UNIVERSIDADE DE EVORA

ARCHMAT

(Erasmus Mundus Master in ARCHaeological MATerials Science)

Mestrado em Arqueologia e Ambiente (Erasmus Mundus –ARCHMAT)

GC-MS ANALYSES OF ARCHAEOLOGICAL SAMPLES OF THE PHANOM SURIN SHIPWRECK FROM THAILAND

Anne-Di Victorino Berdin (m43336)

Thesis Supervisors:

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Elodie Mezzatesta, Ph.D, Co-Supervisor, University of Avignon, IMBE-IRPNC
Cristina Barrocas Dias, Ph.D, Co-Supervisor, University of Evora

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Evora, November 2020

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ABSTRACT

Archaeological samples obtained from Phanom Surin Shipwreck, Thailand were analyzed by Gas Chromatography – Mass Spectrometry (GC-MS) and Fourier Transform-Infared Spectroscopy (FT-IR) for chemical characterization and taxonomic classification. FT-IR is a fast and affordable technique used to identify chemical bonds within the sample while GC-MS analyzes chemical compounds to its molecular level, enabling the detection of biomarkers. Through these techniques, the presence of bituminous material, resinous substances from the genus *Shorea*, and lipid extracts were identified from the three samples analyzed. The information obtained from the samples can aid in establishing trade connections among ancient communities and in identifying the provenances of each raw materials that were utilized during the 7th-8th century CE Asian maritime trade.

Análise por GC-MS de amostras arqueológicas recuperadas do navio naufragado Phanom Surin, Tailândia.

RESUMO

Amostras arqueológicas obtidas do navio naufragado Phanom Surin, Tailândia, foram analisadas por cromatografia gasosa acoplada com espectrometria de massa (GC-MS) e por espectroscopia de infravermelho com transformada de Fourier (FT-IR) para caracterização química e classificação taxonómica das resinas utilizadas. FT-IR é uma técnica rápida e acessível usada para identificar ligações químicas presentes na amostra, enquanto a técnica de GC-MS permite a identificação de biomarcadores individuais. Por meio dessas técnicas, foi identificada nos extractos lipídicos das três amostras analisadas a presença de material betuminoso, e a presença de substâncias resinosas do género *Shorea* da família *Dipterocarpaceae*. As informações obtidas nestas amostras podem ajudar a estabelecer a rede de ligações comerciais entre comunidades antigas, e a identificar a proveniência das matérias-primas utilizadas no comércio marítimo asiático dos séculos VII a VIII d.C.

ACKNOWLEDGMENTS

LIST OF FIGURES

LIST OF TABLES

TABLE OF CONTENTS

For my grandparents, Hugo and Tuning Victorino.

May their souls be at peace, wherever they are…

CHAPTER 1. INTRODUCTION

The research project is a collaborative and multidisciplinary study with a general objective of obtaining the chemical characterization of archaeological organic samples from Phanom Surin Shipwreck (PNS), Thailand. It aims to determine the molecular compounds that make-up the samples by means of Gas Chromatography-Mass Spectrometry (GC-MS) as the primary analytical technique and by Fourier Transformed - Infrared Spectroscopy (FT-IR) as a complementary tool. The organic samples that will be analyzed are expected to yield resins from the *Dipterocarpaceae* family. Dipterocarps are of triterpenic in nature and are endemically found in Southeast Asia and the Indian subcontinent. Due to its abundance, it has long been cultivated and exploited by ancient communities. These resins have also been used as prestige goods in maritime trading and have been a contributing factor in the development of complex societies within the region.

The research was conducted at Avignon University's Mediterranean Institute of Marine and Terrestrial Biodiversity and Ecology (IMBE) - Ecological Restoration of Ecosystems and Cultural Heritage (IRPNC*).* IRPNC's main objective was to develop theoretical approaches that will be used in the analysis of artistic and archaeological materials. To achieve this, IRPNC applies various chromatographic and spectroscopic methods for the identification and characterization of organic materials used in cultural heritage such as resins, dyes, pigments, binding media, etc.

The student/researcher was not able to perform the analysis of the samples due to travel restrictions brought about by the COVID-19 pandemic. With this, both the laboratory analysis and data interpretation were performed by her supervisors, Dr. Elodie Mezzatesta and Dr. Carole Mathe de Souza respectively. Despite the restriction, the student/researcher was tasked to synthesize the findings and relate it to previous studies on organic samples from the Phanom Surin Shipwreck, specifically the research conducted by Dr. Jacques Connan and colleagues

whose bitumen analysis were recently published in the *Journal of Archaeological Science* 117 (2020). The student/researcher also presented how the organic samples obtained from the Phanom Surin Shipwreck can provide new information on possible trading connections and routes along the Indian Ocean between the 7th and 8th century CE.

1.1. Phanom Surin Shipwreck (PNS)

Figure 1. The Phanom Surin Shipwreck. Photo from Bangkok Post.

On September 2013, the 1st Regional Office of Fine Arts Department, Thailand received a call from the Subdistrict Administration of Organization of Pan Thai about a startling new discovery in Samut Sakhon Province. It was reported that local shrimp farm owners, Mr. Surin and Mrs. Phanom Sringamdee discovered a shipwreck's keelson along with its other infrastructures in their property at Wat Klang Klong, Pan Thai, Samut Sakhon Province, Thailand. The shipwreck is situated between the Tha Chin and Chao Praya river deltas, 8 km from the current shoreline of the Gulf of Thailand (Fig.2) (Guy, 2017). The accidental discovery prompted the 1st Regional Office in Ratchaburi and the Underwater Archaeology Division of the Fine Arts Department of Thailand to conduct further investigation and excavation of the site (Jumprom, 2014). The Thai authorities then officially named the discovery as the "**Phanom Surin Shipwreck**" (Fig. 1) in honor of the shrimp farm owners who eventually donated portions of their land for the site's preservation.

Figure 2. Location of PNS. Photo from http://museum.bu.ac.th/Newsletter/SEACM_V8_no1.pdf

There have been two excavations of the Phanom Surin Shipwreck to date (2014 and 2015) with Dr. Tom Vosmer, Research Assistant from the Department of Maritime Archaeology, Western Austalian Museum, Australia and Adjunct Professor at University of Western Australian heading the project. It was mostly devoid of cargoes upon discovery which prompted researchers to hypothesize that the crew have already offloaded somewhere else. Despite this, the wreck can be provisionally assigned between 700-1000 CE, with 700-800 CE as the more conservative dates based on the ceramics that were found onboard. These ceramics belong to different typologies from three origins namely East Asia (Guangdong glazed ceramics), Southeast Asia (Mon earthenware), and West Asia (Persian torpedo jars). Further examination of the ship's timbers and fiber using radiocarbon dating assigned the Phanom Surin Shipwreck to be of mid- to late 8th century CE (Guy, 2019).

1.1.1. Physical Characteristics of the Phanom Surin Shipwreck

Based on its timber formation, the hull of the Phanom Surin Shipwreck (PNS) was stitched (Fig. 3). The planks were drilled allowing the fiber cords to bind, enabling the joints to be sealed by resinous materials to ensure its impermeability from water. The keelson was measured to be 17.67 meters long while one of the two deck mast stood at 17.35 meters. The hulls and masts were made from hardwood

Figure 3. The sewn stich of PNS. Photo by Thailand's Ministry of Culture and Fine Arts.

while the decking and fittings were made from softwood (Fig. 4). Based from its construction, the PNS was identified to be of West Asian in origin. It is the second West Asian ship discovered in

Figure 4. The excavated ship mast. Photo from Thailand's Ministry of Culture and Fine Arts

Southeast Asian waters after the Belitung Wreck in Indonesia which was found in 1998 (Flecker, 2001). Similar with the Belitung Wreck, the PNS is presumed as an Arab *dhow*. *Dhows* were a popular boat type seen transporting goods and people in West Asia and Indian Ocean (Vosmer, 2019). An Arab *dhow* was depicted in *Muqamat al-Hirani*, a 13th century manuscript painting and described as having a stitched hull construction, with a stern rudder, lateen-rigged sail, and composite grapnel anchor (Guy, 2019). It was also depicted in *Ling biaoluyi*, a Late Tang Dynasty source which was a contemporary of the Phanom Surin Shipwreck. It described the PNS having strapped planks with

fibered coil palms with all seams caulked with an olive paste. The 14th century Moroccan traveller, Ibn Battuta also described the Arab *dhow* with a coconut fiber cord called *qandar*, which originated from Maldives (Guy, 2017). Maldives cord or *qandar* was shipped to Yemen which was known for its boatbuilding industry as well as to China during this period. Ibn Battuta further elaborated that sailors navigating the Indian Ocean knew of its many reefs and that ships with iron nails will not be able to withsand collisions with rocks. To resolve this, they sew the cords together preventing the planks to fall apart therefore giving the ship a certain resilience (Guy, 2017).

1.1.2. Ceramic Vessels from the Phanom Surin Shipwreck

Figure 5. Dvaravati Earthenware Pot. Photo from Thailand's Ministry of Culture and Fine Arts

The ceramics that were found in the Phanom Surin Shipwreck were of Chinese, Mon, and Persian in origin. The ceramics were mostly storage jars used to transport liquid goods along the Indian Ocean. The Chinese ceramics were identified coming from the Late Tang Dynasty period,

Guangdong Province. Some of the Guangdong storage jars have Arabic inscriptions indicating that they were bound to West Asian markets. The ancient city of Siraf in Bushehr province, Iran were once a major entrepot for Chinese and Persian trade until 970 CE, where an earthquake devastated the city (Guy, 2017). Aside from the Guangdong jars, there were several Mon earthenwares that were also found in the ship (Fig. 5). The Mon- Dvaravatis who originated from China 3000 years ago, were the first people who inhabited mainland Southeast Asia. They established some of the earliest civilizations in Thailand, Laos, and Myanmar including the Dvaravati (Central Thailand), Sri Gotapura (Central Laos and Northeaster Thailand), Hariphunchai (Northern Thailand) and Thaton Kingdom (Southern Myanmar) (Coedes, 1968). They were also responsible for the popularity of Theravada Buddhism in mainland Southeast Asia which they adapted from Sri Lankan missionaries. The earthenwares recovered from the Phanom Surin Shipwreck had incisions and marks associated with the Mon-Dvaravatis (Guy, 2017). They were most likely used as food containers for the ship's crew since there was an absence of elaborate designs usually associated with upper class and religious authorities.

1.1.2.1. Torpedo Jars

Figure 6. Torpedo Jar. Photo by John Guy (2017).

The last type of ceramics found in the Phanom Surin Shipwreck was the first of its kind found in Thailand. There were 9 large fragments of torpedo jars recovered from the ship. The torpedo jars were commonly used in West Asia and have been discovered in various archaeological sites in the region such as the Great Mosque foundation in Siraf, Busheher Province in Iran and the *Dar Al-Amma* caliphal palace in Samara, Iraq (Guy, 2017 and 2019). Torpedo jars have also been excavated in the African continent specifically in Zanzibar Island, Tanzania, and East Africa. The jars were used as liquid containers for the Indian Ocean trade. Its function is similar to that of amphoras which were containers used in Ancient Greece and Rome

to transport liquids such as wine, olive oil and garum (fish sauce) (Adilbekov, 2016). Torpedo jars recovered from the PNS were sealed with bitumen to prevent leakage. Bitumen was a sticky, viscous material and a form of petroleum with several different functions. Its adhesiveness and water impermeability were highly regarded which is why it was commonly used as a sealing agent for boats and containers alike. There were two main types of torpedo jars based on their morphological make-up. TORP-S is characterized as brownish to orange in color with thinner walls, with mixed sandy grit inclusions while TORP-C is described as cream-colored, less sandy, with thicker walls and a pronounced projecting internal lip (Lischi *et. al.*, 2020). TORP-S appeared to be of earlier class and where found in large quantities in an underwater excavation in the port city of Bushehr which played a significant role in international commerce during the Sassanid Period (224 to 651 CE) (Tofighian, 2019). Samples of TORP-S have also been found in various sites in Iran such as Kush, Jazirat al-Ghanam and Sir Bani Yas; in Fulayj, Oman; and in India and Sri Lanka. TORP-C samples were more associated during the mid- to late eight century CE and were found in Sohar, Manda, and Siraf (Tomber *et. al.,* 2020). Both assemblages were found in the Phanom Surin Shipwreck with TORP-C being the more prevalent one (Connan *et. al.,* 2020)
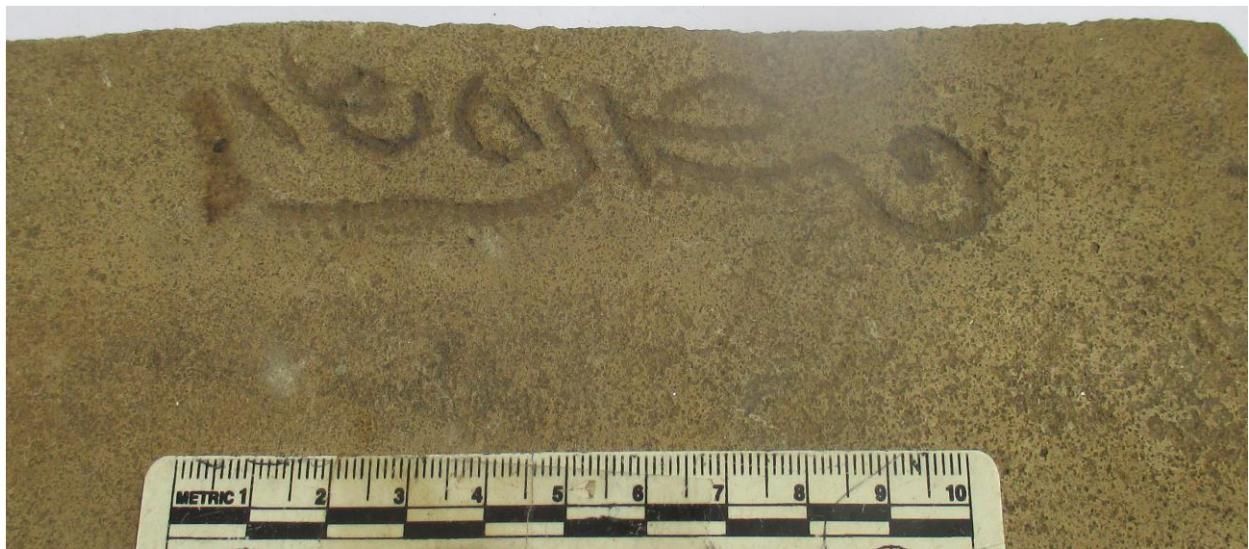
Figure 7. Pahlavi Incription from PNS. Photo from Thailand's Ministry of Culture and Fine Arts.

