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Forensic analysis of fire accelerants in borate treated timber

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Forensic Analysis of Fire Accelerants in Borate Treated Timber

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Acknowledgment

Thanks for Bangor University, School of Chemistry for what they facilitated everything and offered me during all my study time; special thanks for my supervisor and all the faculty members and staff. Finally, I want to express my thanks to my family and my colleagues.

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Abstract

Boric acid is one of the most effective types of wood preservative in that it imparts flame retardancy and has antimicrobial properties. Douglas-fir, Yellow pine, Sapele, and Oak are some of the most common wood types used for lumber purposes. The adsorption of boric acid on the four selected wood types was tested. Standard methods were used to determine the moisture content (MC %), organic matter (OM %), ash content (AC %), density, and pH of each wood type, and the penetration of boric acid was detected using a visual inspection method. The analysis of the wood properties showed that Yellow pine (a softwood) had the highest MC % (11.88 ± 0.36) and OMC % (97.5 ± 1.3). However, the results of the ash residue and wood density analyses indicated that Oak wood has the highest AC % (4.02 ± 0.01) and wood density (0.68 ± 0.06 g/cm^3). From a gravimetric method, Yellow pine wood was shown to have the highest retention quantity of boric acid. Boric acid penetration results have been obtained for Yellow pine, Douglas-fir, and Sapele wood by a colorimetric method. The comparison of thermal decomposition between untreated and treated samples in four wood type indicated that the highest boric acid concentration (0.4 M) has significant effect on the thermal behaviour of yellow pine and Douglas-Fir (softwood) compared to Sapele and Oak species as hardwood.

The residues of the fire accelerants (petrol, kerosene, and diesel) were analysed in fired and unfired debris for each of the four wood types, with wood types treated with different concentrations of boric acid (0.1, 0.2, 0.3, and 0.4 M). Solvent extraction and gas chromatography-mass spectrometry (GC/MS) methods were used to identify the residues.

Petrol, kerosene, and diesel components were most easily observed in Yellow pine wood, followed by Douglas-fir, Sapele, and Oak wood, for fired and unfired wood samples, across all levels of boric acid treatment. Diesel was more easily detected, followed by the kerosene and petrol, across all the wood types in both unfired and fired wood samples.

An adsorption experiment on the four wood species was performed using the batch technique at initial boric acid concentrations of 0.1, 0.2, 0.3, and 0.4 M over a time period of 5 to 250 min. The results showed that Yellow pinewood has the highest ability for boric acid adsorption, followed by Douglas-fir, Sapele, and Oak. The adsorption isotherm studies indicated that the equilibrium data for adsorbed boric acid by all block wood samples fit better with the Freundlich isotherm compared with the Langmuir Equation. The results of the kinetic studies showed that the pseudo second-order kinetics model was more suitable than the first kinetics model for explaining the boron adsorption data.

To conclude, this thesis was shown that fire accelerants (when present) can be detected in wood samples by a GC/MS method and that wood pretreated with boric acid helps to enhance forensic detection of fire accelerants in criminal fires (arson).

Chapter 1.

1 Introductory background

1.1 Introduction

Alternative materials such as plastic, concrete and iron can be used instead of solid wood in different areas, but wood remains superior as a natural engineering material.[1] Even though wood is a combustible material, it can provide centuries of use under good conditions. If these conditions are conducive to significant damage, such as fire or wood-degrading organisms, protection must be provided during processing, merchandising, and use.[2] There is growing interest in wood preservatives using different applications of boron.[2] Boron compounds (boric acid and borax) have shown substantial advantages for wood protection, providing the wood with preservation and fire resistance, including efficacy against fungi and insects, low volatility, low mammalian toxicity and absence of odour and colour.[3-5]

Mixtures of boron compounds have demonstrated little efficacy in resisting fire spread on the surface of wood. In addition, forming the usual char-catalytic effect, these materials have a low melting point, and they form glassy films when exposed to high temperatures in fires.[6,7] Previous research indicates that fire spread is reduced when using borax, but this process can encourage glowing or smouldering.[8] In contrast, boric acid suppresses smouldering, but it has little effect on fire spread of wood.[8] Furthermore, boron compounds are usually used together as mixtures.[8] Fire resistance is essential for the designer of wood buildings. In addition, the char surface of burnt wood is crucial for fire investigators to aid in the determination of a fire's cause.[9] For these reasons, predicting the models for thermal degradation of untreated and boron-treated wood is significant.[8]

Several approaches were taken in order to address the objectives of this study. This study measures the effectiveness of boric acid (H_3BO_3) on diffusion treatments for four wood types in the laboratory. In addition, the fire resistance properties of different woods treated with boric acid are investigated. The models for each species of wood and fire retardant solution were also evaluated. The physical properties of untreated wood were determined for all wood types. The adsorption isotherms of boric acid on the surface of four species of wood were studied in order to obtain information about the effect of wood treated with boric acid. The fire investigation was reported in the forensic arena of wood debris; different fire accelerants (petrol, kerosene and diesel) were used to obtain the forensic analysis found in char debris and control of four wood types.

1.2 The thesis outline

The thesis is divided into six chapters. **Chapter 1** Summarizes the wood chemistry in relation to treatment of boric acid solution and the permeability of wood. This part also provides the borate wood preservatives associated with wood materials combustion; in addition, forensic analysis of the burned wood resulting from fire accelerants fire is reviewed. **Chapter 2** Describes the general experimental methods, including the details of procedures and analytical techniques that were used. **Chapter 3** presents the result of properties of wood samples and gravimetric calculations of treatment procedures. **Chapter 4** Investigates the forensic (chemical) analysis of fire accelerators (petrol, kerosene and diesel) found in char debris and control samples of four wood types, using gas chromatography (GC-MS) techniques. **Chapter 5** Investigates the adsorption of boric acid solution on the surfaces of four wood species using the batch experiment; the adsorption data and the behaviour of boron solution on the wood were represented using the adsorption Equations of Freundlich and Longmuir isotherm in equilibrium, along with kinetics of adsorption first and the second order reaction. The boron as boric acid solution was determined using Inductively Coupled Plasma (ICP). **Chapter 6** Includes discussion, conclusions and future work.

1.3 Wood material

Wood is classified as dead material resulting from living plants; it is also described as a renewable material.[10] Wood has been around for millennia, and it is one of the oldest and most significant resources used for building by countless civilisations.[10]

The structure of ordinary wood naturally consists of different materials, including 16-33% (lignin), 40-44% (cellulose), 27-44% (hemicelluloses); in addition, wood may also include 5-20% extraneous materials and organic extractives, for instance, tannins.[11,12] These materials have similar densities (1.53 g/cm^3).[11,12] These materials change according to plant properties such as age, species, tissue and atmosphere. Cellulose is the essential source of energy for the majority of organisms; it contains sugar units (1,4-β linked glucopyranose), and this sugar has both intramolecular and intermolecular hydrogen bonding, which composes a major part of wood tissues.[13,14]

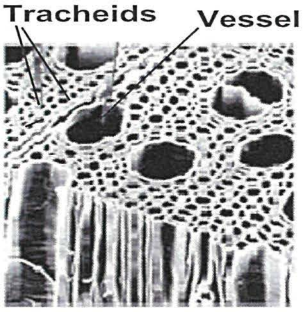


Figure 1.1 Schematic diagram of hardwood, illustrating the relative appearance of vessels and tracheids (vascular cells). Source: adapted from Sojstrom.[15]

The substances of softwood include both tracheids (90-95%) and ray cells (5-10%). The tracheids cells (see Figure 1.1) supply the transported water and the mechanical strength for softwood.[15] There are several types of cells in hardwood tissues. These cells include libriform cells in the supporting tissues, the conducting tissues of vessels with large cavities and ray parenchyma cells in the storage tissues. There are also fibre tracheids cells (hybrid cells).[15] The macroscopic characteristics of wood (hardness, density and bending strength) result from cells and wood tissues. The cellulose and hemicelluloses provide the hydrophilic properties of the cell wall; for instance, both lignin and the agent-cementing cells are classified as hydrophobic molecules.[15,16] Thus, the cell walls of wood have great affinity for water, but the ability of cell walls for adsorbing water is limited. The moisture content (MC) affects the properties of wood, which can decrease the industrial uses of the wood.[17,18,19] The water can exist in two types (free and bound water), as shown in Figure 1.2.[20] Free water is found within the Lumen cells; however, the bound water is adsorbed to both the cellulose and hemicelluloses of the cell wall. The fibre saturation point (FSP) occurs when the cell walls are filled with free water.

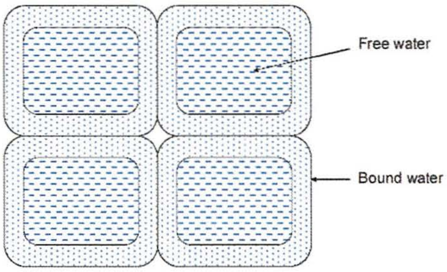


Figure 1.2 Free and bound water within the wood tissues. Source: adapted from Dubey. [20]

Freshly cut wood from trees is green; thus, the MC of green wood can be over 100%, which indicates that the water weight is more than the dry weight of wood cells. Different properties can affect the amount of water within the wood tissues, such as density, porosity, conductivity and diffusivity of wood.[21]

The MC of wood at equilibrium (Equilibrium Moisture Content, or EMC) is a function of temperature (T) and the relative humidity (RH) of the surrounding air; when the thermal conditions of the surrounding environment change, the wood tends to reach a new equilibrium point for moisture content by adsorbing or desorbing water.[22] The MC of softwoods is higher than that of hardwood; this difference is related to the ability of softwood to adsorb more water than hardwood. The moisture content is one of wood's dynamic properties, and a small piece of wood can reach the saturated point of RH at 14 days.[22]

1.4 Constituents of a woody cell wall

The mechanical support of a wood cell wall is mainly composed of cellulose. The empirical formula of cellulose is $(C_6H_{10}O_5)_n$.[22,23] This material is the primary source of wood's hygroscopic property. In addition, wood cells contain cellobiose segments, which have varying molecular lengths; this property can provide the polymolecular structure of wood cells. Each cellobiose segment has a length unit of approximately 10.38 Å, and each length unit of crystalline cellulose cell has two segments with dimensions arranged between 7.9 Å, 8.35 Å and 10.38 Å. The degree of cellulose polymerization is about 10,000, as shown in Figure1.3. This process was conducted using the measurement of light scattering for non-degraded cellulose nitrate.[7] The mean length of this chain was approximately 50,000 Å.[22]

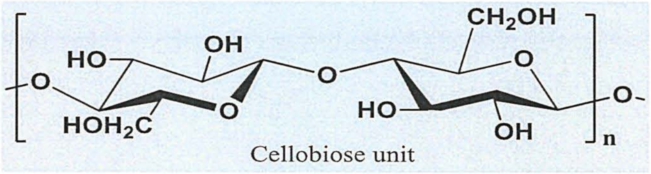


Figure 1.3 The molecular structure of the cellobiose unit of cellulose

1.4.1 Cellulose

Cellulose structure also contains the hydroxyl group (intra- and intermolecular hydrogen bonds).[22] Collections of cellulose molecules can bind together to form crystalline micro fibrils; this includes the formation of hemicelluloses and lignin, as shown in Table 1.1.[19,24,25] The cellulose chains are formed onto micro-fibrils (identical layers of fibre), which constitute the basic framework of the wood cell's resistance to tensile forces. The micro-fibrils characterize about 20-30% of the dry biomass of cell wall wood, and the volume of materials comprises more than 15% of the cell wall. Therefore, the capacity of the cell wall affects the disposition and orientation of micro-fibrils, which can cause deformation of the cell wall.[26,27]

Table 1-1 Chemical composition of the dry woody cell walls.[24,25,19]

Constituent	**(%W) of dry cell wall**
Cellulose	Approximately 50
Hemicelluloses	20 to 35
Lignin	15 to 25
Extractives and extraneous material	0 to 25

As the cell wall reaches the final stages of its formation, in the primary and middle lamella of the cell wall, other wall polymers (lignin) fill the spaces around the polysaccharide of fibrillar elements in order to form lignin.[26,27] The free hydroxyl groups within the cell wall of polymers form hydrogen bonds with water molecules.[19] Thus, water molecules bind to the hydroxyl group via hydrogen bonds. This process causes wood cells (cellulose chains) to swell or shrink as the moisture content increases or decreases in response to changes in the humidity and temperature of the surrounding environment (see Table 1.2).[22]

Table 1-2 Shrinkage values from green to oven dry MC in different directions of wood

Dimension	Radiata pine	Softwoods (North American spp)	Hardwood (North American spp)	European (hardwood and softwood)
Longitudinal	0.2-0.25	0.1-0.2	0.1-0.2	*0.1-0.26
Radial	2-3.4	2.1-5.1	3-7.9	2.3-6.8
Tangential	4-7	4.4-9.1	6.2-12.7	**6-11.8
Volumetric	6.2-10.4	6.8-14	10.19.2	8.5-18.8

Source: (Forest Products Laboratory 1999),[17] *(Black 2005;[28] Bootle 2005;[29] Cown 1992)[30], **(Tsoumis 1991).[19]

As noted above, the decrease of hydrogen bonds at the cellulose surface can be controlled by hydrogen bonds between water molecular and cellulose. Therefore, this process can impact the chain length.[20,31-33]

1.4.2 Hemicelluloses

Hemicelluloses contain a large number of different polysaccharide molecules (~200 sugar), and these chains form a matrix for the cellulose micro-fibrils, including the interactions of these molecules by, for instance, Van der Waals forces and hydrogen bonds. Hemicelluloses classified as low molecular weight of polysaccharides with polymerization degrees arranged in hundreds. These chains constitute more than one monosaccharide chain. These chains consider xylose, arabinose, galactose and mannose as examples of copolymers. Mannose is the most important monomer in softwoods. [25,31] The method of isolation can affect the volume of hemicellulose from a wood sample and change the separated mixture because hemicelluloses can be hydrolysed to sugar and sugar acids via weak acids. [25,31]

1.4.3 Lignin

Lignin is the main material of the cell wall that distinguishes wood from cellulose. It constantly forms together with cellulose.[19,31] Lignin has different properties compared to cellulose, lignin properties include high molecular weight and amorphous substance, and it consists of phenylpropane monomers. However, the details of its structure are still ambiguous, which can be related to difficulties of isolating lignin in its various forms.[19,31]

Lignin protects the wood cell from becoming degraded, and for this reason, some wood types survive much longer than other types. Lignin has two important forms: syringyl and guaiacyl lignin. Guaiacyl demonstrated more ability to resist the degradation impacts than syringyl lignin, which indicates why softwoods (which contain guaiacyl) are less durable than (hardwoods); however, lignin is a mixture of both syringyl and guaiacyl lignin. [22,34]

1.4.4 Wood extractives

These materials are defined as compounds extracted from wood materials via polar and non-polar reagents. The deposition process inside lumens and wood cells resulted in extractives. The composition of these materials includes different chemicals, for instance, oil, gum, resin, sugar, fats, starches, tannins and alkaloids. The percentage of resin acids in heartwood (radiata pine) ranges between 70 and 80% of total materials. However, 41% of sapwood is made up of fatty and resin acids.[25]

One of the main hemicellulose from softwoods contains a backbone polymer of the galactoglucomannans as the principal material (about 20% of dry mass), as shown in Figure1.4. There are other major polymers, such as arabinoglucuronoxylan (AGX) and arabinogalactan, in the softwoods (5-10% of dry wood mass), as shown in Figure1.5.[35,36]

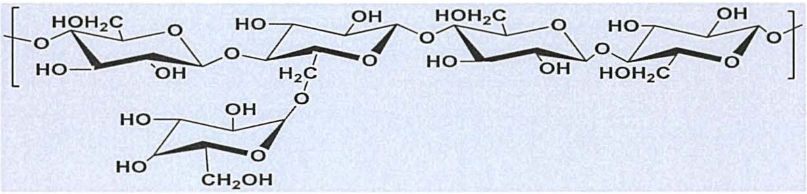


Figure 1.4 The principal chemical structure of galactoglucomannans

Glucuronoxylans is also one of the hemicelluloses polymers in hardwoods. The xylan content is about 15-30% of the dry wood in hardwood, while small amounts (2-5%) of xylan-glucomannan are present in hardwoods.[35-37]

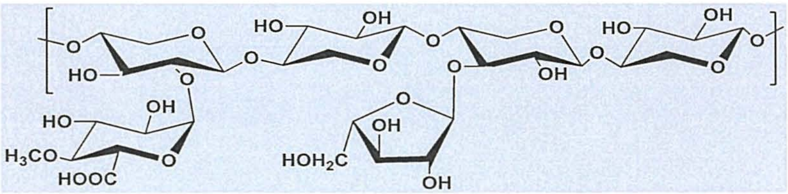


Figure 1.5 The principal chemical structure of arabinoglucuronoxylan

1.5 Wood permeability

Wood has demonstrated varying relative permeability according to the condition and type of saturated fluid. Choosing suitable parameters can change the wood permeability.[38-41] Previous studies have shown that wood preservatives can be controlled by water and petroleum as wood carries. A few researchers have indicated that petroleum hydrocarbons have the ability to penetrate the wood tissues more easily than do water molecular.[42-45] The major reason behind this difference is not completely understood, although certain studies suggest that the hydrogen bonding of the water molecular can impact the ability of liquid to penetrate the wood. This could be related to the capability of water to build strong hydrogen bonds with water molecules, resulting in a structured liquid. Water molecules also have the ability to build hydrogen bonds with hydroxyl functional groups within the wood structure.[22,46,47] Thus, these two hydrogen bonds might form a frictional drag to transfer the water molecules within wood systems, and this process can decrease the rate of liquid flow.[22,38,39,46,47]

As there is no evidence that hydrogen bonding is one of penetrability factors of water and its differences in wood systems, further studies are needed to prove this hypothesis. It has been confirmed that the liquid is able to form bubbles, as previous work indicated that bubbles' presence decreases the rate of liquid flow. Capillary flow within woody vascular structures could be overcome throughout the saturation state.[22,46,47]

There is a significant difference between the organic fluid and water molecules, and previous studies have suggested that the micronuclei of stabilized gas were found in the earlier but not in the final stages of wood permeability. For this reason, organic fluid will not form bubbles if water will not form bubbles. Bailey and Preston discussed the differences between two liquids, and they concluded that these differences could be related to hydrophobic deposition within wood pores.[14] This process can increase water contact sites. They also note that increasing the pressure rate can increase the wood saturation.[22,46,47]

1.6 Chemical treatment of timber

Woods are regularly treated with different types of chemicals to improve their fire retardant performances, to improve their resistance to ignition and to protect them from natural biological degradation using antimicrobial products. Some of the fire retardant treatments, however, can reduce the physical characteristics of wood. In addition, a few fire retardants showed an increase in the degradation process when temperature was increased, especially when used as the roof of truss lumber or sheathing of a plywood roof. Therefore, the impacts of these materials on the properties of wood are immediately associated with different factors such as various pre-treatment, size, wood quality, and treatment and processing after treatment. Several factors comprise chemical type or preservative chemistry, such as initial kiln-drying temperature, preservative retention, pre-treatment incising (if required) and post-treatment drying temperature. Boron solution is one of the most common methods used for wood preservation. Other methods includes different types of inorganic salts based on chromated copper arsenate (CCA), boric acid, borax and other solutions. This method will be elaborated in later Sections.[22,45-49]

1.7 Chemistry of fire retardancy

The main methodology to study the scientific fundamentals of fire retardancy was established by Gay-Lussac.[50,51] This study applies different methods for fire retardants of cellulose using both borax and ammonium phosphates. The use of fire retardants is important to improve fire safety. The rate of fire retardant application was only 2% for wood and paper, 3% for coatings and adhesives, 5% for textiles, 25% for rubber and 65%

for plastics. From the above information, it is obvious that the fire retardant materials have spreads widely over many productions during that period by small companies.[52]

The treatments of fire retardants are classified into two types: (1) those incorporated into wood composite materials or impregnated into the wood, and (2) those applied as paint surface coatings (intumescent or non-intumescent).[53,54] The use of coatings is much easier and a much less expensive product. This type of treatment is used to preserve wood that is already in buildings. There are side effects of these products, including wood cracks and a tendency toward abrasion, which decreases the efficiency of the fire retardant.[22,53]

Impregnating materials is an expensive method because this process requires more fire retardant solution to penetrate the wood structure under pressure conditions. These materials are suitable for new wood before starting the building process. Impregnated products place the fire retardants within wood tissues, and these materials have the ability to reach the inner wood layers, even if the wood surface layers are or have been destroyed.[22,53]

There are two essential types of fire retardants: ‘additive’ and ‘reactive’. Additive compounds interact with a substrate, and their nature is purely a physical property. The reactive compounds have the ability to interact chemically with cellulose, hemicellulose or lignin.[22,55,56]

Additive compounds include phosphate (mono and diammonium), phosphonates, halogenated phosphate esters and inorganic compounds, such as antimony oxide, halogens and ammonium salts (ammonium bromide, ammonium fluoroborate, ammonium polyphosphate and ammonium chloride), amino saps (dicyandiamide, phosphoric acid, formaldehyde, melamine and urea), hydrated alumina, stannic oxide hydrate, zinc chloride and boron compounds (boric acid, borax, zinc borate, triammonium borate, ethyl and methyl borates).[22,55,57,58]

These components decrease the potential of wood fire; however, some additive compounds showed negative effects on wood properties including hygroscopicity, toxicity, strength, adhesion, and the saturation of paint coating.[59,60] The additive and reactive compounds are used to impregnate wood in relatively large doses (10-20 % by weight).[22,61]

Many inorganic fire retardants have disadvantages dependent on salt properties, such as their ability to leach water molecules. Few salts can assimilate moisture from the surrounding environment, and the penetrated water within wood tissues encourages bio-decomposition of wood through fungi; in addition, this process can increase the destruction of building materials and metal joints. Fire retardants depend on boron compounds, and this method provides a long period of wood protection because boron salts deeply penetrate the wood tissues.[57,62-64] Boric acid can perform as a fire inhibitor and reduce the formation of smoke. In addition, previous studies showed that boron compounds demonstrate insecticidal and fungicidal properties when used to treat different types of wood. Synergistic effects, which provide the cellulose stability, are one property of a perfect fire retardant.[57,65,66]

1.7.1 The mechanism of fire retardancy

The majority of wood fire retardants decrease combustible volatile materials during the treatment process; furthermore, the efficiency of a flame is limited with regard to materials' oxidation and combustion, eventually decreasing the wood temperature.[22,53] Various factors can control fire retardancy mechanisms, including chemical compound properties, environmental fire conditions and surrounding environment characteristics; the last factor can stimulate the pyrolysis process. In addition, the type of chemical compound is significant in fire retardants, due to the ability of these compounds to stop producing 1,6-anhydro-glucopyranose compound during their reaction, as they have a highly flammable property with volatile fraction within thermal cellulose decomposition.[22,53]

Browne studied wood fire retardancy using different models of wood.[67] The results of this work indicated that the process of wood fire retardancy involves different steps. The first step is reducing the heat flow to inhibit wood combustion. The second step is flame cooling, and the final step is altering the thermal degradation development.[67] Different types of fire retardant additives have been used for long time, such as boric acid, borates, sodium borate, ammonium phosphates, ammonium sulphate, chloride, zinc chloride, phosphoric acid and dicyanodiamide antimony oxide.[55,68,69]

1.8 Borate wood preservatives

Borates are one of the most effective preservatives to protect wood from fungi, termites, beetles, carpenter ants and other insects. Borates were first used as wood preservatives in the United States in the 1900s; however, other commercial and research developments were conducted elsewhere in the same period.[17,70]

The processing methods of wood can be divided into two general types. The first one is oil-borne preservatives, which includes pentachlorophenol (PCP) as petroleum solutions and creosote.[17,96] The second type is solution-borne preservatives, including sodium octaborate, sodium tetraborate and sodium pentaborate. All of these compounds result from sodium borate in mineral form. These compounds are water-soluble.[17] This method has different properties, such as diffusible materials and excellent penetration in any wood species. However, this compound can easily leach out in the surrounding environment (soil and rainwater) as it is dissolved in a water solution. Borate can only be applied in the areas protected from rainwater (e.g., inside buildings). Treated wood was colourless and odourless, as it has been stained, painted, sprayed, brushed and injected.[70]

Wet wood showed excellent responses to borate preservatives as they diffused into the wood tissues. Consequently, these materials are regularly applied as protective treatments. These treatments are usually used for homes made of wood, hardwood pallets and the finishing of natural wood.[70] The majority of early studies indicated that branded borates had no effects on organisms because these materials have no protection for wood in contact with the ground.[71] Grace and Yamamoto indicated that the formulation of both glycol and borate increased the level of borate in Douglas-fir heartwood than was found with a water-based borate solution.[72]

Several studies confirmed that wood treated using borate solution must not be used in ground contact.[4,5,73,74] Nicholas *et al.* suggested that the borate's leaching properties could prohibit using borate as a wood treatment.[75] However, the treated wood can be used in structures that are protected by a wall or a roof.

Borate is the most important treatment of wood compared to other preservative compounds. Borates widely exist in mineral depositions around the world. A large store of borates is located in the California desert. Borates have used in different manufactured items, such as hand wash and laundry powders. Borates also exist in eye washes, contact lens solutions, ceramics, cosmetics and medicines. They have no health hazards for humans and ecosystems. This could be related to the borate's inorganic structure that has no volatile materials, unlike organic compounds. Volatile organic compounds (VOCs) are one type of air pollutant linked with a number of odour and health issues.[70]

Borate is natural salt derived from the bonding of two elements, boron and oxygen and a cation.[22,96,70] Two significant types of borate are applied to wood preservatives: Sodium borate and zinc borate. Disodium octabora tetrahydrate (DOT) is a sodium borate produced specifically for applications such as lumber wood. Zinc borates have low solubility as borate compounds, and they have been used for hardboard, plastic and fibre matter. The mechanism of wood and borates compounds still requires further study. These materials appear to prevent digestion in organisms (e.g., insects), and this process cause bio-organisms to starve. A different borate mechanism occurs in fungus and deactivates their enzymes at the cellular level.[70]

Previous studies have indicated that 0.2% of sodium borate weight is enough to stop the bio-activation of fungi and insects inside wood. However, higher levels are required for termites; this could be related to the termite species.[70] Forlntek indicated that termite (*Formosan subterranean*) was prevented by borates (2% of weight) in lumber samples. The toxicity of borates is low for mammalian organisms; however, borates do have negative impacts on biological organisms such as fungi and insects.[70]

1.8.1 The mechanism of borate wood preservatives

There are different methods to treat the wood using borated compounds, Zabel and Morrel indicated that suitable methods for wood treatment use both pressure and vacuum process, due to chemicals that can be forced into lumen cells.[2] However, another method does not require pressure and vacuum processes, as this procedure involves steps such as soaking, spraying, brushing and dipping. Both methods have advantages and disadvantages, and they require different materials and equipment. The diffusion process is required to force the preservative into a porous system of wood. Water-borne preservatives were used in both processes to diffuse water in the treatment solution into wood. Wood diffusion depends on the material's tendency to adjust the concentration differences for solutes. There are different diffusible preservatives, as indicated above.[2,70,76]

1.9 Boron chemistry

Boron (B) is one of group 13, and it is the fifth element on the periodic table. The electron configuration for B atoms can be written as $1s^2\ 2s^2\ 2p^1$. Two stable isotopes of boron are found in nature with atomic masses of 10 and 11 respectively. These isotopes occur in a ratio of 20 to 80 % to form an average atomic mass (10.81 g/mol).[2] B has different properties compared to other elements in the same group, due to the fact that its valence shell has no way to fill these outer shells. Boron has only three electrons in the valence shell, and when it forms three single bonds it leaves this atom with six valence electrons rather than an octet. To compensate for this deficiency, B often acts as a Lewis acid.[77,78]

A boron atom basically exists in an oxidation state of trivalent, but under natural conditions, it has no trivalent cation; it exists to bond with oxygen atoms.[3] B can only form covalent bounds, which is related to its high ionic potential and small size. It can also form a coordination number of 3 or 4 when B is found as a natural compound. For instance, the coordination number of B is 3 in boric acid and its salts when it has been bonded with three atoms of oxygen. There are different forms of B bonding with oxygen atoms, for instance, tetrahedral (BO_4^-) structural and trigonal planar (BO_3). Many other B compounds have hydroxyl hydrated borates (B-OH groups), and they might also have interstitial water molecules.[77-79]

B is extensively dispersed in the ecosystem, and it binds with oxygen to form different chemical compounds, including borates. Borates exist at low concentration levels (about 30 ppm) in the environment (rocks and soil). Mellor found that borate levels in surface water were between 0.01 and 2 mg B /L, and in the ocean water were 2 mg B /L.[79]

The application of borates (boric acid, borax) can be used in a number of manufactured products, including fertilizers, wood preservatives, enamels, fire retardants, insecticides, laundry bleaches, cosmetics, glass fibre insulation, ceramics, textile fiberglass, heat-resistant borosilicate glasses and pharmaceutical preparations.[80,81]

In aqueous environments, boron mainly exists as boric acid $B(OH)_3$. This form behaves as a Lewis acid. The hydroxide ion (OH^-) reacts with a hydrogen ion (H^+) with a constant dissociation ($ka=5.8\times10^{-10}$; $pKa= 9.24$ at 25° C). Boric acid accepts electron pairs, instead of transferring protons, as shown in Figure1.6. B moves from hybridization level of sp^2 to sp^3 in the resulting compound.[8,82,83]

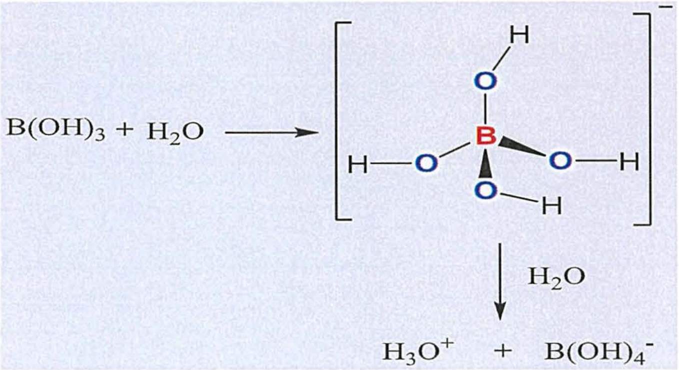


Figure 1.6. Boric acid acting as a Lewis acid.

1.10 The properties of boric acid

The molecular formula of boric acid is $B(OH)_3$, and its molecular mass (MW) is 61.83 g/mol. White needles of boric acid can be obtained from borates or through the hydrolysis of boron trihalides. $B(OH)_3$ molecules are linked to each other through hydrogen bonds to produce infinite layers of almost hexagonal symmetry. The distance between these layers is found to be 3.12 Å, and the cleavage of the crystals is along the interlayer planes.[84] The basic structural units of borates are linear or cyclic polyoxoanions, which are formed when BO_4 and/or BO_3 units are linked with shared oxygen atoms, as shown in Figures 1.7, 1.8 and 1.9.

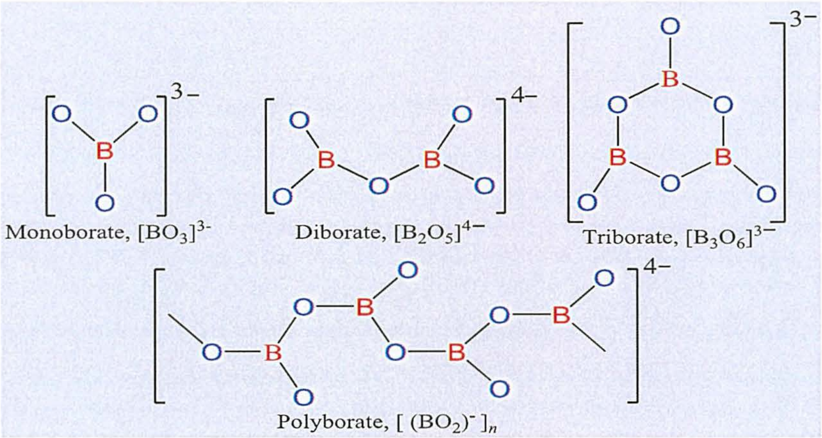


Figure 1.7. Some structures of anions containing boron in planar BO_3 units

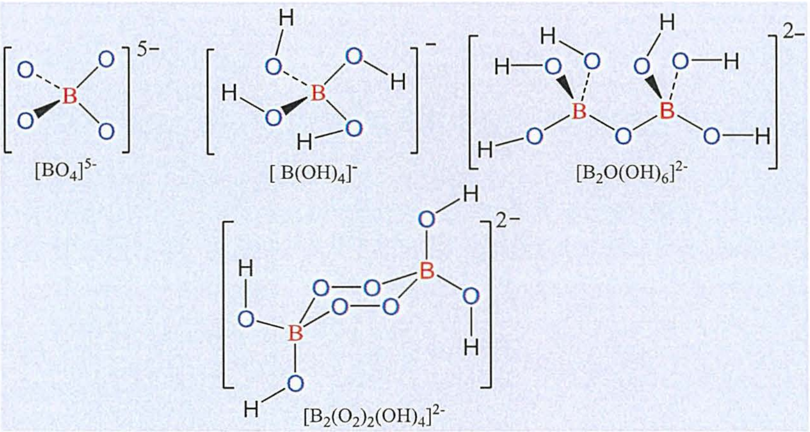
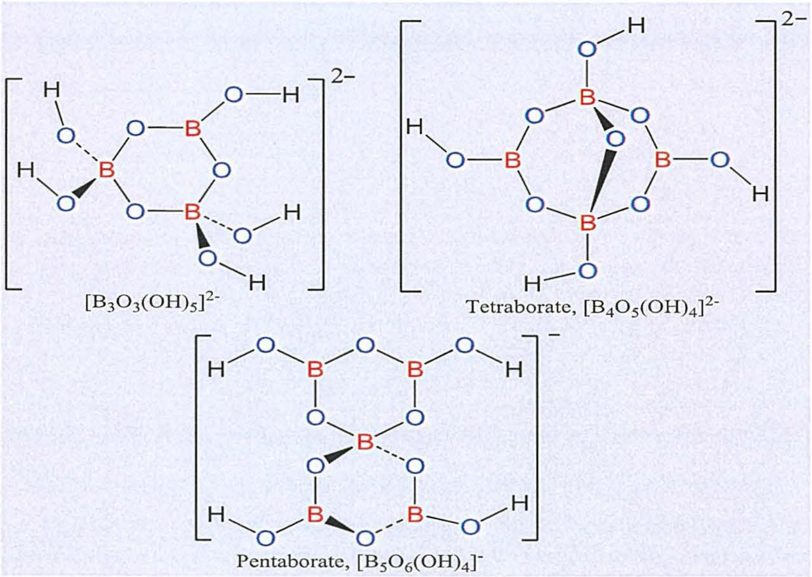


Figure 1.8. The structure of anions containing boron in tetrahedral BO_4 units



$[B_3O_3(OH)_5]^{2-}$

Tetraborate, $[B_4O_5(OH)_4]^{2-}$

Pentaborate, $[B_5O_6(OH)_4]^-$

Figure 1.9. The structure of anions containing boron planar BO_3 and tetrahedral BO_4 units

Upon heating, boric acid gradually loses water and forms one of three different metaboric acids (HBO_2). If this compound is heated to lower than 130° C, then the so-called form-III is obtained. This form demonstrates a layer structure in which rings of B_3O_3 are linked through hydrogen bonds. If the heat (between 130 and 150° C) is sustained for II of HBO_2, then HBO_2-II is formed. This process contains both B_2O_5 groups and BO_4 tetrahedra arranged in chains and joined through hydrogen bonds.[84-86]

If form-II is heated at a temperature above 150° C, form-I (cubic HBO_2) is created with four coordinate of boron atoms. The oxide of boron B_2O_3 is formed as glass on the complete thermal degradation of boric acid. Melted metal oxides can easily be dissolved to provide borate glass. In addition, it also reacts with silica to form borosilicate glass (Pyrex).[84-86]

Condensation of boric acid with alcohols in the presence of sulphuric acid can be transformed to aryl or alkyl orthoborates, $B(OR)_3$. The obtained compounds are generally colourless fluids, and these liquids are changed from alkali metal hydrides or solvents to important agents $[HB(OR)_3]^-$. Modification of R group can be controlled by the selectivity and reactivity of $[HB(OR)_3]^-$.[84-86]

Peroxoborates can be formed by reacting boric acids with sodium peroxide. This reaction results in the formation of peroxoborates and different compounds such as $NaBO_2.H_2O_2.3H_2O$ or $NaBO_3.4H_2O$. Peroxoborates are widely employed in detergent powders due to the release of hydrogen peroxide in solution. The equilibrium of this solution is explained in this reaction (1).[84-86]

$$[B(OH)_3\ (O_2\,H)]^- + H_2O \rightleftharpoons [B(OH)_4]^- + H_2O_2 \quad \text{...........(1)}$$

$[B(OH)_4]^-$ ions have many borate minerals; however, the fusion of boric acid with metal oxides results in complicated compounds of borates such as anion structures. Borates and boric acid can produce very stable compounds by 1,2-diols, as shown in Figure 1.10.

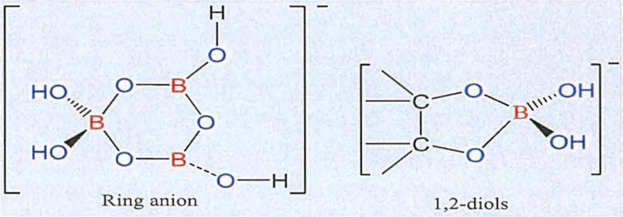


Figure 1.10. The stability of borates and boric acid with 1,2-diols compounds.

Boric acid concentration can be determined by reacting with a diol such as glycerol and followed by titration with sodium hydroxide, as shown in Figure 1.11.

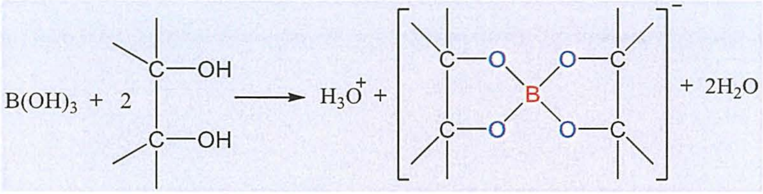


Figure 1.11. Determination of boric acid concentration by reacting with a diol and followed by titration with sodium hydroxide

As noted previously, anions of polyoxoborate are found in concentrated solutions of boric acid. These are formed in the equilibrium case shown below (2).[84-86]

$$2B(OH)_3 + B(OH)_4^- \rightleftharpoons B_3O_3(OH)_4^- + 3H_2O \qquad \text{................(2)}$$

The equilibrium between different borate anions quickly reaches a stability point in solution, as shown by the fast exchange occurring between borates and $B(OH)_3$ labelled with ^{18}O. The large compounds, such as polyoxo anions $B_4O_5(OH)_4^{2-}$ and $B_5O_6(OH)_4^-$ are established using high pH levels. In the case of diluted solutions, depolymerization to mononuclear is found. Therefore, $B(OH)_4^-{}_{(aq)}$ is found if borax is dissolved in a diluted solution.[84-86]

It is interesting to note that boric acid and borate are significant compounds because they have a pair of atypical bases and acids. Conversion of acidic form into conjugate base has no simple deprotonation. Boric acid develops via a number of polyborate anions at a high level of concentration (>0.025 M of B) as a function of pH. This is evident in the reactions from 3 to 6 given below.

