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SPECTROSCOPIC STUDIES OF NUCLEAR
SUBMARINE ATMOSPHERES

II. Infrared Analysis of Major Gaseous
Contaminants

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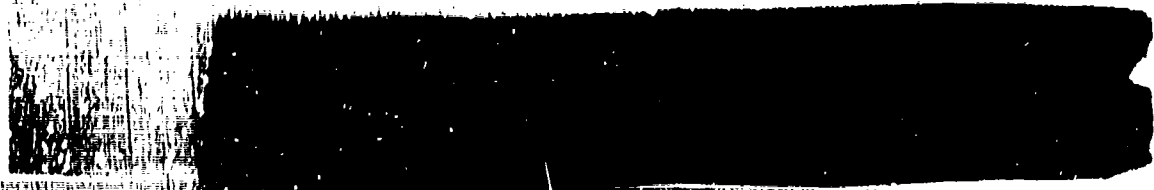
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ABSTRACT

Infrared spectral analyses have been made of compressed submarine air samples taken aboard the USS SEAWOLF during the cruise covering the period 3-26 November, 1966. The following contaminants were detected in the gross samples, i.e., those on which no preliminary separation of constituents was made: carbon monoxide, carbon dioxide, water vapor, Freon-12, methane, methyl alcohol, acetylene and nitrous oxide. Each of these contaminants has been measured quantitatively and found to be well below permissible limits. The way in which the concentration of each of these contaminants is effected by the operation of the Desomatic burner is discussed.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

NRL Problem C07-01
Project NR 477-000, Task NR 477-001

SPECTROSCOPIC STUDIES OF NUCLEAR SUBMARINE ATMOSPHERES

II. Infrared Analysis of Major Gaseous Contaminants

INTRODUCTION

One of the aims of the submarine respiratory habitability program is to determine the constitution of the submarine atmosphere, especially those constituents which might be considered dangerous to personnel after long periods of exposure. Some atmospheric contaminants can be measured aboard an operating submarine by instrumentation such as the Atmosphere Analyzer, which is currently programmed for a relatively few known constituents. Other contaminants can be detected and measured by various chemical tests more or less conveniently. However, these tests are restricted to those few known contaminants for which there is a relatively simple test. Still others can be detected by complicated analytical instrumentation such as infrared and mass spectrometers and the vapor phase fractometers. While such instruments can and have been carried aboard submarines, e.g., the Habitability Cruise of the USS NAUTILUS in 1956, it has been found more practical and convenient to collect samples by various means on the operating vessel and return the samples to the laboratory for subsequent analysis.

There are undoubtedly several hundred atmospheric contaminants from all the various sources on the submarine. For instance, over four hundred contaminants are known to arise from just two of the major sources, tobacco smoke and paint solvents. Over three hundred constituents have thus far been identified in tobacco smoke. Gas chromatography reveals the presence of more than one hundred contaminants, only a few of which have been identified, in the liquid phase of paint solvents recovered from the submarine atmosphere. The identification and determination of the less concentrated contaminants in such a complicated mixture by any means at all would be difficult and time consuming. Fortunately the concentration of these adulterants seems to be well below tolerable limits.

The concentration of most of these impurities, whether in the form of solid or liquid particles or vapor, is maintained at low level by the submarine's air purification system, which consists of aerators, burners, filters, absorbents and precipitators. In addition, the concentration of some of the particulate matter is normally reduced through agglomeration and settling and by collision with surfaces.

Contaminants which build up to significant levels in the submarine atmosphere in spite of these removal methods are of tremendous interest from a toxicological viewpoint. The vapor phase contaminants, which

escape the present removal methods are perhaps the easiest to identify. The three most promising methods of analysis for this purpose are infrared and mass spectrometry and vapor phase chromatography. Of these, the first seems to be the most ideally suited because of its sensitivity and specificity. In general, the highest sensitivity is obtained with the infrared method when the product of absorption path and sample concentration is a maximum. The maximum absorption path length attainable with the equipment at hand is ten meters. This long path is obtained by the use of mirrors which reflect the entering radiation so that it traverses the cell thirty-two times before exiting. The cell has a fairly small volume, 5.5 liters, and can be pressurized safely to 100 psig.

Atmospheric samples can be taken aboard submarines by using a small air compressor to pressurize type A-4 stainless steel bottles, which have a volume of approximately 1.5 liters. Thus when air, compressed into these bottles to a pressure of 400 psig, is later expanded into the evacuated 5.5 liter volume of the ten meter cell, the resultant pressure is about 100 psig.