1.1.2.2. *Ceramic Inscriptions*

Two notable inscriptions were discovered in the ceramics. The first inscription was a Chinese character found in one of the green Guangdong storage jars depicting a "branch office" associated where the jars were probably produced (Guy, 2017). The second one was more unique and was found in one of the torpedo jars. The text was identified as a Pahlavi inscription by Professor Prods Oktor Skjǽrvo of Harvard University which were of Persian origin used by Persians, Zoroastrians, and Christians during the Sasanian Empire (Guy, 2017). The inscription which read as "Yazd – bōzēd" appeared to be a name of a person and speculations about his association with the jars abound. He could have owned the jars, a merchant aboard the ship, the captain of the ship, or the investor who funded the trip. Regardless of his actual profession, it would seem likely that he was Persian and was involved in shipping or trading. The discovery of "Yazd – bōzēd" Pahlavi inscription, the first in Southeast Asia, along with the Guangdong storage jars designated the cargo to be in the second half of 8th century CE which was further supported by the radiocarbon dates of the timbers and fibers which were also assigned in the mid-8th century CE (Guy, 2017).

Figure 8. Interior of torpedo jars with a probable bitumen sealant. Photo from Thailand's Ministry of Culture and Fine Arts

The discovery of the Phanom Surin Shipwreck was notable in many ways. It was the second shipwreck that were of West Asian origin discovered in Southeast Asia after the Belitung Wreck. Its cargoes included the first set of torpedo jars that were found in Thailand. The Pahlavi inscription in the torpedo jars further strengthened the role of Persian merchants in the trade between China, Southeast Asia, and West Asia. The wreck which was strategically located between Tha

Chin and Chao Praya, the two most important river systems in Central Thailand was also an indication that the crew aboard the ship might have an association or have at least interacted with local communities along the Tha Chin since they also utilized Mon earthenwares. The Phanom Surin Shipwreck highlighted the significant role of Persian traders in the West Asia – China trade. Not only that, it also opened up new discussions and researches on trading routes that we have no prior knowledge of, the role of local communities in Thailand when it comes to supplying Persian merchants with international goods, and other unknown markets which can be of source for commodities that can be traded beyond the Gulf of Thailand (Guy, 2017 and 2019).
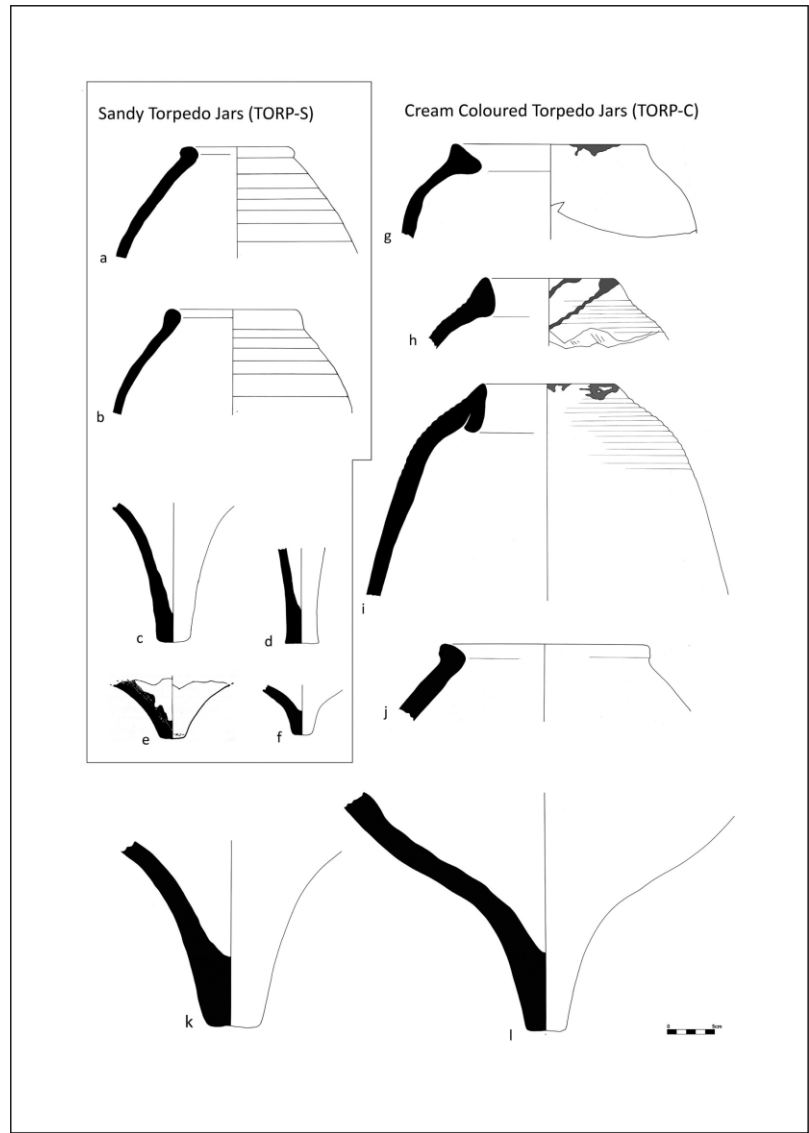
Figure 9. Sandy and Cream Coloured Torpedo Jars. From Connan et. al. 2020

CHAPTER 2. REVIEW OF RELATED LITERATURE

2.1. Organic Residue Analysis (ORA)

Organic Residue Analysis or ORA is the study of amorphous and invisible remains in archaeological sites. It deals with a variety of organic samples which are often found in association with various artefacts (Dunne *et. al.,* 2017). Its amorphous nature sets it apart from other organic remains such as bone, wood, leather, and textiles due to the absence of tangible features. Because of this unique trait, samples have to undergo analytical techniques that can characterise and detect individual compounds called **biomolecules**. These are compounds being investigated to determine the geologic and environmental processes that archaeological remains have endured through the course of its history by analyzing its carbon skeletons that were able to persist and survive over a long period of time. The characterisation of these biomolecules and the succeeding environmental processes that it experienced are the objectives of an approach called the **archaeological biomarker concept** (Evershed, 2008).

The archaeological biomarker concept was developed for the biomolecular analysis of organic archaeological remains therefore providing us with knowledge relating to past human activities. It relies on matching the chemical structures and distributions identified in archaeological remains to those in modern organisms known as **chemical fingerprints** (Dunne *et. al.*, 2017). Biomarkers cover a wide variety of organic compounds including proteins, carbohydrates, lipids, nucleic acids, and amino acids.

Although ORA is known more for the identification of food products that were processed and stored in ceramics, it can also address issues from an array of topics such as historic trading networks (Roffet-Salque *et. al.,* 2017), ancient ceramic technologies (Oudemans, 2007),

acquisition and exploitation of resources (Luong *et. al.,* 2019), ritual ceremonies (Crown *et. al.,* 2012), and ancient foodways (Dunne *et. al.,* 2019). ORA can provide information on various archaeological scales – from site, local, national and global context. ORA can also aide in identifying the organic materials that were used to create boats (Burger *et. al.,* 2011) and ceramics (Rageot *et. al.,* 2019). Most importantly, ORA allows the characterisation of raw materials including terrestrial animal fats wherein isotopic approaches allow us to differentiate between ruminant and non-ruminant fats (Evershed *et. al.,* 2020); aquatic fats from fishes and marine mammals (Craig *et. al.,* 2007 and Heron and Craig, 2015); plant oils and waxes (Colombini *et. al.,* 2005 and Copley *et. al.,* 2005); beeswax (Heron *et. al.,* 1994); resins (Charrie-Duhat *et. al.,* 2011); tars (Mitkidou *et. al.,* 2008 and Rageot *et. al.,* 2019); and bitumen (Connan, 1999). For this specific research, the focus will be the residue analysis of organic substances such as plant resins found in the Phanom Surin Shipwreck and how it relates to the site itself, on a local, national, and even global scale since it was found with a variety of objects from different origins.

2.2. Plant Resins

Resins are highly viscous materials produced in the plant's epithelial cells. Its main chemical constituents are terpenoids and phenolic compounds produced when carbohydrates are broken down to simpler compounds by means of photosynthesis. Terpenoid or terpenes comes from the word, *turpentine* which originally came from the old French word, *ter(e)binth* which means *resins* (Hussein and El-Anssary, 2019). There are several classifications of terpenes depending on the amount of its carbon atoms per molecule. Monoterpenes have 10 carbon atoms per molecule, sesquiterpenes have 15 carbon atoms per molecule, diterpenes have 20 carbon atoms per molecule, and triterpenes have 30 carbon atoms per molecule. Mono- and sesquiterpenes are volatile fractions of terpenoids while di- and triterpenoids are non-volatile fractions. Diterpenoids and triterpenoids have never been found together in the same resin which can be useful in identifying a plant's taxonomy (Bruni and Guglielmi, 2014). Diterpenes are produced by conifers from the *Caesalpinoideae, Leguminoseae, and Araucariaceae* families while triterpenes are produced by angiosperms such as those from the *Burseraceae (elemis), Anacardiaceae (mastic), and*

Dipterocarpaceae (dammar). Resins also consisted of other chemical compounds such as alcohols, aldehydes, and esters (Langenheim, 1990).

Phenols (C_6H_5OH) are aromatic, volatile compounds comprising of phenyl group (-C_6H_5) which is bonded to a hydroxy group (-OH). They are usually found in plants where they significantly affect the color, taste, and flavor of many herbs, foods, and drinks. Phenols or phenolic compounds make up the largest group of secondary metabolites. Secondary plant metabolites are chemical compounds produced by plant cells via metabolic pathways originating from primary metabolic pathways (Hussein and El-Anssary, 2019). Secondary metabolites have healing and therapeutic

Figure 10. Distribution of Dipterocarps Around the World. From Appanah and Turnball (1998)

effects enabling plant resins to be used as antibiotics, antifungal, and antiviral medicines. Furthermore, these therapeutic characteristic of plant resins allows for self-protection from pathogens and leaf damages caused by ultraviolet (UV) rays (Hussein and El-Anssary, 2019).

Resins were primarily obtained by tapping wherein an incision is made from the bark of a tree. It can also be produced naturally when a tree sustains injury from either animal attack or from strong winds. Resins have long been exploited by man in various ways. Apart from its medicinal purposes, resins have adhesive properties suitable for varnishing and paint media in art. Its immiscibility in water allows resins to act as a waterproofing material for amphoraes, ceramics, liquid containers and boats. The oldest known consumption of plant resin was during the late Middle Stone Age in Southern Africa wherein it was used as an adhesive for hafting stone stools (Kozowyk, *et. al.*, 2016).

2.2.1. _Resins from the Dipterocarpaceae Family_

The *Dipterocarpaceae* family is made up of 16 genera and 695 known species (Christenhusz and Byng, 2016). The largest genera is *Shorea* with 196 species, followed by *Hopea* with 104 species, *Dipterocarpus* with 70 species and then by *Vatica* with 65 species (Ashton, 2004). A tree from this family can grow as tall as 40.0-90.0 meters with a *Shorea faguetiana* named "*Menara"* from Danum Valley Conservation Area, Borneo being recorded the tallest at 97.58 meters. The distribution of the *Dipterocarpaceae* family is pantropical and can be found in northern South America to Africa, Seychelles Islands, India, Sri Lanka, Southern China, Southeast Asia and Malesia which consists of Malaysia, Singapore, Brunei, Indonesia, the Philippines, and New Guinea. Borneo which is the largest island in Asia and the third largest in the world has the greatest number of dipterocarp species. The name *Dipterocarpaceae* was of Greek origin which meant "two-winged fruits" (di = two, ptero = wing, carp = fruit) (Ashton, 2004).

Table 1. Phylogeny of the *Dipterocarpaceae* family (Christenhusz and Byng, 2016)

Dipterocarpacea	*Monotoideae*	*Monotes* *Marquesia* *Pseudomontes*	
	Dipterocarpoideae	*Dipterocarpaeae*	*Anisoptera* *Cotylobium* *Dipterocarpus* *Stemenoporus* *Upuna* *Vateria* *Vateriopsis* *Vatica*
		Shoreae	*Dryobalanops* *Hopea* *Neobalanocarpus* *Parashorea* *Shorea*

The Dipterocarps were first described by Karl Ludwig von Blume (1796-1862), a German -Dutch botanist who conducted the first major botanical research in Java, which was then a colony of the Netherlands (Ghazoul, 2016). In 1825, Blume published "*Bijdragen tot de Flora van Nederlandsch Indie*" or "*The Contribution to the Flora of the Dutch Indies*" wherein he described the first four species of *Dipterocarpus* that he encountered in the island (Ghazoul, 2016). The colonial occupation in Southeast Asia also saw the establishments of botanical gardens in Bogor (1817), Penang (1800), and Singapore (1859) where European botanists and ecologists devoted their time in studying various tropical plants and trees endemic to the region. In 1839, the number of dipterocarps rose to 28, 14 of which were recorded by Blume. Korthals then added 11 more species in 1842. De Candolle recorded an additional 126 in 1868. Another 170 species where added in 1874 by Thiselton Dyer while Dietrich Brandis recorded 325 more species in 1894 (Ghazoul, 2016). The abundance and accessibility of Dipterocarps in Asia made it easy for botanists and silviculturalists alike to document its many species, becoming the most well-known trees in tropical rainforestsall over the world.

The Dipterocarps are divided into 2 sub-families, namely *Monotoideae* and *Dipterocarpoideae*. *Monotoideae* which is found in the African mainland and in Madagascar have 3 genera, *Monotes* with 30 species, *Marquesia* with 3 species and *Pseudomonotes* which has a single species called *Pseudomonotestropenbonsii* found in the Colombian Amazon. *Dipterocarpoideae* is the largest among the two sub-families with 13 genera and 470 species. Dipterocarpoideae is divided into 2 groups –*Dipterocarpeae* and *Shoreae* (Christenhusz and Byng, 2016). Dipterocarpeae has 8 genera - *Anisoptera, Cotylelobium, Dipterocarpus, Stemenoporus, Upuna, Vateria, Vateriopsis*, and *Vatica*. *Shoreae* meanwhile has 5 genera - *Dryobalanops, Hopea, Neobalanocarpus, Parashorea, and Shorea*.

