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The Composition of Technical Grade Methyl Chloroform

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ABSTRACT

The compositions of four samples of methyl chloroform solvent have been determined by means of chromatographic, infrared, and mass spectral analysis. Sixteen components, most of them trace contaminants, were identified in these samples. Most of these compounds have been previously found in submarine, spacecraft, and environmental test chamber atmospheres.

PROBLEM STATUS

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

AUTHORIZATION

NRL Problem C07-01
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THE COMPOSITION OF TECHNICAL GRADE METHYL CHLOROFORM

INTRODUCTION

Several of the contaminants which have been found in the atmospheres of Project MERCURY spacecraft have been low molecular weight chlorinated hydrocarbons (1). Several such compounds have also been detected in nuclear submarine atmospheres (2). The identification of the source of these materials is of great importance since some of them may give rise to harmful or toxic decomposition products after passing through elements of the air purification system. Ethylene dichloride, trichloroethylene, and methyl chloroform, commonly used commercial compounds and cold-wash solvents replacing the far more toxic carbon tetrachloride, have all been found in spacecraft, environmental test chambers and submarine atmospheres, and are known to have been used for various purposes within these enclosed spaces before their detection. The origin of several other chlorinated hydrocarbons which have also been found in these atmospheres, however, has been somewhat of a mystery.

METHYL CHLOROFORM

Methyl chloroform is used as a solvent in some brands of contact cement (3). Over a thousand gallons of this material is used in the final fitting out of Polaris submarines for fastening decorative and insulating covering to bulkheads and pipes. At the time of application the submarine is ventilated outboard. Significant quantities of solvent from these cements are retained for longer periods, however, and only slowly diffuse into the submarine atmosphere (4). Significant quantities are also adsorbed on the ship's main charcoal beds during the application period. Later, as the carbon beds become loaded with other higher molecular weight air contaminants, the methyl chloroform is slowly displaced from this source also and reenters the ship's atmosphere (5).

Passage of methyl chloroform contaminated air through the submarine CO/H₂ catalytic burners results in the breakdown of the solvent to form vinylidene chloride and hydrochloric acid. The latter compound, generated slowly but continuously over a long period of time, caused extensive corrosion damage aboard several submarines in areas surrounding the burner discharge before its identity and ultimate source were discovered.

The extensive use of methyl chloroform by the Navy followed a survey of possible substitutes for carbon tetrachloride as nonflammable solvents for shipboard use (6). Methyl chloroform and other low toxicity chlorinated solvents were recommended for shipboard use, however, only when ample ventilation was available and not where the solvents could be retained in closed atmospheres. The use of these solvents on submarines is now discouraged and permitted only in small quantity when adequate outboard ventilation is in effect.

These solvents are still used in and around spacecraft, however, although so far no trouble has been experienced attributable to their use. The air purification system of Project MERCURY spacecraft included activated charcoal which adequately removed this compound from the atmosphere for periods of time in excess of flight durations. Moreover, the MERCURY spacecraft did not incorporate a catalytic burner which might have resulted in the decomposition of chlorinated hydrocarbons in the cabin atmosphere and the formation of corrosive or toxic reaction products.

Some ground test chambers used for simulating space flight and evaluating life support equipment do make use of Hopcalite catalyst burners in their air purification systems, however. In one such chamber study (7), trichloroethylene was found to be one of the major atmospheric contaminants, following its use in and around the chamber for various purposes during pretest activities. Also recovered from the charcoal air sampling canister, which was exposed in the chamber during the test, were traces of chloroacetylene, phosgene, vinylidene chloride, and other chlorinated hydrocarbons. Hydrochloric acid, not readily detected with the procedures used for this analysis, may also have been present. These compounds found in the chamber atmosphere indicate the possibility that decomposition of trichloroethylene occurred in the catalytic burners, such as is known to have occurred with methyl chloroform on submarines. If the decomposition of a chlorinated hydrocarbon were to occur, especially on an actual manned spacecraft on an extended mission, the resultant hydrochloric acid formed could be expected to give rise to possibly serious corrosion of electronic and other equipment as well as causing personal discomfort.

