Navy Experimental Diving Unit
321 Bullfinch Rd.
Panama City, FL 32407-7015

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MEASURING TOTAL HYDROCARBONS IN U.S NAVY DIVING AIR

Author: R. S. Lillo

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14. ABSTRACT: Any "total contaminant" measurement (such as total hydrocarbons [THC] in diving air), whether taken in the laboratory or in the field, can be significantly affected by (1) the specific sensor in the analyzer used to detect the contaminants and (2) the chemical species chosen to calibrate that sensor. Furthermore, when quantifying THC, the type of THC sensor will not only affect the magnitude of the sensor signal representing THC, but also determine what contaminants are detected (and perhaps just as importantly what contaminants are not detected), and thus determine which contaminants are included in the THC measurement. The specific question this document addresses is the following: When measuring THC in U.S. Navy diving air samples using flame ionization detector (FID)-based analyzers, is the current practice of (1) quantifying these THC measurements relative to a methane standard, thus producing a THC value in units of methane "equivalents", and (2) comparing this methane-equivalent value to a THC limit in terms of methane, an acceptable way to judge the chemical safety of an air sample? This report is based on a white paper delivered to the Naval Sea Systems Command Supervisor of Salvage and Diving (NAVSEA 00C) in 2013 that assisted in subsequent change in the diver's breathing air standards (Table 4-1) in revision 7 of the U.S. Navy Diving Manual. Recent feedback from NAVSEA 00C in 2020 has suggested the need to have the information in white papers presented in a more citable and available form. For this report, much of the content of the original white paper is left unchanged in order to keep the information that was delivered to NAVSEA 00C intact. However, some of the exposure limits reported earlier have been updated, and discussion has been added regarding implementation of NEDU's white paper recommendations into revision 7 of the Diving Manual.

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PREFACE

This report is based on a Navy Experimental Diving Unit (NEDU) white paper[1] delivered to the Naval Sea Systems Command Supervisor of Salvage and Diving (NAVSEA 00C) in 2013 that assisted in subsequent change in the diver's breathing air standards (Table 4-1) in revision 7 (and revision 7a) of the U.S. Navy Diving Manual.[2-3] Recent feedback from NAVSEA 00C in 2020 has suggested the need to have the information in white papers presented in a more citable and available form.[4] For this report, much of the content of the original white paper is left unchanged in order to keep the information that was delivered to NAVSEA 00C intact. Any significant updating of the white paper for this report would have required evaluation of new additional samples beyond those originally discussed in the white paper; such evaluation of new samples has not been done. However, some of the exposure limits reported earlier have been updated, and discussion has been added regarding implementation of NEDU's white paper recommendations into revision 7 of the Diving Manual.

BACKGROUND

Diving air samples are commonly taken in the field and sent to shored-based laboratories for analysis of a number of constituents to check on the chemical safety of the gas. These samples are often analyzed in the laboratory for total hydrocarbons (THC) using gas chromatography (GC) with a flame ionization detector (FID), as well as non-GC instruments with FID — although detection modes besides FID are sometimes used. Diving air measurements made with FID are routinely quantified relative to a methane-based calibration standard, and then compared to a THC limit also expressed in terms of methane.

The analytical procedures for diving air samples usually allow for reporting of THC, THC (excluding methane), and methane alone. Alternatively, diving air can be screened directly in the field using portable gas analyzers with FID or other sensors such as photoionization detectors (PIDs). Other approaches to testing of hydrocarbons and related contaminants are often employed in the environment industry, such as using propane or another standard besides methane for quantitation, with the testing and calibration procedures strictly regulated by the government.

THE ISSUES

Any "total contaminant" measurement (such as THC in diving air), whether taken in the laboratory or in the field, can be significantly affected by (1) the specific sensor in the analyzer used to detect the contaminants and (2) the chemical species chosen to calibrate that sensor. Furthermore, when quantifying THC, the type of THC sensor will not only affect the magnitude of the sensor signal representing THC, but also determine what contaminants are detected (and perhaps just as importantly what contaminants are not detected), and thus determine which contaminants are included in the THC measurement.

Examples of the importance of the type of sensor in THC measurements include PID-based analyzers used for screening ambient air in the field. These analyzers are commonly equipped with a 10.6 eV lamp that responds weakly, or not at all, to small, usually nontoxic gases such as methane, ethane, and propane, as well as many halocarbon species including freons. In contrast, the FID used routinely for laboratory measurement of THC responds to virtually all volatile organic compounds (VOCs), including both hydrocarbons as well as other nonhydrocarbon species such as freons. However, whatever the methodology used to measure THC, an important question is what THC limit (in terms of concentration and reference species — e.g., methane or other species) should be used to judge the chemical safety of any air sample.

The FID uses a hydrogen-air flame to ionize the VOCs in the sample gas allowing the detection of these ions (and thus the VOCs present) at the sensor electrodes. In very general terms, the FID in most GC instruments responds proportionately to the number of carbon atoms in the VOC that is being detected: One might predict butane (with its four carbon atoms) would produce four times the FID response as methane (with only one carbon atom). However, in actual practice, the FID response as predicted by carbon number is known to be affected by the presence of heteroatoms (atoms that are not carbon or hydrogen) and different functional groups. Consequently, the concept of “effective carbon number” has been developed, a concept that assigns a contribution to the observed FID response by each of the atoms (including carbon) or functional groups.