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+ \qquad \text{..........(3)}$$

$$3B(OH)_3 \rightleftharpoons B_3O_3(OH)_4^- + H^+ + 2H_2O \qquad \text{..........(4)}$$

$$4B(OH)_3 \rightleftharpoons B_4O_5(OH)_4^{2-} + 2H^+ + 3H_2O \qquad \text{..........(5)}$$

$$5B(OH)_3 \rightleftharpoons B_5O_6(OH)_4^- + H^+ + 5H_2O \qquad \text{..........(6)}$$

Electrochemical techniques and NMR spectroscopy have been used to study the chemical reactions occurring in aqueous boron chemistry.[84-86]

1.11 Combustion of wood materials

When wood is exposed to fire or any high source of heat, the thermal combustion process depends on environmental conditions. The combustion process attached with chemiluminescence to release reaction heat. In contrast, chemiluminescence does not generally take place within the combustion process.[53,88,89]

Chemical bonds that exist in wood are broken down if the wood is heated to 175° C. The heated process stimulates with the increment of temperature.[23] Increasing the wood heat to between 100 and 200° C with the absence of air can result in non-combustible materials, for example, CO_2, CH_3COOH and traces of HCOOH. This thermo-decomposition is completed with water evaporation. The breaking down of wood carbohydrates requires a temperature of more than 200° C in order to produce flammable volatiles and tar materials; these productions disperse in the adjacent environment. Formation of flammable substances (wood material) are completed when the wood temperature reaches over 450° C.[22,90-94]

When the wood's temperature is between 260 and 350° C, the decomposition of cellulose takes place.[17,22,36,45] As pointed above, this decomposition of flammable volatile materials with the presence of oxygen and water can accelerate this operation. The increase of wood temperature decreases cellulose polymerization and produces more carboxyl, carbonyl groups and free radicals and hydroperoxide. The break of the glycosidic linkage causes the initial reaction (depolymerization). The hydrolyzation of glycosidic bonds can occur in the presence of strong acids at room temperature.[17,95]

Hemicelluloses have lower thermal degradation (less stability) compared with cellulose at temperatures of 260-350° C. This decomposition includes less tar and fewer non-combustible gases. The majority of acetic acid resulting from wood pyrolysis is caused by hemicelluloses deacetylation. Hemiculluloses of softwood contain a large amount of xylan and little glucomannan. In contrast, hardwood materials have the opposite proportions of contents.[22,90-52]

Xylan has the lowest thermal stability of hemicelluloses because pentostans materials can simply decompose in the dehydration process. In the dehydration process, the initial thermal reaction of lignin is stimulated at temperatures above 200° C. Alkylether linkages are broken at temperatures in the range of 150-300° C. The chains of aliphatic side separate at 300° C. Eventually, the linkage between two carbon atoms and lignin breaks at 370-400° C.[92-96] There are three steps of heat process in wood as described below.

1.11.1 Preliminary (flameless) stage

This step involves the release of fluid, a dehydration stage and decomposition of volatile materials in wood system by heating. The removal of moisture content can be achieved at 105° C overnight. This reaction occurs at a slow pace (endothermic reaction). After the temperature reaches 200° C, the gas products of the decomposition process start to be released. The bonds of wood become weak, and the gas colour changes to yellow. The lignin decomposition begins at 160° C. Thermal degradation of lignin produces phenols, and the break of ether and C-C bridges produce more char than in cellulose. The majority of the fixed carbon in charcoal is derived from lignin.[97] Hemicelluloses or polysaccharides hydrolysis are established at 180° C.

The thermal stability of hemicelluloses is a lower level than that of cellulose, and they have fewer tarry and more incombustible gases is the released gases are about 70% CO_2 and 30% combustible CO.[95,88,98] This process depends on oxygen availability to form exothermic or endothermic reactions. Exothermic processes are found at 200-260° C. Cellulose is destroyed between 260 and 350° C, and cellulose materials are principally responsible for flammable unstable compounds. The cellulose thermal degradation is stimulated in the presence of oxygen, water and acids. Wood colour changes to brown with pyrophoric carbon formation. However, the rate of reaction is still slow when it is under 260° C.[95,88,97]

1.11.2 Main flame stage

This step involves the ignition of thermal decomposition materials, and combustible gases to spread the flame and increase the heat, causing biomass loss. This is a significant component of the decomposition process. The last reaction develops in the range of 260 to 450° C. As wood reaches the thermal decomposition temperature of 275-280° C, another uncontrolled process begin to release quantities of heat, and the amounts of resulting liquid and gaseous products increased when the wood temperature is increased (280-300° C). These released gases includes methanol, ethanoic acid and its homologues. The amount of carbon dioxide and monoxide is reduced, and mechanical slackening of the wood structure and ignition occurs. After this stage, the wood begins to lose more weight, around 39% of its total mass. Tarry materials are formed at 290° C, releasing more gases and rapidly forming charcoal.

High exothermic reactions occur at temperature levels between 280 and 320° C. The second pyrolysis reaction is classified as the main process because the ignition ability will increase as more gases are released, especially if there is sufficient oxygen access.[88,99]

Combustion materials continue in the gas stage at a small distance from the wood surface instead of on the wood surface itself. From this point, wood can flame significantly even after the heat source is removed. The wood ignition occurs at temperature levels between 300 and 400° C, and the ignition temperature of wood depends on its source. Wood obtained from coniferous trees have an ignition process at 350-365° C. Deciduous wood required less heat 300-310° C. These differences could be related to the high content of lignin in coniferous trees (hardwoods).[88,99]

1.11.3 Final flameless stage

This stage has different wood behaviour, such as the ashing of the remaining matter and the slow burning of the residue. This last stage develops above 500° C; however, as the resulting combustible compounds are small, the formation of charcoal increases. When this reaction is finished, the stoichiometric balance of wood and carbohydrates is formed, as shown in the following Equations (7-9).[57,89,100]

$$\text{Cellulose: } C_6H_{10}O_5 + 6O_2 \rightarrow 6CO_2 + 5H_2O \qquad \ldots\ldots\ldots\ldots(7)$$

$$\text{Hemicellulose: } C_5H_8O_4 + 5O_2 \rightarrow 5CO_2 + 4H_2O \qquad \ldots\ldots\ldots\ldots(8)$$

$$\text{Wood: } C_{1.7}H_{2.5}O_{1.05} + 1.8O_2 \rightarrow 1.7CO_2 + 1.25H_2O \qquad \ldots\ldots\ldots\ldots(9)$$

These steps of heat process in wood could help the investigator to assist the fire behaviour on the location of damaged scene. In addition, heat process can provide the investigator with the fire cause and significant information based on the fire's origin. Therefore, the stages of burned wood are very important to forensic evidences in fire scene.

1.12 Forensic analysis of debris arising from burning of timber

Both fires and natural disasters can cause major damage to human life and property. Deliberate fires intended to destroy human life or properties are some of the hardest cases to investigate because the majority of the significant evidence is removed by the fire. Fire is also one of the major costs for the economic system because it has direct effects on properties and persons. Therefore, providing properties with safety materials such as fire covering and rescue services are necessary. Once the fire-fighters put out the fire, the fire investigators begin to examine all fire-related incidents. This procedure is similar to crime scene examinations in which the investigator must keep the scene secure, collect evidence and analyse materials; however, this practice has more difficulties and danger than other types of crime scene examination. The investigator will survey the damaged scene to find the fire's origin and establish the fire's cause. To successfully test and assess a fire scene, it is very important that the fire investigator has a good knowledge of chemistry concerning the fire's behaviour and its effects.[101-108]

The forensic experts play a significant role in detecting the source of the fire at the site. Determining the cause of the fire as well as its emergence throughout the scene is very important. Inspections of such cases will identify and differentiate the nature of malicious or accidental fires.[108] The forensic expert must collect appropriate samples in order to investigate the possibility of deliberate causes of fire. To identify the existence of Ignitable Liquid Residue (ILR) or any kind of accelerant, these samples must then be examined in a laboratory. In the preliminary analysis, instrumental tools are applied, along with the graphical indications about the fire sources, to reveal the flammable activities and to identify the origin of the fire. Availability of the ILR can be confirmed with the help of the Accelerant Detection Canine (ADC) and staff members. In addition to the fundamental understanding of fire investigation in fire scene, there are still many other familiar and influential procedures pertaining to the fire location itself. The proper detection of the ILR at an alleged burning location holds dual significance. Only successful lab test can reveal the presence of the ILR at the site. The lab efforts can be decreased by using an exact cluster of only the most significant samples by appropriately separating the area containing the ILR. Once it is located, the collection of the residue within the crime scene is of great importance for further proceedings.[108-111] Detecting the ILR at the base of the fire may indicate the presence of accelerants as a cause of the fire. In contrast, identifying the ILR away from the fire source illustrates the nonexistence of an accelerant in deliberately causing the fire. However, the harmless presence of the combustible liquid somewhere else at the fire scene would definitely be discussed, and not at the point of origin.[109,110]

1.12.1 Collection of fire debris evidence

As pointed out above in Section 13 the chemical analysis of fire debris starts at the fire location, and this procedure is followed by detection of origin point using fire investigator evidence. Analytical laboratory tests of samples from the fire scene can clarify whether the debris of the fire includes the ILR. Therefore, the detection of a fire's cause is based on the existence of an ignitable liquid (IL). There are different physical or visual tests that can be applied by a fire investigator, such as point of origin, cause and collection, each of which will be discussed in detail here.[107]

1.12.2 Point of fire origin

The point of fire origin is classified as the specific location where the fire began. Location of this point includes different procedures such as reports of witnesses' observations, the behavior of the fire on the burned wood after the process has ended, the chemical and physical analysis of the fire's beginning and the fire's development at the scene. These tests often provide the required information for detecting the corresponding point of fire origin. The assessment starts with a systematic process for distinguishing areas that have the smallest amount of fire damage followed by the most damage in fire scene. The exact point of fire origin can be characterized depending on the behavior or patterns resulting from the heat movement, smoke and flame. The final conclusion of this test can determine the specific point of the fire's origin, and this point will be where the flame was ignited with ignitable liquid.[107]

1.12.3 Collection

In case of an incendiary fire, the investigator gathers samples from significant points of fire origin as evidence for a suspected incident. Samples collected from fire debris and other resources may include carpet, baseboards, flooring and different parts of furnishings. These fire debris samples may contain residues of ILR. The majority of samples are collected into airtight containers or bags to protect the ILR and show accurate results. The ILR defined as remaining materials of ignitable liquids which could be a possible factor of arson. The result of this test provides the fire investigator with evidence about one suspected cause of the fire.[108-111]

1.12.4 Determining fire cause

The fire cause is detected by recognizing the significant factors and specific situations which caused the fire in the area. This test involves many other key factors, such as equipment, devices, source of ignition, type of materials to ignite first and circumstances; all of these factors can encourage the fire to occur. The fire's cause can been classified as accidental, natural, incendiary and undetermined.[108-111]

The determination of the fire's cause is one of the most important processes in the site of fire debris. This factor can identify the fire's origin after exploring the remaining building structure along with fire debris and ultimately gaining physical proof relevant to the fire's cause.[112,117] An agent is normally involved in the combustible process; it accelerates the rate of fire speed and increases the explosion strength. This type of agent is generally a material that is highly flammable and easily ignited. Hydrocarbon and organic compounds such as kerosene and petrol (gasoline) are normally used to ensure the appearance of a fire. These agents are known as accelerants.[112,114]

There would be an insignificant proof of fire sources or any accelerants involved in this activity if the fire burns for a long time and consumes a significant amount of oxygen and fuel, since the main items have already perished. The expert determines and observes the fire's expansion and can possibly determine the cause through the analysis of burning patterns if the site's basic structure remains. Since fire moves in an upward and outward direction, the investigator holds greater importance for the low-burning areas.[113] The investigator should attempt to reconstruct the area in order to understand the burning patterns on surfaces and furniture. The entire burning site may be used to determine the existence of an accelerant once the source has been established. An accelerated fire is indicated by the presence of an extreme and quick growth that is irregular with the natural fuel loading. An accidental cause of fire is normally disqualified by the presence of multiple areas of origin.[114,115]

If a remaining accelerant could be located at the fire site in a place in which the natural presence of such a material is questionable, for instance, petrol is found in the hallway or on the floor, then the result of any investigation will be greatly helpful to the experts. A main target for the investigation would be to trace and examine residual accelerants in the forensic identification of the fire source.[112,113]

An intentionally ignited fire is revealed by the existence and circulation of a combustible fluid at a fire location. The presence of the accelerant is likely to be discovered by collecting multiple samples. The accelerant can be uncovered by the investigator recognizing the fire's starting point and spreading pattern. The claims of the investigator must be supported by lab tests. Conflicting ideas about the nature of fires can be debated in court; however, the existence of an accelerant can be confirmed by lab findings that are unquestionable and offer certain proof.[112,113]

1.13 Accelerants

Accelerants, or materials that accelerate the burning process and rapidly increase the fire separation simultaneously at many locations, are usually required for deliberate fires. Accelerants consist of ignitable materials such as petrol, which has the ability to burn readily. These kinds of fires are named incendiary fires. Petroleum-based liquids are the most common accelerants in arson. When these materials are poured on surfaces made of carpet or wood, these accelerated materials react as a wick or a matrix.[118,119]

The surfaces of burned materials hold liquids like a sponge. Wood absorbs less liquid than carpet. Evaporation is observed by heating an absorbed liquid. Mixtures of almost 200 or 300 components are used to create petroleum fuels and most accelerants. Diverse chemical and physical properties are associated with these components. The volatility level of each component is different, and the components that evaporate first are the most volatile. Petrol starts to evaporate when its container is left open. There is a similar impact for the heat caused by fire.[118]

A fire cannot start easily if an ignition source is brought into contact with these materials (wood or carpet) because flame retardants have been added to these products to prevent ignition. The components of diesel fuel (liquid and solid materials) are not readily burned. A high temperature is required to produce significant values of volatile materials from carpet and other solids; for this reason, volatile materials are not present at room temperature. The process of combustion develops when vapour is involved with the fuel ignition. A non-volatile matrix such as wood and or carpet material is broken down into volatile materials due to the heat generated by combustion; this is called a pyrolysis process.[118]

The pyrolysis materials may or may not support the ignition process due to their chemical nature. A flame is not expected to spread in cases where the pyrolysis materials are not ignitable. Accelerants can cause fire in wood and these accelerants including flammable pyrolysis, vapours produced by the initial heat; these materials result from the ignition of the accelerant. The heat produced creates more volatile materials on which the flame feeds. When concrete is exposed to the accelerant, it does not burn since this process has no volatile materials.[118,119]

The final stage of this process is fire debris such as partially burnt materials (e.g. tile, wood and carpet). Therefore, samples of the fire debris should be examined using a chemical test in order to determine the components of accelerants. This is not always possible, due to vaporization and other factors. The collection of common accelerants to develop an accelerant library is a common practice for the investigator. The identity of accelerants could be determined by using relevant and helpful data from the accelerant library. The residual accelerant left after the fire incident can be matched with a particular accelerant in some cases. A generic description such as "medium petroleum distillate" may be offered by an investigator.[118]

The analyst must apply methods to verify the presence of an accelerant. The non-existence of accelerant in the fire debris samples may be due to three possible reasons: (1) the accelerant may have been totally consumed in the fire, (2) not enough accelerant may have survived the fire to be tested, and (3) the sample may not contain an accelerant in the first place.[118]

The accidental nature of fire does not signify that there is a 'negative sample'. However, detecting residual accelerant does not usually conclude that a fire has been set deliberately. Therefore, the investigator should have knowledge about components of petroleum and distillates and their behaviour as accelerant materials; this process could affect the selection of scene samples collected as evidence.[118,119]

1.13.1 The nature of accelerants

The most common accelerants are diesel, kerosene, petrol, mineral turpentine and methylated spirits, due to their flammability and availability some accelerants are hardly ever used, such as industrial solvents, and they are readily identified using chemical analysis due their similar chemical properties to those of common accelerants.[112]

Accelerants can include pure or mixed compounds. Pure compounds show a single peak using chromatographic analysis, and many peaks indicate a mixture of compounds; these peaks clarify the fingerprint of each compound in the accelerant. An accelerant containing more volatile materials tends to vaporize at a higher rate than the heavy components; consequently, the total chemical profile of accelerants can change within the fire period and before sampling. The following aspects are likely to control the amount of remaining accelerant at the fire location that is available for sampling purposes:[112]

- The accelerant's volatility.
- The initial loading of the accelerant.
- The fire severity.
- The substrate material porosity.
- The water solubility of the accelerant.
- The elapsed time between sampling and the fire.
- The dryness of the location after the fire.

The aromatic and aliphatic hydrocarbons (e.g., diesel, kerosene and petrol) along with oxygenated compounds like alcohols are the substances of common accelerants. The oxygenated hydrocarbons can be leached during the extinguishing of the fire, since they have a degree of water solubility and a few traces can remain in the solution.[112]

1.14 Suitable matrices for fire debris samples

After detecting the location of fire where an accelerant is expected to have been used, a sample of debris is needed that has the maximum possibility of holding traces of combustible fluid. The forensic expert and fire investigator do not always have matching and consistent requirements. An extremely adsorptive material (no readily pyrolyzing and generate products) is supposed to be the most suitable matrix for the preservation of an accelerant that can be combined with accelerant-based materials. They have low adsorptive capacity of materials, so their ability to store plenty of explosives but also limited for a sufficient amount of volatile materials; however, the matrix is able to release the trapped or adsorbed materials.[118,120,121]

In general, absorbent or adsorbent materials are the best evidence to be collected as samples from the scene. Absorbent materials include carpet, wood, cloth, cardboard, paper, and soil along with concrete (containing a porous structure); these materials have spongy or porous structure. The materials with high adsorption are charcoal and carbon surfaces. The adsorption is process is based "on molecular interaction between the substance to be collected, the volatiles, and collection medium, i.e., the adsorbent".[120] Materials such as plastic and glass have limited adsorbent materials and are less likely to provide positive evidence. Timber and rubber are not usually good sampling materials since the accelerants are depleted during their combustion process. Plastic materials should be avoided because they interfere with accelerants traces and are hard to determine. The main aim of sample preparation methods is to identify volatile materials from the collected samples (fire debris) for subsequent introduction into an analytical procedure. There are two methods for sample preparation based on adsorbent heated headspace enrichment. These methods are the so-called dynamic and static (carbon strip) methods. The first method is the oldest version.[118,120,121]

1.14.1 Ignitable liquids in fire debris samples

One of the most significant tests is the lab test of fire debris, particularly when the investigator hypothesizes that the fire was set using flammable liquids. Examinations of the majority of fire debris are carried out through the ILR-based tests.[103,105] The laboratory analysis of fire debris is the only valid method to conclude that the ILR was used to start a fire. Presently, analytical methods for fire debris analysis of collected samples can determine that a fire was caused by kerosene, gasoline and diesel fuel.[103,105]

1.14.2 Comparable accelerant samples

The majority of fire investigators need to clarify similarities between known flammable and explosive liquids samples obtained from near the fire scene or found in containers and residues of ignitable liquid collected from fire debris. The lab analysis is the only way to conclude the usability of a flammable liquid in a fire scene. The residues of these liquids in collected samples may result from inherent sources to the fire scene, or they could be transported to the scene through different sources; for instance, few pesticides have a petroleum-based carrier. Therefore, comparing the samples from fire debris with liquid samples from these sources, along with similar material samples in a fire scene, may clarify that the materials existed before and after in the scene, which may explain why the fire started and spread in a particular location.[122]

1.15 Extraction of ignitable liquid from fire debris

The fire debris analysts have established committee members to improve and develop methods and other standard practices for the analysis and extraction applications collected from significant scenes of arson. Presently, standard methods for the ILR extraction from fire debris are divided into six practices. These methods involve different patterns, such as extraction of ILR from fire debris, steam distillation, solvent extraction, headspace vapour sampling, and dynamic headspace concentration, passive headspace concentration with activated carbon and headspace concentration with solid phase micro-extraction. This review will focus on the most common methods (steam distillation and solvent extraction) that have been used in studying the fire debris.[107]

1.15.1 Steam distillation

Steam distillation is one of the oldest methods used in the extraction practices. This test is classified as a classical system for the separation and extraction of hydrocarbon-based liquids. The equipment of this method include a container or flask, the size of their mount should be appropriate to introduce the debris materials and a cold finger or condensing column should fit with a distillation trap. The process includes mixing the debris into a specific container along with an appropriate quantity of water, followed by a boiling process. The resulting vapours are condensed in the distillation section. The residues of distillate petroleum are floated on top of a column Section of water, and then these residues are collected as visible liquids.[107]

1.15.2 Solvent extraction

E1386-00 is the second standard procedure for the concentration and separation of ILR from samples of fire debris using different types of solvent extraction.[123] This destructive method can only be used when samples of representative fire debris will be kept for reanalysis. This method is suitable for ILR extraction from the materials that have the ability to absorb liquids and from the surfaces of non-porous materials, for instance, glass surfaces. The collected samples are placed into appropriate beakers along with enough volume of a selected organic solvent to moisturize the samples of debris. The materials are mixed to encourage the IRL extraction followed by removing the solvent from the IRL; the mixture is then passed through an appropriate filter. The evaporation of solvent develops with filtered air and dry nitrogen to condense the collected samples.[107]

The selection of a suitable solvent for the sample isolation is one of the critical factors in terms of the analyst's quality. The American Society for Testing and Materials, (ASTM E1386-00) is an appropriate technique used in solvent extraction to isolate residues from small qualities of the ILR samples. This method is also suitable for ILR extraction with a high ILR absorption using rinsing containers, according to the American Society for Testing and Materials (ASTM).[123]

Carbon disulfide (CS_2) is the most common eluting solvent; it is highly toxic, flammable, explosive, odorous, carcinogenic and teratogenic. It has an infamous reputation for inherent dangers. This compound showed no significant effects when eluting both aliphatic and aromatics almost equally from activated carbon strips. The same behaviour has been demonstrated by diethyl ether.[105] The members of ASTM Committee E30 indicated that carbon disulphide is better than diethyl ether or pentane or other solvents for this action.[124] Previous studies showed small differences between carbon disulphide and diethyl ether when carbon strips were exposed to 10μl of ILR residues.[125] For a fire debris solvent, carbon disulfide was initially chosen due to its high desorption efficiency, and this compound shows a small signal through a flame ionization detector (FID). Therefore, the benefit of a low signal disappears when the mass spectral detector turns off while the solvent is passed through the system.[105] The ability of diethyl ether to develop explosive peroxides is concerning. However, this process can be controlled by keeping ether in a refrigerator and it is use on a regular basis. Explosions of ether cans occur when containers have been stored for many years.[105] Pentane, carbon disulphide and diethyl ether are extremely flammable. On the other hand, carbon disulfide is greatly hazardous with respect to fire since it has the lowest explosion temperature and the largest flammable threshold.[105] The ASTM E1412-00 has reported the comparison of the three recommended solvents as shown in Table 1.3.[126]

Table 1-3 Comparison of three solvents and their properties

Elution solvent comparison			
Properties	**Carbon disulfide**	**Pentane**	**Diethyl ether**
Flash point	-30° C	-40° C	-45° C
Specific gravity(g/cm^3)	1.3	0.78	0.7
Boiling point	40° C	36° C	35° C
Teratogenic	Yes	No	No
FID signal	Small	Very large	Large
LEL (% vol in air)	1.0	1.5	1.9
UEL (% vol in air)	50.0	7.8	48.0
Auotignition tem	90° C	260° C	180° C
Exposure limit, (TWA)	4 ppm	600 ppm	400 ppm
Exposure limit, (STEL)	12 ppm	750 ppm	500 ppm
IDLH	500 ppm	15,000 ppm	19,000 ppm

Note: IDLH, Immediately Dangerous to Life and Health; **LEL**, Low Elution Limit; **UEL**, Upper Elution Limit; **TWA**, Time-Weighted Average; **STEL**, Short Term Exposure Limit.[126]

1.16 Detection of ignitable liquid residues at fire scenes

Petroleum-based liquids are of the ignitable residues, including combustible or flammable materials. These liquids are defined as mixed complexes resulting from hydrocarbons; these complexes contain different materials such as cyclic alkanes, branched, normal and polynuclear aromatics along with aromatic materials. One of these liquids is petrol, which contains over 400 compounds.[127] Crude oil was used to separate the petroleum-based liquids by different chemical steps. Gas chromatography is the most common method for detecting fire debris; this process isolates the hydrocarbons within in the ILR before detection occurs. Different types of detectors can be involved in the gas chromatograph. Therefore, the selection of GC-detector based on sensitivity or the quantity of chemical accuracy is needed in the analytical procedure. The detection methods have different techniques: (1) gas chromatography (GC), (2) gas chromatography-mass spectrometry

(GC-MS), (3) gas chromatography/mass spectrometry/mass spectrometry (GC-MS-MS).[127-130]

1.17 The adsorption of boron on wood surfaces

The adsorption of boric acid and borates by soils, clays and other minerals has been extensively studied.[131-133] At the same time, there is limited information regarding the adsorption of boron on wood surfaces. Moreover, the influences of operational and environmental factors (pH, temperature, concentration and competing ions) on boron adsorption have not been investigated thoroughly, and often there are contradictory results reported in the literature. The mechanism of binding boron to wood when it is treated with borax or boric acid aqueous solutions is unknown. Thus, new investigations on the reaction kinetics of boric acid may help to determine ways of improving the presentation of boric acid as a wood preservative.[131-133]

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Chapter 2.

2 Experiments: Materials, Treatments and Methods of Analysis

2.1 Introduction

This chapter describes the methods and materials that were used in this study to investigate the effect of the treatment of timber with boric acid solution in relation to fire accelerant residue (FAR) for the forensic analysis of fire scenes. Yellow pine *(Pinus elliottii),* Douglas-fir *(Pseudotsuga-menziesii),* Oak *(Quercus petraea)* and Sapele *(Entandrophragma cylindricum)* woods were selected as the main experimental samples because: (1) these species are among the most important fast-growing trees in the world, and they are among the best-selling woods in Saudi Arabia;[1-5] (2) these species are of major importance in terms of forensic evidence at fire scenes;[6] (3) these species are important sources for building materials and furniture;[7] and (4) no study has established the impact of boric acid solution using different fire accelerants for these tested species.

The first Section explains the wood specimens and their preparation for all required studies. The wood treatment was conducted using different concentrations of boric acid solution. More details of the wood treatment and gravimetric calculations are shown in this chapter. The properties of the four wood types were studied, and these characteristics were measured in treated and untreated (control) wood samples. The tests were: moisture content, organic matter, density and pH. The colour of the woods was examined by visual inspection, which is based on colour changes. The depth of boric acid penetration in untreated and treated wood samples was determined to clarify whether the boric acid solution has the ability to achieve maximum levels of penetration in the wood samples. The thermal properties of the treated and untreated wood samples were investigated using thermogravimetric analysis (TGA). The fire tests of each wood sample were examined using petrol, kerosene and diesel as fire accelerates. The ignitable liquid residues (ILR) of each sample were analysed using gas chromatography-mass spectrometry (GC/MS). This technique was used to determine the presence of ILR (petrol, kerosene and diesel) and organic compounds (hydrocarbon) in the wood samples before and after burning. Finally, the adsorption of boric acid was studied on the surfaces of the four wood type's material as adsorbent and boric acid as adsorbate using the batch experiments. Data regarding borate adsorption isotherms and its behavior were reported using mathematical Equation models (Freundlich and Langmuir). In addition, the relationship between borate concentrations and wood types over time was obtained using kinetic reaction models (first and second order).

2.2 Timber collection

Samples of Douglas-fir, Yellow pine, Sapele and Oak were obtained from a timber supplier (Huws Gray Ltd, Llandegai Industrial Estate, UK) as blocks with dimensions of 2×2×5 cm^3, as shown in Figure 2.1.

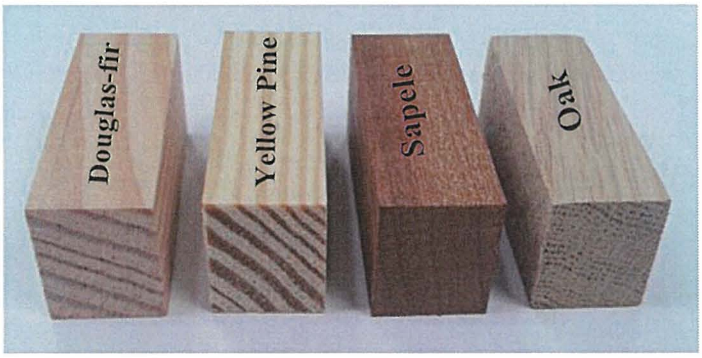

Figure 2.1 The morphology of experimental wood species as sullied from Huws Gray company. The wood species are Douglas-fir, Yellow pine, Sapele and Oak.

2.3 Studied species and sampling

The four wood species and their scientific, vernacular and family names are listed in Table 2.1 below:

Table 2-1 Shows the wood species for experimental samples.

Scientific names	Vernacular names	Family
Pinus elliottii	Yellow pine	Pinaceae
Pseudotsuga-menziesii	Douglas- fir	Pinaceae
Entandrophragma cylindricum	Sapele	Meliaceae
Quercus petraea	Oak	Fagaceae

Source: Shmulsky and Jones (2011).[8]

The wood blocks were divided into four groups depending on species. The samples were stored in plastic boxes to avoid environmental impacts (e.g. temperature and moisture). Because the samples were to be treated with boric acid solution or fire accelerators, they were chosen to be free of wood knots and visible resin concentration; in addition, they had no physical damage, such as colonisation by stain, mold or decomposition from fungi. The weight of each wood block was recorded along with its dimensions for the physical chemical properties analysis. The range of total weight was from 10.55–15.37 g for all wood species, but the weight difference between each sample was no more than 0.5 g.

2.4 Analysis of wood properties

With the above-described details for wood species and sampling preparation, the specimens were examined for the determination of: (1) moisture content and organic matter; (2) wood density; and (3) wood pH. The procedures used are described in the following sections.

2.4.1 Determination of moisture, organic matter and ash content for wood types

Douglas-fir, Yellow pine, Sapele and Oak wood was used to determine moisture content and organic matter. Each wood type was selected as a block section (see Section 2.2). Appropriate porcelain crucibles were carefully washed and rinsed with distilled water and dried in an oven at 105° C. The oven-dried crucibles were then allowed to cool in glass desiccators, and their weights were recorded as W_1 (g). A total of 10 g of each wood sample (blocks) was weighed in oven-dried crucibles and labelled as W_2 (g). Samples were prepared in triplicate for each wood type (*n* = 12), and the samples were placed in an oven at 105° C overnight. The weights of the oven-dried samples and crucibles were recorded as W_3 (g). Finally, the samples were placed in the muffle furnace (Carbolite Limited) at 600° C for 6 hours to measure their organic matter content (OMC). The crucibles were then allowed to cool, reweighed and recorded as W_4 (g). The percentage of MC and OM content of the wood samples was calculated using Equations 2.1 and 2.2, respectively. The AC percentage of each sample was determined using Equation 2.3.[9,10]

$$\mathrm{MC} = \frac{(W2-W3)}{(W2-W1)} \times 100 \qquad \text{Equation 2.1}$$

$$\mathrm{OMC} = \frac{(W3-W4)}{(W2-W1)} \times 100 \qquad \text{Equation 2.2}$$

$$\mathrm{AC} = \frac{(W4-W1)}{(W2-W1)} \times 100 \qquad \text{Equation 2.3}$$

2.4.2 Wood density

Density is a significant property of wood that is interdependent of other properties such as the water amount and the four densities (density at 12% MC, raw, basic density and density at absolute dry weight) were determined. Wood density affects the wood-based composites and quality of solid wood products along with wood yield.[12,13] Therefore, the density and porosity of wood have an impact on its diffusivity and thermal conductivity.[14]

The density of the untreated wood samples was measured according to the water-displacement method to find the wood volume (since water has a density of 1.0 g/cm^3). A glass container (50 ml) was modified to hold the block wood sample. The container was filled with 40 ml of distilled water and placed on an accurate balance (MonoBloc-AB204-S) with four digital numbers. The balance was reset (zero), and the reading was zero. The block wood sample was measured before m (g) then carefully sunk in the water container using a thin needle. The samples were completely submerged, and they were not in contact with the bottom or sides of the glass container. The measured weight of the displaced water was recorded, and this weight was equal to the volume of the wood sample. The process was repeated three times for each wood type. The density (ρ) of the untreated wood samples was calculated using Equation 2.4.[12-15]

$$(\rho)\ \mathrm{g}/(\mathrm{cm})^3 = \frac{m}{V} \qquad \text{............... Equation 2.4}$$

Where m is the mass (g) and v is the volume (*weight of displaced water*) (cm^3).

2.4.3 Measurement of wood pH

The oven-dried blocks of each wood type were divided into very small pieces with a sharp chisel, and the samples were grinded with a stainless steel grinder. Then, 0.5 g of each wood type was placed into a clean glass sample (30 ml). A total of 10 ml of distilled water was added to the wood samples (as a powder) in each tube. The samples were shaken manually for 5 min to ensure that the solution was thoroughly mixed. This process was repeated three times for each sample (*n* = 12). The samples were allowed to settle for 1 hour at room temperature (20° C), then the pH meter (JENWAY 3510) was calibrated using a different range of buffers (pH 10, pH 7 and pH 4). Finally, the pH readings were recorded after 1 hour for each wood type.[16]

2.4.4 Preparation of treatment solution

Boric acid (H_3BO_3) with an analytical grade of 99.5% was used as a wood preservative (Fisher Scientific UK Ltd). The stock solution was prepared by dissolving 49.46 g of boric acid in 2000 ml of distilled water. The concentration of this stock was 0.4 M. Different concentrations of boric acid were prepared from the solution at 0.1, 0.2, 0.3 and 0.4 M. The solutions were then stored in the fridge (approximately 4° C).

2.5 Overview of wood treatments

The wood samples that had been stored at room temperature (20° C) were treated with different concentrations of boric acid. The selected concentrations were 0.1, 0.2, 0.3 and 0.4 M, as described in the previous Section (2.4.4). The details of the treatment procedures and equipment are described in the following Section.

2.5.1 Method of wood treatment

The wet weight of each wood block was recorded for the untreated samples (T_1), and these samples were placed in an oven at 105° C overnight. The oven-dried weight of each untreated sample was recorded (T_2). The wood types were divided into four main groups (Douglas-fir, Yellow pine, Sapele and Oak wood), and each group was divided for six treatments (control, solvent solution, 0.1, 0.2, 0.3 and 0.4 M of boric acid solution). The wood specimens were impregnated with aqueous solutions of boric acid. The control sample was not treated with boric acid. For the solvent solution, the samples were treated with distilled water. The treatment method followed ASTM D 1413-76 procedures.[17] In the impregnation process, four pieces of each wood were placed in 500 ml circular glass troughs. The troughs were located in the vacuum desiccators and were connected to a vacuum pump via a vacuum trap, as shown in Figure 2.2. The vacuum process was applied for 30 min before moving the treatment solution to circular glass troughs. A total of 250 ml of each treatment solution was used for the wood samples. Then, the samples were allowed to soak in the treatment solution for 45 min at room temperature (20°C).[17-18] Figure 2.3 shows the wood block arrangement.

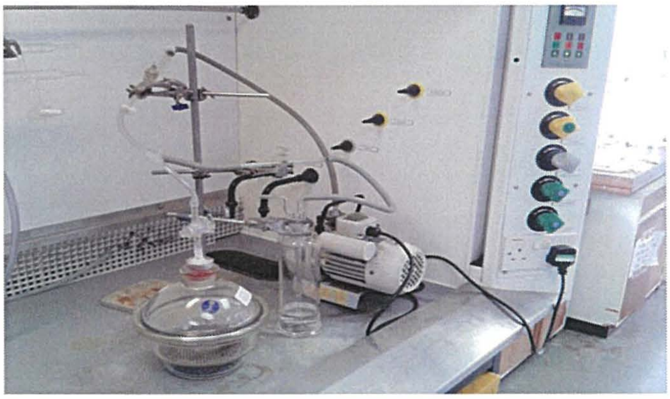

Figure 2.2 The vacuum impregnation appliance.

Figure 2.3 The arrangement of wood samples in the circular glass trough

Each treatment was repeated three times, including the control ($n = 72$). The treated wood samples were used to examine the burning process in each wood type using different ignition accelerators, and the penetration of boric acid solution into the wood tissues was determined. The amount of borate and solution (loading, containing) in the wood materials was calculated, as described in Equations 2.5–2.8:

T_1 (g) = initial weight of each wood sample before drying.

T_2 (g) = dry weight of each sample.

T_3 (g) = weight of each wood sample after treatment.

T_4 (g) = dry weight of each treated wood sample.

$T_5 (g) = T_4 - T_2$ Equation 2.5

$\text{Amount loading } (g\ /\ g)\% = T_5 / T_2 \times 100$ Equation 2.6

$\text{Amount containing in wood material } (g\ /\ g)\% = T_5 / T_4 \times 100$ Equation 2.7

$\text{Amount of borate (mol)} = T_5 / (61.83 \text{ (g/mol) of BA})$ Equation 2.8

For water, the specific gravity is 1.00.[17,18]

2.6 Determination of boric acid penetration in wood

The aim of this experiment was to evaluate the ability of boric acid solution to penetrate into the wood (Yellow pine, Douglas-fir, Oak and Sapele). The wood samples were treated with different concentrations of boric acid (control, solvent, 0.1, 0.2, 0.3 and 0.4 M) as explained in Section (2.4.4). The total wood samples included 24 blocks for all wood types. The examined samples were used to determine the degree of boric acid penetration via the longitudinal section of the samples. Each wood sample was divided into two pieces using a sharp chisel.

Two different solutions were prepared to determine the boric acid solution penetration depth in the four wood types. In the first solution, 10 g of turmeric was dissolved in 90 ml of ethyl alcohol, and the solution was filtered (110 mm filter paper). The second solution was prepared with 20 ml of concentrated hydrochloric acid and 100 ml of ethyl alcohol (dilution), followed by 100 ml of saturated salicylic acid (13 g in 100 ml). The first solution was applied to the surface of the wood specimens using a pipette. The samples were allowed a few minutes to dry. The second solution was supplied in a similar manner to the samples. The colour of wood samples were yellow after adding the first solution. In the presence of boron, the yellow turmeric solution turned red after the application of the second solution. This method is based on the colour change of the wood surface. The penetration depths for the samples were analysed according to standard procedures (AWPA-2003a).[19]

2.7 Test method for fire exposure of timbers

The depth patterns of burned wood have been classified as a relevant factor by fire scene investigators around the world. The depth pattern of fire has significant impacts for forensic evidence in woody buildings.[20-22] This could be related to the rapid thermal decomposition of wood and its ability to hold different liquids when exposed, such as petrol, kerosene and diesel, and to behave as a sponge. These liquids can be adsorbed on wood surfaces, or they may penetrate into the wood system.[23,24] These accelerators are defined as ignitable liquids that are proposed to burn efficiently, and small traces may remain in the residue of fire debris in wood pyrolysis. This is a natural test because post-fire patterns established on wood materials are usually more observable and extensive compared to those found with other commercial construction materials.[22-24]

The aims of this test method were: (1) to investigate and describe the ability of treated and untreated woods (Douglas-fir, Yellow pine, Sapele and Oak) for fire test conditions within a short exposure period after the fire process; (2) to evaluate the ability of borate-treated woods to retain fire accelerants (petrol, kerosene and diesel) for forensic purposes; and (3) to analyse the remaining residues of ignitable fuel in the fire debris of four wood types using GC/MS.