From time to time various submarine atmospheres have been sampled in this manner and spectrally analyzed. These samples were either isolated specimens or were taken after relatively short submergences, and allowed few correlations and conclusions. Recently, however, a particularly interesting series of samples was taken aboard the USS SEAWOLF (by Dr. George W. McLaren) during the cruise 3-26 November 1958. These samples were collected in a systematic manner in an attempt to elucidate certain facts relative to the functioning of the various devices used for maintaining a livable atmosphere.

EXPERIMENTAL PROCEDURES

The stainless steel bottles used for the samples were hydrostatically pressure tested to 600 psi, steamed cleaned at the laboratory prior to use and fitted with teflon coated needle valves. They were evacuated and stored aboard the submarine until ready for use. The procedure for collecting the samples was to connect the bottle to the discharge side of the compressor using a T fitted with a valve and gauge. The compressor was turned on and the discharge side of the line flushed up to the valve on the sample bottle before the latter was opened. All samples were compressed at 400 psig. A length of teflon tubing on the input side of the compressor permitted air to be drawn from practically any desired location. A total of eighteen samples were collected at various locations on the boat during the twenty-three day submergence.

The compressor was charged with a silicone oil instead of a hydrocarbon oil, since silicones absorb very strongly in the infrared and any carry over of the silicone fluid with the sample could be easily detected. No absorption attributable to silicone fluid has ever been observed, however, in the spectra of samples taken as described.

Water vapor is a strong absorber in the infrared. The concentration of water vapor in air of 40% relative humidity, at the pressure and path length used for this analysis, is sufficient to mask out an interesting region of the spectrum. Chilling the sample to 10°K. before expanding it into the 10 meter cell reduces the water vapor concentration to a level where it ceases to be a problem. A small amount of the contaminant gases are undoubtedly retained by solution in the frozen out water. No effort has been made to reduce this loss or to correct the analytical results therefor.

The spectra were obtained over the 2-13 micron region using a Perkin-Elmer Model 21 double beam spectrophotometer.

RESULTS AND DISCUSSION

All of the observed absorption bands have been identified as arising from the following gaseous contaminants: carbon monoxide, carbon dioxide, water vapor, Freon-12, methane, methyl alcohol, acetylene, an unidentified low molecular weight hydrocarbon, and nitrous oxide. All of these contaminants, except nitrous oxide, have been identified in previous submarine atmosphere samples. This is the first time, however, that nitrous oxide has been identified by any analytical means. Reinspection of the spectra obtained of a sample of air taken from the USS NAUTILUS during the trip of April 29, 1958 does reveal the presence of nitrous oxide although its identification was overlooked at that time. It is an easy contaminant to overlook because its strongest absorption band, which is very weak in these spectra, falls between a very strong (intense) CO₂ band and a weaker CO band.

The present series of samples makes the presence of nitrous oxide more obvious, however. It is particularly evident in the spectra of those samples taken at the output of the Desomatic (CO) burner where the absorption arising from CO is zero.

Absorption at 3.42 microns in the spectra of these samples arises from C-H bonds, and is probably due to low molecular weight hydrocarbons. This band is rather weak in the subject spectra, however, and in the absence of other absorption bands attributable to this material no specific identification can be made. It is probably either ethane or propane or a mixture of these gases, both of which have been found in cigarette smoke. For the sake of quantitative measurements the compound is assumed to be propane and calculated as such.

TABLE 1

Analyses of Compressed Submarine Air Samples Taken On
USS SEAWOLF During the Cruise of 3-26 Nov. 1958

