

---

---

# POTENTIAL OPTIONS & MANUFACTURING CHANGES FOR ETHYL ETHER IN SUPPORT OF POLLUTION PREVENTION

*D.J. Watts and I.B. Zimmer, Emission Reduction Research Center, New Jersey Institute of Technology, University Heights, Newark, NJ, 07102-1982, Phone: 201-596-3465*

**ABSTRACT** This project addresses the elimination or reduction of a hazardous substance/toxic chemical, ethyl ether, as listed by the U.S. Environmental Protection Agency in the Toxic Release Inventory. The study focuses on replacing or eliminating the need for the substance in Department of Defense systems (e.g., weapon systems, ammunition manufacturing, propellant manufacturing & processing). An analysis of the processes using ethyl ether, a search for substitutions, and a review of modern techniques are central to this project. The results and procedures form the basis for broader application and chemical change. Ethyl ether is the first of two chemical candidates for replacement and the primary subject of this paper. All conclusions and recommendations require laboratory verification.

**KEY WORDS:** ether, solvent, extraction, peroxide, volatile

---

---

## INTRODUCTION

### *Project definition and objectives*

In support of pollution prevention and under Executive Order 12856 [1] concerning pollution prevention, all federal agencies (e.g., the U.S. Army and DOD) must comply with the Toxic Release Inventory (TRI) chemical release reduction and pollution prevention planning. Frequent occurrence of ethyl ether in an Army chemical data base is the basis for its removal as a hazardous substance. The substance names ethyl ether, diethyl ether, and ether are synonymous for common ether. "Ether" denotes any of the aforementioned names throughout this document, although the other names are used to avoid confusion with other ethers.

Elimination or reduction of ether in manufacturing is the objective. A review of the processes requiring ether is essential for new methods or chemical substitutes to be found. Manufacturing needs of DOD must

still be met when the new procedures are in place. Although a cost analysis is not included, economic aspects are of interest if only briefly noted.

### *Ether as a hazardous substance/toxic chemical*

Commercially, ether is used in chemical manufacturing and as a solvent, extractant, or reaction medium. Use of ethers involves risks of fire, toxic effects, and several unexpected reactions. A review of the properties of ether clarifies its designation as a potential health, safety, and environmental problem. The following section provides such a review.

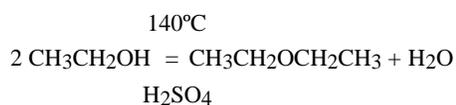
## BACKGROUND

### *Ether properties review*

Ethers are weakly basic compounds with a distinct odor. They have little or no solubility in water, but are soluble in organic compounds.

Most ethers are relatively unreactive compounds because the carbon-oxygen bond is not readily detached. This trait makes them effective solvents in organic synthesis. However, different families of ethers react differently. Most are potentially hazardous chemicals because in the presence of atmospheric oxygen a radical-chain process can occur. This results in the formation of peroxides that are unstable, volatile compounds. Ethyl ether is liable to form explosive peroxides on extended storage and exposure to air and light.

Ethyl ether can be prepared directly by the vapor-phase dehydration of ethanol with a strong acid catalyst and a high reaction temperature:



Most ethers burn in air. Flash points and autoignition temperatures characterize flammability. Ethyl ether particularly is dangerous. For example, the 34.5°C boiling point equates to 94.1°F (possibly room temperature in a lab with failed air-conditioning). Table 1 lists properties of the

different kinds of ether, and Table 2 lists CAS registry numbers.

Upon ingestion, skin contact, or inhalation, ethers can cause drowsiness, lack of coordination, or death. They have a low order of toxicity when ingested. Prolonged skin contact can cause defatting and dehydration leading to dermatitis. Some compounds can penetrate the skin in harmful amounts and are carcinogenic. Inhalation is the most common way for ethers to enter the body. Effects may include narcosis, irritation of the nose, throat, and mucous membranes, and chronic or acute poisoning. Ethers are central nervous system depressants and ethyl ether may still be used as a general anesthetic, although not in the United States (i.e., low toxicity).

Most ethers absorb and react with atmospheric oxygen to form unstable peroxides. These peroxides can detonate with extreme violence when concentrated by evaporation or distillation, when combined with other compounds that give a detonable mixture, or when disturbed by heat, shock, or friction.

