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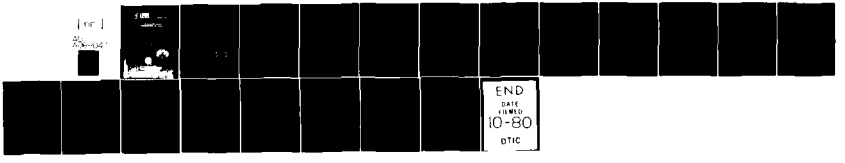

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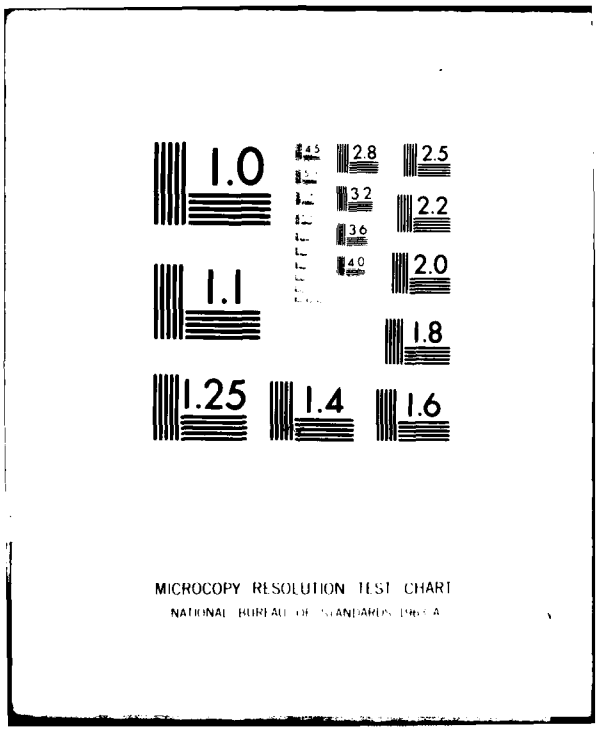
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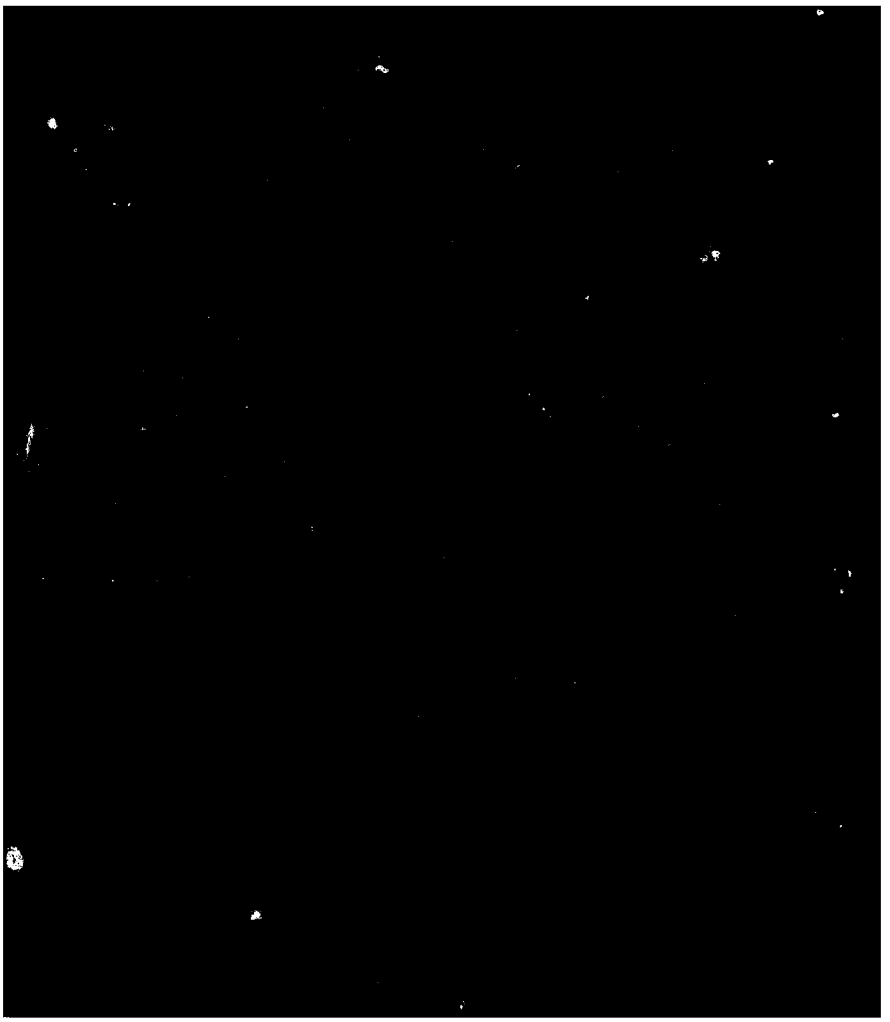