Sample #	Source	Date	Time	Carbon Dioxide %	Carbon Monoxide ppm	Freon 12 ppm	Methane ppm	Methyl Alcohol ppm	Ace
1	Output #1 Deso.	11-6-58	1304	.92	*	30	38	*	
2	Inlet #1 Deso.	11-6-58	1340	.92	38	28	43	1.5	
3	Output #1 Deso.	11-13-58	0930	1.00	*	83	64	*	
4	Inlet #1 Deso.	11-13-58	1000	.88	31	86	65	2.9	
5	Inboard vent #3 gun tank	11-15-58	1230	1.04	29	68	118	*	
6	Torpedo room	11-18-58	1000	1.02	31	66	70	4.5	
7	Control room top of steps	11-18-58	1200	.94	32	57	72	5.2	
8	Eng. room upper level near maneuvering room	11-18-58	1330	.74	32	67	70	5.1	
9	Eng. room lower level near H.O. Evap.	11-18-58	1425	.79	24	67	56	4.5	
10	Exhaust duct from CO ₂ scrubber	11-18-58	1500	.26	36	70	60	6.5	
11	Outlet #2 Deso.	11-18-58	1530	1.06	*	65	72	2.5	
12	Inlet #2 Deso.	11-18-58	1630	.97	30	66	72	4.4	
13	Outlet #1 duct by gyro compass	11-20-58	1000	1.11	28	67	79	3.4	
14	Outlet #1 duct by gyro compass	11-23-58	1200	.95	31	59	75	2.5	
15	Outlet #1 Deso.	11-24-58	1000	.96	*	61	73	*	
16	Inlet #1 Deso.	11-24-58	1100	.90	30	57	68	*	
17	Discharge of CO ₂ scrubber	11-24-58	2305	88.7	*	*	*	*	
18	Outlet #1 air, Whittaker H. Deso.	1-9-59	1200	.04	*	*	*	*	

* Not detected

A

TABLE 1

Analyses of Compressed Submarine Air Samples Taken On
USS SEAWOLF During the Cruise of 3-26 Nov. 1958

Date	Time	Carbon Dioxide %	Carbon Monoxide ppm	Freon 12 ppm	Methane ppm	Methyl Alcohol ppm	Acetylene ppm	Nitrous Oxide ppm	Hydrocarbon as propane ppm
11-6-58	1304	.92	*	30	38	*	*	8.5	*
11-6-58	1340	.92	38	28	43	1.5	0.2	7.0	11
11-13-58	0930	1.00	*	83	64	*	*	18.0	*
11-13-58	1000	.88	31	86	65	2.9	0.4	12.5	9
11-15-58	1230	1.04	29	68	118	*	*	14.5	10
11-18-58	1000	1.02	31	66	70	4.5	*	19.5	8
11-18-58	1200	.94	32	57	72	5.2	*	13.0	10
11-18-58	1330	.74	32	67	70	5.1	0.1	15.5	8
11-18-58	1425	.79	24	67	50	4.5	*	18.0	11
11-18-58	1500	.26	36	70	60	6.5	0.5	20.0	9
11-18-58	1530	1.06	*	65	72	2.5	0.1	20.0	*
11-18-58	1630	.97	30	66	72	3.4	0.1	16.0	8
11-22-58	1000	1.11	28	67	79	2.4	*	27.0	11
11-23-58	1200	.95	31	59	75	2.5	*	19.5	10
11-24-58	1000	.98	*	61	73	*	*	23.0	*
11-24-58	1100	.90	30	57	68	*	*	20.5	9
11-24-58	2345	88.7	*	*	*	*	*	*	*
1-9-59	1200	.04	*	*	*	*	*	*	*

B

The quantitative values given in Table I are calculated on the basis of the best calibrating data at hand, some of which are known to be only approximately correct. More accurate data is presently being acquired and will be used for future analyses. A modified base line system of calculation has been used in the present analysis. That is, an attempt has been made to graphically correct the absorption of each individual constituent for the spectral contribution of all the others. No great accuracy is claimed for this method; however, it is necessary at this time in order to make the analyses manageable.

The concentrations of carbon dioxide listed in the table are in percent by volume. All others are given in parts per million (by volume). An asterisk (*) indicates that the concentration of the contaminant was less than the minimum detectable amount. No quantitative data has been given for water vapor since the concentration of this constituent was deliberately reduced prior to analysis.

Several interesting observations are apparent from these data. In general the carbon dioxide scrubber was able to maintain the carbon dioxide concentration of 1% or less. The concentration of the carbon dioxide in the air exhausted from the scrubber (sample #10) was reduced to 0.26% which would indicate a carbon dioxide removal efficiency of 75% for the operating conditions prevailing in the scrubber at the time of sampling. The samples were not taken with the idea in mind of determining scrubber efficiency, however, nor is it known that the operating conditions prevailing were normal. Actual scrubber efficiency may vary somewhat from this figure. The true efficiency for varying conditions could easily be determined by spectral analysis of scrubber input and output air.

The carbon dioxide concentration is low in the engine room spaces (samples #8 and #9) especially near the maneuvering room because it is in this location that the exhaust of the carbon dioxide scrubber is dumped. The discharge from the scrubber (sample #17), which is normally compressed and pumped overboard, has a carbon dioxide concentration near 90%. This figure is based on a very large extrapolation, and may actually be as high as 100%.