2.7.1 Sample preparation of fire test

Four wood types were tested against the short time fire test. The selected samples were treated with different concentrations of boric acid, including the blank and control samples. These treatments were divided into seven groups: blank, control, solvent (distilled water), 0.1, 0.2, 0.3 and 0.4 M. The blank samples were untreated wood samples without accelerators, while the control samples were untreated wood samples with accelerators. The method of wood treatment was described in Section 2.5.1 The total number of wood samples was 63 for each wood type. Each treatment was repeated three times ($n = 3$). Thus, the total number of samples of the four wood types was 252 blocks. The properties of the test blocks were explained in Sections (2.2-2.4).

2.7.2 Method of fire test

Each block sample of Douglas-fir wood was soaked in a circular glass trough (500 ml) containing 250 ml of petrol. The petrol solution was purchased from a local petrol station in Bangor, Gwynedd, UK. The sample was completely immersed in accelerant solution for 1 min using a tong tool. The block wood sample was removed from the accelerant solution and held by the tong for 2 min. Then, the burning process was conducted using a Bunsen burner for 1 min, as shown in Figure 2.4. Next, the fire was extinguished using distilled water, and the sample was allowed to cool for one hour in a fume cupboard.[25] Finally, the burned samples were stored in glass vials (50 ml) to await the extraction procedure. The entire burning process was conducted under lab conditions. This burn procedure was applied for the three other wood types (Yellow pine, Sapele and Oak), and two other accelerators were used (kerosene and diesel). The diesel was obtained from the same petrol station, and the kerosene was provided by the B&Q store in Bangor, Gwynedd, UK. The extraction method will be described in more detail in the following section.

Figure 2.4 The fire testing method for wood specimens utilising a Bunsen burner.

2.7.3 Extraction method of residue accelerants from burned wood

The extraction method is one of the most important methods for fire scene detectors. This method involves searching for and collecting fire debris containing accelerators such as volatile ignitable compounds. More details of this method can be found in Chapter 1, Section 1.15. This method was applied for all burned wood samples and wood types, as described in the previous Section (2.7.2). The extraction of ignitable (flammable) liquid residues (petrol, kerosene and diesel) from the wood samples was performed using a significant solvent extraction according to ASTM (E1386–10) and Midkiff.[26,27] This procedure has shown significant results when preparing extractions of burned wood samples using gas chromatography. Diethyl ether (DEE) solvent was used to extract ignitable liquid residues from each burned wood sample. 1,3,5-Trichlorobenzene (TCB) was used as an internal standard (IS). This compound should not commonly be encountered within the process of pyrolysis or in the ignitable liquids produced at fire scenes.[28] The stock solvent was prepared by dissolving 0.25 g of TCB in 2 L of DEE. A sufficient amount of solvent was added (25 ml) to the wood samples after burning. The solvent and wood samples were manually mixed for 2 min. to ensure that all samples had adsorbed the solvent. The solutions were filtered using phase separation filter paper (110 mm). A total of 1 ml of each solution was placed in a sealed auto sampler vial with septum (GC/MS vials). Finally, the petrol (hydrocarbons) residues in the extracted solution were analyzed using gas chromatography-mass spectrometry (GC-MS).

2.7.4 Analytical conditions of GC/MS instrumentation

As mentioned earlier, GC techniques have been used extensively for fire debris analysis. The selected parameters have significant effects on the results of ignitable liquid residue analyses; for instance, the separation process must consider the cost, time of analysis and resolution. In addition, it is very important to select the suitable column and its temperature condition according to the mixture type to be analyzed. Therefore, the analytical conditions of GC/MS in the present study were selected according to the standard method. These selected conditions provided perfect separation abilities of the GC technique for all the analysed ignitable liquids.[22,29-32] The used GC/MS conditions are shown in Table 2.2.

Table 2-2 Shows the selected operating parameters of GC-MS technique.

Instrument unit	Descriptions
Gas chromatography (GC)	Thermo Scientific Trace 1300 GC
Mass spectra (MS)	ITQ900 Ion Trap Mass Spectroscopy
Column type	Omega Wax-DB5 capillary column (L30 m×ID0.25 mm×DF0.25 µm) Film
Carrier Gas	Helium
Flow rate	1.0 ml/min
Split value	20 ml/min
Injector	1.0 µl
Transfer line	200° C

Temperature program

Descriptions	Method 1 (gasoline)	Method 2 (kerosene)	Method 3 (diesel)
Initial temperature	35° C	45° C	60° C
Initial hold	2 min	2 min	2 min
Ramp rate	10° C/min	5° C/min	5° C/min
Final temperature	200° C	250° C	300° C
Final hold	3 min	3 min	3 min
Total run time	25 min	46 min	53 min

2.8 Characterisation of accelerant components

The aim here was to obtain the components of chromatographic petroleum liquids (gasoline, kerosene and diesel) within measured peaks using GC/MS. Table 2.3 shows all the standards that were used in these experiments. Components of target compounds were used to identify the patterns of the petroleum liquids compared to those found in the fire debris residues of the ignited wood samples. The components of the used accelerants were toluene, ethylbenzene, *m*-xylene, *p*-xylene and 1,2,4-trimethylbenzene. This method was applied according to Lock *et al.*[28] The retention time (R_t) was obtained to characterise the chromatogram of the standard petroleum components using different temperature programs of GC/MS. The standards or reference peaks were compared with those found in the fire debris residues.

Table 2-3 The preparation of petroleum concentrations and their components.

Compounds	Conc. (ppm)	Density (g/ml)	Standard preparation
Gasoline	500	0.658	381 µl dissolved in 50 ml of DEE
Kerosene	10,000	0.791	632 µl dissolved in 50 ml of DEE
Diesel	10,000	0.835	598 µl dissolved in 50 ml of DEE
Toluene	10,000	0.870	574 µl dissolved in 50 ml of DEE
Ethylbenzene	10,000	0.867	576 µl dissolved in 50 ml of DEE
***m*-xylene**	10,000	0.856	584 µl dissolved in 50 ml of DEE
***p*-xylene**	10,000	0.859	582 µl dissolved in 50 ml of DEE
1,2,4-trimethyl benzene	250	0.655	250 µl dissolved in 50 ml of DEE

Note: Conc represents concentrations and DEE represents diethyl either solvent.

2.9 Analysis of GC/MS data

The chromatographic petroleum peaks were obtained using the GC/MS technique. The (R_t) of all the peaks was integrated using (R_t) of the standard compound (see Table 6.2) presented in the previous Section (2.8). The peak area ratio(PAR) of each measured compound were calculated using Equations 2.9.[30,31] These peak areas were normalised to those obtained using the peak area of the internal standards (IS) (1,3,5-trichlorobenzene)

(TCB). The obtained peaks of GC/MS were analysed with advanced software (Thermo Xcalibur 2.2 SP1.48).

The same procedure was followed for the unburned wood samples, using four wood types, as described in Sections 2.7.2 and 2.7.3 The fire test method was excluded here to allow for comparison between the results of burned and unburned methods using the GC/MS technique.

$$(\mathrm{PAR})\% = \frac{\text{Peak Area}(\mathit{compound})}{\text{Peak Area}(\mathit{Internal\ Standard})} \times 100 \qquad \text{Equation 2.9}$$

2.10 Characterisation of boric acid powder using X-ray diffraction (XRD)

The powder sample was used to determine the crystal structure and morphology of boric acid. In addition, the crystalline degree of treated (0.4 M boric acid) and untreated samples (control) was determined for Yellow pine, Douglas-fir, Oak and Sapele wood. The sliced wood samples were used to observe X-ray diffraction peaks of boric acid. The method for boric acid treatment of wood samples is described in Section 2.5.1 The test samples were dried at 100° C overnight. The diffraction peaks of the boric acid powder and within the wood samples were obtained using powder X-ray diffraction (XRD) with a D/max-2500 X-ray diffractometer using Cu Kα radiation (wavelength Å) ($\lambda = 1.5406$ Å).[33-35]

2.11 Preparation of wood samples for adsorption experiment

Four stock solutions were prepared by dissolving 6.16, 12.36, 18.55 and 24.71g of $B(OH)_3$ in one liter of distilled water. The adsorption isotherm was determined using four different solutions of boric acid (250 ml). The prepared concentrations were 0.1, 0.2, 0.3

and 0.4 M of boric acid. The wood samples were treated with initial boron concentrations from 0.1 to 0.4 M using vacuum impregnation for the standard test method of wood preservatives.[36] Boron adsorption and kinetic studies were performed using batch experiments. A total of 250 ml of each boron concentration was equilibrated with 10± 0.002 g of each wood sample (four types) in the glass beakers (300 ml). The supernatant (25 ml) was collected at different times: 5, 10, 15, 20, 25, 30, 60, 90, 120 and 150 min. The total concentration of boron was measured using inductively coupled plasma (ICP). The amount of adsorbed boron was calculated as the difference between the initial concentration and the final equilibrium concentration adjusted for the solution volume. Each measurement was repeated three times ($n = 3$).[37-42] The amount of adsorbed boric acid (q) mg kg^{-1} was obtained using Equation (2.10)[37]:

$$\text{Amount of adsorbed boron } (\boldsymbol{q}) = (\boldsymbol{C_f} - \boldsymbol{C_i}) \frac{v\ solution}{\boldsymbol{m}\ sorben} \qquad \text{Equation (2.10)}$$

where C_f is the boron concentration in aqueous solution, C_i is the initial concentration (ppm) of boron, $\boldsymbol{m}$ (10 g) is the dry mass of wood and v (25 ml) is the volume of solution was collected in different times (min). The amount of adsorbed boron was calculated as the difference between the initial concentration and the final equilibrium concentration adjusted for the solution volume. Each measurement was repeated three times ($n = 3$).

The Freundlich isotherm Equation is usually applied for a non-homogeneous adsorption process, such as in wood; a physical adsorption of boron on the wood surface with weak forces acting, such Van der Waals and hydrogen bridges, is assumed. The Freundlich isotherm is described in Equation (2.11)[37]:

$$\text{Log}\,(\boldsymbol{q}) = \log \boldsymbol{K_f} + 1/n \log \boldsymbol{C}_{\text{eq}} \qquad \text{Equation (2.11)}$$

Where C_{eq} is the equilibrium concentration, K_f describes the Freundlich equilibrium constant (adsorption capacity) and 1/n is an arbitrary constant (adsorption intensity) evaluated by linearising the equation. The data is plotted in a linear form by taking the log of both sides of Equation 2.12 (Log (q) and log (C_{eq})).

The Langmuir isotherm assumes that that a maximum adsorption of boron corresponds to a saturated monolayer of boron molecules on the adsorbent surface of wood, and the adsorption energy of this reaction is constant; thus, this process has no adsorbate transmigration in the surface plane.[38,39] The Langmuir Equation is represented below (2.12):

$$C/(x/\text{m})\ q = 1/kb + C/b \qquad \text{Equation (2.12)}$$

where q = Amount of B adsorbed per unit of wood (mg/g);

C = Equilibrium B concentration in solution (mg/L);

k = A constant related to the bonding energy of B to the wood surface (L.mg^{-1})

b = The maximum adsorption capacity of wood loading (mg.g-1).

In order to study the controlling mechanism of the boron adsorption process, two kinetic models (pseudo–first and second reactions) were used to examine the adsorption data. The constant rate of adsorbed boron was calculated from the following pseudo–first–order rate expression (Equation 2.13), as given by Lagergreen and Ho and McKay [40,41,42]:

$$\log (q_e - q_t) = \log q_e - (k_1 t / 2.303) \quad \text{Equation (2.13)}$$

where qe and qt are the amounts of adsorbed boron (mg/g) at equilibrium concentration and at time t (min), respectively, and k_1 (min^{-1}) is the constant rate of first–order boron adsorption. The rate of second–order reaction was calculated using Equation (2.14). This model was presented by Ho and McKay[42]:

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{Equation (2.14)}$$

where k_2 is the rate constant of second–order reaction (g/mg.min). The fit of these Equations is examined by each linear plot of log (q_e−q_t) versus t and t/q_t versus t, respectively.

2.12 Statistical analysis

Adsorption data were analysed with a statistical software package (SPSS 20.0 for Windows). The adsorption of boron in four wood types was evaluated using a one-way ANOVA and Tukey's HSD test (*honest significant difference*). A P value < 0.05 was considered statistically significant. The mean average adsorption data were evaluated using the Kruskal–Wallis one-way ANOVA on ranks and Dunn's multiple comparison tests.[43] Data are presented as means ± SE. The mean equilibrium and adsorption errors of each of the three replicates were calculated using Microsoft Excel for precision and absolute accuracy of the modelling results.

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Chapter 3.

3 Determination of Wood Properties and the Method of Wood Treatments

3.1 Introduction

As previously discussed, wood is a unique material, and the majority of its properties are correlated. These interrelated aspects comprise the anatomical features, chemical composition, mechanical and physical characteristics, and natural durability of wood. Many studies established that the properties of wood have a significant effect on their interaction with the environment.[1] Previous studies indicated that the interrelations of wood properties were the main factor in understanding wood behaviour.[2,3] Furthermore, the physical properties of wood are classified as quantitative wood characteristics, and their behaviour is considered affected by external influences, instead of applied forces.[1]

Therefore, the properties were determined for Douglas-fir, Yellow pine, Sapele and Oak (Section 2.4). This part of the study was included in Chapter 2. The studied samples were described in Section 2.2. The characteristics of the four types of wood were measured in untreated (control) wood samples for comparison with the effects in the treated samples; the control samples having received no chemical treatments. The performed properties were moisture content, organic matter, ash content, density and pH parameters, as measured by the method described in Sections 2.4.1, 2.4.2 and 2.4.3. The changes in the colour of the wood were determined by visual inspection. The penetration of boric acid was determined in both untreated and treated wood samples. The maximum degree of boric acid penetration was examined in the wood samples. The treatments of the wood samples were performed using different concentrations of boric acid solutions. The amount of borate in the wood materials was calculated, as described in Equations (2.5 to 2.8).

3.2 Materials and method

3.2.1 Timber collection and studied species and sampling

The collection of samples of Douglas-fir, Yellow pine, Sapele and Oak and their preparation were described in Sections 2.2 and 2.3.

3.3 Results and discussion

3.3.1 Determination of moisture content, organic matter and ash content for wood types

Douglas-fir, Yellow pine, Sapele and Oak were measured for moisture content, organic matter and ash content. The methods used for both parameters were described in Chapter 2, Section 2.4.1. The wet and oven-dried weights of each wood block were recorded to calculate the moisture content and organic matter, as described in Chapter 2, Equations 2.1 and 2.2. In the final step of this process, the percentage of ash content (AC) in each sample was determined using Equation 2.3. The results of the measurements of moisture content (MC), organic matter (OM) and ash content (AC) are shown in Figures 3.1 to 3.3.

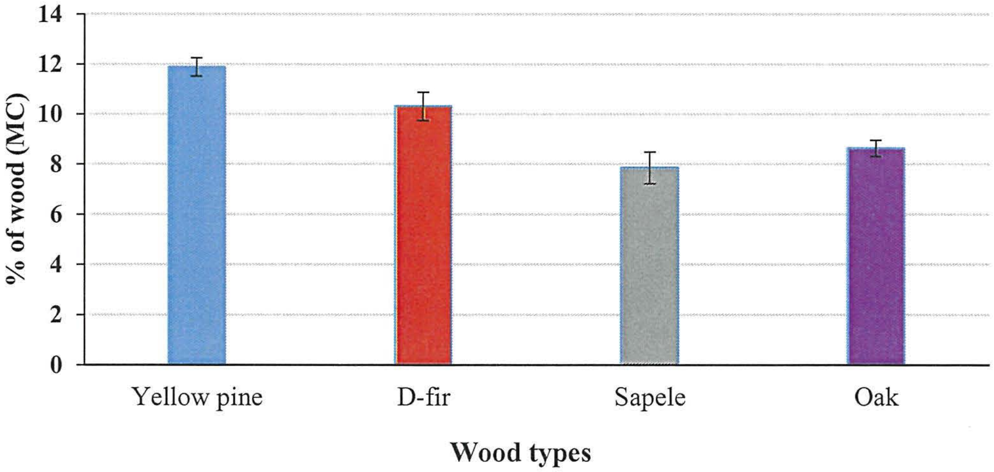

Figure 3.1 The percentage moisture content in the Yellow pine, Douglas-fir, Sapele and Oak samples. The wood samples were not treated with chemicals. The moisture content (MC) was calculated from Equation 2.1. The calculated values are given as mean ±SE ($n = 3$).

The percentage moisture content in Yellow pine (soft wood) was considerably higher than that of Douglas-fir, Oak and Sapele (see Figure 3.1). The moisture content of Yellow pine was 11.88%±0.36, 10.32% ± 0.56 of Douglas-fir, 8.64% ±0.33 for Oak and 7.86% ±0.63 for Sapele. Therefore, Yellow pine showed the highest percentage of moisture content compared to the other wood samples. Possible reasons for its high moisture content may be the dissociation pattern of the wood system and that it is more porous, which increases the ability of Yellow pine to adsorb more water compared with the other three types. On the other hand, a possible reason for the low moisture content in the other three wood samples might be related to the high percentage of heartwood in the wood specimens. Similar wood behaviour in response to water has been obtained from Alaskan Spruce *(Picea glauca)* and Hawaiian Albezia (*Albezia falcataria*).[4] As discussed in Chapter 1 Section 3, moisture content is one of wood's dynamic properties. The moisture content of wood is a property that relies on different factors, such as temperature and the relative humidity of the surrounding air. These factors play a significant role in the equilibrium of the moisture content of wood. For instance, when the thermal conditions of the surrounding environment change, the wood tends to reach a new equilibrium of moisture content by adsorbing or desorbing water.[5] Therefore, the MC of softwood (Yellow pine and Douglas-fir) was higher than those found in hardwood (Oak and Sapele); this difference is related to the ability of softwood to adsorb more water than hardwood.[5]

The results in Figure 3.2 show that the OM content of Yellow pine (soft wood) was the highest followed by Douglas-fir, Oak and Sapele. The OM content of Yellow pine was 97.5% ±1.3, that of Douglas-fir was 93.4% ±0.60, that of Oak was 89.0% ±2.4 and that of Sapele was 88.60% ±1.80. Therefore, Yellow pine showed the highest percentage of OM content compared to the other wood samples.

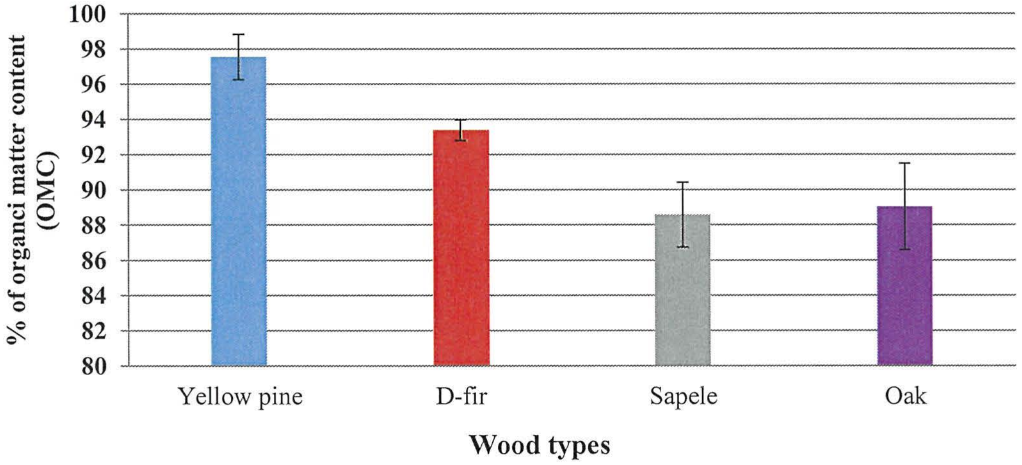

Figure 3.2 The percentage of organic matter content (OMC) in Yellow pine, Douglas-fir, Sapele and Oak samples. The wood samples were not treated with chemicals. The OMC was calculated from Equation 2.2. The calculated values are given as mean ±SE (n = 3).

Ordinary wood has a natural structure of lignin, cellulose, hemicellulose, extraneous materials and organic extractives.[6,7] The chemical bonds of wood separate when it is heated to about 175° C. The heating process is stimulated with the increments of temperature.[8] The thermal decomposition of cellulose occurred at 260–350° C, and the presence of oxygen and water accelerated the decomposition of flammable volatile materials.[4,9,10,11]

In this study, there was a possibility of high OM content in the softwood samples (Yellow pine and Douglas-fir) because softwoods have more cellulose and hemicelluloses than hardwoods do, which increased the carbon content of Yellow pine and Douglas-fir. These materials required low heating values compared to the hardwood samples. A previous study indicated that the carbon content in softwood species was 50–53%, and that of hardwood was 47–50%, which is because of carbon materials, such as cellulose and hemicelluloses. Hard woods however, have more lignin.[12]

Figure 3.3 indicates that the percentage of ash content (AC) for Oak (hardwood) was the highest, followed by Sapele, Douglas-fir, and Yellow pine.

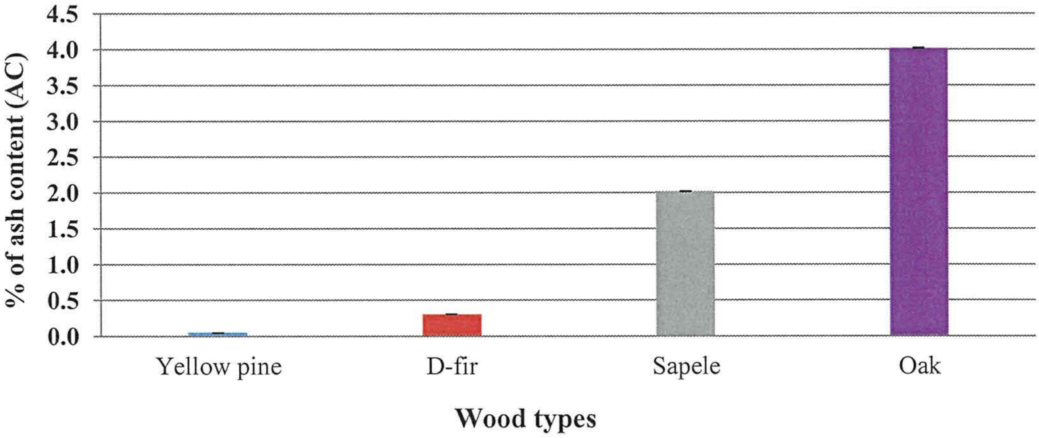

Figure 3.3 The percentage of ash content (AC) in Yellow pine, Douglas-fir, Sapele and Oak. The wood samples were not treated with chemicals. The AC was calculated from Equation 2.3. The calculated values are given as mean ±SE ($n = 3$).

The AC in Oak was 4.02% ±0.01, 2.02% ±0.003 in Sapele, 0.31% ±0.001 in Douglas-fir and 0.05% ±0.0002 in Yellow pine. Therefore, the Oak sample showed the highest percentage of AC, compared to the other wood samples. Previous studies classified ash as a minor constituent of softwood (0.02–1.1 %), compared to hardwood (0.1–5.4). In addition, research confirmed that the ash content of softwood (0.02–1.1 %) was less than that found in hardwood (0.1–5.4). [13-15] These results were supported by the results of the present study.

The mean of ash content varied considerably across the wood types. This significant increase in the ash content of the Oak and Sapele samples could be related to the loss and degradation of their organic content. This could have resulted in the relative increase in their AC, which was higher than in Yellow pine and Douglas-fir. However, the AC of heterogeneous materials (wood) is expected to change and fluctuate.[16] The ACs of Yellow pine and Douglas-fir were lower than those of the other three types were because their high porosity provides more oxygen, which accelerates the thermal decomposition of both wood types.

In a few burned wood samples, the AC was occasionally very high because of impurities, such as sand, stones, minerals and chemical pollution. In addition, other factors can affect the AC of wood, including heat development, degree of temperature and moisture content.[16,17]

3.3.2 Density of wood

Density is one of the most-studied physical properties of wood, compared with other characteristics, such as moisture content, colour and shrinkage.[2,18] Therefore, wood density is classified as the major descriptive property of wood. The combination of cellulose, hemicelluloses and lignin (solid cell wall substance) has shown similar densities (1.53 g/cm^3); thus, the measurement of wood density represents the total density of these compounds.[19] The densities of untreated Yellow pine, Douglas-fir, Sapele and Oak samples were determined in the oven-dried specimens (105° C), as described in Chapter 2, Equation 2.4. The dimensions and weights of the test samples were recorded, according to the density method used (see Chapter 2, Section 2.4.2). The porosity of the wood samples is determined according to the following Equation (3.1):

$$porosity = 1 - (d_1/d_2) \text{.............. Equation 3.1}$$

Were d_1 is the density (g/cm^3) and $d_2 = 1.5$ g/cm^3 (This a constant for all samples of wood and is related to the density of solid cell wall).

Figure 3.4 shows the comparative densities of the Yellow pine, Douglas-fir, Sapele and Oak samples.

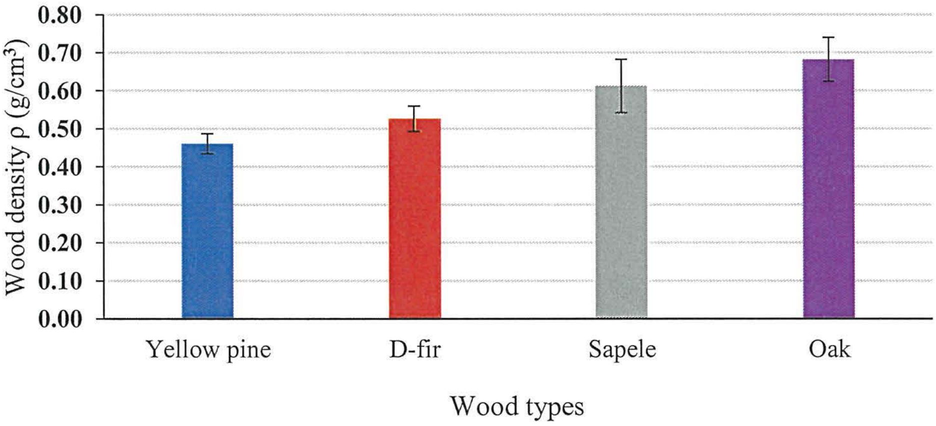

Figure 3.4 The wood density (g/cm^3) of the Yellow pine, Douglas-fir, Sapele and Oak wood samples. The wood samples were not treated with chemicals. The density was calculated from Equation 2.4. The calculated values are given as mean ±SE ($n = 3$).

The results of the analysis of wood density demonstrated that the density of Oak (hardwood) was the highest, followed by the densities of Sapele, Douglas-fir, and Yellow pine, in that order. The density (g/cm^3) of Oak was 0.68 ±0.06, that of Sapele was 0.61 ± 0.07, that of Douglas-fir was 0.53 ±0.03 and that of Yellow pine was 0.46 ±0.03. While the porosity of Oak was 0.56, 0.6 of Sapele, 0.65 of Douglas-fir and 0.7 of Yellow pine wood. Therefore, the Oak sample showed the highest value of density and lowest value of porosity, compared to the other wood types.

Figure 3.4 shows that Oak and Sapele had higher density, strength and hardness than Douglas-fir and Yellow pine. On the other hand, the density of Douglas-fir was close to that found in Yellow pine, which indicated that they have similar strength and hardness but are inferior in hardness, compared to Oak and Sapele, which have high density values. In general, density is one of the most important mechanical properties of wood. Both Oak and Sapele showed higher density than Douglas-fir and Yellow pine. These results demonstrate that the first two species (Oak and Sapele) could be used as hardwood, compared to other two types (Douglas-fir and Yellow pine) softwood. Wood strength is a key factor in wood classification. However, these results may not be generalised, and more research on wood properties is needed. The results regarding wood density agreed with those found by Bootle and Cown, which indicated that the density of hardwood was the highest (0.368–0.977 g/m^3), compared to softwood (0.417–0.769 g/m^3).[20,21]

3.3.3 The pH of wood

The aim of this experiment was to determine the effect of pH on the adsorption of boron in Yellow pine, Douglas-fir, Sapele and Oak. The method used to determine pH was described in Chapter 2, Section 2.4.3. The wood specimens were grinded to obtain a fine powder. The value of the wood pH was determined. A direct method was used to measure the pH values for wood. Table 3.1 shows the pH values of the samples of Yellow pine, Douglas-fir, Sapele and Oak.

Table 3-1 The pH value of Yellow pine, Douglas-fir, Sapele and Oak (n=3).

Wood types	Softwood types		Hardwood types	
	Yellow pine	**Douglas-fir**	**Sapele**	**Oak**
pH values	4.40 ±0.003	5.16 ±0.01	4.36 ±0.003	5.13 ±0.01

The results showed that the pH value of Douglas-fir was the highest, followed by the pH value of Oak, Yellow pine and Sapele. The pH values of four types of wood were in the weak-to-moderate acidic range (4.3–5.1). The pH of wood species indicates their acidic values. This acidic reaction is caused by acidic groups and free acids, which have the ability to split off within the measured solution. These acids include acetyl groups and predominantly acetic acid. Generally, only small differences in the pH values of types of wood have been found.[22]

The pH of wood is one of the most important aspects of wood utilization. It can be affected by many factors, such as corrosion of metals in contact with wood, wood glues and wood protectives.[22] Nimz found that the majority of wood species have naturally acidic values of pH (4.0 and 5.5).[22] These result were supported by the result of the present study.

3.3.4 The absorption of borate by wood species

This part of the present study was carried out to calculate the quantity of borate in the impregnated samples of Yellow pine, Douglas-fir, Sapele and Oak. The wood samples were treated with different concentrations of boric acid solution, as described in Chapter 2, Section 2.4.2: 0.1, 0.2, 0.3 and 0.4 M. The amount of borate (loading and containing) was calculated, as explained in Chapter 2, Equations 2.5 and 2.8. The amount of borate and the percentage of impregnated borate are given in Figures 3.5 and 3.6.

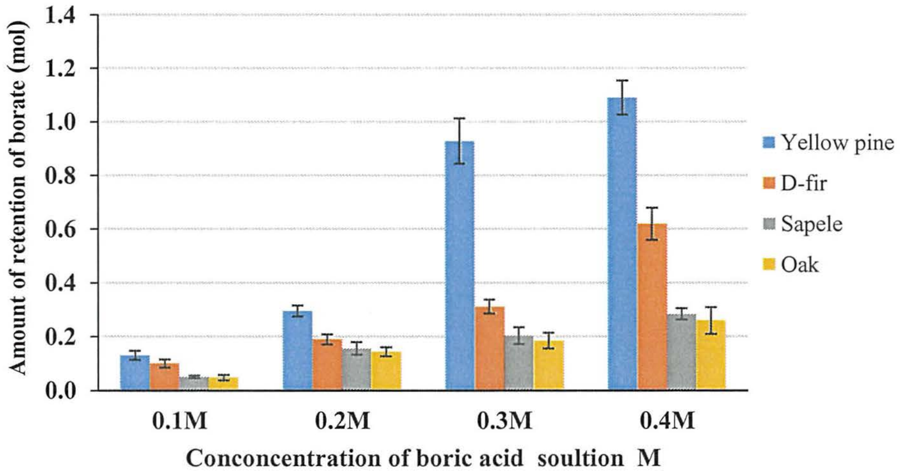

Figure 3.5 The amount of borate (mol) on Yellow pine, Douglas-fir, Sapele and Oak wood samples was calculated from Equation 2.8. The calculated values are given as mean ±SE (*n* = 3). The values of the amount of borate in the wood control (untreated) samples were zero.

Figures 3.5 indicates that the amount of borate (mol) for Yellow pine (softwood) was significantly high at all treatment concentrations, followed by the amount of borate (mol) of Douglas-fir, Sapele and Oak. In addition, the amount of borate increased in all wood types when increased boron concentrations were added.

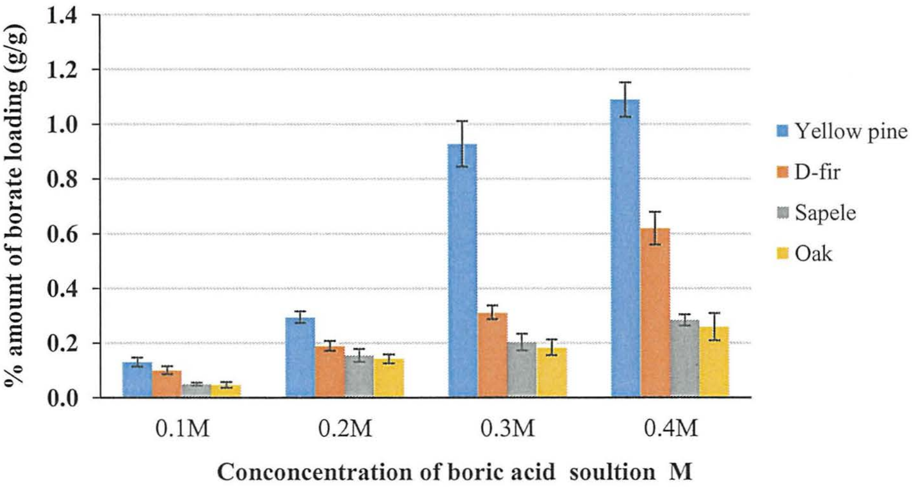

Figure 3.6 The percentage of borate (w_g/w_g) in the Yellow pine, Douglas-fir, Sapele and Oak samples was calculated from Equation 2.6. The calculated values are given as mean ±SE (*n* = 3). The percentage values of borate retained in the wood control (untreated) samples were zero.

Figures 3.6 indicates that the amount of borate loading (w_g/w_g) for Yellow pine (softwood) was significantly high at all treatment concentrations, followed by the amount of borate loading (w_g/w_g) of Douglas-fir, Sapele and Oak. In addition, the amount of borate loading increased in all wood types when increased boron concentrations were added .

The values of amount of borate and its percentage were the highest value in Yellow pine and Douglas-fir and the lowest in Sapele and Oak. Keskin *et al.* found similar results in European Oak.[23] A possible reason why the amount values of Yellow pine and Douglas-fir were different could be due to the wood properties and the structure of the wood material. Therefore, the type of wood material is one of the most significant factors in the amount of impregnation materials absorbed.[23] Another possible reason that the amount of borate in Yellow pine and Douglas-fir could be related to the high diffusion coefficients of boric acid solution in these wood types, which increased with the time of impregnation. The diffusion of boron in a wood system depends on the moisture content of the wood MC, diffusion period, solution strength, diffusion direction, temperature and treatment method.[24-27] Ra *et al.* found that the diffusion coefficients of borate through Southern Pine *(Pinus spp)* were the highest.[28] The results of boron adsorption in the four types of wood studied here confirmed this finding (see Chapter 5, Section 5.4.2).

3.3.5 The penetration of boric acid in wood

The protocol for testing colour change was applied to the samples of Yellow pine, Douglas-fir, Sapele and Oak. The standard method of colorimetric testing was performed using a borate solution for wood specimens in order to determine the depth of the borate penetration. The wood samples were treated with different concentrations of boric acid (control, solvent, 0.1, 0.2, 0.3 and 0.4 M), as explained in Section 2.5.1 Each wood sample was divided into two pieces of longitudinal Section, by using a sharp chisel. The cutting of longitudinal Sections allowed the comparison of borates penetration with respect to the morphology of the wood. In addition, the penetration depths of penetrated borates were compared for wood types and boric acid concentrations. The results of the longitudinal penetrations of borates are shown in Figure 3.7.

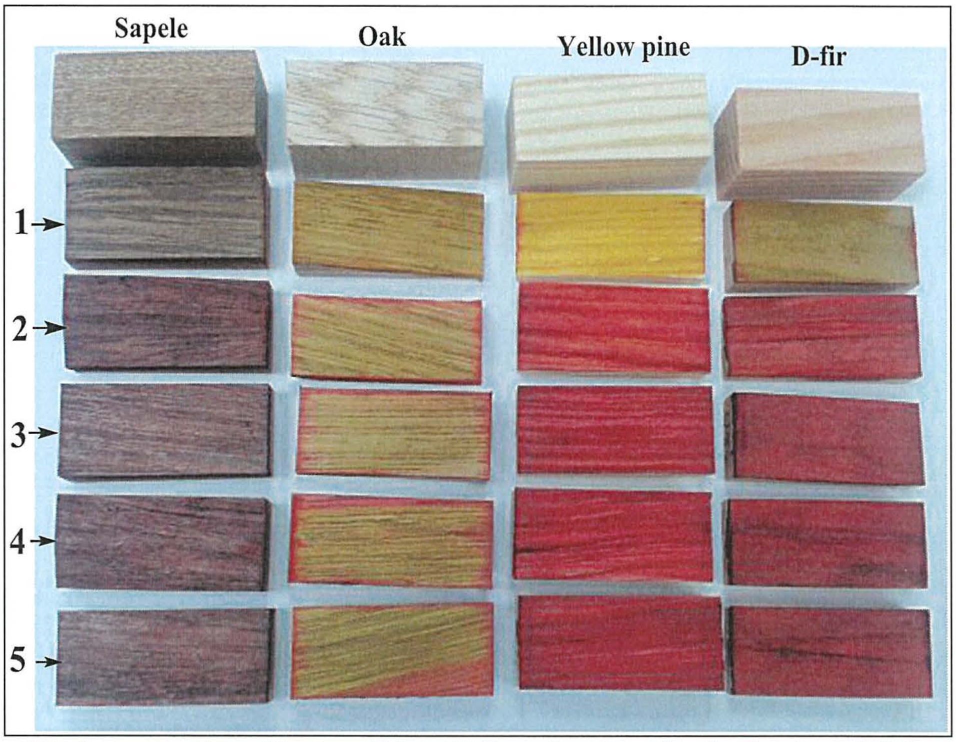

Figure 3.7 The penetration of boric acid into Yellow pine, Douglas-fir, Sapele and Oak samples. This method was based on the colour change of the wood surface using standard titration solutions. The wood samples were treated with different concentrations of boric acid, as follows: control (1), 0.1 M (2), 0.2 M (3), 0.3 M (4) and 0.4 M (5).