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A portable photoionization detector, ~~produced by HNU Systems, Inc.,~~ is being evaluated as a submarine Hydrocarbon Gas Trace Analyzer (TGA). Principals of the photoionization technique and the physical features of the instrument are discussed, and the utility of ~~the HNU~~ instrument as an onboard hydrocarbon analyzer is compared to the Total Hydrocarbon Analyzer (THA) currently deployed on all SSBN's and all 688 Class SSN's. Theoretical and laboratory evaluations show the TGA to be easier to operate, more simple in design and potentially more reliable than the THA.

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20. ABSTRACT (Continued)

Final conclusions regarding suitability of the TGA as a shipboard hydrocarbon analyzer will be reached following sea trials that are now underway.

CONTENTS

I.	INTRODUCTION	1
II.	SELECTIVE DETECTION OF COMPOUNDS WITH PHOTOIONIZATION	3
III.	USING A PHOTIONIZATION ANALYZER AS A TRACE GAS ANALYZER (TGA) ABOARD NUCLEAR POWERED SUBMARINES	4
IV.	ALTERNATIVE USES OF PHOTOIONIZATION IN DETECTION OF SUBMARINE ATMOSPHERIC HYDROCARBONS	8
V.	CONCLUSIONS	8
	REFERENCES	9
	APPENDIX A	10
	APPENDIX B	14

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USE OF A PHOTOIONIZATION DETECTOR (PID) AS A HYDROCARBON TRACE GAS ANALYZER (TGA)

I. INTRODUCTION

Ionization is the process of creating a charged molecule or atom from the neutral molecule or atom. This process occurs whenever the particle absorbs enough energy to move an electron from its normal position to a position far enough from the particle so that there is no longer any interaction between the two. The Ionization Potential (IP) is the minimum energy required to remove the most weakly held electron from a ground state molecule and form an ion. Thus, any energy greater than IP which is transferred to the molecule will result in the ionization of that molecule. The flame ionization detector (FID) uses the hydrogen flame as the energy source to ionize molecules. The flame is energetic enough to ionize practically all organic molecules, including methane, ethane and the freon gases. Photoionization on the other hand, employs an ultraviolet (UV) lamp as an energy source and forms ions by the reaction:

$$RH + h\nu \rightarrow RH^{+} + e^{-}$$

where RH = *trace gas* and

$h\nu$ = *a photon with an energy* $\geq$ *IP of* RH (1, 2, 3, 4)

The unique property of the photoionization technique is not the actual ionization process, but the fact that many different UV lamps can be built using different gases or mixtures of gases and that the photons formed by these different lamps will have different, but specific energies. This property makes it possible to choose the photon energy we wish to use and to selectively ionize some compounds but not other compounds.

Manuscript submitted April 2, 1980.