The original purpose of the equipment now known as the Desomat burner was to convert carbon monoxide and hydrogen to carbon dioxide and water vapor, respectively. As now operated this equipment also converts most of the hydrocarbon contaminants in the entering air stream to carbon dioxide. Obviously the carbon dioxide content of the output air of the Desomat burner should be higher than the input air. For average conditions, however, the difference in carbon dioxide concentration is probably less than the experimental error for this determination. The measured values for carbon dioxide concentration listed in Table I indicate a higher value for burner output air in all instances save one. These differences are probably fictitious, arising from a combination of errors in the sampling and analytical techniques. The carbon dioxide concentration

of outdoor air taken in Washington, D.C. on the date indicated was spectrally determined to be .04%, a figure in good agreement with literature values.

The Desomatic burners, as operated during the cruise, were very efficient in burning carbon monoxide. In each case the concentration of carbon monoxide in the output air of the Desomatic burner was less than the minimum detectable level, which is about 5 ppm. The values for the concentration of carbon monoxide reported here are in fair agreement with those recorded by the Atmosphere Analyzer during the cruise. The average carbon monoxide content of the submarine atmosphere during the cruise was 30 ppm.

It is obvious from the analytical data that no appreciable decomposition of Freon-12 takes place during passage through the Desomatic burners. This gas is readily adsorbed by the activated charcoal filters, however, which tend to keep the concentration of this contaminant reduced, at least until the absorbent becomes saturated.

The data for the concentration of methane at the input and output of the Desomatic burner is somewhat inconsistent. The average, however, appears to support the present contention that no significant reduction in methane concentration takes place in the burners as now operated. This inconsistency in the data probably results from the experimental error in determining this contaminant. Nitrous oxide also absorbs at the wavelength used for determining methane. The accuracy of the determination is lowered even though a correction has been applied for the presence of nitrous oxide. The concentration of methane is significantly higher in the air vented from the sanitary tanks (sample #5). The anaerobic decomposition of sewage is evidently the source of this contaminant, although it is also produced by smoking.

Methyl alcohol, at the levels reported, is not dangerous to personnel. It is effectively removed from the atmosphere by the Desomatic burner. Methyl alcohol is used as a solvent in the office duplicating machine carried aboard the vessel.

Acetylene is also removed from the submarine atmosphere by the Desomatic burner. This gas, possible sources of which are welding and smoking, is present at a very low level, almost at the threshold level of detection for this method of determination. The hydrocarbon reported as propane is also effectively oxidized on passage through the burners.

The presence of nitrous oxide has not previously been known in the submarine atmosphere. This gas, also known as laughing gas, is not very toxic. There is a significant increase in the concentration of this contaminant in the output air of the Desomatic burners. Evidently nitrous oxide is produced by the oxidation of ammonia and other nitrogen containing compounds, such as monoethanolamine, on contact with hot

Hepealite in the Desomatic units. Small amounts of ammonia and monoethanolamine have been detected in the submarine atmosphere chemically, although never by infrared. Nitrous oxide may also be carried aboard in the form of a propellant and whipping agent in canned whipped cream and shaving foam. Various oxides of nitrogen also result from smoking.

SUMMARY AND CONCLUSIONS

Infrared analysis of compressed air samples taken aboard submerged submarines provides a convenient and rapid means of determining the major contaminants in the submarine atmosphere. Such an analysis provides a relatively easy method of studying the efficiency with which these contaminants are removed from the atmosphere by the different components of the submarine's air purification system under various conditions.

For instance, analytical results of air samples taken during a twenty-three day submergence of the USS SEAWOLF indicate a scrubber carbon dioxide removal efficiency of 75% or better for normal operating conditions. Carbon dioxide is maintained at 1% or less without difficulty.

Of the major gaseous contaminants, the Desomatic burners effectively remove carbon monoxide, methyl alcohol, acetylene and hydrocarbons other than methane from the air stream. The Desomatic burners, as presently operated, have negligible effect upon the concentration of Freon-12 and methane. The burners generate nitrous oxide, probably as a result of the oxidation of ammonia and other nitrogen containing compounds in the air stream.

Improved calibrating data would increase the accuracy with which these contaminants could be determined in future analysis. Perhaps additional impurities could be detected if a preliminary separation of the atmospheric constituents were effected by low temperature fractionation.