Ethyl ether is a principal member of the

**TABLE 1.** TYPICAL PROPERTIES OF SELECTED SUBSTANCES [2].

Property	Ether	Ethanol	n-Hexane	MTBE
Chemical Formula	C <sub>4</sub> H <sub>10</sub> O	C <sub>2</sub> H <sub>5</sub> OH	C <sub>6</sub> H <sub>14</sub>	C <sub>5</sub> H <sub>12</sub> O
Boiling Point, °C	34.5	78.3	68.7	55.0
Autoignition Temp, °C	160	423	225	426
Flash Point, °C	-40	14	-22	-30
Molecular Weight	74	46	86	88

**TABLE 2.** CAS REGISTRY NUMBERS [2].

Ether	[60-29-7]
Ethanol	[64-17-5]
n-Hexane	[110-54-3]
MTBE	[1634-04-4]

ether family. It is colorless, extremely volatile, highly flammable with a sweet odor and a burning taste. The flammability and volatility make it dangerous to handle and ship. Its low autoignition temperature and non-conducting property enable it to generate static electrical charges that can result in explosion. Special areas are defined and tools are used when ether is present.

Prevention of health hazards depend on prevention of exposure to toxic atmospheric concentrations and conscientious precautions to prevent fires and explosions.

Ether has a wide range of industrial uses, especially as an organic solvent and as an extractant. It is also a denaturant for several alcohol formulas, a starting fuel for diesel engines, and an entrainer for ethanol dehydration. It is used abundantly for the military production of smokeless powder.

### ***DOD system ether application***

Upon review of military specifications (MILSPEC) provided by Picatinny Arsenal, New Jersey, various system uses of ether are

apparent. All specifications listed deal with extracting a substance and determining its quantity. In only one case, ether is an extractant. In all others, including its use as an extractant, it is an organic solvent. Table 3 lists these applications. Only the last part of the MILSPEC is listed. For the complete number, see the References section. Substance is the chemical extracted. Ether use is “Extractant” or “Solvent.”

The solvent and extraction procedures must be reviewed for each MILSPEC to determine tendencies, if any, for a given chemical. This is the subject of the next section.

## **THE CHEMICAL PROCESS**

### ***Organic solvent procedure***

Ether is a solvent for ethanol in virtually the same procedure for all cases. The essential process follows:

1. Rinse sample with ethanol (few ml).  
(Ethanol used as a solvent).
2. Rinse sample with ether (few ml).

**TABLE 3.** ANALYTICAL CHEMISTRY MILSPEC APPLICATIONS OF ETHER [3].

MILSPEC	Substance to be analyzed	Ether use
11233J	Aluminum	Solvent
46432B	Lead Azide	Solvent
71090	Potassium Perchlorate	Solvent
46462B	Antimony Sulfide	Solvent
50998	Antimony Sulfide	Solvent
382C	Oil & Grease	1) Extractant 2) Solvent
13392B	Antimony Sulfide	Solvent
20449C	Antimony Sulfide	Solvent
12951F	TNT	Solvent
20517H	Black Powder/ Aluminum Powder	Solvent
45474B	Aluminum	Solvent
46647B	Lead Azide	Solvent
48239	Aluminum	Solvent

3. Aspirate sample until there is no odor of ether.
4. Dry the sample in an oven at 80-100°C for 15-60 minutes. (In only one case is 80°C used, all others are around 100°C).
5. Cool sample in a desiccator.
6. Weigh the sample.

This denotes a gravimetric approach for identifying the amount of a substance in a sample. Gravimetry is archaic if not obsolete. Perhaps a more updated method exists for a given substance determination which does not employ ether.

Another detail about the procedure is eye-catching. The ether washes away the ethanol and then the sample is placed in an oven at about 100°C. A look at the boiling points listed in Table 1 for ethanol and ether may provide some insight into the approach.

### ***Extractant procedure***

Ether is an extractant for oil and grease as follows:

1. Extract 50.0 g sample with 250 ml of chemically pure ethyl ether (redistilled over sodium) for one hour in a Soxhlet extractor.
2. Evaporate on steam bath to volume of approximately 50 ml.
3. Filter the extract into a tared 150 ml beaker.
4. (Solvent procedure ensues using 10 ml portions of ether).