Two situations arise which must be understood and accounted for when dealing with low level photoionization energies that do not occur with higher ionization energy sources such as the FID. The first is the photoionization efficiency or sensitivity of a particular compound to ionization and detection. This sensitivity is dependent both upon the molecule's ionization cross-section and the photon energy's relation (slightly higher, slightly lower, much higher, much lower) to the molecule's IP (5) (See Figure 1). For example, with using a 10.2 eV photon source, hexane, which has an IP (10.32 eV) slightly larger than the photon energy, is ionized and detected with a sensitivity of 2.2 (benzene is reference standard with sensitivity of 10.0). This is possible because at ambient temperature, a small fraction of the hexane molecules are in excited vibrational and rotational states, and therefore have a somewhat lower ionization energy. Ammonia, with an IP of 10.15 eV, because of its cross section, has a sensitivity of only 3.0 with the same 10.2 eV source.

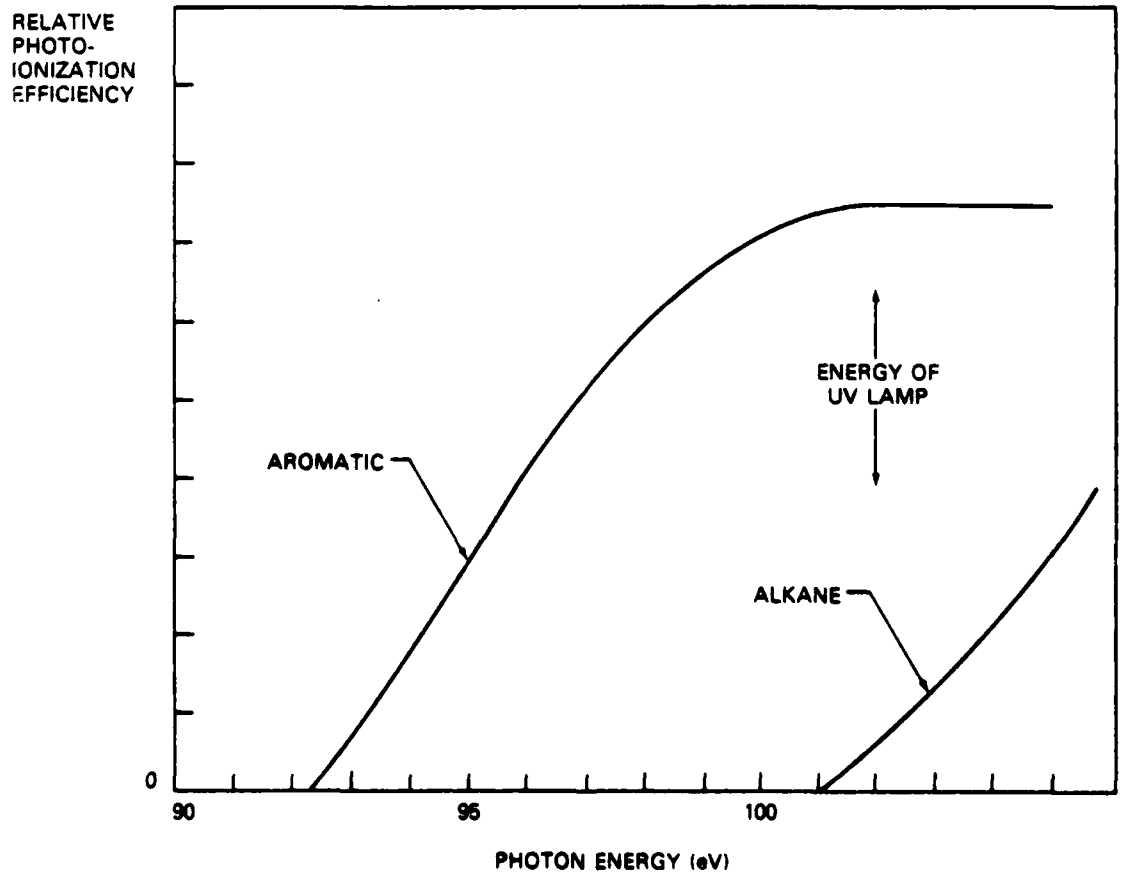

Fig. 1 — Photoionization efficiency curves as a function of photon energy for an aromatic hydrocarbon and an alkane (5)

