

Development and Optimization of Analytical methods for
Sulfolane and BTEX Quantification in Environmental samples

by

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A thesis

presented to the University of Waterloo

in fulfillment of the

thesis requirement for the degree of

Master of Science

in

Chemistry

Waterloo, Ontario, Canada, 2025

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Sulfolane is an industrial solvent widely used in various industries, particularly the petrochemical sector. It is highly mobile in the environment due to its water miscibility at slightly above room temperature and minimal adsorption onto most soil types. Furthermore, sulfolane is a relatively stable compound, with aerobic biodegradation serving as its primary degradation pathway. However, its high mobility allows it to contaminate groundwater, where anaerobic conditions can lead to prolonged persistence. Additionally, sulfolane can migrate into fractured rock structures within groundwater zones, where small pores may trap contaminants, further prolonging environmental contamination. Given the large annual volumes of sulfolane usage, accidental releases are inevitable. Despite significant gaps in toxicological research, sulfolane is recognized as a neurotoxin and may disrupt multiple physiological systems, including the circulatory, hepatic, and reproductive systems. Due to these potential health risks, it is crucial to conduct environmental risk assessments, beginning with the measurement of sulfolane concentrations in environmental matrices.

Sulfolane is rarely used in isolation and is often co-released with other organic solvents and chemicals. Its physicochemical properties, particularly its high solubility in both water and organic solvents, can influence the environmental distribution of co-contaminants. One important group of such co-contaminants commonly associated with sulfolane in the petrochemical industry are BTEX (benzene, toluene, ethylbenzene, and xylenes). BTEX compounds are well-established environmental pollutants with documented adverse effects on human health, including neurotoxicity, hematologic malignancies and damage to multiple organ systems. Therefore, monitoring BTEX alongside sulfolane is essential to understanding potential interactions and cumulative risks.

In this study, two gas chromatography-mass spectrometry (GC-MS) methods were developed, optimized, and validated for the quantification of sulfolane in rock and groundwater samples. The methods were designed to be simple and environmentally friendly, minimizing the use of organic solvents. Due to the distinct characteristics of each matrix, tailored extraction techniques were employed.

For rock samples, a microwave-assisted extraction method using methanol was developed to expedite contaminants extraction. The method was validated, and sulfolane stability in methanol extracts was assessed, confirming its stability for up to one year post-collection. The method was applied to 109

rock core samples from a contaminated site in Alberta, Canada, revealing sulfolane contamination in only one sample, while toluene and ethylbenzene were the most prevalent contaminants.

For groundwater samples, an in-vial extraction method utilizing dichloromethane was developed. The method was validated, and assessed for ruggedness. Benzene was identified as the most susceptible to loss during sample preparation. Stability assessments showed that sulfolane remained stable in refrigerated water samples for up to 23 days. The method was then applied to 97 surface water and groundwater samples collected from a contaminated site in Alberta, Canada. Results indicated that sulfolane concentrations exceeded Health Canada's maximum acceptable contamination levels in 17 out of 50 locations, whereas only a few samples exhibited BTEX concentrations exceeding regulatory guidelines.

Overall, this study successfully developed and validated methods for detecting sulfolane in environmental samples, contributing to a better understanding of its distribution in contaminated sites. However, further sampling and analysis are required to comprehensively assess sulfolane's fate and transport at the study site.

Acknowledgements

I would like to express my sincere gratitude to my supervisor, **Dr. Tadeusz Górecki**, for his invaluable guidance, support, and encouragement throughout the course of this research. His expertise and mentorship have been instrumental in shaping this work.

I am also deeply appreciative of my committee members, **Dr. Scott Hopkins** and **Dr. Wojciech Gabryelski**, for their insightful feedback and constructive guidance, which have greatly contributed to the development of this thesis.

I extend my sincere thanks to **Dr. Beth Parker**, head of the Morwick G360 Groundwater Research Group, for providing me with the opportunity to deeply engage in research and expand my knowledge in this field. Her support has been invaluable in facilitating this work.

I am grateful to **Maria Górecka** for her assistance during the initial phase of this project, particularly for sharing her expertise and experience in the use of laboratory instruments. I also appreciate **Jennie Hansson** for her efforts in sample collection and tracking, as well as for helping me understand the broader context of the project. Additionally, I would like to thank **John Chow** for his invaluable assistance in teaching me the intricacies of the instruments used in this research. My gratitude extends to **Rose Wanyonyi** for her assistance with the analysis of rock samples and to **Alexander Sweet** for his support in the analysis of water stability samples.

Finally, I would like to acknowledge the financial support provided by **Shell** and the **Natural Sciences and Engineering Research Council of Canada (NSERC)**, which made this research possible.

I am deeply thankful to **all those who have contributed to this work** in various ways. Their support and collaboration have been invaluable throughout my academic journey.

Dedication

This thesis is dedicated to:

Niloofer, Zohreh, Farshad, Farzad, Fattaneh,

And

Everyone

who has supported me

throughout my education over the years.

Table of Contents

Author's Declaration	ii
Abstract	iii
Acknowledgements	v
Dedication	vi
List of Figures	xi
List of Tables.....	xii
List of Abbreviations.....	xiii
List of Symbols	xv
Chapter 1 Introduction and literature review	1
1.1 Sulfolane.....	1
1.1.1 Physical and chemical properties of sulfolane.....	1
1.1.2 Toxicological studies of sulfolane.....	2
1.1.3 Environmental contamination of sulfolane.....	3
1.2 BTEX.....	4
1.2.1 Physical and chemical properties of BTEX.....	5
1.2.2 Toxicity of BTEX.....	5
1.2.3 BTEX contamination of the environment	6
1.3 Review of sulfolane analytical methods in the published literature	6
1.3.1 Sampling of environmental matrices.....	7
1.3.2 Sample preparation.....	7
1.3.3 Extraction	11
1.3.4 Separation and analysis techniques	19
1.3.5 Direction for the future work.....	28

1.4 Review of BTEX official analytical methods.....	29
1.4.1 EPA official methods	29
1.4.2 Other methods in literature.....	32
1.5 Low permeability media extraction.....	32
1.5.1 Standard extraction method for low-permeability media	34
1.5.2 Extraction at elevated temperature	34
1.6 Microwave-assisted extraction and its fundamentals	36
1.6.1 Mechanism of heating	36
1.6.2 Microwave extraction instrumentation.....	38
1.6.3 Microwave extraction mechanism.....	38
1.6.4 Factors affecting MAE efficiency	39
1.7 Project objectives	40
Chapter 2 Development and Optimization of a GC-MS Analytical Method for Detecting Sulfolane and BTEX in Rock Samples.....	42
2.1 Materials and methods.....	43
2.1.1 Chemicals and reagents	43
2.1.2 Sample collection	43
2.1.3 GC-MS analysis.....	43
2.1.4 Method validation and characterization	44
2.1.5 Extraction time profile and stability of sulfolane	45
2.1.6 Microwave-assisted extraction	45
2.1.7 Analytical method reproducibility assessment.....	46
2.1.8 Analysis of rock samples.....	46
2.2 Results and discussion.....	47

2.2.1 Sample collection	47
2.2.2 Choice of extraction solvent.....	47
2.2.3 GC-MS method of analysis	48
2.2.4 Method validation and characterization	50
2.2.5 Extraction time profile and stability of sulfolane	51
2.2.6 Microwave-assisted extraction optimization	52
2.2.7 Analytical method reproducibility assessment	55
2.2.8 Analysis of rock samples.....	56
2.3 Conclusions	56
Chapter 3 Development and Optimization of a GC-MS Analytical Method for Detecting Sulfolane and BTEX in Water Samples	58
3.1 Materials and Methods	59
3.1.1 Chemicals and reagents	59
3.1.2 Sample collection	59
3.1.3 Sample preparation.....	60
3.1.4 GC-MS analysis.....	60
3.1.5 Method validation and characterization	61
3.1.6 Method ruggedness testing	61
3.1.7 Sample hold time and analytes' stability	61
3.1.8 Analysis of water samples	62
3.2 Results and Discussion.....	62
3.2.1 Sample preparation method.....	62
3.2.2 GC-MS method of analysis	63
3.2.3 Method validation.....	64

3.2.4 Method ruggedness testing	66
3.2.5 Sample stability test.....	70
3.2.6 Analysis of water samples	73
3.3 Conclusions	79
Chapter 4 Summary and future research directions.....	81
References	82

List of Figures

Figure 1-1. Chemical structure of sulfolane.	2
Figure 1-2. Chemical structures of BTEX.	4
<i>Figure 1-3. Full scan mass spectrum of sulfolane</i>	27
Figure 1-4. Permeability as a function of porosity in different type of rocks	33
Figure 1-5. Schematic illustration of the Soxhlet extraction.	35
Figure 2-1. Sample chromatogram of a spiked rock sample.	50
Figure 2-2. Extraction time profile of sulfolane in methanol extracts.	52
Figure 2-3. Microwave-assisted extraction time profile of sulfolane in contaminated rock samples.	54
Figure 2-4. Microwave-assisted extraction time profile of toluene in contaminated rock samples.	54
Figure 3-1. Chromatogram of spiked water sample.	64
Figure 3-2. Pareto charts of the effects of different factors on the response of the instrument for the target analytes.	67
Figure 3-3. Pareto charts of effects of different factors on the ratio of the response of each target analyte to their surrogate standard.	68
Figure 3-4. Stability of target analytes in water samples kept at room temperature.	72
Figure 3-5. Stability of target analytes in water samples kept at 4 °C.	73

List of Tables

Table 1-1. Chemical and physical properties of sulfolane.....	2
<i>Table 1-2. Chemical and physical properties of BTEX.</i>	<i>5</i>
<i>Table 1-3. Summary of sample preparation methods</i>	<i>8</i>
<i>Table 1-4. Summary of separation and determination methods of sulfolane analysis.</i>	<i>21</i>
<i>Table 1-5. Dielectric constants, dielectric losses, and loss tangents of common extraction solvents for microwave-assisted extraction</i>	<i>37</i>
<i>Table 2-1. Retention times, quantifier, and qualifier ions of target analytes</i>	<i>44</i>
<i>Table 2-2. Method validation and characterization statistics</i>	<i>51</i>
<i>Table 2-3. Limits of detection and quantification of the method for a typical rock sample. ..</i>	<i>51</i>
<i>Table 2-4. Microwave-assisted extraction recovery and reproducibility assessment.</i>	<i>55</i>
<i>Table 2-5. Results of the analysis of rock samples for contaminants</i>	<i>56</i>
<i>Table 3-1. Retention times, quantifier, and qualifier ions of target analytes.</i>	<i>60</i>
<i>Table 3-2. Summary of method performance characteristics</i>	<i>65</i>
<i>Table 3-3. Limits of detection and quantification of the analytical method</i>	<i>65</i>
<i>Table 3-4. Plackett-Burman design for the evaluation of method ruggedness.</i>	<i>69</i>
<i>Table 3-5. Results of stability of target analytes in samples kept at room temperature.</i>	<i>70</i>
<i>Table 3-6. Results of stability of target analytes in samples kept at 4 °C.</i>	<i>71</i>
<i>Table 3-7. Results of analysis of the water samples.</i>	<i>74</i>
<i>Table 3-8. Summary of the result of the analysis of water samples</i>	<i>79</i>

List of Abbreviations

ANOVA – Analysis of Variance

BTEX – Benzene, Toluene, Ethylbenzene, and Xylenes

DCM – Dichloromethane

DMSO – Dimethyl Sulfoxide

DMF – Dimethylformamide

DOE – Design of Experiment

EI – Electron Impact Ionization

FCC – Federal Communications Commission

GC – Gas Chromatography

HAE – Heat-Accelerated Extraction

ID – Inner Diameter

LLE – Liquid-Liquid Extraction

LOD – Limit of Detection

LOQ – Limit of Quantification

MAE – Microwave-Assisted Extraction

MS – Mass Spectrometry

PLE – Pressurized Liquid Extraction

Ppm – Parts per million

QC – Quality Control

RSD – Relative Standard Deviation

SD – Standard Deviation

SIM – Selected Ion Monitoring

SLE – Solid-Liquid Extraction

U.S. EPA – U.S. Environmental Protection Agency

VOC – Volatile Organic Compound

List of Symbols

[Insert List of Symbols here.]

Chapter 1

Introduction and literature review ^a

The advancement of civilizations over the past century has been largely driven by industrial activities. Organic solvents are a crucial component of many industries, where they are used extensively. The high demand for products from these industries has resulted in the widespread use of these solvents. Despite efforts to minimize their release into the environment, accidents and improper waste management practices can nevertheless lead to environmental contamination. The presence of these solvents in the environment can have significant health implications for both humans and the ecosystem, highlighting the need for monitoring their concentrations in the environment. Sulfolane, a commonly used solvent in various industries, has emerged as a concern in recent years due to its potential environmental and health impacts.

1.1 Sulfolane

Sulfolane, also referred to as tetramethylene sulfone and tetrahydrothiophene 1,1-dioxide, is a highly versatile industrial solvent with the molecular formula $C_4H_8SO_2$ (**Figure 1-1**)^[2]. Although first mentioned in the literature in 1916, it was not until the 1960s that it became commercially available. Since then, its usage has steadily increased, and it has found a wide range of applications in various fields^[2]. The evidence lies in the tenfold increase in publications dealing with sulfolane over the past two decades. While a fraction of these articles examines the environmental impact, remediation, synthesis pathways or analytical aspects of sulfolane, the majority is dedicated to unveiling its newfound applications.

Sulfolane has become a desirable solvent for many applications in different fields^[2]. In the oil industry, sulfolane is used as an extractive solvent for the separation of benzene, toluene, and xylenes (aromatic hydrocarbons) from aliphatic hydrocarbons, while in the gas treatment processes, it is effective in removing acidic components such as hydrogen sulfide and carbon dioxide from sour natural gas, particularly in the western parts of Canada due to high concentration of H_2S in the gas resources^[2,3]. Sulfolane is also utilized as a solvent for batteries, a plasticizer, and a solvent in the polymer industry, with an estimated annual production of 18,000 to 36,000 tons, reflecting its versatility of function in different fields^[2,4].

1.1.1 Physical and chemical properties of sulfolane

Sulfolane's rise in popularity can be attributed in part to its unique physical and chemical properties (**Table 1-1**)^[5]. These properties include high boiling point, thermal stability, being miscible with a wide

^a A significant portion of this section is based on my review article, "Sulfolane Analysis in Environmental Samples: A Critical Review", published in the journal *Separations*^[1].

range of liquids including water, toluene, acetone, alcohols, and aromatic solvents, but not very soluble in alkanes^[6].

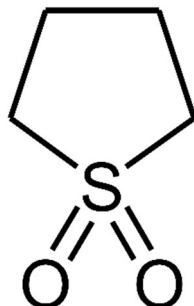


Figure 1-1. Chemical structure of sulfolane.

Table 1-1. Chemical and physical properties of sulfolane

Property	Value	Reference
Molecular formula	C ₄ H ₈ SO ₂	[2]
Molecular weight	120.17 g/mol	[2]
Melting point	28.5 °C	[2]
Boiling point	287.3 °C	[2]
Log P	-0.4	[7]
Solubility in water	Miscible at 30 °C	[8]
pK_a	12.9	[9]
Decomposition temperature	220 °C	[6]

1.1.2 Toxicological studies of sulfolane

Several studies have investigated the toxicity and toxicokinetics of sulfolane over the years. When administered orally, sulfolane is rapidly absorbed in mice and rats, distributed throughout the body, and eliminated with a relatively short half-life^[10]. However, its half-life appears to be dose-dependent, suggesting saturation of the elimination mechanisms at higher doses.

At acute exposure levels, high concentrations of sulfolane exhibit neurotoxic effects. In squirrel monkeys, toxicity manifests as symptoms ranging from vomiting and convulsions to death^[11]. Similarly, dogs exposed

to high, continuous concentrations experienced vomiting, convulsions, and increased aggression^[11]. In rats, sulfolane has been shown to lower the convulsion threshold and induce hypothermia^[12]. While the relevance of these effects to humans remains uncertain, they occur at relatively high doses, typically above 400 mg/kg, with reported LD50 values exceeding 1000 mg/kg^[11–14]. Such dosages are rarely encountered in environmental contamination scenarios and are therefore of limited concern for human health. Instead, the primary concern lies in the potential effects of chronic, low-dose exposure.

In chronic and sub-chronic exposure studies, sulfolane has been found to reduce white blood cell counts and alter hepatic enzyme levels in guinea pigs^[13]. Additionally, inhalation exposure in dogs and rats led to lung inflammation and hemorrhage, although such exposure is unlikely under typical environmental conditions due to sulfolane's high boiling point^[11]. Furthermore, some studies suggest that sulfolane may have reproductive and developmental effects in fetus of rats. While the literature is lacking on the effects of sulfolane on humans and the relevance of such effects to humans is questionable, risk assessment for sulfolane is necessary due to severity of these effects.

1.1.3 Environmental sulfolane contamination

Despite efforts to recover and reuse sulfolane in industrial processes, a small portion of the solvent is lost during each use cycle. For instance, the loss is estimated to be around 5 parts per million (ppm) in the UOP Sulfolane™ commercial process for extracting aromatics from a mixture of hydrocarbons^[15]. This small fraction of sulfolane becomes significant when considering the huge amounts of the solvent used annually. In addition, sulfolane can be released into the environment through direct spillage or improper waste management practices, with reports of sulfolane discharge in different countries including Canada and the US^[4].

Multiple articles and reports have examined fate, remediation, and environmental impacts of sulfolane^[4,16–19]. In brief, due to its chemical stability, sulfolane persists in the environment for a long time when released, and its high solubility in water can lead to contamination of groundwater resources. Furthermore, sulfolane's low adsorption on most soil types means that it can spread over large areas through groundwater after being released into the environment^[16]. For example, at a contaminated site in Waterton, Canada, it is estimated that one square mile around the contamination source has been impacted^[17].

The mobility and toxicity of sulfolane have raised concerns over its spread into environmental media, and natural aerobic biodegradation is the major pathway for sulfolane removal when released into the environment. However, the low oxygen levels in groundwater resources make biodegradation a slow process^[20]. Given the stability of sulfolane under these conditions, it is expected to persist in the environment for a long time after release.

Another concern with sulfolane is that because it is miscible with water and many other organic solvents, such as aromatic compounds, the presence of sulfolane affects the environmental fate of those compounds. One group of compounds that are miscible with sulfolane, frequently found in petrochemical contamination and commonly present along sulfolane in many petrochemical processes, are compounds known as BTEX.

1.2 BTEX

Benzene, toluene, ethylbenzene, and xylenes (**Figure 1-2**), known collectively as BTEX, are classified as volatile organic compounds (VOCs). VOCs are chemicals that have high vapor pressure and hence volatilize easily under ambient conditions. These compounds vary significantly in their environmental or health effects. VOCs have become an increasing concern in recent years due to their wide distribution and persistence in the environment. They are generally characterized by low water solubility, high solubility in lipids, significant vapor pressure, and ability to accumulate in the fatty tissues of living organisms^[21]. BTEX are a group of aromatic hydrocarbons representative of VOCs. They are not only commonly encountered, but in many cases, they are the major component of VOCs.

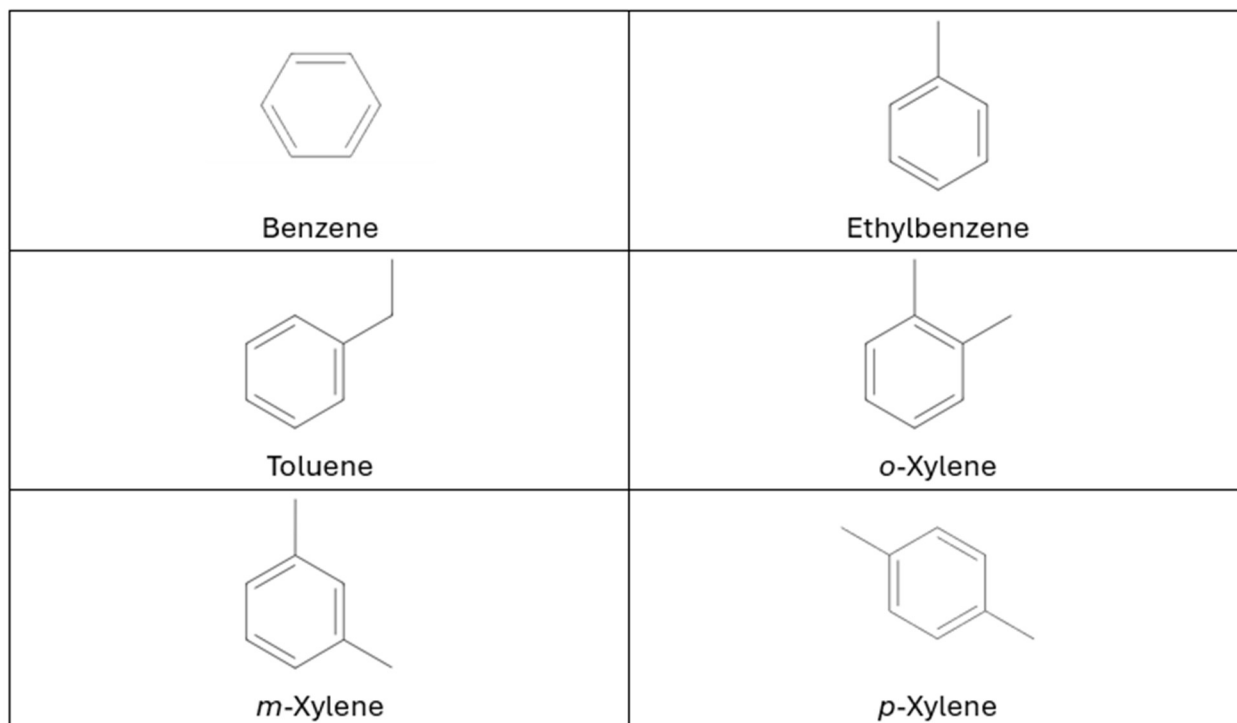


Figure 1-2. Chemical structures of BTEX.

BTEX are crucial petrochemical substances and their usage is very widespread in various industries. They are used in the production of adhesives, dyes, coatings, paints, degreasers, and many other products^[22].

Additionally, they are often used as intermediates in the synthesis of organic compounds and to enhance the performance of gasoline. In fact, as much as 27.5% of high octane gasoline composition might be the BTEX compounds^[23].

1.2.1 Physical and chemical properties of BTEX

The detailed physicochemical properties of BTEX are summarized in *Table 1-2*. Generally, BTEX compounds are characterized by low water solubility, high volatility, and rapid evaporation into the surrounding atmosphere. Furthermore, their high octanol-water partition coefficients (K_{ow}) facilitate bioaccumulation in the lipid-rich tissues of living organisms, owing to their lipophilic nature.

Table 1-2. Chemical and physical properties of BTEX.

	Benzene	Toluene	Ethylbenzene	<i>o</i> -Xylene	<i>m</i> -Xylene	<i>p</i> -Xylene	Reference
Molecular formula	C ₆ H ₆	C ₇ H ₈	C ₈ H ₁₀	C ₈ H ₁₀	C ₈ H ₁₀	C ₈ H ₁₀	-
Molecular weight (g/mol)	78.12	92.15	106.17	106.17	106.17	106.17	-
Boiling point (°C)	80.1	110.6	136.2	138.4	139.1	144.4	[24]
Melting point (°C)	5.5	-95.0	-95.0	13.3	-47.9	-25.2	[24]
Log P	2.13	2.73	3.15	3.12	3.2	3.15	[25]
Solubility in water (mg/L at 25 °C)	1790	526	169	178	161	162	[26,27]

1.2.2 Toxicity of BTEX

BTEX can enter the human body through various routes, including inhalation, ingestion of contaminated food and water, and dermal exposure in cases of direct contact^[28]. They share common adverse health effects, including skin irritation, nervous system disruption and respiratory problems such as bronchitis, as well as headaches and vertigo following acute exposure^[28]. The primary concern associated with BTEX, however, is the risk of chronic exposure, which can have deleterious effects on multiple organ systems, including the central nervous system, respiratory system, and circulatory system^[28–30]. Prolonged exposure to BTEX has been linked to various health problems, including an increased risk of leukemia and other hematologic malignancies^[31]. Additionally, these compounds may impair liver function, as suggested by existing literature^[29].