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LIST OF FIGURES

Fig. 1 Infrared Spectrum of a Typical Submarine Atmosphere Sampled at the Input of the Desomatic Burner

Fig. 2 Infrared Spectrum of a Typical Submarine Atmosphere Sampled at the Output of the Desomatic Burner

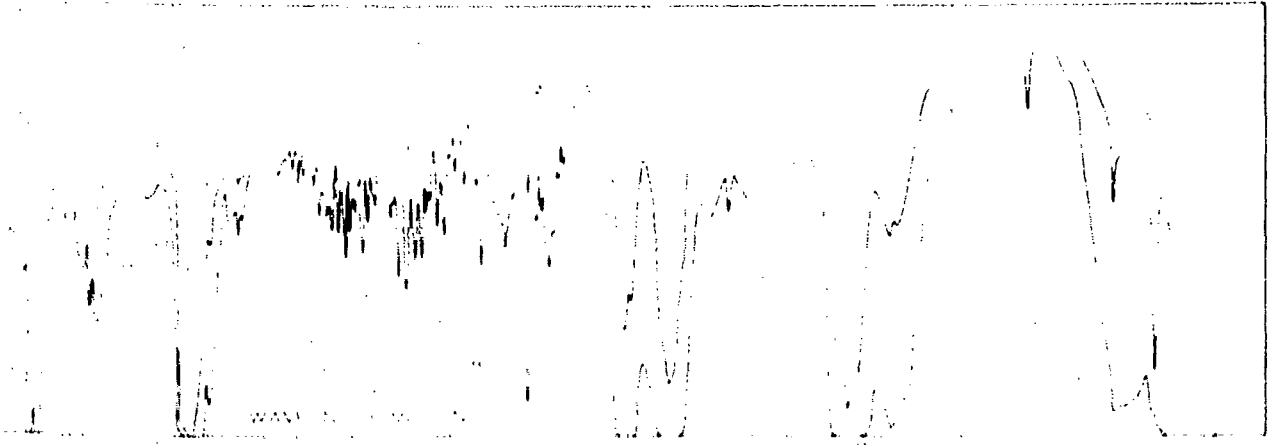


Fig. 1 - Infrared Spectrum of a Typical Submarine Atmosphere Sampled at the Input of the Desomatic Burner

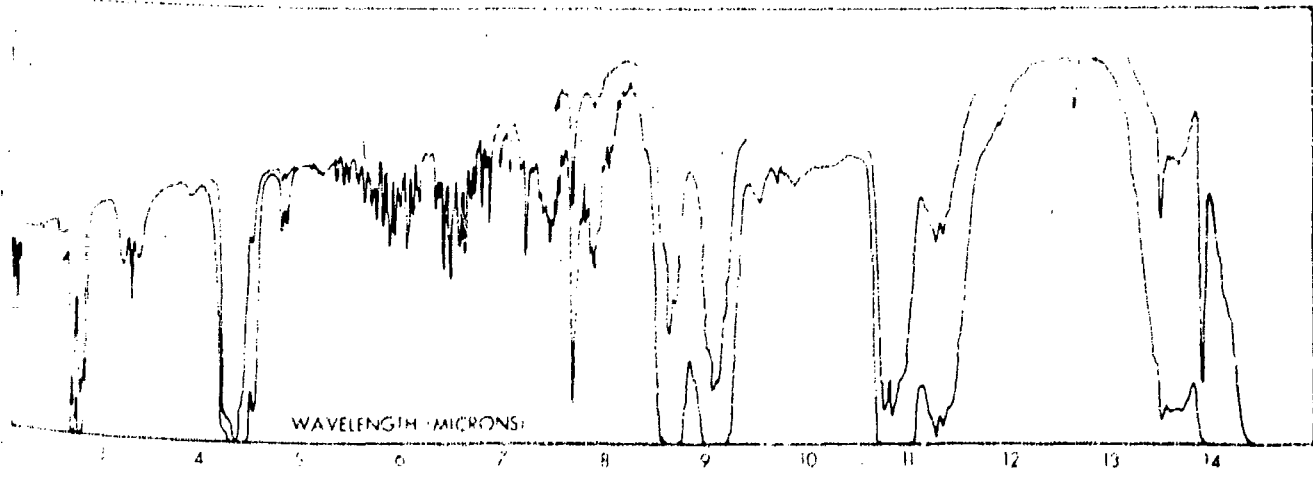


Fig. 2 - Infrared Spectrum of a Typical Submarine Atmosphere Sampled at the Output of the Desomatic Burner