The colour changes in the Yellow pine and Douglas-fir samples were observed carefully after the second solution was applied, compared to the control sample (yellow colour). A dark yellow colour appeared on the untreated samples of Yellow pine; however, a slightly yellow colour appeared on the control samples of the Oak and Douglas-fir cross-longitudinal Sections. The change in the colour of the samples indicates that the wood specimens corresponded to the penetration solution. The colour of the Yellow pine and Douglas-fir samples became red after the yellow turmeric solution was added to all borate treatments. The intensity of colour increased as higher boron concentrations were added.

On the other hand, no yellow colour was observed in the control samples of Sapele. However, a slightly red colour appeared in the Sections of the Sapele samples, which increased as the boric acid concentrations increased. Moreover, the Oak samples showed that the penetration of borate appeared on the surface of the samples, and the red colour occurred on the edge of each sample for all boric acid concentrations. The penetration of borate was less in the Oak samples than in the other three types of wood, as shown in Figure 3.7 The reasons that colour change was obscured could be related to different factors, such as colour of the surface (dark grey, highly weathered). These results agreed with those previously found in hard and softwood.[29]

Many different factors can affect the depth of borate penetration in wood types, including moisture content, temperature, solution concentration, density of wood, and diffusion depths.[30] For instance, concentrations of borate solution could contribute to the final loading in the wood. Thus, increased borate concentration will result in a greater final loading in the wood system.[31,32]

The mechanism of liquid movement within the wood system is well understood. Thus, compared with large diameter tubes, capillary tubes with small diameters have the ability to raise the water.[29] In general, the penetration depths of borate in the Yellow pine and Douglas-fir samples (softwood) were significantly higher than those found in the Sapele and Oak samples (hardwood).

Thus, during the sample preparation, Yellow pine and Douglas-fir showed sponge behaviour in their adsorption of borate. The change in colour was a positive indicator for both wood types; however, changes in the colour of the Sapele and Oak samples were less than those observed in the Yellow pine and Douglas-fir samples. However, diffusion penetration of borate can develop rapidly under constant high temperature, humidity and low wood density. The wood structure of Yellow pine and Douglas-fir could be related to the high penetration of borate. The vessels system of softwood has the ability to transport water more effectively than that of the hardwood tracheids.[4,29] (see Chapter 1, Section 3, Figure 1.1).

3.3.6 Determination of thermal stability in wood types treated with boric acid

The production of industrial wood (modified wood) has been going on for many years. As a result, the problem of wood flammability and how it can be reduced through the use of different chemical treatments has been generating considerable interest among both researchers and industry.[33-35] As pointed out previously, boron compounds are classified as one of the most common basic materials for several fire retardants for wood species and other cellulosic components. These fire retardants have a long history of widespread use due to the ability of borax compounds to decrease flame spread, but they can encourage glowing and smoldering.[36,37] The majority of wood treatments solutions have used a combination of borax and boric acid which forms a protective layer (char) on the surface of wood at high temperatures. Thus, the combustion properties of modified wood are key for understanding their thermal decomposition. Since wood is one of the more prevalent and common flammable materials at the scenes of fires, these properties need to be determined for safety and forensic reasons. The pyrolysis process is when wood materials, cellulose and lignin combust and form gases, vapours and solid charcoal residue. Some studies have focused on the pyrolysis of boric acid treated wood samples.[33-41] Therefore, this is a thermoanalytical study of four boric acid treated wood species

(Yellow pine, Douglas-fir, Sapele, and Oak). The object of this study is to determine whether treating these different types of wood with boric acid has a significant effect on their thermal decomposition when compared with untreated samples of the same types of wood using thermogravimetric analysis (TGA).

3.3.6.1 Materials and method

Yellow pine, Douglas fir, Sapele and Oak samples were selected to conduct the TGA. The wood samples treated with the highest boric acid concentrations (0.4 M) were chosen to be compared with untreated wood samples of each wood type. The method of wood treatment was described in Section 2.5.1. The test samples (10-15 mg each) were crushed into regular wood chips. TGA was performed for each wood sample using the SDT-Q600 instrument with a heat flow from ambient temperature to 1,500° C. Samples of each species were loaded into unsealed alumina crucibles, and the heat ranged from room temperature to 800° C under air atmosphere at a heating rate of 10° C/min. The analyser was calibrated using alumina crucibles as references. The TGA apparatus has the ability to provide a constant measurement of target sample weights as a function of increasing temperature to determine the rate of weight loss for the target samples.[42]

3.3.6.2 Thermal stability of test wood types treated with boric acid

The samples used for TGA were untreated wood and treated wood samples with the highest boric acid concentration (0.4 M). The weight loss of the Yellow pine, Douglas fir, Sapele and Oak samples are shown as percentages of their original weight versus the temperature range in Figures 3.8 to 3.11. The TGA data for the untreated (controls) and treated wood samples, including the percentages of weight loss of hemicellulose, cellulous, lignin and the release of water vapour under different ranges of temperature profiles, are given in the (Table 8.3).

Table 3-2 Percentages of Weight remain for the Untreated and Treated Wood Samples.

Wood types	Weight remaining%		Hemicellulose %		Cellulose %		Lignin %		Charring	
	Untreated	Treated*	untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
(T)° C	25–130° C		140–290° C		300–390° C		400–550° C		560–800° C	
Yellow pine	95.08	95.67	89.04	88.94	47.81	50.95	6.02	19.13	0.01	4.15
Douglas fir	96.20	96.08	90.55	89.43	45.47	49.15	11.04	17.07	-0.03	2.39
Sapele	95.84	96.76	88.77	90.32	45.92	47.62	7.43	14.99	0.02	2.74
Oak	96.18	96.00	89.37	89.06	44.40	42.00	7.84	10.12	-0.35	1.64

*The treated samples were the samples with the highest boric acid concentrations (0.4 M), and the untreated wood samples served as controls.

The gravimetric (TGA) curves of the Yellow pine samples (treated and untreated) are shown in Figure 3.8. The TGA curves of the untreated and treated samples were similar to each other in the gravimetric behaviour at the start of the combustion process (25 to 290° C). The rate of weight loss of hemicellulose, cellulous and lignin was very high after a plateau region at 290° C, and there was a flat tailing section at the highest temperature range (490 to 800° C), which corresponds to a slow charring process of the solid residue for the Yellow pine samples. In the current literature,[38] it has been argued that the two different regions of weight loss detected for the pyrolysis of wood types might correspond to thermal decomposition of hemicelluloses and cellulous at lower temperatures (25 to 290° C).

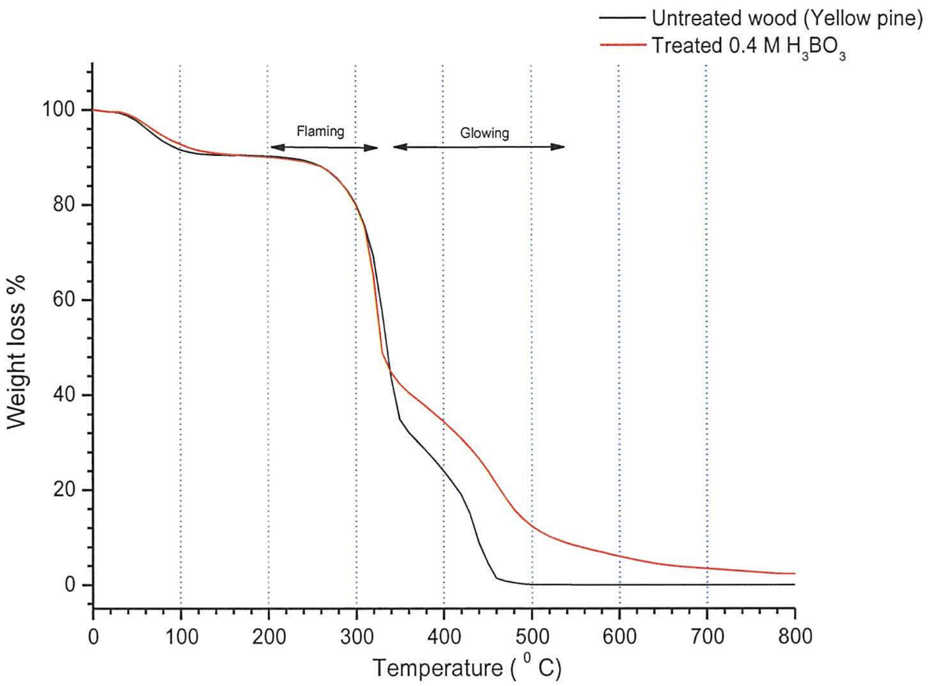

Figure 3.8 Thermal behaviour of untreated and treated Yellow pine samples with a boric acid concentration of 0.4 M using TGA under air atmosphere at a heating rate of 10° C/min. The weight loss, represented as percent versus temperature, start at room temperature and increase to 800° C.

However, in this study, the decomposition of lignin occurred at the highest temperature peak (400 to 550° C).[38] Fung *et al.* studied the degree of cellulose polymerization in wood and found that cellulose treated with acid was depolymerised (DP) and charred very rapidly.[43] In this study, the value of DP for the cellulose was reduced from 1,110 to 650 after just 2 minutes of heat at 150° C. One the other hand, the cellulose treated with borax demonstrated a DP reduction value from 1,300 to 700 after 1 hour of heat at 150° C. Both fire retardants decreased the amount of flammable volatile materials during the application of heat; however, they had different influences on the chain depolymerisation reaction process.[43]

In the present study, the treated and untreated samples of Yellow pine wood decomposed rapidly between 300 and 350° C. After this stage of sharp weight loss, the anti-flammable effect of the highest boric acid concentration (0.4 M) appeared to decrease the weight loss of the treated samples compared to the control. There was a gradual reduction with constant weight loss for the treated samples (additional about 4.15% of starting materials) up to 800° C. However, the percentage of weight loss of the untreated samples rapidly decreased, reaching 0.01% at 800° C. The differences in weight loss between the tested samples was 4.14% and they might be attributed to B_2O_3 which is formed the $B(OH)_3$ at 800 ° C. According to the final stage of organic matter decomposition in wood, the test results showed that the total percent of retention of lignin in the treated Yellow pine sample had the highest value (19.13%) compared to the untreated samples (6.02%) at temperatures between 400 and 550° C, and the differentiation of weight loss between treated and untreated samples was 31.1%.

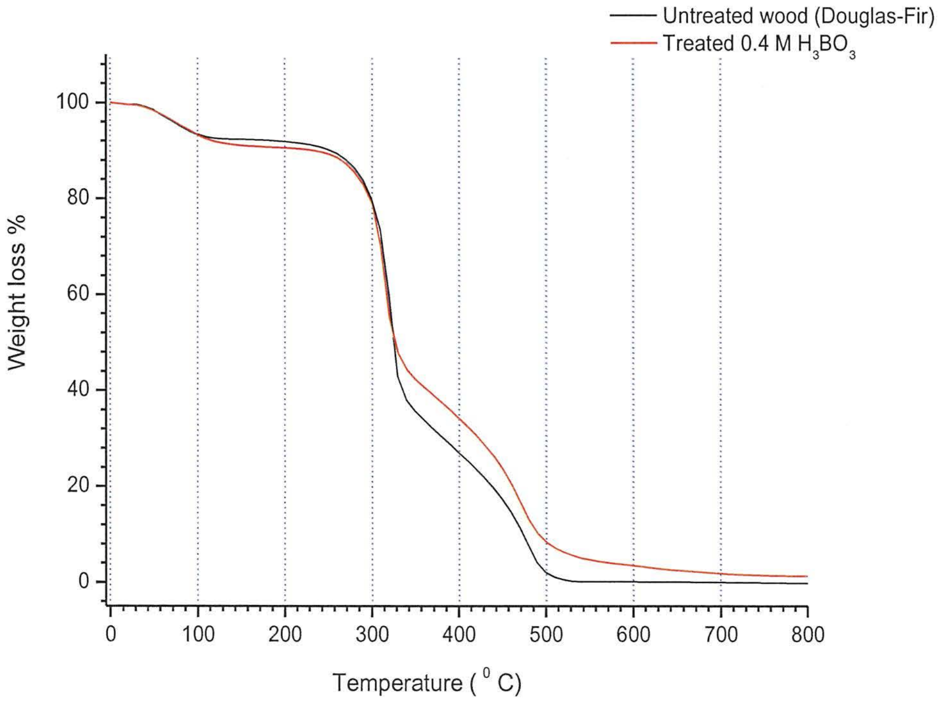

Figure 3.9 Thermal behaviour of the untreated and treated Douglas fir samples with the boric acid concentration (0.4 M) using TGA under air atmosphere at a heating rate of 10° C/min. The weight loss is represented as percent versus temperature start at room temperature up to 800° C.

The TGA results for the Douglas fir samples are shown in Figure 3.9. The TGA's of the untreated and treated samples (0.4 M of boric acid) were similar to those obtained in the Yellow pine wood. However, the remaining amount of organic matter in the treated Yellow pine samples was higher than those obtained in the treated Douglas fir samples. This could be related the high ability of the Yellow pine wood to adsorb more boron than the Douglas fir wood. These results agreed with those obtained in this Chapters, Section 3.3.4 and Chapter 5.Section 5.4.2 The thermal curve of Douglas fir shows the release of water vapour began at temperatures between 0 and 130° C, followed by the combustion of hemicellulose, cellulous and lignin between 130 and 550° C. The charring process of the solid phase took place at temperatures between 550 and 800° C. The thermal decomposition of organic matter in both the treated and untreated Douglas fir samples was achieved between 300 and 350° C, followed by a rapid reduction of organic weight in the untreated sample. However, in the treated sample, the boric acid treatment (0.4 M) appeared to reduce the weight loss compared with the untreated sample. There was also a consistent decrease of weight loss in the treated samples (additional around 2.39% of starting materials) up to a temperature of 800 ° C. The TGA results indicated that the total percentage of remaining lignin in the treated Douglas fir wood had the highest value (17.07%) compared to the untreated samples (11.04%) between 400 and 550° C. The difference of weight loss between the treated and untreated samples was 6.03% residual additional mass of 2.39% probably due to B_2O_3.

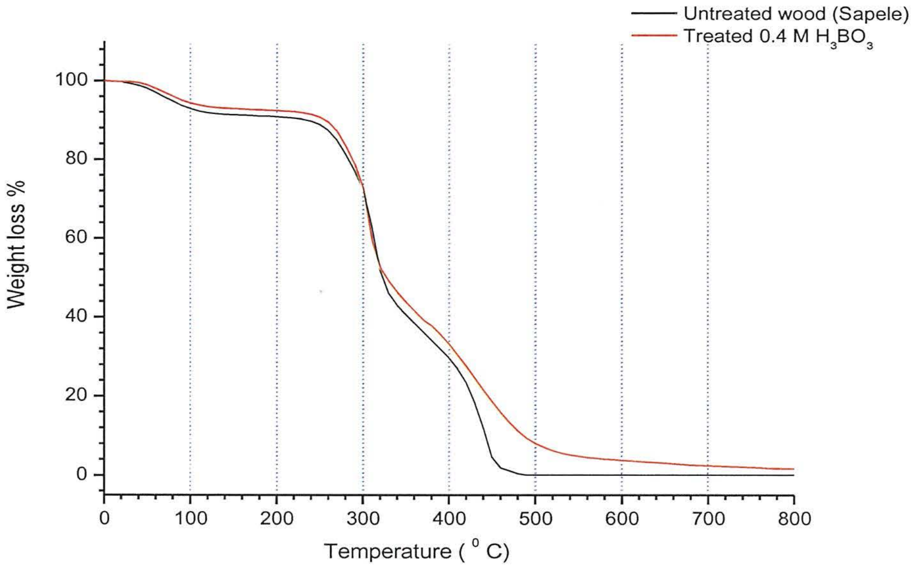

Figure 3.10 Thermal behaviour of untreated and treated Sapele samples with the boric acid concentration (0.4 M) using TGA under air atmosphere at a heating rate of 10° C/min; weight loss is represented as a percentage versus temperature start at room temperature up to 800° C.

The TGA results for the Sapele wood are shown in Figure 3.10 The TGA's of the untreated and treated Sapele samples (0.4 M of boric acid) behaved in a similar manner as the Douglas fir samples in the tested heat range (25 to 800° C). However, the Douglas fir samples (both treated and treated) had less weight loss than the Sapele wood samples. This can be attributed to the Douglas fir samples' ability to adsorb more of the fire retardant (boric acid), which reduced the flammable materials that could be produced on the wood surface and decreased the amount of potential heat process. Similar results were found in the isotherms for adsorption of 'boron' on the surfaces of the four tested wood species (see Chapter 5). The thermal process of hemicellulose, cellulose and lignin and the process of releasing water vapour were performed at similar temperatures (25 to 800° C) to those obtained in the Yellow pine and Douglas fir samples. The organic matter of the treated and untreated Sapele samples decomposed between 300 and 350° C, followed by a charring of the solid residue between 550 and 800° C. The effect of the boric acid was significant on the treated Sapele sample, as it decreased the loss of organic weight compared to the untreated wood sample. The treated sample's weight loss process was also gradually reduced (approximately 2.74% of the starting material) for temperatures up to 800° C compared to the loss weight of the untreated samples (0.02%).

The TGA results also showed that the total percent of remaining lignin in the treated Sapele wood had the high value (14.99%) compared to the untreated samples (7.43%) between 400 and 550° C. The difference of weight loss between the treated and untreated samples was 7.56%. The final residual was 2.74% indicating the present of B_2O_3 in this sample.

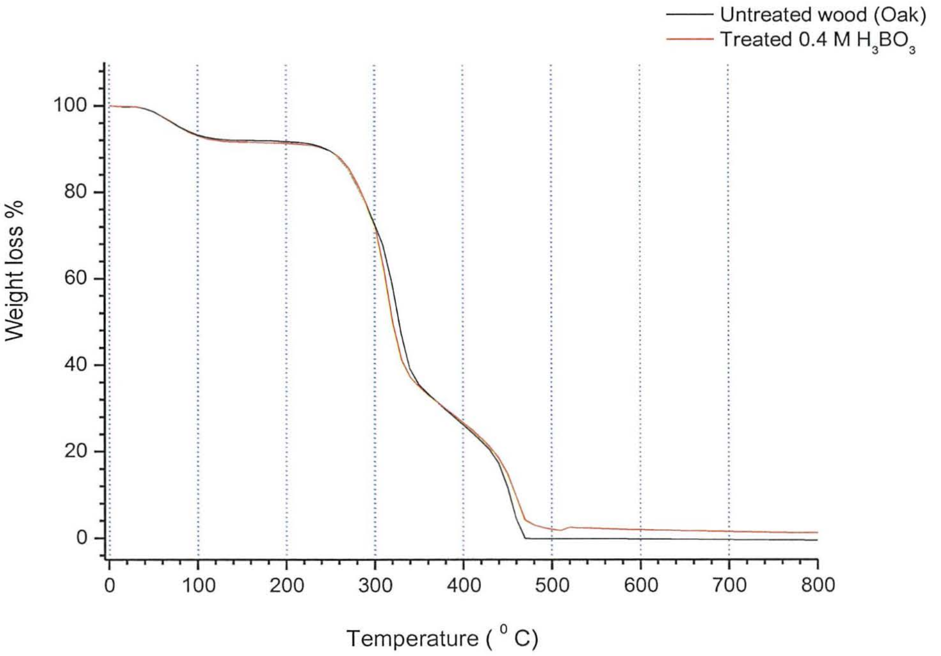

Figure 3.11 Thermal behaviour of the untreated and treated Oak samples with the boric acid concentration (0.4 M) using TGA under air atmosphere at a heating rate of 10° C/min; weight loss is represented as a percentage versus temperature start at room temperatures up to 800° C.

The TGA results for the Oak wood are shown in Figure 3.11 The TGA's of the organic matter in the treated Oak samples (0.4 M of boric acid) was similar to those obtained in the untreated samples (control). This could be related the low level of boric acid in the treated Oak samples, which increased the flammable materials within the heating process. The results of the adsorption experiment (see Chapter 5) showed that the Oak wood has the lowest ability to attract boric acid to its surface. Therefore, the treated Oak samples showed a small difference in weight loss compared to the untreated sample; this relative difference was based on the adsorbed amount of boron treatment in the Oak wood. On the other hand, the thermal process of hemicellulose, cellulous and lignin and the process of releasing water vapour in the Oak samples were completed at a similar range of heating (25 to 800° C) as the Yellow pine, Douglas fir and Sapele wood. Furthermore, the decomposition of organic matter in the treated and untreated Oak samples was similar to those obtained in the other three wood species (300 to 350° C), which was followed by the burning of solid residue between 550 to 800° C. The boric acid had a small influence, resulting in a higher percent of organic weight loss in the treated Oak sample. A significant effect from the boric treatment start to appear in the treatment Oak sample at 470° C, and the process of losing weight in the treated sample was gradually reduced (an addition approximately 1.64% of the starting material) up to 800° C compared to the weight loss of the untreated samples (0%). The TGA results also showed that the total percent of remaining lignin in the treated Oak sample was the highest (10.12%) compared to the untreated sample (7.84%) between 400 and 550° C. The difference in weight loss between the treated and untreated samples was 2.29%.

The comparison of thermal decomposition between the untreated and treated samples showed that the boric acid treatment (0.4 M) had a significant influence on the thermal behaviour of the four wood species. Boric acid is the most common fire retardant and is used commercially for wood products. Because of its solubility and molecular size, it is susceptible to moisture movement and migrates with the movement of water in the wood system.[37-40,44] Many theories have been suggested by Brown and Levan for mechanisms for fire retardants.[39,45] The chemical retardants, including boric acid, significantly change the wood pyrolysis, resulting in a high amount of charring, followed by a reduction in the amount of combustible vapours and volatile materials during the heating process. Thus, the reaction of pyrolysis can alter the thermal decomposition of organic materials that occurred in this study at a lower heating rate in the samples treated with fire retardants compared with the untreated samples.[39,45] In the present study, the pyrolysis of hemicellulose loss and cellulose rapidly decomposed between 300 and 350° C, followed by the thermal decomposition of lignin at a higher temperature (400 to 550 ºC) and the charring process of the solid phase up to 800° C across all wood types and in both untreated and treated wood samples. The TGA curves of the present study agree qualitatively with those obtained in other studies that examined different fire retardants and wood species.[39,42,44,46-48] A significant effect of different fire retardants on the pyrolysis reaction was noted. Furthermore, volatile materials were found to occur at a higher rate at low temperatures, while the mass of residual char was increased.[47] Zaror has also observed the low stage of organic decomposition in wood samples treated with potassium and sodium carbonates and chlorides.[48] In one previous study, the thermal decomposition of organic matter was divided onto two stages. The rapid evolution of volatiles materials was defined as the first stage; this process can be controlled by chemical reactions. Furthermore, the amount of the salt used was found to have a significant influence on the pyrolysis reaction during the first stage. The second stage was classified by the much slower process of losing organic weight. At this thermal level, the organic mass was found to move from the interior of the wood samples to the surrounding environment, and it is possible to be the step of controlling rate. The transferring of organic matter became more significant as the amount of added salt was increased.[48]

Another study investigated the effect of adsorbed salts and their ions exchanging in different wood samples and also noted effects of fire retardants similar to the observation of the present study.[49] That study found that wood doped with Fe^{2+} was the most affected by selected fire retardants; the weight loss of organic matter was decreased at the lowest temperature of the heating process using derivative thermogravimetry (DTG). Moreover, the highest char mass (27% at 390° C). The char was also found to reach 4% at a temperature of 700° C. Similar observation was showed in the present study with four wood types. Thus, all of the treated and untreated wood samples showed similar effects to a smaller extent. Richards and Zheng have attributed the very low DTG maximum with ferrous sulphate to acid-catalysed pyrolysis associated with the sulphate ion.[49]

3.4 Conclusion

The percentages of moisture content and organic matter content were significantly higher in Yellow pine (soft wood) than in Douglas-fir, Oak and Sapele.The reason for the high moisture content could be related to the dissociation pattern of Yellow pine, and its high porous diffusion could increase its ability to adsorb water. Organic matter content was the highest in Yellow pine and Douglas-fir (softwood) because they have higher percentages of cellulose and hemicellulose, than found in Oak and Sapele (hardwoods). The highest percentage of ash content was found in Oak, compared with the samples of Douglas-fir, Yellow pine and Sapele. However, the AC of Yellow pine and Douglas-fir wood was the lowest compared to other two wood (Oak and Sapele) types. A possible reason is that the high porosity of these types of wood facilitates the possibility of more oxygen, which accelerates their thermal decomposition process. The density test indicated that the density of the Oak sample was higher than that of the Sapele, Douglas-fir, and Yellow pine samples.

The amount of borate (mol/kg) quantity and the percentage of borate loading (wg/wg) were the highest in Yellow pine, compared to those found in Douglas-fir, Sapele and Oak. The retention quantity of impregnated borate increased when the initial concentration of boric acid was increased, for all four wood types. The retention values of the softwood (Yellow pine and Douglas-fir) were significantly higher than those found in the hardwood (Sapele and Oak).

As a qualitative test the colour of the samples of Yellow pine, Douglas-fir, Oak and Sapele became red after the yellow turmeric solution was added to all boron treatments. However, the red colour was varied according to the properties of the wood. The penetration of borate appeared to be only on the surface of the Oak samples, and the red colour occurred on the edge of each sample at all boric acid concentrations. In general, all wood types showed that all the wood specimens had showed some penetration of the boric acid solution as indicated by the colour change.

In this study, the comparison of the thermal decomposition of untreated and treated samples in four wood species showed that boric acid treatment (0.4 M) has the highest influence on the thermal behaviour of Yellow pine wood, followed by Douglas-fir, Sapele and Oak wood, respectively. The total percentages of remaining lignin in the untreated and treated samples, respectively, were: 6.02% , 19.13% for Yellow pine, 11.04% and 17.07% for Douglas-fir, 7.43% and 14.99% for Sapele, and 7.84% and 10.12% for Oak. The boric acid treatment also had a significant effect on the residue of the solid phase across all wood types and temperature (550 to 800° C). The total percentages of remaining residue for the untreated and treated samples, respectively, were: 0.01% and 4.15% for Yellow pine, 0% and 2.39% for Douglas fir, 0.02% and 2.74% for Sapele and 0% and 1.64% for Oak. This might be correlated with the amount of B_2O_3 adsorbed. The pyrolysis of hemicellulose loss and cellulose occurred between 300 and 350° C, followed by the thermal decomposition of lignin between 400 and 550° C. The final stage was the charring process of the solid phase up to 800° C across all wood types and untreated and treated wood samples.

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Chapter 4.

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4 Determination of accelerants in the residue of fire debris for different wood types treated with boric acid

4.1 Introduction

Fire accelerants generally arise form refined crude petroleum. Crude petroleum is refined into all types of fuel oils using a fractional distillation process. Petroleum materials are generally divided into three categories according to their distillation properties: heavy distillates and residuum products (heavy fuel oil, lubricating oils, wax, asphalt, etc.), middle distillates (kerosene and diesel) and light distillates (LPG, naphtha and petrol). The classification of these products depends on the method by which crude oils are separated and distilled into different fractions, which are called distillates and their residuum.[1]

Diesel fuel, one of the middle distillate fractions, results from the refining process of crude oil. Additional products of middle distillates include kerosene and aviation fuel. Diesel fuel is classified as the heaviest fraction (about 18%) compared to the petrol fuel; the principal components of diesel are hydrocarbons (*normal*-alkanes) (*n*-C) that range from *n*-C_{10} to *n*-C_{28} with different arrangements of H atoms attached to C atoms. Petrol is categorised under light distillates in the process of oil refining to produce petroleum-derived liquid mixtures; this crude oil fraction is mostly used as fuel in several internal combustion engines. The constituents of bulk petrol are rich in aromatics and range from C_3 to C_{10}.

On the other hand, another study indicated that petrol always contains the C_3-alkylbenzenes, (*m*-, *p*-, *o*-ethyltoluene) (*m*-, *p*-, *o*-xylene) and 1,2,4-trimethylbenzene, whereas kerosene falls between diesel and petrol fuel in weight, in the range of n-C_9 to n-C_{15}; this fraction is usually used as jet engine fuel. The majority of these important fuels contain cycloparaffins and naphthenes (C_nH_{2n}), alkanes (paraffins: C_nH_{2n+2}), alkylbenzenes (aromatics: $C_{6+n}H_{6+2n}$) and alkenes (olefins: C_nH_{2n}).[1-3] Thus, major distillate fractions of kerosene and diesel show overlaps in C number distribution, as kerosene has carbon numbers ranging from n-C_9 to n-C_{18} and diesel has carbon numbers from n-C_{10} to n-C_{28}.[3]

The detection of accelerant residues at fire scenes uses several techniques and has attracted great interest from forensic experts in recent years. Gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) techniques are currently used to separate residual accelerants from samples of fire debris collected at fire scenes.[2] Petrol, kerosene, and diesel have been classified as the most commonly used petroleum accelerants.[2,3] These compounds are basically mixtures of hydrocarbon complexes with similar chemical characteristics, though the boiling points of these materials vary. This variation in boiling point is one of the significant reasons that results in a change in accelerant composition during the process of evaporation.[1-3]

Fire investigators survey the damage at fire scenes to detect the fire's origin, cause and behaviour. Therefore, knowledge of chemistry is very important for the assessment of fire scenes. One of the most common forensic tests is detection of the ignitable liquids residue (ILR) at a fire location, which may indicate the presence of accelerants as a reason for the fire. Partially burnt materials such as tile, wood and carpet may contain accelerant traces. Therefore, samples of the fire debris should be examined using a chemical test in order to determine the accelerant components. However, a fire does not start as easily with materials such wood or carpet that contain flame retardants (e.g. boric acid) added which prevent ignition.[4-12]

4.2 The aims of experiment

The aims of this experiment were: (1) To investigate qualitatively residual accelerants remaining in wood samples (Douglas-fir, Yellow pine, Sapele and Oak) treated with different concentrations of boric acid after exposure to a short period of fire. (2) To evaluate quantitatively the ability of borate treated woods to retain fire accelerants (petrol, kerosene and diesel) for forensic by analyses of the residues in these four wood types using a direct solvent extraction method and GC/MS.

4.3 Materials and method

Douglas-fir, Yellow pine, Sapele and Oak wood samples were tested against the fire compared with unburned wood samples. The selected samples were treated with different concentrations of boric acid, as follows: blank (untreated wood sample without accelerants), control (untreated wood sample with accelerants), and treated (with 0 (water), 0.1, 0.2, 0.3 and 0.4M boric acid) see an example (Figure 6.34: Appendix **B**). The procedures of sample preparation and the fire test methods were described in Chapter 2, Sections 2.2 and 2.7.2, respectively.

Extraction of ignitable liquids residues (ILR) from each wood sample was performed using solvent extraction according to ASTM (E1386 – 10) and Midkiff, as described in Chapter 2, Section 2.7.3.[13,14] A GC/MS technique was used to analyse the petrol, kerosene and diesel content in liquid residues from burned and unburned wood samples. Components of target compounds (standards) were used to identify the patterns of petrol, kerosene and diesel liquids and to compare with those found in fire debris residues in ignited and unignited wood samples. The components of the petrol accelerant were: toluene, ethylbenzene, *o*,*m*-xylene, *p*-xylene, and 1,2,4-trimethylbenzene. These standards represent the majority of petrol components as they are the most persistent following the high temperatures generated by fire. Consequently, these materials may be highly concentrated and simply detected in the ILR (petrol). Analytical grade (C_9-C_{18}) and (C_{10}-C_{28}) hydrocarbon standards (fresh liquids) were used to verify the residual components of kerosene and diesel, respectively, in all samples. In addition, 1,3,5-trichlorobenzene (TCB) (0.025 M) was used as an internal standard (IS) for all accelerants, as described in Chapter 2, Section 2.8. The peak area ratios for all isolated compounds (percentage area) were normalised to the TCB, the internal standard.

The peak area ratios of all compounds were calculated using Equation 2.9, as detailed in Chapter 2, Section 2.9. The selected operating parameters of the GC-MS technique were detailed in Chapter 2, Section 2.7.2. All methods used in the present work are described in Chapter 2, from Section 2.7.1 to Section 2.9.

4.4 Statistical analysis

The peak area ratios data for petrol, kerosene and diesel accelerants in burned and unburned wood samples for Douglas-fir, Yellow pine, Sapele and Oak wood treated with different concentrations of boric acid solution were analysed with a statistical software package (SPSS 20.0 for Windows). The peak area ratios of all accelerants in the four wood types were evaluated using a one-way ANOVAs and Tukey's HSD test (*honest significant difference*). Two-way ANOVAs were used to compare the peak area ratios of each accelerant for four wood types at all the boric acid concentrations. A p-value < 0.05 was considered statistically significant. The mean averages of each accelerant were used to compare between the four wood types. Data are presented as means ± SE. The mean peak area ratios and standard errors of each of three replicates were calculated using Microsoft Excel for precision and absolute accuracy of the results.

4.5 Results and discussion

4.5.1 Detection of accelerants in unfired and fire debris samples

The detection of petrol, diesel and kerosene for the forensic investigation of unburned and fire debris samples was performed using solvent extraction and gas chromatography (GC/MS) for the four wood types treated with different concentrations of boric acid (blank, 0 (solvent), 0.1, 0.2, 0.3 and 0.4 M). The wood properties are given in Table 4.1.

Table 4-1 physical and chemical properties of Yellow pine, Douglas-fir, Sapele and Oak wood

Wood property	**Wood types**			
	Yellow pine	**Douglas-fir**	**Sapele**	**Oak**
MC %*	11.88 ±0.36	10.32 ± 0.56	7.86 ±0.63	8.64 ±0.33
OMC %**	97.5 ±1.3	93.4 ±0.60	88.60 ±1.80	89.0 ±2.4
AC %***	0.05 ±0.0002	0.31 ±0.001	2.02 ±0.003	4.02 ±0.01
pH	4.40 ±0.003	5.16 ±0.01	4.36 ±0.003	5.13 ±0.01
Density (g/cm^3)	0.46 ±0.03	0.53 ±0.03	0.61 ± 0.07	0.68 ±0.06

***MC**; Moisture Content, ****OMC**; Organic Matter Content *****AC**; Ash Content.

Sealed auto sampler vials with septa (GC/MS vials) were used to hold the unfired and fired debris samples (1ml of each sample) and to determine the components of each accelerant in the four wood types. Each fire debris sample was tested three times; one representative chromatogram was selected as a result of the experiment to determine the impact of burning time. The accelerant types and types of unburned and burned materials are shown in Figures (6.1.A–6.8.A, 6.9.A–6.16.A and 6.17.A–6.24.A), Appendix (A), Comparison of calculated PAR (%) was used to determine the relative availability of three accelerants (petrol, kerosene and diesel) for each of the four wood types (burned and unburned), as presented in Figures (4.2 and 4.3), (4.5 and 4.6) and (4.8 and 4.9), respectively. The results of each accelerant (petrol, diesel and kerosene) were represented as total average of their components using the peak area ratio Equation 2.9 (see Chapter 2, Section 2.9).

4.5.2 Quantitative analysis of petrol

The chromatogram is the optical output of a GC separation. In the event of an optimal GC separation, different patterns or peaks on the curve correlate with different materials from the separated accelerants. The retention time (R_t) (min) is plotted on the x-axis, and the y-axis represents the peak area (PA) or relative abundance of the compound in the system of GC/MS. Figures 4.1 showed the results of pure petrol components remaining in the wood samples. These peaks are shown matched to five compounds as fingerprints for a petrol accelerant (Table 4.2).

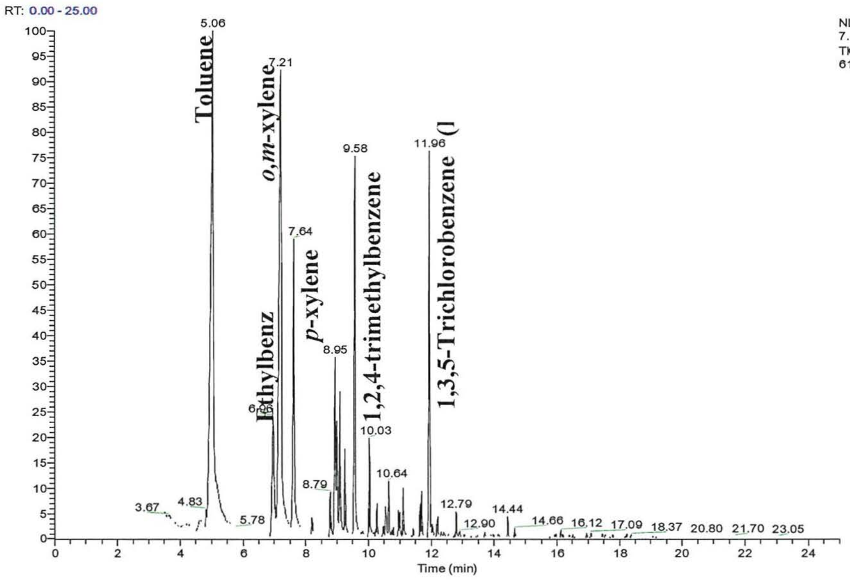

Figure 4.1 Typical GC-MS total chromatogram for fresh petrol components at concentration of 500 ppm. The isolated compounds are: toluene, ethylbenzene, *o,m*-xylene, *p*-xylene, 1,2,4-trimethylbenzene and 1,3,5-trichlorobenzene (TCB) as an internal standard (IS). The identity of each peak is shown in Table 10.4.

Table 4-2 Peak identification of isolated components from a petrol sample

Accelerant	Retention time (R_t) min.	Component
petrol	5:06	toluene
	6:96	ethylbenzene
	7:21	*o,m*-xylene
	7:64	*p*-xylene
	9:58	1,2,4-trimethylbenzene
Internal Standard (IS)	11:96	1,3,5-trichlorobenzene (TCB)

GC-MS chromatograms obtained from petrol components and the effects of boric acid (fire retardant) on burned and unburned samples for Douglas-fir, Yellow pine, Sapele and Oak wood are shown in Figures (6.1.A–6.8.A), Appendix (A), and the results are summarized in the next Section. The statistical analysis showed highly significant differences ($p < 0.01$) in the total peak area ratio of the major petrol components across all of the unburned wood types and their boric acid concentrations (0–0.4 M) compared to control samples Figure (6.1.A–6.4.A) Appendix (A). Figure (4.2 and 4.3) shows that total amount of all petrol components recovered from in the residue of unburned and burned Yellow pine wood samples treated with different concentrations of boric acid. However, different relative amounts were obtained compared to those found in the standard petrol components.

4.5.3 Comparison of total petrol in the residue of unburned and burned wood

The result of Table 4.3 showed that the total PAR (%) of the major petrol components was highest in Yellow pine wood followed by Douglas-fir, Sapele and Oak wood, respectively, across all of the boric acid concentrations in both unburned and burned wood samples. The average overall petrol PAR (%) values for unburned and burned samples, were 78.40 ±9.50 and 51.20 ±7.19, respectively, for Yellow pine, 60.93 ±7.53 and 22.72 ±3.61 for Douglas-fir, 46.30 ±6.91 and 12.91 ±1.91 for Sapele and 36.93±5.59 and 6.50 ±1.22 for Oak wood.

The statistical results of ANOVA (Two-way) showed highly significant differences ($p < 0.01$) in the total peak area ratio of petrol components in unburned wood types compared to those found in burned types.