It is essential to note that each BTEX compound has a distinct toxicity profile. For example, long-term exposure to toluene can cause permanent damage to the central nervous system^[32]. More significantly, benzene is a known human carcinogen, exposure to which can increase the risk of cancer, whereas toluene, ethylbenzene, and xylenes are considered possible human carcinogens^[31]. All BTEX compounds can cross the placental barrier, posing a risk to fetal development if a pregnant woman is exposed^[33]. This is particularly concerning for benzene, which can harm a developing fetus^[31]. Given the severe health consequences associated with BTEX exposure, it is crucial to monitor and potentially remediate environmental contaminations to prevent human exposure.

1.2.3 BTEX contamination of the environment

BTEX can contaminate the environment through three primary sources. The first source is pyrogenic processes, where BTEX are formed during the pyrolysis of coal, petroleum, and other similar materials^[34]. Incomplete combustion of these materials can result in significant releases of BTEX. Another source of BTEX contamination is the petrochemical industry, where leaks or accidents during oil transportation, storage or processing can lead to environmental releases. Additionally, BTEX compounds are used as building blocks in chemical production and are present in various products, such as paints. Improper disposal of chemical waste can also introduce these compounds into the environment. The abundance and widespread use of these compounds make their release into the environment practically inevitable.

Once released, BTEX can pollute various environmental media, including air, water, and soil. The distribution of BTEX between these media depends on the mode of introduction and other factors specific to each medium^[35]. Generally, BTEX tend to partition quickly into the air, where they can be destroyed through processes such as photodegradation^[36]. They can also be biodegraded under aerobic conditions^[37]. However, if released into water-saturated soils, BTEX compounds can exhibit high mobility, contaminating groundwater and potentially leading to persistent pollution^[38]. The limited aerobic conditions in groundwater aquifers can slow down biodegradation, allowing BTEX to persist in the environment. Furthermore, BTEX compounds can penetrate and become trapped in porous rock formations, generating a continuous source of groundwater contamination. Due to these factors, monitoring BTEX contamination in these areas is crucial.

1.3 Review of sulfolane analytical methods in the published literature

Sulfolane is a well-established chemical with a long history of use. As a result, there is a body of research in the literature focused on the measurement of sulfolane in environmental samples. Although these studies did not specifically target the analysis of sulfolane in rock samples, their findings and methodologies can

provide valuable insights for the development of a new analytical approach. To leverage this existing knowledge, a comprehensive literature search was conducted at the outset of the project.

Upon literature examination, only one review article on the subject was identified, dating back more than 20 years^[39]. Subsequently, numerous advancements in analytical techniques and methodologies have emerged and been applied to sulfolane analysis. This literature review aims to offer insights into the present state of sulfolane analysis and its progressive developments over the years, and critically evaluate the methodologies employed.

To obtain the relevant literature on sulfolane analysis, the Web of Science database was utilized with appropriate keywords. A total of 49 articles were selected, which provided methods for analyzing sulfolane. Moreover, an exhaustive search for official methods and governmental guidelines for sulfolane analysis was conducted, which yielded two official methods of analysis. The reported parameters of the analytical methods were organized into different stages of the analytical process and are summarized in the subsequent sections.

1.3.1 Sampling of environmental matrices

Sampling in analytical chemistry is defined as the process of collecting a representative fraction of a material, so that it can be analyzed to determine certain characteristics of the bulk of that material. This step is crucially important in the analytical process because of its immense and immediate effect on the validity of the results^[40]. To achieve representativeness, different matrices require different sampling techniques. There are well-established official sampling procedures for semi-volatile compounds such as sulfolane in different matrices published by the U.S. EPA (Environmental Protection Agency), which must be followed to ensure minimizing the error introduced into the analysis by inappropriate sampling^[41,42].

1.3.2 Sample preparation

Sample preparation is a critical step in sulfolane analysis, as it involves addressing the challenges of low analyte concentrations, and potential co-contaminants that may be present in the sample. Similar to other analytical procedures, sample preparation plays a pivotal role in ensuring accurate and reliable results. The key parameters that vary among different sample preparation procedures include the extraction method, concentration step, and the utilization of internal standards for error correction. These parameters for the reviewed publications are summarized in *Table 1-3*. In the subsequent sections, a selection of these procedures is discussed which reveals useful insights into the proposed research.

Table 1-3. Summary of sample preparation methods. See below for the meaning of the acronyms.

Sample type	Method of extraction	Extraction phase	NO. of extraction aliquots	Solvent to sample ratio (mL:mL or mL:g)	Centrifuge	Filtration	Salting out agent (saturation %)	Water removal of extract	Solvent evaporation (concentration factor)	pH adjustment	Internal standard	Recovery (%)	Reference
Aqueous solution	AQ direct injection	N/A	N/A	N/A	Yes	Filter paper	No	No	No	No	No	N/A	[43]
Aqueous solution	LLE	DCM	3	2:5	No	No	No	No	No	No	No	60 to 70	[44]
Aqueous solution	LLE	DCM	1	2:5	No	Yes	NaCl (80%)	No	No	No	Ethylene glycol butyl ether	N/A	[45]
Aqueous solution	LLE	DCM	1	1:1	No	No	No	No	No	No	No	80	[46]
Aqueous solution	LLE	DCM	1	2:5	No	N/A	No	No	No	No	No	N/A	[47]
Aqueous solution	LLE	DCM	1	2:1	No	No	No	No	No	No	No	80	[48]
Aqueous solution	LLE	Ethyl acetate	1	2:1	No	No	No	No	No	No	No	N/A	[49]
Aqueous solution	LLE	DCM	1	3:5	No	Yes	No	No	No	No	No	80±5	[50]
Aqueous solution	LLE	DCM	1	3:5	No	Yes	No	No	No	No	No	80±5	[51]
Aqueous solution	LLE	Toluene	1	2:1	No	No	No	No	No	No	Sulfolane-d8	N/A	[18]
Aqueous solution	LLE	DCM	1	3:5	No	Yes	No	No	No	No	No	80±5	[52]
Aqueous solution	LLE	DCM	1	3:5	No	Yes	No	No	No	No	No	80±5	[53]
Aqueous solution	LLE	DCM	1	3:5	No	Yes	No	No	No	No	No	N/A	[54]
Aqueous solution	LLE	DCM	1	3:5	No	Yes	No	No	No	No	No	80±5	[55]
Aqueous solution	LLE	DCM	1	1:1	No	0.2 µm PTFE filter	No	No	No	No	No	N/A	[56]
Aqueous solution	LLE	DCM	1	1:1	No	0.2 µm PTFE filter	No	No	No	No	No	N/A	[57]
Aqueous suspension	AQ direct injection	N/A	N/A	N/A	Yes	0.22 µm nylon filter	No	No	No	No	No	N/A	[58]

Sample type	Method of extraction	Extraction phase	NO. of extraction aliquots	Solvent to sample ratio (mL:mL or mL:g)	Centrifuge	Filtration	Salting out agent (saturation %)	Water removal of extract	Solvent evaporation (concentration factor)	pH adjustment	Internal standard	Recovery (%)	Reference
Aqueous suspension	LLE	DCM	3	N/A	N/A	N/A	No	No	No	No	Sulfolane-d8 and nitrobenzene-d8	N/A	[59]
Aqueous suspension	LLE	DCM	1	1:10	No	0.22 µm Teflon filter paper	NaCl (100%)	No	No	No	No	N/A	[60]
Aqueous suspension	LLE	DCM	1	3:5	No	0.45 µm membrane syringe	No	No	No	No	No	N/A	[54]
Biochar	Soxhlet extraction	Ethyl acetate	6	N/A	No	No	No	No	N/A	No	N-butanol	43 to 50	[61]
Ethanol/water (1:1) mix	LLE	Chloroform	1	1:5	No	No	No	Na ₂ SO ₄	No	No	Dicyclohexylmethanol	45.5	[62]
Homogenized water plant tissue mixture	LLE	Toluene	3	5:1	Yes	0.2 µm cellulose acetate membrane filter	No	No	Yes (15)	No	No	80±12	[63]
Homogenized water plant tissue mixture	LLE	Toluene	3	5:1	Yes	0.2 µm cellulose acetate membrane filter	No	No	Yes (15)	No	No	80±12	[64]
Homogenized water plant tissue mixture	LLE	DCM	3	2:5	No	0.2 µm membrane filter	No	No	No	No	No	50 to 60	[44]
Plasma	LLE	Ethyl acetate	1	5:1	Yes	No	Yes	No	Yes (8)	NaOH	Sulfolane-d8	93	[65]
Plasma	LLE	Ethyl acetate	1	5:1	Yes	No	Yes	No	Yes (8)	NaOH	Sulfolane-d8	75 to 89	[66]
Plasma	LLE	Ethyl acetate	1	5:1	Yes	No	Yes	No	No	NaOH	Sulfolane-d8	>85	[67]
PPSF polymer	SLE	Acetonitrile	1	20:1	No	No	No	No	No	No	Dicyclohexylmethanol	N/A	[62]
Soil	SLE	Water	2	5:1	Yes	No	No	No	No	No	No	65 to 102	[68]
Soil	SLE	Water	1 to 3	1:1 to 3:1	Yes	0.45 µm filter	No	No	No	No	No	82 to 99	[69]
Soil	SLE	DCM	1	1:1	Yes	No	No	Na ₂ SO ₄ and NaCl	No	No	Sulfolane-d8	80-120	[70]
Soil	SLE	DCM	3	5:2	Yes	Yes	No	Na ₂ SO ₄	If required	No	Sulfolane-d8	70-120	[71]

Sample type	Method of extraction	Extraction phase	NO. of extraction aliquots	Solvent to sample ratio (mL:mL or mL:g)	Centrifuge	Filtration	Salting out agent (saturation %)	Water removal of extract	Solvent evaporation (concentration factor)	pH adjustment	Internal standard	Recovery (%)	Reference
Soil	Soxhlet extraction	DCM	1	30:1	No	No	No	Na ₂ SO ₄	Yes (3)	No	Sulfolane-d ₈	70-120	[71]
Soil Slurry	AQ direct injection	Water	N/A	N/A	Yes	No	No	No	No	No	No	N/A	[3]
Soil slurry/soil water mix	LLE	DCM	3	1:2	Yes	No	NaCl (80%)	Na ₂ SO ₄	Yes (N/A)	No	Dibenzothiophene	N/A	[72]
Soil water mix	LLE	Toluene	3	5:1	Yes	0.2 µm cellulose acetate membrane filter	No	No	Yes (15)	No	No	126	[64]
Water	AQ direct injection	N/A	0	N/A	Yes	No	No	No	No	No	No	N/A	[73]
Water	AQ direct injection	Water	N/A	N/A	Yes	No	No	No	No	No	No	N/A	[74]
Water	LLE	DCM	1	1:1	Yes	0.2 µm membrane filter	No	Na ₂ SO ₄	No	No	No	N/A	[16]
Water	LLE	DCM	1	1:1	Yes	0.2 µm membrane filter	No	No	No	No	No	N/A	[75]
Water	LLE	DCM	3	1:20	No	Glass wool	No	Na ₂ SO ₄	Yes (15)	NaOH to pH 10	No	N/A	[76]
Water	LLE	Toluene	3	5:1	Yes	0.2 µm cellulose acetate membrane filter	No	No	Yes (15)	No	No	127	[64]
Water	LLE	DCM	1	1:1	No	0.2 µm membrane filter	No	Na ₂ SO ₄	No	No	No	N/A	[77]
Water	LLE	DCM	1	1:10	No	No	NaCl (100%)	No	No	Na ₂ CO ₃ to pH 5-8	No	N/A	[78]
Water	LLE	DCM	1	1:10	No	No	NaCl (100%)	No	No	Na ₂ CO ₃ to pH 5-8	No	N/A	[79]
Water	LLE	DCM	1	5:2	No	0.45 µm PTFE	No	No	No	No	No	N/A	[20]
Water	LLE	1,2-dichloroethane	1	1:1	No	No	No	No	No	No	No	N/A	[80]
Water	LLE	DCM	2	1:1	No	No	Yes	Na ₂ SO ₄	Yes (200)	Yes (pH<2)	Sulfolane-d ₈	80-120	[70]

AQ: Aqueous extract, DCM: Dichloromethane, LLE: Liquid-liquid extraction, SLE: Solid-liquid extraction.

1.3.3 Extraction

Extraction is a widely used process that takes advantage of the differences in chemical distribution between two immiscible phases to separate the constituents of a sample. The ideal objective of extraction is to partition the analytes of interest into one phase while keeping other sample constituents in the other phase, resulting in simplified sample composition and reduced interference from other compounds. The extraction itself might lead to analyte concentration if the volume of the extractant is lower than the sample volume and extraction is exhaustive, i.e. most of the analyte is removed from the sample into the extraction phase^[40].

For sulfolane analysis, two common extraction techniques are liquid-liquid extraction (LLE) and solid-liquid extraction (SLE). In both techniques, a solvent is added to the sample phase, and the analyte partitions into the solvent, which is the extraction phase. The recovery of the extraction process is defined as the fraction of the original analyte that is removed from the sample phase, and transferred to the extraction phase^[40]. The goals of the extraction process are to isolate and concentrate the analyte, and to exchange the sample matrix for one that is compatible with the analytical instrument.

There are several factors that can affect the recovery in sulfolane extraction, which will be discussed in the following sections. Understanding these factors is crucial in optimizing the extraction process for sulfolane analysis, ensuring accurate and reliable results.

1.3.3.1 Extraction solvent

The choice of the extraction solvent plays a crucial role in the recovery and sensitivity of the analysis in various ways. The partitioning of the analyte into the extraction phase is influenced by the characteristics and volume of the extraction solvent, which in turn impacts the fraction of the analyte that gets extracted. To increase the extraction efficiency, multiple aliquots of the solvent can be used to extract the sample repeatedly. This will result in higher recovery of the analyte and by removing most of the analyte into the extraction phase, exhaustive extraction can be achieved. Additionally, higher sensitivities can be achieved by increasing the amount of analyte extracted.

Blowing down the solvent is a technique in which a gentle stream of an inert gas, typically nitrogen, is applied above the sample. This process effectively removes solvent molecules that have evaporated from the liquid surface, preventing their return and thereby accelerating solvent evaporation. As a result, this technique can be employed to preconcentrate analytes. Blowing down the solvent is particularly effective in increasing analyte concentration in the extract and enhancing sensitivity, especially when combined with

multiple aliquot extractions to maximize analyte recovery. However, this approach may not be practical with high boiling point solvents such as water because of the long evaporation time and higher energy requirements. Moreover, when the boiling point of the solvent is high, there is a greater risk of analyte loss due to evaporation, particularly if the boiling point of the analyte is lower than that of the solvent. On the other hand, solvents with low boiling points can be easily evaporated to concentrate the extract or dried to reconstitute the sample in another solvent, resulting in higher concentration and higher sensitivity.

It's important to note that the choice of the extraction solvent also affects gas chromatography (GC) analysis. Typically, the extraction solvent is the same as the final sample solvent. If high boiling point solvents are used for the extraction, it can result in co-elutions with some sample components, leading to the inability to detect some analytes. This highlights the need to carefully consider the boiling point and other characteristics of the extraction solvent in order to optimize the recovery and sensitivity of the analysis. The specific solvents used for the extraction of sulfolane are discussed in the following sections.

1.3.3.1.1 Dichloromethane

As illustrated in *Table 3-1*, dichloromethane (DCM) has been commonly used for the extraction of sulfolane from solid and liquid samples in numerous studies. Despite extensive literature research, no information on the solubility of sulfolane in DCM was found. Nevertheless, reported recovery rates for sulfolane extraction using DCM ranged from 50% to 80% which falls within the acceptable range based on the only two available official methods for sulfolane determination in environmental samples^[70,71]. Despite the acceptable extraction performance demonstrated in various studies, DCM is widely recognized as one of the most harmful solvents to the environment^[81]. One of the reasons for this negative reputation is that DCM has been found to contribute to the delay in the recovery of the ozone layer in the Earth's stratosphere^[82].

For water samples, most studies utilized a single aliquot of DCM for the extraction, with DCM-to-sample ratios ranging from 1:20 ^[76] to 5:2 ^[20], with most being around 1:1. Notably, except for Kim et al., none of the studies exploited the easy evaporation capability of DCM to further concentrate the final samples^[76]. The decision to exclude this step could be attributed to achieving adequate sensitivity in their analyses.

On the other hand, in a study conducted by Doucette et al., water samples were extracted with three aliquots of DCM at a DCM-to-sample ratio of 2:5, and the combined extract was reserved for analysis^[44]. The reported recovery ranged from 60% to 70%, which barely meets the acceptance criteria set by the only two official guidelines for sulfolane analysis in water^[70,71]. The use of three aliquots of solvent for extraction should result in higher extraction efficiency. However, when the reported recovery by Doucette et al. is

compared to similar studies conducted using single aliquot extraction with lower cumulative solvent volumes, such as the studies by Izadifard et al. and Khan et al., the achieved recovery was 10% to 20% lower^[44,46,51]. This is unexpected, as the absolute recovery should be directly proportional to the fraction of the analyte partitioned from the sample into the extraction phase, and theoretically, more aliquots of extraction solvent and higher cumulative volumes should result in higher recoveries.

Since the samples used in the study by Doucette et al. were water samples that did not contain particles for the sulfolane to sorb onto, one explanation for the lower recovery could be the possible difference in extraction temperature, as can be inferred from the study by Li et al.^[44,80]. In this study, they aimed to inspect the suitability of 1,2-dichloroethane for the extraction of sulfolane from an aqueous phase, and they created a ternary system consisting of water, 1,2-dichloroethane and sulfolane in varying proportions. They measured the distribution of sulfolane between the organic and aqueous phases and found that at low concentrations of sulfolane, it tended to be enriched in the organic phase up to 120 times. Additionally, there was an inverse relationship between sulfolane enrichment in the organic phase and temperature in the range of 15 °C to 35 °C. The effect was significant, as the enrichment decreased from 120:1 at 15 °C to 32:1 at 35 °C^[80]. Although no such study has been done for DCM extraction of sulfolane, it can be expected that DCM and 1,2-dichloroethane behave similarly due to their similar structure and properties. This relationship between temperature and sulfolane distribution could be the reason for the significant difference in recoveries observed when using seemingly similar extraction procedures. Furthermore, it would be interesting to explore if and to what extent the distribution of sulfolane in other water-immiscible solvents, such as toluene and ethyl acetate, is affected by temperature.

In another study conducted by Greene et al.^[3], DCM was used for soil sample extraction. The extraction was carried out using a Soxhlet apparatus for 6 hours. Soxhlet extraction is an example of a SLE technique where the analyte is continuously removed by the solvent at its boiling point (Soxhlet extraction is described in detail in Section 1.5.2.2). This method allows higher recoveries, especially for challenging samples, due to the high extraction temperature and circulation of the distilled solvent over the sample^[83]. Following the extraction, the solvent was concentrated using a rotary evaporator, as described by Greene et al.^[74]. Notably, this extraction method is similar to the official soil extraction method used by the government of Alaska, which will be discussed later in this section.

DCM is also the solvent recommended by the only two official guidelines available for sulfolane analysis. In the lab manual for sulfolane analysis by the government of British Columbia, a 100 mL water sample is adjusted to a pH below 2 and then extracted with two aliquots of 100 mL of DCM. The extracted samples are then treated with sodium sulfate to remove water, followed by complete evaporation of the solvent and reconstitution of the sample in 1 mL of isooctane^[70]. Although this procedure results in concentration of

sulfolane in the extract by around a factor of 200, the environmental impact of using 200 mL of DCM for every sample is significant. Scaling down the extraction procedure and reevaluating the need for such high analyte concentration rate may be strategies to reduce solvent usage, especially considering that reasonably low limits of detection (LODs) have been achieved with simpler and less environmentally hazardous procedures^[64]. However, if these methods are to be replaced, extensive validation procedures must be undertaken to ensure their reliability. In contrast, the government of Alaska has not specified any particular method of extraction for water samples but has designated the required performance parameters for the extraction^[71].

For soil samples, the extraction procedure described in the BC lab manual involves adding 1 mL of water to 10 to 12 g of field-moist sample, followed by extraction with 10 mL of DCM. Sodium sulfate, and sodium chloride are added for their water removal, and salting out effect (described in Section 1.3.3.3), respectively. After centrifugation, 1 mL of the extraction phase is reserved for analysis^[70]. Although this method uses much less DCM compared to the official water method, it does not include a concentration step. It may be possible to increase sensitivity by taking a larger portion of the DCM extract and concentrating it through evaporation.

On the other hand, the government of Alaska suggests using EPA method 3550C or preferably 3540C for soil samples^[71]. The EPA method 3550C involves mixing 40 g of soil sample with 60 g of sodium sulfate to remove water, followed by extraction with three 100 mL aliquots of DCM while being sonicated for 3 minutes. The extracts are then filtered and centrifuged to remove any particles^[84]. The EPA method 3540C for soil samples involves mixing 10 g of soil sample with sodium sulfate to remove water, followed by Soxhlet extraction with 300 mL of DCM for 16 to 24 hours. The solvent is then evaporated and reconstituted in 100 mL to 125 mL of DCM^[85]. Both methods use large amounts of solvents and achieve a subtle increase in the concentration of the analyte in the final extracts. Furthermore, Soxhlet extraction is time-consuming and energy-intensive, and is prone to analyte loss for volatile compounds.

For plant tissues, the Alaskan government requires the sample to be ground, frozen using liquid nitrogen, pulverized, and then extracted with water, followed by extraction with DCM^[71]. This method is based on the method by Headley et al., discussed later in Section 1.3.3.1.3, with the difference being that toluene has been replaced by DCM as the extraction phase^[64].

1.3.3.1.2 Water

In order to optimize water extraction conditions for soil samples, Brandao et al. investigated the effects of extraction time, number of extraction steps, and soil-to-water ratio on recovery^[69]. They concluded that

increasing the extraction time from 30 to 90 minutes did not significantly affect the recovery. However, increasing the water-to-soil ratio from 1:1 to 3:1 resulted in an increase in recovery from 82% to 93%. Additionally, three cycles of extraction with a water-to-soil ratio of 2:1 resulted in increased recovery from 85.2% for the first cycle to 97.2% for the second cycle, and 98.9% for the third cycle. To confirm the remaining sulfolane content in the soil after water extraction, Soxhlet extraction with DCM was used^[69]. Although using two or three aliquots of water for the extraction resulted in better recoveries, it may negatively impact sensitivity due to the impracticality of evaporating water and concentrating the final extract. In cases where higher sensitivities are required, a single aliquot of water can be used. However, using only one aliquot of water may result in incomplete extraction, as the recovery is dependent on the partitioning equilibrium, which is influenced by the distribution constant^[83]. The distribution constant can be affected by various factors, such as temperature, the composition of the soil sample, the presence of ionic species in the soil sample, and co-contaminants, all of which add uncontrollable parameters to the analysis.