Dipterocarps from Asia and *Sarcolaenaceae*, a tree family endemic to Madagascar have a common ancestor from the southern supercontinent of Gondwana. The ancestor of both Asian Dipterocarps and *Sarcolaenaceae* was found in the ancient landmass shared by the modern nations of India, Madagascar, and Seychelles millions of years ago. This ancestor was transported by India northward which eventually collided with the large Asian landmass allowing it to spread across Southeast Asia. The first ever Dipterocarp pollen was discovered in Myanmar which was once part

of the Indian plate, was dated from the Upper Oligocene Period (about 23 to 34 million years before the present) (Morley, 2000). This pollen ancestor eventually became more abundant and diverse in the region during the Mid-Miocene Period (16 to 11.6 million years ago).

Regardless of the species, the Asian Dipterocarps were also known by its local name, *dammar,* a term of Malay origin. Dammars have long been utilized by locals in various ways. It is used for medicinal purposes, illumination, dyeing, adhesion, construction and waterproofing boats and houses (Gianno, *et. al.,* 1987). Dammars are easily utilized not only because of its accessibility but also due to its transportability. They can be packaged, shipped, and transported to long distances without affecting its properties (Hale, 1998).

Resins were often traded in the region along with other prestige goods such as beads, ceramics, rattans, silk cloths, and metals (Gianno, *et. al.,* 1987). It was suggested that dammars and other luxury items were responsible for the development of states and polities during the Protohistoric Period in Southeast Asia (200 CE – 1400 CE) (Gianno, *et. al,.* 1987). *Pinus merkusii* or Sumatran Pine was attributed to the emergence and expansion of Sriwijaya, the earliest known state in the region that flourished between 7th to 13th century CE in what is now Indonesia. The Sriwijayans monopolized and traded extensively this resin which resulted to economic prosperity. The Semalai people of Tasek Bara, Malaysia also used dammars for various manufacturing processes such as torches, blowpipes, boats, baskets; for hafting knives and spears; and for medicinal purposes (Gianno, *et. al.,* 1987)The people of Champa Kingdom (2nd to 19th century CE) in Central and Southern Vietnam used dammars as binding agents for the mortars and plasters in the construction of temples in My Son (Tamburini*, et. al.*, 2017). A wreck found 40 km off the coast of Brunei, believed to be from the Hongzi Era (1488-1506 CE) contained dammars from 2 different *Dipterocarpus* species, namely *D. intricatus Dyer* and *D. cf. dyeri* (Burger, *et. al.,* 2011) Dammars alongside with pitch and bitumen were also utilized to caulk a Portuguese warship found in the Straits of Malacca which was destroyed during the Battle with the Achenes in 1538 CE (Burger, *et. al.,* 2009). Lastly, dammars were also found during a 2006 excavation in Khao Sam Kheo, Thailand belonging to *D. obfusifolius Teysm* and *Dipterocarpus cf. dyeri*. (Burger, *et. al.,* 2017). Dammars were first brought to Europe in 1829 and had been used extensively since 1844 for varnishing, decorating, and painting purposes (Langenheim, 2003).

2.2.1.1.Botanical Description

Dipterocarps are small and large evergreen trees dominating the Southeast Asian rainforests. Stems can either have plagiotropic (horizontal) or orthotropic (vertical) branching. The genus *Hopea* and *Shorea* have plagiotropic branching while *Dipterocarpus* have orthotropic branching. Barks can vary depending on species, but they can either be smooth, dippled, has shallow fissured, deep fissured, scaly, surface rotten or laminated. Distinction among bark types can only be observed when a tree grows into maturity or when it reaches a height of 30 meters. Leaves of Dipterocarps are simple, but its shapes and sizes vary depending on species. Shapes can either be lanceolate, elliptical, oblong, ovate, and abovate (Ghazoul, 2016). The leaves of the genus *Shorea* are usually small. The leaf venation pattern of Dipterocarp trees is an important identification marker. Many leaves of *Dipterocarpus*, *Hopea*, and *Shorea* trees have veins that run parallel to each other and lie perpendicular or diagonal to the secondary veins (Ghazoul, 2016). The flowers are hermaphrodite wherein female and male reproductive organs are present. They are also scented with a sweet smell that secretes nectar. Ovaries of *Dipterocarps* are 3-celled except for *Pakaraimaea* with 5-cells, *Marquesia* and *Monotes* with 4 to 5 cells, and *Stemenoporus* with 2 cells. The fruits contain a nut with 2 or more wings. The wings are often unequal wherein *Shorea* have 3 long wings and 2 short ones, while *Dipterocarpus* have 2 long wings and 2 short ones. The shape of the nut can either be globose or elongated and its size can also help determine the species. Both *Shorea* and *Hopea* have imbricate sepals in fruits while *Dipterocarpus* has valvate sepals. The resin canals in both *Shorea* and *Hopea* have tangential bands while *Dipterocarpus* has scattered resin canals. Lastly, the genus *Shorea* and *Hopea* have a basic chromosome number 7 while *Dipterocarpus* has a basic chromosome number 11 (Gamage, *et. al.,* 2005).

2.2.1.2. Main Chemical Constituents of *Dipterocarpaceae*

Dammar is a generic term that corresponds to a number of resinous materials. The wide usage of the term had a few shortcomings and oftens leads to confusion in identifying its botanical origins. Regardless of the semantics, dammars are mostly made up of triterpenoids (C30) and a small amount of sesquiterpenoids (C15). Dammars also contain **polycadinene** (Fig. 11), a polymer

consisting of polysesquiterpene with a cadinene carbon skeleton structure (van der Doelen, 1999). Triterpenoids that have been analyzed in dammars were of the **tetracyclic dammarane derivatives** (Fig. 12) (van Aarssen, *et. al.,* 1993 and van der Doelen, 1999). **Pentacylic oleanane** (Fig. 12), **ursane** (Fig. 12), **and hopane derivatives** (Fig. 12) can also be detected in dammars (Mills and White, 1977; van der Doelen, 1999; Burger, *et. al.,* 2017; and Tamburini, *et.al.,* 2017). These compounds also act as biomarkers for further identifying the species of a plant resin.The genera *Shorea* and *Hopea* can be distinguished from *Dipterocarpaceae* with the **tetracylic dammarane series, pentacylic ursolic acids, and aldehydes** (Langenheim, 2003). The compounds, **α-amyrene-3-one**(Fig. 13 and **β-amyrene-3-one** (Fig. 13) were also found in the genus *Shorea* (Burger, *et. al*., 2011). Bisset, *et. al.,* (1971) did an analysis of the sesqui- and triterpenes of 35 species under the genera *Shorea* wherein they identified that the association of sesquiterpene hydrocarbons **copaenes** (Fig. 14)**, β-caryophyllene** (Fig. 14), and **β-elemene** (Fig. 14) with **triterpenic shoreic acid** (Fig. 14) was the key to distinguish the genus *Shorea* from other dipterocarps.
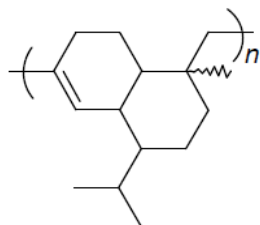
Figure 11.. Molecular structure of Polycadinene. From van der Doelen G.A. (1999)

The genus *Dipterocarpaceae* contains volatile sesquiterpenes and non-volatile triterpenes. For the *Dipterocarpus* species, the biomarker **betulonal 13** (Fig. 15) (Burger *et. al.,* 2009; 2010; and 2017) must be present to differentiate it from other dipterocarps. Burger *et. al.,* (2011) also identified several compounds to differentiate two species of *Dipterocarpus* resins found in the Chinese junk discovered off the coast of Brunei. **Dammarane derivatives** (Fig. 12) have also been found in other families other than Dipterocarpaceae such as in *Olea madagascariensis* (Bianchini, *et. al.,* 1988) from *Olaceae* family and *Boswellia frereana* (Fattorusso, *et.al.,* 1985) from *Burseraceae* family which are also angiosperms.
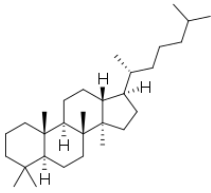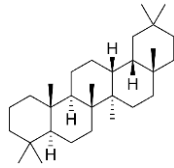
Dammarane   Oleanane   Ursane   Hopane
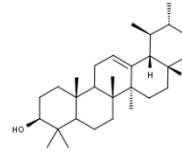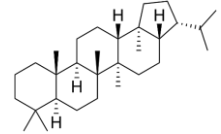
Figure 12. Triterpenoids found in Dammars
(Langenheim, 2003)

α-amyrene
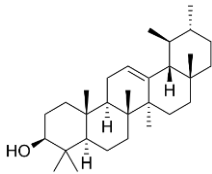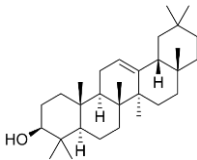
β-amyrene

Figure 13. Triterpenoids found in
the genus Shorea
(Burger et.al, 2011)
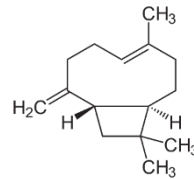
β-caryophyllene   Copaenes
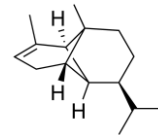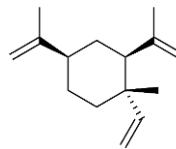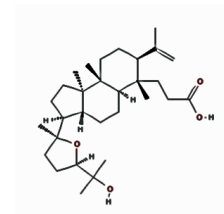
β-elemene   Shoreic Acid

Figure 14. Sesquiterpenoids and triterpenoids found in the genus
Shorea (Bisset, et. al.,1971)
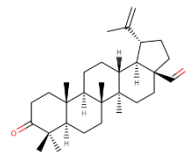
Betulonal

Figure 15. Biomarker for Dipterocarpus spp.
(Burger et. al, 2009, 2010, and 2017)

18

2.2.2. *Resins from the Araucariaceae Family*

Figure 16. Tane Mahuta or Lord of the Forest (Agathis australis) by W. Bulach.

Araucariaceae is one of the most ancient families of coniferous trees dating back to Jurassic and Cretaceous Periods. Also known as the Araucarians, it is mostly found in the Southern Hemisphere except for some of its species which propagate the Southeast Asian rainforests. It has 3 living genera with 41 species, and these are *Araucaria, Agathis, and Wollemia*. *Araucaria* has 19 species which are distributed in New Caledonia, Norfolk Island, Australia, New Guinea, Argentina, Chile, and Brazil, while *Wollemia* has 1 living species endemic to Australia. With 21 species, *Agathis* has the greatest distribution among the three and can be found in New Zealand, Australia, Vanuatu, New Caledonia, Papua New Guinea, Indonesia, Malaysia, and the Philippines (Fu *et. al.,* 1999).

Even though the Araucarians are found in the Southern Hemisphere today, they were also present in the Northern Hemisphere before they started to disappear during the Cretaceous-Paleogenic extinction event (Poinar and Brown, 2018). There where evidence that *Araucariaceae* once existed in Late Cretaceous Turkey which was once part of the supercontinent Laurasia (Kutluk *et. al.,* 2012). They flourished in forests near off the coast of the Tethyan Ocean which divided Laurasia from the southern supercontinent of Gondwana (Kutluk *et. al.,* 2012).

Araucarians are typically tall, evergreen conifers that can grow up to 60 meters or more. A giant kauri tree found in New Zealand called *Tane Mahuta* in Maori which means "God of the Forest" from the *Agathis australis* species has a height of 45.2 meters tall, with a diameter at breast height

of 491 cm, and a total wood volume of 516.70m^3 is the third largest conifer ever recorded after Sequioa and Sequoiadendron which are both from the Cupressaceae family, *Sequioideae*. Like any other conifers, it produces cones. Araucarians can either be monoecious or dioecious (Carr, n.d.). Both male and female cones are the largest among the coniferous trees. Due to their size and weight, they can cause injury if they hit a person. Cones of the *Araucaria bidwillii* weighs up to 4.5 - 6.8 kg which is about the same weight as a pineapple and can drop from a height of 23.0 meters (Armstrong, n.d.).

Popularly known as kauri or dammara, *Agathis* trees are easily recognizable not only because of their towering height but also due to their cylindrical, unbuttressed, columnar boles (Whitmore, 1980). The surface color of *Agathis* can vary from black, brown and purple with an everpresent orange hue. It has a monopodial crown with a single trunk while its roots are big and swollen. They are mostly utilized for their timber due to their finely grained, silky texture and lustrous surface (Whitmore, 1980). *Agathis*' timbers are also ideal for boatbuilding specifically for masts construction. It is also used to make furniture, instruments such as guitars and ukulele, artificial limbs, and paper pulps.

Aside from its timber, *Agathis* also produces a clear, whitish resin known colloquially as Manila copal (*A. philippinensis)*. Endemic to the Philippines, Sulawesi, and Halmahera, Manila copal (local name is *almaciga*) is mostly used for varnishes due to its elasticity and luster. Aside from varnishing, it is also used for incense, fuel for lamps and torches, as a sealing agent, paint driers, linoleum, printing inks, floor polish, shoe polish, and lacquers. Even though it came from a completely different family, Manila copal is also sometimes called dammar in Melanesia. Manila copal just like other dammars are obtained by tapping the tree. In some parts of Malaysia and New Zealand, an incision will be applied on the limbs of a tree to acquire a bigger volume of resins which can yield up to 10 -12 kg per tree annually (Whitmore, 1980).
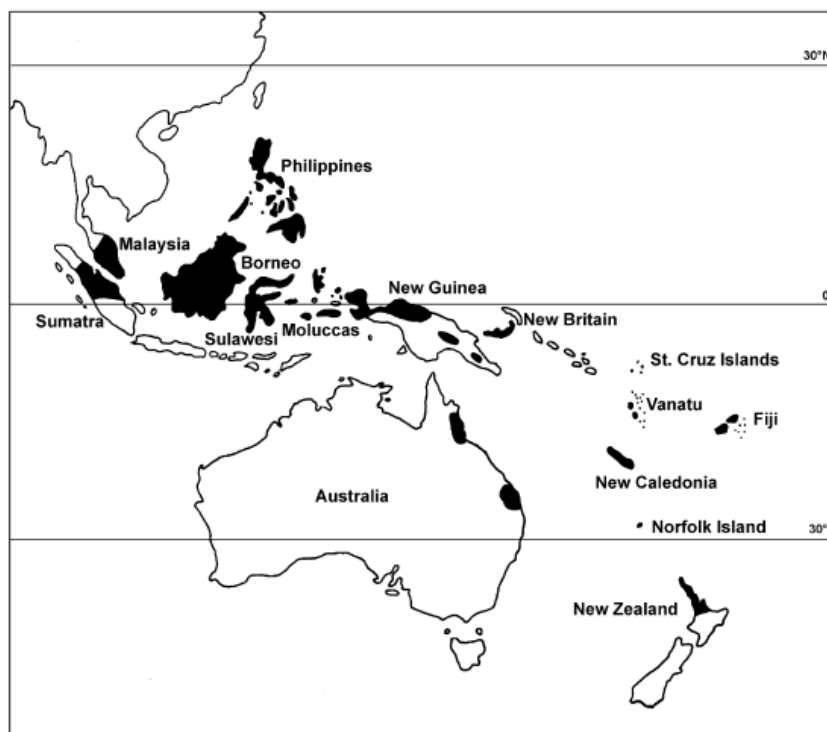
Figure 17. Distribution of Agathis genus. From Kunzmann (2007).

