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TRACE CHEMICAL CONTAMINANTS IN A NEW HUMAN PRESSURE CHAMBER

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The Naval Medical Research Institute received a large human pressure chamber complex in 1977 and began human exposures in 1981. An early incident of organic chemical contamination led to an evolution of contaminant analysis, control, and removal. On the suspicion that poor interior paint was the major problem, the chambers were waterblasted and repainted. Many initial attempts to understand the problem were frustrated by incomplete documentation and conflicting analyses. A persistent level of benzene, toluene, xylenes, and refrigerant-113 led to decontamination by flushing and evacuation. A series of saturation dives were finally performed in 1985 with a certifiably clean chamber. One contamination incident during these dives was quickly recognized and remedied. [illegible]

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BACKGROUND

Closed ecological systems present unique problems in human toxicology. The major problematic systems are nuclear submarines, manned spacecraft, and saturation diving systems. In each case, men are restricted to an environment that does not exchange with "fresh air" for periods of days to weeks. Large development programs have been beneficial to submarines and spacecraft, but few findings have been translated to the diving environment. The Naval Research Laboratory (NRL) has pursued submarine contamination studies since 1958 (Saalfeld & Saunders, 1979) and NASA has maintained an interest since manned spacecraft projects in the 1960's (Conkle et al., 1970). The diving community has been much less involved, with essentially only one document now addressing the issue (NAVMAT, 1976). The contamination problem in diving systems is compounded by exposure to higher total pressures, which amplifies the hazard of contaminants in compressed breathing gas. Because the higher pressures are provided by compressed helium or nitrogen which dilutes the toxic gas, greater analytical sensitivity is required to detect the same toxic partial pressure of the contaminant. Sensitive chemical analyses of closed environments can detect several hundred individual organic compounds (Saalfeld and Saunders, 1979), but even an excellent laboratory would require months to evaluate such a complex chemical profile.

Even though the need to monitor contaminants in a pressure chamber has been acknowledged for years, several incidents have occurred. Because of the overall lack of suitable instrumentation, all incidents that have been reported were first recognized by the divers reporting symptoms.

The first occurred at the Experimental Diving Unit in 1974. A new whip (flexible high pressure hose), certified by the manufacturer as "oxygen-clean," was actually filled with several ounces of liquid trichloroethylene,

$C_2H_3Cl_3$, a cleaning solvent. The whip was placed into service connecting breathing masks in the chamber to an experimental gas bank while the inhabitants were at 1000 fsw (feet of sea water) or about 31 atmospheres of pressure. The problem was first identified by unsteadiness in the divers breathing from the masks, followed by a diver's report of an unusual odor, "like perfume." It was quickly determined that all emergency breathing gas banks, as well as the "make-up" tube truck and banks of 100% helium, had been contaminated. Thus, it was not possible to place the divers on emergency breathing gas or to maintain the depth of the chamber allowed to decompress by passive leakage for three days while a new source of clean helium was obtained. The entire chamber atmosphere was then replaced and normal decompression resumed. At all times during the casualty, management was complicated by conflicting reports from several laboratories on the nature of the contaminant(s) present and the levels to which the divers had been exposed (Flynn, E.T. unreported observations).

The second reported incident occurred on an Experimental Diving Unit operation at the facilities of Taylor Diving and Salvage Co. (Thalmann, 1973). Again, a cleaning solvent, Refrigerant-113, was accidentally spilled into the chamber. The chamber was at about 400 fsw and a worst case calculation showed a possible concentration over 1200 ppm. The operation was delayed for decontamination although final analysis gave about 30 ppm of the solvent. Luckily, neither incident resulted in known mortality or morbidity, but standard procedures could not prevent a reoccurrence (see incident reported below). At least two other chamber contamination incidents have apparently occurred, one at a Navy facility in California, the other in Norway. Neither case has been reported in detail.

Early History of the NMRI Chamber

During 1977 two separate chambers with total volume of 2300 cu ft were delivered: a two-chamber complex rated at 1500 psig (3365 fsw) were designated chambers A and I, and a three-chamber complex rated at 1000 psig (2245 fsw). Over the next 3 years, both sets were installed, connected to piping systems (of mild carbon steel), and tested against certification standards. Gas samples analyzed during this period showed compliance with the then existing standard (< 25 ppm total hydrocarbon) but testing details are unavailable. Other file evidence shows a controversy about detection methodology, i.e. detector tubes vs. gas chromatograph. No comprehensive test plan is evident in the records.