Using the effective carbon number approach to predict the FID response with GC for any VOC has been reported by one highly regarded expert to produce response predictions that are accurate only to within ~20%.[5] However, restricting the estimates of FID responses to members of a homologous series (e.g., straight chain alkanes or straight chain 1-alkenes), or to compounds with a limited number of heteroatoms, produces much better accuracy — a conclusion widely accepted among the analytical community. Nevertheless, the ability to reliably predict FID response factors can be significantly degraded by the failure to correctly set GC gas flows to the FID.

For FIDs used in non-GC instruments specifically designed for THC or total VOC measurements in the laboratory, or for FIDs used in portable analyzers for field monitoring, the different hardware configurations of the FID in some of these instruments may produce responses to VOCs that are less affected by carbon number than those responses with GC.[6-7] Thus, THC measurements of identical air samples can be very different when comparing FID measurements from GC to non-GC instruments, even if these measurements are quantified relative to the same VOC (e.g., methane or another species).

Thus, it seems important to clearly define the analytical method (including calibration standards and instrumentation) used to produce measurements of THC as THC results are so dependent on these methodological details.

THE QUESTION ADDRESSED IN THIS DOCUMENT

The specific question this document addresses is:

When measuring THC in U.S. Navy diving air samples using FID-based analyzers, is the current practice of (1) quantifying these THC measurements relative to a methane standard, thus producing a THC value in units of methane “equivalents”, and (2) comparing this methane-equivalent value to a THC limit in terms of methane, an acceptable way to judge the chemical safety of an air sample?

Notes:

1. Although this report discusses the question of quantitation of THC in diving air, for FID-based analysis this report more correctly discusses quantitation of *VOCs* and comparison of these measurements to a *VOC* limit — as the FID, as already mentioned, responds to nearly all VOCs.

2. This report provides only limited references to some of the statements made herein — as most, if not all, of the information presented on the FID and its operating characteristics is well known and generally well accepted in the analytical community. What has been less discussed in the past are the implications of using the FID for quantitation of THC in diving air samples.

3. This report tries, where possible, to limit discussion of the technical aspects of analysis although some details have been included to support the arguments made in this document. Hopefully, these details do not overly confuse the readers, some of whom may be limited in their chemical background. However, if needed, more technical information about the analytical methodology used by TRI Air Testing (Round Rock, Texas; referred subsequently in this report as “TRI”) and NEDU is available beyond what is contained in this document. Specifically, NEDU’s analysis of air samples was based on procedures given in reference 8 that NEDU previously provided upon request to NAVSEA 00C.

4. Some of the text in this document dealing with VOC profiles of diving air is taken with little, or no, change from NEDU’s previously published report dealing with the

development and evaluation of an online air quality monitor (Diveair2), an analyzer NEDU was then helping to develop to allow testing of diving air in the field by the Navy.[9]

WHAT DO DIVING AIR SAMPLES TELL US

To help address the questions about the current practice of measuring VOCs in diving air with FID, this report will review some data on the VOC profiles of diving air previously summarized in reference.[9] NEDU collaborated with TRI from 2002 to 2004 to collect these data to assist with the development of the VOC limit using the Diveair2. At that time, NEDU could not locate any detailed reports on VOC profiles of diving air, and is still unaware of any similar data on VOC profiles of diving air existing elsewhere.

During the time of NEDU's collaboration, TRI (at that time, the contract laboratory analyzing samples under the U.S. Navy Diver's Air Sampling Program) identified 36 samples collected by field personnel per the Air Sampling Program, samples that each had THC values (minus methane) greater than 10 ppm as determined from TRI's routine testing for the Navy. Using gas chromatography/mass spectroscopy (GC/MS), as well as other procedures, both TRI and NEDU subsequently analyzed these air samples to characterize the specific VOCs present. However, this report emphasizes that normally no detailed analysis of the VOCs is done in connection with the Air Sampling Program, and that the additional analysis by GC/MS was done via a special Navy contract with TRI that authorized and funded this work. Furthermore, as analysis of the samples proceeded, NEDU contacted the field personnel involved with taking some of the samples to try to determine possible reasons for the elevated THC measurements. Discussed directly below some of the results of the GC/MS testing as they pertain to the question of THC quantitation.

Table 1, at the end of this document, presents some of the results from the 36 samples analyzed. In nearly all cases (except sample #35 where some NEDU results are included), the results are taken from TRI documents and include data from their normal air analysis per the Air Sampling Program (e.g., THC, methane, CO, and CO2) as well as limited results from the GC/MS analysis. The unique information in Table 1 includes values of "total petroleum hydrocarbons" (TPH) derived from the GC/MS analysis. Strictly speaking, TPH describes a large group of several hundred hydrocarbons that originally came from crude oil; however, for this work the analysis is limited to the more volatile species that would be likely contaminants in diving air. So, for the analysis discussed in this document, TPH can be considered as a measure of VOCs in diving air determined by GC/MS.