2.2.2.1.<u>Botanical Description</u>

Agathis have large trunks with minimal branching from the crown. The bark is smooth with light gray to gray-brown coloring. The bark normally peels into irregular flakes once the tree matures (Whitmore, 1977). Leaves from juvenile trees are often larger than in adult trees with a coppery-red color and can have an ovate or lanceolate shape while adult leaves are thick and leathery. Leaf arrangements can either be alternately or spirally. The presence of male pollen cones can be detected on larger trees while female pollen cones appear on short, lateral branches that have reached maturity after 2 years. Female pollen cones are often oval, or globe shaped (Whitmore, 1977).

The leaves are also covered with a thickly circularized and well-developed epidermis. The continuity of the epidermis is hampered by several sunken stomata of the haplocheilic type. The leaves in *Agathis* also possess a sclerenchymatous hypodermis which is present with

monocotyledon stems (Dhote, n.d.). *Agathis* also has a spongy parenchyma and its vascular bundles are surrounded by a well-developed endodermis. Leaves from coniferous trees like *Agathis* also possess transfusion tissues. Transfusion tissues are mostly made up of transfusion tracheids that have dead cells with thick and lignified walls as well as transfusion parenchyma cells that contain tannins.
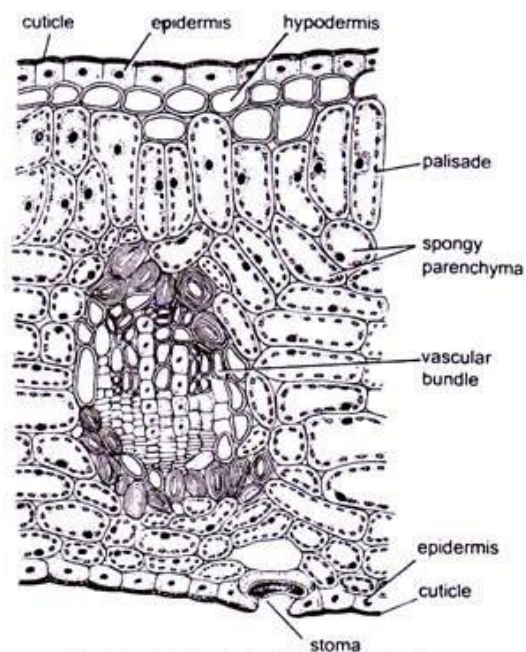
Figure 18. Leaf of Agathis robusta.
From: Biology Discussion.com

2.2.2.2.Main Chemical Constituents of Agathis

Trees belonging to the genus *Agathis* exude a complex mixture of mono-, sesqui-, and diterpenoids. The monoterpenes commonly found in Agathis are **limonene**, **myrcene**,**α-pinene**, and **β-pinene** (Fig.19). Agathis along with other Auracarians also contain **sandaracopimaric acid** (Fig.20) (Mills and White, 1977). Manila copal and kauri also have large volumes of **agathic acid** (Fig 20). Meanwhile both kauri and the Australian species also have **abietic acid** (Fig.20) which is not present in Manila copal (Mills and White, 1977).
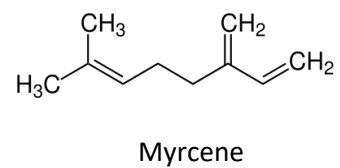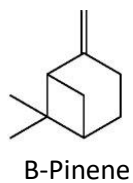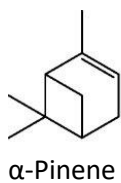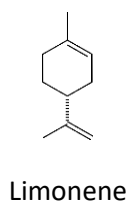
Figure 19. Monoterpenoids found in Agathis genus
(Millls and White, 1977)

Figure 20. Diterpenoids found in Agathis genus
(Mills and White, 1977)

2.3.   Analytical Techniques Applied in Resin Analysis

Two of the most well-known analytical techniques in organic residue analysis are the Fourier Transform – Infrared Spectroscopy or FT-IR and Gas Chromatography-Mass Spectrometry (GC-MS). FT-IR is a sensitive and microdestructive tool popularly applied to the analysis of different organic and inorganic materials in the field of Cultural Heritage (Pińa-Torres, *et. al*., 2018). GC-MS is used for the characterization, identification, and separation of chemical compounds. GC-MS can also be applied for the molecular analysis of organic compounds and for the detection of various alteration processes such as evaporation and leaching, biodegradation, and pyrolysis within a sample (Burger *et. al.,* 2009 and 2017). In this section, the working mechanisms, the advantanges and disadvantages of both techniques will be discussed to further understand their importance in organic residue analysis specifically, to resin analysis.

2.3.1.   Fourier Transform – Infrared Spectroscopy (FT-IR)

One of the most popular and useful techniques that has been used in the analysis of organic materials is Fourier Transform – Infrared Spectroscopy or FT-IR. In organic residue analysis, FT-IR detects and characterizes resins by producing spectra for each chemical bond found in the substance (Matheson and McCollum, 2014). The spectrum obtained from the analysis can then be categorized according to their terpenoid nature. Since diterpenoids and triterpenoids are produced by two different plant families – conifers and angiosperms, the identification of the terpenoids present in the resin is essential in determining its taxonomy. FT-IR is also used in the analysis of organic compounds due to its affordability, availability, and portability. It is also non-labor intensive and can yield fast results. It can be used in *in-situ* analysis and there is no need for prior treatment of samples unlike in other techniques.

2.3.1.1. The Principles of Fourier Transform – Infrared Spectroscopy

Infrared spectroscopy relies in the interaction of matter and infrared radiation. Infrared radiation is part of the electromagnetic spectrum that has a longer wavelength than visible light. Along the electromagnetic spectrum, as the wavelength increases, the energy decreases. Infrared is subdivided into three categories – near, mid, and far infrared. When the term IR spectroscopy is used, it often refers to the mid-infrared region. For over seventy years, infrared spectroscopy is the chosen analytrical technique in various laboratories around the world. When an IR radiation passes through a sample, some of the radiation will be absorbed while the rest will just pass through (transmitted). This absorption and transmission by the sample produces a chemical fingerprint. No two fingerprint will yield the same results making the detection of individual compounds possible. Infrared spectroscopy represents a fingerprint sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material (Adilbekov, 2016).
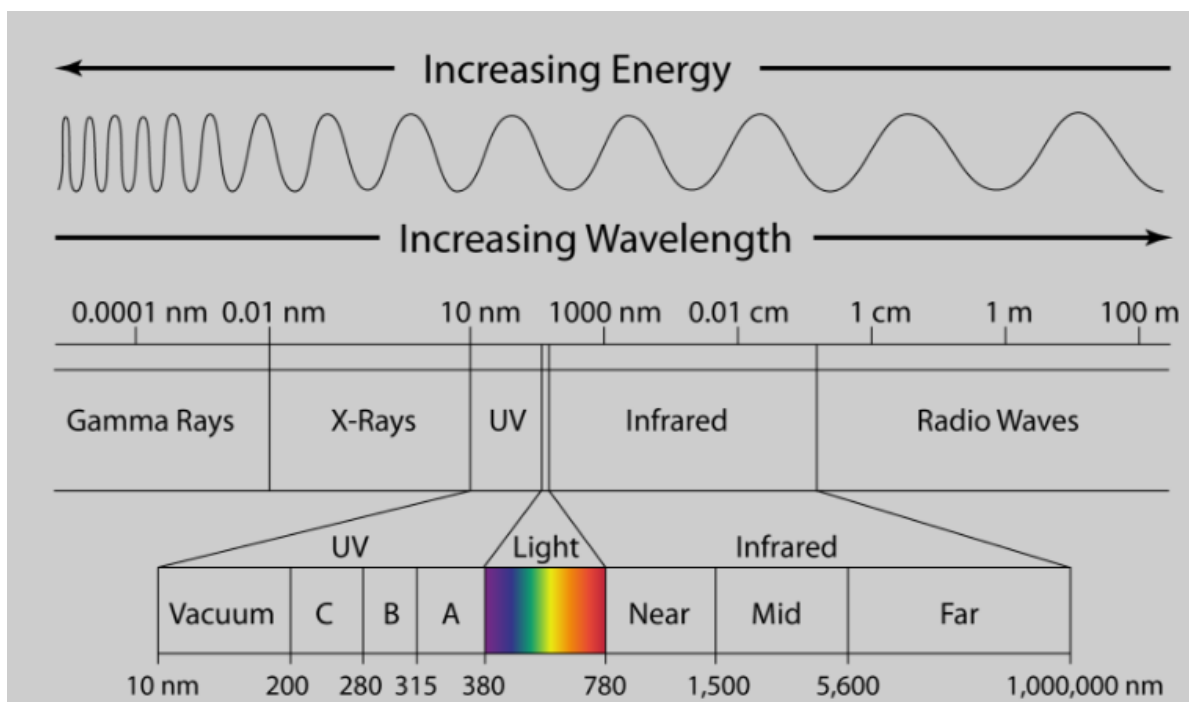
Figure 21. The Electromagnetic Spectrum. From Quora.com

The development of Fourier Transformed-Infrared Spectroscopy was a response to address the slow scanning process of dispersive instruments. Dispersive instruments were the original infrared technology used to identify individual compounds. Despite being effective, the process was time-consuming. A tool was developed called **interferometer** to address the tediousness of dispersive instruments**.** Interferometer was a simple optical device that produces a unique signal containing all the encoded infrared frequencies needed to yield a fast result, usually in a second. This device lessened the waiting time immensely wherein a signal can be detected in a matter of seconds compared to minutes that dispersive instruments perform.

Interferometers have a **beamsplitter** that absorbs infared beams that split them into two optical beams. Due to the differences on how each beam travel, one is travelling at a fixed rate while the second beam is moving constantly due to a reflecting mirror, the signal that comes out of the interferometer is the result of the two beams "interfering" with one another. The signal that results from this interference is called the **interferogram.** When measuring the interferogram, all frequencies are also being captured simultaneously, allowing the interferometer to yield speedy results.

In order to fully capture and interpret the signals produced by the interferometer, a frequency spectrum must be produced. In order to realize this, an infrared spectroscopy is always connected to a **Fourier transformation**, a mathematical operation performed by a computer to generate the spectral information needed for the analysis. With Fourier Transform – Infrared Spectroscopy or FT-IR, the identification and separation of individual compounds have enabled users to make a fast-paced but in-depth analysis of archaeological samples throughout the world.
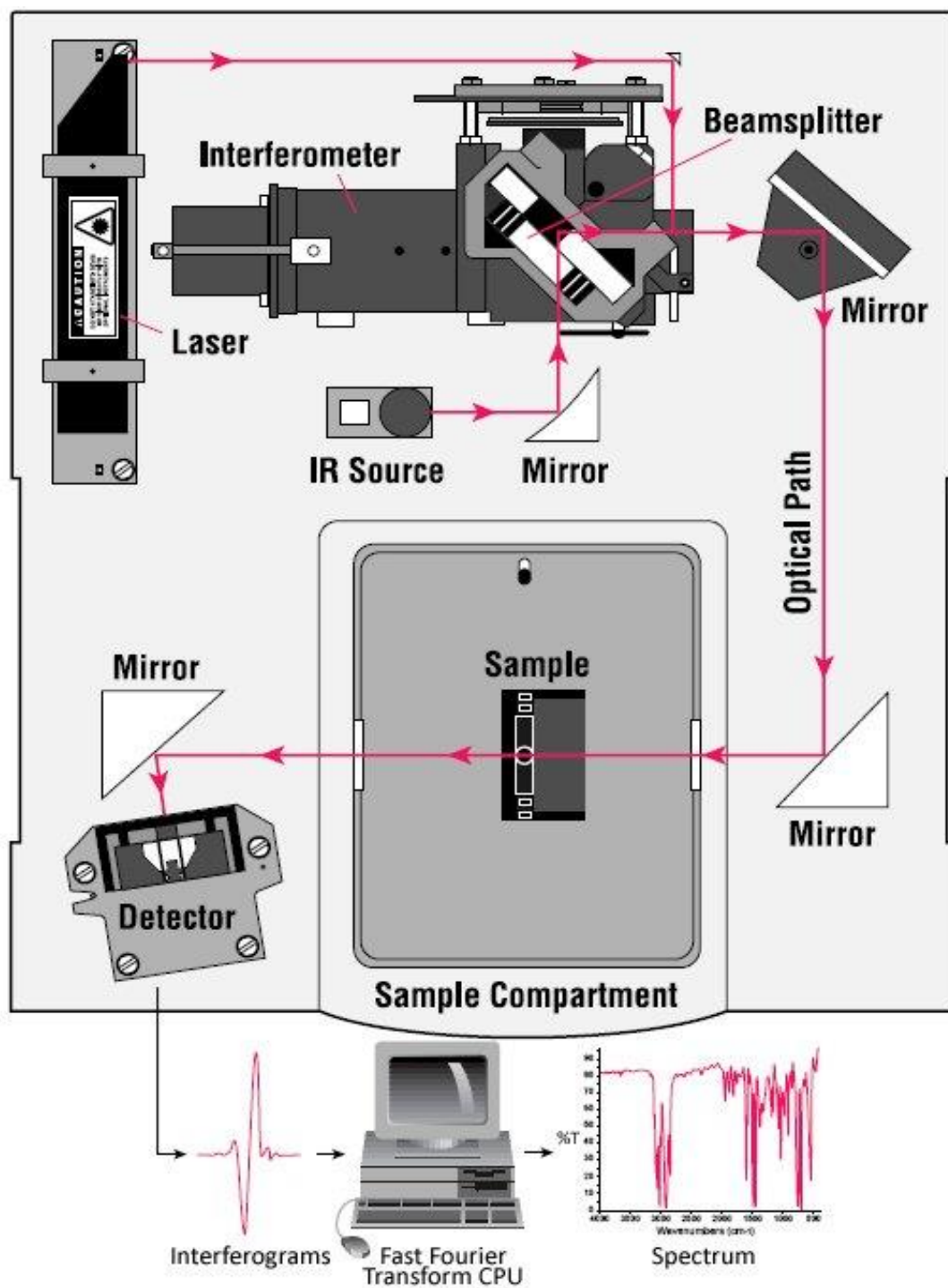
Figure 22. A Simple Spectrometer Layout.
From https://www.chem.uci.edu/~dmitryf/manuals/Fundamentals/FTIR%20principles.pdf

2.3.1.2. Interpreting IR Spectra

FT-IR is primarily used to identify the functional groups found in a given compound or mixture. It is important to identify the location of each functional groups in the transmission spectrum that the Fourier Transform will produce. The spectrum falls between 4000 to 500 cm $^{-1}$ and is divided into two main regions: the fingerprint region between 1500 to 500 cm $^{-1}$ and the functional group between 4000 to 1500 cm^{-1}. Several chemical bonds can be detected along the functional group such as the OH region between 3700 cm^{-1}-3200 cm^{-1}; the CH region between 3200 cm^{-1}-2400 cm^{-1}; and the carbonyl region at 1800 cm^{-1}-1550 cm^{-1} (Azémard, *et. al.,* 2014). The fingerprint region from 1500 to 500 cm-1 represents various bond stretching and bending vibrations of C-O, C-C, and C-N single bond nature.

