

Final Report

Evaluation of new high-flashpoint hydrocarbon dry cleaning solvents

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Research Services Team

This report was prepared by the Hazardous Waste Management Program in King County, Washington, a coalition of local governments. Our customers are residents, businesses and institutions with small quantities of hazardous wastes. Our mission is: to protect and enhance public health and environmental quality in King County by reducing the threat posed by the **production, use, storage and disposal** of hazardous materials.

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CONTENTS

Executive Summary	1
Introduction	3
Background.....	3
Solvents evaluated in this study	3
Optima DCF TM	3
Sensene TM	4
Intense [®]	4
Current study	4
Methods.....	5
Sample collection and storage.....	5
Chemical analyses.....	5
Fish bioassays	5
Results	7
Chemical analyses.....	7
Target analytes	7
Chromatogram and TIC review	8
Fish bioassays	8
Discussion.....	13
Conclusions.....	15
Acknowledgments.....	17
References	19

Tables

Table 1. Analytes detected above MDLs in one or more samples	7
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Figures

Figure 1. Chromatogram from GC/MS analysis of Optima DCF TM	9
Figure 2. Chromatogram from GC/MS analysis of Sensene TM	10
Figure 3. Chromatogram from GC/MS analysis of Intense [®]	11

Appendices

Appendix A: Safety Data Sheet for Optima DCF™

Appendix B: Safety Data Sheet for Sensene™

Appendix C: Safety Data Sheet for Intense®

Appendix D: Target Analyte Results

Appendix E: TIC Results

Appendix F: Fish Bioassay data

ACRONYMS AND ABBREVIATIONS

°C	Degrees Celsius
CAS	Chemical Abstract Service
Ecology	Washington State Department of Ecology
°F	Degrees Fahrenheit
GC/MS	Gas Chromatography/Mass Spectrometry
KCEL	King County Environmental Laboratory
LD50	The median lethal test dose that kills 50 percent of test organisms
MDL	Method Detection Limit
µg/L	Micrograms per liter
mg/L	Milligrams per liter
MRL	Method Reporting Limit
NFPA	National Fire Protection Association
NYSDEC	New York State Department of Environmental Conservation
PERC	Perchloroethylene / Tetrachloroethylene
RDL	Reporting Detection Limit
SDS	Safety Data Sheet
TIC	Tentatively Identified Compound

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EXECUTIVE SUMMARY

In 2018-2019, three new high-flashpoint hydrocarbon solvents were brought to the attention of the Hazardous Waste Management Program (Haz Waste Program) in King County: Optima DCFTM (EIL Industrial Co., Ltd, South Korea), SenseneTM (Dow Chemical Company, United States), and Intense[®] (Seitz GmbH, Germany). Although we have previously evaluated the two most frequently used high-flashpoint hydrocarbon dry cleaning solvents used in Washington state (ExxonMobil's DF-2000TM and Chevron-Phillips' EcoSolv[®]) and another relatively new product (Technichem's CalypsolvTM), we were not aware of any analytical- or bioassay- data for these three new products.

Consequently, we collaborated with the King County Environmental Laboratory (KCEL) to perform chemical analyses and derive LD50s for these solvents using an acute fish toxicity test. In this case, the LD50 is defined as the median lethal concentration of solvent that kills 50 percent of the test fish within 96 hours.

All three solvents were confirmed to be primarily complex mixtures of high molecular weight aliphatic hydrocarbons. Although lower molecular weight substituted alkanes were present at low concentrations, benzene was not detected. Optima DCFTM contained a cyclopentane compound. As specified on their Safety Data Sheets (SDSs), SenseneTM and Intense[®] were confirmed to also contain alkoxypropanols and a glycol, respectively.

It was not possible to define LD50s for these solvents because they all failed to kill fish at the highest tested concentration (100 mg/L). This result is identical to that achieved previously with DF-2000TM, EcoSolv[®], and CalypsolvTM.

We conclude that SenseneTM and Intense[®] are likely safer alternatives to perchloroethylene (PERC) for use in dry cleaning. Although Optima DCFTM also appears to be a safer alternative, it would be valuable to have additional information about the source of the petroleum feedstock used to manufacture this product and the catalytic cracking process.