In August 1981 a saturation dive was aborted when diver-subjects reported paint blisters bursting on the inside of the chamber and releasing fumes. One diver (a medical officer with a biochemistry Ph.D.) suspected that the fumes were probably ketone. No systematic analysis of that atmosphere was performed, and diver health was presumed not threatened because the depth was shallow enough to permit immediate surfacing. Later, the suspect paint was water blasted and touched-up. Faulty initial painting of the chamber appeared to be the problem. Samples of paint flakes were much thicker than called for in original chamber specifications.

Many chamber refurbishments and sub-saturation air (short exposure) dives were performed over the next several years. About 6 spot samples of chamber atmosphere were analyzed during that time by commercial laboratories using both gas chromatography and mass spectrometry. Records of equilibration time, sample location, chamber pressure at time of sampling, etc., were incomplete. At one time or another benzene, toluene, xylenes, methylethyl ketone, methylisobutyl ketone, dimethyl formamide, isopropyl alcohol, hexane, acetone, and refrigerant R-113 ($C_2 Cl_3 F_3$) were reported in disturbingly high concentrations. Several other unidentified ketones, alcohols, aromatics and aliphatics were reported in levels > 0.1 ppm. No consistent pattern was discernible either in the identification or quantity of chemicals but concentrations of 0.5 to 50 ppm were suspected. Duplicate samples sent to different laboratories produced conflicting results. Similar disagreement had been reported by NASA (Conkle, et al., 1970).

Suspected sources for the contaminants were too numerous to isolate the problem(s). One sample with a very high isopropyl alcohol level was later determined to have been drawn through a pressure gauge line that "had a liquid discharge when first opened". (This alcohol is commonly used in pressure gage connections when the gage is cleaned and calibrated, but the calibration procedures also specify solvent removal). A variable but high R-113 level was reported; the highest from a large scuba bottle used occasionally for sampling. The bottle had been cleaned using a R-113 procedure at a time when an instrument to monitor those vapors was not available. Benzene, xylenes, and toluene were commonly found, but not in constant amounts. The chamber paint contained toluene and o-xylene as solvents, as did several adhesives used for many applications in the chamber and in a maintenance shop 20 feet away. The shop was also used in off-hours for personnel to work on automobile parts, including soaking parts in auto fuel (unleaded gasoline contains many aromatics). Many standard chamber items at that time (breathing masks, hoses, noise protector earmuffs, etc.) were constructed of rubber and plastic materials. Once these materials had been exposed to solvent vapors, they would serve as long term sources of contaminants by the well known but difficult to predict process of polymer sorption (Williams, 1970; Vind and Mathews, 1970).

Analytical Methods

To solve the contamination problem, it was necessary to first establish the actual nature and amount of chemicals in the chambers. Toxicology standards (Wands, 1968) provide upper limits to allowable compounds in the parts per million (ppm) range. Most instruments associated with diving operations do not have nearly that high a sensitivity. Furthermore, the toxicology standards are interpreted as a partial pressure at 1 ATA (atmospheres absolute) total pressure. To detect a contaminant with a room pressure instrument drawn from a 1000 fsw dive (31 ATA), the instrument reading needs a 31-fold correction to obtain the actual partial pressure.

One simple instrument available is the photoionization detector (PID) (Spain et al., 1980) (Model PI 101, HNU Corp.). This device, soon to be issued to the submarine fleet, has parts per million sensitivity to many compounds. A lamp with well defined photon energy ionizes any molecules with a sufficiently low ionization potential (typically 10.2eV) and the ion current is amplified as output. Since the major background gases (O_2, N_2, He) and many contaminants that can reach high levels (CO_2, CH_4, low alcohols) do not ionize that easily, the device has low background; however, it has high sensitivity for double bond and aromatic ring structures. The device is simple to operate and regular use by enlisted men is possible. Its single channel output, however, makes interpretation impossible when multiple contaminants are present.