The second situation that arises is directly related to low energy photons and the compound's photoionization sensitivity. A FID gives a nearly uniform detector response to all carbon atoms, and is independent of the nature of the chemical bonding. If a high energy photon is used in photoionization then this detector also detects all types of carbon compounds with about equal sensitivity. With lower energy photons though, the sensitivity of aromatic compounds to detection becomes much higher than alkene or alkane molecules (5). For example, with a 10.2 eV photon source, the PID is 5-10 times more sensitive to aromatic compounds than it is to alkane compounds, while the detector's sensitivity to alkenes is midway between its sensitivity to aromatic compounds and alkanes (1,2,3,5).

II. SELECTIVE DETECTION OF COMPOUNDS BY PHOTOIONIZATION

Sections I-VII of Appendix A give the ionization potential for some compounds as well as the sensitivities of some of these to detection using a PID equipped with a 10.2 eV, (hydrogen lamp) photon source. The compounds are grouped into the tables on the basis of their chemical classes. From the tables, it is easy to see the general trend that IP decreases with both increase in molecular weight within classes and with an increase in carbon chain branching.

An examination of the IP of various classes reveals that if one is interested only in the detection of some general classes of compounds and not in the detection of specific compounds, a PID can be used for this purpose—if proper selection of the photon source is made. Any knowledge about what the sampled atmosphere can and cannot contain is, of course, very useful in analyzing the output of a PID. The ideal situation would be one in which only one possible compound could be responsible for the signal generated. This type situation might arise where a reaction is being carried out and one compound, reactant or product, has a lower IP than the other compounds involved in the situation. In this case, selection of a photon source that will ionize only the one compound is made and thus an accurate and easily understandable signal is obtained. Unfortunately, general atmospheric monitoring with a PID is not as straightforward as is this limited industrial application.

Significant atmosphere contaminant monitoring is possible with a PID but only if some assumptions can be made and the types of contaminants present can be reasonably predicted. The photon

source must be energetic enough to ionize the compounds for which monitoring is desired yet not energetic enough to ionize other types of compounds with higher IP's which are present in the atmosphere. If other contaminants with an IP less than the photon energy are present, then it must be reasonable to assume either that the concentration of these contaminants is too low to introduce significant error in the measurement, or that the concentration of these contaminants has some known relationship to the compounds of interest. In the first case, the concentration contribution of the unwanted compounds can be ignored. In the second case, the concentration contribution can be subtracted from the indicated concentration to yield the total concentration of the class of compounds being monitored. This subtraction must be done carefully and thoughtfully, however, with consideration given to the different detector sensitivities of these classes of compounds. In all cases, the total concentration of the class of compounds must be a meaningful figure because a PID is incapable of detecting individual compounds within chemical classes unless it is coupled with other techniques such as gas chromatography or mass spectroscopy.

III. USING A PHOTOIONIZATION ANALYZER AS A TRACE GAS ANALYZER (TGA) ABOARD NUCLEAR POWERED SUBMARINES

The Naval Research Laboratory (NRL) has been active for many years in testing submarine atmospheres and in designing, developing and/or testing instruments for onboard atmosphere monitoring. The Total Hydrocarbon Analyzer (THA) was developed by NRL to monitor hydrocarbon concentrations. The THA, which is based on proven principles and techniques, and showed promise in its laboratory evaluations, has been plagued with poor performance and maintainability since its deployment (6). Therefore, NRL has been examining all possible alternatives for a trace hydrocarbon monitor. Ultraviolet lamps and readout devices are commercially available and seem very promising for use as a trace hydrocarbon, photoionization detector. Thus, PI is under evaluation as a technique to monitor trace hydrocarbons with the idea of using this method to either supplement or replace the THA which is currently deployed on all SSBN's and all 688 Class SSN's. Additionally, if this detection method proves accurate and reliable for detecting hydrocarbons then consideration would be given to equipping other submarines with the detector in order to give them a capability for detecting hydrocarbons.

