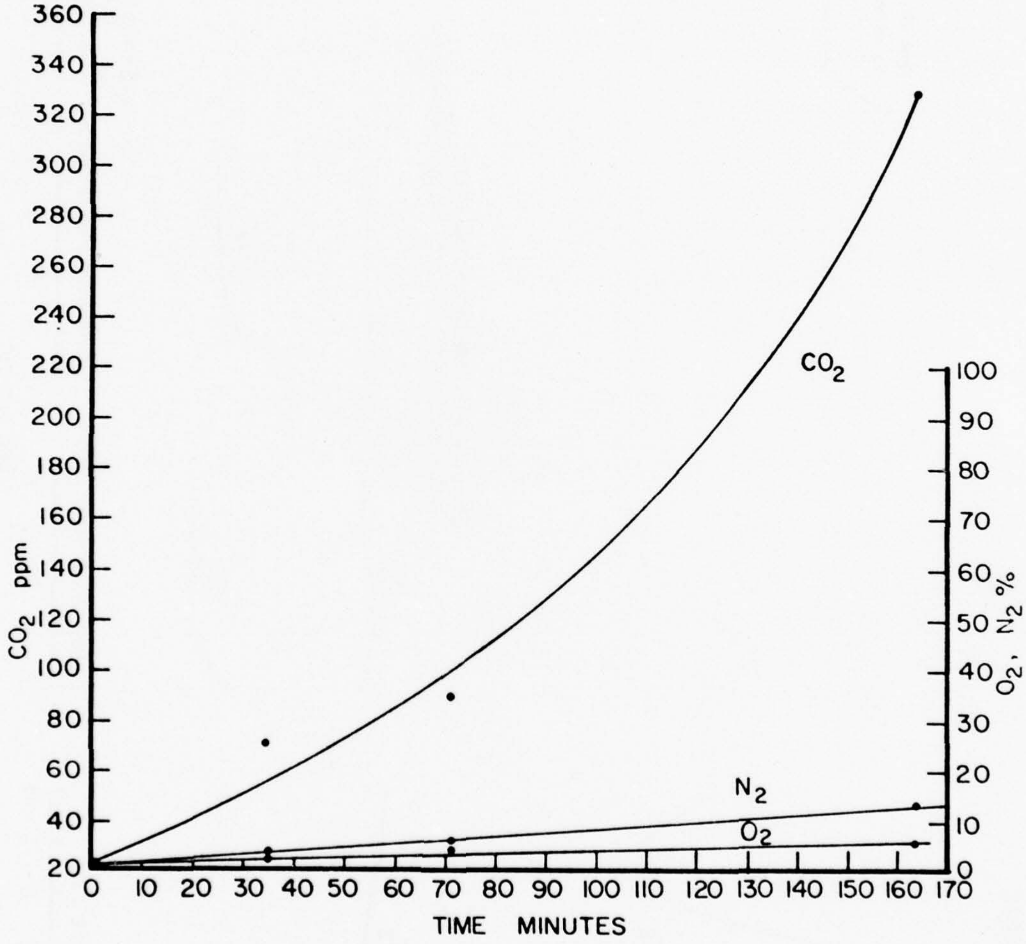


Figure 17. Recovery of N_2, O_2 and CO_2 in a sealed helium flushed sea ice hole.