Once again, an updated method for the gravimetric approach appears appropriate.

Alternative techniques for the solvent and extraction procedures are assembled through a literature search based on the particular substances extracted.

## **RESULTS AND DISCUSSIONS**

### ***Organic solvent procedure***

From an examination of Table 3 and the organic solvent procedure, two improvements come to mind. The first is an observation of the boiling points of ethanol and ether; the second, an investigation into possible alternative methods for the gravimetric approach.

The boiling point of ethanol is 78.3°C and of ether is 34.5°C. Based on the 100°C oven temperature, both solvents will boil away. Actually, the ethanol would boil away without the ether present because the boiling point of ethanol is less than the oven temperature. The ether is extraneous and may be left out entirely. Oven temperatures and times may need adjustment, but most likely will remain the same. These statements may be verified in the laboratory.

If results indicate that a solvent is required for the ethanol, Eaton, *et al.* [4], prescribes an alternative solvent of 80% n-hexane and 20% methyl-tert-butyl ether (MTBE) for gravimetric methods. These substances are not on the TRI. Hexane is flammable and requires appropriate handling precautions. It is a central nervous system depressant. The vapors are mildly irritating to mucous membranes. Exposure may cause dizziness, unconsciousness, prostration, and death. Main uses include fuel applications and oil extraction.

MTBE, although an ether, has a uniquely stable structure that contains no secondary or tertiary hydrogen atoms. Therefore, it is resistive to oxidation and peroxide formation (less prone to explode). Its higher autoignition temperature and narrower flammability range make it comparably safer to use than ethyl ether. MTBE's chief uses

are as a fuel additive and a solvent. It also has medical applications.

A literature search for determination methods for the chemicals in Table 3 reveals that analytical methods such as spectroscopy and voltammetry are available. Spectroscopy uses instrumental analysis to identify elements by measurement of the radiant energy absorbed or emitted by a substance. Specialized and sophisticated techniques include, but are not limited to: Raman spectroscopy, nuclear magnetic resonance, nuclear quadrupole resonance, dynamic reflectance spectroscopy, microwave and gamma-ray spectroscopy, and electron paramagnetic resonance.

Voltammetry, an electrochemical method, is common for lead azide determination and renders high accuracy. It also has applications for other propellants and high explosives. Asplund [5] describes the determination of azide based on the oxidation of azide at a carbon paste electrode and that of lead on reduction of lead at a dropping mercury electrode in a 0.1 M acetate solution at pH 4.6. The solubility of lead azide in pure water is very low, but in an acetate solution adequate amounts of lead azide dissolve.

Other methods are specified in the References section. Their discussion is beyond the scope of this project. However, the relevant articles are included because of their importance in establishing precedence for alternative methods to gravimetry (and therefore ether). Additionally, they provide a beginning for follow-on research.

### ***Extraction procedure***

In Eaton, *et al.* [4], section 5520 "Oil and Grease" contains information pertinent to replacing ether as an extractant. Five methods are described in detail. Although

none of the methods uses ether, the listed reagents should be checked against the current TRI before use. Most of the methods use the n-Hexane/MTBE mixture.

The partition-gravimetric method, the partition-infrared method, and the Soxhlet method are designed for oil and grease extraction in liquid samples. The partition-infrared method is recommended for low levels of oil and grease (<10 mg/l) because gravimetric methods do not provide the required precision. A modified Soxhlet method is provided for the extraction of sludge samples. Lastly, a hydrocarbon method is given for use with any of the above methods to obtain a hydrocarbon measurement in addition to or instead of the oil and grease measurement.

## **CONCLUSIONS AND RECOMMENDATIONS**

### ***Recommended actions***

The objective of reducing or eliminating a hazardous substance from the environment and improving a chemical process is complete. Upon laboratory confirmation, the following recommendations are provided:

1. Eliminate the use of ether as an organic solvent for ethanol; ethanol alone suffices. The cost of the ether is saved. If lab results indicate ether's necessity, substitute an 80% n-hexane, 20% MTBE mixture for the ether.
2. Explore the implementation of more sophisticated techniques to gravimetry. Methods include spectroscopy and voltammetry. Results will be more accurate. Availability of equipment and funds is a factor.
3. Use the methods described in Eaton, *et al.* [4], for oil and grease extraction.