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INTRODUCTION

Background

High-flashpoint hydrocarbons are the most frequently used solvent alternatives to perchloroethylene (PERC) in dry cleaning.⁽¹⁻⁵⁾ These organic chemicals ignite at relatively high temperatures (i.e., high-flashpoint) and contain only carbon and hydrogen (i.e., hydrocarbons). They are generally classified by the National Fire Protection Association (NFPA) as Class IIIA solvents (i.e., flashpoints at or above 140 °F and below 200 °F).

High-flashpoint hydrocarbon dry cleaning solvents are manufactured under several trade names, and the products used most frequently in King County are EcoSolv® (Chevron Philips Chemical Company, LLC) and DF-2000™ (ExxonMobil Corporation).^(2,3) While the detailed chemical specifications are proprietary and vary by product, these solvents typically contain between 11 and 14 carbons as their primary structural backbone (i.e., C11 to C14).

Our previous evaluations of high-flashpoint hydrocarbon solvents (DF-2000™, EcoSolv®, and Calypsolv™) revealed that they do not contain detectable levels of toxic aromatic hydrocarbons and are not acutely toxic to fish.⁽¹⁾ Based on this information, and a detailed toxicological evaluation of this product class, we concluded that these three solvents are likely safer alternatives to PERC for use in dry cleaning.

Solvents evaluated in this study

Optima DCF™

This solvent was brought to the attention of the Haz Waste Program by a dry cleaning solvent manufacturer in December 2018.^a The manufacturer representative was concerned that this solvent, which is manufactured by EIL Industrial Co., Ltd in South Korea, contained “...an appreciable amount of cyclic hydrocarbon (cyclopentane or cyclohexane).” Cyclic hydrocarbons can be present in hydrocarbon solvent products if the catalyst used in the manufacturing process is not very efficient.

The SDS for Optima DCF™ (Appendix A) states that this solvent is 100% Naphtha (petroleum), hydrotreated heavy (Chemical Abstract Service number (CAS No.) 64742-48-9).

No other technical or marketing information was available from Internet searches.

^a Personal communication with Mark Ng, Technichem, Inc., Hayward, California. December 12, 2018.

Sensene™

We were asked to evaluate Sensene™ by a vendor in Washington state.^b Sensene™ is described as a “modified alcohol solvent” on the SDS (Appendix B) and is manufactured by The Dow Chemical Company (Midland, Michigan).

According to our vendor contact, Sensene™ is used by uniform cleaning facilities to remove heavy greases.^c Marketing materials for this solvent assert that “Sensene combines excellent oil and fat-solubilization properties due to its lipophilic groups with the ability to dissolve polar materials due to its hydrophilic groups.”⁽⁶⁾

The SDS states that Sensene™ contains the following ingredients:

- 50-70% alkoxypropanol formulation (CAS no. not provided/trade secret) and
- 30-50% Hydrocarbons, C11-C13, isoalkanes, <2% aromatics (CAS no. 64742-48-9)

Intense®

The Washington state vendor described above also asked us to evaluate Intense®.^c This product is manufactured by Seitz GmbH in Germany. Marketing materials for this solvent state that Intense® can remove moisture and thus facilitates removal of water-soluble stains while also safely dissolving grease and wax-based stains.⁽⁷⁾

The SDS states that this solvent is comprised of two ingredients (Appendix C):

- 60-80% Alkanes, C12-14-iso- (CAS no. 68551-19-9) and
- 10-30% propylene glycol ether (CAS no. not provided/trade secret)

Current study

The goal of this study was to evaluate the chemical composition and acute aquatic toxicity of Optima DCF™, Sensene™, and Intense® and compare these findings to our previous results for other high-flashpoint hydrocarbon dry cleaning solvents. This information will be used to determine whether these three solvents are safer alternatives to PERC for dry cleaning.

^b Personal communication with Susan Kim, S.K.Y. & COMPANY, Auburn, Washington. March 25, 2019.

^c Personal communication with Susan Kim, S.K.Y. & COMPANY, Auburn, Washington. March 28, 2019

METHODS

Sample collection and storage

We were provided a sample of Optima DCF™ by Technichem, Inc. (Hayward, California). Samples of Intense® and Sensene™ were provided by S.K.Y. & Company (Auburn, Washington). All samples were delivered in secondary glass containers at room temperature and then refrigerated in the Haz Waste Program's laboratory. The containers were delivered to the King County Environmental Laboratory (KCEL) at room temperature; copies of the chain-of custody form are included in Appendix F.