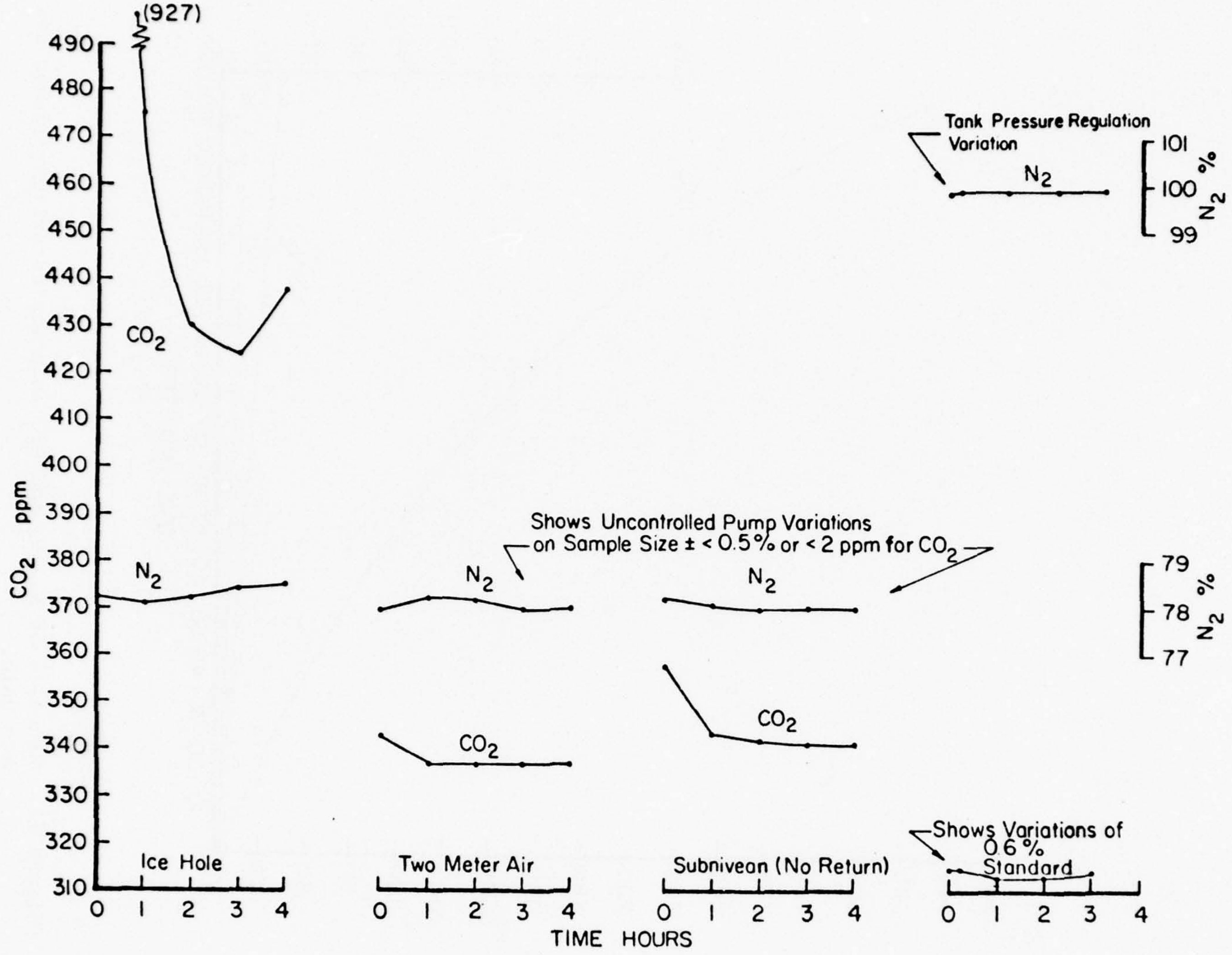


Figure 18. Pressure uncontrolled but standard calibrated same four hour record. On 17 March 1977.

Part of our work was to develop an automatic sampling system for a gas chromatograph that would accurately control the sample size of a gas to be reasonably competitive with the accuracy of an infrared system. The infrared system is continuous and somewhat more accurate, but not as versatile as the gas chromatograph. The results shown in Figure 18 are for a free running system working on the four sources, through different pumps and a pressurized tank. The pressure controlling feature for the sample loop was not in operation. The large variation in the CO_2 level in the ice hole (as in Fig. 16) is still evident, and the rapid decrease in the subnivean level due to pumping without a return line. Fluctuations in the nitrogen levels for the ice hole, 2-m air and subnivean are attributable to pump variations. The stable nitrogen level for the pressurized tank standard reveals that the thermal conductivity detector was stable throughout. The flame ionization detector response for CO_2 (CO_2 converted to methane) shows a 0.6% variation possibly due to the low attenuation and greater sensitivity of the detector.

A similar five-hour record, with the pressure controlling device operational, (Figs. 1, 3) shows only a ± 0.17% variation in the standard CO_2 analysis and ± 0.26% for the 2-m air. Thus the prototype device is successful. The system will be improved by the elimination of an electronically noisy relay chip, an overall electronics improvement by a factor of 2-4, the selection of a better control valve, and a faster drive motor. Once these practices have been resolved, the system can be considered patentable.

The system functions by having a pressure transducer in the line after the pumps, switching valves and sample loop. The transducer is set to measure 1000 mm of pressure (absolute) and becomes a variable resistor in the electronic circuitry which drives a motorized precision metering valve on stream below the transducer. The valve opens when the pressure is too high and closes if the pressure drops. Atmospheric pressure variations are compensated for in the transducer.

F. Gases injected under and into sea ice

Last year we injected gas into sea ice and spiked holes adjacent to sample holes. This year carbon dioxide and neon were chosen for injection under the ice. Carbon dioxide was chosen because of its importance and uniqueness as a trace atmospheric gas, and in order to investigate what was thought to be an apparent shortcut that CO_2 used to propogate itself through sea ice similar to proton transfer through water. The latter effect does not appear to be the case, but is still open to question. Neon was chosen because it is not reactive to water as is carbon dioxide, and is rapidly resolved and detected by the thermal conductivity detector portion of the gas chromatograph in submicroliter quantities, and is nondetectable in the normal environment.

The ice depth around the field laboratory was mapped by drilling a series of holes. A dome area was found under a snow drift and was chosen as a useful area because the gas pocket would not be likely to drift away. Two sampling horizons were chosen, a hole at 70-cm depth (ice was 137 cm thick) and the subnivean. The sea ice under the insulating snow drift was relatively warm (-6°C) compared to the ambient air -28°C. This led to some problems in that brine filled the hole at the rate of about 5-10 cm/hour. A loosely capped (watertight) copper tube was frozen into the ice about a meter away from the probe holes. The tube extended well below the bottom of the ice. The CO_2 level in the ice hole was quite stable (not like the previous month as shown in Figs. 16 and 18) and produced a pronounced rise a little more than an hour after the steady slow stream of CO_2 was started. The flow of carbon dioxide was stopped, and the increased concentration decreased slowly overnight. Arrival of CO_2 in the subnivean layer did not occur for about six hours indicating that either the CO_2 was diffusing away laterally at a significant rate, or it met with diffusion resistance in the top 10-15 cm of ice which is devoid of brine.

Attempts to repeat the experiment on the second day were thwarted because the CO_2 pocket had leached a hole through a brine channel in the sea ice and would rapidly escape into the ice hole and subnivean.

Neon was not observed in either horizon, probably due to the lower sensitivity of the TCD ($\sim 10^3$ less sensitive) than the FID. On the other hand, neon injected into the ice about 20 cm below a chamber sealed to the sea ice surface showed the presence of neon after 45 minutes. If neon was injected into a leaking spiking hole at 6 psi, it showed up in the sealed chamber after 10 minutes. The surface opening of the injection hole was about 30 cm downwind from the sample can which was frozen to the sea ice surface.

G. Chemical analysis of sea ice and brines

During the course of the investigation of gases in sea ice, routine chlorinity samples of whole ice were determined by wet chemical methods for comparative purposes. Non-routine results were obtained (Fig. 19). Using instrumentation and chemicals at hand, sodium, potassium and sulfate were also determined for three separate cores. Only the 28 February sample displayed a "standard" profile.