Per TRI procedures, TRI calculated TPH by first integrating the entire GC/MS signal of the air sample (integrating the "total ion chromatogram" [TIC]), and then dividing this value by the "average response" of the GC/MS to the 54-species calibration standard used for the analysis. This "average response" is calculated by dividing the total area of the TIC of the calibration standard by the total concentration of all the 54 species — at concentrations of ~10 ppb each — in the standard (i.e., ~10 ppb species1 + ~10 ppb species2 + …. + ~10 ppb species54). In essence, the GC/MS measurement of total VOCs is being quantified by the average response of the 54 calibration species — in contrast to the THC measurement by FID that is quantified relative to a single species (methane) per the Diving Air Sampling Program.[10]

The standard chosen for this work by TRI contained a broad mixture of aliphatic and aromatic hydrocarbons, from ethene to trimethyl benzenes, (i.e., from the earliest to latest species eluding from the GC column), and detection of the full range in species in this standard should ensure detection of most, if not all, contaminants in diving air. TRI's GC/MS analysis is able to measure from butane to beyond the upper range in volatility of the calibration standard. However, to measure low molecular, highly volatile species with less than 4 carbon atoms (e.g., ethane, propane, some freons), TRI performed an additional, special GC/FID analysis which measured unsubstituted species (containing only carbon and hydrogen) with less carbons than butane. In addition, the analysis done by NEDU was also designed to lessen the chances that there would be contaminants in the air samples that might be missed in the gap between TRI's low molecular analysis and its GC/MS analysis.

Because the TPH approach used for the GC/MS analysis has important bearing on the question of THC quantitation of air samples, clarification of the TPH methodology — by presenting an analogous procedure for FID measurements of air samples — may be useful. Such an alternative way to quantify THC might be to divide the total FID response for the air sample by the average response of an alternative calibration standard containing a range of different VOCs. For this example, the following standard has been chosen: ~1 ppm each of n-butane, n-pentane, n-hexane, n-heptane, and n-octane, or ~5 ppm total. So, as with the GC/MS analysis, the total FID response to the alternative 5-species standard would be divided by the ~5 ppm total concentration of the standard to produce the average FID response for the mixture per ppm, and this average response would be used to quantitate the THC for the sample. Again, this way to quantitate THC using a mixture contrasts with the way quantitation is now being done for the Diver's Air Sampling Program, using the one species methane.

Importantly, there is one big difference between using a calibration mixture of VOCs to quantitate THC (GC/FID) in diving air compared to using such a mixture to quantitate TPH (GC/MS). In both cases, such a mixture should preferably contain a broad range of species representative of the contaminants expected to be in diving air. By using such a mixture representative of expected contaminants (and consequently with a range in molecular size and volatility), one may better estimate the average analytical response of the contaminants — thus increasing the accuracy of the THC or TPH value. However, in contrast to the large effect that molecular size has on the GC/FID response due to increasing numbers of carbon atoms, the GC/MS response is well known to exhibit much less variability in total ion response with increasing molecular weight than GC/FID — a phenomenon confirmed by the TRI data from its calibration standard with GC/MS.

Thus, using a single calibration species with GC/MS would be expected to introduce much less error into the TPH values, compared to using a single calibration species with FID to produce THC values, when quantifying a broad range of volatile contaminants such as those found in diving air.

Clearly, the THC value calculated in the alternative manner as presented using the n-butane to n-octane mixture, or in another manner using a different quantitation standard, would be much different from the THC calculated the traditional way using methane. Quantitation using methane, with only a single carbon atom producing a relatively small FID response, significantly magnifies the THC of any air sample compared to THC quantitation using most, if not all, other single or multiple species. This realization returns us to the question of whether methane is an appropriate gas standard for quantitation of THC — for FID analysis done with or without GC. However, the selection of a calibration standard for the total TPH is much less of concern due to the smaller dependence of the GC/MS response on molecular weight.

TABLE 1 RESULTS

Columns 2 to 5 of Table 1 present measurements relevant to VOCs: THC (GC/FID), methane, TPH (GC/MS), and the ratio of THC to TPH. When methane is added back to the THC values (the THC values as listed now in Table 1 exclude methane to allow a more accurate comparison to the TPH values which also do not include methane), there were 16 THC values above the THC limit of 25 ppm in Table 4-1 per revision 6 of the Diving Manual.[10] However, when methane is excluded from the THC values, only ten samples fail the 25 ppm limit; these elevated "THC minus methane" values have been marked in Table 1 in bold along with an "F" (i.e., Fail). NEDU emphasizes that although the revision 6 THC limit does not exclude methane, earlier versions of Table 4-1 excluded methane from the 25 ppm limit — this change in the definition of THC apparently occurring sometime in the early 2000's during a revision of the Diving Manual, although it's unclear from discussions with 00C why this change was made.[11]

With two exceptions, all the THC values (GC/FID, excluding methane) are greater than their corresponding TPH (GC/MS) values with the ratio of THC/TPH ranging from 1.0 to 18.6. The individual ranges for THC, methane, and TPH were 10.2 to 158 ppm in methane equivalents, 1.7 to 6.6 ppm, and 1.0 to 23.9 ppm, respectively. Other constituents in Table 1 include CO (ranging from <1 to 9 ppm, with no failures per revision 6 Table 4-1 and CO2 (ranging from <25 to 3,800 ppm, with four failures). However, as reported previously, there appears to be few multiple failures (e.g., THC and CO2) with any of the gas measurements reported by the Air Sampling Program, so little correlation is expected between any of the failure rates.[12]