Table 2. Characteristic of IR Absorptions of some functional groups (Adilbekov, 2016)

alkane	C-H	2850-3960 (m-s)		
alkene (arene)	C(sp2)-H	3020-3100 (m-s)	C=C	1620-1680 (m-w)
alkyne	C(sp)-H	~ 3300 (s)	C≡C	2100-2260 (m-w)
alcohol (ether)	O-H free O-H	3200-3700 (s, br) 3590-3650 (m)	C=O	1050-1250 (s)
aldehyde (ketone)	C(O)-H	~2720 and 2820 (w)	C=O	1630-1750 (s)
carboxylic acid	O-H	2500-3300 (s, br)	C=O	1710-1780 (s)
amine	N-H	3300-3500 (m, br)	C-N	1020-1230

Note:

Absorption bands are given in cm-1, with indications of their intensities in parenthesis with strong (s), Medium (m), Weak (w), and Broad (br).

2.3.2. Gas Chromatography – Mass Spectrometry (GC-MS)

One of the most reliable and useful technique in analyzing organic residues is Gas Chromatography-Mass Spectrometry or GC-MS. GC-MS is an analytical tool that separates and identifies a very large amount of organic compounds (Mezzatesta *et. al.,* 2020). Chromatography is derived from the Greek words, *chroma* which means "color" and *graphein* which means "to write" (Pecci, 2018). The technique was first performed by Russian-Italian botanist Mikhail Tsvet in the beginning of the 20th century to separate plant pigments such as chlorophyll, carotenes, and xantophylls which all possess different colors – green, orange, and yellow respectively (Ettre and Sakodynskii, 1993). The first half of the century saw the development of various separation techniques but it was further enhanced in the 1940s and 50s by the works of Archer John Porter Martin and Richard Laurence Millington Synge who were awarded the Nobel Prize for Chemistry in 1952 for their contribution in inventing partition chromatography. Their research and success paved the way for new chromatographic techniques such as paper chromatography, gas chromatography, and high-performance liquid chromatography.

2.3.2.1. The Principle of Gas Chromatography-Mass Spectrometry (GC-MS)

Gas Chromatography is an analytical technique used in organic residue analysis to separate samples into its individual chemical components. In some cases, it will isolate all organic compounds from one another so that individual chemical identification can occur. GC-MS is also the most common technique for the identification of terpenes in plant resins (Bruni and Guglielmi, 2014). The main parts of a gas chromatogram are the capillary column which is arranged in a coil; the stationary phase which is located in the inner wall of the column; the mobile phase which is a carrier gas (either a helium or nitrogen) that transports the sample across the stationary phase all the way to its last component, the detector.

Depending on the objectives of a research, it is essential to determine first if any treatment should be applied to the samples before it undergoes chromatographic analysis to ensure its volatility and thermal stability. This is done by applying the appropriate reagent for derivatization purposes such as trimethylsilyl (TMS), Bis(trimethylsilyl)acetamide (BSA) N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA), N-Methyl-bis [trifluoroacetamide] (MBTFA) and triflouroacetic anhydride (TFAA) (Dias, 2018). Sample preparation is an important step towards chromatography to protect the quality of the data and to avoid undesirable adsorption effects within the samples.

After the initial preparation, a small amount of the sample is injected into the injection port of the GC device where it is immediately volatized and mixed with the carrier gas. The mobile phase carries the sample to move forward down the capillary column where the stationary phase is located. The separation of molecules takes place in the stationary phase wherein molecular compounds travel in different speeds depending on their mass and volatility. Some compounds travel fast along the column to the detector while others do not. Individual molecular compounds elute in different retention times. The different retention times per molecule allows us to identify and separate them from one another, therefore helping us to determine and specify various substances found in an archaeological organic sample.
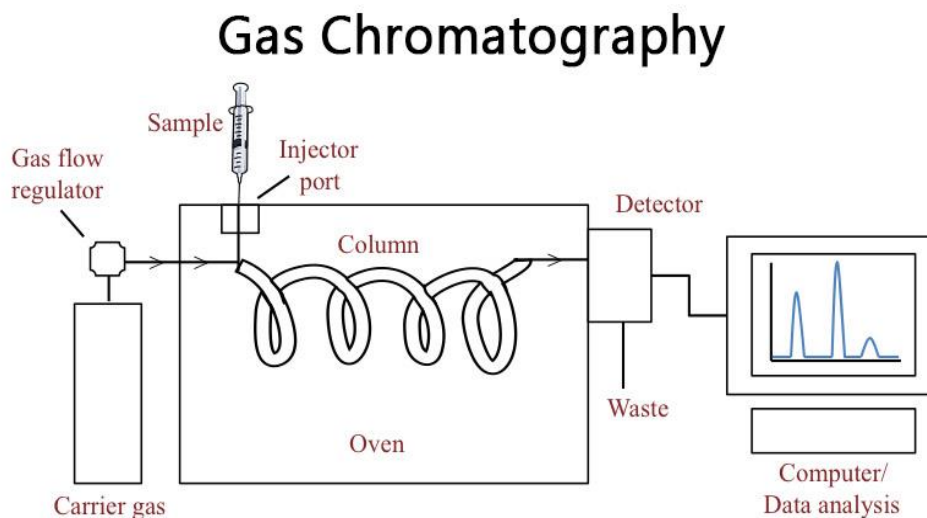

Figure 23. Gas Chromatography from https://microbenotes.com/gas-chromatography/

Gas chromatography is often used together with mass spectrometry (MS) for a more successful analysis and identification of molecular compounds. MS is a highly selective, specific, and sensitive technique that separates ions according to their mass to charge *(m/z)* ratios (Pecci, 2018). MS works by ionizing chemical compounds to generate charged molecular fragments and measuring their mass-to-charge *(m/z)* ratios. After passing through the GC column, the molecules are heated and bombarded with electrons at 70 electron volts causing them to be ionized. Through ionization, the molecules will now become positively charged particles called cations. These ions will now get accelerated to enter the magnetic field that filters them based on their mass to charge *(m/z)* ratio. The detector will then count the number of ions related to a specific mass. The information is sent to a computer and a mass spectrum is created showing the ions with different masses that traveled through the filter. To determine and validate the spectra, it will then be compared and matched against standard references available in the database. If a match is found within the database, the unknown compound will now be tentatively identified.

GC-MS has been utilized for the analysis of archaeological resins. It is the universal technique of choice when it comes to the identification of terpenoids in plant resins due to its selectivity and sensitivity. It can be used to identify the botanical source of the resin (Colombini *et. al.,* 2000), chemical composition (Assimopoulou and Papageorgiou, 2005 and Mathe *et. al.,* 2004), taxonomic classification (Burger *et. al.,* 2009, 2010, 2011, and 2017), ways of acquiring resins (Tamburini *et. al.,* 2017), and the extent of its degradation (van der Doelen *et. al.,* 1998). GC-MS can also determine the extent of degradation either due to oxidation or hydrolysis on a given substance (Mezzatesta *et. al.,* 2020 and Mizzoni and Cesaro, 2007).

Despite being highly favored in the field of organic residue analysis, the application of GC-MS has some drawbacks. It is a destructive technique making repetition of the analysis impossible. Solvents of high purity are always needed to perform sample preparations. It is also expensive, time-consuming, and cannot be conducted in-situ analysis.

2.3.3. FT-IR Spectroscopy and GC-MS Analysis as Complimentary Techniques for Resin Analysis

FT-IR Spectroscopy and GC-MS analysis have been used to analyze archaeological resins in several studies. Some studies even combine them with other techniques for a more intensive and multi-analytical approach. Natural resins applied in 16th and 17th century paintings as final protective coatings were analyzed using FT-IR and GC-MS analysis (Cartoni *et. al.*, 2003). Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FT-IR) and GC-MS were used for the identification of native plant resins from Australian Aboriginal artefacts from the Anthropology Museum at the University of Queensland, Australia (Matheson and McCollum, 2014). The organic material found in a glass vessel recovered in Pompeii was analyzed using FT-IR, direct exposure mass spectrometry (DE-MS), and GC-MS techniques (Ribechini *et. al.,* 2008). Sixteen ancient projectile weapons from the Holocene Period in northwest Canada were analyzed using FT-IR, GC-MS, scanning electron microscopy – energy dispersive spectrometry (SEM-EDS), Raman spectroscopy, and polarized light microscopy (PLM) to identify the botanical source of its adhesives (Helwig *et. al.,* 2014).

GC-MS and FT-IR analysis are reliable methods in identifying resinous substances in the archaeological record. Both techniques are effective tools that provide comprehensive understanding of the botanical source of resins, plant exploitation practices, use of natural materials, development of technologies, and their impact on cultural practices (Matheson and McCollum, 2014). The application of GC-MS and FT-IR analysis can aid in identifying which resinous materials where exploited by ancient communities as well as where and to whom it was traded. Resin as a product is crucial in determining exchanges between ancient societies since it can help in establishing previously unknown trade connections in the past. Lastly, resin identification can also provide information on the environmental and geological knowledge of past societies and the technologies they developed to modify and process these organic materials for their own benefits.

CHAPTER 3. MATERIALS AND METHODS

3.1. Materials

All three (3) archaeological samples will be analyzed from the Phanom Surin Shipwreck:

a. Sample 3190
b. Sample 3194
c. Sample 3195

Figure 24. Sample 3190. Picture from Connan et. al. (2020)

Sample 3190 was obtained inside a torpedo jar together with other samples (Samples 3191, 3192, 3193, and 3196) that were already analyzed by Connan *et. al,.* (2020). Based on previous microscopic analysis, it was of yellowish color with some vegetal debris.

Samples 3194 and 3195 were also recovered from the PNS and both were made up of resin-like material. They were not obtained inside the torpedo jar nor in other earthernware materials recovered from the PNS.

Figure 25. Sample 3194

3.2. Fourier Transform – Infrared Spectroscopy (FT-IR)

Figure 26. FTIR at IRPNC, IMBE. Photo by Carole Mathe De Souza

Archaeological samples were mixed and homogenized with 100 mg of KBr (VWR International, USA) which were then pressed under 10 T/cm^{-2} to obtain a KBr pellet. The analysis were performed with a Thermo-Nicolet iZ10 FT-IR spectrometer in transmission mode with OMNIC software. All FT-IR spectra were collected in the middle infrared (400 to 4000 cm^{-1}) recording 32 scans

3.3. Gas Chromatography – Mass Spectrometry (GC-MS)

3.3.1. Preparation of samples

Ten (10) mg of samples were extracted with 1 mL of dichloromethane then an ultrasound were applied during 10 min. The solution was then centrifuged at 6000 rpm for 10 minutes. The supernatant was set aside to extract again the solid pellet. This step was repeated twice. The three fractions were collected, combined and evaporated to dryness under a stream of nitrogen. All of the extractives were trimethylsilyled with 200 μL of BSTFA/TMCS (99/1 v/v) and heated at 70°C for 30 min. The mixture was again evaporated to dryness and then dissolved in 0.2 to 1 mL of a hexane/DCM mixture (1/1, v/v) and filtered on a polytetrafluoroethylene cartridge (PTFE, 0.45 μm, VWR) (Mezzatesta *et. al.*, 2020). One (1)μL of the solution was injected in GC-MS apparatus.

Figure 27. GC-MS at IRPNC, IMBE.
Photo by Carole Mathe De Souza

3.3.2. Apparatus

Figure 28. GC-MS at IMBE.
Photo by Carole Mathe De Souza

GC-MS analysis was performed with a Thermo Scientific Focus gas chromatographic system composed of a Thermo Scientific Al 3000 auto-sampler coupled with an ITQ 700 ion trap mass spectrometer (Thermo Fisher Scientific). A GC fused silica capillary column Thermo trace GOLD TG-5MS (5% diphenyl / 95% dimethylpolysiloxane, 30 m length × 0.25 mm i.d. × 0.25 μm film thickness) was used. The carrier gas was helium with a constant flow of 1 mL.min^{-1}. 1μL of each sample was injected in splitless mode. Mass spectra were recorded in electron impact mode with an electron ionization voltage of 70 eV, an ionization time of 25,000 μs and a mass range of 40–650 *m/z,* while the temperature of the injector was set at 250 °C. Transfer line, ion trap and manifold temperatures were respectively set at 300 °C, 200 °C and 50 °C. The separation was achieved with the following temperature program: 50 °C with a 2 min hold, increased at 10°C.min^{-1} to 200 °C, then increased at 2.5 °C.min^{-1} to 310 °C, then increased at 8°C.min^{-1} to 330 °C and held isothermally for 3 minutes. All of the injections were realized in triplicate. Peak identification was implemented following established protocol in the form of comparison with mass spectra and retention times of pure standard compounds, as well as using NIST database (NIST MS Search 2.0)

CHAPTER 4. RESULTS AND DISCUSSION

4.1 FT-IR Results

Below are the results of the FT-IR analysis done in each archaeological sample (Samples 3190, 3194, and 3195) obtained from the Phanom Surin Shipwreck (PNS). Sample 3190 was recovered from the TORP-C torpedo jar from the PNS. Torpedo jars are ceramic vessels of West Asian in origin that used to transport amorphous goods for trading purposes. Both Samples 3194 and 3195 were of resin-like material with vegetal origin (Connan et.al., 2020).