An alternative solution to address the issues of using water as the extraction solvent is to use a water-immiscible solvent to extract sulfolane from the aqueous extract, as demonstrated by Fedorak et al.^[72]. While this approach may be beneficial in certain scenarios, such as when there are numerous hydrophobic compounds that require clean-up, the limitation of water as an extraction phase in terms of its inability to extract hydrophobic co-contaminants remains unresolved. Moreover, the addition of an additional extraction step introduces another potential source of errors, which can adversely impact the analytical reliability.

Water samples can be directly injected into analytical instruments for analysis without any pretreatment, if the analyte concentration is high enough for detection. This approach, known as direct injection of aqueous samples, eliminates the sample extraction step, which minimizes errors introduced during extraction. However, the samples must be clean and free from excessive constituents, as this method is susceptible to contamination of the analytical instrument. Therefore, this method may not be suitable for “dirty” samples such as wastewater. To extend the applicability of this technique, centrifugation and sample filtration can be employed to separate the aqueous phase for samples that may contain particles, such as soil slurries^[3]. In cases where filtration is used, it is important to confirm that the analyte does not adsorb onto the filter, as demonstrated by Yu et al. in their study for nylon filters^[58].

In an uncommon and novel extraction method, water was used in an ordinary espresso machine to extract sulfolane from biochar. The authors concluded that ground biochar extraction with water in an espresso machine is more efficient than ethyl acetate extraction with Soxhlet for six solvent cycles or dispersion of biochar in ethyl acetate for 48 hours with initial ultrasonication for 45 minutes. They also reported a loss of sulfolane when they tried to evaporate water at 60 °C or 104 °C in the presence of biochar due to unknown

reasons^[61]. This method of extraction is a simple and inexpensive setup for PLE. Considering the 10 to 20 bars of pressure offered by these machines, they can be considered low-pressure liquid extractors. However, since the extraction is performed with water just below its boiling point, it cannot be used for the simultaneous extraction of volatile co-contaminants. Additionally, although the authors achieved reproducible recoveries based on their limited set of experiments, it is interesting to see how reproducibly this machine performs over time, as most of these machines lose pressure as they age.

1.3.3.1.3 Toluene

Toluene has been utilized as a solvent for extracting sulfolane from water samples^[64]. Notably, it has been employed for the back-extraction of sulfolane from soil or plant tissue extracts. The reported recoveries for direct water extraction and the extraction of water extract from soil samples were remarkably high at 127% and 126%, respectively^[64]. However, no explanation was provided for these high recoveries, but it is possible that matrix effects, non-symmetric solubility of sulfolane in the toluene-water system formed during the extraction and the high extraction efficiency of toluene for sulfolane contributed to these results^[86]. It should be noted that the high boiling point of toluene may hinder the analysis of volatile co-contaminants by GC.

The high extraction efficiency of toluene for sulfolane has been effectively utilized in the extraction of sulfolane from plant tissue samples by Headley et al.^[64]. In their procedure, they homogenized plant tissue in Mili-Q water to extract the sulfolane into the aqueous phase. In a slightly different approach, they ground the plant tissue to a fine powder using liquid nitrogen and then suspended it in Mili-Q water. In both cases, the tissue was left in water for 40 minutes with intermittent swirling. Subsequently, they centrifuged and filtered the supernatant to remove any particles. Next, they back-extracted the aqueous extract with three aliquots of toluene. The toluene portions were combined, and the extract was concentrated 15 times using nitrogen blowdown before being reserved for analysis by GC-MS. The average recovery achieved was 80.3% with an RSD of 11%. Notably, the method's performance was maintained over a period of 18 months, indicating its ruggedness^[64].

The decision to use water as an intermediate extraction solvent for plant tissue is reasonable due to the hydrophilic nature of plant tissue. By leaving the tissue in an aqueous solution, water can penetrate and swell the tissue, allowing for better dissociation and partitioning of the analytes into the bulk of water. Aprotic organic solvents, on the other hand, do not swell the tissue and poorly penetrate it, resulting in poor extraction efficiency. Since these compounds have low water solubility, using water as an intermediate extraction solvent can help minimize their interference. Therefore, water is a preferable choice over other protic solvents, such as methanol. Additionally, the use of water as an intermediate solvent also serves as a clean-up step. However, the relatively low recovery rate of 80% compared to soil and water samples in the

study suggests possible adsorption of sulfolane onto the plant tissue, which needs to be monitored when developing a method for plant tissue analysis.

1.3.3.1.4 Ethyl acetate

Ethyl acetate has been successfully used for plasma sample extraction with good recoveries, as demonstrated in a study by Versace et al.^[65]. Considering that plasma is a complex aqueous solution with many constituents, it is reasonable to explore the use of ethyl acetate for sulfolane extraction from water samples, and potentially environmental samples. Moreover, ethyl acetate is known to have minimal impact on the environment^[81].

In the study by Versace et al., the extraction procedure involved adjusting the pH of 100 μL of plasma by adding 50 μL of 1 M sodium hydroxide, resulting in a highly basic pH that caused aggregation of plasma proteins. Subsequently, the plasma was extracted with 500 μL of ethyl acetate, followed by centrifugation to separate the organic phase. Next, 50 μL of isopropanol were added to the ethyl acetate extract, and the ethyl acetate was evaporated using N_2 gas to concentrate the extract approximately by a factor of 5. The remaining isopropanol extract was reserved for analysis. Despite the complexity of the plasma sample and the abundance of constituents in the matrix that could potentially sorb sulfolane, the study achieved a remarkable recovery rate of 93%^[65].

The addition of sodium hydroxide facilitates protein denaturation and reduces the matrix effects typically associated with plasma samples. However, the resulting high pH can lead to hydrolysis of ethyl acetate, producing ethanol and acetic acid. This transformation is undesirable, as it may be non-reproducible and subject to variability due to multiple experimental factors. A notable feature of this extraction procedure is the use of small volumes of samples and solvents, which is evident upon inspection. Additionally, as mentioned earlier, the environmental impact of ethyl acetate is comparatively low. When compared to the government of Alaska official method for sulfolane extraction from soil samples, the solvent usage in the study by Versace et al. is three orders of magnitude lower^[65,71]. Furthermore, similar studies, such as the one by Silinski et al., support the possibility of using ethyl acetate for sulfolane analysis^[66]. In fact, Heydari et al. used ethyl acetate for water sample extraction, although no information about the extraction performance was provided in their publication^[49]. However, it is worth noting that DCM has been used as a replacement for ethyl acetate in their recent publications^[19,53]. This may be due to the inadequate extraction performance of ethyl acetate in their procedure, possibly resulting from the lack of addition of a salt or other ionic strength modifier (discussed in Section 1.3.3.3)^[49].

1.3.3.2 Other solvents

Acetonitrile has been utilized as an extraction solvent to extract residual sulfolane content from ground polyphenyl sulfone polymers, as reported by Eckardt et al.^[62]. In the same study, chloroform was also used for extracting sulfolane from an ethanol-water (50:50) mixture to analyze the sulfolane leaching extent from bottles using the ethanol-water mixture as a food simulant. Although efficiency parameters were not reported, all three solvents - ethanol, acetonitrile, and chloroform - have the potential to be used as extraction solvents for sulfolane^[62]. It's worth noting that while chloroform is as hazardous to the environment as DCM, acetonitrile is less hazardous, and ethanol is considered one of the most environmentally friendly solvents^[81].

On the other hand, 1,2-dichloroethane has been investigated as an extraction solvent for sulfolane from water samples. However, it poses environmental hazards similar to DCM and has a higher boiling point, resulting in longer blowout time, greater risk of analyte loss, and increased risk of co-elution with volatile compounds in GC analysis.

1.3.3.3 Salting out effect

In two-phase solvent systems used for extraction, a fraction of the organic phase can dissolve in the water phase. This fraction can be significant, reaching up to 8% for solvents like ethyl acetate^[87], while for highly non-polar solvents like toluene, it is typically below 1%^[86]. This dissolved organic phase can reduce the activity coefficients of the analytes in water and the partitioning coefficients of the solutes between the organic phase and water. To mitigate this effect, an electrolyte can be added to the aqueous phase, which limits the fraction of the organic phase that dissolves in water and increases the aqueous activity coefficients of the analytes, thus improving the extraction efficiency^[87]. For instance, sodium chloride at 80% of its saturation concentration ^[45,72] or at its saturation concentration ^[60,78,79] has been used to enhance the partitioning of sulfolane into DCM, which served as the organic phase. Similarly, in the study conducted by Versace et al., adjusting the pH of water by adding sodium hydroxide increased the ionic strength, which consequently improved the extraction efficiency of sulfolane^[65].

1.3.3.4 pH adjustment

If a species undergoes dissociation at the extraction pH, mostly the undissociated fraction of the analyte will actively participate in the partitioning equilibrium, while the ionized species will predominantly remain in the aqueous phase^[40]. Hence it is crucial to adjust the pH in a way that most of the analyte stays in the non-dissociated form during the extraction procedure. However, because of the high pK_a value (12.9), sulfolane does not dissociate significantly in the pH range typical of environmental samples. Hence, pH

adjustment might not be necessary for most samples. It should be pointed out that it is required by the official method suggested by the government of BC for water samples^[70]. One of the possible reasons for using pH adjustment in sulfolane analysis might be to limit the extraction of matrix co-contaminants. For instance, this principle has been exploited by Versace et al., Shipkowski et al., and Silinski et al. in plasma samples to aggregate and discard proteins present in the matrix^[65–67].

1.3.4 Separation and detection techniques

Despite the various extraction methods discussed in the literature, there has been limited diversity in the separation and analytical techniques utilized for the determination of sulfolane. Almost all researchers have employed GC to analyze sulfolane due to the low sensitivity of common LC detectors for this compound. Sulfolane does not absorb UV light at wavelengths that can be distinguished from the mobile phase, and thus cannot be detected by UV-DAD detectors. Furthermore, it is not efficiently ionized by ESI, leading to inadequate sensitivity of LC-MS systems^[63]. In contrast, sulfolane is completely compatible with the two most widely used GC detectors, FID and MS. In the following sections, the conditions and configurations reported for the GC analysis of sulfolane are summarized.

1.3.4.1 GC inlet

All of the reviewed studies utilized the split/splitless type of inlet. In this inlet system, the temperature must be high enough for all sample components to have sufficient vapor pressure to be transferred effectively into the column. As shown in **Table 1-4**, temperatures in the range of 165 °C to 300 °C were successfully employed for sulfolane analysis.

With the split/splitless inlet system, different modes of injection can be used for introducing the sample into the GC column. Several studies have utilized split mode injection, as shown in **Table 1-4**. In this injection mode, the sample is vaporized, but most of the vapor exits the inlet through a split vent, and only a small fraction of the vapor is transferred into the capillary column. This injection mode is ideal for injecting high-concentration samples, often eliminating the need for sample dilution. Additionally, thanks to a narrow injection band, narrower peaks can be achieved in this mode^[88]. However, since the concentration of sulfolane is typically low in environmental samples, more concentration must typically be performed in the sample preparation step to analyze the samples in this mode.

In most studies, the splitless mode of injection has been used, as indicated in **Table 1-4**. In this mode, most of the sample vapor is carried by the carrier gas into the column. Since the transfer of the vapor into the column could take several seconds to minutes depending on the carrier gas flow rate and inlet volume, the initial temperature of the column oven must be lower than the boiling point of the sample solvent to refocus the injection band on the column head through solvent effect and prevent peak widening due to

wide initial injection band^[88]. Since most of the analyte is transferred into the instrument, this type of injection results in higher sensitivity and is useful when the analyte concentration in the sample is low.

Table 1-4. Summary of separation and determination methods of sulfolane analysis. See below for the meaning of the acronyms.

Sample type	Sample solvent	Carrier gas	Carrier gas flow rate/Pressure	Mode of injection	Injection volume	Inlet temperature (°C)	Type of column	Column stationary phase	Column dimensions	Detector	LLOD	LLOQ	detector temperature (°C)	Reference
Aqueous solution	DCM	N ₂	10 mL/min	N/A	N/A	N/A	WCOT	DB-5	30m×0.45mm×0.25µm	FID	N/A	N/A	N/A	[44]
Aqueous solution	Water	N ₂	360 mL/min	Splitless	N/A	280	SCOT	OS-138	7.5m×0.51mm	FID	6 mg/L	N/A	N/A	[43]
Aqueous solution	DCM	He	1 mL/min	Splitless	1	250	WCOT	DB-WAXetr	30m×0.32mm×1µm	MS	N/A	N/A	N/A	[45]
Aqueous solution	DCM	He	250 KPa	Splitless	2	165	WCOT	ZB-5	N/A	FID	1 mg/L	N/A	250	[46]
Aqueous solution	DCM	He	10 mL/min	Splitless	2	250	WCOT	ZB-5	N/A	FID	N/A	N/A	320	[47]
Aqueous solution	DCM	He	250 kPa	Splitless	2	165	WCOT	ZB-5	N/A	FID	1 mg/L	N/A	250	[48]
Aqueous solution	Ethyl acetate	N/A	N/A	N/A	N/A	N/A	WCOT	ZB-5	N/A	FID	N/A	N/A	N/A	[49]
Aqueous solution	DCM	He	1.07 mL/min	Splitless	1	250	WCOT	ZB-5	N/A	MS	10 µg/L	N/A	N/A	[50]
Aqueous solution	DCM	He	1.07 mL/min	Splitless	1	250	WCOT	ZB-5	N/A	MS	10 µg/L	N/A	N/A	[51]
Aqueous solution	Toluene	He	1 mL/min	Splitless	0.5	285	WCOT	DB-5	30m×0.25mm×0.25µm	MS	20 µg/L	70 µg/L	Ion source: 285	[18]
Aqueous solution	DCM	He	1.07 mL/min	Splitless	1	250	WCOT	ZB-5	N/A	MS	10 µg/L	N/A	N/A	[52]
Aqueous solution	DCM	He	1.07 mL/min	Splitless	1	250	WCOT	ZB-5	N/A	MS	10 µg/L	N/A	N/A	[53]
Aqueous solution	DCM	He	N/A	Splitless	1	165	WCOT	ZB-5	N/A	FID	0.3 mg/L	1 mg/L	330	[89]
Aqueous solution	DCM	He	1.07 mL/min	Splitless	1	250	WCOT	ZB-5	N/A	MS	10 µg/L	N/A	N/A	[55]

Sample type	Sample solvent	Carrier gas	Carrier gas flow rate/Pressure	Mode of injection	Injection volume	Inlet temperature (°C)	Type of column	Column stationary phase	Column dimensions	Detector	LLOD	LLOQ	detector temperature (°C)	Reference
Aqueous solution	DCM	He	1.07 mL/min	Splitless	1	165	WCOT	ZB-5	N/A	FID	N/A	N/A	330	[56]
Aqueous solution	DCM	He	1.07 mL/min	Splitless	1	165	WCOT	ZB-5	N/A	FID	N/A	N/A	330	[57]
Aqueous suspension	Water	He	N/A	Splitless	1	165	WCOT	ZB-5	N/A	FID	1 mg/L	N/A	250	[58]
Aqueous suspension	DCM	N/A	N/A	Pulsed-splitless	N/A	N/A	WCOT	RTX-200	30m	MS	N/A	40 µg/L	N/A	[59]
Aqueous suspension	DCM	N ₂	N/A	Splitless	1	200	WCOT	Stabliwax	30m×0.53×1µm	FID	N/A	N/A	250	[60]
Aqueous suspension	DCM	He	N/A	Splitless	1	N/A	WCOT	5-MSI	N/A	FID	N/A	N/A	330	[54]
Biochar	Ethyl acetate	He	N/A	Split (10:1)	1	N/A	WCOT	ZB-Wax-Plus	30m×0.32mm×0.5µm	FID	10 mg/L	N/A	N/A	[61]
Ethanol/water (1:1) solution	Chloroform	He	1 mL/min	Splitless	1	N/A	WCOT	HP-5	30m×0.25mm×0.25µm	MS	10 µg/Kg of Ethanol/water (1:1)	N/A	N/A	[62]
Homogenized water plant tissue mixture	Toluene	He	25 cm/s	Splitless	N/A	250	WCOT	DB-5	25m×0.25mm×0.25µm	MS	90 ng/g of wet plant tissue	300 ng per g of wet plant tissue	Ion source: 280	[63]
Homogenized water plant tissue mixture	Toluene	He	25 cm/s	Splitless	N/A	250	WCOT	DB-5	25m×0.25mm×0.25µm	MS	90 ng/g of wet plant tissue	300 ng per g of wet plant tissue	Ion source: 280	[64]
Homogenized water plant tissue mixture	DCM	N ₂	10 mL/min	N/A	N/A	N/A	WCOT	DB-5	30m×0.45mm×0.25µm	FID	N/A	N/A	N/A	[44]
Plasma	Isopropanol	He	1 mL/min	Splitless	1	250	WCOT	ZB-5	15m×0.25mm×0.25µm	MS/MS	N/A	20 µg/L	Ion source: 200	[65]
Plasma	Isopropanol	He	1 mL/min	Split (50:1)	1	250	WCOT	DB-5	30m×0.25mm×0.25µm	MS	0.516 µg/L	20 µg/L	Ion source: 230	[66]

Sample type	Sample solvent	Carrier gas	Carrier gas flow rate/Pressure	Mode of injection	Injection volume	Inlet temperature (°C)	Type of column	Column stationary phase	Column dimensions	Detector	LLOD	LLOQ	detector temperature (°C)	Reference
Plasma	Ethyl acetate	He	1 mL/min	Split (50:1)	1	250	WCOT	DB-5	30m×0.25mm×0.25µm	MS	1.25 µg/L	N/A	Ion source: 230	[67]
PPSF polymer	Acetonitrile	He	1 mL/min	Splitless	1	N/A	WCOT	HP-5	30m×0.25mm×0.25µm	MS	N/A	N/A	N/A	[62]
Soil	Water	He	25 mL/min	Splitless	2	250	Packed	Tenax-GC coated with 5% polyphenyl ether	1.2m×0.32cm	FID	1 mg/L	N/A	250	[68]
Soil	DCM	He	250 KPa	Splitless	1	250	WCOT	ZB-5	N/A	MS	<1 mg/L	<1 mg/L	330	[69]
Soil slurry	Water	He	24 mL/min	Splitless	2	250	Packed	Tenax-GC coated with 5% polyphenyl ether	2m×0.3cm	FID	0.5 mg/L	N/A	250	[3]
Soil slurry or soil water mixture	DCM	N/A	N/A	Split (20:1)	N/A	250	WCOT	DB-5	25m×0.25mm×0.25µm	FID	N/A	N/A	250	[72]
Soil water mixture	Toluene	He	25 cm/s	Splitless	N/A	250	WCOT	DB-5	25m×0.25mm×0.25µm	MS	90 ng/g of wet plant tissue	N/A	ion source: 280	[64]
Water	Water	N ₂	30 mL/min	Splitless	2	250	Packed	Tenax-GC coated with 5% polyphenyl ether	1.8m×0.32cm	FID	5 mg/L	N/A	250	[73]
Water	Water	He	25 mL/min	Splitless	2	250	Packed	Tenax-GC coated with 5% polyphenyl ether	1.2m×0.32cm	FID	1 mg/L	N/A	250	[74]
Water	DCM	He	1.7 mL/min	N/A	N/A	300	WCOT	DB-5	30m×0.25mm×0.25µm	FID	N/A	N/A	350	[16]
Water	DCM	He	N/A	N/A	N/A	N/A	WCOT	DB-5	30m×0.25mm×0.25µm	FID	N/A	N/A	N/A	[75]
Water	DCM	He	1.7 mL/min	Split (N/A)	5	300	WCOT	DB-5	30m×0.25mm×0.25µm	FID	N/A	N/A	350	[76]

Sample type	Sample solvent	Carrier gas	Carrier gas flow rate/Pressure	Mode of injection	Injection volume	Inlet temperature (°C)	Type of column	Column stationary phase	Column dimensions	Detector	LLOD	LLOQ	detector temperature (°C)	Reference
Water	Toluene	He	25 cm/s	Splitless	N/A	250	WCOT	DB-5	25m×0.25mm×0.25µm	MS	1 ng/mL	N/A	ion source: 280	[64]
Water	DCM	He	1.7 mL/min	N/A	N/A	300	WCOT	DB-5	30m×0.25mm×0.25µm	FID	N/A	N/A	350	[77]
Water	DCM	He	N/A	N/A	0.2	200	WCOT	Stabliwax	30m×0.53×1µm	FID	N/A	N/A	250	[78]
Water	DCM	He	N/A	N/A	0.2	200	WCOT	Stabliwax	30m×0.53×1µm	FID	N/A	0.44 mg/L	250	[79]
Water	DCM	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	FID	1 mg/L	N/A	N/A	[20]
Water	1,2-dichloroethane	N ₂	4.5 mL/min	Split (8:1)	0.2	250	WCOT	DB-FFAP	30m×0.53×1µm	FID	N/A	N/A	250	[80]

DCM: Dichloromethane, LLOD: Lower limit of detection, LLOQ: Lower limit of Quantification, SCOT: Support coated open tubular column, WCOT: Wall coated open tubular column.

In a study by Kasanke et al., pulsed splitless mode of injection was utilized^[59]. In this mode, the pressure, and consequently the carrier gas flow rate, is raised temporarily. The vaporized sample is transferred into the column faster and more effectively by the increased flow of the carrier gas, and the injection band is consequently narrower. Additionally, since the pressure in the inlet is higher at the time of injection, solvent expansion volume is smaller, and larger volumes of sample can be injected. The larger injection volume and narrower injection band both lead to increased sensitivity^[90].

1.3.4.2 GC column

In earlier publications, there are reports of using packed columns for GC analysis of sulfolane. However, recent studies have exclusively employed capillary columns due to their higher separation efficiency. In the following sections, the properties of these capillary columns are outlined. For complete specifications of the columns used in each study, please refer to *Table 1-4*.

1.3.4.2.1 Stationary phase

The majority of studies on sulfolane have utilized non-polar columns coated with (5%-phenyl)-methylpolysiloxane as the stationary phase. This type of stationary phase results in weak retention of sulfolane, and consequently, the elution time is quite short. However, if other polar compounds or volatile non-polar compounds are present in the sample, they may co-elute with sulfolane. On the other hand, several researchers employed columns with more polar stationary phases, specifically polar polyethylene glycol^[45,61], and mid-polar trifluoropropyl methyl polysiloxane^[59].

Due to the high polarity of sulfolane, polyethylene glycol columns retain it strongly, and the analysis time is typically longer due to the lower maximum temperature limit of these columns. Therefore, the use of polyethylene glycol columns is only justified when there are polar components in the sample that need to be separated from sulfolane for reliable analysis.

In the study by Kasanke et al., mid-polar trifluoropropyl methyl polysiloxane columns were used to exclude hydrocarbon co-contaminants that might have been present in the samples^[59].

1.3.4.2.2 Column dimensions

The dimensions of the capillary columns used for sulfolane analysis vary in length from 15 m to 30 m, in inner diameter (ID) from 0.25 mm to 0.53 mm, and in film thickness from 0.25 μm to 1 μm (*Table 1-4*). While longer columns may provide better separation, they result in prolonged analysis time, which

can lead to band broadening and reduced sensitivity. Therefore, it is recommended to choose the shortest column that can separate the sample components^[88].

Columns with narrower diameters and thinner films result in higher chromatographic resolution, but have lower sample capacity. This is not a major issue for detection with MS, which is characterized by high analytical sensitivity. In the case of FID detectors, thicker stationary phases may be preferred to achieve higher sensitivity through the use of larger injection volumes ^[88].

1.3.4.3 GC detectors

Both MS and flame ionization detectors (FID) are commonly used for sulfolane analysis. However, MS provides superior sensitivity and selectivity compared to FID. In fact, reported LODs for MS range from 0.516 µg/L to 20 µg/L, while FID LODs range from 500 µg/L to 6000 µg/L in aqueous samples. Additionally, MS allows for the use of isotopically labeled internal standards, which results in better accuracy and precision.