Complex mixtures are more easily analyzed if the components can be separated, thus gas chromatography (GC) is a common technique. For a modestly complicated mixture (e.g. a dozen compounds) whose identities are known, GC can be a sensitive (approximately 0.1 ppm) and precise (relative error < 10%) technique. Its drawbacks include the inability to identify unknown components, except by trial and error matching of elution times, and the need for trained experienced operators.

Another available instrument is the mass spectrometer (MS). This device ionizes and fragments gas molecules and senses the molecular weight of the fragments. Qualitative identification of the parent molecule is rather easily achieved by a skilled operator. The difficulty increases greatly as the number of compounds present increases although computerized "library" search and match programs aids in the process. The instruments are difficult to maintain and to use in a quantitative mode.

The best choice for messy samples is a hybrid gas chromatograph-mass spectrometer (GC-MS). Even complex mixtures can be separated by the GC into sub-samples which the MS can identify. Not surprisingly, such an instrument is expensive and difficult to operate and maintain. When the number of components gets very large (100 or more) the prospects for total identification diminish. For example, in samples of submarine atmospheres, several hundred compounds can be found, most of which have not been identified (Saalfeld and Saunders, 1979).

An additional processing step can be used when the expected concentrations are quite low. Absorption of organic molecules on activated charcoal or Tenax (Tenax is polymeric 2, 6-diphenyl-p-phenylene oxide, sold by Applied Science, State College, PA) can serve to concentrate the contaminants when they are subsequently flash desorbed onto the GC (Rippstein and Coleman, 1983). Some quantitative precision is lost by the additional processing steps, but sensitivity to "well behaved" compounds can increase by a factor of 100 or more.

Part of the overall analysis problem concerns the details of gas handling. Instruments do not operate in the pressure chambers, so gas samples must be brought to the instrument. Gas movement through tubing, valves and regulators, and storage in metal or plastic containers, can both add and remove contaminants if extreme care is not exercised. Evaluation of the entire sampling and analysis process is a laborious but quite necessary step.

At the time the chamber problems came to light, none of the instruments and procedures discussed above were available in-house. Advice and instruments had to be sought elsewhere. The final equipment and procedures development for a local contamination monitoring program will be presented in another report.

Baseline Studies

Early in 1984 a systematic procedure was instituted to establish the contamination status of the chambers. All possible non-metal components were removed and a complete inventory of remaining items was taken. Component chambers were flushed with high purity helium and held at a modest pressure (35 to 100 fsw) for 7 days. The 3 chambers (designated "A", "D", and "R") under study were kept isolated by pressure differences across inter-chamber doors and the contents mixed periodically by blowers in the 3 life-support loops. Normal purification beds of a caustic scrubber Sodasorb (High Performance Sodasorb, Dewey and Almy Chemical Division, W.R. Grace Co., Lexington, MA), a mixed alkali metal hydroxide for CO_2 removal, and Purafil (Purafil II, Purafil Inc., Atlanta, GA), a permanganate chemisorbant for "odor removal" were deliberately omitted during this test.

Samples were taken into aluminum cylinders similar to those successfully used for long term storage by the National Bureau of Standards for Standard Reference Materials (SRM) reference gases. These cylinders were said to be valved and cleaned by the same procedures used for SRM cylinders. However, these sample cylinders were smaller than SRM cylinder and were later found to be internally coated by an unidentified semi-solid black layer produced by a different preparation treatment by the manufacturer. In practice, the small cylinders were found to exhibit a "memory" for previous gases in the cylinder, presumably by adsorption to the interior surfaces. For their initial use however, they were cleaned by heating under vacuum and thus false positive information was not a problem. The cylinders were subsequently returned to the supplier and replaced with stainless steel cylinders.

Analyses were run on a GC-MS system at NRL with a Tenax absorbent in a semi-quantitative mode. The analysis was not set to maximally recover all gases present so results were precise to within about a factor of 3. Also, for the first time at this command, quality control of the analysis was attempted. Duplicate cylinders of each sample and several commercially purchased calibration gas samples were also submitted; all with only a numerical identification. Table 1 summarizes the results from the chamber samples. Benzene, toluene and xylenes were the only gases found despite running a long GC exposure. Duplicates agreed within about a factor of 4. Only one chamber seemed to have a benzene contamination. An attempt to check outgassing kinetics by comparing early samples with those taken after 3 and 7 days of incubation were frustrated by low precision.