Some of the discrepancy between THC and TPH values is undoubtedly due to the use of different analytical procedures. NEDU suspects that integration of the total GC/MS signal (TIC) may be imperfect (as integration commonly is) and influenced by the amount of noise in the TIC baseline due to low level VOCs. In one case (sample #34) with 4.0 ppm toluene, the TPH is 3.3 ppm whereas the sum of the detected and identified GC peaks (presumably a subset of TPH) is greater than the TPH at 4.2 ppm. Other possible errors with the GC/MS procedures include losses in VOCs that may be occurring during the trapping the contaminants on a solid adsorbent and subsequent thermal desorbing into the GC/MS, losses that are often unavoidable. Unfortunately, the more sophisticated and complex procedures required for GC/MS commonly lend themselves to these types of errors, with the potential loss of some of the contaminants. On the other hand, NEDU is less concerned about the possibility of missing some of the highly volatile species that are not measured with TRI's GC/MS as both TRI and NEDU found few, if any, of these compounds during GC/FID analysis, and then only at concentrations generally well below 1 ppm (see Note 3 at the bottom of Table 1 indicating that TRI reported values for unsubstituted species with two or three carbons were <0.2 and <0.5 ppm respectively in all samples).

Most importantly, NEDU believes how total VOCs are quantified plays a major role in the THC vs. TPH discrepancy, and that quantitation of THC with GC/FID, using a calibration standard based on the expected contaminants in diving air samples, may be a better approach than the current one based on methane. Consequently, this report will review the diving air samples presented in Table 1 with respect to VOC profiles to provide direction on how to answer the quantitation questions raised by this document.

VOC PROFILES OF DIVING AIR

VOC profiles described in this document are based on TRI results, with identification done by TRI using standard methodology of GC/MS search software and quantitation based on their 54-species standard, again each species at ~10 ppb. Species detected in samples, but not contained in the standard, were quantified relative to the closest eluting component from the standard (a fairly routine approach in laboratories). TRI results were then compared to results from NEDU analysis (where NEDU data was available as NEDU did not reanalyze all samples) with both results agreeing closely in most cases in terms of specific contaminants identified and concentration (for the few species that NEDU was able to directly quantify using gas standards that NEDU held in its laboratory at the time of analysis).

Where discrepancies between TRI and NEDU existed, NEDU deferred to TRI's results as there were a number of known limitations associated with the analysis done by NEDU after receiving the sample cylinders from TRI. These potentially error-introducing limitations with NEDU analysis included: cylinders sometimes being received from TRI with very low or no pressure requiring NEDU repressurizing prior to analysis and subsequently correcting results for dilution, all sample cylinder septums being previously punctured by TRI as required for its analysis undoubtedly hastening sample degradation, and TRI cylinders not being designed for long-term storage of low level (<1 ppm) or reactive species (e.g. aldehydes and ketones). The latter concern about the suitability of the sample cylinders for low level VOCs reflects the reality that TRI used procedures that were in place at its facilities to do the GC/MS analysis for the Navy without spending a lot of time and money to fine tune their analytical methods to meet NEDU's needs. NEDU and NAVSEA 00C accepted this approach and the resulting limitations associated with the analysis.

As expected, the VOCs detected in the 36 air samples included a broad range of aromatic and aliphatic species — at levels up to ~9 ppm for any one species — although most species were at relatively low levels (<0.1 ppm). However, despite detection of some highly volatile, low molecular weight compounds in the samples, the large majority of contaminants were heavier VOCs containing six to nine carbon atoms or more. Although these results, as well as NEDU's experience with diving air samples during the past 30 years, suggest that the VOCs that might be found in diving air probably number in the thousands, listed in the rightmost column of Table 1 are a few of the predominant species found by GC/MS based on TRI results. NEDU arbitrarily defined predominant species in each sample as the three species at the greatest concentrations, while excluding species <0.5 ppm. Consequently, some of the samples in Table 1 show no predominant species if none were at 0.5 ppm or greater. The only exception to using TRI results in Table 1 is with sample #35's listing of 1.0 ppm Freon 114 as reported by NEDU, as no GC/MS results were provided by TRI for this sample.

Contamination of the compressor intake air appears to be a likely reason for the elevated VOC levels in many of the 36 samples. Ten of these samples were taken from compressors or air banks on submarines, the air of which originates from the submarine atmosphere and thus is prone to contamination from shipboard sources (see reference 12 for a discussion of the relatively high failure rates by submarine air samples). For many samples not from submarines, it seems likely from NEDU's follow-up discussions with field personnel that VOCs were introduced by (1) the actions by the person(s) sampling the air (e.g., wiping the sampling fitting with a cleaning solution that introduced VOCs into the air sample), (2) the nearby environment (e.g., locating the compressor near exhaust sources from other engines), or (3) contaminated hardware upstream from the sample site (e.g., sampling from a compressor with an intake manifold recently repaired with glue).

The results from the 36 air samples reported here suggest that the wide range in molecular weight, and thus carbon content, of the VOCs found in these samples has a large potential to produce discrepancies between THC and TPH values (Table 1). This conclusion is based on the premise that THC is strongly influenced by the carbon content of the species, whereas the TPH derived from GC/MS is less affected by the carbon content or molecular weight. Therefore, TPH should be a better estimator of the total ppm concentration of VOCs, compared to THC, although considerable variation should be expected in the THC/TPH ratio with different samples (as seen in Table 1) as the specific VOCs, and consequently their carbon contents, vary with each sample.