Chemical analyses

Samples were analyzed by KCEL staff using Purge and Trap Gas Chromatography-Mass Spectrometry (GC/MS) using EPA Method EPA SW846 8260C (volatile analysis). A 5-mL aliquot of sample was diluted in 50 mL of reverse osmosis water and shaken for 2 minutes. The aqueous portion of the sample/water mix was removed and loaded into a 40-mL capacity VOA vial. Helium gas was bubbled through the aqueous portion at ambient temperature. After purging was completed, the trap was heated and back-flushed with helium to desorb the purgeables onto a gas chromatographic column (J&W DB-VRX column, 30 m long, 0.250 mm ID with a 1.4 um coating thickness).

The gas chromatograph was temperature-programmed to separate the purgeables, which were then detected with a mass spectrometer (Agilent 5975C/7890A GC/MS with a Teledyne Tekmar Atomx autosampler).

D4-Dichlorobenzene, Fluorobenzene, and D5-Chlorobenzene were used as internal standards. D8-Toluene, D4-1,2-Dichloroethane, and 4-Bromoflorobenzene were used as surrogates.

Analysis for Tentatively Identified Compounds (TICs) was performed on peaks that were >3% of the D4-Dichlorobenzene internal standard.

Fish bioassays

Acute aquatic toxicity tests were conducted by KCEL staff according to the Washington State Department of Ecology's (Ecology's) *Biological Testing Methods for the Designation of Dangerous Waste*.⁽⁸⁾ This test involved exposing juvenile rainbow trout to solvent samples for 96 hours at two concentrations (10 mg/L and 100 mg/L) in a "non-renewal" static acute fish toxicity bioassay (i.e., Ecology's Part A: Method 80-12).

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RESULTS

Chemical analyses

Target analytes

Complete analytical data are presented in Appendix D. Summary information for target analytes that were detected above Method Detection Limits (MDLs) in at least one solvent sample are presented in Table 1.

Table 1. Analytes detected above MDLs in one or more samples			
Analyte	Analyte Concentration (ug/L) in Solvents		
	Optima DCF™	Sensene™	Intense®
2-Butanone (MEK) ^a	<MDL	36.9	20.5
Acetone ^b	28.4	63.3	54.3
Acrolein ^a	<MDL	<MDL	7.1
Chloroethane ^c	<MDL	<MDL	9.57
Chloromethane ^c	<MDL	1.3	20.5
Tetrachloroethylene ^c	<MDL	3.76	<MDL
Toluene ^c	<MDL	<MDL	1.9
^a MDL = 5 ug/L; RDL = 10 ug/L ^b MDL = 2.5 ug/L; RDL = 10 ug/L ^c MDL = 1 ug/L; RDL = 2 ug/L Where MDL = Method Detection Limit / RDL = Reporting Detection Limit			

Target analytes from the EPA Method SW846 8260C analysis for volatile organics were present at low concentrations. Acetone was detected in all samples and was likely a laboratory contaminant.^d Both Sensene™ and Intense® contained detectable levels of 2-butanone (MEK)

^d Personal communication with Michael Doubrava, King County Environmental Laboratory, Seattle, Washington. August 1, 2019.

and chloromethane. Sensene™ also contained a trace of tetrachloroethylene (PERC) and Intense® contained acrolein, chloroethane, and toluene.

Chromatogram and TIC review

Chromatograms for Optima DCF™, Sensene™, and Intense® are presented in Figures 1, 2, and 3, respectively. TIC data are presented in Appendix E.

Optima DCF™ displayed chromatographically as multiple peaks within a mound, starting at an approximate Retention Time (RT) of 19 minutes. A review of the TICs from 19.027 minutes onwards revealed that they were C5 to C11 compounds. It is noteworthy that one TIC, methyl cyclopentane, was observed at a RT of 6.611 minutes.

The chromatogram for Sensene™ also displayed as a mound starting at approximately 19 minutes. The TICs from 19.603 minutes onwards were C7 to C14 compounds. However, Sensene™ also displayed several large peaks between 18.008 and 18.759 minutes, two of which were tentatively identified as alkoxypropanol compounds.