Though this test was only partially successful at characterizing the baseline status of the chambers, some information was gained. The level of total aromatic hydrocarbons in D chamber appeared to exceed the 90-day limit recommended for submarine atmospheres (NAVMAT 1976) and desired for long saturation dives.

Decontamination

Rather than commit the time and resources to verify and further quantify contamination, a series of steps was initiated to lower the amount of hydrocarbons in the entire system.

The most heavily contaminated was chamber, D, the largest chamber by virtue of the associated 550 feet^3 wetpot. Chamber D had the greatest problem in paint adhesion and several areas had been covered with numerous touch-up coats. The bolted joint connecting the main chamber and the wetpot had a

TABLE 1

1984 Chamber Baseline Analysis
(all in ppm v/v after depth correction)

Sample location and chamber depth	Benzene	Toluene	Xylene(s)
Chamber A			
day 0, 75 fsw	-	-	-
	-	-	-
day 7, 40 fsw	2.6	10.4	4.2
	< 2	2.7	3.6
Chamber D			
day 0, 102 fsw	-	-	-
	-	< 2	< 2
day 3, 85 fsw	-	9.1	5.4
	-	4.7	3.8
day 7, 56 fsw	-	11.0	6.1
	-	3.9	< 2
Chamber R			
day 0, 75 fsw	-	-	-
	-	2.1	-
day 3, 58 fsw	-	-	-
	-	< 2	< 2
day 7, 36 fsw	-	< 2	< 2
	-	< 2	< 2

- = no measurable reading

Notes: 1. No gas added during exposure period.
2. Depth change during exposure due to gas loss from closed chambers.

recess that had been repeatedly spray painted to an unknown depth. These poorly characterized paint layers were suspected as a persistent source of solvent vapor.

The applications of heat and vacuum were considered for chamber decontamination. Since the chamber had many fittings designed to seat properly when internal pressure exceeded ambient, initial evacuation was frustrated by a sequence of leaks that were individually found and then remedied. A 760 l/min rotary vane pump (Leybold-Heraeus model D30A) was eventually required to achieve an evacuation to about 0.01 ATA. A vapor trap of 1 liter of alumina was placed in-line to prevent oil back streaming. Evacuation continued for about one week. Heat application was not very extensive due to limited available equipment and concern over exceeding thermal limits specified in the system certification procedure. Initial gas heating and pipe heating in the recirculation loops were all that could be consistently used. Maintenance of several hundred gallons of hot water in the wet pot served at one point to demonstrate the low boiling point of H_2O at reduced pressures.

Components, especially rubber face masks and hoses, were also highly suspect as solvent sources. They would have absorbed and slowly released all organic vapors over the course of an unknown history. To attempt removal of some of their contaminants, the components were placed in a small chamber which had been cleaned and found nearly free of organic vapor. Over the course of at least 4 days the chamber was evacuated to less than .001 ATA, backfilled with pure N_2 at about 40 psi for a day, and evacuated again. Analysis was performed on samples after a final 48 h cycle of pure gas exposure.

Gas Purity on Saturation Dives

Three saturation dives of 7-21 days duration were scheduled for summer of 1984. Before the first dives began, a final check of total system purity was performed. For this test the two chambers designated were equipped with all the operational and experimental apparatus that would be present during the dive. The chambers were then flushed with bulk helium and held at approximately 3-4 ATA for five days. The chambers were again mixed using the life support unit pumps without any absorbents in-line. After the exposure, original and post-exposure gases were analyzed by a GC with a flame ionization detector (FID). Unmarked calibration gas samples of about 10 ppm each of benzene, toluene, and xylene were included in the samples sent to NRL for analysis. The calibration gases were accurately identified. The chamber and flush gas samples were found to be free of those compounds at a sensitivity of about 0.5 ppm. However, R-113 reappeared in the chamber samples at < 1 ppm. The freon was again attributed to components recently cleaned with that solvent. The chambers were deemed safe for occupancy from a contamination standpoint.