A few of the VOCs commonly observed in the samples are listed in Table 2, along with their 2013 threshold limit value–time-weighted averages (TLV–TWAs) given by the American Conference of Governmental Industrial Hygienists (ACGIH).[13] These VOCs are presented as examples of contaminants, although they represent only a small number of expected species. In addition to the 2013 TLV-TWA values given in the original white paper,[1] 2018 ACGIH values have been added to Table 2 in this report to bring the TLV-TWA values up to date.[14] The TLV–TWAs are time-weighted concentrations, based on a normal 8-hour workday and 40-hour workweek, to which it is believed that nearly all workers can be repeatedly exposed, day after day, without adverse effect. For this discussion, it is assumed that the ACGIH TLV–TWAs have some relevance to divers' exposures to VOCs.

Most of Table 2 contaminants are relatively nontoxic based on their TLV-TWA values, all of which are no lower than 20 ppm for both 2013 and 2018 ACGIH documents. However, if desired, these TWA values can be corrected for other variables that might be relevant to diving air. For example, to reflect the actual partial pressure exposure of divers to the contaminant, one important correction would be for diving depth. Depth correction would be made by dividing the TWA values by the maximum depth in atmospheres absolute (ATA) for an operation. Current Navy experience indicates that use of air for diving might commonly be at depths down to 5 to 6 ATA. Besides depth, another concern about using TWA values to judge safety of diving air would be the reality that contamination of diving air would presumably involve mixtures of VOCs that introduce more complexity into the situation, an issue NEDU does not address in this document.

Only one of the 36 air samples contained a mixture of aldehydes and ketones (sample #12) with 0.7 ppm acetone, 0.5 ppm methyl ethyl ketone, and 0.2 ppm of the very toxic methyl vinyl ketone (butenone) — consistent with the VOC profiles NEDU previously reported for two actual compressor failures.[15-16] Although sample #12 passed all revision 6 Table 4-1 limits, results from analysis of the earlier two compressor incidences by the Naval Medical Research Institute suggested that air samples from both of these compressors would have failed THC, odor, and in one case CO2 and CO — although neither sample was analyzed by the Air Sampling Program. Thus, based on the occurrence of presumably only one compressor failure among the 36 samples examined, VOC contamination seemed to be overwhelmingly an intake air problem rather than a compressor operating problem.

In addition to the GC/MS analysis, NEDU previously completed a brief review of the composition of fuels and petroleum products that might be present at a salvage site — for example, after a plane or ship accident. The petroleum products, which would have the potential to contaminate diving air charged on site during such operations, include the following (all of which are complex aliphatic/aromatic mixtures): (1) gasoline, C_4-C_{12} (chemicals containing 4 to 12 carbon atoms); (2) jet fuel JP-5 and JP-8, C_8-C_{18}; (3) diesel, C_9-C_{20}; (4) bunker oil, C_{12}-C_{36}; and (5) lube oil, C_{16} and beyond. By one definition, VOCs are those with vapor pressure of 10^{-1} torr (10^{-4} atm) at 760 torr and 25 ºC (method TO-15, Environmental Protection Agency).[17] By this definition, the cutoff for volatile species from these petroleum products is ~C_{12} for aliphatics and aromatics. However, the actual composition and concentration of VOCs in the air at a dive site would be influenced by other factors such as (1) the partition coefficients for the VOCs in water and (2) the ambient temperature, humidity, and wind that would influence the transport and dispersion of the fuels.

CONCLUSIONS

1. The range of aliphatic and aromatic hydrocarbons represented by the VOC profiles of the 36 air samples reported in this document, as well as by the petroleum products listed in the preceding paragraph, suggests that broadly screening for VOCs is a clear need. VOC measurement using FID provides that screening, although presenting results in terms of THC introduces concerns about quantitation and how THC limits should be defined.

2. Because of the influence of carbon content on the FID response in GC and many non-GC instruments, contaminants have an increasing effect on THC measurement as their molecular weight goes up. This overweighting effect by heavier species on THC distorts the estimation of the actual concentration of VOCs. The effect of this distortion is to reduce the ability (1) to estimate potential exposure risk to contaminants and (2) to compare Navy THC limits and measurements to those limits and measurements based on alternative procedures.

3. One of the potentially most hazardous exposures to diving air would involve a true compressor failure, which experience has shown can produce highly toxic species, including at least one contaminant (methyl vinyl ketone) that at sub-ppm levels exceeds industrial workplace guidelines for even short-term exposures. Fortunately, many of the possible contaminants in diving air have relatively low toxicities, as judged by their exposure limits set for the industrial workplace, or are present in very low amounts. Therefore, the primary focus of the THC limit should be directed toward avoiding exposure to the more toxic species, whether from contamination of the intake air or from the rare compressor failure.

4. Since the THC value provides a single measurement of VOCs without identifying specific contaminants, it is virtually impossible to distinguish normal low-level THC readings from similar readings that might occur when trace levels of highly toxic VOCs are present. Consequently, NEDU emphasizes that is impossible to guard against all cases of air contamination that may be of concern no matter how much effort is devoted toward contaminant screening. However, NEDU's experience suggests that high levels of a range of VOCs may be produced during a compressor failure, as well as when there is contamination of the intake air to a compressor. Both conditions are often accompanied by a higher than normal THC value.

5. Lastly, the apparent overwhelming contribution to high THC values by compressor intake air and the rare compressor failure provides additional support for real-time

monitoring of diving air in the field — as the reporting of air quality results per the current Air Sampling Program that occurs often days after initial sampling does not address these contamination issues.

RECOMMENDATIONS

Based on the conclusions in the preceding section, NEDU makes the following recommendations for measuring THC in U.S. Navy diving air samples per any future revision of the Diving Manual beyond revision 6.