4.1.1 Sample 3190

#3190
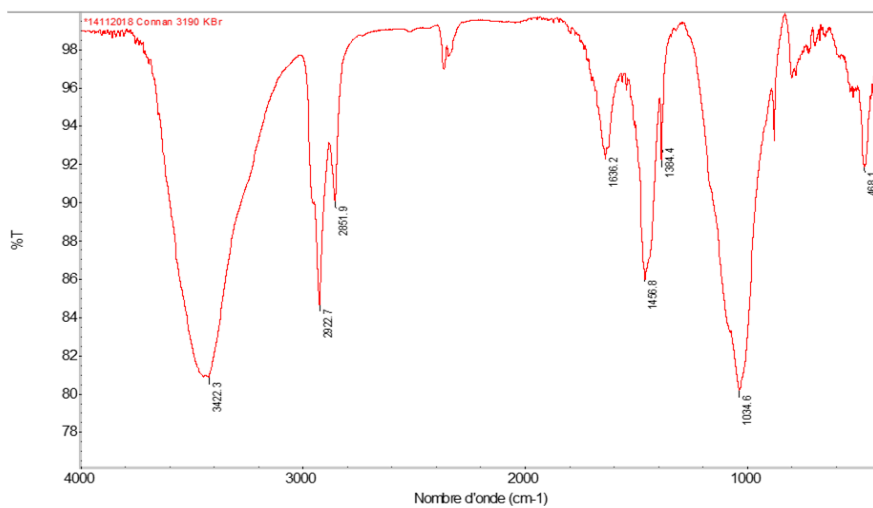
Figure 29. Sample 3190 FT-IR Result

The FT-IR spectra of Sample 3190 is shown in Fig 29. It is possible to observe the O-H (alcohol) stretching band at around 3422.3 cm^{-1}. C-H (alkane) stretch can also be observed in exposant at 2922.7 cm^{-1} and at 2851.9 cm^{-1}. A C=C stretch can also be observed at 1636.2 cm^{-1}. In the fingerprint region, it is possible to observe the stretching bands at 1456.8 cm^{-1}, 1384.4 cm^{-1}, 1034.6 cm^{-1}, and 468.1 cm^{-1}. Notably, the C-H stretch at 2922.7 cm^{-1} is indicative of a bituminous subtance wherein an asymmetric and symmetrical CH_2 elongation vibration occurs, as well as the bands at 1456.8 cm^{-1} and 1384.4 cm^{-1} which were both attributed to C-H bond strain vibrations (Derrick *et. al.,* 1999).

4.1.2 Sample 3194

#3194
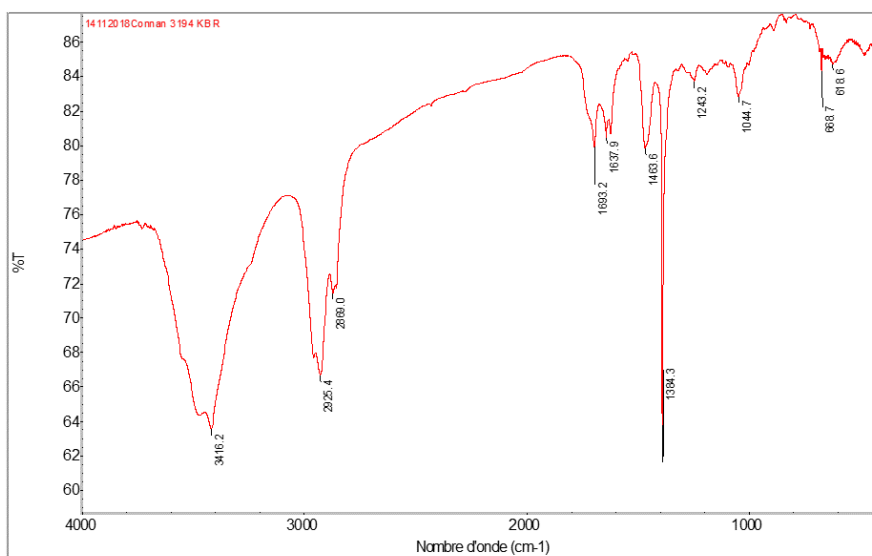
Figure 30. Sample 3194 FT-IR Result

Figure 30 shows the FT-IR spectra for Sample 3194 from the Phanom Surin Shipwreck. It can be observed that there is an O-H stretch occurring at 3416.2 cm^{-1}. C-H (alkane) stretching can also be observed at 2925.4 cm^{-1} and at 2669.0 $cm^{-1,}$ respectively. In the carbonyl region (C=O), a stretching occurred at both 1693.2 cm^{-1} and at 1637.2 cm^{-1}. Stretching bands also appear in the fingerprint region at 1463.6 cm^{-1}, 1384.3 cm^{-1}, 1243.2 cm^{-1}, 1044.7 cm^{-1}, 668.7 cm^{-1}, and at 618.6

38

cm^{-1}. The bands at 1463.6 cm-1 and 1384.3 cm-1 characterized a deformation vibration of CH_2 and CH_3 (C-H bending) (Russo and Avino, 2012 and Bonaduce *et. al.,* 2016). The band at 1044.7 cm-^{1} represented a stretching vibration in alcohol (Popescu *et. al.,* 2012) which could refer to a resin from the *Dipterocarpaceae* family (Gianno, *et. al.,* 1987). All these bands were indicative of a resinous substance.

4.1.3. Sample 3195

#3195
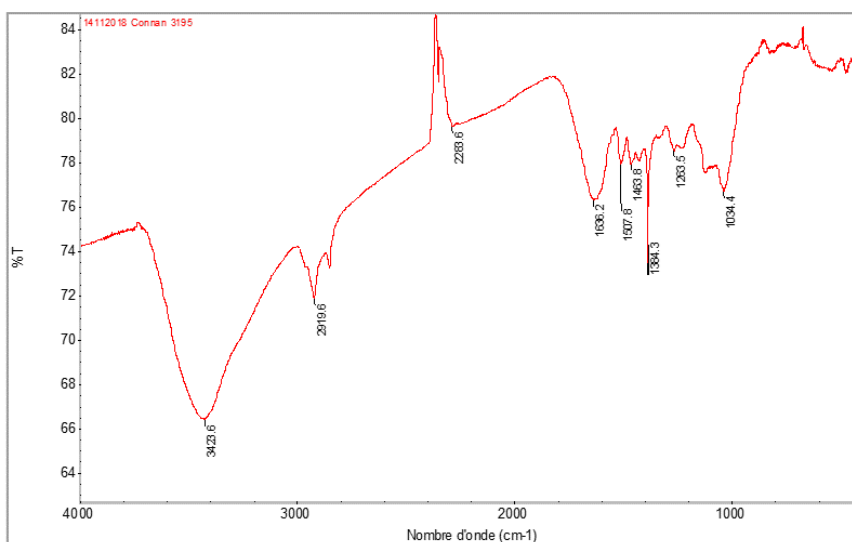
Figure 31. Sample 3195 FT-IR Result

It can be observed in Figure 31 that an O-H stretching occurred at 3423.6 cm^{-1}. It can also be seen that there is a C-H stretching at 2919.6 cm^{-1} and at 2283.6 cm^{-1}. It is also possible to observe a C=C stretching at 1636.2 cm^{-1}. In the fingerprint region, it is possible to observe stretchings at 1463.8 cm^{-1}, 1384.3 cm^{-1}, 1263.5 cm^{-1}, and at 1034.4 cm^{-1}. The O-H bond at 3423.6 cm-1 and the C-H stretching at 2929.6 cm-1 both characterized natural resin (Font *et. al.,* 2007). Bands at 1463.8 cm-1 and 1384.3 cm-1 were also indications of an organic resinous sample (Russo and Avino, 2012 and Bonaduce *et. al.,* 2016).

4.2 GC-MS Results

<u>4.2.1. Sample 3190</u>

#3190 – GC-MS chromatogram at *m/z* 191+217
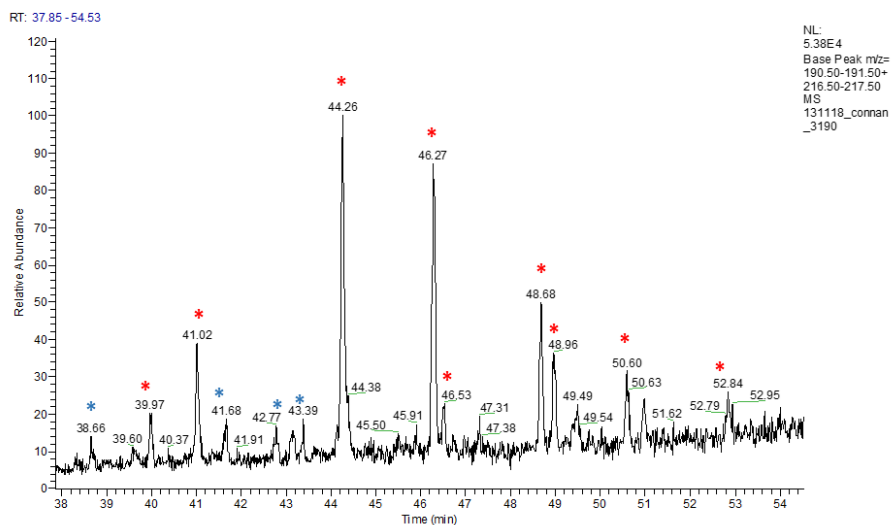
Figure 32. Sample 3190 GC-MS Result. With presence of hopanes and steranes.

Based on the chromatogram above, it can be observed that the peaks were either **hopanes** (Fig. 68) or **steranes** (Fig.32) which are known biomarkers for bitumen. The detection at *m/z* 191 (**hopane**) and *m/z* 217 (**sterane**) is used for the characterization of bitumen. Alkanes compounds were also detected at *m/z* 89. This finding supported the previous study conducted by Connan *et. al.* (2020) on the other samples obtained inside the torpedo jars from the PNS which all yielded **hopanes** and **steranes** based on their chromatographic study. Further exhaustive analysis is required to investigate the different compounds within this sample.

Hopanes and **steranes** are the two of the most used biomarkers in the study of organic geochemistry (Wu and Geng, 2016). **Hopane** ($C_{30}H_{52}$) is an organic triterpenic compound and its name is derived from the genus *Hopea* of the *Dipterocarpaceae* family. **Sterane** is a compound

from steroids via diagenetic and catagenetic degradation and saturation. **Sterane** contains 21 to 30 carbon atoms. **Steranes** were derived from steroids and can be found in eukaryotic membranes of plants enabling strength and water impermeability (Connan, 1999). Common examples of compounds with sterane skeleton are cholesterol, progesterone, aldosterone, cortisol, and testosterol. The presence of **steranes** in low or very low abundances within the chromatogram signifies an alteration process. Both decreasing series of **hopane** and **sterane** can be attributed to the biodegradation of bituminous material. (Lischi *et. al.,* 2020).

Because of their abundance in West Asia, bituminous materials have been widely used in the region since the Neolithic Period. Bitumen has been used in antiquity and prehistory serving as mortar for construction projects, waterproofing boats and vessels, sealing agent for tools, ornaments, sculpture, and for mummification. It is an organic fossil material originating from petroleum (Connan, 1999). The chemical composition of bitumen depends largely on its provenance and age. By analyzing bituminous substances in vessels such as in TORP-C of the Phanom Surin Shipwreck, it is possible to determine its origin as well as trace the locations where it travelled. By characterizing bitumen, we can identify trade networks of a given historical period and geographical area. Lastly, it can also assist in establishing previously unknown trading relations and in the case of the Phanom Surin Shipwreck, hypothesize the trade relations of South East Asian communities such as the Mon-Dvaraviti people of Thailand with Persia during the 8th century CE.

Hopane   Sterane

Figure 33. Biomarkers for Bitumen (Wu and Geng, 2016)
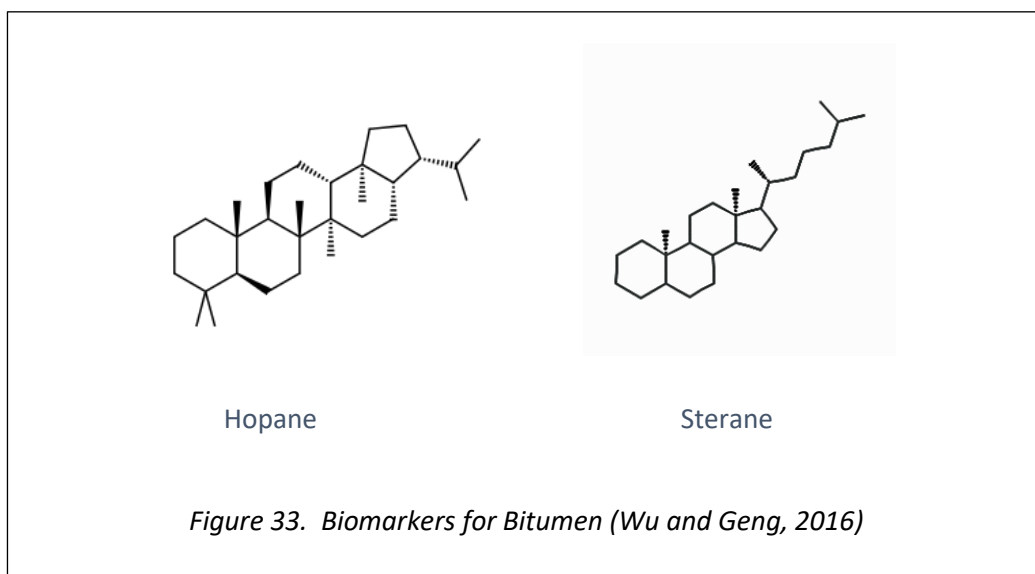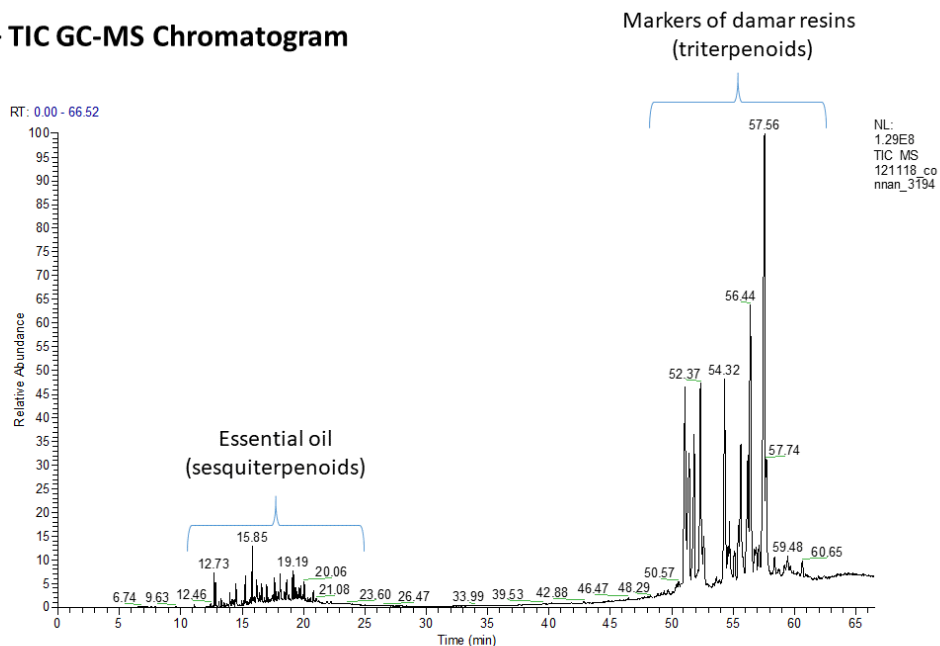
4.2.2. Sample 3194