Special attention was paid to components used in chamber experiments. For example, cardio-respiratory experiments called for gas bags, tubing, mouthpieces, etc. that totalled several pounds of rubber, most of it assembled by adhesives. To prevent secondary contamination of the chamber, none of this equipment was permitted on the dive unless it completed a several day off-gassing test. Most components appeared satisfactory in that test, but some electrical connections recently potted for watertight integrity were not allowed in the chamber because of substantial emission of a mixed solvent. Desired components with an unavoidable solvent were treated differently. These include electrode paste, adhesive tape, etc. Samples were first checked for off-gassing to identify the volatile species. For a set of EKG electrodes and their adhesives, toluene and iso-octane were found. Chamber use of materials in this category was permitted in short time intervals. Electrodes were sent into the chamber immediately prior to experimental use and removed immediately afterward.

A contamination surveillance program was maintained throughout the dives. Samples of chamber gas were checked with the PID daily. Since that instrument is quite sensitive to aromatic compounds, an early recurrence of benzene or toluene problems could be detected. In fact, this PID showed no such problem during any of the three saturation dives. A number of samples were also taken of chamber gas for GC/FID analysis. With the striking exception described later, these samples also appeared free of any hydrocarbons at 1 ppm or greater.

Procedures during the dives can reduce contaminants below the level found in a prolonged unmanned exposure. Initially the gas should be rather clean since bulk helium and oxygen are used. These gases tend to arrive from the supplier after an intrinsically clean cryogenic separation process. Build-up of off-gassing products from the chamber and equipment are partially diluted by the numerous air-lock runs and tests of emergency gas supplies that result in deliberate loss of chamber gas with clean replacement. Also, a proprietary "odor control" absorbent is used in the gas recirculation system.

Contamination Incident

One experiment on the first of the 1984 saturation dives (200 fsw) required divers to exercise while breathing a gas different from chamber gas. A diver-subject exercising for 6 minutes on a stationary bicycle while breathing the test gas by face mask reported a "funny taste", and became dizzy. Other divers assisted him in removing the gas supply mouthpiece. Within 30 minutes, a contaminated gas supply was suspected and all divers were in an isolated adjacent chamber, ordered to don emergency face masks, and breathe from an emergency gas supply.

The source of test gas in this experiment was a 1.7 cu ft cylinder. It was owned by this Command but had recently been sent to a gas supplier to be cleaned and re-valved. Upon its return the cylinder was charged here with a mixture of 5% oxygen in helium. Continuous measurement of O_2 was performed during and again after mixing. A number of other cylinders were prepared and charged the same way. No post-mixing analysis for hydrocarbons was performed on any of these or other cylinders used for experiments.

When the incident occurred, the cylinder was closed and a PID reading taken on the distribution header. The instrument showed a deflection equivalent to about 20 ppm isobutylene in air, the local calibration gas. To avoid the instrument sensitivity to background gas, the PID was recalibrated with a benzene/helium mixture. The contaminated cylinder had 5 ppm equivalent of that gas. Steel sample cylinders were sent to two other institutions having a GC-MS capability. In the meantime the gas was bled into a local quadropole mass spectrometer (UTI-100 C Analyzer) which had not previously been used to identify unknown samples. Significant peaks were found at mass units 61, 97, and 99. Searching tabulated mass spectra (Cornu and Massot, 1975) and consulting other chemists, a tentative identification of methyl chloroform was achieved. Since the PID response to this compound was expected to be quite low, and since the divers were exposed at 7-fold increase in partial pressure, their exposure was feared to be in the anesthetic range for the compound, about 2000 ppm, surface equivalent (Carchman et al., 1984). Analysis of chamber gas showed a very low reading on the PID. Because no sensitive way to determine actual chamber levels of methyl chloroform was available, all chamber gas was vented after the divers were moved to an adjacent chamber at the same depth. Divers were permitted to breathe chamber gas once it had all been replaced six hours later.