The THA is a gas chromatograph that detects methane and the freons and then normally reverses the direction of carrier gas flow (backflushing) to reform all remaining components into one peak that is used as an indication of the total hydrocarbon concentration less methane. Laboratory analyses of submarine atmospheres has established that most submarines have about 25% aromatic and 75% aliphatic hydrocarbons (7) so 25% of the THA peak is attributed to aromatic hydrocarbons and the rest to aliphatic hydrocarbons. In addition to the normal practice of backflushing the THA, the instrument can also be run as a normal gas chromatograph and thus the capability (a capability that is almost impossible to realize on the shipboard THA being operated by someone inexperienced with gas chromatography) exists to help identify individual compounds based upon their retention times.

The THA also has the capability of detecting and monitoring methane and freons. This capability is no longer essential because the Central Atmosphere Monitoring System (CAMS) monitors the freons and the methane concentration is not considered to be a serious concern (7,8). Also, although there is concern about keeping all hydrocarbon concentrations as low as possible aboard submarines, the proven toxicity and suspected carcinogenicity of the aromatic hydrocarbons cause them to be of much greater concern than the aliphatic hydrocarbons.

Two configurations of the photoionization detector are under examination for use as a Trace Gas Analyzer (TGA) for hydrocarbons. One of these configurations is equipped with a 10.2 eV (Hydrogen) lamp while the other one has a 9.5 eV (Nitrogen) lamp. This examination is structured to evaluate the use of one or the other of these probes as a TGA, as well as using both in order to produce a more versatile TGA.

A summary of the components that will give an instrument response at particular ionization energies is presented in Figure 2. Of particular interest is the fact that methane, which can reach a concentration of 600 ppm (see Table 1), and the freons, which are present at the ppm level, are not ionized or detected using the TGA and therefore do not interfere with measurement of other low-level compounds. This is important because the sensitivity of the THA to these substances contributes to one of the THA's major maintenance problems (6). The THA uses a heated catalyst followed by an acid