The chromatogram for Intense® also displayed as a mound, but it started at approximately 17 minutes. The early peaks were primarily C6 to C9 compounds, with the remainder primarily C10 to C11. A peak for a glycol compound also was present at 20.573 minutes.

Fish bioassays

None of the solvents were acutely lethal at the highest test concentration (100 mg/L). Detailed results are provided in Appendix F.

Figure 1. Chromatogram from GC/MS analysis of Optima DCF™

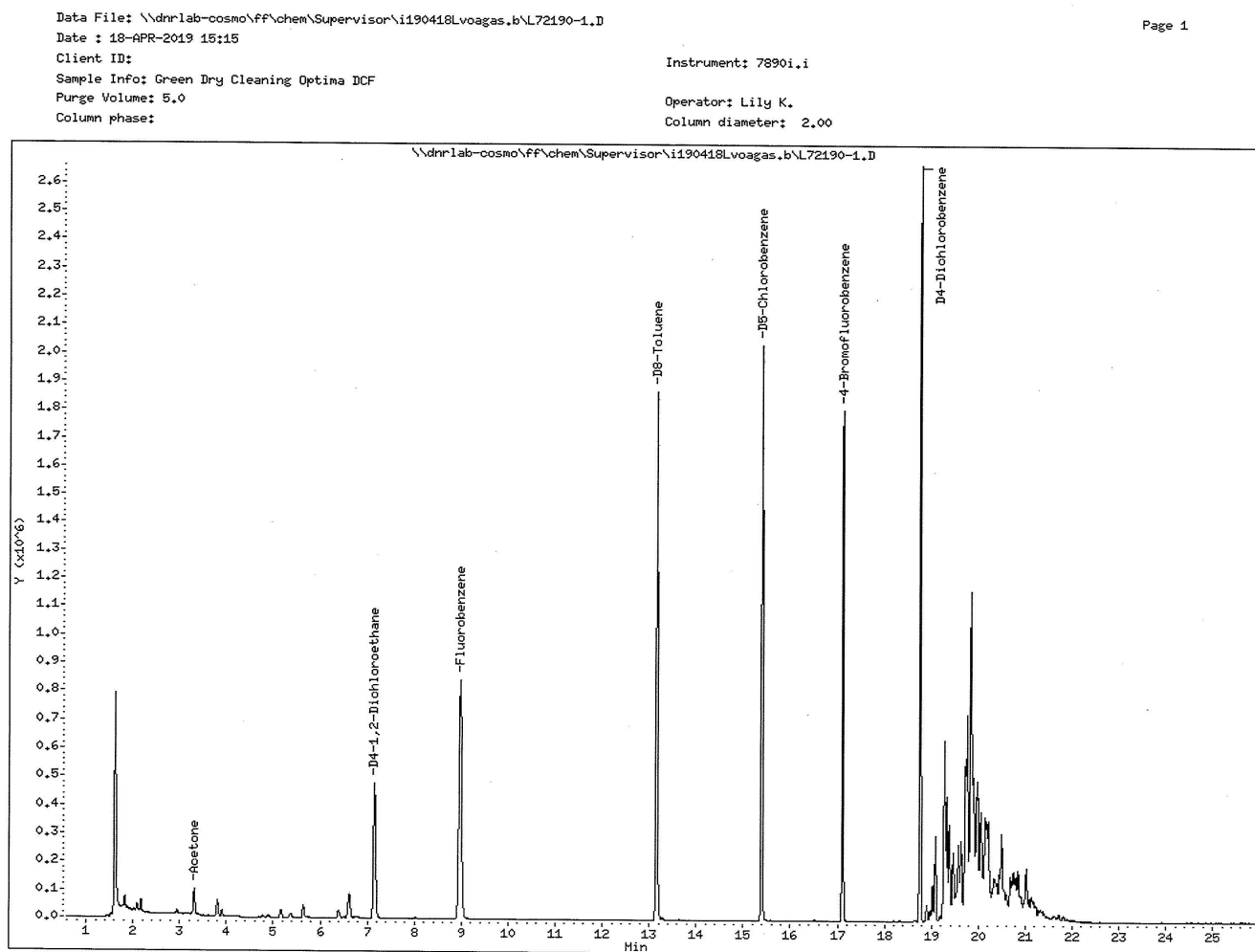


Figure 2. Chromatogram from GC/MS analysis of Sensene™

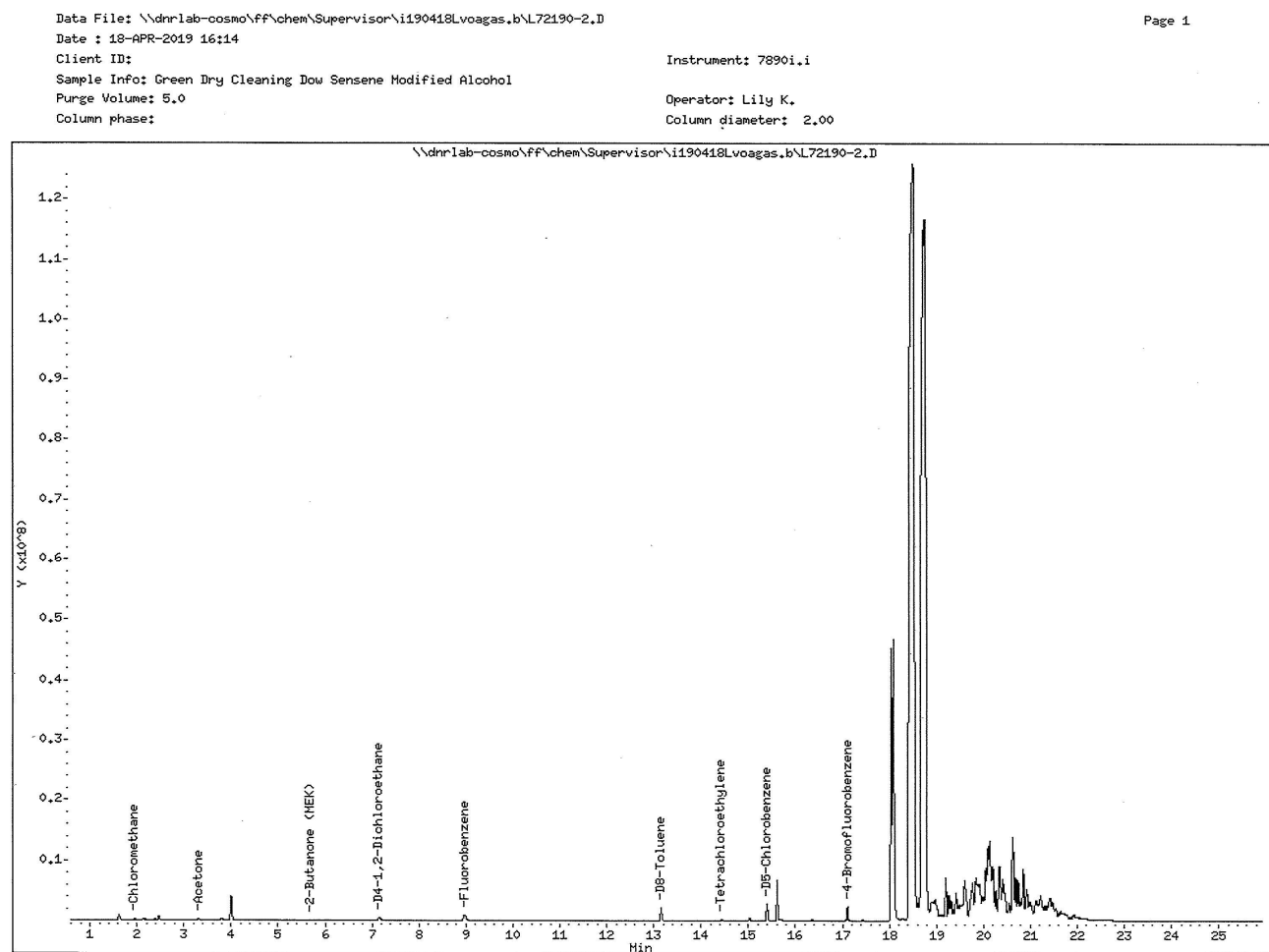
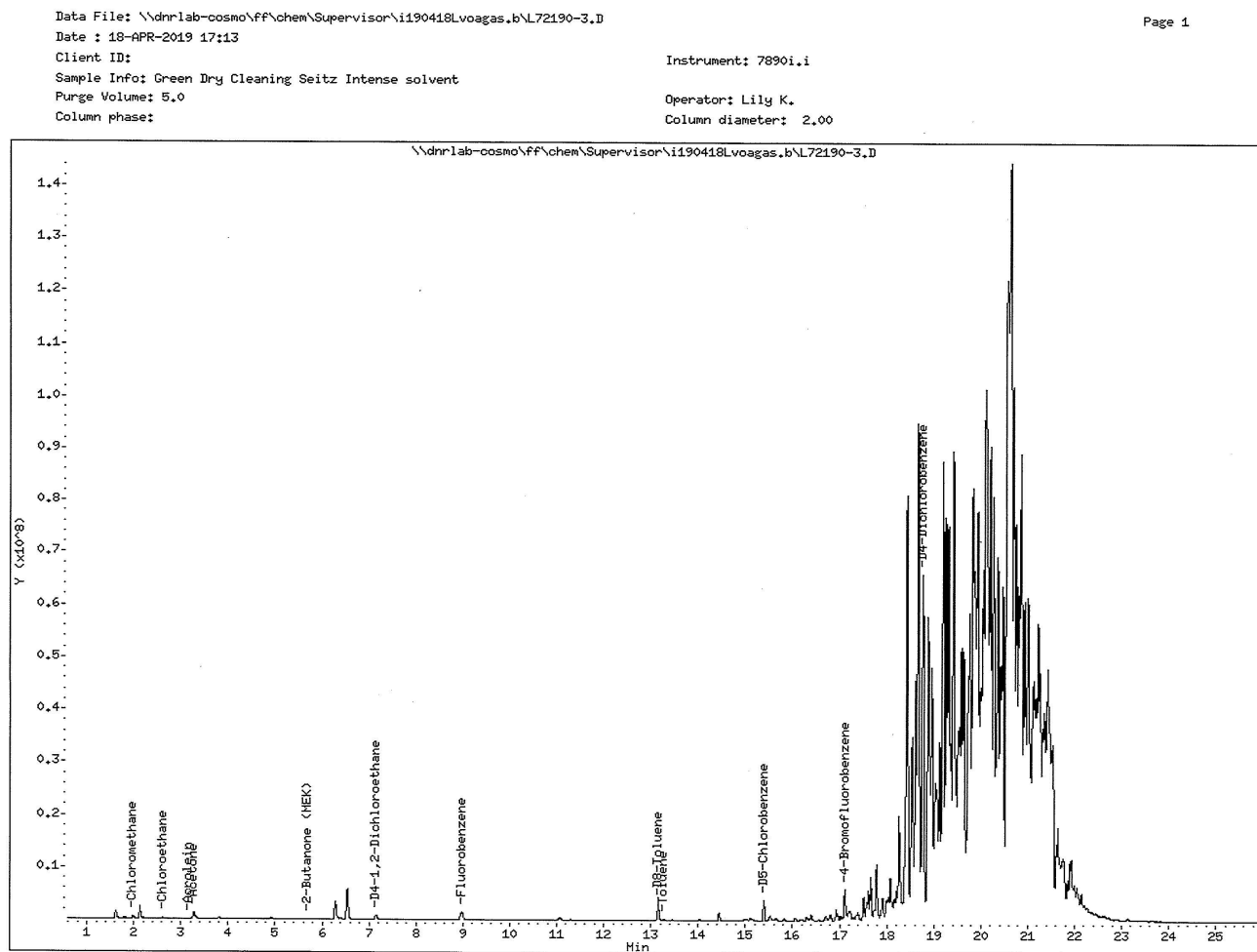