Table 4-3 The total (PAR) % of the major petrol components in the residues of unburned and burned wood treated with different concentrations of boric acid

Accelerants	Borate Treatment	Fire Test	Sum of peak area ratio (PAR) % for the major petrol components in the residue of wood types			
			Yellow pine	Douglas-fir	Sapele	Oak
Petrol	**Control**	Unburned	34.76 ±0.78	17.85 ±0.44	10.85 ±0.36	5.99 ±0.35
	Solvent		37.38 ±2.04	37.48 ±0.24	17.67 ±0.23	11.98 ±0.18
	0.1M (BA)		49.78 ±0.30	41.89 ±0.50	55.39 ±2.37	28.62 ±0.27
	0.2M (BA)		100.35 ±0.65	71.86 ±1.93	51.80 ±0.55	50.31 ±0.60
	0.3M (BA)		117.50 ±1.30	91.57 ±0.82	73.82 ±0.69	57.09 ±0.40
	0.4M (BA)		130.57 ±0.91	104.92 ±0.21	83.28 ±1.03	67.60 ±1.27
	Average petrol		**78.40 ±9.50**	**60.93 ±7.53**	**46.30 ±6.91**	**36.93 ±5.59**
	Control	burned	10.07 ±0.11	6.89 ±0.08	3.70 ±0.03	0.81 ±0.05
	Solvent		37.00 ±5.57	8.70 ±0.15	6.01 ±0.08	3.03 ±0.10
	0.1M (BA)		75.91 ±1.17	12.36 ±0.64	8.95 ±0.22	3.17 ±0.04
	0.2M (BA)		91.46 ±0.32	26.61 ±0.90	13.55 ±0.31	6.63 ±0.07
	0.3M (BA)		78.10 ±0.66	34.36 ±2.26	18.91 ±0.74	9.56 ±0.15
	0.4M (BA)		94.35 ±0.58	47.40 ±0.53	26.34 ±0.54	15.80 ±0.38
	Average petrol		**51.20 ±7.19**	**22.72 ±3.61**	**12.91 ±1.91**	**6.50 ±1.22**

The results for the total major petrol components also showed that the relative amounts were increased with increasing concentrations of added boric acid solution for all the wood samples; however, the total petrol was reduced after the burning process across all wood types and boric acid treatments, as shown in Table 4.3 and Figures 4.3.

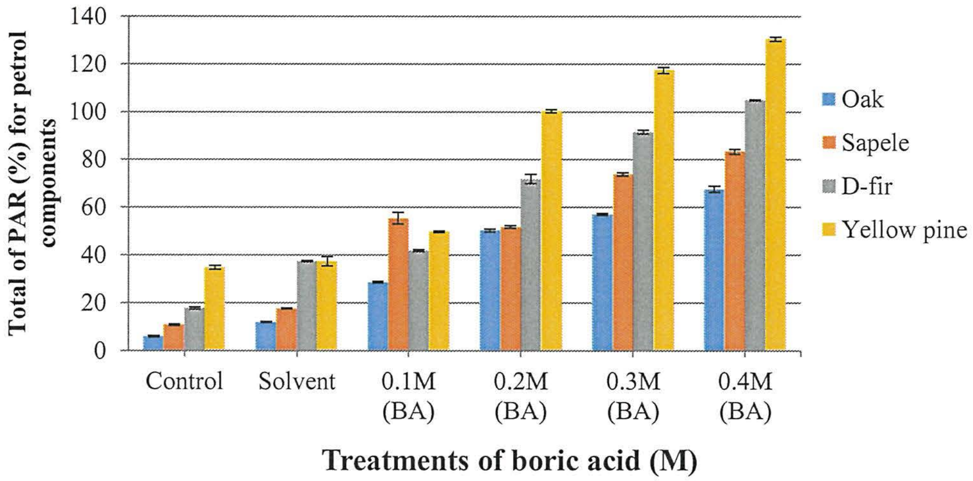

Figure 4.2. Comparison of total petrol components in unburned samples of Yellow pine, Douglas-fir, Sapele and Oak wood treated with different concentrations of boric acid. PAR (%) represents the peak area ratios of isolated petrol compounds in the four types of unburned wood samples.

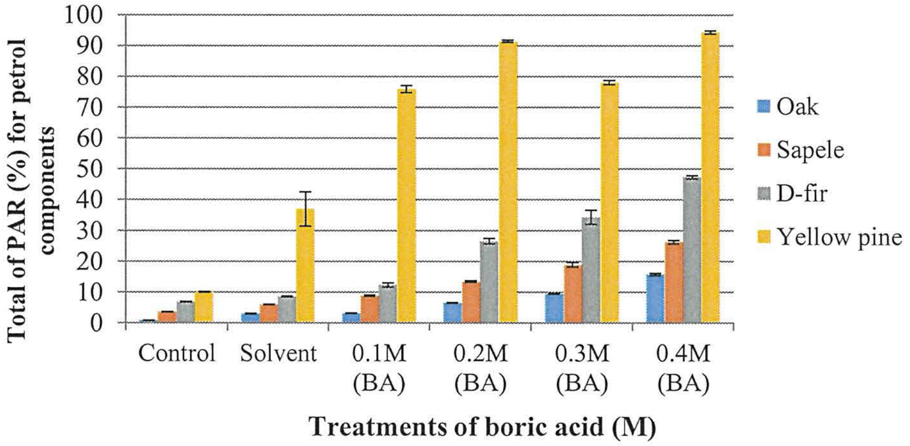

Figure 4.3 Comparison of total petrol components in burned samples of Yellow pine, Douglas-fir, Sapele and Oak wood treated with different concentrations of boric acid. PAR (%) represents the peak area ratios of isolated petrol compounds in the four types of burned wood samples

4.5.4 Quantitative analysis of Kerosene

The GC results obtained for kerosene analysis showed the distribution of various carbon fractions in the range (n-C_9 – n-C_{18}) across pure and 'standard' kerosene components, as shown in Figure 4.4. The samples were analysed using a GC-MS technique to identify the carbon fractions (*normal*-alkanes) from kerosene. Various fractions of carbon number distribution in the fresh kerosene standard samples are given in Table 4.4.

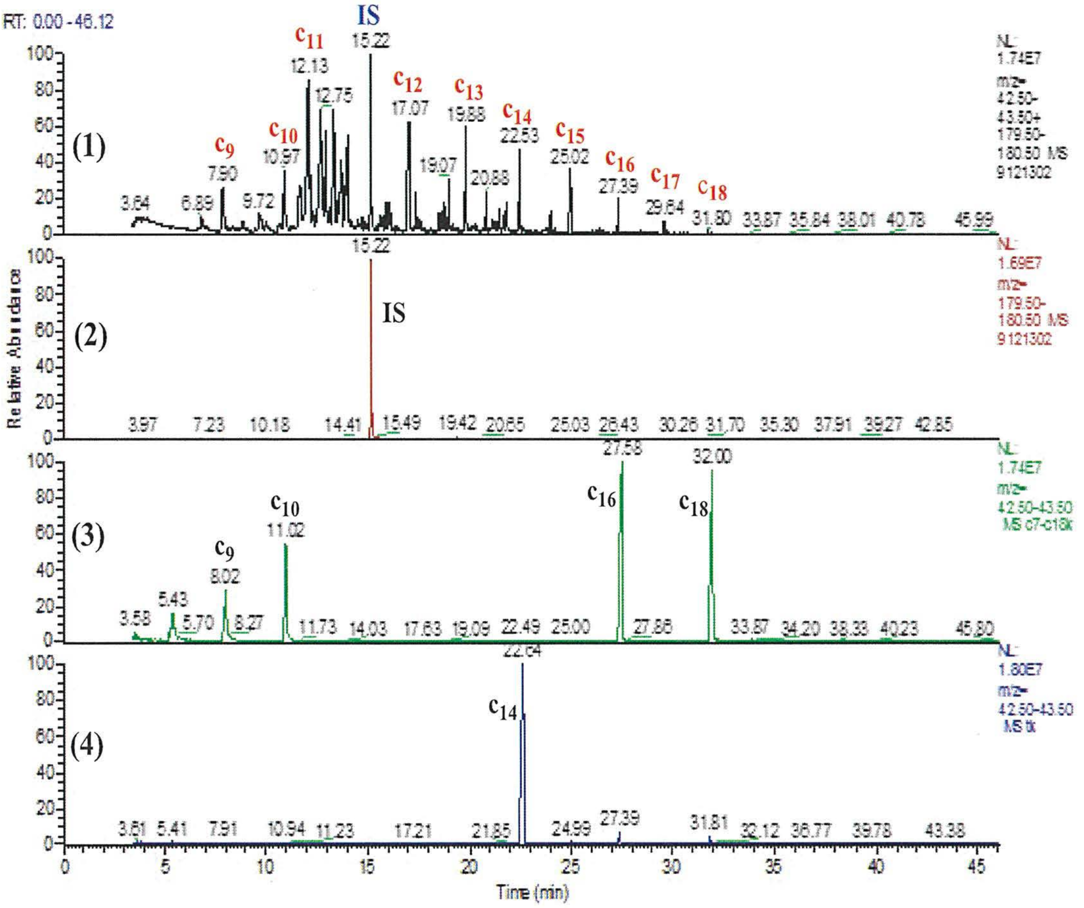

Figure 4.4 GC-MS chromatogram of (**1**) the fresh liquid of kerosene (Medium Product rang; *n*-C_9 to *n*-C_{18}) at concentration of 20,000 ppm. The internal standard (1,3,5-trichlorobenzene) is represented in curve (**2**). (**3**) calibration standards of normal-alkaline (*n*-C9, *n*-C10, *n*-C16, *n*-C18, and (**4**) calibration standard of *normal*-alkaline (*n*-C_{14}). Curve (**1**) represents various types of compounds (alkanes, cycloalkanes, aromatics and condensed ring aromatics).

The obtained results for pure (fresh) kerosene components were in good agreement when compared to those of the reference of standard kerosene as shown in Figure 4.4 and detailed in Table 4.4.

The majority of the hydrocarbons in pure kerosene were identified by comparison with peaks obtained for standard hydrocarbons. The results of pure kerosene showed a distribution (n-C_9–n-C_{18}) with analysis of 10 major hydrocarbon peaks. However, overlap occurred for a number of peaks for kerosene and diesel; for instance, kerosene fractions were obtained at C_9 to C_{18} for and diesel fractions at C_{12} to C_{28}.[2]

Table 4-4 Peak identification of the pattern components found in the range n-C_9 to n-C_{18} in kerosene

Accelerant	Retention time (R_t) (min).	Component
Kerosene	7:90	n-C_9 Nonane
	10:97	n-C_{10} Decane
	12:75	n-C_{11} Undecane
	17:07	n-C_{12} Dodecane
	19:88	n-C_{13} Tridecane
	22:53	n-C_{14} Tetradecane
	25:02	n-C_{15} Pentadecane
	27:39	n-C_{16} Hexadecane
	29:64	n-C_{17} Heptadecane
	31:80	n-C_{18} Octadecane
Internal Standard (IS)	15:22	1,3,5-trichlorobenzene (TCB)

The results of GC-MS chromatograms for kerosene components and the effects of boric acid (fire retardant) on burned and unburned samples of Douglas-fir, Yellow pine, Sapele and Oak wood are shown in Figures (6.9.A–6.16.A) Appendix (A).

The majority of the components in the range n-C_9 to n-C_{18} of kerosene components were found in the residues of unburned and burned wood samples for all of the four wood types and for all of the boric acid treatments (0.1–0.4 M). However, different relative amounts

(PA) were observed compared to those found in the calibration standards of kerosene components, as shown in Table 4.5. The results also showed that the total peak area ratios for kerosene components increased with increasing doping of boric acid when compared with control samples for all four wood types. Statistical analysis showed highly significant differences ($p < 0.01$) in the total peak area ratio of kerosene components across all of the unburned wood types and boric acid concentrations (0–0.4 M), compared to control samples (Figure 4.5-4.6).

4.5.5 Comparison of the total major kerosene components in the residues of unburned and burned wood treated with different concentrations of boric acid.

Table 4.5 shows that the total PAR (%) of the major kerosene components was highest in Yellow pine wood, followed by Douglas-fir, Sapele and Oak wood for all boric acid dopant levels in both the unburned and burned wood samples. The statistical results of ANOVA (Two-way) showed highly significant differences ($p < 0.01$) in the total peak area ratio of kerosene components in unburned wood types compared to those found in burned wood types.

The kerosene analysis showed that the majority of the kerosene patterns were recovered from the residue of unburned and burned wood samples within the retention time period of about 8.0 to 30.0 min, and the IS was detected within time of around 15.08 to 15.27 min, as shown in Figures (6.9.A–6.16.A) Appendix (A). Therefore, the characteristic profiles of the major kerosene compounds were obtained only often a longer time period (30 min) compared to petrol components (10 min) across all unburned and burned samples, wood types and boric acid treatments.

Table 4-5 Kerosene components in the residues of unburned and burned wood treated with different concentrations of boric acid

Accelerants	Borate Treatment	Fire Test	Sum of peak area ratio for kerosene components in the residue of wood types			
			Yellow pine	**Douglas-fir**	**Sapele**	**Oak**
Kerosene	**Control**	**Unburned**	619.09 ±11.78	509.35 ±55.47	530.55 ±4.52	475.39 ± 5.09
	Solvent		637.12 ±25.84	610.49 ±5.07	541.34 ±3.77	499.35 ±2.88
	0.1M (BA)		637.12 ±9.30	619.84 ±5.19	576.54 ±3.86	494.44 ±1.05
	0.2M (BA)		681.79 ±1.78	617.01 ±0.67	591.51 ±1.96	513.11 ±1.30
	0.3M (BA)		696.52 ±5.32	597.34 ±4.10	559.91 ±3.51	521.50 ±2.84
	0.4M (BA)		702.04 ±0.23	629.08 ±2.73	573.07 ±3.90	550.31 ±2.54
	Average kerosene		**662.21 ±8.94**	**597.19 ±12.58**	**562.15 ±5.23**	**509.02 ±5.79**
	Control	**burned**	88.97 ±1.91	41.72 ±3.55	11.62 ±0.67	12.74 ±0.23
	Solvent		138.04 ±4.26	70.25 ±0.28	91.19 ±0.12	24.40 ±0.10
	0.1M (BA)		170.23 ±4.34	67.64 ±1.21	9.78 ±0.54	5.29 ±0.17
	0.2M (BA)		224.94 ±3.01	88.03 ±0.74	12.35 ±0.05	15.68 ±0.17
	0.3M (BA)		220.71 ±4.88	147.97 ±0.52	19.16 ±0.12	5.95 ±0.11
	0.4M (BA)		299.17 ±3.16	64.51±0.99	15.03 ±0.12	119.09 ±1.87
	Average kerosene		**523.68 ±5.02**	**80.12 ±8.09**	**30.53 ±9.72**	**26.52 ±8.09**

The results for total kerosene components also showed that the total relative amount increased with increasing concentrations of doped boric acid for all the wood samples. The total (PAR) % of kerosene components was reduced after the burning process across all wood types and boric acid treatments, as shown in Table 4.5 and Figures (4.5–4.6). The signal intensity of kerosene components showed a low level of target peaks in burned samples for Sapele and Oak wood (hardwood).

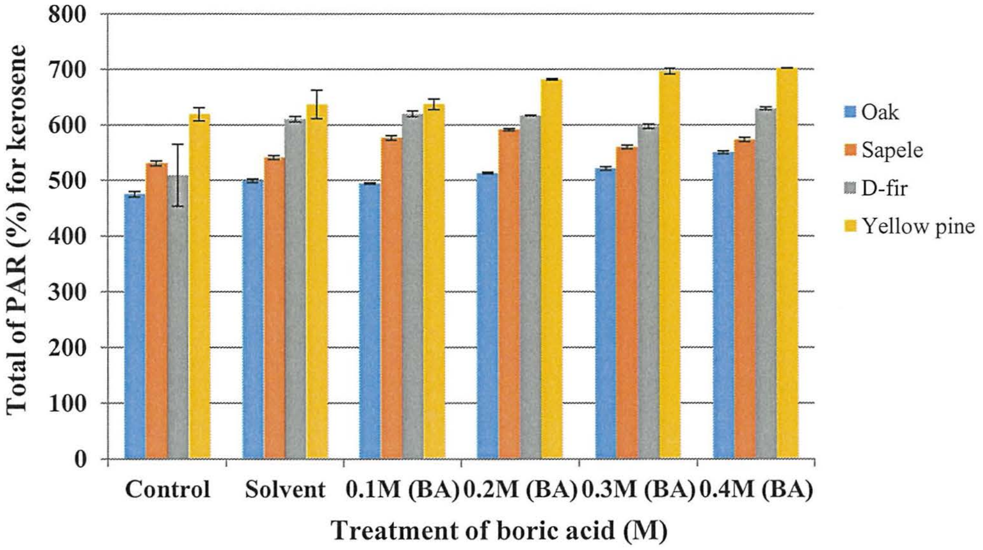

Figure 4.5 Comparison of total kerosene components in unburned samples of Yellow pine, Douglas-fir, Sapele and Oak wood treated with different concentrations of boric acid. PAR (%) represents the peak area ratios of isolated kerosene compounds in the four types of unburned wood samples.

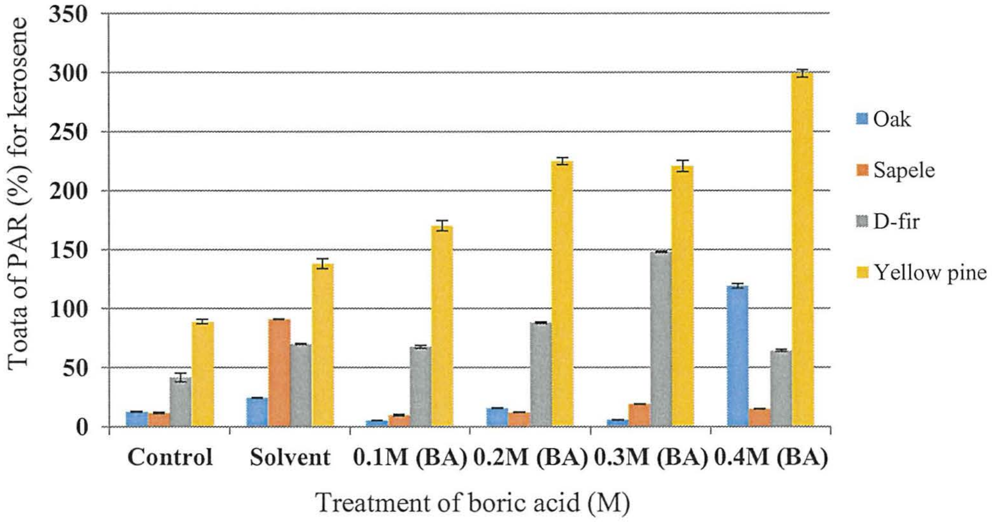

Figure 4.6 Shows the comparison of total kerosene components in burned samples for Yellow pine, Douglas-fir, Sapele and Oak wood treated with different concentrations of boric acid. PAR (%) represents the peak area ratios of isolated kerosene compounds in the four types of burned wood samples

4.5.6 Quantitative analysis of Diesel

The GC/MS results of diesel analysis showed the hydrocarbon peaks in the range from *n*-C_{10} to *n*-C_{28} for both the pure and the calibration standards of diesel, as shown in Figure 4.7. The distribution of carbon fractions (hydrocarbons *n*-alkanes) in the diesel components for standard samples is shown in Table 4.6.

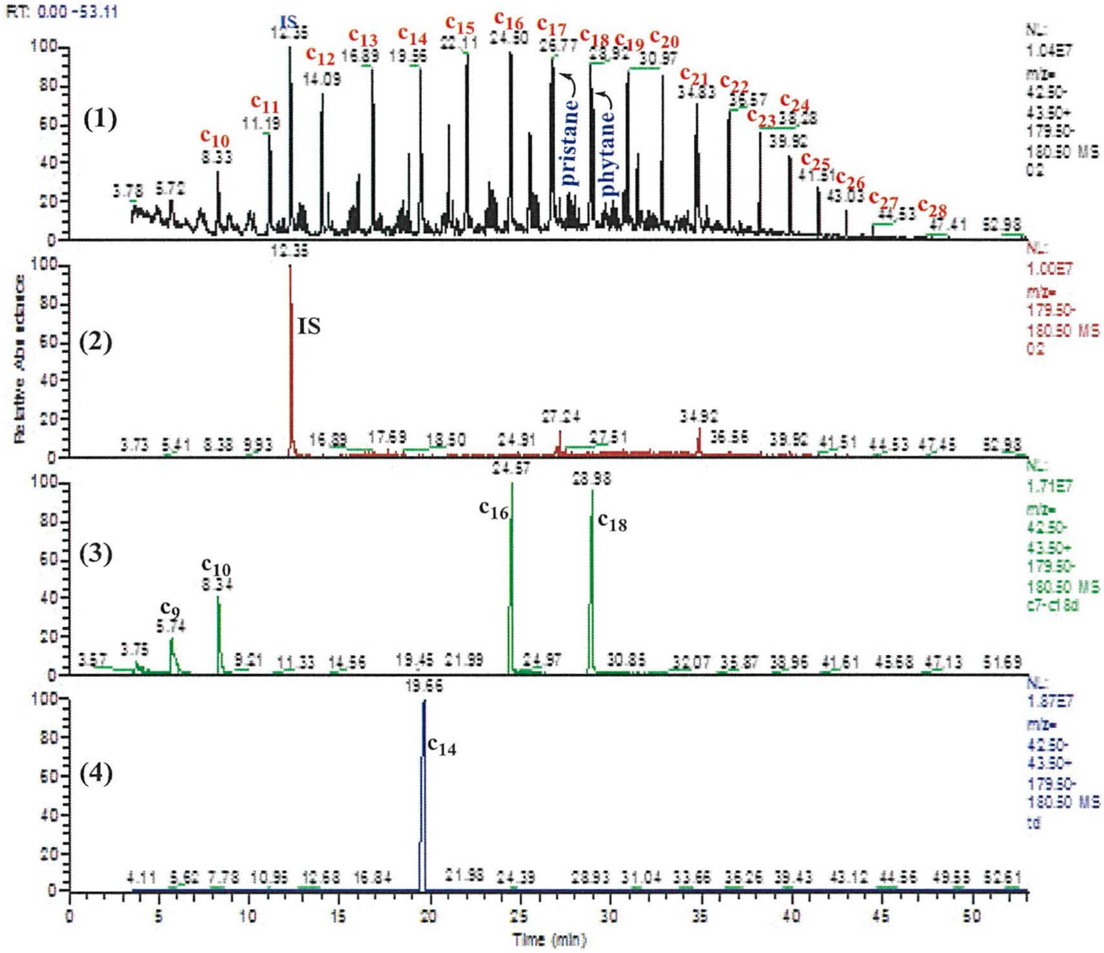

Figure 4.7 GC-MS chromatogram of (**1**) the fresh liquid diesel (Heavy product range from n-C10 to n-C28) at a concentration of 20000 ppm. The internal standard (1,3,5-trichlorobenzene) is represented in curve (**2**) at a retention time of 12.35. Curve (**3**) calibration standards of normal-alkaline (*n*-C9, *n*-C10, *n*-C16, *n*-C18. Curve (**4**) calibration standard of normal-alkaline (*n*-C14).. Curve (**1**) represents various types of compounds (alkanes, cycloalkanes, aromatics and condensed ring aromatics).

The component patterns for fresh diesel were in agreement with those obtained for the standard diesel samples. The results for pure diesel showed that most of the pattern occurs in the range from *n*-C_{13} to *n*-C_{25} enabling analysis of 15 hydrocarbons across all the samples.

As pointed out previously, overlapping occurs for carbon fractions (*n*-C_{17}–*n*-C_{18}) of kerosene and diesel; therefore, pristane and phytane compounds were used to identify the carbon fractions for *n*-C_{17} and *n*-C_{18}, respectively (see Table 4.6). The ratios of C_{17} to pristane and C_{18} to phytane are well recognised as suitable biodegradation indicators using GC/MS techniques.[2,3,5]

Table 4-6 The retention time (Peak identification) of the pattern components found in the range from *n*-C_{10} to *n*-C_{28} in diesel

Accelerant	(R_t) min.	Component
Diesel	8:33	*n*-C_{10} Decane
	11:19	*n*-C_{11} Undecane
	14:09	*n*-C_{12} Dodecane
	16:89	*n*-C_{13} Tridecane
	19:56	*n*-C_{14} Tetradecane
	22:11	*n*-C_{15} Pentadecane
	24:50	*n*-C_{16} Hexadecane
	26:77	*n*-C_{17} Heptadecane
	26:91	2,6,10,14-tetramethyl pentadecane (Pristane)
	28:93	*n*-C_{18} Octadecane
	29:11	2,6,10,14-tetramethyl hexadecane (Phytane)
	30:97	*n*-C_{19} Nonadecane
	32:93	*n*-C_{20} Cosane
	34:83	*n*-C_{21} Uncosane
	36:57	*n*-C_{22} Docosane
	38:28	*n*-C_{23} Tricosane
	39:92	*n*-C_{24} Tetracosane
	41:51	*n*-C_{25} Pentacosane
	43:03	*n*-C_{26} Hexacosane
	44:53	*n*-C_{27} Heptacosane
	45:98	*n*-C_{28} Octacosane
IS	12:35	1,3,5-trichlorobenzene (TCB)

The GC-MS chromatogram results of diesel components and the effect of boric acid concentrations as a fire retardant on burned and unburned samples for Douglas-fir, Yellow pine, Sapele and Oak wood are shown in Figures (6.17.A–6.24.A) Appendix (A). The majority of diesel hydrocarbons in the range from n-C_{13} to n-C_{25} were recovered in the residues of all samples for all four wood types and for all boric acid dopant concentrations (0.1-0.4 M). The total peak area ratios of carbon number distribution for a diesel accelerant were increased with increasing dopant concentrations of boric acid when compared with the control samples for all the wood types. The results of statistical analysis indicated highly significant differences ($p < 0.01$) in the total peak area ratio of diesel components across all unburned and burned wood types and boric acid concentrations (all treatments) (0 Solvent–0.4 M) when compared to control samples (Figure 4.8–4.9).

4.5.7 Comparison of the total major diesel components in the residues of unburned and burned wood treated with boric acid at different concentrations.

Table 15.4 shows that the total PAR (%) of the major diesel components was highest in Yellow pine wood, followed by Douglas-fir, Sapele and Oak wood across all boric acid dopant concentrations for both unburned and burned wood samples.

The statistical results of ANOVA (Two-way) showed highly significant differences ($p < 0.01$) in the total peak area ratio of diesel components in unburned wood types compared to those found in burned wood types. The results indicated that the characteristic patterns of all examined diesel components were recognisable within the retention time period of about 8.0 to 44.0 min and the IS was detected within time of around 12.35 min, as shown in Figures (6.17.A–6.24.A) Appendix (A) Therefore, the characteristic profile of all diesel compounds was distinguished only for the longest time period (45 min) for all wood types or boric acid treatments.

Table 4-7 The total (PAR) % of diesel components in the residue of unburned and burned wood treated with different concentrations of boric acid

Accelerants	Borate Treatment	Fire Test	Sum of peak area ratio (PAR)% for diesel components residue in wood types			
			Yellow pine	Douglas-fir	Sapele	Oak
Diesel	Control	Unburned	2045.4 ±57.46	1468.2 ±77.3	1044.4 ±58.26	810.2 ±47.89
	Solvent		2161.5 ±34.04	1831.7 ±66.55	1086.6 ±26.33	924.6 ±40.12
	0.1M (BA)		2258.4 ±42.33	1750.5 ±25.87	1348.9 ±16.28	788.2 ±19.90
	0.2M (BA)		2324.3 ±33.28	1884.2 ±13.4	1397.1 ±35.53	819.6 ±66.41
	0.3M (BA)		2422.9 ±27.87	1910.4 ±44.9	1421.0 ±63.67	1037.2 ±19.18
	0.4M (BA)		2433.3 ±79.85	1818.5 ±27.69	1275.3 ±19.48	1117.7 ±58.40
	Average diesel		**2274.41 ±37.44**	**1777.32 ±39.4**	**1262.28 ±38.3**	**916.23 ±32.55**
	Control	burned	368.89 ±19.42	283.59 ±21.94	184.66 ±4.56	99.99 ±3.62
	Solvent		673.51 ±8.52	317.49 ±10.82	213.47 ±1.59	273.91 ±8.85
	0.1M (BA)		673.51 ±6.08	315.32 ±20.87	178.54 ±0.52	138.91 ±0.94
	0.2M (BA)		690.69 ±16.72	358.33 ±3.55	123.77 ±8.17	65.71 ±2.83
	0.3M (BA)		755.34 ±8.84	328.39 ±6.74	214.71 ±20.91	172.99 ±9.20
	0.4M (BA)		762.38 ±12.14	294.95 ±2.67	298.70 ±18.95	77.73 ±1.80
	Average diesel		**670.75 ±34.27**	**316.34 ±7.44**	**202.21 ±13.44**	**138.21 ±17.27**

The results for total diesel components also showed that the relative amounts of these components increased with increasing dopant concentrations of boric acid compared to control samples; however, this total decreased after the burning process across all wood types and boric acid treatments, as shown in Table 4.7 and Figures 4.8 and 4.9

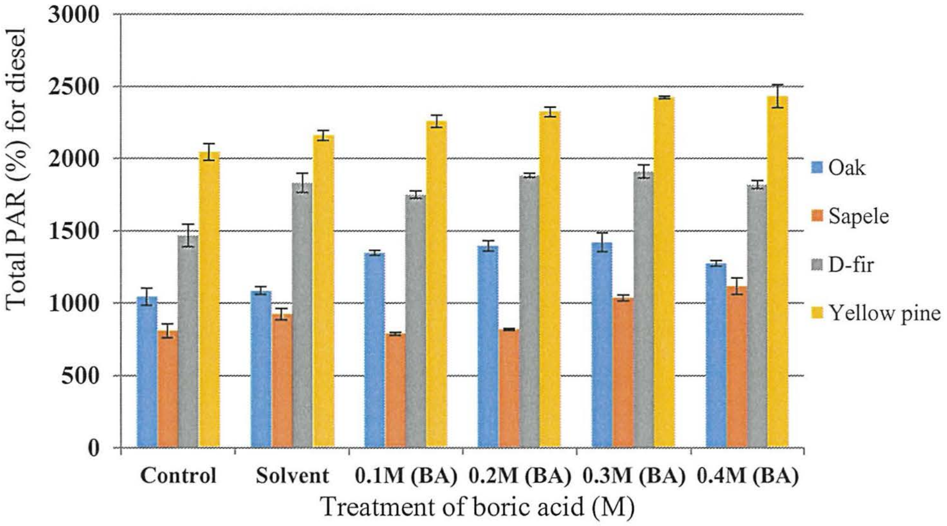

Figure 4.8 Comparison of total diesel components in unburned samples for Yellow pine, Douglas-fir, Sapele and Oak wood treated with different concentrations of boric acid. PAR (%) represents the peak area ratios of isolated diesel compounds in the four types of unburned wood samples.

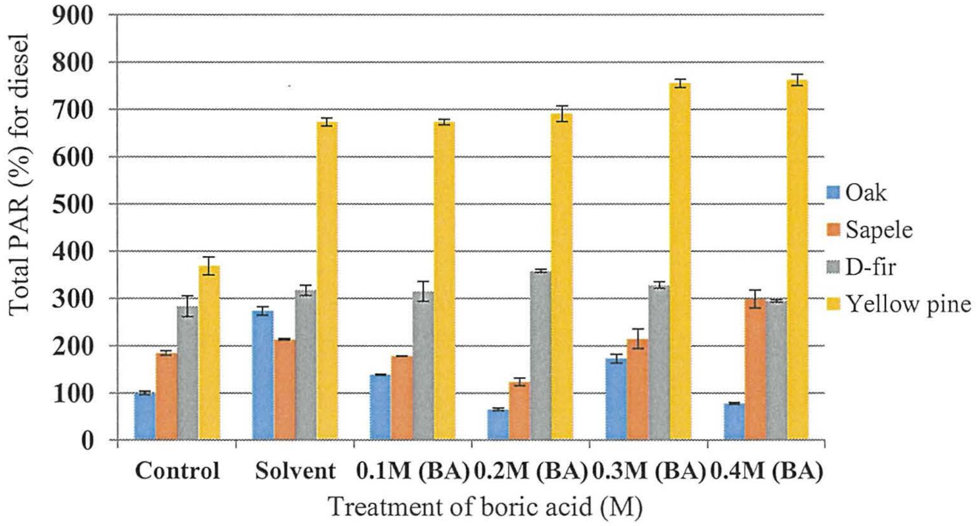

Figure 4.9 Comparison of total diesel components in burned samples for Yellow pine, Douglas-fir, Sapele and Oak wood treated with different concentrations of boric acid. PAR (%) represents the peak area ratios of isolated diesel compounds in the four types of burned wood samples.

4.6 Forensic analysis:

As described in Sections 4.5.2, 4.5.4, and 4.5.6, the relative abundance (peak area) (PA) and retention time (R_t) are two significant parameters used to characterise the patterns of accelerants. The GC/MS results of petrol, kerosene and diesel in unburned and burned wood types (debris) treated with different dopant concentrations of boric acid showed that a principal task of arson investigation is to identify the commonly targeted accelerants when they exist in test samples of unfired and fired debris. The extraction and the employed GC/MS methods successfully separated the majority of volatile debris components across all test accelerants and wood types. A previous study failed to establish the presence of all accelerants in the fire debris of carpet swatches with padding, plywood chips and floor tile fragments.[15] Nevertheless, the relative PAR value and retention time of representative standard accelerants were similar to those obtained in the present study. This suggested that the GC/MS peaks of pyrolysis products (non-accelerants origin) are sufficient in size and number to obscure the patterns of diagnostic accelerants. In the previous study, mass spectrometry (MS) was recommended to distinguish accelerant-related types with high background samples to limit the interference of non-accelerant components in the fire debris.[15]

In this present study, the characteristic patterns of petrol, kerosene and diesel components in unburned and burned samples treated and untreated were recognisable based on the standards across all investigated time periods. However, the relative abundance of kerosene components was low in burned hard wood samples, Sapele and Oak wood, across all boric acid dopant concentrations. In addition, the relative abundance of diesel showed similar results in burned Sapele and Oak wood samples. One possible reason is that this low level of kerosene and diesel is related to a decreased ability of hardwoods (Sapele and Oak) to absorb accelerants compared to softwoods (Yellow pine and Douglas-fir). Another significant reason could reflect the high value of PAR for internal standards compared to those obtained for wood samples. Therefore, the burned wood samples treated with the highest boric acid solution were selected to represent the total peaks of kerosene and diesel in Sapele and Oak wood.

The fingerprint ratios of petrol, kerosene and diesel components in calibration standards and wood samples were reasonably insensitive to change, which was affected by many factors such as incomplete sample recovery and evaporation processes. The target compounds can be divided onto two groups: (1) compounds that require a long time to evaporate because they have low vapour pressures (boiling point); (2) neighbouring compounds (low boiling point) that need a short time to evaporate, so the long term compounds show greater abundance ratios compared to the short time compounds. Due to these variations, long-term compounds are more acceptable than short-term compounds for matching the visual patterns, as the latter might give questionable results.[15]

The method of solvent extraction was successful at separating the majority of the accelerants examined, allowing their detection at their predicted retention times across all wood types, boric acid concentrations for both burned and unburned samples. The extraction method for petrol, kerosene and diesel components in calibration standards and wood samples, the characteristic peaks of petrol compounds had the shortest retention times (10 min) compared with those obtained for kerosene (30 min) and diesel (45 min). As explained previously, accelerants with prolonged retention times (kerosene and diesel) showed similar chromatograms to those obtained with their standards; however, a few irregularities in relative quantities and signal levels could be observed in the chromatograms.

The effectiveness of chromatographic separation can be affected by several significant factors including the system temperature, selected column and sample concentration.[16] Therefore, these factors can affect the relative amount of a component and its retention time for ILR in the stationary phase. All examined accelerants were distinguished in burned wood samples even after the fire exposure. The short time of fire exposure (1 min) and uncharred materials remaining are possible reasons for the ready recognition of accelerants in burned wood using the GC/MS technique.

The total PAR (%) for petrol, kerosene and diesel components was highest in Yellow pine wood followed by Douglas-fir, Sapele and Oak wood across all boric acid concentrations and unburned and burned wood samples, as given in Table (4.3, 4.5 and 4.7). The strong adsorption of all target accelerants in Yellow pine wood is attributed to its structural properties compared to other three wood types, as shown in Table 4.1. The Yellow pine wood had the highest moisture content (MC) (11.88% ±0.36) compared to other wood types. One possible reason for this high MC could the cavity size and more diffuse porosity in the wood structure. These factors would increase the ability to adsorb liquid compared with the other tested wood species. On the other hand, the fewer cavities and diffuse pores and the high density of hardwood cells (Sapele and Oak wood) would result in less diffusion space for liquids, as would the low MC.

These wood properties were confirmed in Chapter 3, Section 3.3.1. Similar wood behaviour towards water were obtained from Alaskan spruce (*Picea glauca*) and Hawaiian albezia (*Albezia falcataria*).[17] Therefore, the MC of wood types is a characteristic that depends on different significant factors including temperature and the relative humidity of the surrounding air. These factors can control the equilibrium of wood MC.[18] The MC was higher in softwoods (Yellow pine and Douglas-fir) than in hardwoods (Oak and Sapele wood); this difference is related to the ability of softwoods to adsorb more water or liquids than hardwood.[17] Another significant factor for the high content of all target accelerants in Yellow pine samples could be related to the high organic matter content (OMC) (97.5% ±1.3) compared to other three wood types. The OMC can provide more active sites (functional groups) to bind the components of target accelerants. The high OMC in Yellow pine may indicate that this species contains more cellulose and hemicellulose than is found in hardwoods, which would increase the carbon content of Yellow pine and Douglas-fir softwoods.[18-23] The results of Chapter 3, Section 3.3.4 established that the adsorption of boric acid was highest for Yellow pine wood, followed by Douglas-fir, Sapele and Oak wood. These results confirm that Yellow pine wood has the ability to adsorb more boric acid compared to other wood types. Similar results were obtained for all wood types in the present study.

The total peak area ratio of petrol, kerosene and diesel components was increased with added boric acid across all wood types and in burned and unburned samples. Boric acid solution is one of the most common wood preservatives and also acts as a fire retardant.[17,18,24,25] Therefore, the amounts of total petrol, kerosene and diesel components were highest at the concentration of 0.4 M boric acid across all wood types and burned and unburned samples, as shown in Tables 4.3, 4.5 and 4.7.