COMPOSITION OF COMMERCIAL METHYL CHLOROFORM

In view of the wide use of methyl chloroform in closed atmospheres, and the several other chlorinated hydrocarbons of unknown origin which have been found in submarine and spacecraft atmospheres it seemed of interest to determine the composition of a few technical grade samples of methyl chloroform taken from government stock and other sources. Four brands were chosen: Octagon Process Co., Fisher Chemical Co., Phillips and Jacobs Chemical Co., and Eastman Kodak Co.

Analysis was made by passing the solvent through a vapor phase chromatographic column (Ucon 50HB-2000 on 30-60 mesh Chromasorb at 100°C), which resolved the various components of the solvent as shown in the chromatograms in Figs. 1 to 4. The eluted

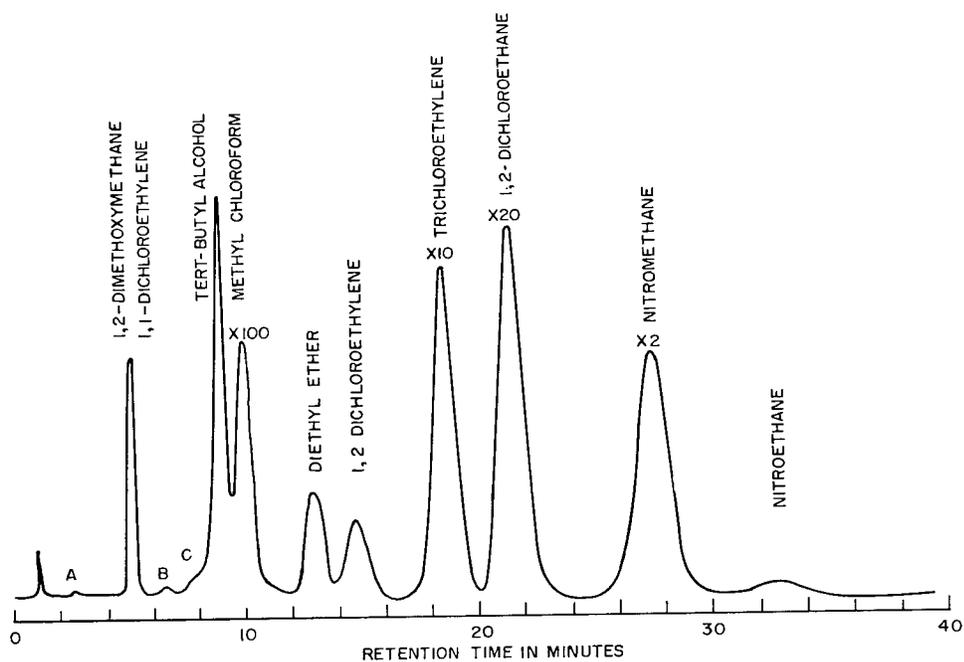


Fig. 1 - Chromatogram of methyl chloroform (Octagon Process Co.)