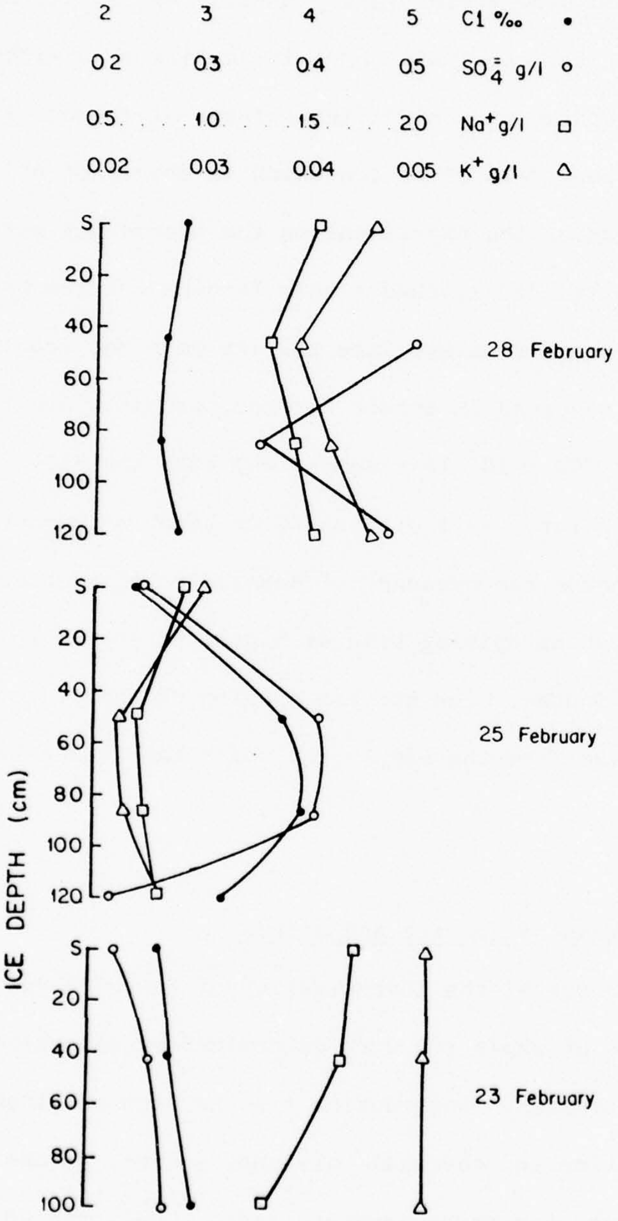


Figure 19. Chemical profiles of sea ice.

The chlorinity values for whole sea ice samples are normal in their range of 2.5-3 + °/oo which was about 1/6 that of the seawater at 18.6°/oo. Potassium should and does behave conservatively in that it does not readily form any insoluble salts as the other components are doing at the temperatures involved. The non "routine" behavior of the other components will be investigated next year when time and resources can be devoted to it.

Two other facets also came to light in the course of this brief investigation of the wet chemistry of sea ice. On one occasion the brine which slowly fills protected holes in sea ice was sampled and observed to outgas significantly due to the slight partial vacuum in the pipette. It is assumed that the gas was chiefly CO_2. The other is that the chlorinity values of the pure brine (no sea ice to dilute it to 2-3°/oo) were very large and are shown in Table 3. The warming trend influence on the brine is evident from the last two entries in Table 3. The brine channels are opening up and are diluted by melting sea ice. By July, sea water can actively flow up to and over the surface of depressed ice via the leached out brine channels.

TABLE 3. Chlorinity of sea ice and brines and the temperature of the system.

Date	Description of Ice	T(°C)	Cl °/oo
2 April	Annual ice (brine)	-17°	114.6
10 April	Annual ice (brine)	- 6°	66.4
15 May	Annual ice (brine)	∿- 3°	38.5
8 July	Rotted Annual	∿ 0°	< 0.05
March	Annual Ice	∿-15°	2.5-3.9

II. Tundra Lake Ice Gases

Several tundra and alpine lake ices were sampled for purposes of comparing the gas content of the ice, and of their overlying subnivean atmospheres with both the sea ice and with North Meadow Lake (71°N) for which a large backlog of data had been acquired in the past.

Fresh water ice is markedly different from sea ice in its hardness. Cores fracture quite readily, and the occluded gases are truly trapped; frequently under pressure. Two alpine lakes (ca 2500-3000 ft elevation) were sampled; No Luck Lake, about 180 miles due south of NARL, and Chandler Lake, near Anaktuvuk Pass. Three tundra lakes were also sampled; North Meadow Lake, by NARL, a lake about 60 miles south of NARL (Lake A) and a lake about 120 miles (∿ 1 hour flying time) out of Anaktuvuk Pass towards NARL, and north of the Colville River (Lake B).

The gas content of the ices was highly varied. Ice from North Meadow Lake was rich in bubbles near the bottom, whereas the other two tundra lakes (A and B) had relatively few bubbles as did the ice from Chandler Lake. Ice from No Luck Lake was normal except for several very large (estimated 1 cm x 3 cm) bubbles below the surface. The one phenomenally large value for rotting North Meadow Lake is paralleled (by an order of magnitude less) by coastal sea ice (Table 1).

Trace gas analyses for the five lakes are given in Table 4. Composition is again by using O_2, N_2 values to correct for helium dilution and are for total (acidified) CO_2.

The only exception data for CO and CH_4 are those from North Meadow Lake, and for CO_2 the surface sample from lake B and North Meadow Lake. The total CO_2 for North Meadow Lake ice is comparable with glacier ices

TABLE 4. Trace gas analysis for tundra and alpine lakes (corrected for helium dilution).

Date	Lake	ppm		
		CO	CH_4	CO_2 (total)
25 March	Chandler - surface ice	0.3	7	890
	- below surface	ND	4	680
6 April	No Luck			288
25 February	North Meadow	50	520	1800
6 April	A	<0.8	<0.2	102
25 March	B - surface ice	0.1	5	3020
	- below surface	trace	<2	850
10 June	N. Meadow - rotting ice	102	1024	-

even though this value is probably low because it is not a thoroughly stripped sample.

Likewise the subnivean air values for the lake sites (Table 5) are not particularly outstanding for CO or CH_4 except for their omnipresence. The elevated CO_2 figures are, however, of significance showing that the arctic tundra in general may be a source of CO_2.

TABLE 5. Subnivean trace gas analysis at tundra and alpine lakes.

Date	Lake	ppm		
		CO	CH_4	CO_2
25 March	Chandler	0.2	1	340
25 March	Anaktuvuk Pass	0.8	1	329
25 February	North Meadow	-	-	360
6 April	A	0.6	1.8	570
25 March	B	0.2	2.3	390

III. Summer Atmospheric Work

There have been indications that high carbon dioxide levels persist over the Arctic Ocean after the CO_2 recorded at Barrow descends rapidly in the late spring. Six flights of opportunity from NARL were taken in 1972 to obtain atmospheric samples for carbon dioxide. Carbon monoxide and methane were also monitored, but were always too low in concentration to be mentioned further in this report. Three of the flights went north over the ice; one along the Beaufort coast; one was to high altitude near NARL, and one southwest of the Bering Sea. In all cases elevated CO_2 levels were found and are discussed below.