Electron impact ionization (EI) is the preferred method for all mass spectrometric techniques. The mass spectrum shown in Figure 2 indicates that the molecular ion for sulfolane appears at m/z 120, with two abundant fragment ions at m/z 41 and 56, corresponding to the loss of SO_2CH_3 and SO_2 , respectively. Different publications have used either the ion at m/z 120 or 41 for quantification, but Headley et al. reported 5 times higher sensitivity when using m/z 41 as the quantifier ion^[63]. The molecular ion at m/z 120, however, offers significantly higher selectivity, as it is more specific to sulfolane.

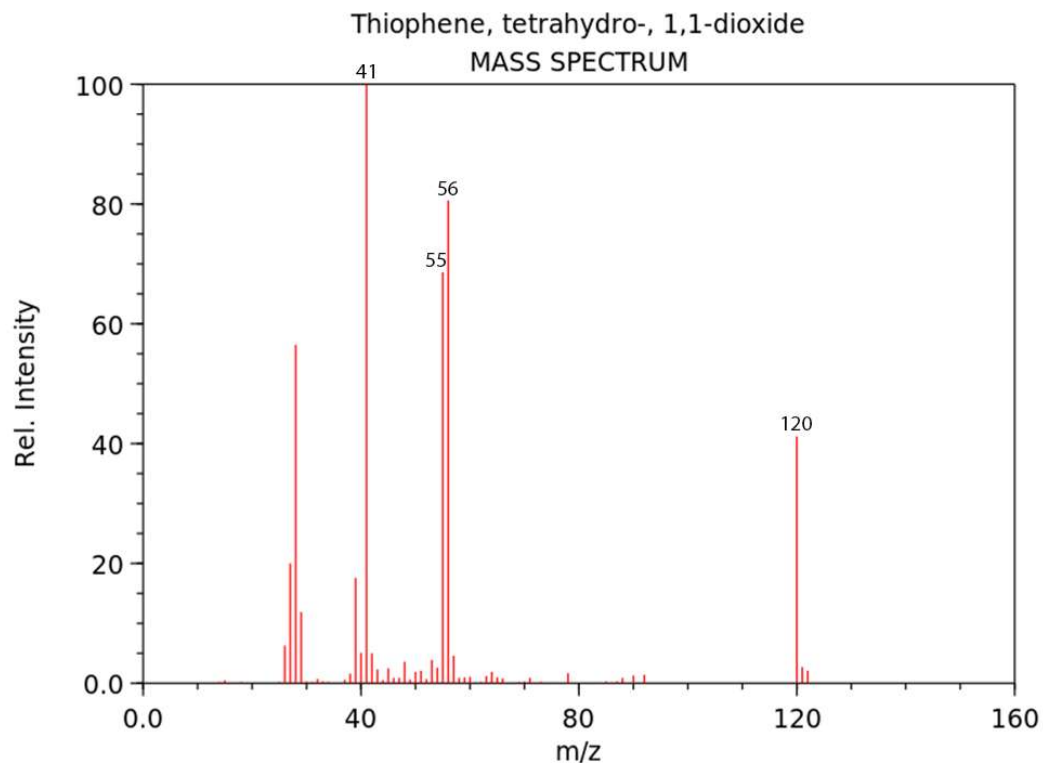


Figure 1-3. Full scan mass spectrum of sulfolane. The spectrum is taken from NIST website (Thiophene, Tetrahydro-, 1,1-Dioxide, 2014)^[91]. The most abundant fragment ions appear at m/z 41, 56, and 55, and the molecular ion appears at m/z 120.

In the official method by the government of Alaska, the molecular ion of sulfolane, which appears at m/z 120 in the mass spectrum, is required to be used as the quantifier ion for sulfolane detection. Additionally, the ions at m/z 41, 55, and 56 are specified as qualifier ions, corresponding to the loss of CH_3SO_2 , $\text{C}_2\text{H}_4\text{SO}_2$, and $\text{C}_2\text{H}_5\text{SO}_2$ fragments, respectively^[71]. On the other hand, the official method by the government of BC does not specify any particular ion for the detection of sulfolane using MS^[70].

1.3.4.4 Internal standard

An internal standard is a compound added at a known level to samples, standards, and blanks to correct for analysis errors. Two approaches are employed for adding internal standards. In the first approach, internal standards are added before sample processing (surrogate standards). This method allows the standards to correct errors at all stages of the analysis, including sample preparation,

separation, and final determination. However, it's crucial to choose an internal standard that would not be present in the samples, and mimics the partitioning, injection, separation, and detector response profile of the original compound. This can be challenging when using a non-selective detector, such as FID^[40].

In contrast, when using mass spectrometry (MS), isotopically labeled compounds can serve as internal standards. These compounds have the same molecular structure as the analyte, but some of their atoms are replaced by their stable isotopes. This method provides a close match between the chemical and physical properties of the internal standard and the original compound, but MS can separate the former from the analyte due to its different molecular weight and slightly different retention time^[40]. A common isotopically labeled internal standard for sulfolane analysis is sulfolane-d8, which has been employed in several studies listed in *Table 1-4*, and is required by the official methods for sulfolane analysis^[70,71].

The second approach involves adding the internal standard directly to the final sample before injection and analysis. This type of internal standard addition is mostly used to correct errors introduced by the analytical instrumentation, such as uncertainty in injection volume or differences in analysis conditions at different times. In this case, any compound that would not be present in the samples can serve as an internal standard. Naphtalene-d8 is required as this type of internal standard in the Alaskan government's official method for sulfolane analysis^[71].

1.3.5 Direction for the future work

Upon examining the existing literature on sulfolane analysis, it becomes apparent that there is a noticeable gap when it comes to analytical methods that can simultaneously determine potential co-contaminants along with sulfolane. This is true for all environmental matrices including soil and water. Furthermore, aside from the official method based on Soxhlet extraction approved by the government of Alaska, other sample preparation procedures have overlooked the heat stability of sulfolane and the potential benefits of extracting it at elevated temperatures for quicker extraction. While this may not be essential for water and highly permeable soil samples due to the already rapid extraction procedures, it becomes evident that elevated temperature could prove advantageous when dealing with plant tissue and low permeability media such as rocks. In Section 1.5, the principles and the complexity of low permeability media extraction are detailed.

1.4 Review of BTEX official analytical methods

Unlike sulfolane, BTEX compounds are well-established environmental contaminants that have been extensively studied in the scientific literature. The U.S. Environmental Protection Agency (EPA) has developed standardized methods for analyzing VOCs in environmental matrices, including BTEX.

1.4.1 EPA official methods

The EPA-approved methods for VOC analysis in environmental samples include Methods 5021A, 5030C, 5032, 8015C, 8021B, and 8260D, all of which explicitly specify their applicability to BTEX analysis. A concise overview of these methods is provided in the following section.

1.4.1.1 Sample preparation and introduction

EPA Methods 5021A, 5032, 5030C, and 5035 outline the sample preparation procedures for analyzing BTEX compounds in environmental samples^[92]. These include vacuum distillation, as well as static and dynamic headspace analysis.

1.4.1.1.1 Static headspace analysis

EPA Method 5021A describes the static headspace technique for analyzing various VOCs in aqueous and soil samples. In this approach, samples containing the target analytes are heated to 85 °C and stirred to facilitate analyte partitioning into the headspace, allowing equilibrium to be reached between the headspace and the sample. Next, the carrier gas transports a defined volume of the headspace sample into the GC column, where the analytes are separated and detected.

Headspace sampling requires specific sample preparation procedures. For water samples, field collection must be conducted in vials with no headspace to prevent sample degradation. Upon arrival at the laboratory, subsamples are taken using gas-tight syringes and transferred into headspace analysis vials. At this stage, any necessary matrix modifications or internal standard additions are performed before the vials are analyzed via GC using a headspace sampler.

For soil samples designated for direct headspace analysis (low-concentration samples), intermediate extraction steps are avoided to maintain sample integrity. Since transferring soil samples between vials would require opening the container, samples must be collected directly into headspace vials in the field. Upon laboratory arrival, matrix-modifying agents and internal standards are added directly to the vial before analysis.

For high-concentration soil samples, an extraction solvent (typically methanol) is added in the field to preserve analytes. In the laboratory, a subsample is taken using a gas-tight syringe, diluted with a matrix modifier or analyte-free water, and subsequently analyzed by GC.

Static headspace sampling offers several advantages for sample introduction. It effectively removes non-volatile matrix components, reducing potential matrix interferences. Additionally, matrix-modifying agents, typically water-soluble salts, can be added to enhance analyte partitioning into the headspace without the risk of introducing these agents into the GC system, as they remain in the sample phase. Furthermore, injecting a large volume of headspace gas into the GC can improve sensitivity compared to direct liquid injection^[93]. However, for ultra-low concentration samples, the analyte concentration in the static headspace may be insufficient to achieve satisfactory sensitivity.

1.4.1.1.2 Dynamic headspace (purge-and-trap) analysis

EPA Methods 5035 and 5030C describe purge-and-trap techniques for analyzing solid and aqueous samples, respectively. In these methods, a carrier gas is bubbled through the sample, volatilizing the target analytes, which are then captured on a sorbent trap. The trapped analytes are subsequently desorbed by heating and introduced into the gas chromatograph (GC) for final analysis.

The use of a sorbent trap allows for preconcentration of the analytes, significantly enhancing the method's sensitivity^[93]. Additionally, similar to static headspace analysis, non-volatile matrix components do not reach the GC, minimizing potential interferences. Sensitivity can be further optimized by adjusting the purge temperature and sample volume.

Despite its advantages, purge-and-trap analysis is not readily suitable for high-concentration samples due to its high concentration factor. Samples with excessively high volatile component concentrations can lead to sorbent trap contamination, affecting subsequent analyses. To mitigate this risk, it is recommended that samples be pre-screened using a less sensitive method, such as static headspace analysis, ensuring that only low-concentration or diluted samples undergo purge-and-trap analysis. However, this additional screening step increases both the time and effort required for the overall analysis.

1.4.1.1.3 Vacuum distillation

EPA Method 5032 describes the vacuum distillation technique for analyzing VOCs in various sample types, including soil and aqueous samples. In this method, the sample is subjected to a vacuum (10

torr), causing the evaporation of volatile analytes along with some other sample components, such as water. The vaporized components then pass through a condenser coil maintained at -10 °C or lower, where water and other low vapor pressure compounds are removed. The more volatile analytes are subsequently captured in a cryogenic trap made of stainless-steel tubing, cooled to -196 °C. To introduce the analytes into the gas chromatograph (GC), the trap is heated, releasing the captured compounds.

This technique is particularly effective for highly volatile analytes and has demonstrated better recoveries than purge-and-trap for these compounds^[94]. However, for BTEX analysis, its sensitivity is generally lower or, at best, comparable to purge-and-trap. Additionally, the sample preparation process is significantly more complex, making vacuum distillation a less favorable choice for BTEX analysis. As a result, this method is primarily reserved for highly volatile analytes rather than being a first-line approach for BTEX detection.

1.4.1.2 Chromatographic separation methods

After sample preparation using the described methods, chromatographic separation is required. All EPA-approved methods rely on GC for separation, with different detectors specified for analyte detection.

None of these methods mandate the use of a specific GC column; however, DB-624 and DB-5 columns are among the recommended options. EPA Method 8015C allows for both capillary and packed columns, whereas other methods recommend only capillary columns. However, packed columns have largely been phased out in modern GC trace analysis due to their inferior performance compared to capillary columns.

EPA methods suggest three different detectors for BTEX analysis: FID, MS, and photoionization detector (PID). FID is a robust and cost-effective detector; however, it relies solely on chromatographic separation for selectivity. If interferences appear in the chromatogram, the EPA method recommends verifying the analysis using an alternative technique or a GC column with a different stationary phase. Additionally, FID has lower sensitivity for aromatic compounds, such as BTEX, compared to PID and MS^[95].

PID operates similarly to FID but ionizes compounds using ultraviolet (UV) light at a specific wavelength, hence energy^[95]. This selective ionization allows PID to detect certain species, including

aromatic hydrocarbons, with greater sensitivity than FID. The emitted energy can be adjusted to selectively ionize target analytes, improving selectivity. MS offers superior sensitivity and selectivity compared to FID and PID. However, it is less robust, requires more frequent maintenance, and has higher operational costs. Each detector has advantages and limitations, with the choice depending on the analytical requirements, sample complexity, and available instrumentation.

1.4.2 Other methods in literature

Over the years, numerous methods have been introduced in the literature for detecting BTEX in environmental samples. While many of these methods are similar to the EPA-approved techniques, some employ direct aqueous or organic extract injections. Additionally, advanced extraction and preconcentration techniques, such as solid-phase microextraction (SPME), have been successfully applied to BTEX analysis. For a more comprehensive review of these analytical methods, refer to the review article by Yu et al.^[34].

1.5 Low permeability media extraction

Sulfolane does not significantly adsorb onto most soil types^[17]. Therefore, when extracting it from soil samples, the partitioning of the analyte into the extraction solvent is not an issue. Soil is primarily composed of densely packed individual particles. However, the bulk of the soil is permeable, allowing the extraction solvent to penetrate between the soil particles and extract the analyte from their surfaces. However, this is not the case with rock samples and other low-permeability media.

Permeability is defined as the ability of a fluid to pass through the pores of a solid. It is typically modeled using Equation 1-1^[96].

$$k = c\phi r^2 \quad (\text{Equation 1-1})$$

In this equation, k represents permeability, ϕ represents porosity, r represents pore radius, and c represents the geometric factor that accounts for the shape, connectivity, and other variations of the pores^[96]. As the equation shows, the pore radius plays a pivotal role in determining the extent of permeability.

Total porosity refers to the amount of void volume inside a rock relative to its total volume. Effective porosity, on the other hand, is the ratio of the volume of interconnected pores to the total void volume inside a rock^[97]. While permeability represents how easily fluids and potential contaminants can

penetrate the rock, effective porosity represents the amount of space available for contaminants to be deposited inside the rocks. As illustrated in **Figure 1-4**, certain types of rocks have high porosity but low permeability.

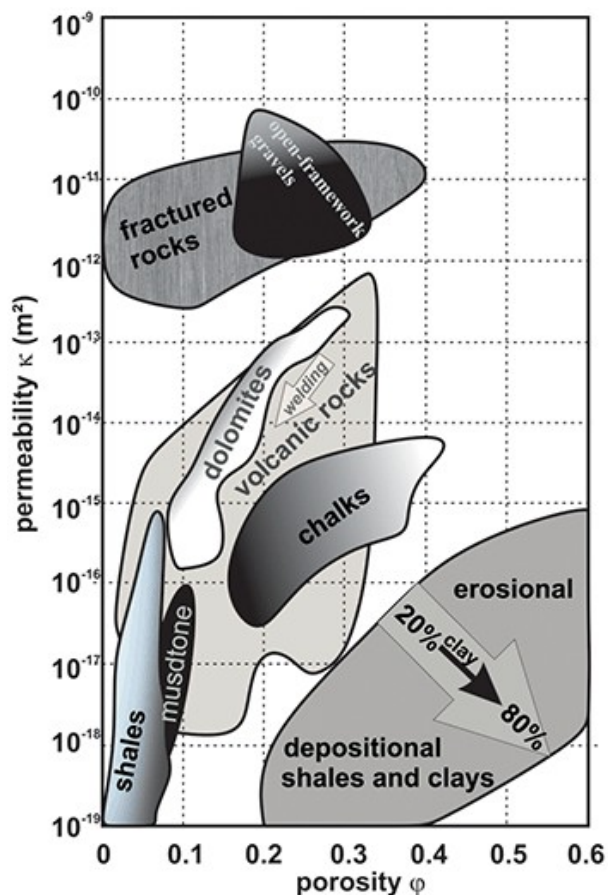


Figure 1-4. Permeability as a function of porosity in different type of rocks (Reproduced from *Fundamentals of Rock Physics*^[97]).

This indicates that given enough time, contaminants can penetrate into the pores. However, during extraction, due to very low permeability, it takes a significant amount of time for the extraction solvent to penetrate the pores and for the contaminants to diffuse through the pores and partition into the bulk of the solvent. Consequently, the main mechanism by which contaminants are transported through the pores is diffusion.

1.5.1 Standard extraction method for low-permeability media

To ensure the maximum extractable analyte is obtained, the shake-flask extraction method is usually employed for extracting low-permeability media at the Morwick G360 laboratory in the School of Engineering of the University of Guelph. In this method, the sample (e.g., crushed rock or clay) is immersed in an extraction solvent, such as methanol, and the container is sealed. The containers are regularly shaken to enhance the mixing of the sample with the extraction phase. Aliquots of the extract are collected and analyzed at specific time intervals until no further increase in analyte concentration is observed. This approach establishes the maximum extractable amount of analytes. While the shake-flask method is a reliable technique for contamination analysis in low-permeability media, it is time-consuming and carries the risk of contamination and analyte loss during the repeated sampling.

To develop a faster and potentially more efficient extraction method, it is crucial to increase the diffusivity of the analyte. Diffusion is dependent on the concentration gradient and the molecular diffusion coefficient^[83]. The concentration gradient varies throughout the extraction process and cannot be easily manipulated to accelerate the process without compromising the sensitivity. The molecular diffusion coefficient, on the other hand, depends on temperature, which can be easily adjusted^[83]. Therefore, heat-accelerated extraction (HAE) methods can expedite the process. The following section provides a brief overview of the suitability of these techniques.

1.5.2 Extraction at elevated temperature

Increasing the temperature results in a higher molecular diffusion coefficient, potentially speeding up the extraction process^[83]. Pressurized liquid extraction (PLE), Soxhlet extraction, and microwave-assisted extraction (MAE) are common HAE techniques used for extraction in environmental analysis.

1.5.2.1 Pressurized liquid extraction

In this technique, the sample is heated with an extraction solvent inside a closed pressurized cell and kept for a certain period. The closed nature of the extraction cell allows the temperature to exceed the solvent's boiling point at atmospheric pressure, thereby reducing the solvent's viscosity and enhancing molecular mobility, leading to faster extraction^[98]. To collect the samples after extraction, the extraction cell is purged with a stream of an inert gas followed by a small volume of the extraction phase, with the hot extract collected in an open flask. Consequently, the collection stage can result in the loss of volatile co-contaminants.

1.5.2.2 Soxhlet extraction

Soxhlet extraction involves placing a solid sample and the extraction solvent in the Soxhlet apparatus (**Figure 1-5**), heating the solvent, and allowing the hot solvent to pass through the sample repeatedly after its vapors condense and drip on top of the sample. Once the condensed solvent reaches a certain level in the extraction vessel, it is siphoned back into the boiling flask, and the process is repeated for several cycles^[99]. Soxhlet extraction requires a significant amount of solvent, and the extraction temperature is limited by the atmospheric boiling point of the solvent. Additionally, volatile analytes may be lost due to the open nature of the extraction vessel.

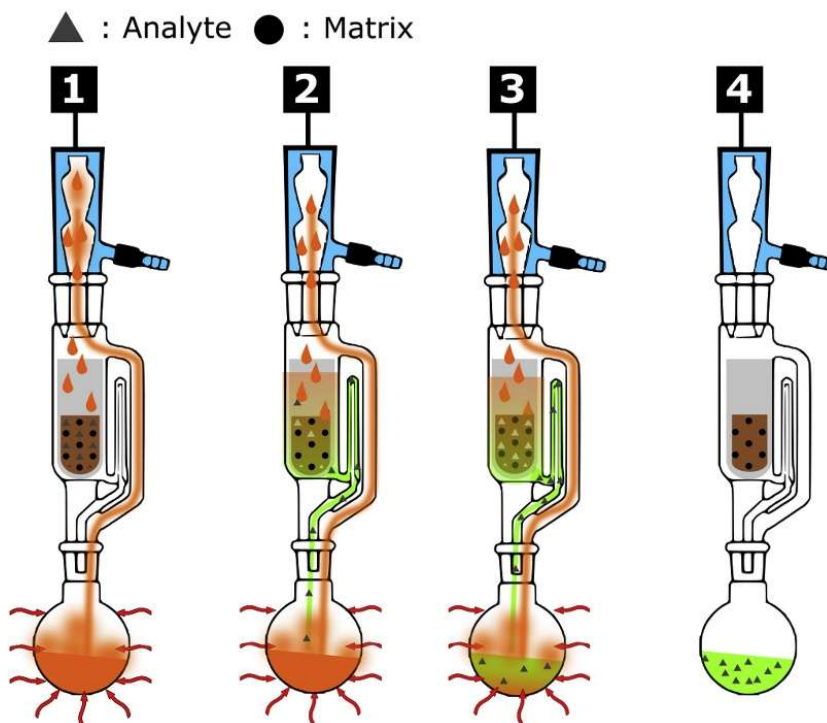


Figure 1-5. Schematic illustration of the Soxhlet extraction, reproduced from Chapter 5 of the book “Basic Multidimensional Gas Chromatography^[100]. 1) The solid sample is placed in the Soxhlet thimble, and the solvent is heated under a reflux condenser. 2) The distilled fresh solvent percolates through the sample, dissolving the target analytes. 3) Once the solvent reaches a certain level, it is siphoned into the reservoir, where it is continuously evaporated, condensed, and recycled back onto the sample, repeating the extraction cycle multiple times. 4) The extracted analytes accumulate in the solvent within the reservoir.

1.5.2.3 Microwave-assisted extraction

Microwave-assisted (MAE) extraction involves using microwaves to heat the sample and the extraction solvent, allowing extraction to be performed at elevated temperatures. In brief, MAE offers almost all the advantages of PLE, without the concern of losing volatile analytes during the collection stage. Hence, MAE is expected to be a promising technique for expediting the extraction of sulfolane and its volatile co-contaminants from low-permeability media.

1.6 Microwave-assisted extraction and its fundamentals

Microwaves are defined as electromagnetic radiation with frequencies ranging from 0.3 GHz to 300 GHz^[101]. When microwaves interact with matter, they induce molecular motions, leading to an increase in temperature. In the following sections, the fundamental principles of microwave extraction (MAE) are described.

1.6.1 Mechanism of heating

There are two recognized mechanisms for the heating capability of microwaves: ionic conduction and dipole rotation. In solutions containing ions, the application of an electromagnetic field causes the electrophoretic migration of ions. This induces movement of the ions within their surrounding medium, and the resulting friction generates heat. Similarly, when the field is applied to dipoles, they align themselves with the field's direction. As the direction of the field changes based on the frequency of the microwaves, the dipoles constantly realign themselves and their rotation in response to changes in magnetic field polarity generates friction against surrounding molecules, resulting in heat production. For instance, at the standard microwave oven frequency of 2.45 GHz, realignment occurs at a rate of 4.9×10^9 times per second^[102].

This induced molecular and ionic mobility results in heating due to friction with the surrounding molecules. In most extraction solvents, where ion concentration is low, the principal mechanism of MAE is assumed to be dipole rotation. Consequently, more polar compounds with higher separation of charges and stronger dipoles can be heated more quickly by the microwave oven. Two factors affecting the interaction between different materials and microwaves are dielectric loss (ϵ''), an indication of how microwaves can be dissipated by the material, and dielectric constant (ϵ'), which represents the material's ability to obstruct microwaves passing through it. The dissipation factor (loss tangent),

defined as the ratio of the two, directly affects the heating ability of microwaves for a certain material (Equation 1-2)^[102].