The majority of wood fire retardants, including boric acid, reduce combustible volatile materials during the treatment process. The efficiency of a flame can be controlled by the oxidation of target materials and the combustion process, time of sample burning and the wood properties.[25,26] In addition, the mechanisms of fire retardancy can be affected by many different factors such as the properties of chemical compounds, conditions of environmental fire and surrounding environment characteristics, which can stimulate the pyrolysis process. The type of chemical compound also is significant key for fire retardants, due to the ability of retardants compounds to stop producing 1,6-anhydro-glucopyranose compounds during the fire process, as this compound is highly flammable in the volatile fraction during thermal cellulose decomposition.[25,26-36]

In cases of forensic evidence, the component patterns for petrol, kerosene and diesel accelerants were identified in the unburned and burned (debris) samples of all wood types by comparison to those obtained from standard samples. The total PAR (%) of diesel components showed the highest value followed by total PAR (%) of kerosene and petrol across all wood types and unburned and burned samples. The average overall PARs (%) for diesel, kerosene and petrol in unburned and burned samples, respectively, were as follows: 1557.54 ±36.92 and 331.90 ±26.50 for diesel, 582.64 ±7.86 and 165.19 ±27.86 for kerosene and 55.64 ±4.13 and 23.33 ±2.89 for petrol. The components of diesel and kerosene showed the highest values compared to petrol, since the diesel and kerosene accelerants required high temperatures to begin the evaporation process for their components compared to petrol, which readily burned.

The volatility levels of each petroleum component differed, and the first evaporated components were classified as the most volatile materials. As explained in Chapter 2, Section 2.8, petrol readily evaporates when its container is left open. Therefore, the impact of the heating process is more significant during a fire test.[37-43]

One the other hand, the components of diesel and kerosene fuels (liquid and solid materials) were not as readily burned compared to petrol. Thus, a higher temperature is required to produce significant values for volatile materials from wood samples; for this reason, volatile materials are not present at room temperature. The process of combustion develops when vapour is involved in fuel ignition. A non-volatile matrix such as wood and or carpet material is broken down into volatile materials due to the heat generated by combustion; this reaction is termed a pyrolysis process.[39] Therefore, the residual of each accelerant left after the fire incident can be used as forensic evidence to be matched with a particular accelerant in some cases.[37]

4.7 Conclusion

The results of fire test GC-MS chromatograms indicated that the relative amount of total PAR (%) for petrol, kerosene and diesel components could be recognised in four wood types across all boric acid concentrations in both unburned and burned wood. The solvent extraction method was successful in extracting the residue of ILR components remaining in wood samples (debris) for comparison to representative accelerant standards. The resulting GC/MS profiles for all target accelerants matched those provided of accelerant standards. The total PAR (%) of petrol, kerosene and diesel components was highest in Yellow pine wood followed by Douglas-fir, Sapele and Oak wood across all boric acid concentrations and in unburned and burned wood samples. The structural properties of Yellow pine wood increased its ability to adsorb liquids compared with other three wood species. This was related to fire retardants (boric acid), which reduced combustible volatile materials during the fire process. The total PAR (%) of diesel components showed the highest value followed by total PAR (%) of kerosene and petrol across all wood types and in unburned and burned samples. The characteristic peaks of petrol compounds had the shortest retention times (10 min) compared with those obtained for kerosene (30 min) and diesel (45 min) across all wood types and standard accelerants, because the diesel and kerosene accelerants need high temperatures for the evaporation process compared to petrol which readily burns when exposed to flame.

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Chapter 5.

5 Adsorption of boron on wood surfaces

5.1 Introduction

In recent years, there has been a rapid increase in the application of chemicals to wooden materials to improve their physical, mechanical, biological and fire-retardant properties.[1] Therefore, a systematic research program is now underway within the wood industry and at the Forest Products Laboratory to assess the relative importance of these factors and the ways they contribute to the effects on wood treated with fire retardants.[1]

Boron is widely dispersed from natural and anthropogenic sources in the ecosystem and is one of the most abundant trace elements in soil management.[1] Low concentrations of boron are essential for plant growth, and the element becomes toxic at concentration levels higher that than the recommended range.[2] This element is found in the forms of boric acid and borate salts. The constant of boric-acid dissociation plays a significant role (at 25° C and $pKa = 9.24$) and H_3BO_3 is the major form at low and neutral pH levels while $B(OH)_4^-$ is seen at high pH levels. Both forms (H_3BO_3 and $B(OH)_4^-$) may exist in equilibrium at a pH range of 7.0–11.5 and are used in the industrial manufacturing of porcelain and glass, carpets, cosmetics, leather and photographic chemicals.[1] They are also used in wire drawing, for fireproofing fabrics, weatherproofing and preserving wood, and manufacturing fire-retardant materials.[2,4] Moreover, compounds containing boron are used in some plant fertilizers for boron-deficient soils. Because H_3BO_3 has mild bactericidal and fungicidal environmental properties, it is also used as a food preservative and disinfectant. In addition, it can be used for wood control on railways and other industrial sites. Borax is also a major industrial material used for metal brazing and welding.[3-9]

The European community has considered several legislative changes because of the environmental effects and high toxicity of some extensively used chromium(VI)- or arsenic-based wood preservative compounds, such as the so-called CCA formulations (Cr(VI)-Cu-As), which have been banned for use as wood preservatives.[10] Boron has a low environmental impact, and boron-based formulations have been revealed as new preservation methods for wood systems.[11] Boron has significant plant toxicity and is effective as a fungicide and insecticide.[12] However, the biological resistance of treated wood can decrease rapidly under certain conditions, owing to the high boron leachability.[13]

The adsorption of boron by soils, clays and other minerals has been extensively studied. However, there is limited information in the literature about the adsorption of boron on wood surfaces. The influences of operational and environmental factors (pH, temperature, concentration and competing ions) on boron adsorption have not been investigated thoroughly, and there are contradictory results reported in the literature.[2]

The mechanism that binds boron to wood when treated with borax or boric-acid aqueous solutions is unknown. Thus, new investigations on the reaction kinetics of boron may increase understanding of the behaviour of boron on wood surfaces and improve wood preservation using boric acid. This method could maintain the mobility and biocidal effectiveness of boron on wood. This work is considered the first research in this area.

5.2 The aims

This experiment seeks to:

- Determine the reaction kinetics and thermodynamics of boric-acid (H_3BO_3) absorption from aqueous solution with different types of exemplar woods [softwood (*Yellow pine* and *Douglas-fir*) and hardwood (*Oak* and *Sapele*)].

- Monitor the reaction kinetics of boron (as boric acid) with block wood samples, through the evolution at various boric acid concentrations, over a 2.5 h period.
- Determine the amount of boric acid adsorbed by wood samples at different aqueous boric-acid solution concentrations.
- Evaluate adsorption isotherms, descriptive constants of boric acid (as boron from inductively coupled plasma (ICP) in wood using the Freundlich and Langmuir adsorption isotherm models.
- Test the experimental data of the adsorption process using pseudo-first-order and pseudo-second-order kinetic models.

The amount of boron adsorbed from the boric acid solution (**q**) mg.g^{-1} was obtained using the Equation (2.10) see Chapter 2 Section 2.11.[15] Each measurement was repeated three times ($n = 3$).

The Freundlich isotherm Equation is usually applied for a non-homogeneous adsorption processes, such as in wood; it is assumed that the physical adsorption of boron on the wood surface with weak forces acting such Van der Waals and hydrogen bonds. The Freundlich and Langmuir isotherm model is described in Equation (2.11 and 2.12) respectively, see Chapter 2 Section 2.11.[15-17]

To study the controlling mechanism of the boron adsorption process, two kinetics models (pseudo-first and pseudo-second reactions) are used to analyze the experimental adsorption data. The rate constant of adsorbed boron is calculated from the following (pseudo-first and pseudo-second order rate) expression (Equation 2.13 and 2.14) respectively, as given by Lagergreen , Ho and McKay. [18-20] See Chapter 2 Section 2.11.

5.3 Statistical analysis

Adsorption data were analyzed with a statistical software package (SPSS 20.0 for Windows®). The adsorption of boron on four wood types was evaluated using a one-way ANOVA and Tukey's honest significant difference (HSD) test. A P value < 0.05 was considered statistically significant. The mean averages of the adsorption data were evaluated using the Kruskal-Wallis one-way ANOVA on Ranks and Dunn's multiple comparison test.[21] Data are presented as means ±SE. The mean equilibrium and adsorption errors of each three replicates were calculated using Microsoft Excel for precision and absolute accuracy of the modelling results.

5.4 Results and discussion

5.4.1 Phase and morphology analysis of boric acid and wood samples

The phase of H_3BO_3 was examined by the X-ray diffraction (XRD) pattern of the compound, as shown in Figure 5.1. All of the diffraction peaks can be readily indexed as H_3BO_3 [space group, P1 (No. 2)].[22]

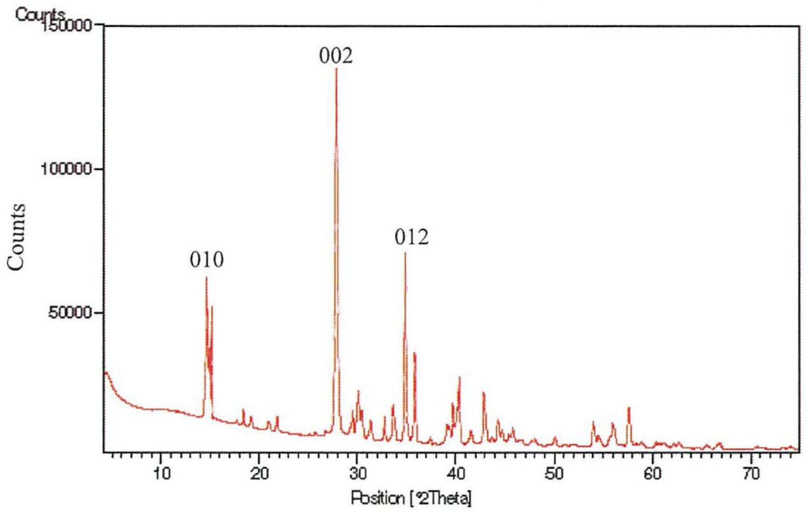

Figure 5.1 X–ray diffraction patterns of the H_3BO_3 structure as pure powder exposed to heat treatment at 100 °C overnight (for reference).

This result is in agreement with the structures found in previous studies.[22-24] Figure 36.5. shows that the greatest intensity of XRD patterns for boric acid were at $2\theta = 14.63°$, $28.02°$ and $33.916°$. The reflection planes of boric acid proved the crystal structure (planes: 010, 002 and 012, respectively). This result is similar to the XRD patterns of the B_2O_3/H_3BO_3 examined in previous works.[22-25]

The diffraction peaks of treated and untreated wood samples (Douglas-fir, Yellow pine, Oak and Sapele) were obtained, as shown in Figures 5.2, 5.3, 5.4 and 5.5, respectively.

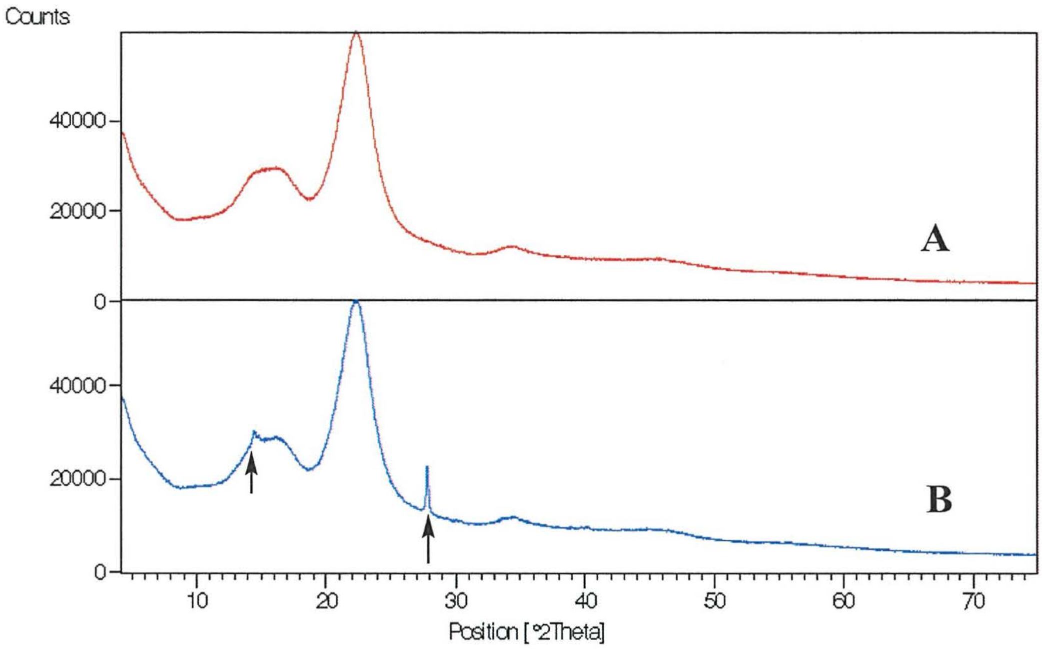

Figure 5.2 XRD peaks of uncoated Douglas-fir samples. (A) Control wood sample and (B) Sample exposed to the highest borate treatment (0.4 M)

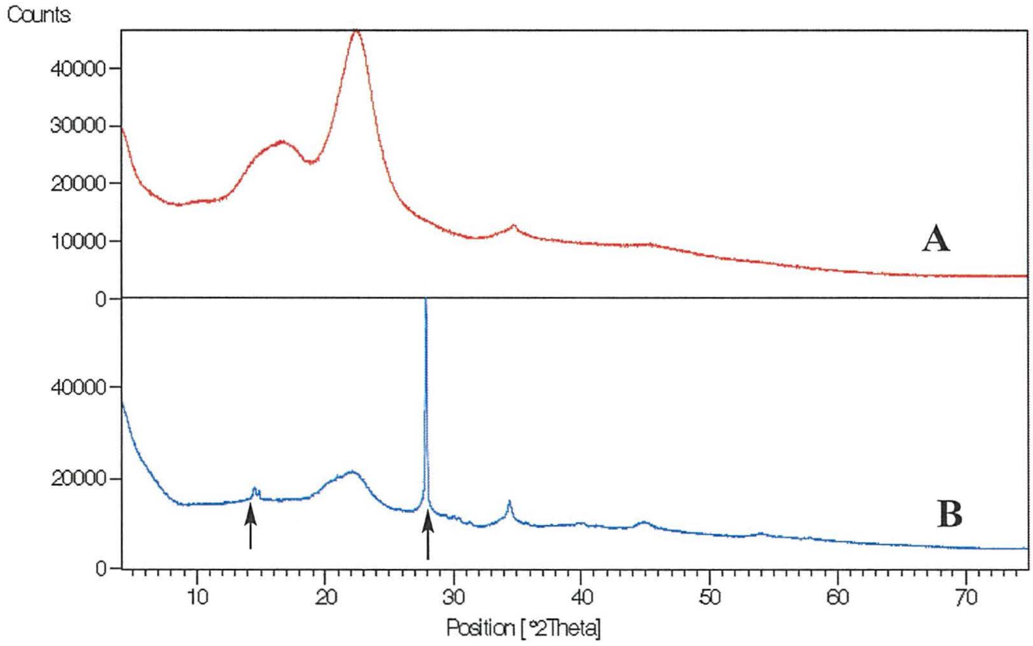

Figure 5.3 XRD peaks of uncoated Yellow pine samples. (A) Control wood sample and (B) Sample exposed to the highest borate treatment (0.4 M)

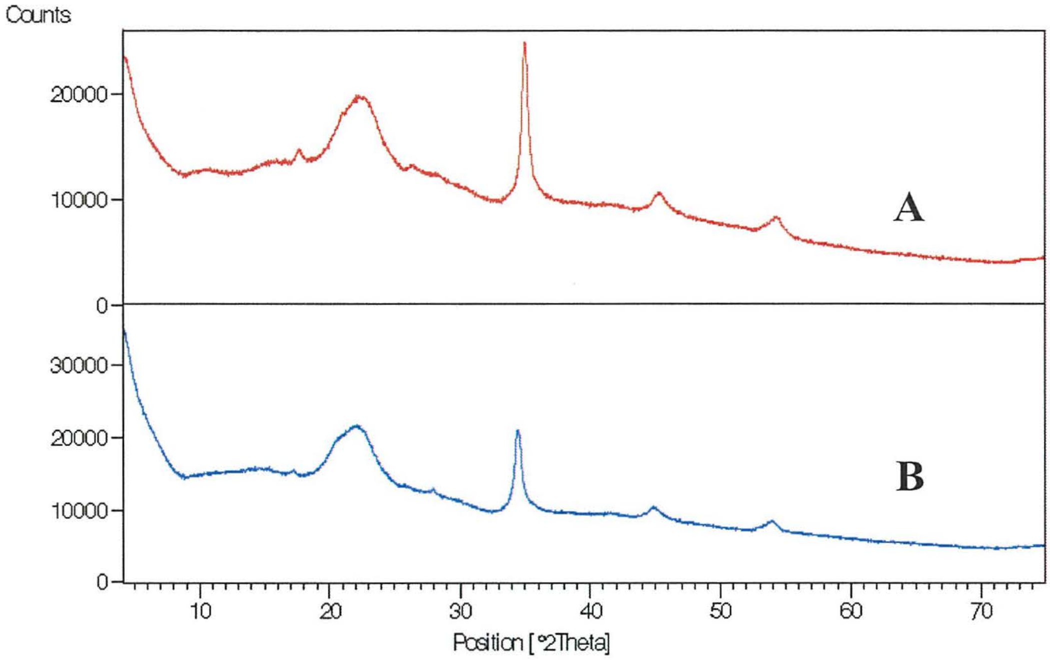

Figure 5.4 XRD peaks of uncoated Oak samples. (A) Control wood sample and (B) Sample exposed to the highest borate treatment (0.4 M)

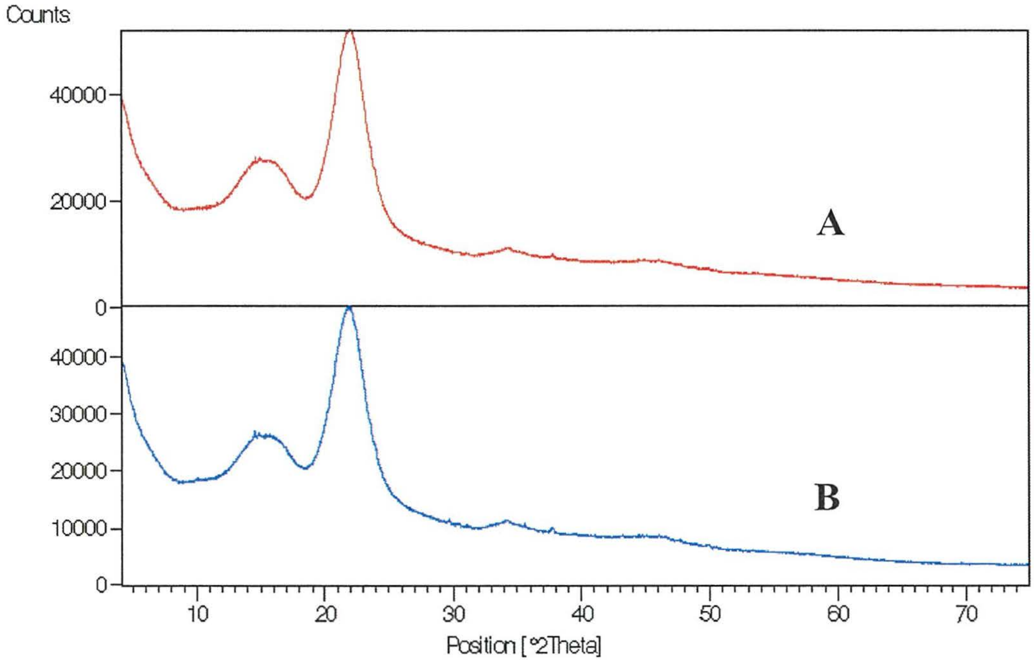

Figure 5.5 XRD peaks of uncoated Sapele samples. (A) Control wood sample and (B) Sample exposed to the highest borate treatment (0.4 M)

The diffraction peaks of boric acid in Douglas-fir were obtained at $2\Theta = 14.60°$ and 28.03°; the reflection planes of these peaks were 010 and 002 respectively (see Figure 5.2). However, the control samples revealed no diffraction peaks compared to the boric-acid sample, as shown in Figure 5.1. The Yellow pine sample showed the same results as the Douglas-fir; however, the intensity of the X-ray for boric acid was higher in Yellow pine than in Douglas-fir, as shown in Figure 5.3. These results indicate that the adsorption of boric-acid solution was higher in Yellow pine than in Douglas-fir.

The X-ray results of Oak and Sapele showed no boric-acid diffraction peaks compared to the control and boric acid samples, as shown in Figures 5.4 and 5.5. This result could be related to the small amount of boric-acid solution adsorbed onto the Oak and Sapele samples.

5.4.2 Quantifying the amount of boron adsorption

The reaction of boric acid with Yellow pine, Douglas-fir, Oak and Sapele was revealed. Different boric-acid solution concentrations (0.1, 0.2, 0.3 and 0.4 M) were mixed with tested woods until the equilibrium of this reaction was reached at room temperature. The equilibrium time of each wood was obtained from kinetic studies. The equilibrium concentration of boron in each boric-acid solution was measured and, from a mass balance, adsorbed concentrations were obtained. Results of the adsorbed boron as boric acid per gram of each wood versus boric acid at different concentrations of boron in solution are presented in Figure 5.6. This curve is the adsorption isotherm (the relation between the amount of adsorbed boric acid and the solution concentration). The amount of adsorbed boron (**q**) $mg.g^{-1}$ was calculated using Equation 5.1.

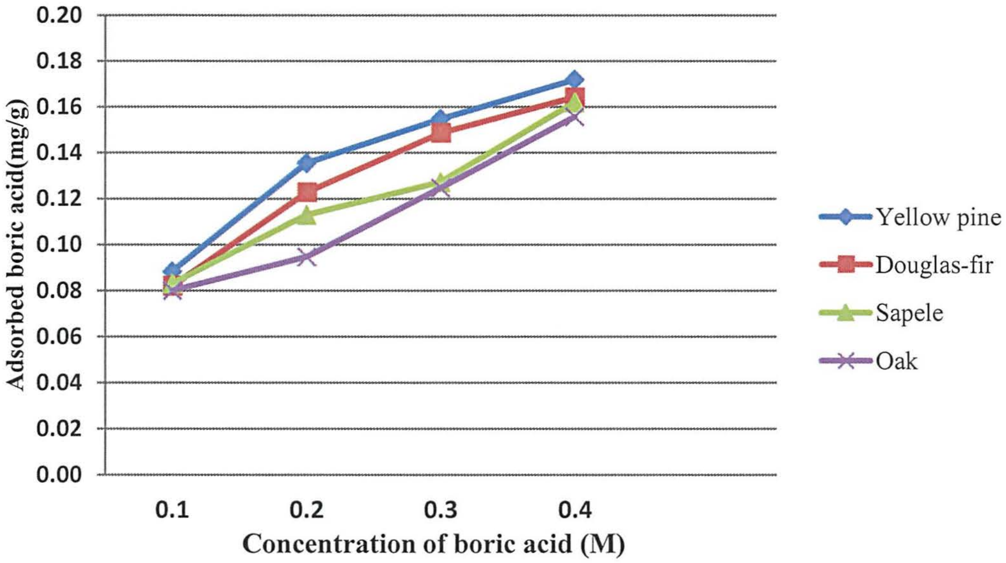

Figure 5.6 Adsorption isotherms of boron on surfaces of Yellow pine, Douglas-fir, Oak and Sapele. Each wood was mixed with a different concentration of boric-acid solution (0.1, 0.2, 0.3 and 0.4 M). The calculated values are given as mean ± SE (*n* =3).

Figure 5.6 shows that the adsorption of boric acid was highest on Yellow pine, followed by Douglas-fir, Sapele and Oak, respectively. The average boric acid adsorption was 0.138 $mg.g^{-1}$ ± 0.032 for Yellow pine, 0.129 $mg.g^{-1}$ ± 0.033 for Douglas-fir, 0.121 $mg.g^{-1}$ ± 0.033 for Sapele and 0.114 $mg.g^{-1}$ ± 0.030 for Oak. However, boric acid adsorption showed small differences between all the wood types, and the amounts of adsorbed boron were also small compared to the initial concentrations of boron used to treat the different woods. The adsorbed boron increased with increased boric acid concentrations. The statistical comparison of adsorbed boron showed no significant differences ($p > 0.05$) for all woods. The adsorption of boron on the Yellow pine surface could be related to the high diffusion coefficients of boron in this wood, which increased with time. The diffusion of boron in wood is based on different significant factors, such as the wood's moisture content (MC), diffusion period, solution strength, diffusion direction, temperature and treatment method.[26-29]

Ra *et al* demonstrated the constant radial diffusion coefficients of boron through southern pine *(Pinus* spp.). The result showed a potential easy way to predict the boron diffusion coefficients for dip-diffusion treatment.[30]

Borate compounds can be adsorbed on the wood surface in sufficient quantities for subsequent diffusion below the surface. Thus, boron diffusion is the transportation of this element from an area of high to low concentration. The initial penetration of the element is in the wood's top layer, followed by diffusion below the surface based on the presence of free water molecules in the wood cells.[29]

5.4.3 Adsorption Isotherm Models

The Freundlich and Langmuir adsorption isotherm models (Equations) were used to describe mono layer adsorption; therefore, they are useful to interpret chemical adsorption data as described in Equations 2.11 and 2.12. The Freundlich isotherm (Equation 2.11) is a brief empirical Equation often used to characterize adsorption data. This isotherm describes physical adsorption of elements from liquids.[31]

An alternative Equation (Langmuir) was developed assuming a fixed number of accessible sites available on the adsorbent surface; all of these sites have the same energy. In addition, the adsorption process is reversible, and mono-layer adsorptions can occur.[31] In this type of adsorption process, the adsorbed boron normally forms a layer over the surface of the wood, which is only one molecule thick.[32] Freundlich and Langmuir isotherm parameters for adsorption of boron by Yellow pine, Douglas-fir, Oak and Sapele are presented in Table 5.1.

Table 5-1 Freundlich and Langmuir parameters for the adsorption of boron (B) onto different types of wood

Wood type (adsorbent)	**adsorbate**	**Freundlich isotherm constants**			**Langmuir isotherm constants**		
		K_f(mg.g^{-1}) capacity	1/n	R^2	b (mg g^{-1}) capacity	k_L(L.mg^{-1})	R^2
Yellow pine	B	986.51	0.996	0.996	3.56	0.203	0.955
Douglas-fir	B	400.11	1.0	1.0	6.667	3.571	0.973
Sapele	B	400.11	1.0	1.0	5.00	4.56	0.821
Oak	B	400.11	1.0	1.0	6.061	4.34	0.625

The results shown in Figure 5.7-5.10 that good fits of the Freundlich isotherm to the boron adsorption system were found for all wood types. This means there is almost no limit to the amount of adsorbed boron and there is a multilayer of boron adsorption. The applicability of the Freundlich isotherm Equation (linear form) to a particular case is tested by plotting $log\ q_e$ against $log\ C_e$ from the logarithmic form of Equation 2.11. The correlation coefficients (R^2 value) for the Freundlich isotherm model Equation were linear (0.996–1.0), and this model fit well with the adsorption data shown in Figures 5.7-5.10.

Yellow pine showed the highest capacity for boron adsorption (K_f = 986.51 mg.g^{-1}) followed by the other three woods, which showed the same behaviour of boron adsorption as shown in Table 5.1. The adsorption capacity was 400.11 for Douglas-fir, Sapele and Oak.

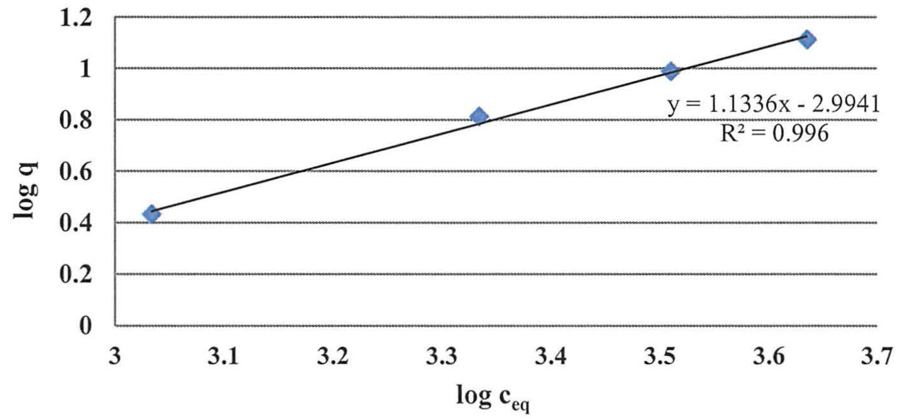

Figure 5.7 Linear fitting of equilibrium isotherms for the adsorption of boron on Yellow pine using the Freundlich Equation

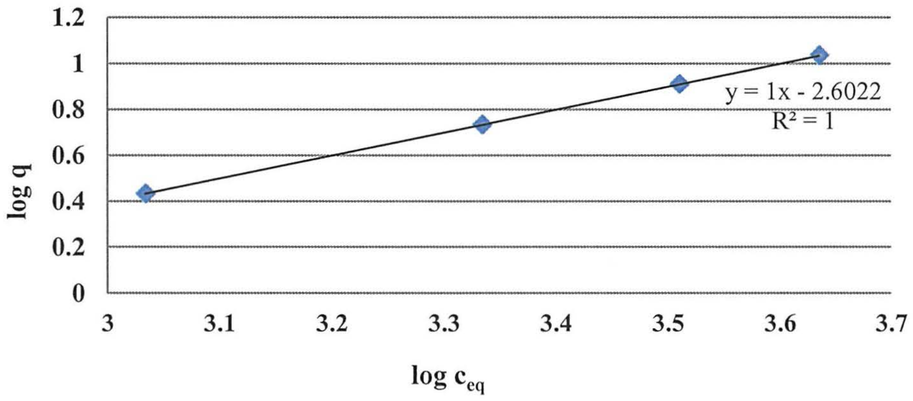

Figure 5.8 Linear fitting of eq uilibrium isotherms for the adsorption of boron on Douglas-fir using the Freundlich Equation

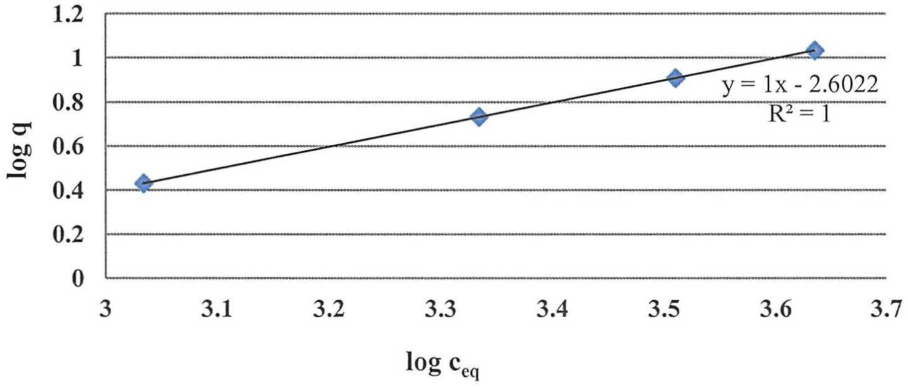

Figure 5.9 Linear fitting of equilibrium isotherms for the adsorption of boron on Oak using the Freundlich Equation

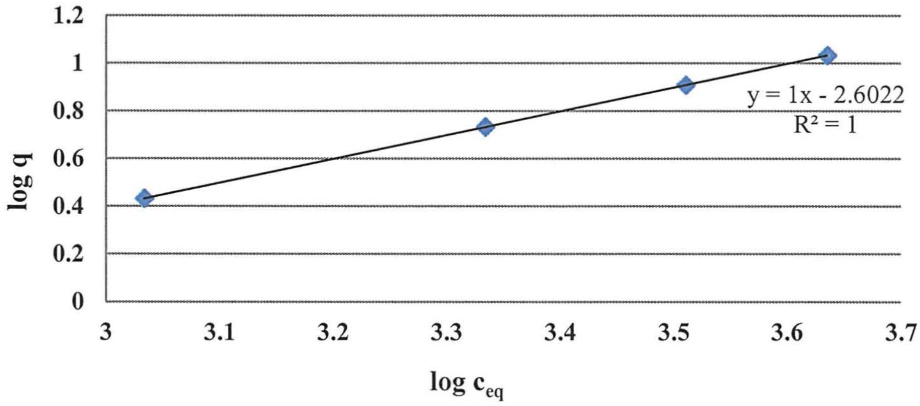

Figure 5.10 Linear fitting of equilibrium isotherms for the adsorption of boron on Sapele using the Freundlich Equation

However, the Langmuir adsorption isotherm model (linear form) is tested by plotting C/q against C from of Equation 2.12. It was not able to describe the relationship between the adsorbed amount of boron and the four wood types compared to the Freundlich adsorption isotherm model. The correlation coefficients (R^2) value for the Langmuir Equation were (0.973, 0.955, 0.821 and 0.625) as shown in Figures 5.11, - 5.14.

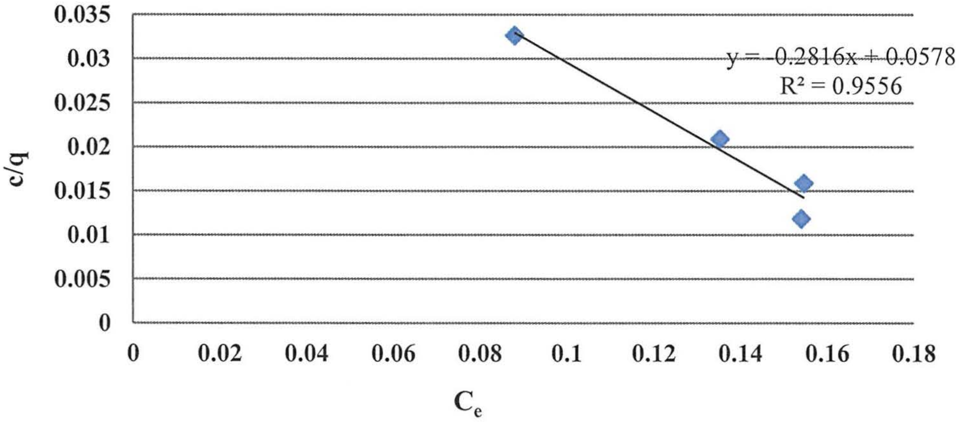

Figure 5.11 Plotting of Langmuir adsorption isotherms of boron onto Yellow pine wood

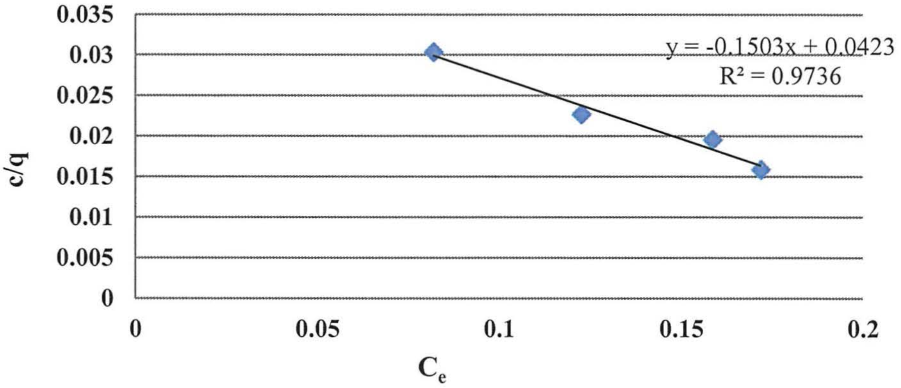

Figure 5.12 Plotting of Langmuir adsorption isotherms of boron onto Douglas-fir

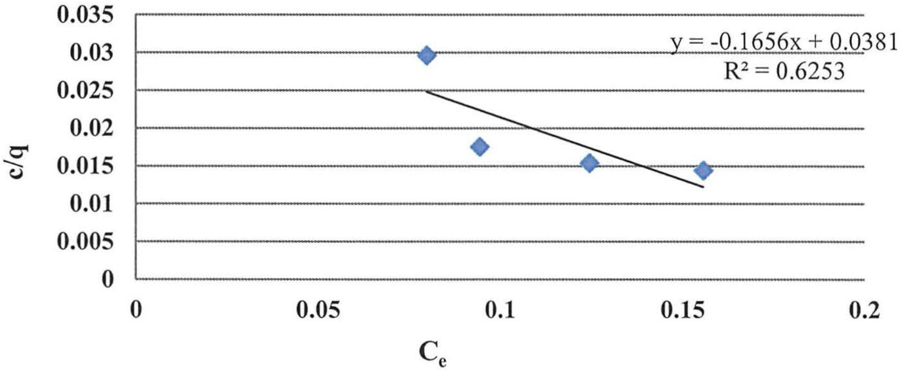

Figure 5.13 Plotting of Langmuir adsorption isotherms of boron onto Oak

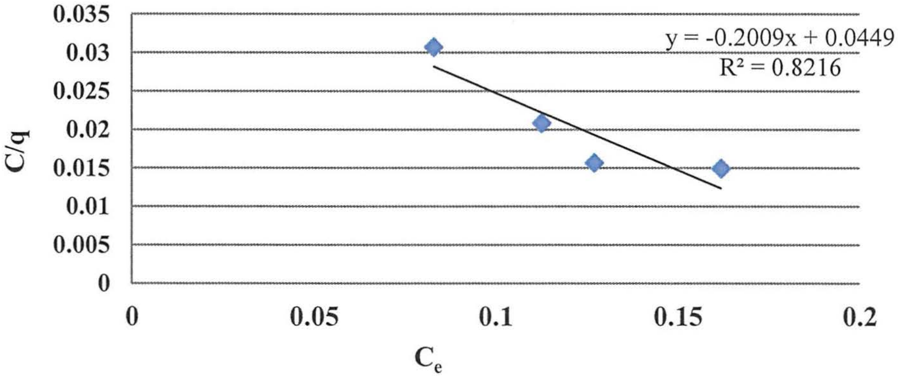

Figure 5.14 Plotting of Langmuir adsorption isotherms of boron onto Sapele

5.4.4 Adsorption Kinetics Models

To evaluate the controlling mechanisms of boron adsorption, the pseudo-first-order and pseudo-second-order adsorption kinetics models were used to test the experimental data. The rate constants of boron adsorption were calculated from Equations 2.13 and 2.14, as described above. The results of these models are presented in Tables 5.2-5.5.