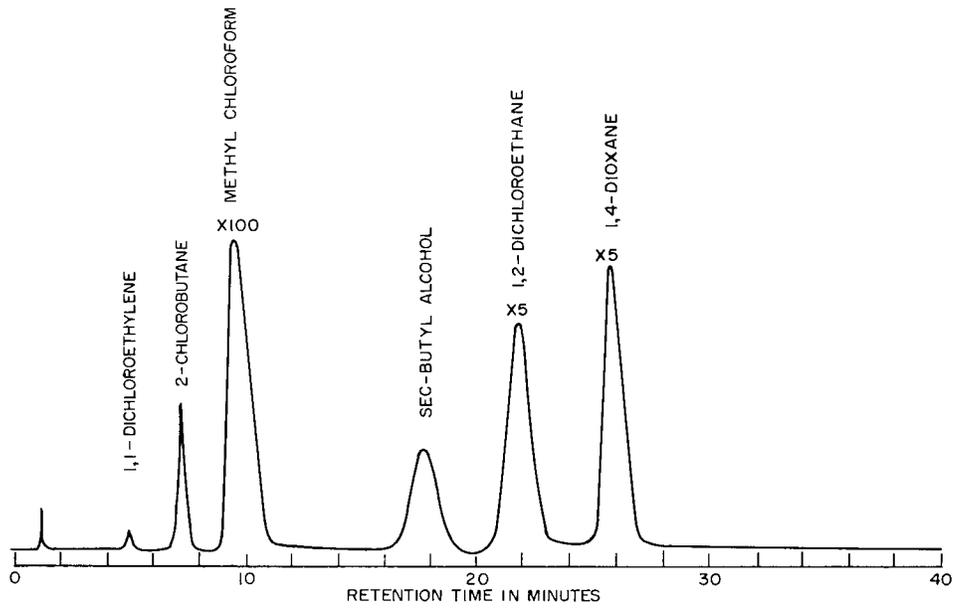


Fig. 2 - Chromatogram of methyl chloroform (Fisher Chemical Co.)

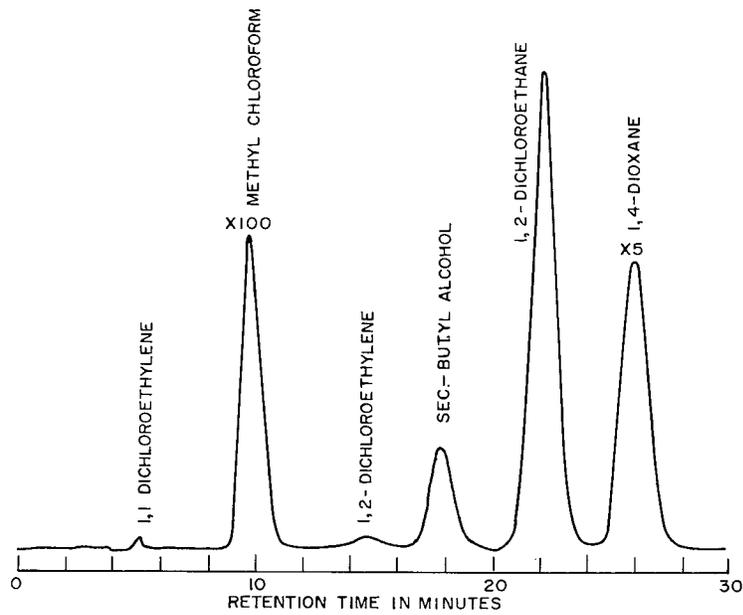


Fig. 3 - Chromatogram of methyl chloroform (Phillips-Jacobs Chemical Co.)

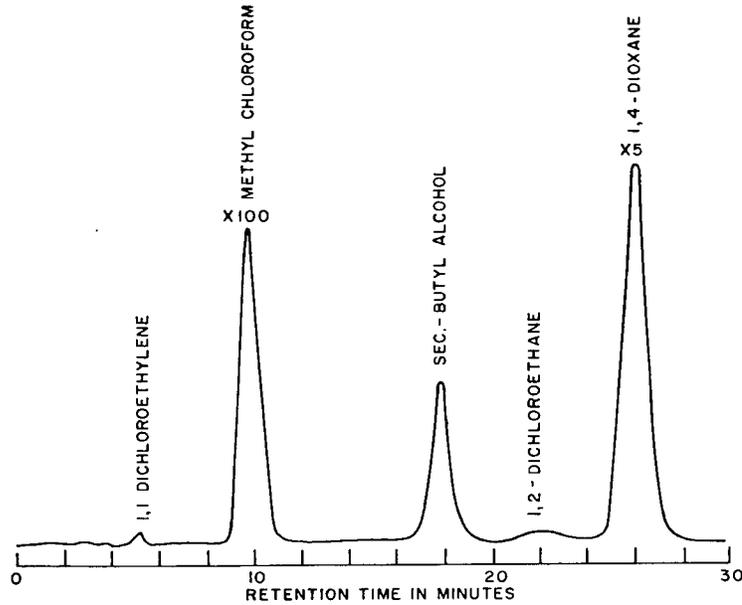


Fig. 4 - Chromatogram of methyl chloroform
(Eastman-Kodak Co.)