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \quad (\text{Equation 1-2})$$

Materials with higher dissipation factors absorb microwaves more efficiently and can be heated up more efficiently. In fact, materials can be classified into three types based on their interaction with microwaves. Conductors, such as metals, reflect microwaves and do not allow their penetration. Insulators are transparent to microwaves and do not interact with them. For example, non-polar solvents like hexane do not absorb microwave energy and remain unaffected. On the other hand, microwave absorbers are dielectric materials with dipole moments. Hence, they interact with and absorb microwave energy, resulting in heating. Water, a typical polar solvent with high dipole moment, efficiently absorbs microwaves and heats up quickly^[103]. The loss tangents (dissipation factors) for several common solvents are presented in **Table 1-5**.

Table 1-5. Dielectric constants, dielectric losses, and loss tangents of common extraction solvents for microwave-assisted extraction (Reproduced from an article titled “Dielectric properties in microwave-assisted solvent extraction—present trends and future outlook” by Ibrahim et al.^[103]).

Solvent	Dielectric constant (ϵ)	Dielectric loss (ϵ')	Loss tangent ($\tan \delta$)
Water	80.4	9.89	0.123
Dimethyl sulfoxide (DMSO)	45.0	37.1	0.825
Dimethylformamide (DMF)	37.7	6.08	0.161
Ethylene glycol	37.0	50.0	1.35
Methanol	32.6	21.5	0.856
Ethanol	24.3	22.9	0.941
Chloroform	4.80	0.437	0.0910
Toluene	2.40	0.0960	0.0400
Hexane	1.90	0.0380	0.0200

It is evident that in microwave absorbing samples, where the energy is directly applied to the constituents of the solution, heat transfer is much more efficient compared to traditional heating methods, which rely on conduction and convection. Consequently, microwave heating allows faster heating of solutions^[98]. Moreover, this direct heating mechanism enables the application of energy to microwave absorbing constituents of the sample, even if parts of the sample are transparent to microwaves.

1.6.2 Microwave extraction instrumentation

A typical microwave extraction instrument consists of several parts. The magnetron produces microwaves, which are then directed through a waveguide to a mode stirrer. The mode stirrer distributes the radiation throughout the microwave oven, where the samples absorb the radiation and heating occurs. Two types of extraction technologies are available based on the vessel type: open vessel and closed vessel MAE. In open vessel MAE, the extraction vessels are under atmospheric pressure and can exchange constituents with the surrounding air. In contrast, closed vessel MAE involves heating samples in closed, hermetically sealed vessels, making it possible to perform extraction under elevated pressures at temperatures higher than the atmospheric boiling point of the solvent^[98].

Closed vessel MAE offers several advantages over open vessel MAE. The high temperature enhances molecular motion (thus increases diffusion coefficients), accelerating the extraction process. Additionally, the decrease in solvent viscosity at higher temperatures allows more efficient penetration of the solvent into the pores of solid samples, resulting in quicker analyte extraction^[102]. Furthermore, if the vessels are cooled before opening, volatile compounds can be extracted while minimizing the risk of analyte loss.

1.6.3 Microwave extraction mechanism

The extraction of analytes from low permeability medium in MAE occurs through two distinct mechanisms depending on the nature of the extraction solvent and the analytes. If the extraction solvent is transparent to microwaves and the analytes are microwave absorbers, the microwaves directly heat up the analytes. As a result, they vaporize and their molecular diffusion coefficient increases, allowing them to migrate out of the sample pores and partition into the extraction solvent. In contrast, if the analytes are unable to absorb microwave energy, by using a transparent extraction solvent, the water content of the sample can be heated, causing the water to heat the sample. This heating prompts the

molecules to move out of the pores and partition into the extraction solvent. In both cases, there is no significant increase in solvent temperature. In both cases, however, the dependence on variable sample factors has led to inconsistencies in reproducibility, making this approach unsuitable for extraction.

On the other hand, if a microwave absorber solvent such as methanol is used for the extraction, the microwaves are mainly absorbed by the solvent molecules. The increase in temperature and the corresponding decrease in viscosity both facilitate faster extraction. In this case, MAE provides advantages over traditional methods by enabling more efficient and rapid heating. Furthermore, when closed-vessel MAE is employed, the elevated vessel pressure allows the solvent temperature to exceed its atmospheric boiling point, which further increases the extraction efficiency.

1.6.4 Factors affecting MAE efficiency

Based on the extraction mechanism, several factors influence the extraction efficiency for a given sample. These factors include the nature of the extraction solvent, temperature, pressure, extraction time, and microwave power and frequency^[102]. Optimizing these factors is crucial for developing an efficient MAE method.

1.6.4.1 Temperature and pressure

Increasing the temperature of the extraction solvent enhances the mobility of solvent molecules and reduces overall solvent viscosity. This, in turn, increases the diffusivity of the extraction solvent, leading to more efficient extraction. Higher temperature also may improve the solubility of analytes in the solvent, further enhancing extraction efficiency^[102]. However, it is important to avoid exceeding the maximum tolerable pressure of the extraction vessels when heating solvents, as increasing the temperature causes pressure inside the vessels to increase as well. Exceeding the maximum pressure may lead to partial or complete loss of analytes if the vessel depressurizes, and poses a safety risk due to the potential explosion of the extraction vessel, which often contains flammable solvents. Fortunately, commercial extraction vessels are equipped with safety devices that make the latter scenario unlikely. Moreover, elevated temperatures can lead to analyte degradation. Although sulfolane can withstand typical MAE extraction temperatures, it is essential to consider the thermolability of target co-contaminants.

1.6.4.2 Extraction time

A longer extraction time generally leads to higher extraction efficiency, as molecules have more time to partition into the extraction solvent. However, the optimal extraction time depends on factors such as the solvent type, target analytes, and sample matrix, and must be carefully optimized. Special attention is required for thermolabile analytes, as prolonged extraction can increase their degradation. A shorter extraction time helps minimize degradation, improving both sensitivity and overall analysis efficiency^[102]. In this regard, the reduced extraction time, particularly in closed-vessel MAE, offers a significant advantage over traditional extraction methods.

1.6.4.3 Microwave power

The total microwave power can be adjusted in MAE systems and some home microwave ovens. However, the power applied to the extraction medium, assuming constant total power, depends on the number of vessels in the microwave cavity and their contents^[102]. Therefore, ensuring uniform sample and solvent content throughout all the vessels is important to minimize temperature and pressure differences among them.

1.6.4.4 Microwave frequency

Microwave frequency affects the penetration and energy transfer into samples. However, the choice of frequency is limited due to radio frequency spectrum regulation and prevention of interference with other instruments^[101]. For non-communication industrial, scientific and medical purposes, including home microwave ovens and MAE instruments, the Federal Communications Commission (FCC) has set the microwave frequency at 915 MHz and 2450 MHz. However, in practice, the 2450 MHz frequency is nearly universally used for both purposes.

1.7 Project objectives

As discussed in Section 1.3.5, various methods have been reported in the literature for the analysis of sulfolane in soil and water samples. However, none of these methods have focused on the analysis of sulfolane co-contaminants, which is a significant oversight. The fate of sulfolane contamination and its co-contaminants can be interconnected, and analyzing both is crucial to understand their relationships. BTEX compounds are potential co-contaminants of sulfolane, often found together in the

petrochemical industry. While it is possible to develop separate methods for each group of analytes, a single method that can analyze both groups simultaneously would be more beneficial, as it would reduce costs, time, and uncertainty associated with replicate analysis.

Furthermore, due to the differences between rock and soil samples, despite their chemical similarities, a method specifically designed and validated for rock samples is necessary to assess contaminant levels. To the best of the author's knowledge, there is no reported methodology for the analysis of sulfolane in rock samples, and therefore, no prior information is available on the extraction behavior of sulfolane from these matrices.

Consequently, based on these gaps in the literature, the following main objectives were established:

- Develop and optimize an analytical method for the simultaneous determination of sulfolane and BTEX in rock and water samples.
- Validate the method, assess its ruggedness, and identify the critical factors that affect the results to control them more carefully during analysis.
- Evaluate the stability of the analytes in the samples and determine the hold time.
- Assess the extraction profile of sulfolane for rock samples and develop an accelerated extraction procedure if necessary for prompt sample analysis.
- Minimize the use of organic solvents due to their negative environmental impact, particularly chlorinated solvents, which have more severe environmental consequences.
- Transfer the methods developed to the Morwick G360 Groundwater Research Group, enabling their use for contamination assessment at potentially contaminated sites.

The subsequent Chapters will detail how these objectives were achieved and the challenges that were overcome. Note that the next two Chapters are based on manuscripts intended for publication, and minor modifications have been made to accommodate them in this thesis.

Chapter 2

Development and Optimization of a GC-MS Analytical Method for Detecting Sulfolane and BTEX in Rock Samples^b

As described in Section 1.3.5, several methods have been reported in the literature for the analysis of sulfolane in soil samples, and numerous studies have focused on the determination of BTEX in soil^[68–71,104–109]. However, to the best of our knowledge, no method has been reported that simultaneously analyzes both BTEX and sulfolane. Developing a single analytical method for both analytes would be beneficial in terms of time and cost. Moreover, the analysis of rock samples is distinct from soil samples, despite their relatively similar chemical nature.

When porous rock structures are exposed to contaminants, these compounds penetrate the rock pores via diffusion and become trapped, with potentially very long residence times. As a result, the release of contaminants from these structures is slow, resulting in environmental pollution that can persist long after the primary source of contamination has been mitigated or removed. The same phenomenon occurs during laboratory extraction, where contaminants may require a long time to be fully extracted from porous rocks into the solvent. Consequently, analytical methods suitable for soil samples may not provide sufficient time for complete extraction, resulting in an underestimation of contaminant concentrations in rock samples.

To ensure complete extraction of analytes, the standard method for rock sample analysis at the University of Guelph's Morwick G360 laboratory is shake-flask extraction. In this method, samples of the rock cores collected by drilling are crushed and preserved in an organic solvent, with occasional shaking. The solvent is sampled at regular intervals and analyzed until the response for the analytes plateaus. Although this technique is effective, frequent sampling can lead to analyte losses or sample contamination. Furthermore, multiple analyses are required for each sample, and extraction can take several weeks (typically 6-8 weeks for VOCs). Therefore, an accelerated extraction technique can not only expedite the analysis, but also reduce costs by minimizing the need for frequent analysis.

^b A significant portion of this section is adapted from my article, "Development and Optimization of a GC-MS Analytical Method for Detecting Sulfolane and BTEX in Rock Samples", prepared for submission to *Journal of Chromatography Open*.

Consequently, the objective of this stage of the project was to develop a simple and fast method for the simultaneous analysis of sulfolane and BTEX in rock samples.

2.1 Materials and methods

2.1.1 Chemicals and reagents

Analytical-grade sulfolane ($\geq 99\%$ purity) was obtained from MilliporeSigma Canada Ltd. (Oakville, ON, Canada) and used to prepare calibration standards and spiking samples. A residual solvent sulfolane standard was purchased from Restek Corporation (Bellefonte, PA, USA) and employed for quality control (QC) sample preparation. BTEX solution analytical standard and BTEX high-concentration mix certified reference material were acquired from MilliporeSigma Canada Ltd. (Oakville, ON, Canada) to prepare calibration standards and QC samples. Sulfolane-d8 ($\geq 95\%$ purity) was obtained from Toronto Research Chemicals (Toronto, ON, Canada) and used as the internal standard. Methanol (SupraSolv®) for gas chromatography-mass spectrometry (GC-MS) was purchased from MilliporeSigma Canada Ltd. (Oakville, ON, Canada) and used for extraction and standard preparation.

2.1.2 Sample collection

Rock core samples were collected from a contaminated site in Alberta, Canada, and subsequently crushed using a manual hydraulic press. The crushed rock was then transferred to pre-cleaned 40 mL vials, which were transferred to the lab and stored at $-8\text{ }^{\circ}\text{C}$ until further processing. These samples were utilized for the development of the sulfolane extraction method, as no prior data were available on the extraction time profile of sulfolane. For the analysis of target samples using the final method, rock core samples were collected and crushed in the same manner. However, to preserve the volatile target analytes, the crushed rocks were immediately transferred to 40 mL vials containing 15 mL of methanol, thereby minimizing the potential losses of these compounds.

2.1.3 GC-MS analysis

A GC-MS method was developed using an Agilent 6890 GC coupled with a 5793N MS system as the detector. The GC system utilized helium as the carrier gas, a split/splitless straight liner with wool ($4\text{ mm} \times 6.3\text{ mm} \times 78.5\text{ mm}$) in the injection port, a 2-meter polar retention gap, and a Restek Rxi®-624Sil MS column ($60\text{ m} \times 0.32\text{ mm ID} \times 1.8\text{ }\mu\text{m}$ film thickness) as the stationary phase. The

autosampler was configured to inject 1 μL of DCM from below the surface of the water layer in a 1:1 split mode. A small split ratio was preferred over splitless injection to improve peak shape. The autosampler needle was rinsed three times with methanol, followed by DCM, before each injection. The inlet temperature was maintained at 240 $^{\circ}\text{C}$.

The carrier gas flow rate was set to 4.0 mL/min for the first 1.5 minutes and then reduced to 2.0 mL/min for the remainder of the run. The oven temperature program began at 45 $^{\circ}\text{C}$, held for 1.0 minute, then increased to 150 $^{\circ}\text{C}$ at 14 $^{\circ}\text{C}/\text{min}$, followed by a ramp to 215 $^{\circ}\text{C}$ at 5 $^{\circ}\text{C}/\text{min}$, and finally increased to 240 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C}/\text{min}$, where it was held for 5 minutes. Compound retention times are provided in *Table 2-1*.

Table 2-1. Retention times, quantifier, and qualifier ions of target analytes

Target analyte	Retention time (min)	Quantifier ion (m/z)	Qualifier ion 1 (m/z)	Qualifier ion 2 (m/z)
Benzene	7.1	78	77	N/A
Toluene	8.8	91	92	N/A
Ethylbenzene	10.4	91	106	N/A
<i>m/p</i> -Xylene	10.5	91	106	N/A
<i>o</i> -Xylene	11.0	91	106	N/A
Sulfolane-d8	20.9	46	128	N/A
Sulfolane	21.1	41	56	120

For the detection of eluted compounds, an Agilent 5793N MS was employed with an EI ion source. The transfer line temperature was set to 240 $^{\circ}\text{C}$, while the ion source temperature was maintained at 230 $^{\circ}\text{C}$ with an ionization energy of 70 eV. The mass analyzer temperature was set to 150 $^{\circ}\text{C}$. The MS was operated in selected ion monitoring (SIM) mode to ensure maximum sensitivity. At least two ions were included in the SIM method for each compound, with one serving as the quantifier and the other as the qualifier. These ions are listed in *Table 2-1*.

2.1.4 Method validation and characterization

The method was validated following the EPA method validation guideline for chemical methods of analysis^[110]. In summary, the linear response range was evaluated and confirmed to span from 10 $\mu\text{g}/\text{L}$

to 8000 µg/L for all compounds. An initial linearity assessment was performed by visual inspection, followed by confirmation using the lack of fit F-test. To characterize the method's performance, two sets of 10 spiked rock extracts were prepared at two distinct concentrations. These samples were analyzed using the method developed and bracketed by two sets of calibration standards, repeated on three different days. The trueness/bias and precision of the method were evaluated by calculating the recovery and relative standard deviation (RSD) for these samples, respectively. Additionally, the standard deviation (SD) was calculated, and the limit of detection (LOD) and limit of quantification (LOQ) were determined as three times and ten times the SD of the spiked sample at the lower concentration, respectively. Notably, the concentration of the spiked sample was very close to the determined LOQ, ensuring that the method's LOQ was evaluated at a relevant concentration level.

2.1.5 Extraction time profile and stability of sulfolane

To evaluate the stability of sulfolane in methanol extracts and determine its extraction time profile in rock samples, a total of 190 rock samples were analyzed to identify the contaminated ones. Briefly, 5.00 mL of methanol was added to 5 g aliquot of each rock sample, and the resulting mixtures were initially stored at room temperature, with occasional vortex shaking. Among the analyzed samples, only 9 were found to be contaminated with sulfolane at quantifiable levels. Over the course of a year, sub-samples were collected at regular intervals from these vials, analyzed using the validated GC-MS method, and the results were used to determine the extraction time profile of sulfolane and establish its stability in the rock extracts, with the rock matrix present.

2.1.6 Microwave-assisted extraction

Based on the results of the extraction time profile determination and the delayed release of sulfolane, it was determined that an accelerated extraction technique was desirable for prompt processing and analysis of samples. Due to the benefits described in the Introduction, MAE was selected as the preferred method.

For method development, a reconfigured home microwave oven was utilized in conjunction with commercial O.I. Analytical moderate pressure microwave digestion vessels. The microwave oven was equipped with a 689-0010 temperature controller system manufactured by Bernant Company (Barrington, IL, US). The microwave extraction system consisted of 11 extraction vessels and one reference vessel. The reference vessel contained the same volume of solvent and analytes as the other

vessels. A thermocouple, connected to the temperature controller system, monitored the temperature of the reference vessel and regulated the magnetron operation to maintain the set temperature within ± 1 °C. Although the extraction vessels lacked individual thermocouples, it was assumed that, due to the uniform composition of their contents, the microwave heating effect was consistent across all vessels, ensuring similar temperature conditions. The method developed was subsequently transferred to a commercial microwave extraction system, the ETHOS SEL microwave extraction system manufactured by Milestone Srl (Sorisole, Italy).

To optimize the MAE procedure, a set of 6 samples that were previously determined to be contaminated with sulfolane and exhibited slow release in their extraction time profiles were selected. Twenty gram aliquots of each sample were accurately weighed and placed in microwave vessels, followed by the addition of 7.5 mL of methanol. The vessels were sealed, and after a 5-minute equilibration period, they were reopened and a subsample was taken from each vessel. The vessels were then resealed and subjected to microwave radiation at a temperature of 120 °C for a duration of 50 minutes. After cooling to room temperature, the vessels were opened, and the samples were analyzed. To ensure that the extraction of all target analytes was complete, the same samples were re-heated in the microwave oven and re-analyzed repeatedly, for a total extraction time of 110 minutes. To assess potential solvent losses during the extraction process, the vessels were weighed before and after microwave exposure, and the weights were recorded.

2.1.7 Analytical method reproducibility assessment

To evaluate the reproducibility of the analysis, a set of samples was prepared by spiking clean rock samples with known amounts of analytes. These spiked samples were then subjected to the MAE extraction procedure and analyzed. This process was repeated 3 times over three different days for a total of 21 samples. The resulting data were analyzed, and the average recovery and RSD of the results were calculated as a measure of the analytical method's accuracy and reproducibility, respectively.

2.1.8 Analysis of rock samples

Rock samples that had been collected and preserved in methanol were analyzed using the validated method, which employed microwave extraction. To do so, the contents of each sample were completely transferred into microwave extraction vessels and subjected to microwave radiation for 50 minutes at 120 °C. After cooling to room temperature, a 1.0 mL aliquot was taken from each vessel. Subsequently,

sulfolane-d8 was added as the internal standard to each sample, which was then analyzed by the GC-MS method. The internal standard was introduced post-MAE to address concerns regarding the stability of the deuterated compound and the potential for deuterium-hydrogen exchange.

2.2 Results and discussion

2.2.1 Sample collection

As described in Section 2.1.2, the samples collected for method development and validation were crushed and placed in vials without any preservation. This was necessary to determine the extraction time profile of sulfolane, as the porous rock samples may have had varying pore sizes. The size of the pores and the tendency of different chemicals to adsorb onto the rock matrix could cause the target analytes to become trapped within the pores. As a result, a prolonged extraction time is required to allow the analytes to diffuse into the bulk solvent, a process that involves the penetration of the solvent into the pores, followed by the diffusion of the analytes into the bulk of solvent. If the samples had been preserved in methanol, the extraction process would have started immediately after collection, making the estimation of the extraction time profile unreliable. In the analysis of the actual samples, the rock samples analyzed by the method were preserved in methanol in the field immediately after crushing to minimize losses of volatile compounds.

2.2.2 Choice of extraction solvent

To the best of our knowledge, there is no reported methodology for the analysis of sulfolane in rock samples in the literature. However, for soil samples, several solvents, including DCM and toluene, have been suggested for sulfolane extraction^[64,69]. Nevertheless, these solvents are not miscible with water, which can hinder their ability to penetrate rock samples with high water content, potentially hindering the extraction process. This limitation may be less significant for soil samples, where the smaller particle size and shorter diffusion distances facilitate more efficient extraction.

Among the commonly available solvents, methanol is capable of dissolving both sulfolane and other target compounds. It is a protic solvent capable of acting as a hydrogen bond donor, which contributes to its increased affinity for sulfolane when compared to non-protic solvents. Additionally, methanol is more environmentally friendly compared to chlorinated solvents, and is available at high purities^[81]. Its miscibility with water also enables it to penetrate samples with high water content effectively. Due to these advantages, methanol was selected as the extraction solvent. However, injecting methanolic

extracts directly into a GC system can be challenging, and certain measures were necessary to address the corresponding issues. These challenges and solutions to them are discussed in the following section.

2.2.3 GC-MS method of analysis

Direct injection of samples dissolved in methanol into a GC system can be challenging. Methanol is often injected into the GC using on-column mode of injection, which offers several benefits, including the ability to inject larger volumes of extract compared to split injection, lack of discrimination towards analytes with different boiling points, and no need for injection band re-focusing through solvent re-condensation in the column^[11]. However, on-column injectors are not widely available and require more frequent maintenance, particularly when dealing with complex samples that may contain low-volatility chemicals that can contaminate the system. Therefore, it was decided to develop a method utilizing a split/splitless injector instead.

Using splitless injection for methanol poses several issues. Firstly, the relatively large vapor volume of methanol limits the injection volume and subsequently the sensitivity of the analytical method. If the vapor volume exceeds the liner volume, it can contaminate the injector system, leading to issues such as cross-contamination and baseline elevation. To maximize the injection volume, a higher flow rate at the start of the run, and consequently a higher pressure, can help contain the vapor volume within the liner. In fact, it would not be possible to inject 1 μL of methanol into the described setup using optimized flow rates. Additionally, the higher flow rate would facilitate the transfer of analytes into the analytical column, resulting in narrower peaks and higher resolutions. Finally, by reducing the flow rate to the optimized value after the target analytes have been transferred to the column, the separation can be performed with minimal compromise to resolution.

Another issue with methanol is its polar nature, which hinders its ability to properly wet non-polar GC columns. This leads to poor solvent refocusing efficiency and broad, distorted peak shapes, thereby increasing the risk of co-elutions and compromising the sensitivity and quantification reliability of the method. One potential solution is to employ a highly polar GC column, which would better accommodate the polar properties of methanol. However, since simultaneous analysis of non-polar BTEX compounds was one of the key objectives of the study, the use of a highly polar column was not feasible as it would result in poor or no separation of these compounds. Furthermore, the high polarity of sulfolane would likely result in long analysis times if a highly polar column were used. Therefore, the careful selection of a suitable GC column was essential to the success of the analysis.

Initially, a DB-5 column was tested due to its wide availability. However, the DB-5 column failed to retain sulfolane effectively, and the sulfolane-d8 peak shape was significantly affected by the concentration of sulfolane, which could have caused non-linearity in the calibration curve when the ratio of the analyte to the internal standard peak area was used. Therefore, other columns were tested, and among the tested columns, the polar DB-WAX column was able to effectively focus sulfolane and produce sharp and narrow symmetrical peaks. Additionally, *m*-xylene was distinguishable from *o*-xylene on this column. However, benzene and toluene co-eluted with methanol, making quantification impossible. Many other columns were tested, and finally, the DB-624 column was able to separate all compounds except *m*- and *p*-xylene successfully. However, the peak shape for more volatile species, particularly benzene and toluene, was broad and skewed.