1. First, clearly define the methodology for measuring THC in the following, or equivalent, terms: Analysis in the laboratory should be done using an FID detector with or without GC, but with both types of analysis using the same calibration species for defining THC measurements and the THC limit. The calibration standard and THC limit is defined below in recommendation #3.

Rationale:

a. The rationale and justification for various THC limits used throughout the diving community (including the various militaries throughout the world) are unclear, and the THC limits are rarely, if ever, linked to an analytical method. As should be evident from the discussion in this document, any THC limit not tied to a well-defined analytical method is meaningless due to the strong dependence of THC measurements on the procedures used to produce those measurements.

b. Because FID analysis is well-suited for THC measurement and has been traditionally widely used for diving air samples, NEDU sees no reason to change from FID, and does not encourage at this time approval of other detection modes for laboratory analysis of THC, due to the expected complexity associated with ensuring that measurements derived from different procedures are similar.

c. Although this document does not specifically address screening of diving air in the field, for THC measurement in the field, in the future the Navy may consider alternatives to FID measurement such as PID (e.g., with the Diveair2 or other portable monitor) or other detection modes. However, non-FID detection analysis may require THC limits that differ from the FID-based THC limits discussed here and should be clearly defined in terms of methodology.

d. Requiring the same calibration standard for GC and non-GC FID analysis may help to ensure their THC measurements are closer in agreement — as will be explained below in recommendation #3.

2. Exclude methane from the THC measurement AND therefore from the THC limit.

Rationale:

a. Again, the reason why non-hazardous methane was added back into the THC limit by 00C in the early 2000s is unclear, and methane should now be removed to produce a THC limit more reflective of contaminants of concern.

b. Reexamination of the three data sets from the Air Sampling Program previously discussed by NEDU in the fall 2011 indicates that 1 to 3% (depending on the data set) of the total samples had methane values from 3 to 5 ppm — while emphasizing that normal methane in "clean air" is ~2 ppm.[12] Higher levels of methane were rare (i.e., from 0.1 to 0.2% of the total samples, again depending on data set) with one value of 28 ppm methane, four values from 6 to 8 ppm methane, and six values from 6 to 21 ppm methane, found in the three data sets.

c. So, exclusion of methane from THC should not be expected to have a large effect on THC measurements, However, methane should still be removed from THC measurements and the THC limit in keeping with NEDU's previously stated conclusion (#3) that "the primary focus of the THC limit should be directed toward avoiding exposure to the more toxic species, whether from contamination of the intake air or from the rare compressor failure."

3. Change the current THC limit from the current 25 ppm THC in methane equivalents to an interim limit of 5 ppm in n-hexane equivalents.

Rationale:

a. NEDU's results from detailed analysis of the 36 air samples indicated that the VOCs included a broad range of aromatic and aliphatic species. Although there were some highly volatile, low molecular weight compounds in the samples, the large majority of contaminants were heavier VOCs containing six to nine carbon atoms or more.

b. Expressing THC measurements (and therefore also the THC limit) in terms of a species such as n-hexane or n-octane (with 6 and 8 carbons respectively) should (1) produce THC readings using FID more accurately representing actual concentrations of VOCs in diving air and (2) reduce the increasing effect (in terms of the ppm contribution by an individual contaminant) on THC measurements by VOCs as their molecular weight increases. However, at this time NEDU would discourage basing any THC limit or measurement on a substituted hydrocarbon or an aromatic species to avoid introducing any more complexity to the solution. NEDU arbitrarily chose n-hexane, but n-heptane or n-octane may also be options.

c. Based on the relative GC/FID response to methane compared to n-hexane (i.e., approximately 1 to 6), a n-hexane-based THC limit might be estimated at ~4 ppm (i.e., 25 ppm/6; ignoring the confounding issue of methane being included presently in the Tables 4-1 and 4-2 THC limit of revision 6 of the Diving Manual). NEDU arbitrarily selected 5 ppm n-hexane to "round up the limit" to the nearest 5 ppm to emphasize that defining this new n-hexane-based limit is not an exact science due to all the uncertainties about contaminants and their FID response factors. Thus, this approach converts the current 25 ppm limit (after exclusion of methane per the preceding recommendation #2) to an equivalent limit based on n-hexane. However, this approach makes no assumptions about the correctness of the current Navy THC limit, a limit that has resulted in less than a 0.5% failure rate for THC values by over 6000 Navy air samples from May 2004 to August 2011.[12]

d. The observed variation in the THC/TPH ratios for the 36 air samples reported in this document is expected, as discussed earlier. Therefore, this variation in THC/TPH should not raise concern over the recommendation to change to a n-hexane-based limit. The important point is that the THC/TPH ratio suggests that THC values are commonly higher, and sometimes much higher, than would be expected based on GC/MS results, results that should be much more reflective of the actual VOC concentrations than THC values are.

e. To put NEDU's proposed n-hexane-based THC limit in context, screening air bank gas on submarines prior to diving use using NEDU-produced procedures has proved practical for more than ten years when using a 5 ppm limit for both PID and FID measurements with the portable Toxic Vapor Analyzer (TVA-1000).[18] The TVA methane-free FID measurement, quantified with isobutylene, would be equivalent to ~8 ppm when expressed in terms of n-hexane based on response factors in the TVA-1000 manual**[7]** — remembering that responses to VOCs in non-GC analyzers such as the portable TVA are often much less effected by carbon number than the typical GC/FID used by TRI for the Navy Air Sampling Program.