Figure 3. Chromatogram from GC/MS analysis of Intense®



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DISCUSSION

All three solvents were confirmed to contain primarily high molecular weight, multicomponent hydrocarbons, which is consistent with our previous findings for DF-2000TM, EcoSolv[®], and CalypsolvTM.⁽¹⁾

Although benzene was not detected in any samples, several potentially hazardous chemicals were present, albeit at low concentrations. However, the source of these trace levels of target analytes is unclear. We previously detected low levels of PERC in a single sample of EcoSolv[®] and tentatively concluded that it originated from cross-contamination of solvent distribution equipment at the vendor warehouse.⁽¹⁾

Optima DCFTM contained a compound tentatively identified as methyl cyclopentane, which is consistent with the observation made by the chemical manufacturer who brought this solvent to our attention.^e The presence of cyclic hydrocarbons may indicate the use of an inefficient cracking catalyst during petroleum refining.

Intense[®] was confirmed to contain a glycol, which was tentatively identified as a tripropylene glycol compound. However, the CAS no. assigned to this TIC (999157-71-7) does not appear to be valid and likely reflects a limitation associated with the TIC library used by KCEL.^f The CAS no. typically assigned to tripropylene glycol is 24800-44-0 and a search of the EPA Safer Choice database revealed that this is a “Green circle” solvent (i.e., the chemical has been verified to be of low concern based on experimental and modeled data).⁽⁹⁾ In addition, following a review of proprietary ingredient information by the New York State Department of Environmental Conservation (NYSDEC), Intense[®] was approved for use in New York based on a finding of low toxicity.^g

The SDS for SenseneTM states that this product contains a proprietary alkoxypropanol formulation. Examples of this chemical class include propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, and tripropylene glycol monomethyl ether. Although none of these specific compounds were identified in our analyses, several of the TICs found in SenseneTM appeared to belong to this chemical class. Dipropylene glycol methyl ether is also regarded by EPA as a “Green circle” solvent.⁽⁹⁾ As was the case with Intense[®], NYSDEC approved SenseneTM for use in New York following a review of proprietary ingredient information.^g In addition, in its review of dry cleaning solvents, The Toxics Use Reduction Institute assigned propylene glycol ethers to the same mid-level hazard category as pure high-flashpoint hydrocarbons.⁽¹⁰⁾

^e Personal communication with Mark Ng, Technichem, Inc., Hayward, California. December 12, 2018.

^f Personal communication with Michael Doubrava, King County Environmental Laboratory, Seattle, Washington. September 3, 2019.

^g Personal communication with Donald Ward, New York State Department of Environmental Conservation. August 16, 2019.

Although these solvents contained several additional ingredients, the fish bioassay results were identical to the findings from our previous studies with DF-2000™, Calypsolv™, and EcoSolv®. None of these solvents were acutely lethal at the maximum test concentration of 100 mg/L and LD50s could not be determined.

CONCLUSIONS

To our knowledge, this study is the first to evaluate the chemical composition and acute aquatic toxicity of Optima DCF™, Sensene™, and Intense®. Our chemical analyses confirmed that these are complex hydrocarbons that do not contain detectable concentrations of benzene, a common contaminant of petroleum-based solvents. We also found that these solvents are not acutely toxic to fish.

However, we recognize the following limitations of this study:

1. We only evaluated single samples of each solvent, which were provided by vendors in secondary containers. Therefore, we cannot exclude the possibility that the samples were incorrectly labeled or adulterated.
2. A more comprehensive evaluation would involve testing samples from multiple manufacturer's lots. Consequently, it is not clear whether the low concentrations of MEK, acrolein, chloroethane, chloromethane, PERC, and toluene represent product ingredients or contaminants from solvent distribution equipment or another source.
3. Because our chemical analyses focused primarily on volatile organic compounds, other hazardous constituents may be present in these products that would not be detected using our analytical methods.
4. The fish bioassay used in this study was Ecology's standard method for evaluating acute aquatic toxicity and does not address chronic effects. A more comprehensive evaluation of aquatic toxicity would include longer-term tests with a more sensitive test species, such as *Daphnia*.

We conclude that Sensene™ and Intense® are safer alternatives to PERC for dry cleaning. Although Optima DCF™ also appears to be a safer alternative, it would be valuable to have additional information about the source of the petroleum feedstock used to manufacture this product and the catalytic cracking process.

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The following individuals provided a critical review of this report:

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Myles Perkins (Ecology)

Rachel Shaffer (Haz Waste Program and University of Washington)

Don Ward (New York State Department of Environmental Conservation)

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