To resolve this issue, a 2-meter polar retention gap was attached before the analytical column. This polar retention gap increased the efficiency of methanol solvent refocusing, improving the peak shape. Additionally, a small split ratio of 1:1 was introduced to reduce the initial peak width. While ideally it is preferable to use splitless mode to maximize sensitivity, the dissimilar polarity of sulfolane and BTEX necessitates compromises, and in this case, the reliability of the method was prioritized over maximum sensitivity. A sample chromatogram of a spiked sample can be found in **Figure 2-1**.

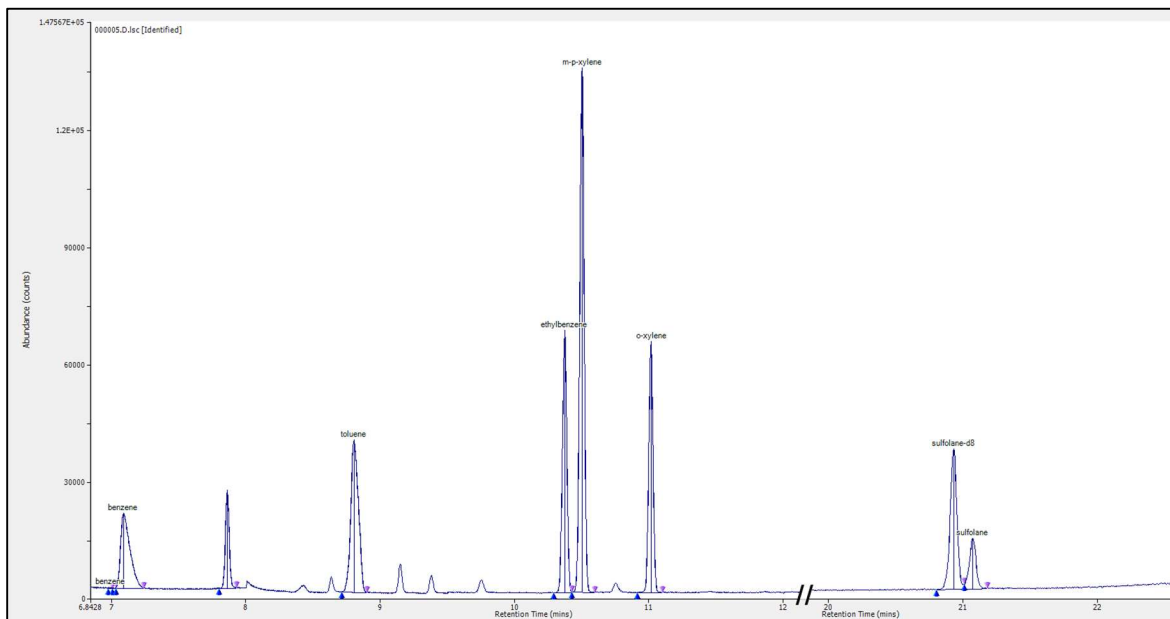


Figure 2-1. Sample chromatogram of a spiked rock sample. From left to right, benzene, toluene, ethylbenzene, m/p-xylene, o-xylene, sulfolane-d8, and sulfolane. Notably, sulfolane-d8 peak elutes earlier than sulfolane peak due to the increased polarity of deuterated compounds^[112].

2.2.4 Method validation and characterization

The results of the method validation are summarized in **Table 2-2**. The selectivity of the method was deemed satisfactory, grounded in the use of an MS detector and the verification of ion ratios, as well as the absence of interference in the analyzed samples. The response linearity was confirmed with the Lack-of-fit F-test. The method was found to be accurate, with recoveries of spiked samples ranging from 86% to 115% of their nominal concentrations, falling within the acceptable range of 70% to 120%^[110]. The precision of the method was evaluated by calculating the RSD of the spiked samples, which was found to be 7.9% or less, well within the acceptable limit of 20%.

Table 2-2. Method validation and characterization statistics

Target analyte	Linearity lack of fit test				Spiked samples replicates			
	F (Calculated)	F (Critical)	P	Significance	N	Nominal concentration (µg/L)	Average recovery (%)	RSD (%)
Benzene	0.05	5.41	0.99	No	3×10	4.32	107%	3.6%
					3×10	2877	99%	3.9%
Toluene	0.04	5.41	0.99	No	3×10	4.39	95%	1.6%
					3×10	2928	97%	5.0%
Ethylbenzene	0.02	5.41	1.00	No	3×10	4.42	91%	2.1%
					3×10	2946	96%	5.9%
<i>m/p</i> -Xylene	0.02	5.41	1.00	No	3×10	17.62	104%	4.4%
					3×10	5874	115%	7.9%
<i>o</i> -Xylene	0.01	5.41	1.00	No	3×10	4.42	86%	2.5%
					3×10	2946	94%	5.6%
Sulfolane	0.02	5.41	1.00	No	3×10	4.47	92%	8.0%
					3×10	2982	95%	1.0%

The limits of detection (LOD) and quantification (LOQ) for all compounds ranged from 0.20 to 1.2 µg/kg and 0.66 to 4.0 µg/kg of wet mass, respectively (**Table 2-3**). Notably, the LOD and LOQ values would vary slightly depending on the sample mass in each vial. The values reported in **Table 2-3** are based on a typical sample composition, assuming 40 g of rock in 15 mL of methanol.

Table 2-3. Limits of detection and quantification of the method for a typical rock sample.

	Benzene (µg/Kg)	Toluene (µg/Kg)	Ethylbenzene (µg/Kg)	<i>m/p</i> -Xylene (µg/Kg)	<i>o</i> -Xylene (µg/Kg)	Sulfolane (µg/Kg)
LOD	0.49	0.20	0.25	1.2	0.29	0.98
LOQ	1.6	0.66	0.84	4.0	1.0	3.3

2.2.5 Extraction time profile and stability of sulfolane

The extraction time profile of sulfolane in rock samples is illustrated in **Figure 2-2**. This figure demonstrates that the response for sulfolane reached a plateau and remained stable for up to a year after the initiation of extraction when the samples were stored at -8 °C. The confirmation of sulfolane's stability was crucial, as some of the sampling took place prior to the development of the method, and the validity of the results from those samples was verified through this stability study.

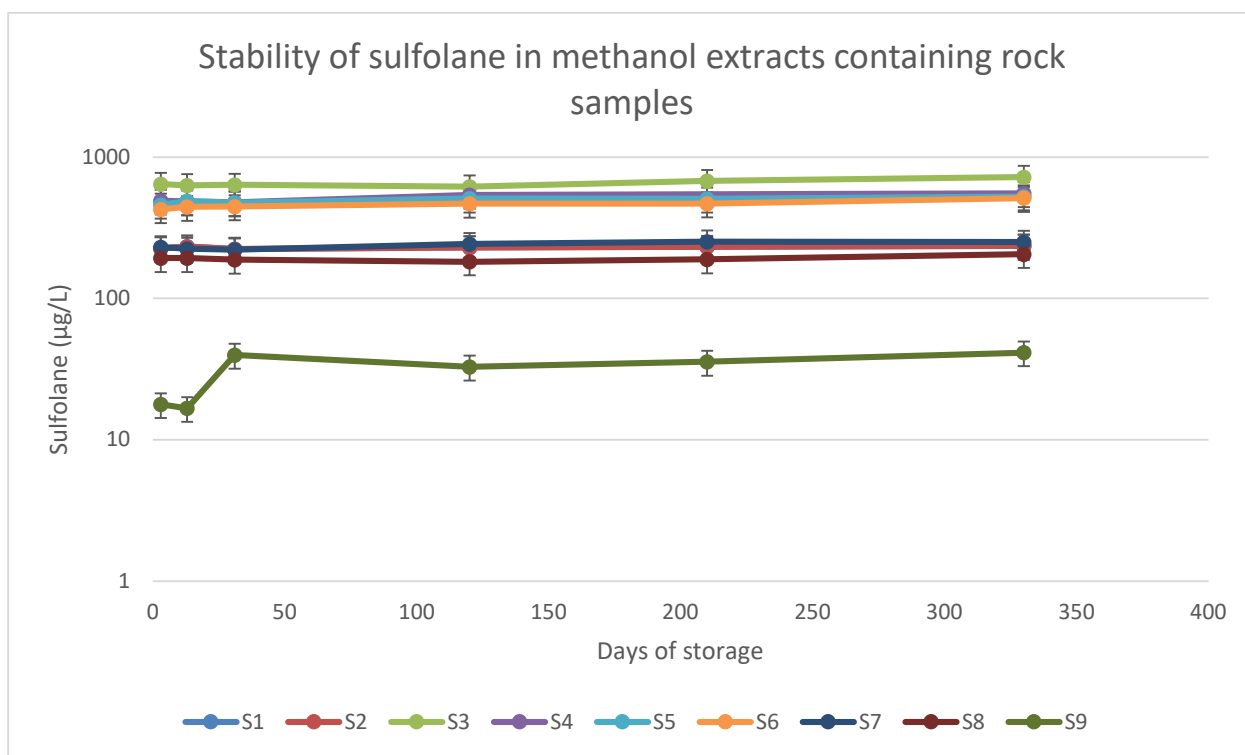


Figure 2-2. Extraction time profile of sulfolane in methanol extracts.

Figure 2-2 also reveals that some sulfolane samples require prolonged extraction times. Notably, the S9 sample reached a plateau after 31 days of extraction. This indicates that some samples must be extracted in methanol for at least 4 weeks before they can be processed and injected for analysis, which is not ideal. Based on these findings, if prompt sample processing is required, an accelerated extraction method should be considered to reduce the extraction time.

2.2.6 Microwave-assisted extraction optimization

MAE, Soxhlet extraction, and PLE are commonly employed as accelerated extraction techniques for environmental solid samples. Among these methods, MAE was selected for this analysis due to its advantages over other available methods. Soxhlet extraction is time-consuming, uses large volumes of solvent, and is limited in its ability to process multiple samples simultaneously, with the added risk of volatile compound loss through the recondensation column^[99]. PLE, while offering benefits such as rapid extraction, high throughput, and compatibility with in-line cleanup methods, can result in the loss of volatile analytes during the final stage of extraction, where the cell content is removed by purging with an inert gas^[113]. MAE offers many of the benefits of PLE, such as quick extraction and high

throughput^[114]. Additionally, in a closed-vessel MAE system, if the vessels are allowed to cool to room temperature before opening, the loss of volatile target analytes can be minimized^[115]. Furthermore, methanol, the chosen extraction solvent, is fully compatible with MAE and does not require any additional sample processing^[116]. MAE has been successfully applied for the extraction of chlorinated solvents from clay^[117] and rock samples^[118], and at the Morwick G360 laboratory, tens of thousands of rock samples have been analyzed over the years using these methods.

Despite its advantages, MAE also has certain limitations. If filtration of the extracts is necessary, it must be performed as an additional step after extraction^[119]. However, in this study, after allowing the vessels to cool, clear sub-samples could be collected without disturbing the settled rock particles. Therefore, filtration was considered unnecessary for sample preparation.

The optimization of MAE extraction time and temperature is crucial as different compounds might show varying responses to microwave energy, influencing their extraction efficiency. The MAE extraction profiles for sulfolane and toluene are presented in **Figures 2-3** and **Figure 2-4**, respectively. This analysis was conducted on samples that were previously demonstrated to require long extraction times. As shown in the graphs, sulfolane extraction reached a plateau after 50 minutes of microwave exposure at 120 °C, establishing this as the optimized extraction time for MAE. Ideally, samples containing all target contaminants would have been preferable; however, none were found to be significantly contaminated with BTEX compounds, except for toluene. Nevertheless, since the physico-chemical properties of BTEX are similar, toluene can be considered a good proxy for all BTEX compounds.

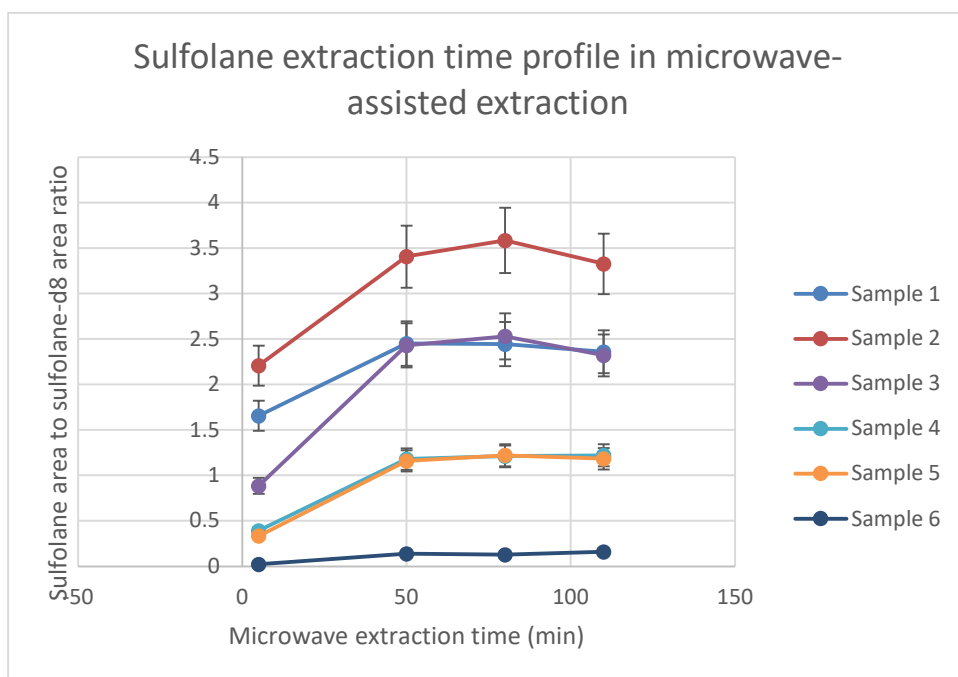


Figure 2-3. Microwave-assisted extraction time profile of sulfolane in contaminated rock samples.

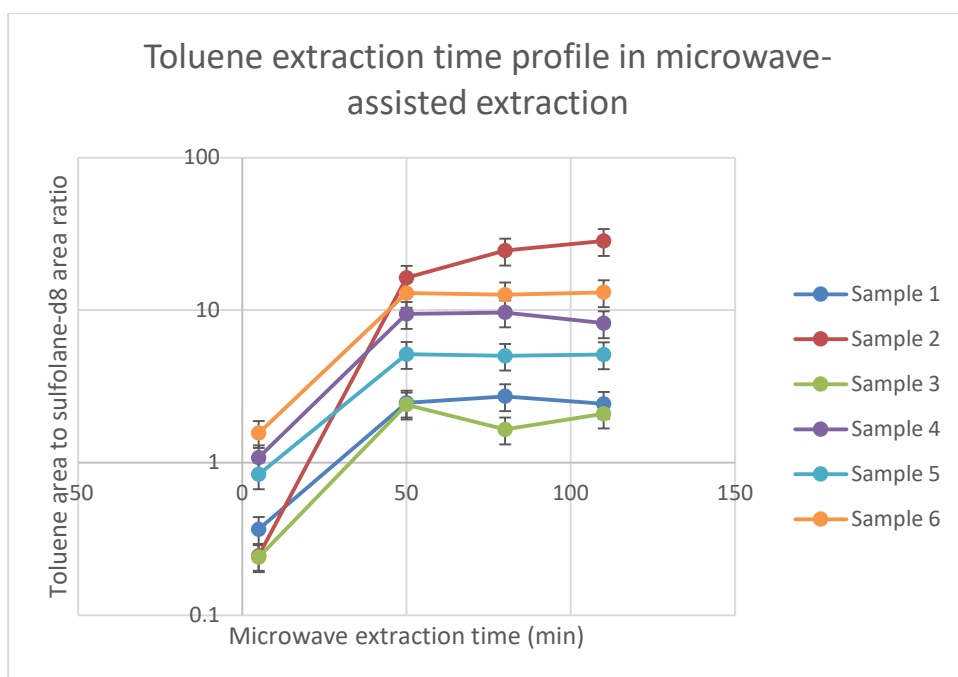


Figure 2-4. Microwave-assisted extraction time profile of toluene in contaminated rock samples.

2.2.7 Analytical method reproducibility assessment

The reproducibility of the analytical method was a critical aspect to evaluate, as several steps in the procedure can significantly impact the results. Ideally, this assessment would be performed through replicate analysis of identical samples. However, the rock samples are heterogeneous, exhibiting large variations in pore and particle size across different portions of the same crushed sample. To address this challenge, a set of rock samples that were free from the target analytes were selected, spiked with the analytes of interest, extracted using MAE and analyzed by the method developed. As shown in *Table 2-4*, inter-day recoveries ranged from 72% to 109%, with RSDs ranging from 3% to 17%, demonstrating satisfactory recovery and reproducibility of the method.

Table 2-4. Microwave-assisted extraction recovery and reproducibility assessment.

		Benzene	Toluene	Ethylbenzene	<i>m-p</i> -Xylene	<i>o</i> -Xylene	Sulfolane
Day 1	N	7	7	7	7	7	7
	Average calculated concentration	183	235	188	378	181	111
	Average recovery	97%	121%	97%	97%	93%	75%
	SD	10.58	53.8	8.03	16.5	6.90	4.18
	RSD	6%	23%	4%	4%	4%	4%
Day 2	N	7	7	7	7	7	7
	Average calculated concentration	179	200	183	367	176	105
	Average recovery	94%	103%	94%	95%	91%	71%
	SD	6.40	20.4	6.04	12.6	5.95	5.29
	RSD	4%	10%	3%	3%	3%	5%
Day 3	N	7	7	7	7	7	7
	Average calculated concentration	176	200	173	345	165	103
	Average recovery	93%	103%	89%	89%	85%	70%
	SD	2.64	21.0	2.40	4.37	2.39	2.58
	RSD	2%	11%	1%	1%	1%	3%
Inter-day	N	3 × 7	3 × 7	3 × 7	3 × 7	3 × 7	3 × 7
	Average calculated concentration	179	211	182	363	174	106
	Average recovery	94%	109%	93%	94%	90%	72%
	SD	7.48	36.2	6.12	12.6	5.57	4.27
	RSD	4%	17%	3%	3%	3%	4%

2.2.8 Analysis of rock samples

A total of 109 rock samples were analyzed using the method developed. Only one sample was found to be contaminated with sulfolane, and the concentration was below the LOQ. However, all samples contained toluene at quantifiable levels. The maximum detected concentration of toluene in these rock samples was 227 µg/kg, with an average concentration of 21.1 µg/kg. Xylenes and ethylbenzene were also detected in many samples, as summarized in **Table 2-5**. Notably, none of the contaminants exceeded the Alberta Tier 1 soil remediation guideline values.

Table 2-5. Results of the analysis of rock samples for contaminants

	N, Not detected	N, Detected < LOQ	N, > LOQ	Maximum (µg/Kg)	Average (µg/Kg)
Benzene	105	0	4	11.5	6.06
Toluene	0	0	109	227	21.1
Ethylbenzene	20	8	81	12.2	3.19
<i>m/p</i>-Xylene	65	6	38	93.4	14.3
<i>o</i>-Xylene	61	0	48	51.7	8.35
Sulfolane	108	1	0	N/A	N/A

2.3 Conclusions

In this study, a GC-MS analytical method was developed for the detection and quantification of sulfolane and BTEX in rock samples. The samples were extracted using methanol, and the resulting extracts were analyzed by GC-MS. Despite the challenges associated with injecting methanol in split/splitless mode, these were mitigated through careful optimization of the flow rate, selection of a suitable stationary phase, and the incorporation of a polar retention gap.

This method was applied to assess the extraction time profile of the target analytes into methanol. Due to the observed slow extraction of the analytes from rock samples, an MAE method was proposed and optimized to enhance the extraction process. The MAE technique enables faster sample processing and analysis.

Additionally, the stability of sulfolane in methanol extracts containing rock was investigated, revealing that sulfolane remains stable for up to one year under these conditions. The method developed was then applied to analyze 109 real rock samples from a suspected contaminated site in Alberta, Canada.

Results indicated that the percentage of samples contaminated with sulfolane, benzene, toluene, ethylbenzene, *m*-xylene or *p*-xylene, and *o*-xylene were 1%, 4%, 100%, 82%, 40%, and 44%, respectively. All detected contaminants were below Alberta's Tier 1 guideline limits. Notably, the analyzed samples were collected from shallow depths, highlighting the need for further research and sampling at greater depths to obtain a more comprehensive understanding of the contamination profile.

Chapter 3

Development and Optimization of a GC-MS Analytical Method for Detecting Sulfolane and BTEX in Water Samples^c

The simultaneous analysis of sulfolane and BTEX in water samples necessitates a determination technique that is compatible with both classes of compounds. Sulfolane and BTEX are commonly analyzed using GC-MS due to their sufficient volatility for GC^[70,71,120]. The incorporation of MS enhances the selectivity of the method, which is crucial given the potential presence of interfering co-contaminants. However, the primary distinction between their analyses lies in the sample preparation techniques.

For sulfolane analysis in water samples, two official methods have been established, both of which rely on very large volumes of chlorinated solvents^[70,71]. Additionally, various alternative methods have been reported in the literature, most of which employ DCM or toluene for sulfolane extraction prior to GC-MS analysis^[16,20,64,73,78]. These techniques often involve complex sample preparation procedures.

In contrast, BTEX analysis typically requires preconcentration using solvent-free extraction techniques such as purge-and-trap^[120–122]. While these methods enhance sensitivity, they also demand specialized instrumentation and involve elaborate sample preparation. Moreover, purge-and-trap is not suitable for sulfolane analysis, as sulfolane exhibits low volatility and does not partition into the headspace in significant amounts.

In this study, we developed a GC-MS method for the simultaneous quantification of sulfolane and BTEX in water samples with very simple sample preparation. While numerous studies have focused on these compounds individually, to the best of our knowledge, no existing research has examined both sulfolane and BTEX simultaneously in water. The objective of this study was to establish a simple and straightforward GC-MS-based analytical approach with minimal organic solvent use, enabling efficient detection of both compound classes.

^c A significant portion of this section is adapted from my article, “Development and Optimization of a GC-MS Analytical Method for Detecting Sulfolane and BTEX in Water Samples”, submitted to the journal “Separations”.

3.1 Materials and Methods

3.1.1 Chemicals and reagents

Analytical-grade sulfolane (purity: $\geq 99.8\%$) was obtained from MilliporeSigma Canada Ltd. (Oakville, ON, Canada) and used for the preparation of calibration standards and spiking samples. A certified sulfolane residual solvent standard was sourced from Restek Corporation (Bellefonte, PA, USA) for the preparation of QC samples. Analytical standards of BTEX and a high-concentration BTEX certified reference material were also procured from MilliporeSigma Canada Ltd. and employed in the preparation of calibration standards and QC samples, respectively. Sulfolane-d8, used as a surrogate standard for sulfolane, was supplied by Toronto Research Chemicals (Toronto, ON, Canada). Toluene-d8, used as a surrogate standard for BTEX, was obtained from Cambridge Isotope Laboratories, Inc. (Tewksbury, MA, USA). DCM (SupraSolv® grade for GC-MS) was purchased from MilliporeSigma Canada Ltd. and used for extraction and standard preparation. Blank samples were prepared using tap water.

3.1.2 Sample collection

A total of 97 surface and groundwater samples, including 47 duplicate samples, were collected in June 2024 from a contaminated site in Alberta, Canada. Surface water samples were obtained from a spring at the contaminated site. The samples were collected with a peristaltic pump in pre-cleaned 40 mL glass vials, filled to the brim to minimize the loss of volatile compounds and sealed with airtight caps. To produce duplicate samples, two vials were filled alternately. The downside of this approach was that the vials remained open to the atmosphere for a longer time, potentially increasing losses of volatile compounds. However, this was deemed an acceptable compromise. In the case of groundwater collection, the procedure was similar, except that in some cases the amount of groundwater that could be drawn at one time was insufficient to fill the vials, and the collection had to be resumed at a different time. Samples collected in this way cannot be treated as true duplicates.