The results of the three flights to the north over sea and sea ice are shown in Figure 20. The flight of 26 June 1977 occurred during the first 10 days of rapidly declining CO_2 values recorded at the NOAA site at NARL. The NOAA values had previously reached a fairly steady value of about 343 ppm concentration mixing level. The NOAA value for atmospheric CO_2 on 26 June was 333.8 ppm. The flight was from about 60 miles inland over wet tundra to 200 nm: out to sea over melting, but almost continuous ice cover. The abrupt change for 26 June is evident in Figure 20. The trend is still evident for the same flight path on 7 July 77. Sea ice conditions were mostly open water out to 50 miles, broken ice to about 100 miles and ∿10% open water at 200 miles. The flight of 20 July shows almost constant CO_2 values out to 500 miles north of NARL. The NOAA site CO_2 values for 7 and 20 July were 329.9 and ppm respectively. Another north-south profile is effectively present in the data discussed below for the east-west transect, again showing increased atmospheric CO_2 for stations out to sea.

Figure 21 shows an east-west profile for 18 July 77 between Barrow and Deadhorse, Alaska. Station 1 was overland near Deadhorse. Station 2 was also overland, but in a high particle count* plume from Deadhorse

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* The particle count information comes from Dr. Ken Rahn's and Mr. R. Bory's instrumentation for whom this flight was designed, and our information supplements.

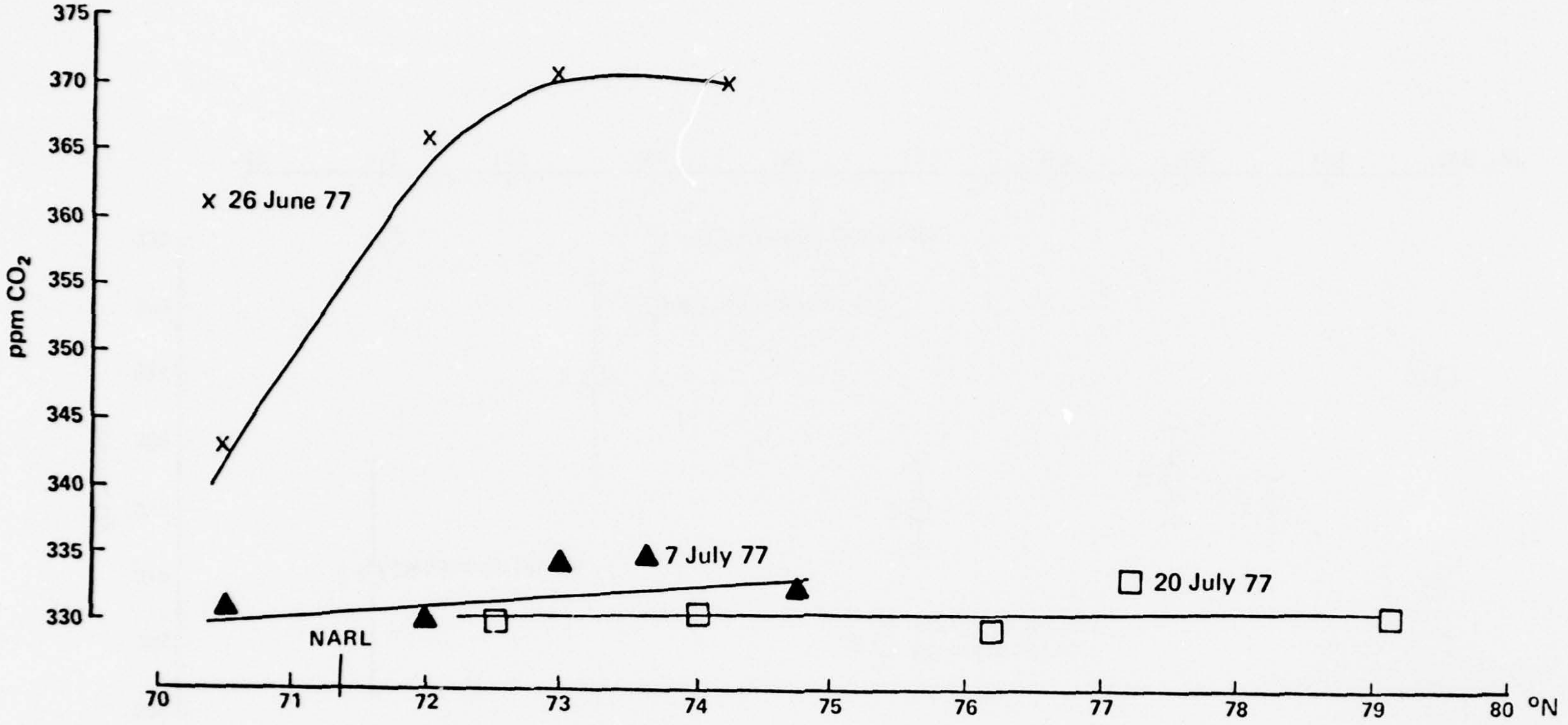


Figure 20. Atmospheric profiles for CO_2 northward over Arctic Oceans. June-July, 1972.