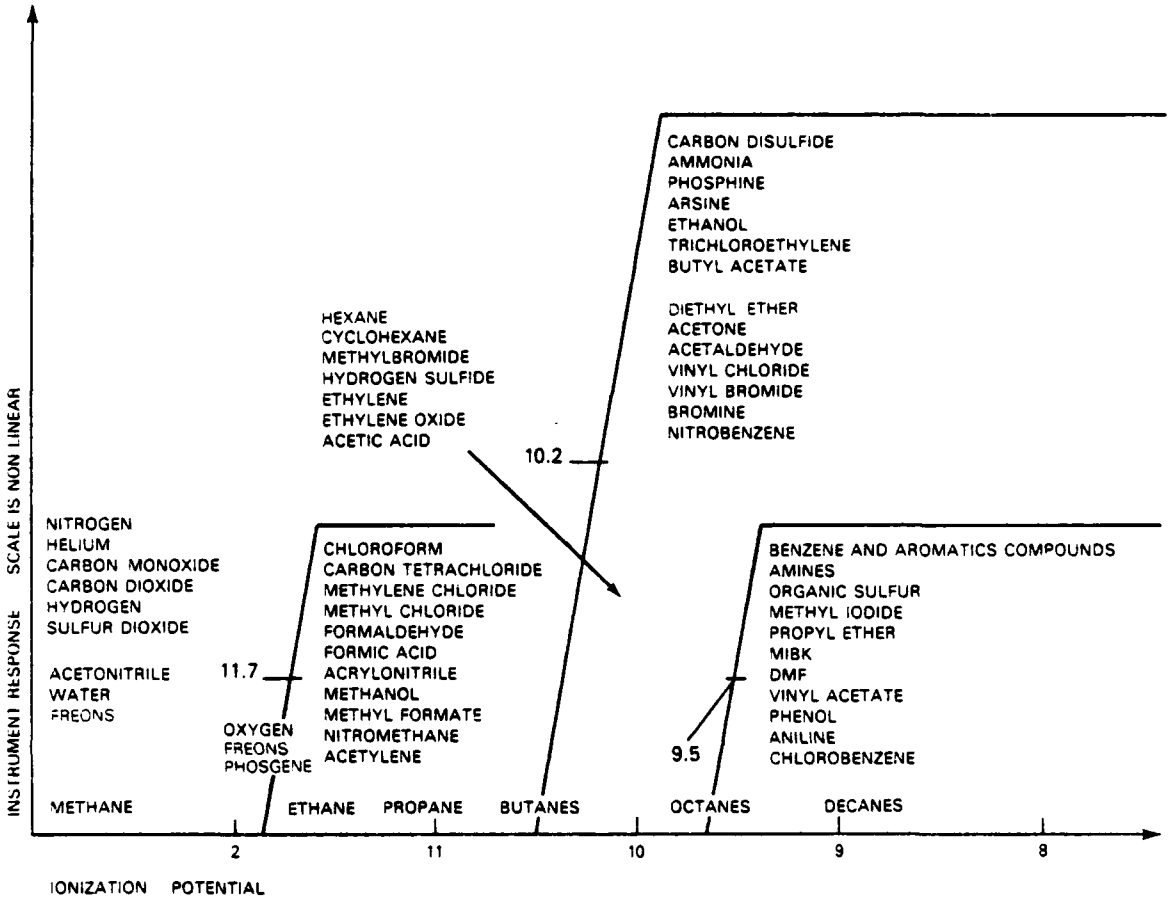

Fig. 2 — Instrument Response vs Ionization Potential for Several Classes of Compounds

scrubber to remove methane and the freons from submarine air which is then used as a carrier gas. These components have been the cause of the majority of the THA failures and thus a device such as the TGA, that can totally ignore these components, is of utmost interest as a submarine hydrocarbon analyzer.

The compounds listed in Sections I-VII of Appendix A are representative of the chemical classes of contaminants observed in submarine atmospheres (7,9,10). A review of the sensitivities for various compounds indicates that use of a 10.2 eV photon source would result in a TGA capable of detecting total hydrocarbons less C1-C-4 alkanes, freons, and acetylene. Although a few additional compounds would also be detected and bumped into the category "Higher Organics," (Table 1), the number of these compounds are few (see Section I of Appendix B) and any error introduced into the TGA measurement would always result in a false positive, providing an additional margin of safety.

Another important factor that would have to be addressed is the TGA's difference in sensitivity to different classes of hydrocarbons (see Table 2). For example, consider the situation in which the submarine atmosphere might contain 1 ppm of aromatic hydrocarbons and 3 ppm of aliphatic hydrocarbons. This situation corresponds to the general empirical finding that a submarine's atmosphere contains three times as many aliphatic hydrocarbons (less methane) as aromaric hydrocarbons (7). With the FID we would expect to read about 4 ppm. With the TGA, however, we would read approximately 1.6 ppm or 8 ppm, depending on whether the span adjustment was made using an aromatic or an aliphatic compound, respectively, as the calibration gas. Although possibly a little confusing, this would not constitute a problem as long as a correction for this factor was always made. Another solution would employ a calibration gas containing a mix of aromatic and aliphatic hydrocarbons (1:3) that approximates the contaminant levels in submarine atmospheres.

Use of a 9.5 eV photon source with the TGA would result in an aromatic hydrocarbon sensor. As before, some additional compounds would be included (see Section II, Appendix B), but again this error would be on the side of safety and therefore more acceptable. The difference is that sensitivities of compounds increases as the ionization energy approaches their I.P.'s (see Figure 1). Thus, although a 9.5 eV probe would not detect alkanes, the different sensitivities of the compounds it does detect might become a significant factor. Thus, further investigation into this question would be warranted before assuming that a 9.5 eV probe on the TGA would result in an accurate reading for total aromatic hydrocarbons.