All samples were transported to the laboratory in the University of Waterloo in an insulated cooler within 48 hours of collection. Sample processing and analysis were completed within 72 hours of arrival, ensuring a total holding time of less than five days.

3.1.3 Sample preparation

To simplify the sample preparation procedure, an in-vial extraction method was employed. For the extraction of sulfolane and BTEX from water samples, 0.500 mL of DCM containing 400 µg/L of sulfolane-d8 and toluene-d8 as surrogate standards was added to a GC vial. Subsequently, 1.00 mL of the water sample was dispensed into the vial using an automatic pipette. The vial was capped and vortex-shaked for 30 seconds to ensure thorough extraction and partitioning of the analytes into the DCM phase. Samples prepared in this way were then loaded onto the instrument's autosampler tray for injection and analysis.

3.1.4 GC-MS analysis

A GC-MS method for the analysis of sulfolane and BTEX was developed using an Agilent 6890 GC coupled with a 5973N MS detector. The configuration of the GC-MS method developed was identical to that of the method for methanol extracts, except for the addition of toluene-d8 as a surrogate standard for water samples. The retention times, as well as the quantifier and qualifier ions used for each compound, are described in *Table 3-1*.

Table 3-1. Retention times, quantifier, and qualifier ions of target analytes.

Compound	Quantifier ion (m/z)	Qualifier ion 1 (m/z)	Qualifier ion 2 (m/z)	Retention time (min)
Benzene	78	77	N/A	7.1
Toluene-d8	100	98	N/A	8.7
Toluene	92	91	N/A	8.8
Ethylbenzene	91	106	N/A	10.4
<i>m/p</i> -Xylene	91	106	N/A	10.5
<i>o</i> -Xylene	91	106	N/A	11.0
Sulfolane-d8	46	128	N/A	20.9
Sulfolane	41	56	120	21.0

3.1.5 Method validation and characterization

The method was validated in accordance with the EPA Method Validation Guidelines for Chemical Methods of Analysis^[110]. In summary, the linearity of the response was evaluated across a range of 10 µg/L to 8000 µg/L for all compounds. Initial assessments were performed through visual inspection, followed by confirmation using a lack-of-fit F-test. Precision and accuracy were characterized by preparing a set of samples consisting of 10 blank tap water samples spiked at two different concentrations. These spiked samples were analyzed, bracketed by two sets of calibration standards, with the procedure repeated three times over three separate days. Data from these analyses were processed to validate and characterize the method's performance.

Selectivity was demonstrated by employing MS detection and confirming the absence of interferences in spiked samples. Method bias and trueness were assessed through the average recovery of spiked samples, which fell within the acceptable range of 70% to 120%^[110]. Precision was quantified by calculating the RSD of the spiked samples, with all compounds exhibiting RSD values below 20%. The LOD and LOQ were determined as three times and ten times the SD of the lowest concentration spiked samples, respectively. It is important to note that the spiked concentration did not exceed three times the calculated LOQ.

3.1.6 Method ruggedness testing

To assess the ruggedness of the analytical method, a Plackett-Burman experimental design with 11 factors was developed using Minitab®. The study included several factors: the presence or absence of vortex-shaking, reinjection from a pierced vial, a 24-hour delay before injection, sample temperature during preparation, needle washing with methanol only, and the use of 0.45 mL of DCM for extraction. The experimental results were subsequently imported into the software, and analysis of variance (ANOVA) was conducted to interpret the findings.

3.1.7 Sample hold time and analytes' stability

To assess the stability of the water samples, two sets were prepared and stored under different conditions. The first set was stored at room temperature (21–25 °C) on a laboratory bench throughout the duration of the study. The second set was refrigerated at 4 °C. Both sets of samples were analyzed at designated intervals, extending up to 23 days.

3.1.8 Analysis of water samples

The water samples collected were analyzed using the validated method. For samples with replicates, analyses were performed on different days to evaluate the method's robustness and the reproducibility of results. Prior to each analysis, the MS was tuned. Sample analyses were bracketed by calibration standards, with a total of 12 QC samples injected at regular intervals to ensure result validity. Reagent blanks were injected before and after the calibration standards and once every 10 samples to check for injector carryover. Any results below the LOD were disregarded, while results between the LOD and the LOQ were considered positive detections.

3.2 Results and Discussion

3.2.1 Sample preparation method

The sample preparation method was designed with a focus on simplicity, aiming to minimize the number of steps involved. The most straightforward approach would be direct aqueous injection into the GC, eliminating sample preparation entirely. This technique has been successfully employed in a few studies for sulfolane analysis. However, it requires an on-column injection system, which presents several challenges. Firstly, on-column injectors are less commonly available compared to split/splitless injectors. Secondly, direct injection of water samples, particularly those from contaminated sites, can introduce a high level of matrix contaminants, leading to increased maintenance requirements for the GC system. For these reasons, a split/splitless injector was selected due to its widespread availability and robustness.

With split/splitless injection, direct aqueous injection is not feasible. Water's high vapor expansion significantly limits the injection volume, reducing sensitivity. Additionally, the MS detector is not well-suited for direct water injections, as water can disrupt the vacuum inside the mass analyzer and interfere with ionization. To address these limitations, an extraction step was incorporated to transfer the target analytes into an organic solvent prior to GC-MS analysis. To further simplify the process, the extraction was designed to take place directly within the GC vials, eliminating the need for phase separation and sample transfer before analysis. This approach minimizes the risk of analyte loss, particularly for volatile compounds such as BTEX.

While a non-chlorinated solvent would have been preferable to mitigate environmental concerns, DCM was selected due to its high density, which allows it to form a distinct layer beneath the aqueous

phase. This property enabled automated sampling directly from the DCM layer without the need for an additional transfer step, reducing sample handling and potential losses. Although autoinjectors can be set up to aspirate only from the upper layer of a vial if a solvent less dense than water is used, this setup requires precise adjustments. Even minor variations in vial dimensions could lead to unintended water aspiration, which would introduce excessive vapor volume into the GC inlet, causing contamination and requiring extensive cleaning. Additionally, the water layer above the DCM phase acts as a barrier, reducing solvent evaporation and potentially enhancing sample stability while stored on the autosampler tray before the injection.

To expedite analyte partitioning into the organic phase, a vortex-shaking step was incorporated into the sample preparation method. While the results in Section 3.2.4 indicate that vortex-shaking had minimal impact on the quantified analyte concentrations when surrogate standards were used, it did influence analyte response, thereby improving the overall sensitivity of the analytical method.

3.2.2 GC-MS method of analysis

The split/splitless injection system was selected due to its greater availability and reduced maintenance requirements. While splitless injection would have been preferable for maximizing sensitivity, it resulted in peak tailing for the more volatile compounds, such as benzene and toluene. Apparently, these compounds were not effectively re-focused by the solvent recondensing in the column. Peak tailing can compromise method robustness, increase the risk of co-elution, and interfere with accurate quantification. To address this issue, a small split ratio of 1:1 was implemented, which significantly improved peak shape. However, introducing a split ratio inevitably reduces sensitivity, partially offsetting the preconcentration achieved during sample preparation. Despite this trade-off, the enhanced reliability and improved quantification accuracy were deemed more critical.

Additionally, while the optimum flow rate for separation was determined to be 2.0 mL/min, a higher flow rate of 4.0 mL/min (the maximum allowable for the MS) was maintained during the first 1.50 minutes of the run. This elevated flow rate facilitated the rapid transfer of analytes from the inlet to the column, resulting in narrower peaks with improved shape and resolution.

The GC-MS method developed successfully resolved all target compounds with acceptable peak shapes. A representative chromatogram of a spiked sample is shown in *Figure 3-1*. In spite of all the measures, the benzene peaks exhibited a tailing factor of 1.6, likely due to the limited solvent-focusing effect of DCM. Regardless, the tailing remained within acceptable limits and did not hinder the

identification or quantification of benzene. It is worth noting that as observed in the chromatogram, the column was unable to separate *m*-xylene from *p*-xylene; therefore, the method quantifies the combined concentration of both isomers.

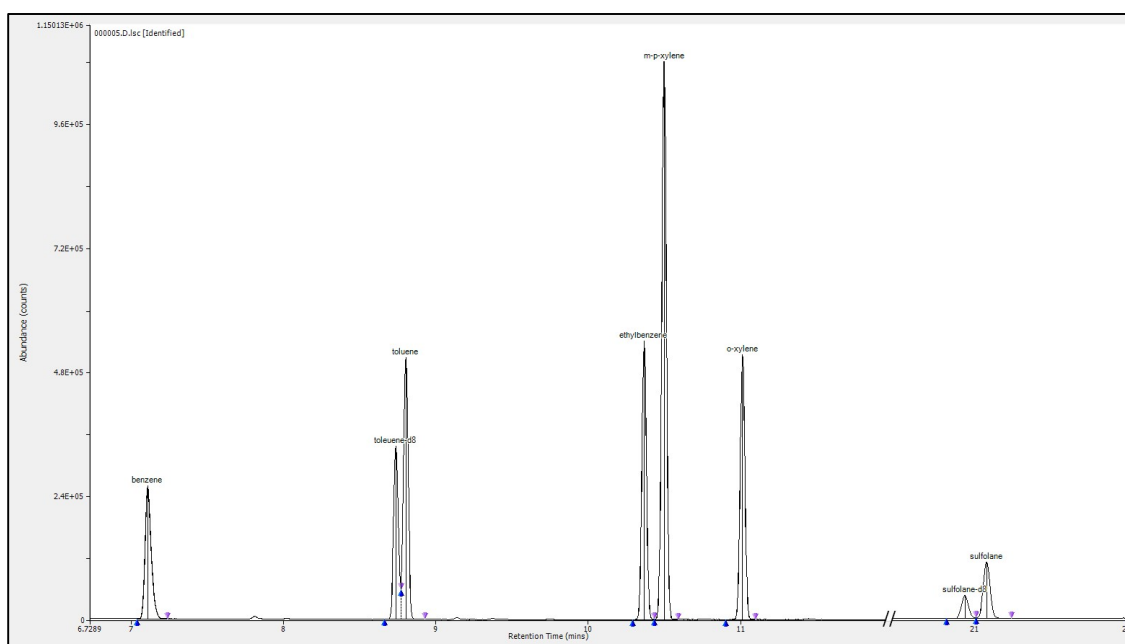


Figure 3-1. Chromatogram of spiked water sample. Peaks from left to right: Benzene, toluene-d8, toluene, ethylbenzene, *m*-xylene and *p*-xylene, *o*-xylene, sulfolane-d8, and sulfolane. Notably, sulfolane-d8 peak elutes earlier than sulfolane peak due to the increased polarity of deuterated compounds^[112].

3.2.3 Method validation

The method validation results are summarized in **Table 3-2**. The method demonstrated good selectivity, correctly identifying and accurately quantifying all target compounds in the spiked samples. Recoveries ranged from 86% to 103%, with RSDs between 0.5% and 8.1%. LODs and LOQs were between 0.5 µg/L and 2.6 µg/L, and 1.8 µg/L and 8.8 µg/L, respectively, as shown in **Table 3-3**. While lower LODs and LOQs could be achieved by focusing on a single compound class (i.e. BTEX or sulfolane alone), the dissimilar polarities of these analytes necessitated methodological compromises. These included using a 1:1 split injection ratio and selecting a column that could accommodate both

compound groups rather than a specialized column for individual analytes. Additionally, sample preparation was kept straightforward, with no preconcentration steps applied. Given these trade-offs, the observed LOD and LOQ values are well within acceptable limits and sufficiently sensitive for their intended purpose, as the current regulatory thresholds for these compounds are higher than the method's LOQs.

Table 3-2. Summary of method performance characteristics

Analyte	Nominal concentration (µg/L)	N	Average recovery (µg/L)	Average recovery (%)	SD (µg/L)	RSD (%)
Benzene	11.51	3×10	10.87	94%	0.34	3.1%
	767.2	3×10	789.5	103%	20.26	2.6%
Toluene	11.71	3×10	10.54	90%	0.22	2.1%
	780.8	3×10	778.4	100%	8.55	1.1%
Ethylbenzene	11.78	3×10	10.47	89%	0.19	1.8%
	785.6	3×10	760.4	97%	9.36	1.2%
<i>m/p</i>-Xylene	23.50	3×10	20.53	87%	0.45	2.2%
	1566	3×10	1544	99%	29.36	1.9%
<i>o</i>-Xylene	11.78	3×10	10.12	86%	0.18	1.8%
	785.6	3×10	744.9	95%	9.90	1.3%
Sulfolane	11.93	3×10	10.77	90%	0.88	8.1%
	795.2	3×10	746.6	94%	3.50	0.5%

Table 3-3. Limits of detection and quantification of the analytical method

	Benzene	Toluene	Ethylbenzene	<i>m/p</i> -Xylene	<i>o</i> -Xylene	Sulfolane
LOD (µg/L)	1.0	0.7	0.6	1.3	0.5	2.6
LOQ (µg/L)	3.4	2.2	1.9	4.5	1.8	8.8

3.2.4 Method ruggedness testing

Method ruggedness can be evaluated by examining how small changes in experimental parameters that might occur during sample preparation and analysis affect the final results. A design of experiments (DOE) approach was implemented to assess the ruggedness of the method and identify the most influential factors affecting analytical results. When properly selected, these designs enable efficient optimization by significantly reducing the number of experimental runs required. A 12-run Plackett–Burman design was chosen, as it allows the evaluation of 11 factors with only 12 experimental runs, making it a highly efficient screening method. However, every experimental design has limitations, and in the case of the Plackett–Burman design, it assumes that interactions between factors are negligible. This assumption must be considered when interpreting the results.

The interpretation of the Plackett-Burman design results is presented in pareto charts in **Figure 3-2** and **Figure 3-3**, with factors included in **Table 3-4**. The analysis highlighted the significance of vortex shaking on the response of all compounds except sulfolane. However, when accounting for losses by plotting calibration curves using the ratios of BTEX compounds to toluene-d8 and sulfolane to sulfolane-d8, respectively, none of the compounds, except benzene, appeared to be influenced by the experimental factors tested.

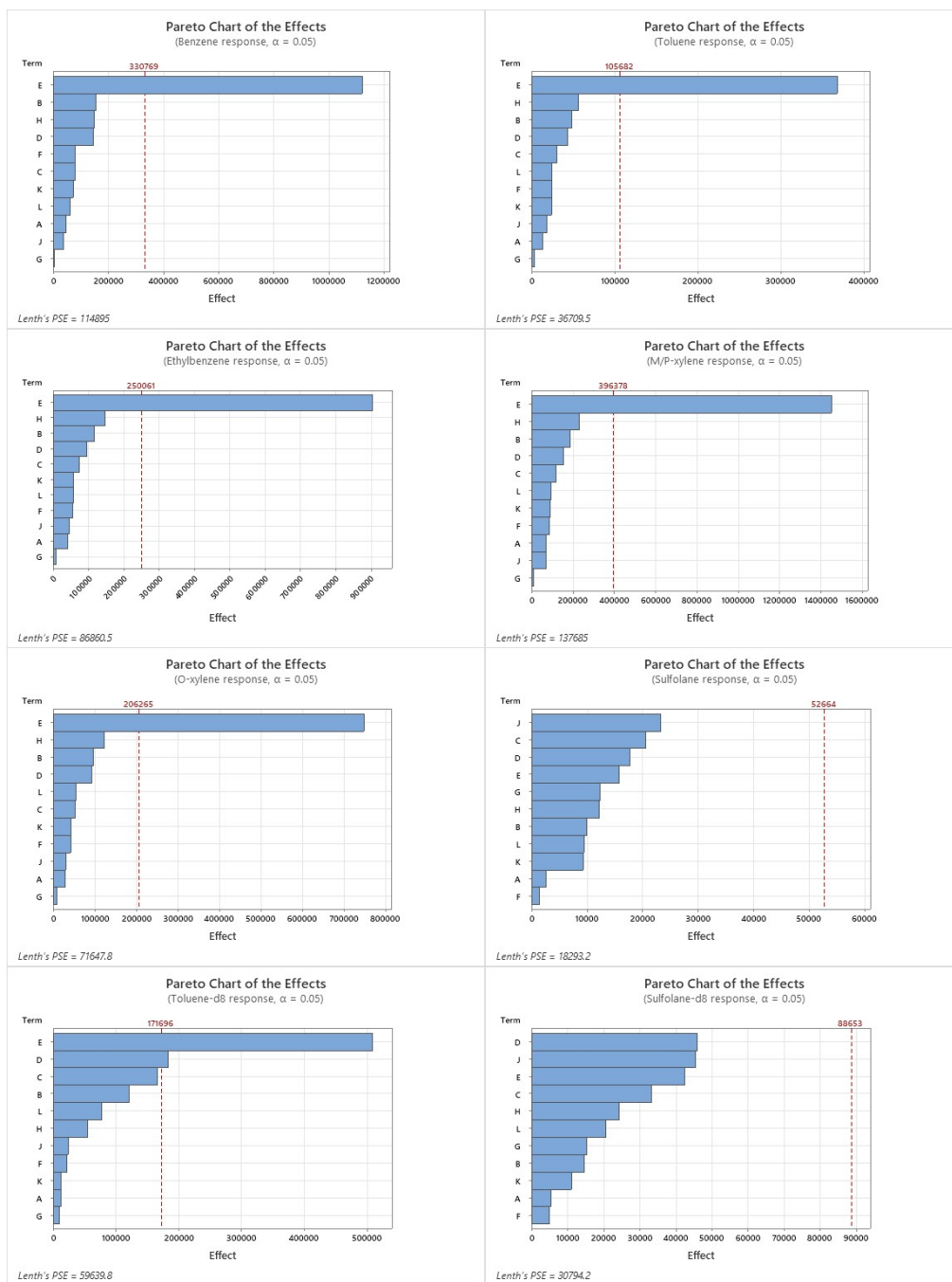


Figure 3-2. Pareto charts of the effects of different factors on the response of the instrument for the target analytes. Factors are described in **Table 3-4**.

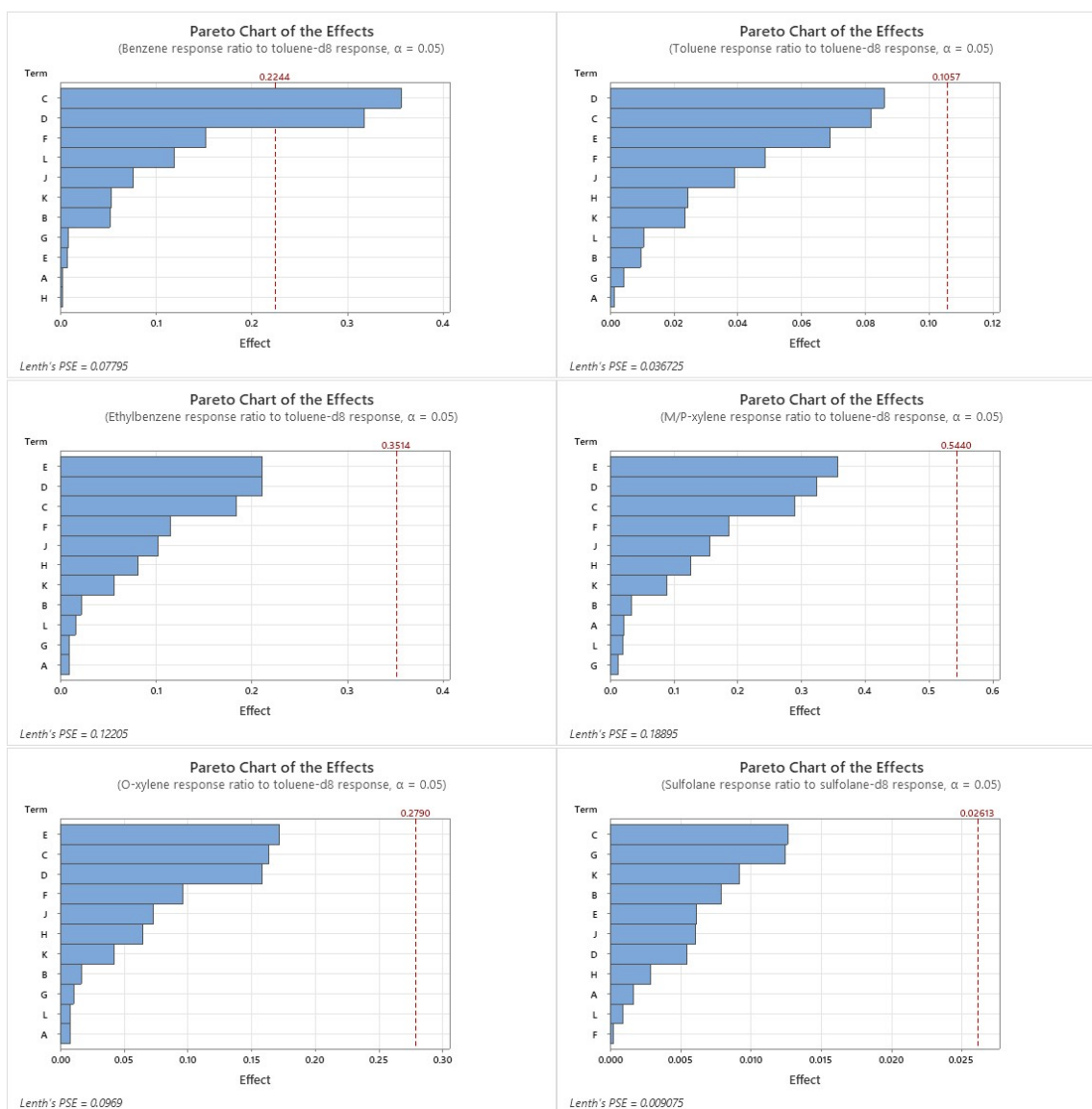


Figure 3-3. Pareto charts of effects of different factors on the ratio of the response of each target analyte to their surrogate standard. Factors are described in **Table 3-4**.

Table 3-4. *Plackett-Burman design for the evaluation of method ruggedness.*

Factor	Description	-1 (Low Level)	1 (High Level)
A	Sample temperature	4 °C	30 °C
B	Discarding the first portion of drawn water	No	Yes
C	Time between opening the sample vial and adding water to DCM	15 sec	90 sec
D	Volume of DCM	450 µL	500 µL
E	Vortex shaking applied	No	Yes
F	Use of already pierced septa	No	Yes
G	Methanol wash only (DCM replaced with methanol in the autosampler)	No	Yes
H	Injection performed 24 h after sample preparation	No	Yes
J	Tool used for sampling water	Syringe	Automatic pipette
K	Dummy factor (for experimental design)	N/A	N/A
L	Order of addition	Water sample to DCM	DCM to water sample

Benzene, even after correction with the surrogate standard, showed significant sensitivity to both the time taken to add the water sample to the DCM and the volume of DCM used. This sensitivity can be attributed to the higher vapor pressure of benzene compared to other BTEX compounds^[123]. Its elevated vapor pressure allows benzene molecules to escape from the water more readily, making delays in handling the sample critical to its concentration. To mitigate this issue, it is recommended to add surrogate standards directly to the DCM and immediately transfer water samples into the DCM in the injection vial upon opening the sample vials.

3.2.5 Sample stability test

Table 3-5. Results of stability of target analytes in samples kept at room temperature.