### *Suggestions for further study*

Considerable laboratory work is needed for all the above recommendations. The intent of the MILSPEC must be satisfied. Ample literature exists concerning alternative substance determination techniques.

Applicable techniques must be explored and feasibility studies performed as necessary.

1,1,1-Trichloroethane (methyl chloroform) is the follow-on chemical candidate for replacement for this study. These two chemical studies will form the basis for a chemical replacement strategy/protocol.

The removal of hazardous substances from the environment is not necessarily difficult. In the long run, the benefits surpass the cost.

### **REFERENCES**

1. Executive Order 12856, Federal Compliance with Right-to-Know Laws and Pollution Prevention Requirements, National Defense Center for Environmental Excellence, 1993.
2. Kirk-Othmer, 1994, Encyclopedia of Chemical Technology, Wiley, New York, 4<sup>th</sup> ed., 1994, 9: 812-14, 860-73, 13: 826-29.
3. Military Specifications, U.S. Army, Department of Defense, (1) MIL-C-11233J, Cartridge, Photoflash, M112A1, 1990. (2) MIL-D-46432B, Detonator, Stab, M18, 1988. (3) MIL-C-71090, Canister Smoke, 155MM, M804E1, 1995. (4) MIL-D-46462B, Detonator, Stab, M192A2, 1988. (5) MIL-D-50998, Detonator, Stab, M76, 1992. (6) MIL-M-382C, Magnesium Powder, 1988. (7) MIL-P-13392B, Primer, Percussion, M54, 1987. (8) MIL-P-20449C, Primer, Percussion, M61, 1988. (9) MIL-P-12951F, Primer, Percussion, M39A1, 1985. (10) MIL-S-20517H, Simulator, Projectile, Airburst, M74A1, 1991. (11) MIL-C-45474B, Charge, Spotting, For Warhead, M38, 1991. (12) MIL-D-46647B, Detonator, Stab, XM58, 1988. (13) MIL-P-48239, Powder Photoflash, 1990.
4. A.D. Eaton, L.S. Clesceri, and A.E. Greenberg, Standard methods for the examination of water and wastewater, American Public Health Association, 19<sup>th</sup> ed., 5 (1995) 30-35.
5. J. Asplund, Voltammetric determination of azide and lead in lead azide, Proc. Int. Pyrotech. Semin., 9 (1984) 15-28.
6. J. Asplund, Some examples of modern voltammetric analysis methods for the inspection of propellants and high explosives, Int. Jahrestag.—Fraunhofer-Inst. Treib-Explosivst., (1983) 313-35.
7. C.A. Clausen, Principles of Industrial Chemistry, Wiley, New York, 1978.
8. S.N. Deming and S.L. Morgan, Experimental Design: A Chemometric Approach, Elsevier, Amsterdam, 1993.
9. D. Guo, and L. Xiang, Application of oscillopolarographic titration to analysis of explosives, Fenxi Shiyanshi, 10:1 (1991) 43-5.
10. S.S.M. Hassan, F.M. El Zawaway, S.A.M. Marzouk, and E.M. Elnemma, Poly(vinyl chloride) matrix membrane electrodes for manual and flow injection determination of metal azides, Analyst (Cambridge, U. K.), 117:11 (1992) 1683-9.
11. S.S.M. Hassan, M.A. Ahmed, S.A.M. Marzouk, and E.M. Elnemma, Potentiometric gas sensor for the

selective determination of azides, Anal. Chem., 63:15 (1991) 1547-52.

12. K.K. Ospanov and E.Z. Aitkhozhaeva, Selective determination of antimony compounds, Otkrytiya, Izobret., Prom. Obrgetiv Tovarnye Znaki, 48 (1983) 165.
13. I. Pawlowska and S. Kwiatkowski, Determination of lead azide in an aqueous suspension by conductometric titration, Zavod. Lab., 54:8 (1988) 5-6.
14. A.R. Samo, Y.M. Khahawer, S. Ali Arbani, and G. Ali Qureshi, Quantitation of azide and lead in lead azide by voltammetric method, J. Chem. Soc. Pak., 15:3 (1993) 187-90.