Figure 34. Sample 3194 GC-MS Result

Sample 3194 was a resin-like material recovered from the PNS. It can be observed from the chromatogram on Figure 34 the presence of sesquiterpenoids and triterpenoids both of which were indicative of plants from the *Dipterocarpaceae* family. In the triterpenic area shown in Figure 35, it is possible to see the presence of **Lup-12-en-3-ol** (Fig. 36); **24-Nor-oleane-3, 12-diene** (Fig. 36); **α-amyrin** (Fig. 13); **epi-Lanosterol** (Fig. 36); and **β-amyrin** (Fig. 13). **Lupeol** is a pentacylic triterpenoid found in variety of fruits and vegetables and has a chemical formula of $C_{30}H_{50}O$. It also acts as an anti-inflammatory drug and as a metabolite for plants. **Lanosterol** is a tetracylic triterpenoid and a compound where both animal and fungal steroids come from. Its chemical formula is $C_{30}H_{50}O$. It also acts as a metabolite for animals, bacteria, humans, and plants. **Amyrins** are compounds which are triterpenic in nature with a chemical formula of $C_{30}H_{50}O$. These are **α-amyrin** (ursane skeleton) and **β-amyrin** (oleanane skeleton). In the biosynthesis of plants, ursolic acid originally comes from **α-amyrin** while oleanolic acid is derived from **β-amyrin**, which are

both pentacylic triterpenoids. Other triterpenoids found in Sample 3194 are **hydroxydammarane derivative, 20, 24-epoxy-25-hydrodammaran-3-one, 3-hydroxydamma-20,24-diene, and 20-hydroxy-3-oxodammara-x-24-ene** which are all dammarane derivatives. **Oleanolic acid** (Fig. 12) and **oleanolic aldehyde** can also be observed along with **ursonic aldehyde** (Fig 12). It is possible to identify based from the chemical compounds that were detected that Sample 3194 belonged to the genus *Shorea* of the *Dipterocarpaceae* family.
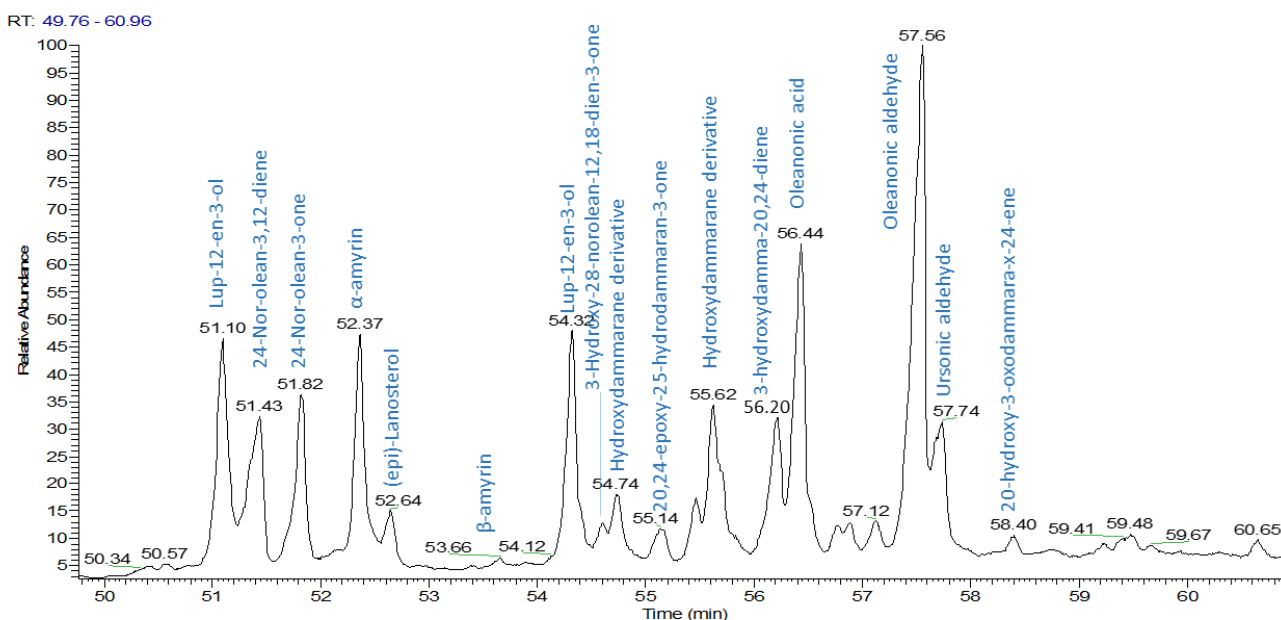
Figure 35. Sample 3194 GC-MS Result (Triterpenic Area)

Lup-12-en-3-ol   24-Nor-oleane, 12-diene   epi-Lanosterol
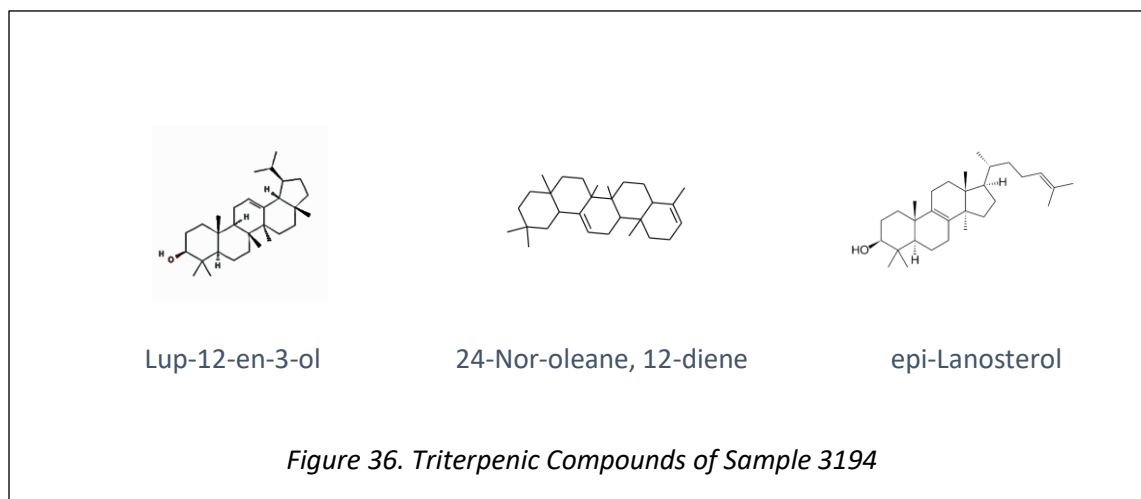
Figure 36. Triterpenic Compounds of Sample 3194

Table 3. Identified Compounds by GC-MS Analysis of Sample 3194

#	Compound	Retention Time (mins)
1	Sesquiterpenoids	12.73
2	Sesquiterpenoids	15.85
3	Sesquiterpenoids	19.19
4	Sesquiterpenoids	20.06
5	Sesquiterpenoids	21.08
6	Lup-12-en-3-ol	51.10
7	24-Nor-oleane-3, 12-diene	51.43
8	24-Nor-oleane-3, 12-diene	51.82
9	a-amyrin	52.37
10	(epi)-Lanosterol	52.64
11	B-amyrin	53.66
12	B-amyrin	54.12
13	Lup-12-en-3-ol	54.32
14	Hydroxydammarane derivative	54.74
15	20,24-epoxy-25-hydrodammaran-3-one	55.14
16	Hydroxydammarane derivative	55.62
17	3-hydroxydamma-20,24-diene	56.20
18	Oleanonic acid	56.44
19	Oleanonic aldehyde	57.56
20	Ursonic aldehyde	57.74
21	20-hydroxy-3-oxodammara-x-24-ene	58.40

4.2.3. Sample 3195

#3195 - TIC GC-MS Chromatogram

Mono- (*MAG*) and diacylglycerols (*DAG*)
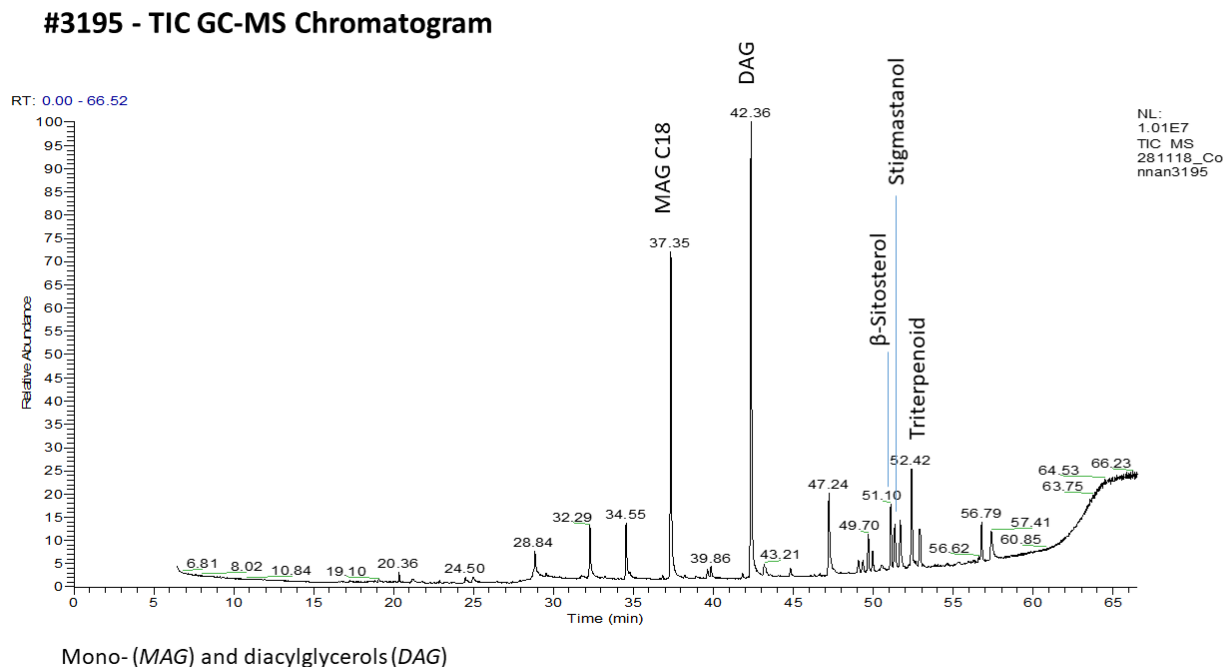
Figure 37. Sample 3195 GC-MS Result

Based from the analysis done by GC-MS, it can be observed that the following compounds were present in Sample 3195: **MAG C18, DAG, β-Stistosterol, stigmastanol,** and **triterpenoid. MAG C18** and **DAG** stand for monoglyceride and diacylglycerol respectively. **Monoglyceride or MAG** is composed of glycerides linked to a fatty acid via an ester bond. It is a result of the enzymatic hydrolysis (the use of water by enzymes to break down molecular compounds) of both triacylglycerides and diglycerides. **MAG** is also a by-product from the biodiesel process relating to sedimentation problems occurring at low temperature environment (Aisyah *et. al.,* 2018). It is present in olive oils, rapeseed or canola oils, and cottonseed oils. **Diacylglycerol lipase or DAG Lipase, DAGL, or DGL** is an enzyme that stimulates the hydrolysis of diacylglycerol which eventually releases free fatty acids and monoacylgylycerol. **β-Sitosterol** is a phytosterol or plant sterol which has a similar chemical structure to cholesterol. It can be found in various plants all over the world as well as in vegetable oil, nuts, and avocadoes. **Stigmastanol** is also a sterol found in various plant families. **Stigmastanol** is a by-product of the reduction of **β-sitosterol** and the

hydrogenation of stigmasterol. **Triterpenoids** are terpenoids consisting of 30 carbon atoms per molecule and produced by plants from the *Burseracereae* (elemis), *Anacardiaceae* (mastic), and *Dipterocarpaceae* (dammar) families. With fatty acids (MAG and DAG) and plant sterols (β-sitosterol and Stigmastanol) being detected from Sample 3195, it is possible to identify it as a lipid extract.

Table 4. Identified Compounds by GC-MS Analysis of Sample 3195

#	Compound	Retention Time (mins)
1	MAG C18	37.35
2	DAG	42.36
3	β-sitosterol	51.10
4	Stigmastanol	51.12
5	Triterpenoid	52.42

Lipids are the most common biomarkers from archaeological sites since it can endure for a long period of time. Lipids are also hydrophobic which means that they do not quickly dissolve in water due to its large quantities of saturated hydrocarbons. This unique property also enables lipids found in underwater archaeological sites to be resistant against water leeching. They are mainly composed of hydrogen, carbon, and oxygen and a small amount of phosphorous, nitrogen, and sulfur. Lipids can form a variety of chemical structures such as fatty acids, wax esters, sterols, phospholipids, and triacylglycerides (mono-, di-, and triglycerides) all of which can be used as biomarkers in identifying organic samples in the archaeological record. Lipids are also the main constituents of plant and animal cells along with carbohydrates and proteins therefore, making up the building blocks of their structure and function (Dunne *et. al.,* 2017).