Table 5-2 The first-order reaction correlation and second-order reaction for Yellow wood

adsorbate	Conc. (ppm)	q (ex) (mg.g-^{1})	Pseudo-First order constant			Pseudo-Second order constant		
			k_1 (min^{-1})	q (cal) (mg.g^{-1})	R^2	k_2 (g.mg^{-1}.min-^{1})	q (t) (mg.g^{-1})	R^2
B	1081	0.09	0.0001	0.985	0.311	4.66	0.079	0.995
	2162	0.14	0.0001	1.0	0.210	11.89	0.140	0.997
	3243	0.16	0.057	1.01	0.608	2.55	0.169	0.995
	4324	0.46	0.026	1.03	0.132	17.31	0.462	0.999

Table 5-3 The first-order reaction correlation and second-order reaction for Douglas-fir wood

adsorbate	Conc. (ppm)	q (ex) (mg.g-^{1})	Pseudo-First order constant			Pseudo-Second order constant		
			k_1 (min^{-1})	q (cal) (mg.g^{-1})	R^2	k_2 (g.mg^{-1}.min-^{1})	q (t) (mg.g^{-1})	R^2
B	1081	0.08	0.012	1.01	0.115	13.56	0.078	0.999
	2162	0.13	0.012	1.02	0.353	10.36	0.121	0.998
	3243	0.16	0.0002	1.02	0.050	16.92	0.157	0.993
	4324	0.18	0.0002	1.01	0.402	1.29	0.141	0.990

Table 5-4 The first-order reaction correlation and second-order reaction for Sapele wood

adsorbate	Conc. (ppm)	q (ex) (mg.g-^{1})	Pseudo-First order constant			Pseudo-Second order constant		
			k$_{1}$ (min^{-1})	q (cal) (mg.g^{-1})	R^{2}	k$_{2}$ (g.mg^{-1}.min^{1})	q (t) (mg.g^{-1})	R^{2}
B	1081	0.08	0.138	1.00	0.002	25.64	0.078	0.999
	2162	0.12	0.00002	0.968	0.584	4.43	0.108	0.996
	3243	0.12	0.115	1.035	0.003	17.91	0.134	0.972
	4324	0.23	0.00012	1.020	0.138	2.35	0.169	0.998

The results of both kinetics models indicated that the fit of these Equations is examined by each linear plot of log ($q_e - q_t$) versus t and t/q_t versus t, respectively. In addition, the regression coefficient comparison for each model for Yellow pine, Douglas-fir, Oak and Sapele wood is presented. The result reveal that the rate expression of the pseudo-first-order reaction did not fully represent the adsorption data of boron for all wood types, as shown in Tables 5.2–5.5.

Table 5-5 The first-order reaction correlation and second-order reaction for Oak wood

adsorbate	Conc. (ppm)	q (ex) (mg.g-^{1})	Pseudo-First order constant			Pseudo-Second order constant		
			k$_{1}$ (min^{-1})	q (cal) (mg.g^{-1})	R^{2}	k$_{2}$ (g.mg^{-1}.min-^{1})	q (t) (mg.g^{-1})	R^{2}
B	1081	0.080	0.012	0.99	0.384	28.32	0.082	0.999
	2162	0.095	0.0023	0.77	0.297	10.18	0.110	0.986
	3243	0.125	0.00002	1.03	0.004	11.04	0.131	0.987
	4324	0.156	0.023	0.997	0.001	11.05	0.157	0.998

Low correlation coefficients of the pseudo-first-order reactions are shown in the Appendix (B) Figures (6.25.B-6.29.B). There is good agreement of the boron adsorption data with the pseudo-second-order reaction (Tables 5.2–5.5). The values of constant rate (k_2) and q_e for the second-order model were calculated from the slopes and intercepts of the plots, as described in Equations 2.13 and 2.14. These parameters of both models are shown in Table 5.2–5.5. The majority of correlation coefficients (R^2) values for the second-order reaction are higher than 0.98 compared to those found in the first-order reaction. The theoretical q_t values (calculated from the Equations) agreed perfectly with the experimental q(ex) values (obtained from Equation 2.10). These results indicate that the adsorption of boron represented by the pseudo-second-order kinetic model compared to the first-order reaction.

The results of the evolution of adsorbed boron at different times are shown in Figures 5.15 – 5.18. These results for boron adsorption at different times, as related to reacted boron and wood types, are valid. Figures 5.15 –5.18 show that there is variation in boron consumption with time in the reaction with Yellow pine, Douglas-fir, Oak and Sapele.

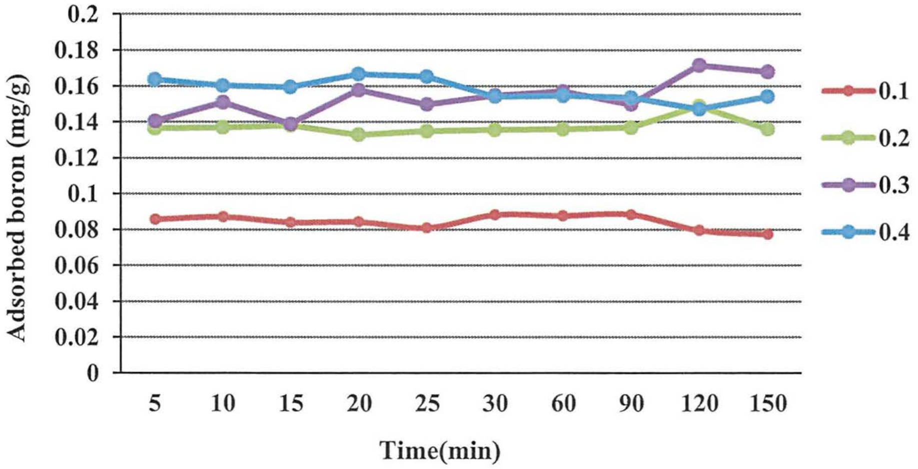

Figure 5.15 Adsorption kinetic curve of adsorbed boron on Yellow pine at different *time* intervals; calculated values are given as mean ± SE ($n = 3$)

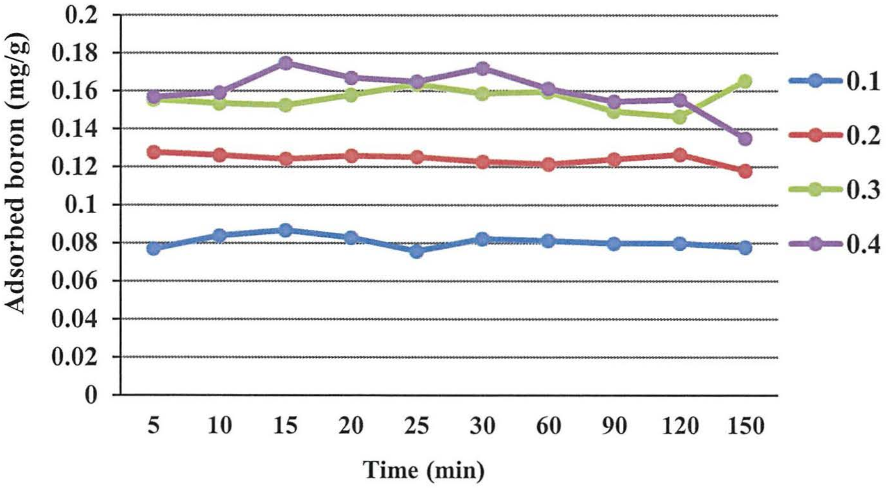

Figure 5.16 Adsorption kinetic curve of adsorbed boron on Douglas-fir at different *time* intervals; calculated values are given as mean ± SE ($n = 3$)

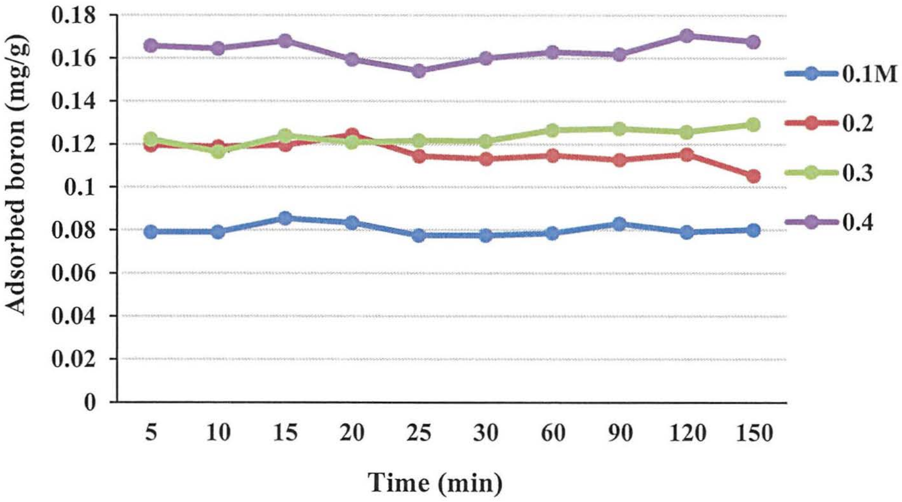

Figure 5.17 Adsorption kinetic curve of adsorbed boron on Sapele at different *time* intervals; calculated values are given as mean ± SE ($n = 3$)

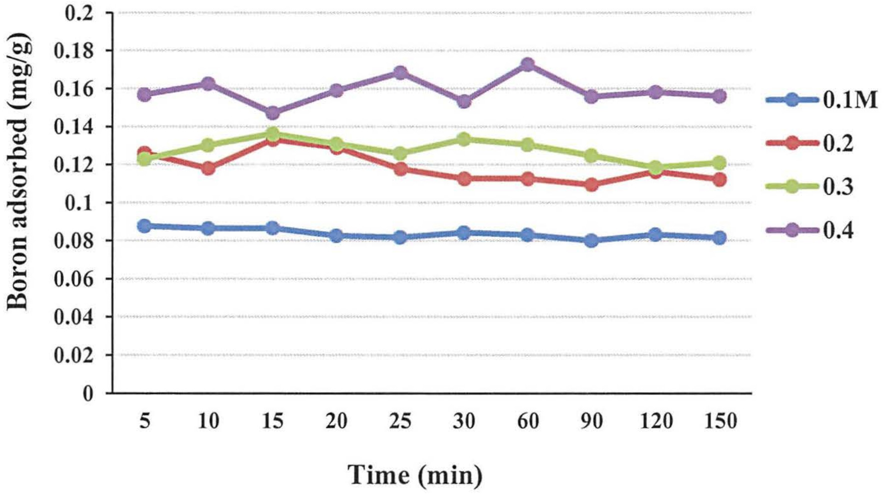

Figure 5.18 Adsorption kinetic curve of adsorbed boron on Oak at different time intervals; calculated values are given as mean ± SE ($n = 3$)

The results showed that 30 min is the reaction time needed to reach the equilibrium in Yellow pine and Douglas-fir wood. In the wood reaction, the equilibrium time is about 30 min. However, Sapele and Oak wood required 90 min to reach equilibrium. This could be related to the required time for boric acid to penetrate the diffusion layers around the wood system, followed by diffusion through the wood pits and, finally, adsorption. This is consistent with previous work.[33]

5.5 Conclusion

Boron adsorption was very similar for Yellow pine, Douglas-fir, Sapele and Oak. The amount of adsorbed boron was small for all wood types compared to the initial concentrations of added boron. The adsorbed boron was highest on Yellow pine, followed by Douglas-fir, Sapele and Oak, respectively. In the majority of the wood types, the adsorbed boron increased with increased boron concentration in the solution. The Freundlich isotherm fit well with the adsorption data for boron compared to the Langmuir isotherm. The highest values for maximum boron adsorption were seen in Yellow pine;

this value correlated with the amount of total boron. Thus, the Freundlich isotherm confirmed that adsorption of boron was a physical process in all the wood types.

It was observed that the boron adsorption data conforms to the pseudo-second-order kinetics model more than to the first-degree kinetics model, as a better correlation ($R^2 = 0.99 \approx 1.0$) was obtained from the second-order reaction than from the second reaction. The adsorption data showed that Yellow pine and Douglas-fir woods reached equilibrium in a shorter time (30 min) than the other two wood types (90 min).

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Chapter 6.

6 General Conclusion and Future Work

6.1 General conclusions

This thesis was divided into four main experiments. The first provides an analysis of some of the chemical and physical properties of Douglas-fir, Yellow pine, Sapele, and Oak wood samples. The properties that were analysed were moisture content (MC %), organic matter (OM %), ash content (AC %), density, and pH. The absorption of boric acid by these wood samples has been studied. The penetration of boric acid was examined using the visual colour method, and the loaded amount of boric acid in all the wood types is described in Chapter 3.

The third part of this study was aimed of determining the ability of boric acid treated woods to retain fire accelerants for forensic purpose and to evaluate the effect of wood type on the absorption of the fire accelerants (petrol, kerosene, and diesel). Forensic analysis of the ignitable liquid traces of fired wood debris was conducted using a GC-MS technique. The ability of unfired wood samples to retain fire accelerants was examined using the same technique, and these results were compared to those of the fired wood samples, as described in Chapter 4.

The final part of the study was conducted to investigate the capacity of the surfaces of Douglas-fir, Yellow pine, Sapele, and Oak wood samples to adsorb boric acid. The transport and rate of the kinetic process of boric acid adsorption by the four wood species were determined by applying the Freundlich and Langmiur adsorption models. The data adsorption of boric acid was evaluated using pseudo-first- and second-order kinetic models, as described in Chapter 5.

The results of the tests of the wood properties showed that Yellow pine (a softwood) has the highest percentage of MC and OMC, followed by Douglas-fir, Oak, and Sapele wood. The dissociation patterns, along with high diffusion porosity, are significant factors that increase the adsorption of liquids within the Yellow pine system compared to the other three species. Furthermore, the high OMC percentage was attributed to the increased amount of organic materials (including cellulose, hemicellulose and extractives) in softwoods (Yellow pine and Douglas-fir) compared to hardwoods (Oak and Sapele). Therefore, softwoods required a higher temperature for thermal decomposition compared to hardwoods.

The results of the ash residue test indicated that Oak was highest, followed by Sapele, Douglas-fir, and Yellow pine wood. One possible reason for this order is the high porosity system of softwood, which increases the availability of required oxygen for the thermal decomposition process. The classification of wood depends on different factors, including their strength and hardness properties, which are directly proportional to wood density; thus, the density measurements indicated that Oak has a higher density than Sapele, Douglas-fir, and Yellow pine. Oak and Sapele are denser than Douglas-fir and Yellow pine and are classified as hardwoods.

The pH of Douglas-fir was highest, followed by Oak, Yellow pine, and Sapele wood. This high pH value can be related to the fact that Douglas-fir wood has more acidic groups and free acid compared to the other three wood types.

The absorption test (gravimetric method) showed that Yellow pine wood has the highest retained quantity of boric acid, followed by Douglas-fir, Sapele, and Oak wood. Moreover, the retention of boric acid increased as the dopant concentration of boric acid was increased, and the applied to all wood types. The retained amount of boric acid was considerably higher in the softwood (Yellow pine and Douglas-fir) than in hardwood (Sapele and Oak wood) samples. On the other hand, the boric acid penetration results indicated that the response of Yellow pine, Douglas-fir, and Sapele wood was positive, as the colour changed to red after adding the colorimetric reagent. The penetration of borate appeared to reach the deep layers of the longitudinal wood section for the latter three wood types. Oak however, showed that the penetration of borate was not deep in the longitudinal section. It appeared to be on the external surface of the wood, across all boric acid concentrations and the penetration of boric acid increased as the added concentration of dopant boric acid solution increased.

The results of thermogravimetric analysis (TGA) concluded that the fire retardant (boric acid 0.4 M) has significant influence on the thermal decomposition of organic materials in yellow pine wood followed by Douglas-Fir, Sapele and Oak wood respectively. The total percent of organic residues (hemicellulose, cellulous, lignin and char) including the process of releasing water vapour was higher in the treated wood described in Chapter 3 samples compared to untreated wood samples across all wood types. The pyrolysis of hemicellulose and cellulose was rapidly decomposed between 300 and 350°C and the thermal decomposition of lignin was performed between 400-550 °C followed by the final stage which is the charring process of the solid residue up to 800 °C across all wood types and untreated and treated wood samples.

The results of the identification of accelerants in the fire debris of wood samples are as follows: a GS/MS technique was able to detect the hydrocarbons components of petroleum distillates (petrol, kerosene, and diesel). The calculated PAR percentages of the petrol, kerosene, and diesel components were determined for all wood types, with fired and unfired samples, and various boric acid dopant treatments. The sample preparation and extraction method described succeeded in providing a better outcome for each selected accelerant under the GC-MS conditions.

Yellow pinewood had the highest total PAR percentage for the petrol, kerosene, and diesel components, followed by Douglas-fir, Sapele, and Oak wood, across fired and unfired wood samples and various boric acid dopant treatments. This result confirmed the findings about the wood properties described in Chapter 3, which suggested that Yellow pine wood has significantly higher MC and OMC values than other wood types. These factors, along with the dissociation patterns and the high diffusion porosity of its wood system, increase its ability to adsorb more liquid compared to the other three wood species.

The calculated total PAR percentages of each accelerant increased significantly as the boric acid treatment concentrations increased across all wood species and for both unburned and burned samples. It is well known that these wood types are treated with boric acid to decrease the bio-decomposition process and reduce their combustibility when a fire begins. The diesel accelerator had the highest total PAR percentage, followed by the kerosene and petrol accelerants, across all wood types for both unfired and fired wood samples.

The comparison of retention time for the selected accelerants indicated that petrol compounds required a shorter time to be detected (10 min) compared to kerosene (30 min) and diesel (45 min) across all wood types. Both diesel and kerosene are classified as heavy accelerants, which require a longer time and higher temperatures to evaporate compared to petrol, which burned more readily. Therefore, the methods of collecting the samples (physical evidence) from fire debris, and the methods of extracting and the analytical technique used play an important role in the forensic analysis. The appropriate selection of these factors can result in a successful analytical outcome that can assist the course of justice. The laboratory analysis described in this study has demonstrated that it can be useful for detecting evidence of arson in selected samples.

The results of the batch experiment (Chapter 5) showed that Yellow pinewood has the highest ability for boric acid adsorption, followed by Douglas-fir, Sapele, and Oak. These results agreed with the findings about the properties of the different wood types in Chapter

3 and the detection of accelerants in Chapter 4. However, the adsorbed boron was small when compared to the initial concentrations of added boric acid. Furthermore, the way that each wood type behaved toward boric acid was similar, as the value of adsorbed boric acid was similar in all four wood species, with Oak absorbing lowest.

The amount of adsorbed boric acid was directly proportional to the initial concentrations of added boric acid solution. The analysis of the different adsorption isotherms indicated that the equilibrium data for adsorbed boric acid across all wood types fit better with the Freundlich isotherm model compared to the Langmuir Equation. It is well known that the Freundlich isotherm describes the physical adsorption of solutes on the surface of the solid phase. Yellow pinewood was shown to have the maximum capacity (K_f) of adsorbed boron, which agreed with the results of the adsorption data. The result of the kinetic studies showed that the pseudo second-order kinetics model was more suitable for the analysis of the boron adsorption data than the first kinetics model. The pseudo second-order Equation showed a higher correlation ($R^2 = 0.99$) for boric acid adsorption compared to the second-order across all wood types and boric acid treatments. The results of the kinetic studies indicated that Yellow pine and Douglas-fir wood required a shorter period (30 min) to reach the equilibrium time compared to the other two wood types (90 min). These times insured saturated samples (softwood and hardwood).

6.2 Future work

Although the present work has met its research aims and demonstrated significant results, it could be further developed in a number of ways based on the findings presented here. Further research is recommended along the following lines:

- The physical and mechanical properties of wood are not completely understood. More detailed tests are needed to determine wood strength, stiffness, hardness, durability, fungal resistance, colour evaluation, water vapour sorption, swelling, and shrinkage in order to better understand the structure of each type of wood. There is great complexity in the chemistry of the components of each of the wood types studied; thus, it would be useful to determine the lignin, cellulose, and hemicellulose content of each selected wood type in order help understand some of the results that were obtained in this study. The evaluation of colour changes using a Konica Minolta CM-2500d surface reflectance spectrophotometer would provide more accurate results compared to the visual inspection method. This was not available to us for these studies.
- All the studies here had a fire exposure of 1 min. It would be useful to determine the residue of each accelerant in each of the four wood types using different times for fire exposure (more than 1 min). It would also be important to investigate the use of an accelerants on different materials treated with boric acid in order to build a database of combustible materials for fire investigators and forensic laboratories.
- Another area for future work is to investigate the adsorption of boric acid by the powdered wood types in order to increase the surface area of the wood materials. This should provide more activity or binding sites and mobility for the boric acid.

Appendix (A)

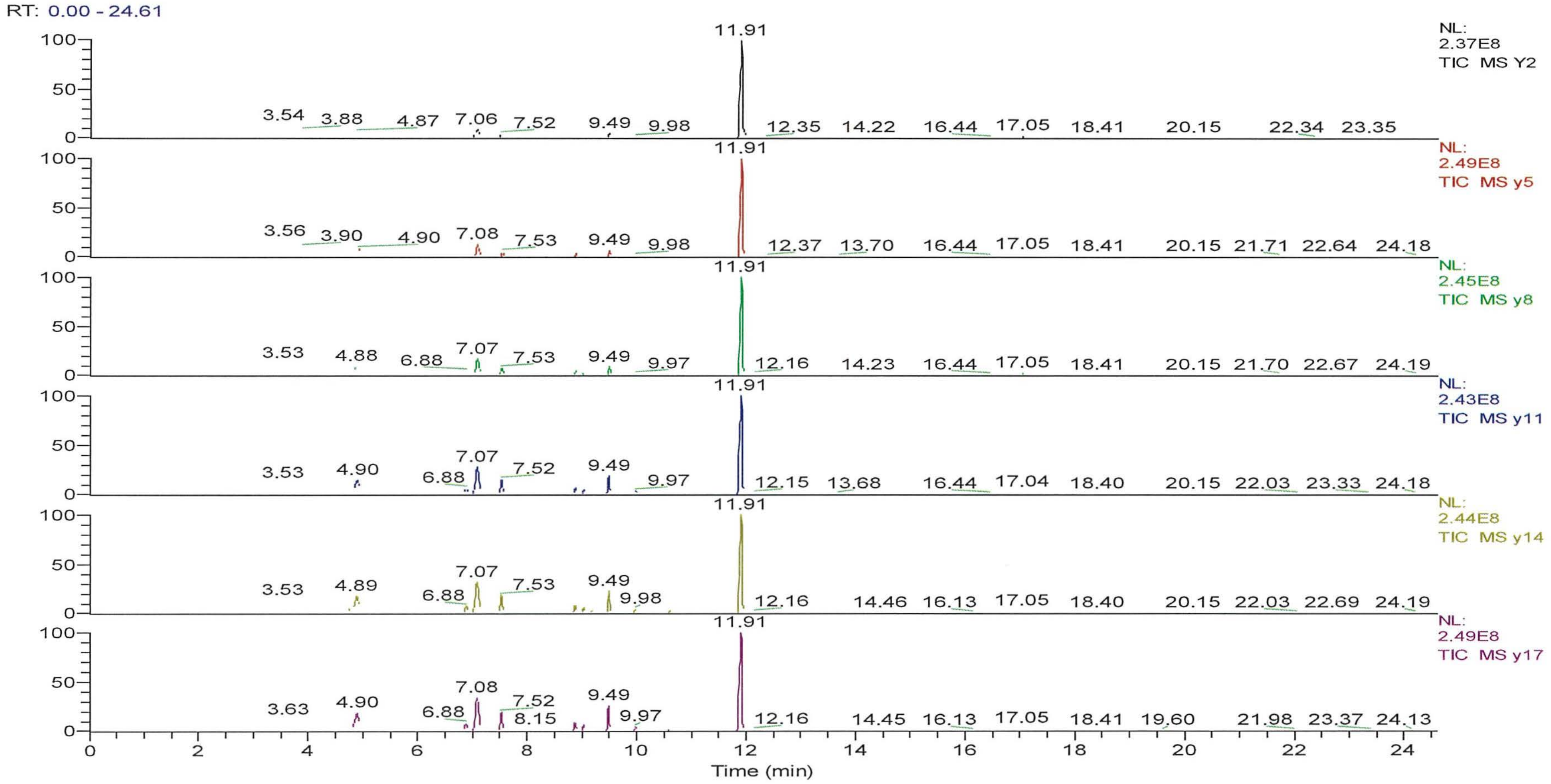

Figure 6.1.A Exemplary GC/MS chromatogram obtained from the residue of unburned Yellow pine samples using petrol fuel as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M.

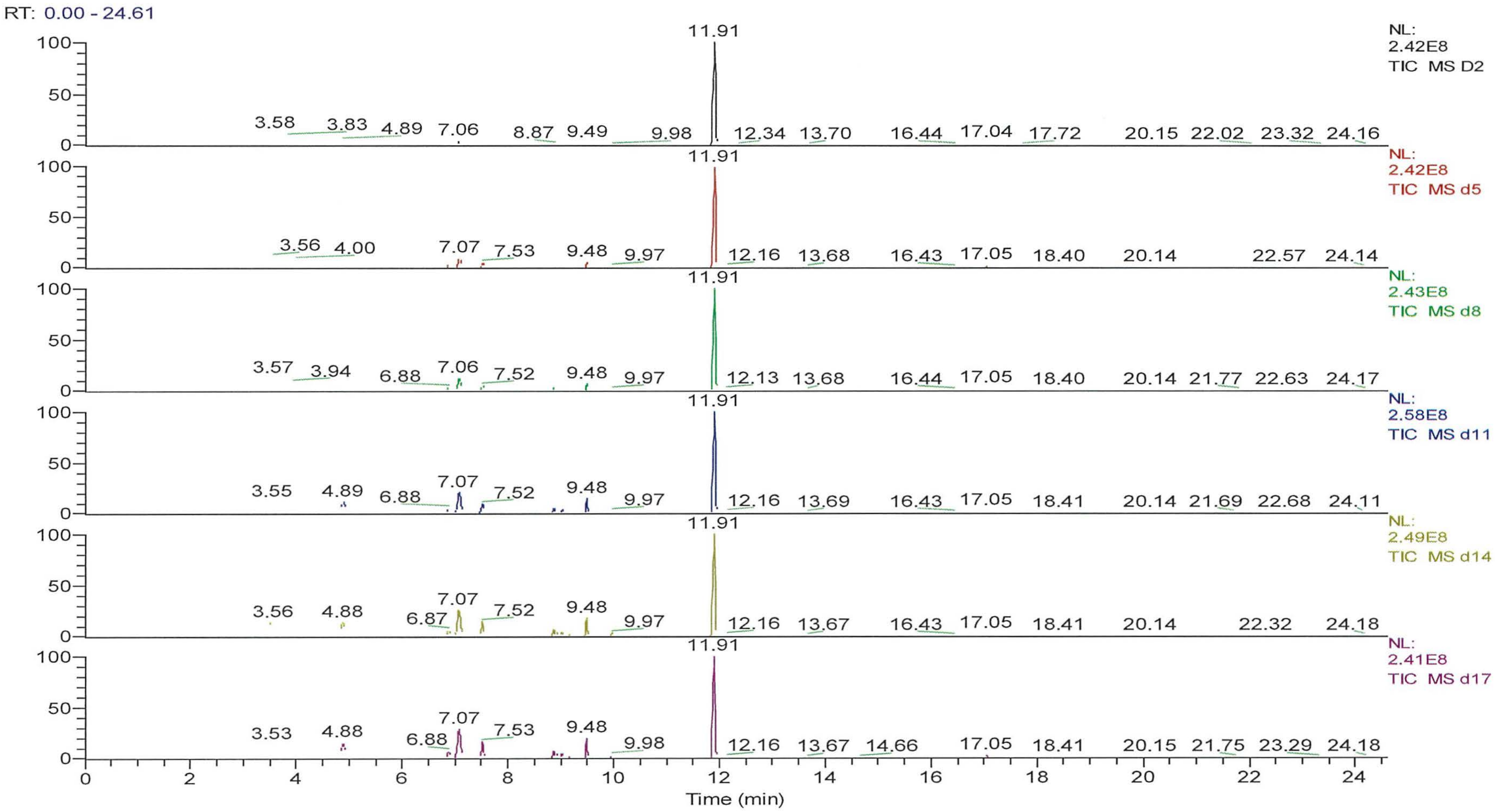

Figure 6.2.A Exemplary GC/MS chromatogram obtained from the residue of unburned Douglas-fir wood samples using petrol fuel as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M.

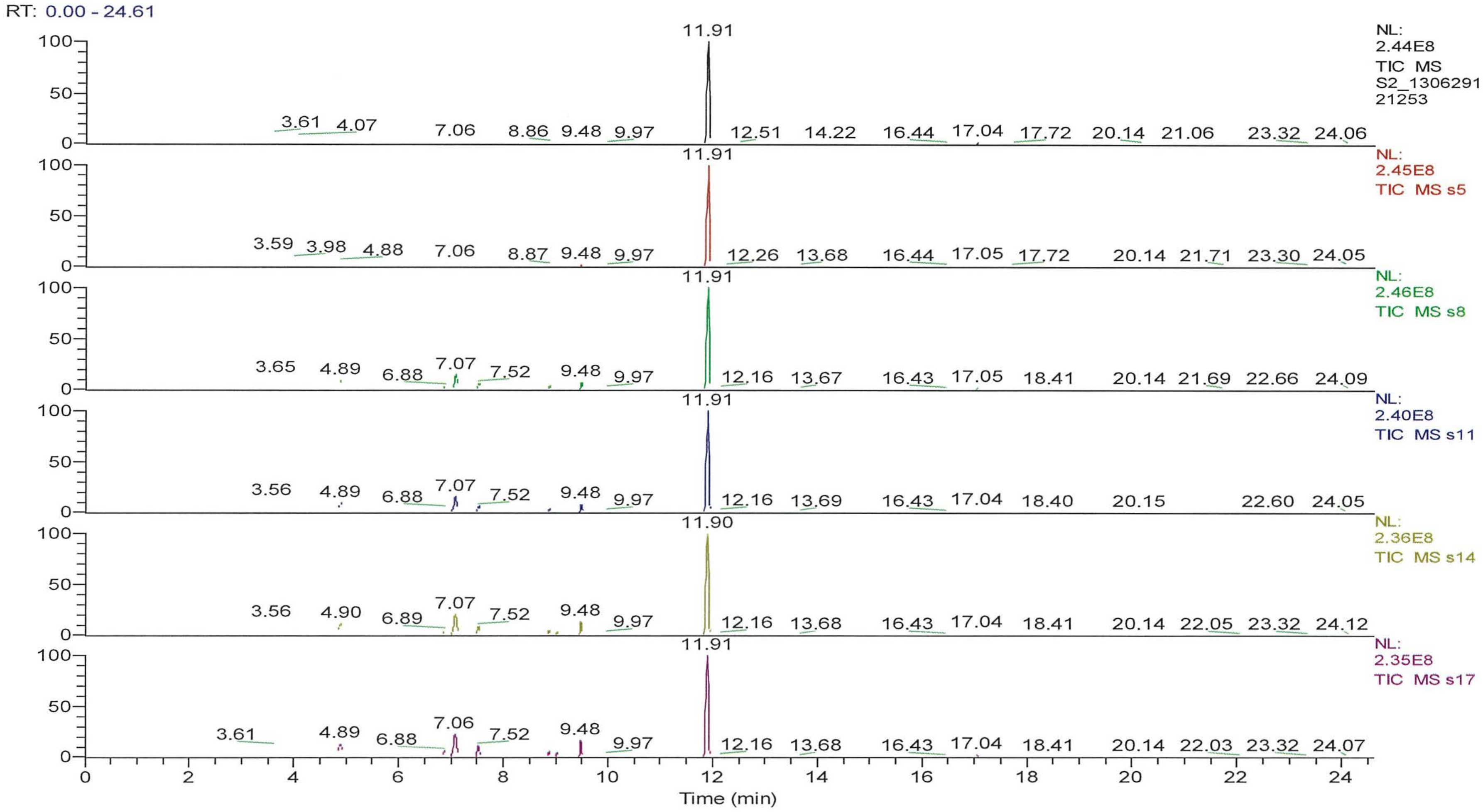

Figure 6.3.A Exemplary GC/MS chromatogram obtained from the residue of unburned Sapele wood samples using petrol fuel as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M.

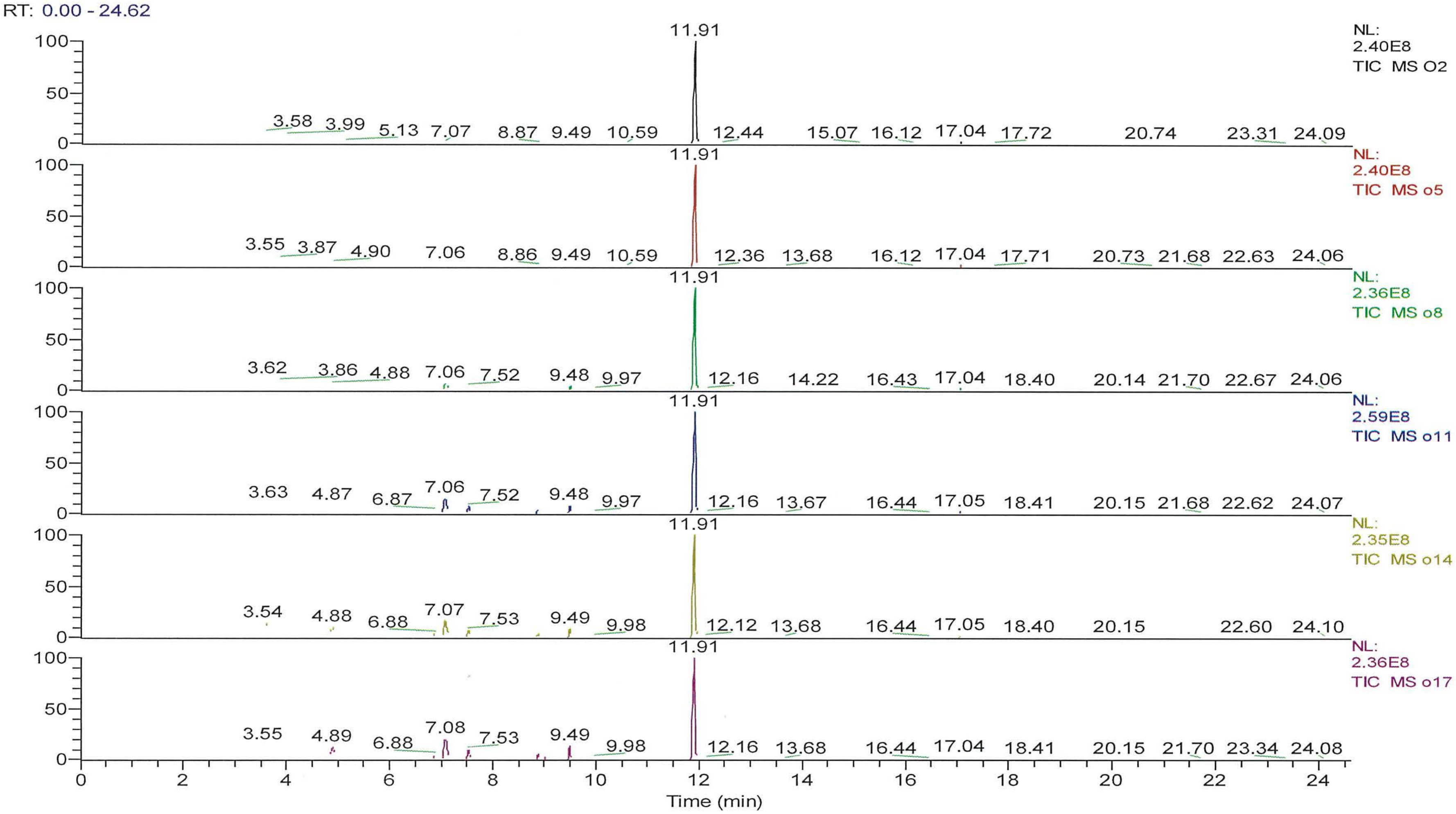

Figure 6.4.A Exemplary GC/MS chromatogram obtained from the residue of unburned Oak wood samples using petrol fuel as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M.

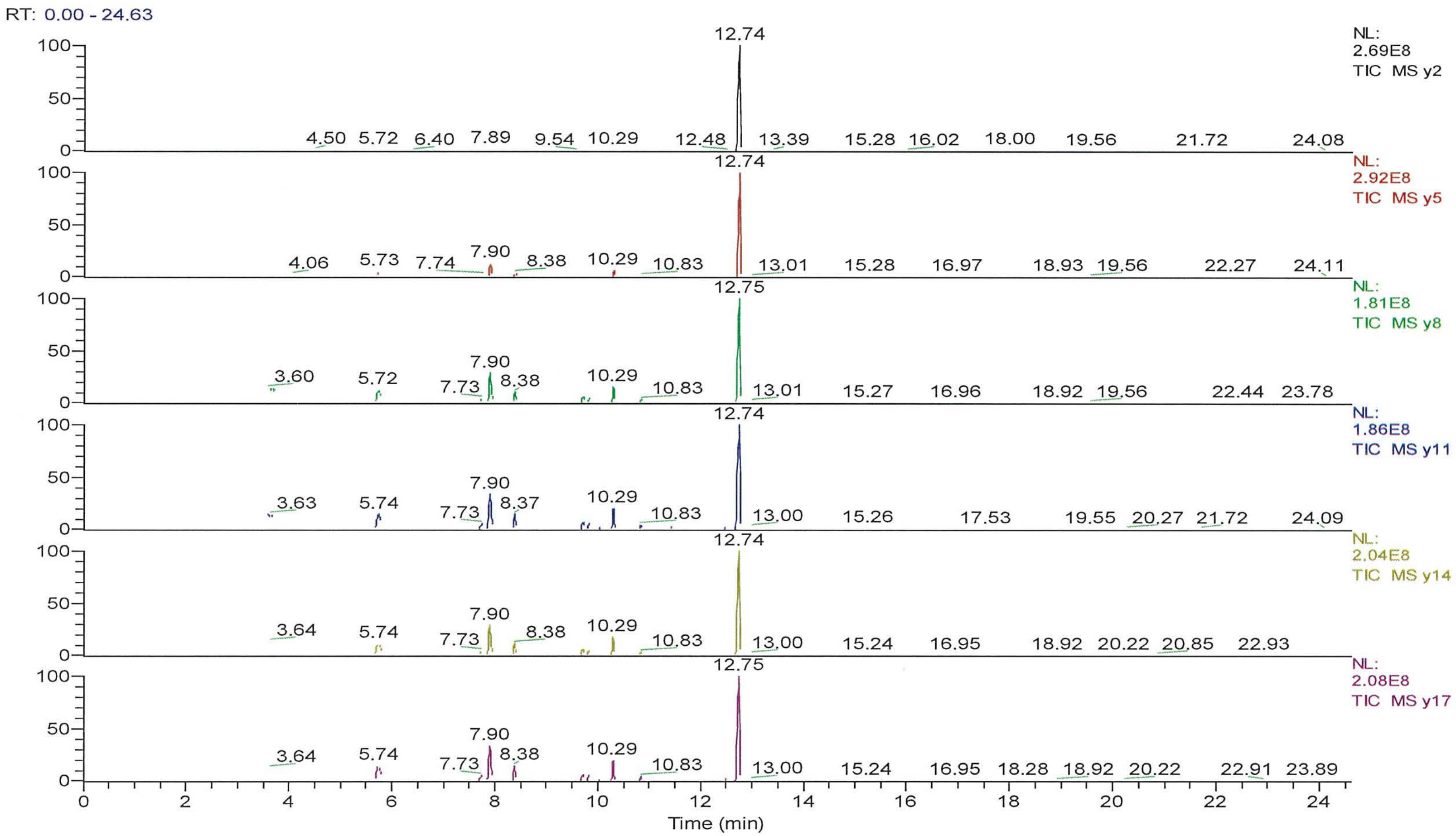

Figure 6.5.A Exemplary GC chromatogram obtained from the fire residue of burned Yellow pine wood samples using petrol fuel as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M.