f. Another calibration option would be is to base the THC limit on a mixture of species with a range in the number carbon atoms more closely related to expected air contaminants. For example, similar to the 54-species calibration standard used by TRI, the Navy might select a 3-species standard such as ~2 ppm each of n-hexane, n-octane, and n-decane, or ~6 ppm total — with the calibration response calculated as discussed earlier with regard to TRI's analysis. However, use of a mixture probably adds no benefit over choosing one species with a response more representative of the diving air contaminants than that of methane, and commercial preparation of 3-species gas standards for use in the laboratory would introduce added complexity, analytical error, and cost into the process.

g. Some non-GC FID analyzers may be less affected, when compared to GC analyzers, by a change from using methane to a higher molecular weight species such as n-hexane, due to the smaller effect by carbon content on their readings. However, the change to n-hexane should be expected to produce better agreement between GC and non-GC THC measurements due to the reduced effect (in terms of ppm) of carbon content on the GC THC measurements.

4. NEDU recommends that any change to the proposed n-hexane-based limit, or any other THC limit, be done on an interim basis — with the stipulation that this limit is subject to change depending on experience with actual air testing results.

IMPLEMENTION OF 2013 WHITE PAPER RECOMMENDATIONS

Revision 7 (and revision 7a) of the U.S. Navy Diving Manual combined revision 6 Tables 4-1 (“U.S. Military Diver’s Compressed Air Breathing Purity Requirements for AMU Approved or Certified Sources”) and 4-2 (“Diver’s Compressed Air Breathing Requirements if from Commercial Source”) into one new Table 4-1 (“U.S. Navy Diving Breathing Air Requirements”).[2-3] Again, revision 6 specification for THC was 25 ppm in methane equivalents (including methane) in both Table 4-1 and Table 4-2.[10] Revision 7 (and revision 7a) Table 4-1 allowed for any one of the three following three specifications for total VOCs (replacing THC):

1. 25 ppm in methane equivalents when measured by a laboratory-based FID calibrated with methane and methane excluded.

2. 5 ppm in n-hexane equivalents when measured by a laboratory-based FID calibrated with n-hexane and methane excluded.

3. 10 ppm when measured by a portable PID containing a 10.6 eV lamp and calibrated with isobutylene (includes Analox ACG+ analyzer).

Revision 7 VOC specification #2 (i.e., VOCs in n-hexane equivalents) implements NEDU’s recommendation #3. Importantly, revision 7 specification #1 (i.e., VOCs in methane equivalents) allows for the revision 6 VOC specification (although excluding methane) to avoid — at least for the immediate future — disruption to commercial laboratories that had been analyzing air samples for THC in terms of methane equivalents.

Revision 7 VOC specification #3 implements an earlier NEDU recommendation regarding an interim VOC limit of 10 ppm for the previously evaluated portable air monitor (PAM) Diveair2 with a 10.6 eV PID, when calibrated with isobutylene.[9] A newer PAM now on the ANU list (Analox ACG+, also with a 10.6 eV lamp) would now also be governed by this specification.[19]

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Table 1. Results from analysis of air samples with elevated THC values (all gas values are in ppm).

Sample # - Date TRI Analyzed	**THC (GC/FID)**	**Methane**	**TPH (GC/MS)**	**THC/TPH**	**CO**	**CO2**	**Sample Info**	**Predominant Species**
Range	**10.2 – 158**	**1.7 – 6.6**	**1.0 – 23.9**	**1.0 – 18.6**	**<1 – 9**	**<25 – 3,800**		
1 - 4/23/02	12.9	2.4	1.0	12.9	<1	535	sub air bank	
2 – 4/23/02	14.2	2.5	1.4	10.1	<1	532	sub air bank	
3 – 4/25/02	**35.3F**	2.6	1.9	18.6	<1	<25	sub HPAC	1.1 Freon 114
4 – 4/25/02	24.9	3.3	1.6	15.6	<1	<25	sub HPAC	1.2 Freon 114
5 – 4/25/02	20.8	2.3	2.0	10.4	<1	375	LPAC	0.9 toluene
6 – 5/1/02	15.3	2.8	2.0	7.7	<1	<25	sub HPAC	
7 – 5/1/02	**31.3F**	2.7	2.0	15.7	<1	<25	sub HPAC	1.2 Freon 114
8 – 5/23/02	11.3	2.8	2.3	4.9	<1	**1,272F**	HPAC	
9 – 5/23/02	14.2	2.7	3.4	4.2	2	**1,252F**	HPAC	
10 – 5/23/02	11.9	3.2	1.9	6.3	<1	**1,571F**	sub air bank	
11 – 6/13/02	17.9	2.0	3.6	5.0	<1	364	LPAC	1.9 toluene
12 – 6/20/02	15.7	2.2	3.5	4.5	9	407	HPAC	0.7 acetone, 0.5 methyl ethyl ketone

Notes:
1. THC (GC/FID): excluding methane, but quantitated in methane equivalents.
2. Predominant species: 3 species with highest concentrations but each >0.5 ppm.
3. C2/C3: <0.2 / <0.5 for all samples per TRI GC analysis.
4. **BOLD+F** = failed Table 4-1 limit per revision 6 of the Diving Manual.