Analysis of gas samples performed at two different laboratories confirmed the major contaminant as methyl chloroform at a level of about 250 ppm v/v. Both labs also reported other contaminants. One lab suggested the presence of dioxane, but reported difficulties in confirming the specific isomer present. The other lab reported the presence of vinylidene chloride as well as dioxane. Both of these compounds are found in industrial grades of methyl chloroform (Saunders, 1965).

The source of the problem was traced to the cleaning vendor. The vendor had been in the process of changing quality control managers at the time, and the solvent (industrial methyl chloroform) had not been properly purged from 2 of the 13 cylinders that were processed. Medical follow-up of the diver who inhaled the gas showed no evidence of liver or bone marrow toxicity. Rubber components that had been contaminants were discarded. The affected piping systems were flushed until residual methyl chloroform fell to < 10 ppm at the start of the next dive.

Conclusion

Chemical contamination of manned diving systems is a recurring problem. Incidents of gross contamination are probably under-reported. Long term low level problems may be very common because detection programs are non-existent at most installations. Regulations only require a serious evaluation at initial system certification, and even this process can miss many problems.

Monitoring of chemical contamination at this facility has evolved with little guidance from existing Navy publications. Mistakes and changes of direction were inevitable. Some lessons were learned quickly, such as the importance of complete documentation of test conditions and the desirability of clean habits over decontamination. Other lessons are learned more slowly, such as how a believable and efficient surveillance program should be conducted. A set of standard procedures will be the subject of a subsequent report. Knowledge of historical problems and their solutions can increase the safety of all Navy hyperbaric chamber operations.

REFERENCES

1. Spain D, JJ DeCorpo, JR Holtzclaw. Use of a photoionization detector as a hydrocarbon trace gas analyzer. Navy Research Laboratory, Memorandum Report No. 4239, 1980.
2. Vind HP, C Mathews. Toxicity of off-gassing from divers' hoses. In: Proceedings, Purity standards for divers breathing gas symposium NAVSHIPS Report No. 6-70 (Batelle) 1970; pp 14-1 to 14-34.
3. Conkle JP, JD Adams, WE Mabson, P Wolf, HJ Zeft, and BE Welch. Detailed study of contaminant production in a space cabin simulator at 258mmHg. Aerosp Med 1970; 41: 1031-1038.
4. Wands RC. Philosophy of 100-day and 1000-day limits for space cabin atmospheres. In: Proceedings of the Fourth Annual Conference on Atmospheric Contamination in Confined Spaces. Dayton: Aerojet General Corp, 1968; AMRL TR 68 175, pp 7-13.
5. Thalmann ED. Freon contamination at 400 feet during a saturation dive. In: Proceedings 1973 Divers' Gas Purity Symposium. Report No. 2-73, Battelle, 1973; pp IX-1 to IX-8.
6. Trigger AW, and RD Neil. Some specific case histories of U.S. Navy breathing gas systems contamination In: Proceedings 1976 Divers' Gas Purity Symposium. Report No. 7-76, Battelle, 1976; pp. 15-1 to 15-8.
7. Rippstein WJ, and ME Coleman. Toxicological evaluation of the Columbia spaecraft. Aviat Space Environ Med 1983; 54:S60-S67.
8. Williams FW. Sources of contaminants in diving systems. In: Proceedings, Purity standards for divers breathing gas symposium. NAVSHIPS Report No. 6-70 (Batelle) 1970; pp 6-1 to 6-12.

9. Saalfeld FE, and RA Saunders. Analysis of encapsulated environments. In: Mass Spectrometry, Part A, C. Merrit, C.N. McEwen, eds., Dekker, NY, 1979, pp 119-144.

10. Saunders RA. The composition of technical grade methyl chloroform. NRL Report No. 6206, Feb 1965.

11. Carchman R, Davidson IWF, Greenberg MM, Parker JC, Benignus V, Singh DL, and Fowle JR. Health assessment document for 1,1,1-trichloroethane (methyl chloroform). U.S. Evnrionmental Protection Agency Report EPA-600/8-82-003F, Feb., 1984.

12. NAVMAT Systems certification procedures and criteria manual for deep submergence systems. NAVFAC P-9290, June 1976.

13. Cornu A and R Massot. Compilation of mass spectral data. Second edition; London: Heyden, 1975.