A more versatile use of a TGA could be developed by employing both the 9.5 and a 10.2 eV probe. Knowledge of the different contaminant sensitivities especially the aromatic ones, is still required, however use of two probes would enable a cross-correlation between their readings and should result in a more accurate determination of hydrocarbon concentrations. An even simpler use of the two probe technique would operate the 9.5 eV probe only when the 10.2 eV probe indicated a hydrocarbon concentration close to or above the hydrocarbon limits. This would simplify routine measurements, but would retain the capability of more accurate determination for those instances when it is most needed.

IV. ALTERNATIVE USES OF PHOTOIONIZATION IN DETECTION OF SUBMARINE ATMOSPHERIC HYDROCARBONS

Two possibilities exist for modifying existing submarine hydrocarbon monitors in order to incorporate a PID. One modification might reduce some of the problems currently experienced by the THA while the other would only add to the complexity of the THA.

One possible modification would be replacement of the FID with a PID. This would remove the need for the hydrogen flame and consequently remove the potential explosion hazard and the need to catalytically purify the air for use as a carrier gas. The catalytic burner on the THA, designed to remove methane, hydrocarbons, and the freon gases from the carrier gas (atmospheric air), could therefore be replaced with a simple filter of activated charcoal to scrub any PID detectable hydrocarbons from the carrier gas.

A second modification that would greatly increase the capability of the THA to identify specific compounds incorporates both a TID and PID in the gas chromatographic THA. The dual detector arrangement would provide the operator information about saturation of the hydrocarbon contaminants (5) and when coupled with the retention time might possibly allow an accurate qualitative analysis of the compounds passing the detector. However, this modification requires the addition of a PID as well as a device to split the carrier stream at the output of the THA, while not solving any of the problems currently experienced by the THA.

Either of these modifications would be quite extensive and are probably not warranted considering the development of the Central Atmosphere Monitoring System—MK II (CAMS-II) that should be operational in about five years and will be capable of monitoring hydrocarbons (8).

V. CONCLUSIONS

The PID is an innovative device that is able to detect higher molecular weight hydrocarbons simply yet accurately. The use of an ultraviolet lamp and a relatively low energy photon eliminates both

the need for a hydrogen flame (and Hydrogen) as well as often unwanted interferences from such compounds as methane and the freons. Deployment of a photoionization detector as a shipboard Trace Gas Analyzer looks very promising from theoretical considerations and laboratory evaluations of the instrument by NRL and others (2,3,4). The most important consideration must, however, be drawn from the evaluation of several sea trials. A final report containing the results of both the NRL Laboratory evaluation, shipboard evaluations, and any recommendations will be submitted upon completion of the sea trials now in progress.

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Appendix A

THE IONIZATION POTENTIALS AND SENSITIVITIES OF SOME OF THE SUBSTANCES IDENTIFIED IN SUBMARINE ATMOSPHERES

(1,2,7,9,10)*

I. Inorganic Compounds

Compound	IP (eV)	Sensitivity
ammonia	10.15	0.3
argon	15.68	0
carbon dioxide	13.79	0
carbon monoxide	14.01	0
chlorine	11.48	0
helium	24.46	0
hydrogen	15.43	0
nitrogen	15.58	0
nitrogen dioxide	9.78	0.02
nitrous oxide	12.90	0
oxygen	12.075	0
ozone	12.80	0
sulfer dioxide	12.34	0
water	12.59	0

*Ionization potential (I.P.) given in electron volts (eV) and sensitivities given to a 10.2 eV photoionization detector (PID) using benzene as a standard and assigning benzene a sensitivity of 10.0.

II: Aliphatic Hydrocarbon Compounds

Compound	IP(eV)	Sensitivity
methane	12.98	0
ethane	11.65	0
n-butane	10.63	0
n-pentane	10.57	0
i-pentane	10.35	1.5
n-hexane	10.32	2.2
n-heptane	10.18	1.7
n-octane	10.08	2.5

III: Aromatic Hydrocarbon Compounds

Compound	IP(eV)	Sensitivity
benzene	9.245	10.0
toluene	8.82	10.0
o-xylene	8.56	–
m-xylene	8.56	11.2
p-xylene	8.445	11.4
ethyl benzene	8.76	–
n-propyl benzene	8.72	–
i-propyl benzene	8.69	–
butyl benzenes	8.68	–
napthalene	8.12	–