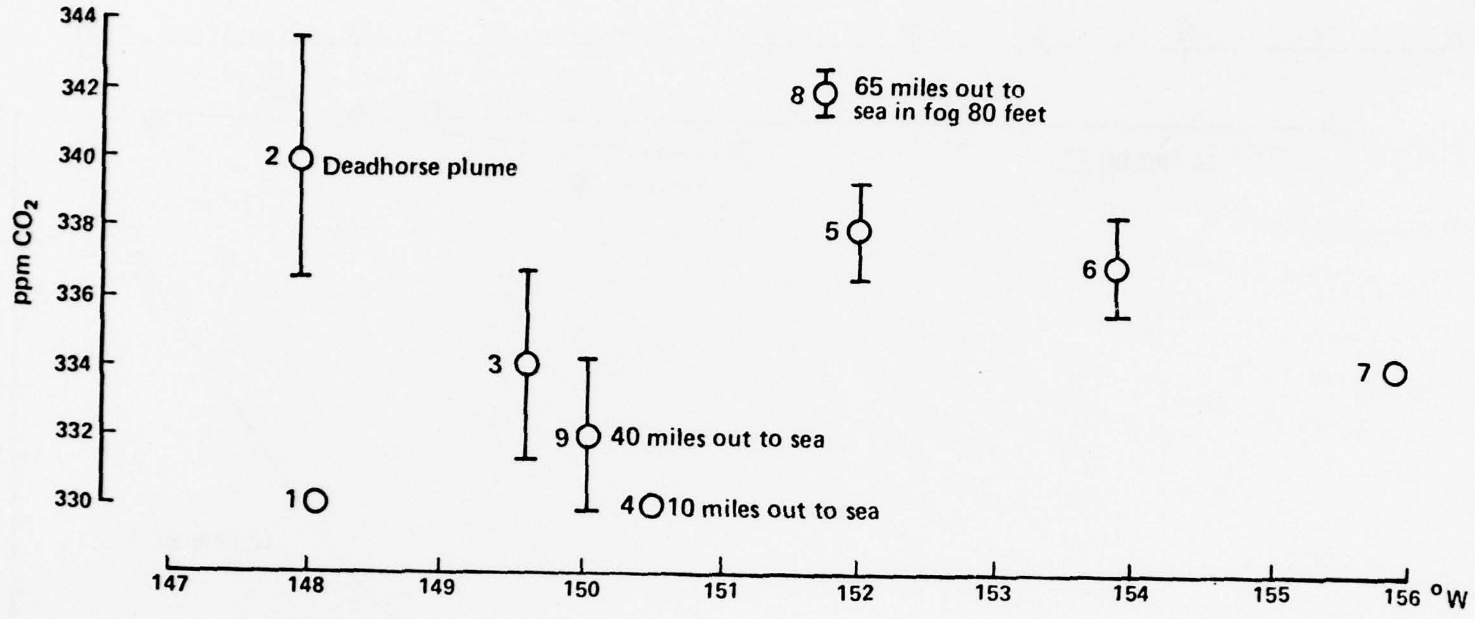


Figure 21. Carbon dioxide values between Deadhorse and Point Barrow, Alaska, 18 July 1977.

(Prudhoe Bay petroleum activity). Most of the sampling was done at an altitude of about 450 ft. The high data point for Station 8 about 70 miles offshore at an altitude of 77 ft was in a surface fog. Note, Stations 4, 8 and 9 form a north-south profile out to sea and again show the increased CO_2 values out to sea.

Figure 22 shows the vertical profile of CO_2 near Point Barrow to 12,000 ft for 16 July 77. Gas chromatographic methods are not plagued by pressure broading errors associated with infrared systems because the samples analyzed are brought to the same pressure before analysis. Figure 22 shows a definite trend toward CO_2 enriched air at altitude; a layering enrichment may be attributable to the trapping oc CO_2 in the upper atmosphere from the large number of forest fires in northern Alaska this year.

Figure 23 is a plot of samples taken on a flight between NARL and Gambell on St. Lawrence Island in the North Bering Sea on 12 July 1977. Stations 1-3 were at 10,500 ft over land, station 4 at 6,500 ft over the ocean, and station 5 on the ground at Gambell. The rise in the CO_2 concentration was attributed to the effect of forest fires in the general area of the Seward Peninsula. Sample number 2 was taken in a region of a brown haze. The fires and the haze may be part of the reason for the large deviation observed. The wind at Barrow on that date was out of the east.

These data again indicate an area for future research and support the hypothesis that the arctic oceans are a source of CO_2 through the sea ice.

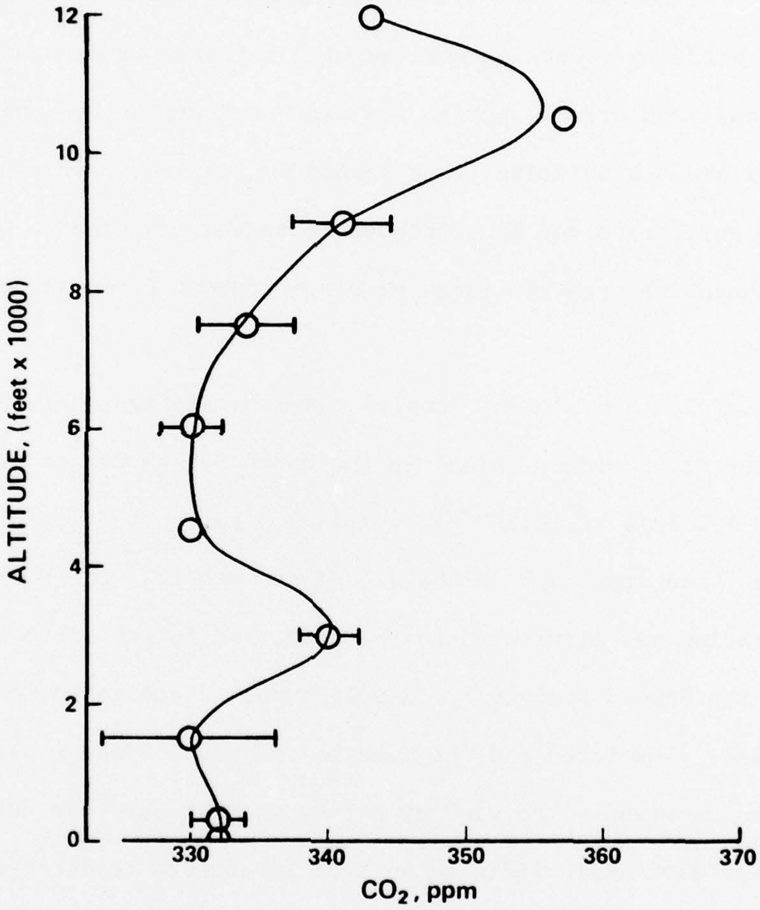


Figure 22. Vertical profile to 12,000 ft of CO_2 near Point Barrow, Alaska, 16 July 1977.