Table 1 (cont.). Results from analysis of air samples with elevated THC values (all gas values are in ppm).

Sample # - Date TRI Analyzed	THC (GC/FID)	Methane	TPH (GC/MS)	THC/TPH	CO	CO2	Sample Info	Predominant Species
13 – 10/31/02	13.6	2.0	3.7	3.7	<1	406	LPAC	1.4 toluene
14 – 11/22/02	11.0	2.1	2.8	3.9	<1	379	LPAC	2.3 toluene
15 – 12/12/02	12.1	2.1	2.8	4.3	<1	374	LPAC	1.4 toluene
16 – 12/20/02	**158F**	2.0	11.2	14.1	<1	364	HPAC	9.4 butyl cellosolve
17 – 1/26/03	12	3	4.3	2.8	<1	690	sub HPAC	0.5 trimethyl benzenes
18 – 1/26/03	11	3	5.9	1.9	<1	752	sub HPAC	0.9 trimethyl benzenes
19 – 1/26/03	**75F**	3	6.0	12.5	<1	<25	HPAC	2.4 toluene, 0.7 methyl octane, 0.6 n-octane
20 – 5/8/03	**89.3F**	1.7	13.8	6.5	<1	389	HPAC	1.9 D-limonene, 0.8 n-undecane
21 – 5/8/03	**95.3F**	1.7	19.3	4.9	3	413	HPAC	2.6 D-limonene, 1.0 cellosolve, 1.0 n-undecane,
22 – 5/17/03	15.1	1.9	4.9	3.1	<1	382	HPAC	3.6 toluene
23 – 5/17/03	**32.2F**	2.8	7.2	4.5	<1	373	LPAC	0.7 n-pentane
24 – 5/17/03	**38.3F**	2.7	17.0	2.3	<1	370	LPAC	2.3 n-pentane, 1.7 methyl hexane, 0.6 methyl heptane

Notes:

1. THC (GC/FID): excluding methane, but quantitated in methane equivalents.
2. Predominant species: 3 species with highest concentrations but each >0.5 ppm.
3. C2/C3: <0.2 / <0.5 for all samples per TRI GC analysis.
4. **BOLD+F** = failed Table 4-1 limit per revision 6 of the Diving Manual.

Table 1 (cont.). Results from analysis of air samples with elevated THC values (all gas values are in ppm).

Sample # - Date TRI Analyzed	THC (GC/FID)	Methane	TPH (GC/MS)	THC/TPH	CO	CO2	Sample Info	Predominant Species
25 – 5/28/03	22.8	2.9	10.0	2.3	3	440	LPAC	
26 – 5/28/03	24.9	2.8	12.7	2.0	2	446	LPAC	0.7 methylene chloride, 0.5 dimethyl heptane
27 – 7/7/03	**30.3F**	6.6	6.2	4.9	2	**3,800F**	sub air bank	0.7 Freon 114
28 – 7/8/03	23.6	5.1	23.9	1.0	<1	379	HPAC	1.3 D-limonene, 0.9 n-undecane
29 – 8/19/03	23.0	2.1	10.3	2.2	M	380	LPAC	6.0 toluene
30 – 10/19/03	13.6	2.1	8.9	1.5	<1	367	LPAC	
31 – 11/22/03	21.3	3.8	21.6	1.0	2	387	HPAC	1.7 D-limonene, 1.5 n-undecane, 0.5 n-dodecane
32 – 11/29/03	10.2	2.4	4.2	2.4	<1	481	HPAC	0.9 n-hexane
33 – 12/20/03	**28.7F**	2.2	21.6	1.3	<1	373	LPAC	2.1 toluene, 1.3 methyl pentane 1.3 xylenes
34 – 12/30/03	21.5	2.0	3.3(4.2)	6.5	<1	374	HPAC	4.0 toluene
35 – 1/28/04	~17	M	M	M	M	M	LPAC	1.0 Freon 114 (NEDU)
36 – 2/3/04	~12	M	M	M	M	M	LPAC	M

Notes:

1. THC (GC/FID): excluding methane, but quantitated in methane equivalents.
2. Predominant species: 3 species with highest concentrations but each >0.5 ppm.
3. C2/C3: <0.2 / <0.5 for all samples per TRI GC analysis.
4. **BOLD+F** = failed Table 4-1 limit per revision 6 of the Diving Manual
5. For sample #34: TPH = 3.3 ppm; sum of detected and identified peaks = 4.2 ppm.
6. M= missing data.

Table 2. TLV-TWA values for a few selected VOCs commonly observed in the 36 samples analyzed in detail by TRI and NEDU.

Species	**TLV-TWA (ppm, ACGIH 2013)**	**TLV-TWA (ppm, ACGIH 2018)**
Ethyl methyl benzene (Cumene)	50	50
Freon 114	1000	1000
Methyl decane	NA	NA
Methyl ethyl ketone (MEK)	200	200
Methyl isobutyl ketone (MIBK)	50	**20**
Methylene chloride (dichloromethane)	20	**50**
n-Butanol	20	20
n-Hexane	50	50
n-Nonane	200	200
n-Octane	300	300
n-Pentane	600	**1000**
Toluene	20	20
Trimethyl benzenes	25	25
Xylenes	100	100

Notes:
1. TLV-TWA values (2013) taken from reference 13.
2. TLV-TWA values (2018) taken from reference 14.
3. NA = not available.
4. 2018 **BOLD** values changed from 2013 values.