IV: Unsaturated and Alicyclic Compounds

Compound	IP(eV)	Sensitivity
acetylene	11.41	0
ethylene	10.515	1.0
propylene	9.73	4.0
1-butene	9.13	
isoprene	8.845	

V: Chlorinated Compounds

Compound	IP(eV)	Sensitivity
carbon tetrachloride	11.47	0
chloroform	11.42	0
dichloromethane	11.35	0
methyl chloride	11.28	0

VI: Refrigerants and Aerosol Propellants

Compound	IP(eV)	Sensitivity
R-11 (CCl_3F)	11.77	0
R-12 (CCL_2F_2)	12.31	0
R-113 (CCl_2FCClF_2)	11.79	0

VII: Miscellaneous Organic Compounds

Compound	IP(eV)	Sensitivity
acetaldehyde	10.21	–
acetic acid	10.37	0.1
acetone	9.69	6.3
ethyl acetate	10.11	–
ethyl alcohol	10.48	0
formaldehyde	10.87	0
methyl alcohol	10.85	0
methyl ethyl ketone (MEK)	9.53	5.7
methyl isobutyl ketone (MIBK)	9.30	5.7
phenol	8.50	–
i-propyl alcohol	10.16	–

Appendix B

REPRESENTATIVE COMPOUNDS IN A SUBMARINES ATMOSPHERE DETECTABLE WITH A PHOTOIONIZATION TRACE GAS ANALYZER (1,2,7,9,10)

I: Compounds Detectable with a 10.2 eV Photon Source

Compound Type	Sample Compounds
Hydrocarbon-Alkane (larger than C_4)	pentane
	hexane
	heptane
Alkene (except acetylene)	ethylene
	propylene
Aromatic (all)	benzene
	toluene
	napthalene
Aldehydes and Ketones	acetaldehyde
	acetone
	methyl ethyl ketone
	methyl isobutyl ketone
Alcohols	i-propyl alcohol
	phenol
Esters	ethyl acetate
Inorganic*	ammonia
	nitrogen dioxide

*These are the only inorganic compounds known to be detectable and these have a very low sensitivity

II: Compounds Detectable with a 9.5 eV Photon Source

Compound Type	Sample Compounds
Hydrocarbon-alkene (C_4 and larger)	butene, isoprene
aromatic (all)	benzene, toluene, napthalene
Aldehydes and Ketones (C_3 and larger)	methyl ethyl ketone
	methyl isobutyl ketone
Aromatic Alcohols	phenol

Table 1 — Submarine Atmosphere Composition

Substance	Amount (Approx., Dry Basis)	Ionization Potential (eV)
N_2	78%	15.580
O_2	19-21%	12.075
CO_2	08.13%	13.79
Ar	0.9%	15.68
He	0	24.46
CO	25 ppm	14.01
CH_4	0-600 ppm	12.98
H_2	0-0.35%	15.426
Higher Organics	30 mg/m^3	$\leqslant 10.2$

Table 2 — Relative Photoionization Sensitivities for Various Gases

Chemical Grouping	Relative Sensitivity	Examples
Aromatic	10.0	Benzene, Toluene, Styrene
Aliphatic Amine	10.0	Diethyl amine
Chlorinated, Unsaturated	5-9	Vinyl Chloride
		Vinylidene Chloride
		Trichloroethylene
Carbonyl	5-7	MEK, MIBK, Acetone
Unsaturated	3-5	Acrolein,Propylene
		Cyclohexane, Allyl Alcohol
Sulfide	3-5	Hydrogen Sulfide,
		Methyl Mercaptan
Paraffin (C_5–C_7)	1-3	Pentane, Hexane
		Heptane...
Ammonia	0.3	
Paraffin (C_1–C_4)	0	Methane, Ethane...

*Sensitivities in ppm (v/v), 10.2 eV photoionization detector

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