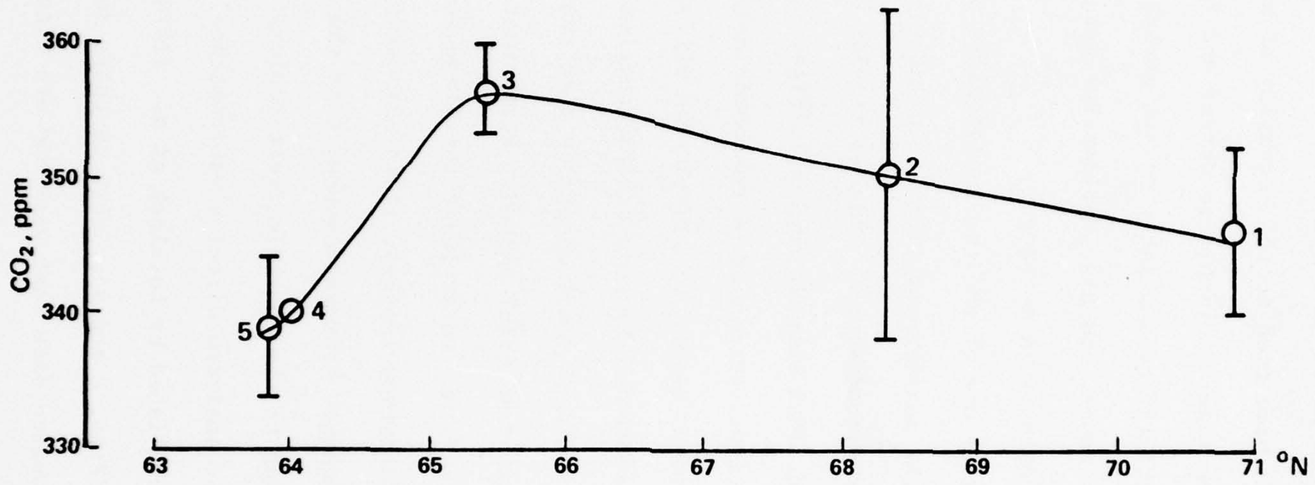


Figure 23. Carbon dioxide profile between Point Barrow and St. Lawrence Island on 12 July 1977.

IV. Coulometry

A. General

In all of our past work, either by infrared or gas chromatographic methods, we have been tied to the necessity of having on hand fairly expensive, cumbersome, difficult to obtain and frequently unreliable, gas standards. There is now available on the market a coulometric detector for combustible gases, and also devices for quantitative reduction of CO_2 and CO to combustible methane.

Coulometry is one of the few analytically absolute methods since it only requires the measurement of the flow of electrons, a relatively simple task for picoammeters. This particular device from Reaction Coulometers Ltd. (Maidenhead, England) (Figs. 8, 9) accomplishes the analyses in an indirect manner by coulometrically generating oxygen, using the generated oxygen to combust the effluent of a gas chromatograph, and then electrochemically reducing the remaining oxygen. The net flow of electrons, followed continuously by electronics, is the absolute measure of the quantity of material passed. Furthermore, not only does the device have sensitivity equal to at least the flame ionization detector of a good gas chromatograph (<ppbv), it is also suitable for the otherwise difficult to measure hydrogen component of the environment.

In addition to the above indirect coulometric method, it appears that hydrogen may be analyzed directly coulometrically, by the application of some work published by Lovelock *et al.* (1970) discussed below in section IV-C (Figs. 8 and 9). Work on these devices has only begun because of the late funding date last year and are discussed separately below.

Free hydrogen is a simple primal micro component of the environment like methane and carbon dioxide, etc., but is very difficult to determine by existing analytical instrumentation. It can be done with great accuracy and sensitivity by a mass spectrometer, but these devices are very expensive, usually bulky, and for the most part, unless modified, are not designed to look at masses less than 4-12. Helium ionization detectors on gas chromatographs are capable of the task, but are prone to leak and contamination problems. Flame ionization detectors are ruled out because it operates by the combustion of hydrogen.

B. The reaction coulometer

A reaction coulometer has been set up in the laboratory at IMS in Fairbanks for the purpose of verifying its sensitivity and calibrating the system. It is currently set up to do only hydrogen on a continuous basis by placing it downstream from a water stripper and hydrogen transfer device, instead of downstream from a gas chromatograph (Fig. 24). Initial nonoptimized results show that the system will readily detect 0.02 μl of hydrogen when the hydrogen is injected directly upstream of the coulometer. Normal seawater concentrations of hydrogen are on the order of 0.01 μl/ℓ (Seiler and Schmidt, 1974). There is a loss if the hydrogen transfer device barrier must be crossed. This is due to either dirt in the transfer device, or traces of oxygen in the carrier. An oxygen getter device will be required in order to eliminate the latter possibility.

Final results of this work are not anticipated before this report is to be submitted. An interim updating report to interested personnel will follow in October-November.

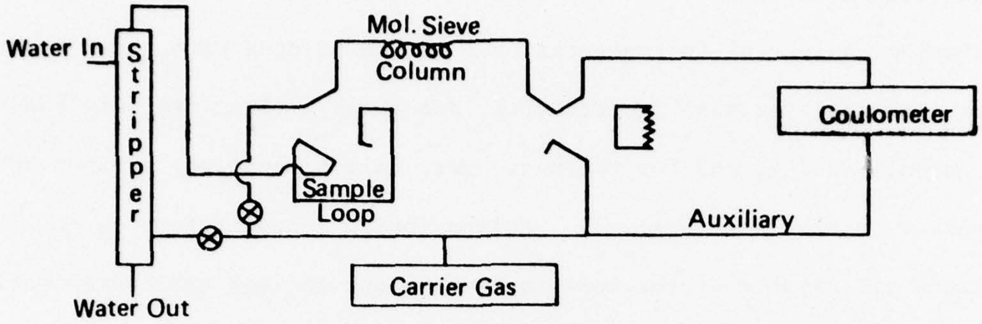


Figure 24. Current flow scheme for hydrogen detection in water with the reaction coulometer.