We can also distinguish plant from animal remains by characterizing the sterols present within the sample. Cholesterol is the most abundant sterol among animals while compesterol and sitosterol are the two major plant sterols (Evershed, 1993). The main form of lipid found in living organisms are triacylglycerols (TAG) which are composed of glycerol molecules that were linked together by three fatty acid chains. The by-product of triacylglycerols after undergoing hydrolysis are

diacylglycerols (DAG) and monoglycerides (MAGs). These are also the two fatty acids usually preserved in vessels discovered in archaeological sites indicating that triacylglycerols (TAG) have been completely degraded (Budja and Ogrine, 2017).

Analyzing fatty acids are applied to distinguish animal fats from plant oils, adipose fats from milk fats, and ruminant fats from non-ruminant fats. This can aid in determining diet and consumption in prehistoric times since fatty acids can be preserved in cooking vessels and storage jars. By studying lipids, we can also determine which natural products were utilized in other activities such as in tool repairs, waterproofing of boats and storages, illumination, cosmetics, healing, and embalming. There are many possibilities on how Sample 3195 were utilzed by crew members of the Phanom Surin boat and further studies are needed to determine its usage.

1-monoglyceride

1,2-diacylglycerol

β-Sitosterol

Stigmastanol

Figure 38. Sample 3195 Compounds
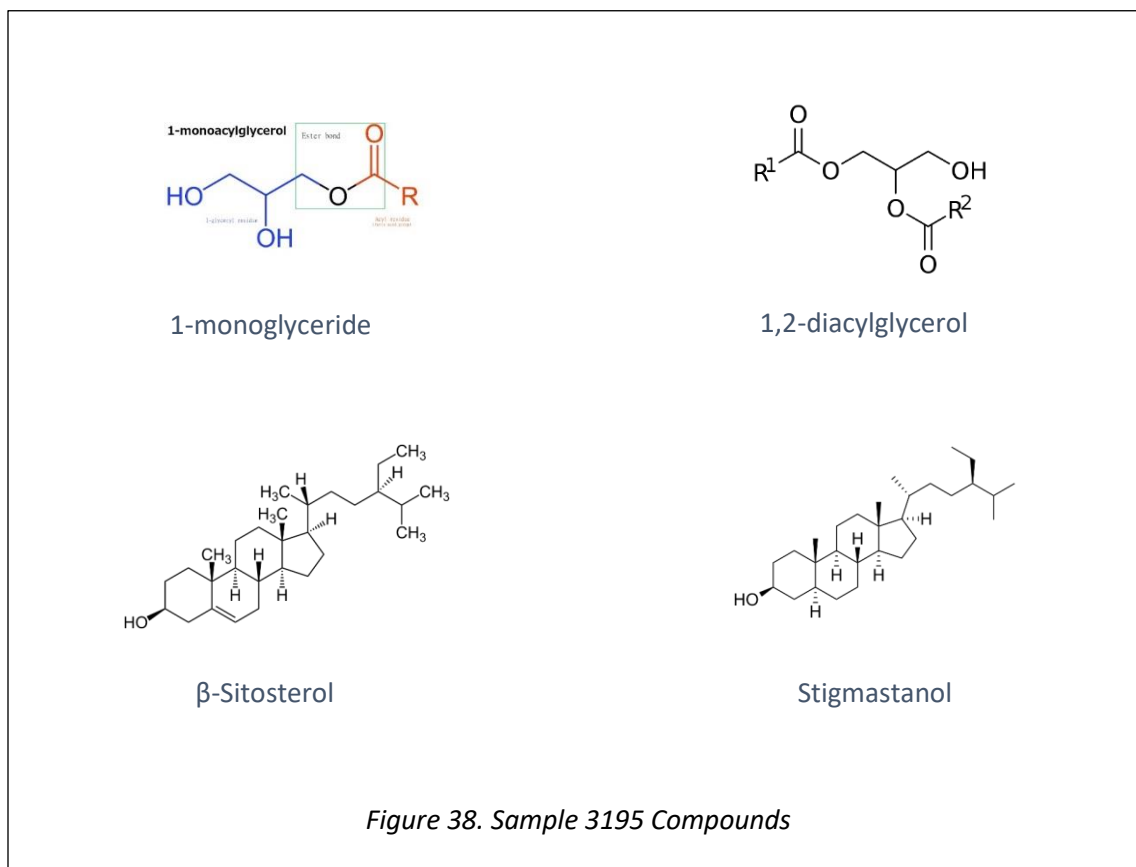
4.3. Interpretation of FT-IR and GC-MS Results

Overlay spectra #3190, 3194 and 3195
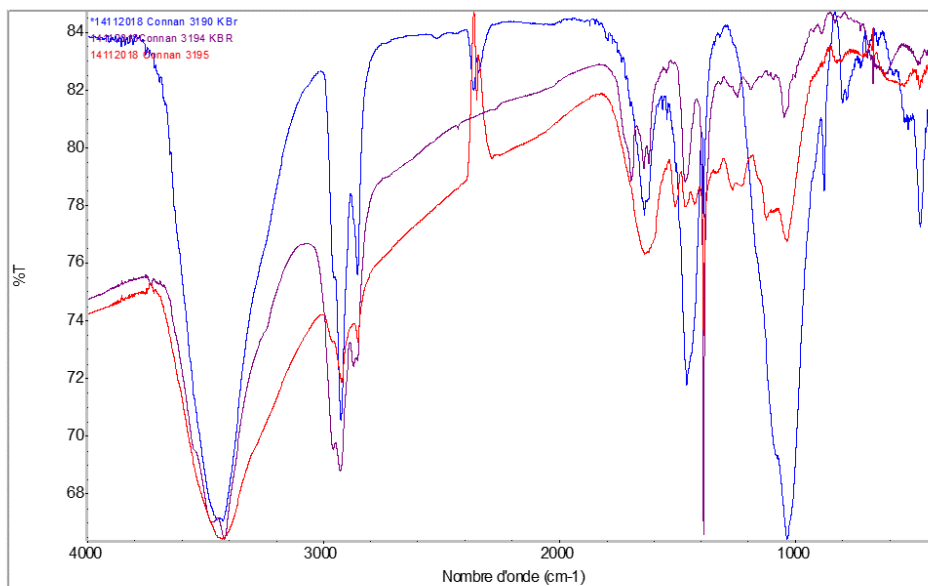
Figure 39. Overlay Spectra of Samples 3190, 3194, and 3195

The results of both FT-IR and GC-MS analysis have complemented each other. Sample 3190 yielded a spectra indicating the presence of bitumen which was corroborated by its chromatographic result that produced hopanes and steranes which were biomarkers for bitumen. These findings confirmed the previous work done by Connan *et. al.* (2020) with the other bitumen samples recovered from the Phanom Surin Shipwreck. Further studies need to be taken to exhaustively determine specific compounds in this sample. Sample 3194 produced a spectra indicating that the sample were of a resinuous substance belonging to the *Dipterocarpaceae* family, a tree family endemic to Southeast Asia. Sample 3194's GC-MS result yielded both sesquiterpenoids and triterpenoids which were characteristics of dammar, a resinous substance associated with the *Dipterocarpaceae* family.

FT-IR analysis of Sample 3195 yielded spectra confirming that it was of an organic, resinous substance while its GC-MS result was able to show molecular compounds rich in fatty acids – monoglyceride (MAG) and diacylglycerol (DAG) which were by-products of hydrolysed triacylglycerides (TAG). TAG is one of the main forms of lipids which are organic substances commonly found in archaeological sites. Lipids are also major components of plant and animal cells. The chromatographic result of Sample 3195 also yielded compounds related to β-sitosterol and stigmastanol which were the two most common plant sterols.

Both FT-IR and GC-MS analysis allowed us to identify and distingush organic archaeological samples of the Phanom Surin Shipwreck from one another. FT-IR is an affordable technique that facilitates the identification of chemical bonds of organic substances in the archaeological record without sample preparations. With the use of FT-IR, we can classify taxonomically plant samples since angiosperms and conifers possess two different terpenoic nature. Angiosperms such as the Dipterocarps possess triterpenoids while conifers such as the Araucarians have diterpenoid compounds. Meanwhile, GC-MS provided a more in-depth analysis of molecular compounds of the sample wherein we can identify a plant resin to its genus level. We can also analyze the quantity of a given compound within the sample. We were able to detect that the amount of hopanes and steranes in Sample 3190 were in low to very low abundance signifying that the sample have undergone degradation. We were able to identify that Sample 3195's chemical compounds underwent hydrolysis since we detected both monoglyceride (MAG) and diacylglycerol (DAG) which were by-products of a hydrolised TAG, and β-sitosterol, a compound resulting from the hydrogenation of stigmastanol.

4.4. Archaeo-Historical Implications of the Samples Obtained from the Phanom Surin Shipwreck

Based from the samples analyzed from the Phanom Surin Shipwreck (PNS), we can observe that the provenance of these organic substances did not come from one geographic region alone. Bituminous substances have long been exploited in West Asia since the Neolithic period, especially in the territories of present-day Iran and Iraq (Connan, 1999). The *Shorea* genus of the *Dipterocarpaceae* family is endemic to Malaysia, Indonesia, the Philippines, and India. The archaeological samples from the Phanom Surin Shipwreck were a testament to the extent of the ancient maritime trading route during the 7th to 8th century CE spanning the Indian Ocean, Gulf of Thailand, and South China Sea. With the other samples previously obtained and analyzed, such as the Guandong ceramic jars and the Mon earthenwares, it is possible to trace the trade network that flourished between West, South, Southeast, and East Asia during this period. The trade between India and China have long been established as well as the influence of both nations to the culture and politics of Southeast Asia as a whole (Paine, 2014). The trade between the Islamic Umayyad (661-750) and Abbasid (750-1258) caliphates with China's Tang Dynasty (618-907) is also well-documented (George, 2015). With Southeast Asia's strategic location, the region has been sourced for raw materials for these lucrative exchanges. Persian merchants were involved in substituting products wherein they will acquire goods from Southeast Asia and label them as Persian goods before selling it to their Chinese counterparts (Guy, 2017). Based from the materials found, the Phanom Surin Shipwreck have already offloaded its products possibly to Guandong, China since there were no goods of prestige standings that have been recovered as of this writing. The location of the shipwreck is worth noting since it lies between the two river deltas of Chao Praya and Ta Chin in Thailand, an area where the Mon-Dvaravati people inhabited with their moat settlements. Lastly, the discovery of a *dhow* ship in the Gulf of Thailand further strengthened Persian-Siam connection, even predating by 600-700 years the establishment of Persian settlements during the Ayutthaya Period (1350-1767) (Marcinkowski, 2014)

CHAPTER 5: CONCLUSION

Organic samples from the Phanom Surin Shipwreck in Thailand were analyzed by Fourier Transform Infrared Spectroscopy (FT-IR) and Gas Chromatography-Mass Spectrometry (GC-MS) for chemical characterization. FT-IR is an affordable and fast technique that identifies chemical bonds within a given sample. With FT-IR analysis, we were able to distinguish if resinous samples were from conifers such as *Caesalpinoideae, Leguminoseae,* and *Auracariaceae* or from angiosperms *Burseraceae (elemis), Anacardiaceae (mastic),* and *Dipterocarpaceae (dammar)* since they produce two very distinct terpenoids – diterpenoids with the former and triterpenoids with the latter. We were able to determine triterpenic compounds in the spectra that both Samples 3194 and 3195 yielded.

GC-MS allowed a more in-depth analysis of organic samples. Through GC-MS, we were able detect molecular compounds and degradation processes that occurred within a sample. GC-MS also enabled the identification of biomarkers that will help in determining a plant resin's taxonomy to its genus level. For Samples 3190, we were able to identify the presence of hopanes and steranes which were biomarkers for bitumen. This supports the previous study conducted by Connan *et. al.* (2020) wherein he conducted analysis on other bituminous substances found in the Phanom Surin Shipwreck. Further investigation should be done in order to exhaustively identify specific compounds found in Sample 3190 but we were able to observe from its chromatogram that the quantity of both hopanes and steranes were decreasing which is attributed to their degradation. For Sample 3194, we detected compounds that are associated with the *Shorea* genus of the *Dipterocarpaceae* family. For Sample 3195, we identified several compounds that usually characterize lipid extracts, the most common biomarkers found in archaeological sites. Sample

3195 possessed monoglyceride (MAG) and diacylglycerol (DAG); the plant sterols stigmastanol and β-sitosterol which are all characteristics of lipids.

By analyzing the molecular compounds of a given archaeological sample, it is possible to identify the source of raw materials used in a given object enabling the establishment of ancient trade connections and networks. Organic residue analysis, the study of amorphous and invisible remains found in archaeological sites can provide us with evidences that can corroborate historical sources as well as geopolitical relations in the past. By characterizing the compounds called biomolecules, we were able to detect the botanical and geological origin of these samples. Through the biomarkers found from the samples of the Phanom Surin Shipwreck, we were able to provide information of their provenance - the bitumen originating from West Asia while the genus *Shorea* from Southeast Asia. Organic residue analysis can also aid in determining subsistence practices of ancient communities as well the different technologies they developed to adapt to their surroundings. It can also determine the botanical origin of trade goods; how it was acquired and and prepared for trading; and its geographical provenience (Evershed, 2008).

With the organic samples obtained from the Phanom Surin Shipwreck as well as the torpedo jars, Guangdong glazed ceramics, Mon-Dvaravati vessels, the Pahlavi inscription, and even the Arab sewn-planked technique applied to the ship itself were testaments to the extent of the vast Indian Ocean Maritime trade around 7th to 8th century CE. It is also a possibility that communities in Southeast Asian such as the Mon-Dvaravatis were already participants in a highly-globalized world engaging in trade and commerce with their Persian counterparts. Further analysis has yet to be taken to look at this supraregional connection spanning vast geographic locations within the Asian continent, with the archaeological samples from the Phanom Surin Shipwreck as testimonies to this interconnectivity among ancient communities during this period.

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