Table 1
Composition of Commercial Methyl Chloroform
(Octagon Process Company)

Compound	% by volume
1,2 -dimethoxymethane	0.24
1,1-dichloroethylene	0.06
tert-butyl alcohol	3.64
1,1,1-trichloroethane (methyl chloroform)	~65.
diethyl ether	trace
1,2-dichloroethylene (acetylene dichloride)	trace
1,1,2-trichloroethylene	7.6
1,2-dichloroethane (ethylene dichloride)	22.0
nitromethane	1.3
nitroethane	trace
1,1,2-trichloroethane (vinyl trichloride)	trace

Table 2
Composition of Commercial Methyl Chloroform
(Fisher Chemical Company)

Compound	% by volume
1,1-dichloroethylene	trace
2-chlorobutane	trace
1,1,1-trichloroethane (methyl chloroform)	~ 94.
sec-butyl alcohol	0.2
1,2-dichloroethane	2.1
1,4-dioxane	3.6

Table 3
Composition of Commercial Methyl Chloroform
(Phillips-Jacobs Chemical Co.)

Compound	% by volume
1,1-dichloroethylene	trace
1,1,1-trichloroethane (methyl chloroform)	~95.5
1,2-dichloroethylene	trace
sec-butyl alcohol	0.2
1,2-dichloroethane	0.8
1,4-dioxane	3.4

Table 4
Composition of Commercial Methyl Chloroform
(Eastman-Kodak Company)

Compound	% by volume
1,1-dichloroethylene	trace
1,1,1-trichloroethane (methyl chloroform)	~95.
sec-butyl alcohol	0.3
1,2-dichloroethane	trace
1,4-dioxane	4.5

components, represented by the various peaks of the chromatograms, were individually recovered from the effluent stream of the chromatograph in the manner described in a previous report (8). The identity of each of these components was then determined by means of its infrared and/or mass spectrum. No identifications were made solely on the basis of chromatographic retention time. The compositions of the four solvents and the proportions of the predominant components are given in Tables 1 to 4. Some of the less concentrated components were not identified, i.e., those represented by the weak peaks at A, B, and C in Fig. 1 and a trace component eluted at the same time as the tertiary butyl alcohol. One component of this sample, 1,1,2-trichloroethane, had a long retention time and is not shown in the chromatogram (Fig. 1).

The quantitative data presented in Tables 1 to 4 are based upon the amount of pure reference compounds required to give the same peak areas for the given column conditions. There may have been other components in the solvents examined which were not eluted from the chosen column in reasonable retention times and, therefore, were not detected. Quantitative data are given only for the major constituents. Quantitative estimates of the less significant components can be inferred by comparing chromatographic peak areas for these components with those of other similar constituents for which quantitative values are given.

Commercial grades of methyl chloroform generally contain one or more stabilizers or inhibitors, such as p-dioxane, to prevent decomposition and the formation of hydrochloric acid. In spite of such additives, samples of methyl chloroform taken from government stock have been known to cause corrosion of metal, especially aluminum (9). Chlorinated solvents should not be used indiscriminately, therefore, for general cleaning of spacecabin components or of Polaris or other missile parts.

SUMMARY AND CONCLUSIONS

Methyl chloroform and other low toxicity chlorinated solvents have been used in closed submarine spaces in considerable quantity with subsequent deleterious effects on equipment. These solvents are still being used in and around spacecraft and environmental test chambers. Some commercial grades of methyl chloroform have been shown to contain appreciable quantities of other more toxic chlorinated hydrocarbons. The relatively high concentrations of the more toxic chlorinated hydrocarbons in such grades of methyl chloroform may raise the toxicity levels of these solvent mixtures above that of the pure compound. It is obvious that the use of such technical grade solvents in closed atmospheres can add several unsuspected and perhaps undesirable contaminants to the atmosphere, in addition to the labeled compound.

Since methyl chloroform and trichloroethylene are known to decompose under certain conditions on passage through a submarine CO/H₂ catalytic burner with the formation of additional chlorinated hydrocarbons and highly corrosive hydrochloric acid, the use of chlorinated hydrocarbon solvents should be prohibited in those spacecraft and environmental test chambers utilizing catalytic burners as air purification devices.

An analysis of other solvent systems whose use may be necessary in submarines, spacecraft, or other analogous closed spaces, followed by restrictions on the use of those materials which contain or which might produce deleterious substances, is also recommended.

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