C. Study of direct coulometry of hydrogen

A palladium pump system similar to the one published by Lovelock *et al.* (1970) has been assembled and initially tested. Aside from electrolyte contamination problems, the cell was functional, but was far from coulometric in the amount of external current passed when small quantities of hydrogen were introduced to the gas stream. Work is underway to apply a stable bucking potential to the system in order to raise the efficiency of the method to the required 100%. An updating note will have to follow to interested personnel on this phase of our research. Basically the cell works, but has to be debugged. Precedence will be given to the reaction coulometer aspect since it is more universal in its application, and is closer to being perfected.

V. Miscellaneous

A. Gases in holes drilled in tundra by North Meadow Lake

During the winter (1977) two holes were drilled in the tundra by North Meadow Lake to sample gases in connection with our interest in subnivean gases. At the bottom of the holes 2-foot sections of 2-inch pipe, open on the bottom and capped on top, were refrozen and buried. Two 1/8" O.D. lines from the caps to the surface were also incorporated to obtain samples. The soil was organic gravel and a deep layer of clay. This summer an addition horizontal pipe section was set in at approximately a 5-cm depth over the pipe.

Some flow problems, possibly frost in the lines, caused sampling difficulties. The results for the samples 72 hours after the holes had been completed are given below in Table 6 along with spring and summer values. The only significant variation between the new hole winter values and the spring summer are the elevated CO_2 values in the spring and the continued consumption of oxygen, possibly accounting for the decreased CO value in the summer.

TABLE 6. Analysis of air chambers in holes in tundra by North Meadow Lake.

		(%)		ppm		
Date	Sample	O_2+Ar	N_2	CO	CH_4	CO_2
21 March 1977	9 m hole	14	83	150	450	1180
	1 m hole	20	78	0.4	2	475
	Subnivean	22	78	<0.1	<1	1060
10 June 1977	1 m hole	-	-	0.05	2.3	2100
1 August 1977	5 cm chamber	-	-	trace	1.2	2000
	1 m hole	-	-	trace	1.4	392
	9 m hole	3	90	1.0	580	2500

A question arises, if CO_2 is escaping from the tundra into the subnivean, why aren't CO and CH_4 doing likewise. A discussion of this phenomena is given in section V B,2.

B. Carbon monoxide

1. In CO_2 standards

The accuracy of infrared analysis of CO_2 depends on the availability of reliable standards. Kelling's laboratory at the Scripps Institute of Oceanography supplies such standards as determined by manometric methods. We have used those same standards in this work to calibrate our gas chromatographic system and to intercalibrate other commercial standards. The presence of carbon monoxide in these standards is of no consequence to the accuracy of either the manometric or gas chromatographic methods, but is of concern to the infrared system since both gases have bands which narrowly overlap. It was observed that both old and new standards contain CO, as well as traces of methane. Sample number 11 was a primary standard. The levels are not sufficient to cause problems with current levels of infrared work at ± 0.3 ppm, but are if the ± 0.05 ppm level is sought.

Table 7 shows CO levels in 11 randomly selected CO_2 standard tanks.

2. Carbon monoxide, ozone and the subnivean

In the process of attempting to explain the high values of CO_2 and relatively low values of CO and CH_4 in the tundra subnivean environment compared to the gases present in the holes in the tundra, the possibility of ozone oxidation was considered. Kelley and McTaggart-Cowan (1973) have reported in the past that there is a variable quantity of ozone in the first few meters above the snow, with higher concentrations near the

TABLE 7. Carbon monoxide and methane levels in randomly chosen CO_2 standards.

Sample No.	CO (ppm)	CH_4 (ppm)
1	1.5	0.3
2	0.8	0.2
3	0.8	0.1
4	1.2	0.1
5	0.6	not detected
6	0.8	trace
7	0.7	0.2
8	0.7	0.1
9	1.8	0.4
10	1.9	0.1
11*	1.1	trace

*this standard was classified as a primary standard.

snow surface (possibly due to the double path length of reflected incident radiation). Routine observations at the NOAA site in Barrow confirm this increase in concentration of ozone near the snow surface. If the atmospheric ozone, of which there is a nearly continuous supply, diffuses through the snow pack and oxidizes CO and CH_4 escaping from the tundra surface, the resultant CO_2 will of course be enriched there, and because of the interaction of carbon dioxide with water (the snow surfaces) its diffusion out may be retarded, thus the high CO_2 and low CO, CH_4 subnivean concentrations. One experiment with helium flushed snow in a tube did suggest that CO_2 is indeed held up by snow surfaces, as perhaps is some CO. Several experiments were done with a CO standard in a quartz tube injected with sufficient ozone in the air to approximate an ozone-rich normal atmosphere (about 0.1 ppm). A sample was withdrawn and analyzed for CO immediately for a starting point reference and the tube placed in the sun. The CO was always reduced to approximately half the starting concentration within an hour.

This is yet another facet of this work which warrants further investigation.

C. Modification of equipment

Based on the assumption that our research will be refunded, certain equipment modifications planned last year, but not possible because of late funding are being implemented. Figures 25 and 26 are drawings of two new metal stripping devices which will operate at the new gas chromatographs working pressure of 50 psi. The sea ice stripper will allow chips of ice to be flushed with helium (through needles and septa) before melting and the assumed total stripping of all gases, both before and after acidification. The sea water stripper will permit the injection of $\mu\ell$ quantities of sea water for total stripping, with and without acid, and not overwhelm the detectors.

Columns and valves are being investigated to allow for the monitoring of C_2-C_4 hydrocarbons as well as methane. Moderate success has been achieved, but renewal funding will be necessary to be able to install the proper valves.

CONCLUSIONS

This year we have demonstrated that the sea ice is apparently a continuous source of CO_2, CO, and CH_4. There is also reason to believe that the high CO_2 levels found in the subnivean environment over sea is linked to the concentrated brines in the sea ice, and pressure exerted on the ice. Atmospheric perterbations over sea ice extends well into the summer months.