Day	Statistic	Toluene-d8	Sulfolane-d8	Benzene	Toluene	Ethylbenzene	<i>m/p</i> -Xylene	<i>o</i> -Xylene	Sulfolane
0	N	3	3	3	3	3	3	3	3
	Mean	1441613	726457	2.25	0.66	1.66	2.64	1.38	0.55
	SD	101057	16728	0.14	0.04	0.10	0.16	0.08	0.02
	RSD	7%	2%	6%	6%	6%	6%	6%	3%
3	N	3	3	3	3	3	3	3	3
	Mean	1143753	577020	2.30	0.66	1.60	2.51	1.35	0.50
	SD	67812	16330	0.05	0.02	0.04	0.07	0.03	0.01
	RSD	6%	3%	2%	3%	3%	3%	2%	3%
8	N	3	3	3	3	3	3	3	3
	Mean	1320023	609492	1.94	0.54	1.27	1.96	1.12	0.46
	SD	32754	29046	0.08	0.03	0.07	0.12	0.04	0.02
	RSD	2%	5%	4%	5%	6%	6%	4%	4%
14	N	3	3	3	3	3	3	3	3
	Mean	1167060	435533	1.77	0.48	1.06	1.64	1.00	0.51
	SD	67691	9500	0.06	0.02	0.03	0.05	0.03	0.02
	RSD	6%	2%	3%	3%	3%	3%	3%	4%
23	N	3	3	3	3	3	3	3	3
	Mean	1175603	440954	1.64	0.42	0.85	1.32	0.89	0.48
	SD	47252	36560	0.23	0.07	0.14	0.22	0.12	0.01
	RSD	4%	8%	14%	16%	17%	17%	13%	3%

Table 3-6. Results of stability of target analytes in samples kept at 4 °C.

Day	Statistic	Toluene-d8	Sulfolane-d8	Benzene	Toluene	Ethylbenzene	<i>m/p</i> -Xylene	<i>o</i> -Xylene	Sulfolane
0	N	3	3	3	3	3	3	3	3
	Mean	1723903	358646	1.64	0.86	1.33	2.15	1.13	0.91
	SD	32454	5076	0.11	0.06	0.10	0.15	0.08	0.03
	RSD	2%	1%	7%	7%	7%	7%	7%	3%
3	N	3	3	3	3	3	3	3	3
	Mean	1647095	344945	1.72	0.89	1.36	2.20	1.16	0.94
	SD	86780	16258	0.13	0.07	0.11	0.17	0.08	0.05
	RSD	5%	5%	7%	8%	8%	8%	7%	6%
8	N	3	3	3	3	3	3	3	3
	Mean	1688260	361630	1.60	0.83	1.26	2.02	1.08	0.89
	SD	74115	19287	0.08	0.05	0.08	0.12	0.05	0.05
	RSD	4%	5%	5%	6%	6%	6%	5%	5%
14	N	3	3	3	3	3	3	3	3
	Mean	1361130	321169	1.92	0.97	1.38	2.29	1.26	0.99
	SD	196047	23679	0.30	0.15	0.24	0.34	0.19	0.09
	RSD	14%	7%	15%	15%	17%	15%	15%	9%
23	N	3	3	3	3	3	3	3	3
	Mean	1618825	383752	1.61	0.80	1.19	1.89	1.04	0.86
	SD	57163	13176	0.12	0.06	0.11	0.16	0.08	0.01
	RSD	4%	3%	8%	8%	9%	9%	7%	2%

The results for the samples stored at room temperature and 4 °C are summarized in **Figures 3-4** and **Figure 3-5**, respectively, with detailed data provided in **Tables 3-5** and **Table 3-6**. For both storage conditions, the data show that sulfolane remains stable for up to 23 days, as expected, given its non-

volatile nature and minimal degradation potential in water under these storage conditions. In contrast, the loss of BTEX compounds begins immediately after sample collection.

For samples stored at room temperature, the most significant losses were observed for *m*-xylene and *p*-xylene, which showed a 26% reduction in concentration after 8 days. Ethylbenzene exhibited a 23% loss over the same period. In contrast, samples stored in the refrigerator showed no significant losses up to 23 days. Based on these findings, it is recommended to store water samples in the refrigerator to preserve the target analytes. However, if refrigeration is not feasible, it is essential to process and analyze the samples within 7 days to limit analytes' losses to less than 25%.

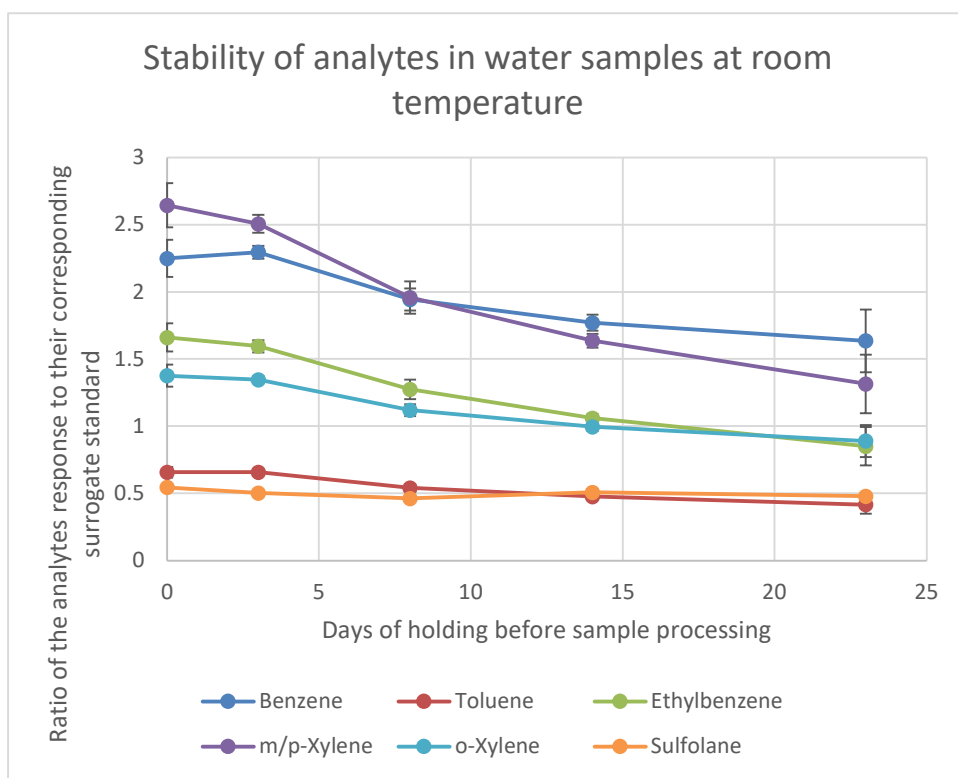


Figure 3-4. Stability of target analytes in spiked groundwater samples kept at room temperature. Error bars represent one standard deviation ($\pm$ SD).

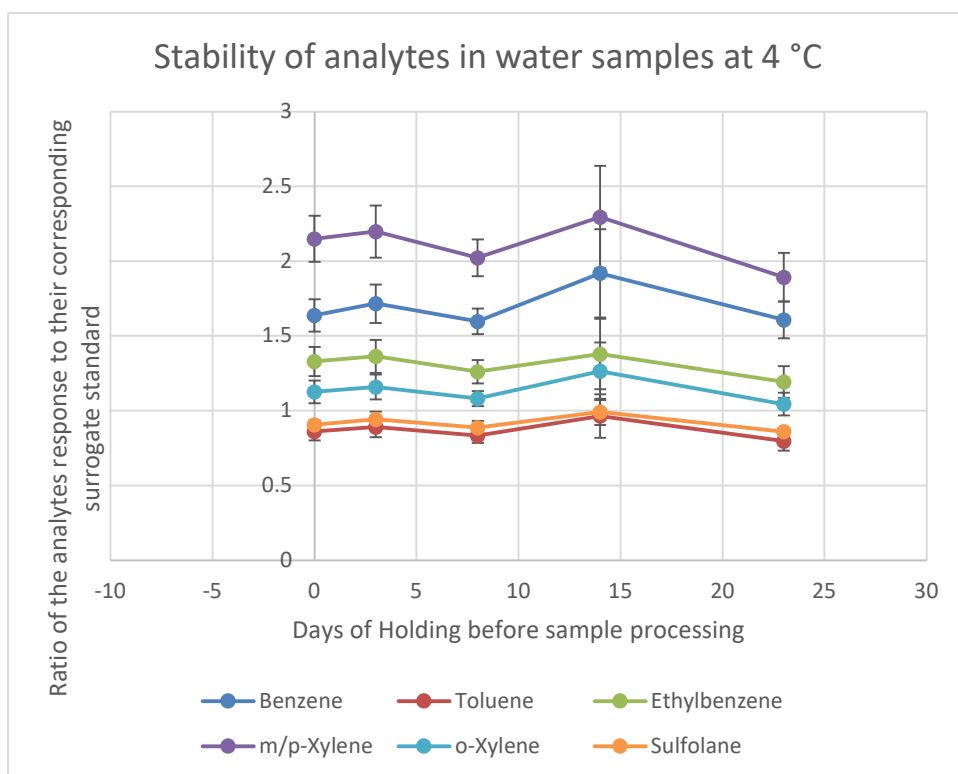


Figure 3-5. Stability of target analytes in spiked groundwater samples kept at 4 °C. Error bars represent one standard deviation ($\pm SD$).

3.2.6 Analysis of water samples

The results of the water sample analyses are presented in **Table 3-7**. In most cases, the duplicate samples exhibited consistent results as expected. Any inconsistencies were carefully examined, with the conclusion that these discrepancies likely resulted from sampling variability rather than analytical determination errors. This variability is unavoidable when working with real-world samples, as obtaining identical duplicates in the field can be challenging. Groundwater samples present a particular challenge, as they must be collected using a pump, leading to variations in collection times. Also, the amount of groundwater that could be drawn from a particular layer of the aquifer was in some cases insufficient to fill two vials at the same time. In cases like these, the collection had to be resumed at a different time, hence the samples could not be treated as true replicates. Finally, the use of a peristaltic pump can influence the concentration of BTEX compounds since the pump's internal tubing is made of

silicone rubber, which can absorb these analytes. However, the limited contact time and rapid sample collection should help minimize these effects.

Table 3-7. Results of analysis of the water samples.

Sample ID	Sample type	Toluene-d8 (area)	Sulfolane-d8 (area)	Benzene (µg/L)	Toluene (µg/L)	Ethylbenzene (µg/L)	m/p-Xylene (µg/L)	o-Xylene (µg/L)	Sulfolane (µg/L)
FS1	Surface water	2.43E+06	5.61E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS1D	Surface water	2.35E+06	5.91E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS2	Ground-water	2.74E+06	5.99E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS2D	Ground-water	2.41E+06	5.98E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS3	Ground-water	2.65E+06	5.86E+05	N.D.	2.59E+01	N.D.	N.D.	N.D.	5.20E+02
FS3D	Ground-water	2.54E+06	6.19E+05	N.D.	6.65E+00	N.D.	N.D.	N.D.	4.40E+02
FS4	Ground-water	2.22E+06	5.46E+05	N.D.	N.D.	N.D.	N.D.	N.D.	1.02E+03
FS4D	Ground-water	2.43E+06	6.41E+05	N.D.	N.D.	N.D.	N.D.	N.D.	9.62E+02
FS5	Ground-water	1.70E+06	4.35E+05	N.D.	N.D.	N.D.	N.D.	N.D.	3.19E+01
FS6	Ground-water	2.62E+06	5.38E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS7	Ground-water	2.62E+06	5.61E+05	N.D.	N.D.	N.D.	N.D.	N.D.	8.38E+01
FS7D	Ground-water	2.49E+06	6.24E+05	N.D.	N.D.	N.D.	N.D.	N.D.	8.57E+01
FS8	Ground-water	2.45E+06	5.47E+05	N.D.	N.D.	N.D.	N.D.	N.D.	9.69E+00
FS9	Ground-water	2.32E+06	5.50E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS9D	Ground-water	2.18E+06	6.13E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS10	Ground-water	2.25E+06	5.30E+05	N.D.	N.D.	N.D.	N.D.	N.D.	2.41E+02
FS10D	Ground-water	2.59E+06	6.07E+05	N.D.	N.D.	N.D.	N.D.	N.D.	2.30E+02

FS11	Ground-water	2.39E+06	5.53E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS11D	Ground-water	2.78E+06	6.38E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS12	Ground-water	2.66E+06	5.62E+05	N.D.	N.D.	N.D.	N.D.	N.D.	6.15E+01
FS12D	Ground-water	2.75E+06	6.43E+05	N.D.	N.D.	N.D.	N.D.	N.D.	5.91E+01
FS13	Ground-water	2.53E+06	5.61E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS13D	Ground-water	2.38E+06	6.22E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS14	Ground-water	2.25E+06	5.36E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS14D	Ground-water	2.12E+06	5.99E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS15	Ground-water	2.13E+06	5.34E+05	N.D.	N.D.	N.D.	9.35E+00	N.D.	3.86E+02
FS15D	Ground-water	2.39E+06	6.21E+05	N.D.	N.D.	N.D.	positive	N.D.	3.72E+02
FS16	Ground-water	2.23E+06	5.38E+05	N.D.	N.D.	N.D.	N.D.	N.D.	6.35E+02
FS16D	Ground-water	2.61E+06	6.43E+05	N.D.	N.D.	N.D.	N.D.	N.D.	6.27E+02
FS17	Ground-water	2.35E+06	5.40E+05	N.D.	N.D.	N.D.	N.D.	N.D.	positive
FS17D	Ground-water	2.60E+06	6.35E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS18	Ground-water	2.48E+06	5.18E+05	N.D.	N.D.	N.D.	N.D.	N.D.	3.71E+02
FS18D	Ground-water	2.63E+06	6.36E+05	N.D.	N.D.	N.D.	N.D.	N.D.	3.20E+02
FS19	Ground-water	2.52E+06	5.72E+05	N.D.	N.D.	N.D.	N.D.	N.D.	2.21E+03
FS19D	Ground-water	2.65E+06	6.43E+05	N.D.	N.D.	N.D.	N.D.	N.D.	2.07E+03
FS20	Ground-water	2.27E+06	5.49E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS20D	Ground-water	2.43E+06	5.82E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS21	Ground-water	2.32E+06	5.49E+05	N.D.	N.D.	N.D.	N.D.	N.D.	1.59E+03

FS21D	Ground-water	2.63E+06	6.35E+05	N.D.	N.D.	N.D.	N.D.	N.D.	1.50E+03
FS22	Surface water	2.32E+06	5.24E+05	N.D.	N.D.	N.D.	N.D.	N.D.	positive
FS22D	Surface water	1.96E+06	5.91E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS23	Ground-water	2.50E+06	6.09E+05	N.D.	N.D.	N.D.	N.D.	N.D.	5.65E+02
FS23D	Ground-water	2.34E+06	5.38E+05	N.D.	N.D.	N.D.	N.D.	N.D.	6.06E+02
FS24	Ground-water	2.55E+06	6.17E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS24D	Ground-water	2.09E+06	5.37E+05	N.D.	2.55E+01	N.D.	N.D.	N.D.	N.D.
FS25	Ground-water	2.38E+06	5.73E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS25D	Ground-water	2.52E+06	6.24E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS26	Surface water	2.47E+06	5.76E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS26D	Surface water	2.93E+06	6.27E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS27	Ground-water	2.28E+06	5.68E+05	N.D.	N.D.	N.D.	N.D.	N.D.	positive
FS27D	Ground-water	2.56E+06	6.34E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS28	Ground-water	2.65E+06	5.85E+05	N.D.	N.D.	N.D.	N.D.	N.D.	9.88E+02
FS28D	Ground-water	2.65E+06	6.52E+05	N.D.	N.D.	N.D.	N.D.	N.D.	8.12E+02
FS29	Surface water	2.73E+06	6.02E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS29D	Surface water	2.63E+06	6.13E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS30	Surface water	2.41E+06	5.61E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS30D	Surface water	2.30E+06	5.86E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS31	Surface water	2.29E+06	5.56E+05	N.D.	N.D.	N.D.	N.D.	N.D.	8.89E+00
FS31D	Surface water	2.28E+06	6.17E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

FS32	Surface water	2.18E+06	5.48E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS32D	Surface water	2.74E+06	6.23E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS33	Ground-water	2.55E+06	5.92E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS33D	Ground-water	2.32E+06	6.00E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS34	Ground-water	2.46E+06	6.03E+05	N.D.	N.D.	N.D.	N.D.	N.D.	7.79E+02
FS34D	Ground-water	2.53E+06	6.49E+05	N.D.	N.D.	N.D.	N.D.	N.D.	4.20E+01
FS35	Surface water	2.44E+06	5.41E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS35D	Surface water	2.41E+06	6.53E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS36	Ground-water	2.52E+06	5.67E+05	N.D.	1.87E+01	N.D.	N.D.	N.D.	N.D.
FS36D	Ground-water	2.18E+06	6.26E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS37	Ground-water	2.60E+06	5.71E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS37D	Ground-water	2.41E+06	6.39E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS38	Surface water	2.65E+06	5.72E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS38D	Surface water	2.76E+06	6.27E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS39	Ground-water	2.54E+06	5.76E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS39D	Ground-water	2.45E+06	5.89E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS40	Ground-water	2.58E+06	5.53E+05	N.D.	9.97E+01	N.D.	N.D.	N.D.	N.D.
FS40D	Ground-water	2.66E+06	6.47E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS41	Surface water	2.58E+06	5.56E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS41D	Surface water	2.77E+06	6.52E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS42	Ground-water	2.62E+06	5.65E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

FS42D	Ground-water	2.05E+06	6.10E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS43	Ground-water	2.64E+06	5.73E+05	N.D.	1.35E+01	N.D.	N.D.	N.D.	N.D.
FS43D	Ground-water	2.50E+06	6.61E+05	N.D.	6.01E+00	N.D.	N.D.	N.D.	N.D.
FS44	Surface water	2.47E+06	5.99E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS44D	Surface water	2.75E+06	6.57E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS45	Ground-water	2.87E+06	6.07E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS45D	Ground-water	2.51E+06	6.21E+05	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
FS46	Ground-water	2.64E+06	6.09E+05	N.D.	2.03E+02	N.D.	8.36E+00	N.D.	9.34E+02
FS46D	Ground-water	2.62E+06	6.35E+05	N.D.	1.93E+02	N.D.	6.85E+00	N.D.	7.61E+02
FS47	Surface water	2.67E+06	6.05E+05	N.D.	N.D.	N.D.	N.D.	N.D.	1.12E+03
FS47D	Surface water	2.48E+06	6.16E+05	N.D.	N.D.	N.D.	N.D.	N.D.	1.07E+03
FS48	Ground-water	2.63E+06	5.92E+05	N.D.	N.D.	N.D.	N.D.	N.D.	3.90E+02
FS48D	Ground-water	2.73E+06	6.43E+05	N.D.	N.D.	N.D.	N.D.	N.D.	4.61E+02
FS49	Ground-water	2.53E+06	5.97E+05	N.D.	5.86E+01	N.D.	N.D.	N.D.	1.52E+03
FS49D	Ground-water	2.48E+06	6.19E+05	N.D.	1.64E+01	N.D.	N.D.	N.D.	8.64E+02
FS50	Surface water	9.43E+05	5.68E+05	N.D.	N.D.	N.D.	N.D.	N.D.	positive
FS50D	Surface water	2.69E+06	6.03E+05	N.D.	N.D.	N.D.	N.D.	N.D.	positive

**Samples marked with 'D' were collected from the same location, but not always at the same time in the case of groundwater because of the occasionally limited amount of water that could be drawn from the aquifer.*

The current federal long-term water quality guideline for preservation of aquatic life, as defined by Environment and Climate Change Canada, are 0.59 mg/L for benzene, 0.03 mg/L for toluene, and 0.07 mg/L for both ethylbenzene and total xylenes. Similarly, the Government of Alberta sets a maximum

level of 0.09 mg/L for sulfolane in groundwater. As shown in **Table 3-8**, 17 samples contained sulfolane at concentrations exceeding the recommended screening level. In contrast, few samples showed detectable BTEX, with only three samples exceeding the long-term guideline concentration for toluene. Environmental factors, including seasonal variations, rainfall, and temperature, may influence these contamination levels. Therefore, regular monitoring is recommended to develop a more comprehensive understanding of the contaminant profile in this area.

Table 3-8. Summary of the result of the analysis of water samples

Contaminant	Benzene	Toluene	Ethylbenzene	<i>m/p</i> -Xylene	<i>o</i> -Xylene	Sulfolane
Positive samples, N	0	6	0	2	0	24
Positive samples, %	0%	12%	0%	4%	0%	48%
Quantified samples, N	0	6	0	2	0	20
Average concentration, positive samples (µg/L)	N/A	70.0	N/A	8.85	N/A	673
Concentration range, positive samples (µg/L)	N/A	13.5 - 203	N/A	8.36 - 9.35	N/A	8.89 - 2206
Quantified samples above long-term guideline, N	0	3	0	0		17

3.3 Conclusions

An analytical method for the simultaneous determination of BTEX and sulfolane in a single run was developed and validated. The method demonstrated good selectivity and sensitivity, with LOQs ranging from 1.8 µg/L to 8.8 µg/L for the analytes in water. The calibration range extended from the LOQ up to 8000 µg/L for all compounds.

Method ruggedness was evaluated using the Plackett-Burman experimental design. Among the factors studied, benzene was significantly affected by the time elapsed between exposing the water sample to air and adding the extraction solvent, highlighting the compound's volatility.

Sample holding time was assessed at both room temperature and refrigerated conditions by preparing two identical sets of spiked samples and analyzing them over a three-week period. Based on the results, it is recommended to process and analyze samples within 7 days of collection, as BTEX losses exceeded 25% beyond this time frame in the worst-case scenario (storage at room temperature).

Finally, the method was used to analyze 97 surface water and groundwater samples from a contaminated site in Alberta, Canada. The analysis indicated that water from 17 out of 50 locations contained sulfolane concentrations above Health Canada's recommended screening level for drinking water, while two locations exhibited toluene levels exceeding the MAC set by Health Canada. Overall, the method is suitable for its intended purpose and effective for monitoring BTEX and sulfolane in water samples. However, for a more comprehensive understanding of the contamination profile and associated risks, additional sampling and more frequent monitoring are recommended.

Chapter 4

Summary and future research directions

This research addressed the recognized gaps in the literature by developing analytical methods for the determination of sulfolane and BTEX in environmental samples, with a focus on minimizing organic solvent usage and sample manipulation where possible. The methods were designed to analyze water and rock core samples, and were subsequently validated to confirm their reliability and ruggedness. They were then used to investigate the stability of the analytes in the samples and establish the hold times for each sample type.

To optimize the extraction of sulfolane, an extraction time profile was established, which revealed that some of the samples took a long time to reach steady state. In response, an MAE method was developed and optimized to enable prompt sample analysis. The extraction efficiency of the MAE-based method was evaluated and found to be satisfactory.

The methods developed were successfully transferred to the Morwick G360 Groundwater Research Institute at the University of Guelph, where they have been integrated into their routine analytical protocols since August 2024. As a result, all the objectives of the project have been successfully achieved, providing a contribution to the field of environmental analysis.

Future research directions include the analysis of a larger number of samples from contaminated sites to elucidate the fate and transport of sulfolane in the environment. Furthermore, there is a notable gap in the development of analytical methods for the determination of sulfolane in biological tissues, such as plant and animal tissues, which is essential for understanding the potential bioaccumulation and toxicity of this compound. Additionally, the limitations of the GC-MS technique used in the methods restrict the analysis of co-contaminants without significantly compromising sensitivity. Since these co-contaminants are often present at trace levels, a more comprehensive analytical approach, such as comprehensive two-dimensional gas chromatography-mass spectrometry (GC×GC-MS), is advantageous for detecting all relevant co-contaminants with minimal loss of sensitivity. This would provide valuable information for a more detailed risk assessment and a better understanding of the environmental and health implications of sulfolane contamination.

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