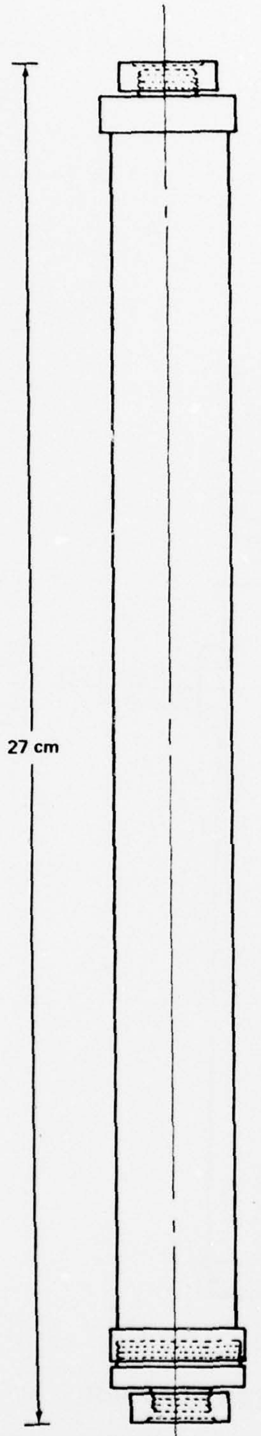
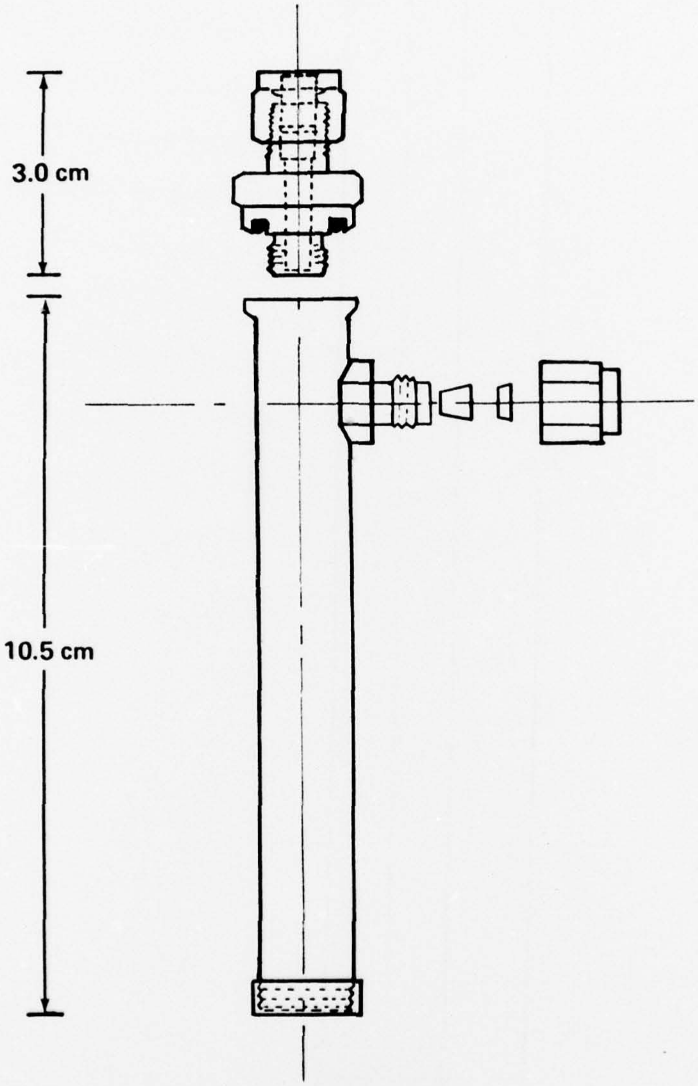


Figure 25. Design of metal sea ice stripper to work at 50 psi. Septa caps are located on each end.



SEA WATER STRIPPER

Figure 26. Design of metal sea water stripper to work in line at 50 psi.

Coulometric work has proved feasible for hydrogen work, and will eventually do away with the needs for multiple standard gases since the method is absolute.

PROPOSED FUTURE WORK

We will endeavor to monitor sea ice over relatively long periods of time as a function of several simultaneous physical and chemical measurements to better understand the cause of the pumping of gases from the sea to the atmosphere. We also hope to do more detailed chemical analysis of both various types of sea ice, and of the brine in them. Furthermore, funds permitting, we hope to begin a survey of other trace gases in the arctic oceans, ices and atmosphere. These gases would include hydrogen C_2-C_4 hydrocarbons, oxides of nitrogen and ozone.

REFERENCES

Coyne, P. I., and J. J. Kelley, Jr. 1974. Variations in carbon dioxide across an arctic snowpack during spring. *J. Geophys. Res.* 79:799-802.

Gosink, Thomas A., J. G. Pearson and J. J. Kelley. 1976. Gas movement through sea ice. *Nature* 263:41-42.

Hemmingsen, E. 1959. Permiation of gases through ice. *Tellus* 11:355-359.

Kelley, J. J., Jr., D. F. Weaver and B. P. Smith. 1968. The variation of carbon dioxide under the snow in the arctic. *Ecology* 49:358-361.

Kelley, J. J., Jr., and J. D. McTaggart-Cowan. 1973. Vertical gradient of net oxidant over the ground surface at Barrow, Alaska. *J. Geol. Res.* 73:3328-3330.

Lovelock, J. F., P. G. Simmonds and R. G. Shoemake. 1970. The palladium generator-separator a combined electrolytic source and sink for hydrogen in closed circuit gas chromatography. *Anal. Chem.* 42:969-973.

Oeschger, H., B. Stauffer, P. Bucher and M. Moell. 1976. Instruments and methods. Extraction of trace components from large quantities of ice in bore holes. *J. Glaciol.* 17:117-128.

Riley, J. P. and G. Skirrow. 1965. Chemical Oceanography. Academic Press p. 230, Vol. 6. Reference to Miyahe and Matsuo.

Seiler, W. and U. Schmidt. 1974. Chapter 7, Dissolved nonconservative gases in sea water. *In: The Sea*, Vol. 5, E. Goldberg (ed.). Wiley, Interscience.

Swinnerton, J. W., V. J. Linnenbom and C. H. Cheek. 1969. *Environ. Sci. Tech.* 3:836-839.

Swinnerton, J. W., V. J. Linnenbom and R. A. Lamontagne. 1970. *Sci.* 167: 984-986.

Weiss, R. F., P. Bucher, H. Oeschger and H. Craig. 1972. Compositional variations of gases in temperate glacier. *Earth and Planet. Sci. Lett.* 16:178-184.