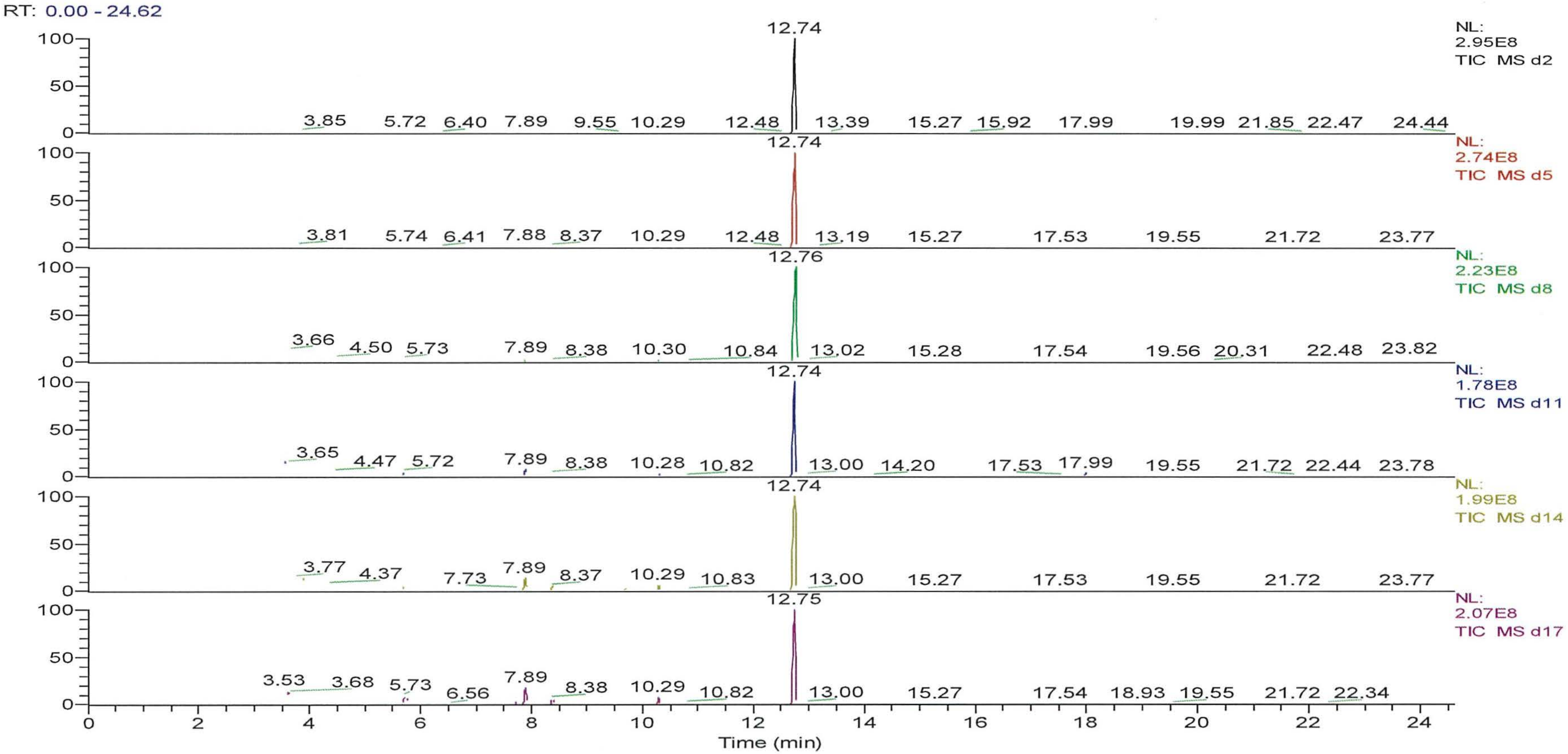

Figure 6.6.A Exemplary GCMS chromatogram obtained from the fire residue of burned Douglas-fir wood samples using petrol fuel as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M.

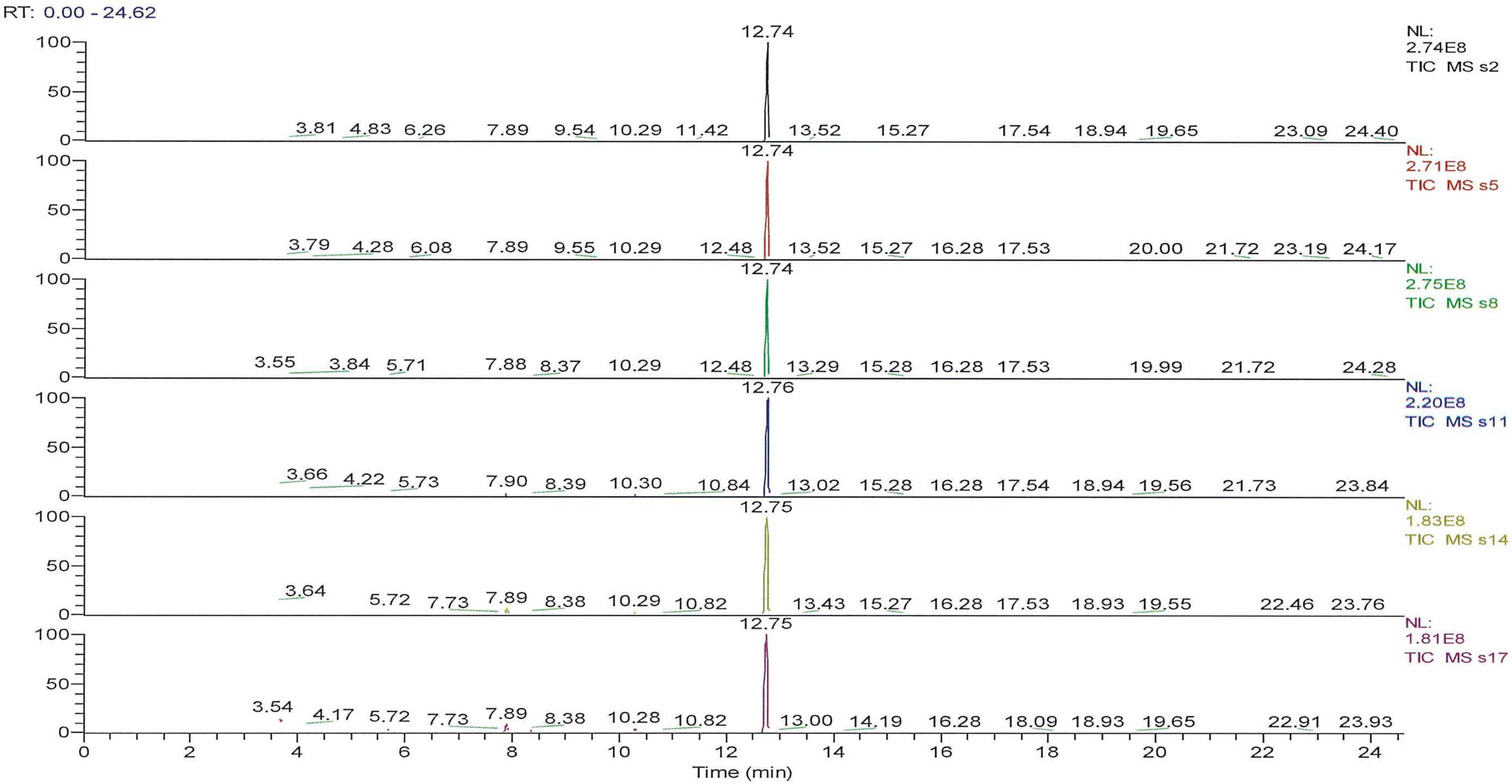

Figure 6.7.A Exemplary GC/MS chromatogram obtained from the fire residue of burned Sapele wood samples using petrol fuel as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M

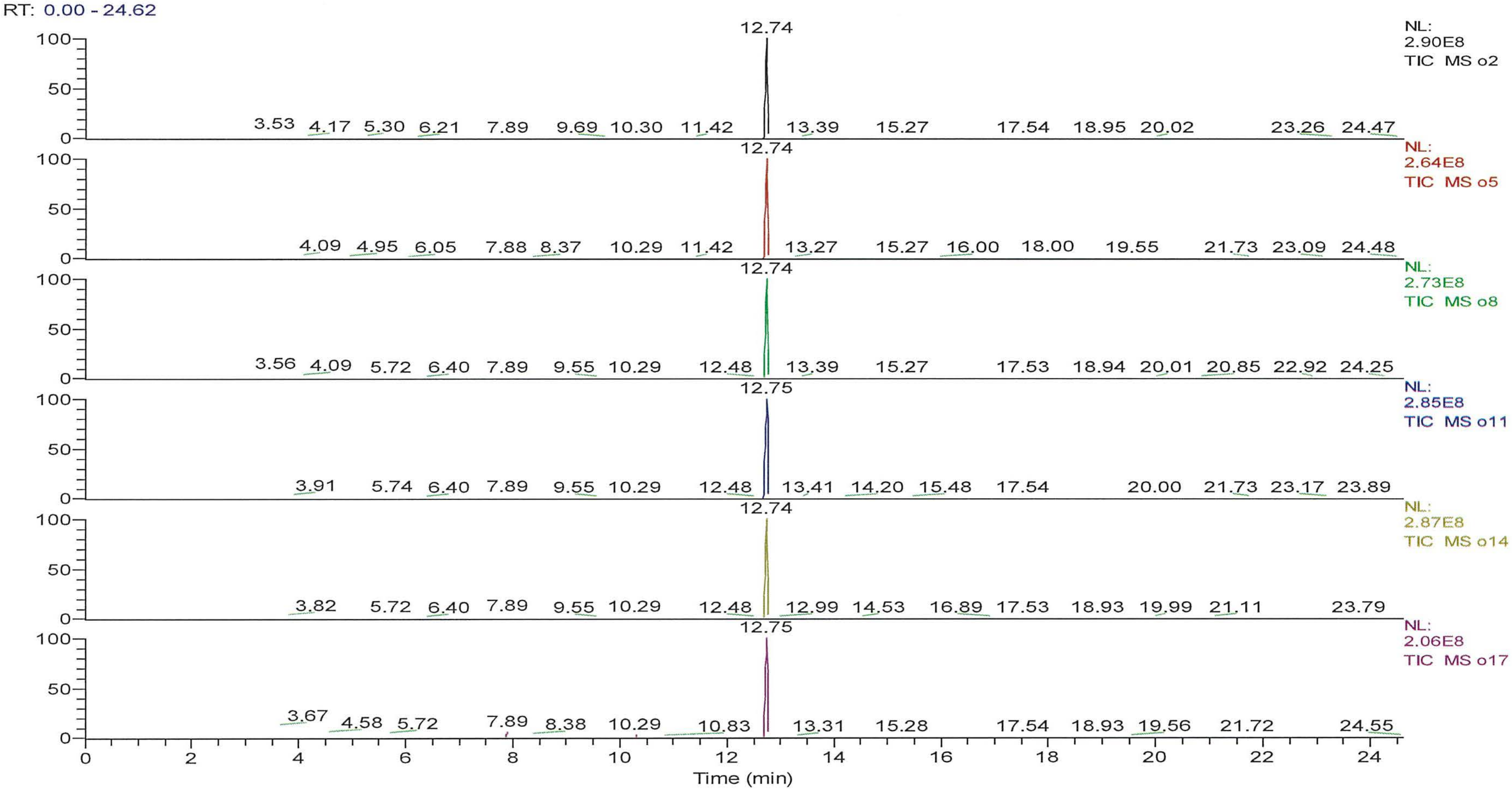

Figure 6.8.A Exemplary GC/MS chromatogram obtained from the fire residue of burned Oak wood samples using petrol fuel as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M.

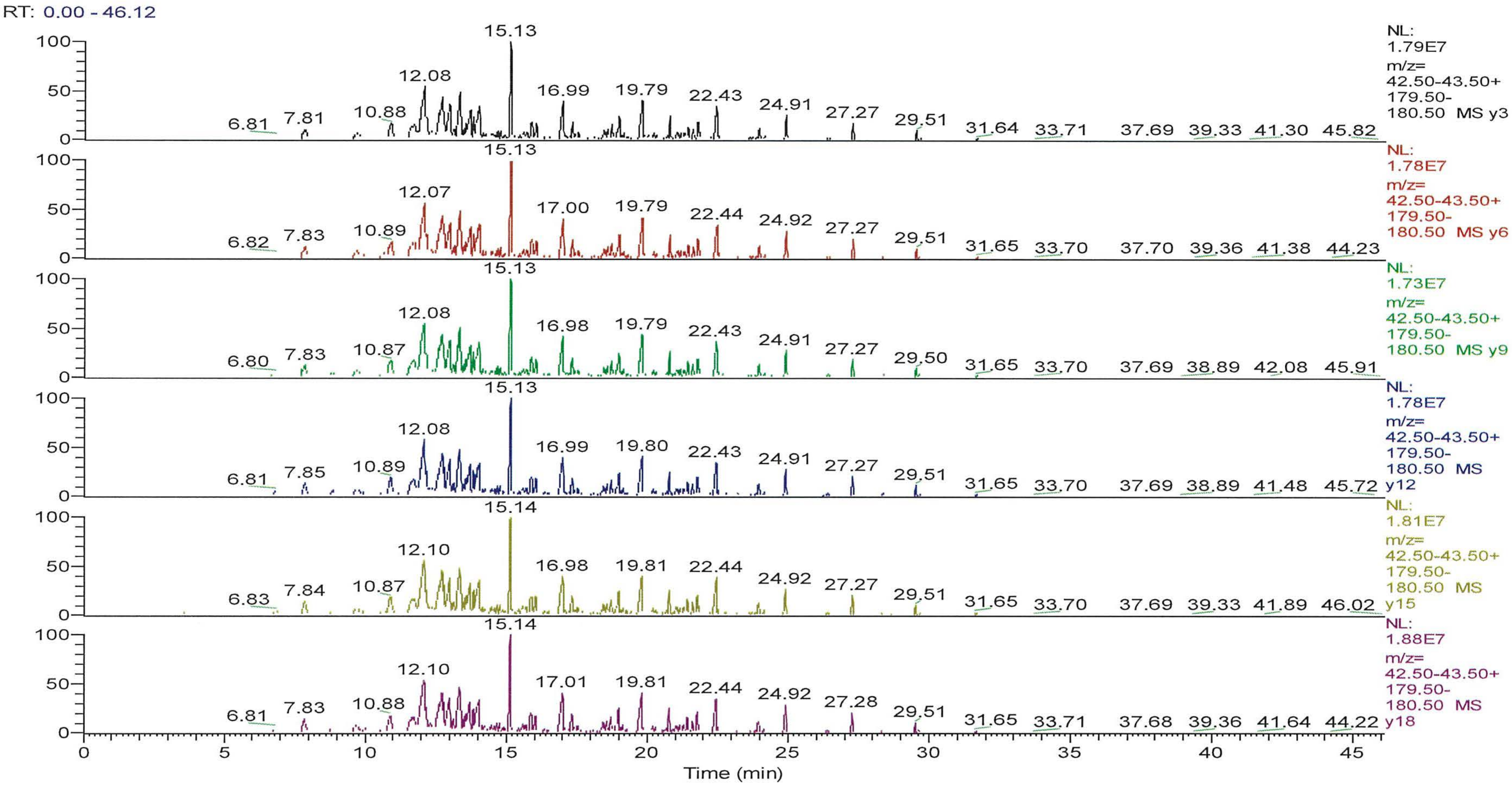

Figure 6.9.A Exemplary GC/MS chromatogram obtained from the residue of unburned Yellow pine wood samples using kerosene as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M.

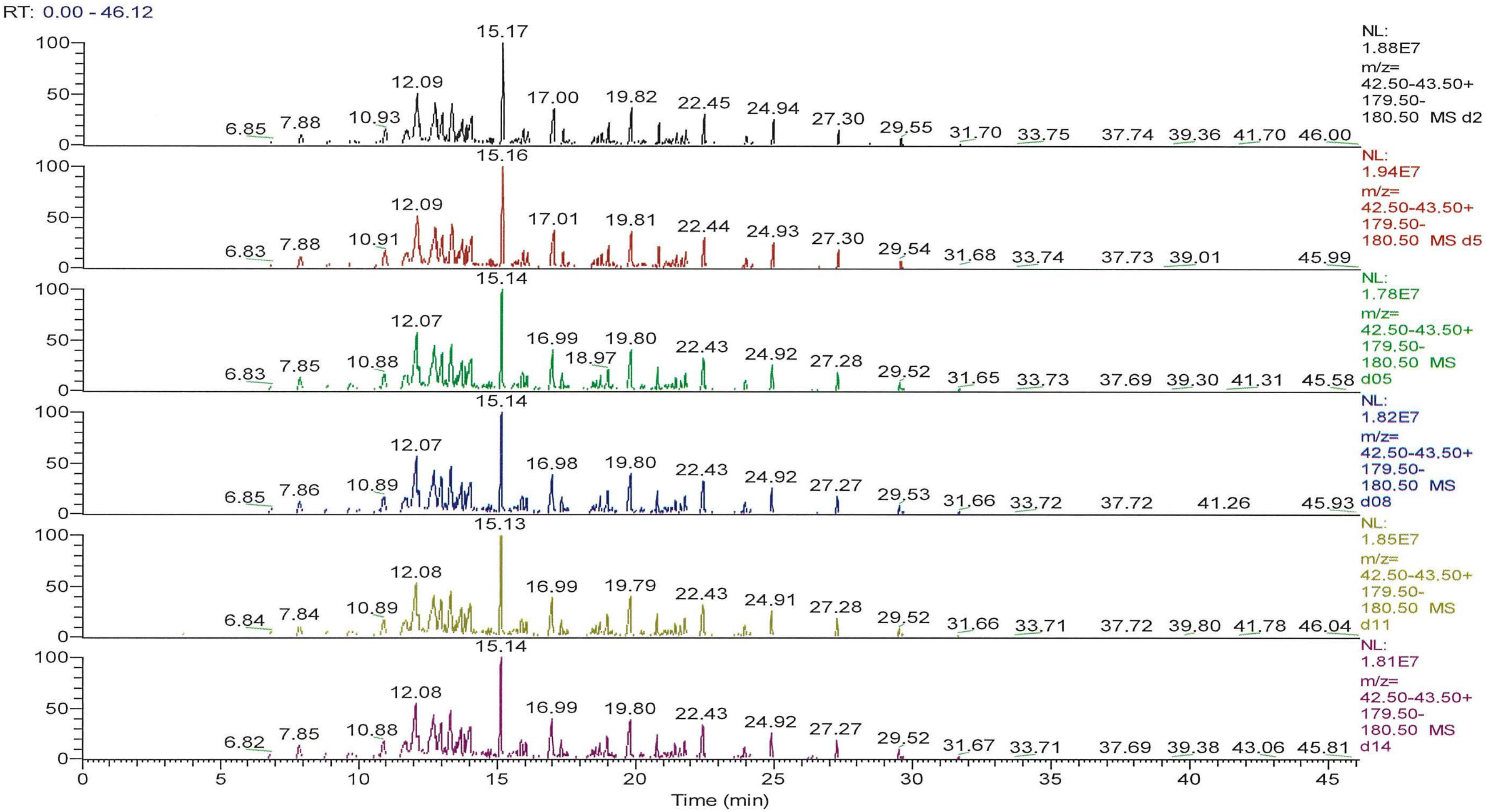

Figure 6.10.A Exemplary GC/MS chromatogram obtained from the residue of unburned Douglas-fir wood samples using kerosene as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M.

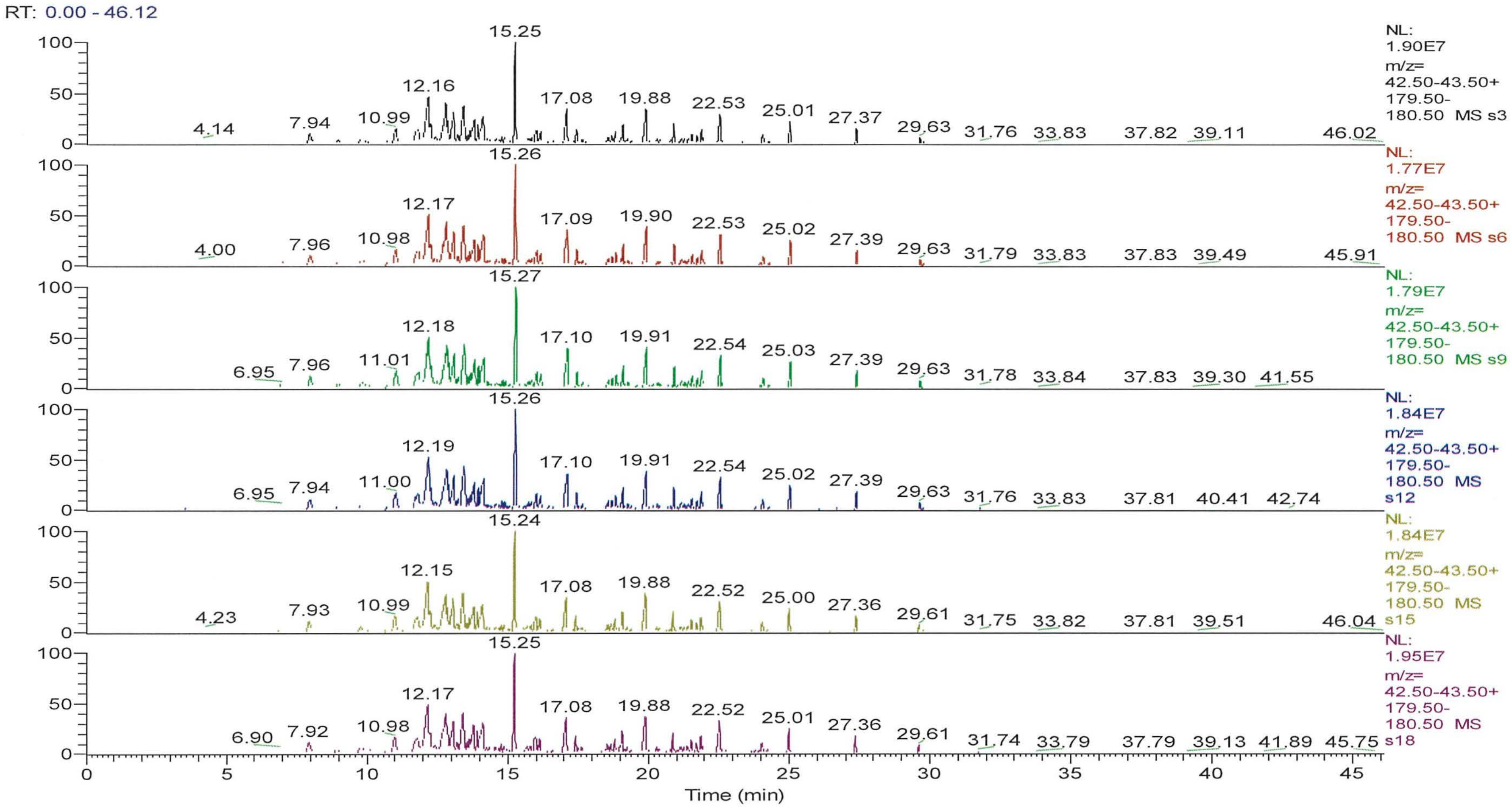

Figure 6.11.A Exemplary GC/MS chromatogram obtained from the residue of unburned Sapele wood samples using kerosene as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M.

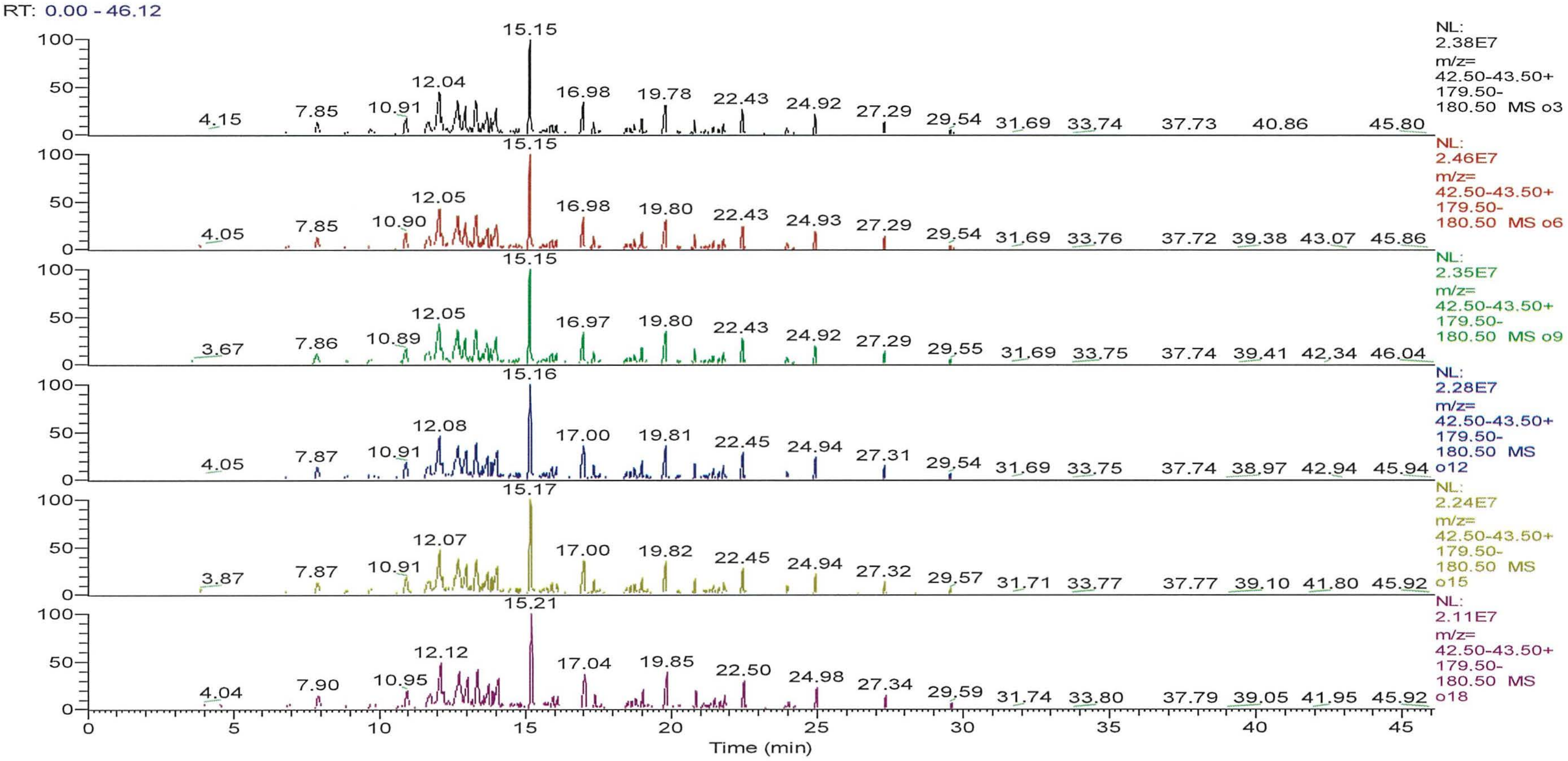

Figure 6.12.A Exemplary GC/MS chromatogram obtained from the residue of unburned Oak wood samples using kerosene as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M.

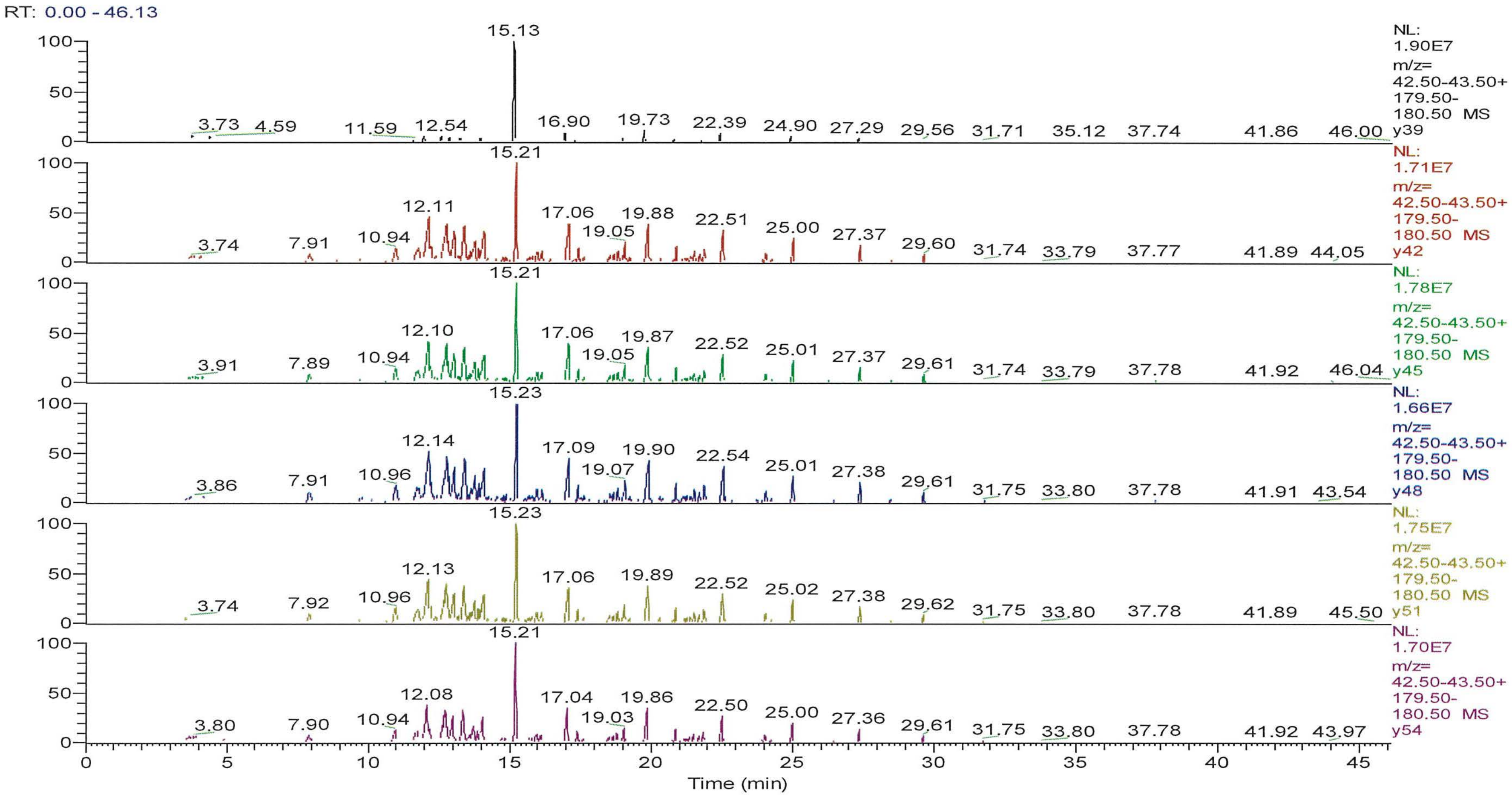

Figure 6.13.A Exemplary GC/MS chromatogram obtained from the residue of burned Yellow pine wood samples using kerosene as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M.

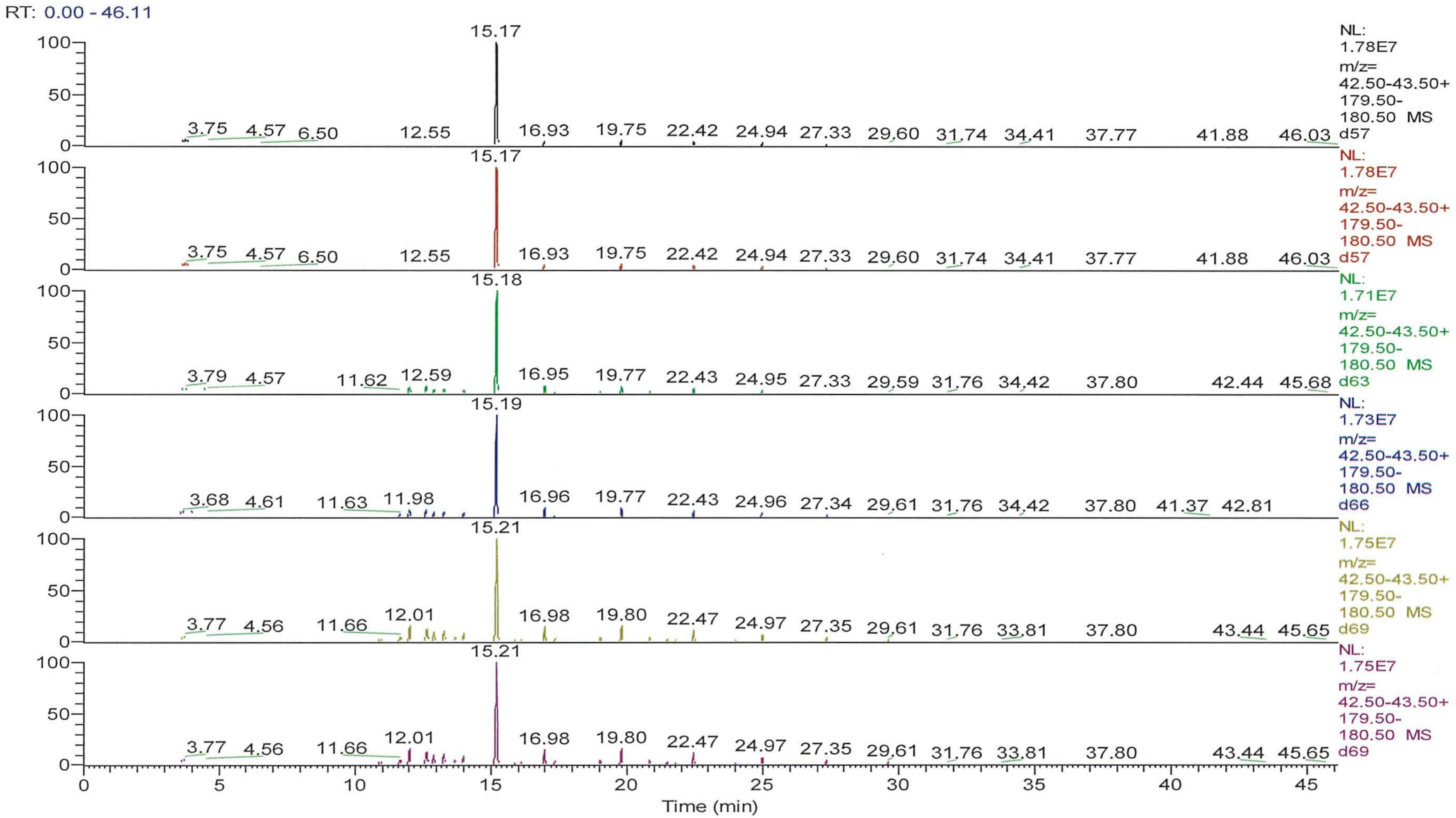

Figure 6.14.A Exemplary GC/MS chromatogram obtained from the residue of burned Douglas-fir wood samples using kerosene as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M.

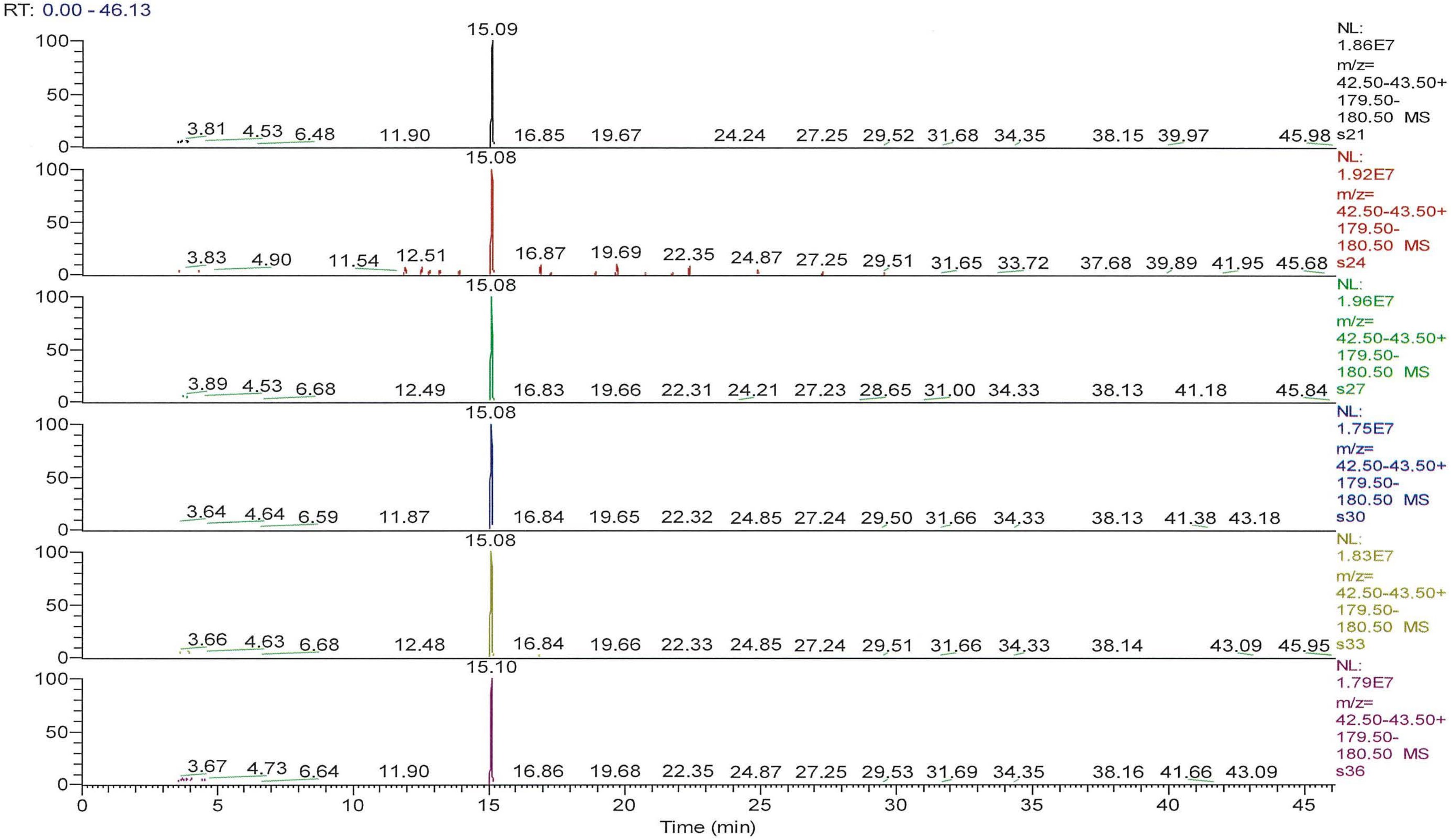

Figure 6.15.A Exemplary GC/MS chromatogram obtained from the residue of burned Sapele wood samples using kerosene as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M

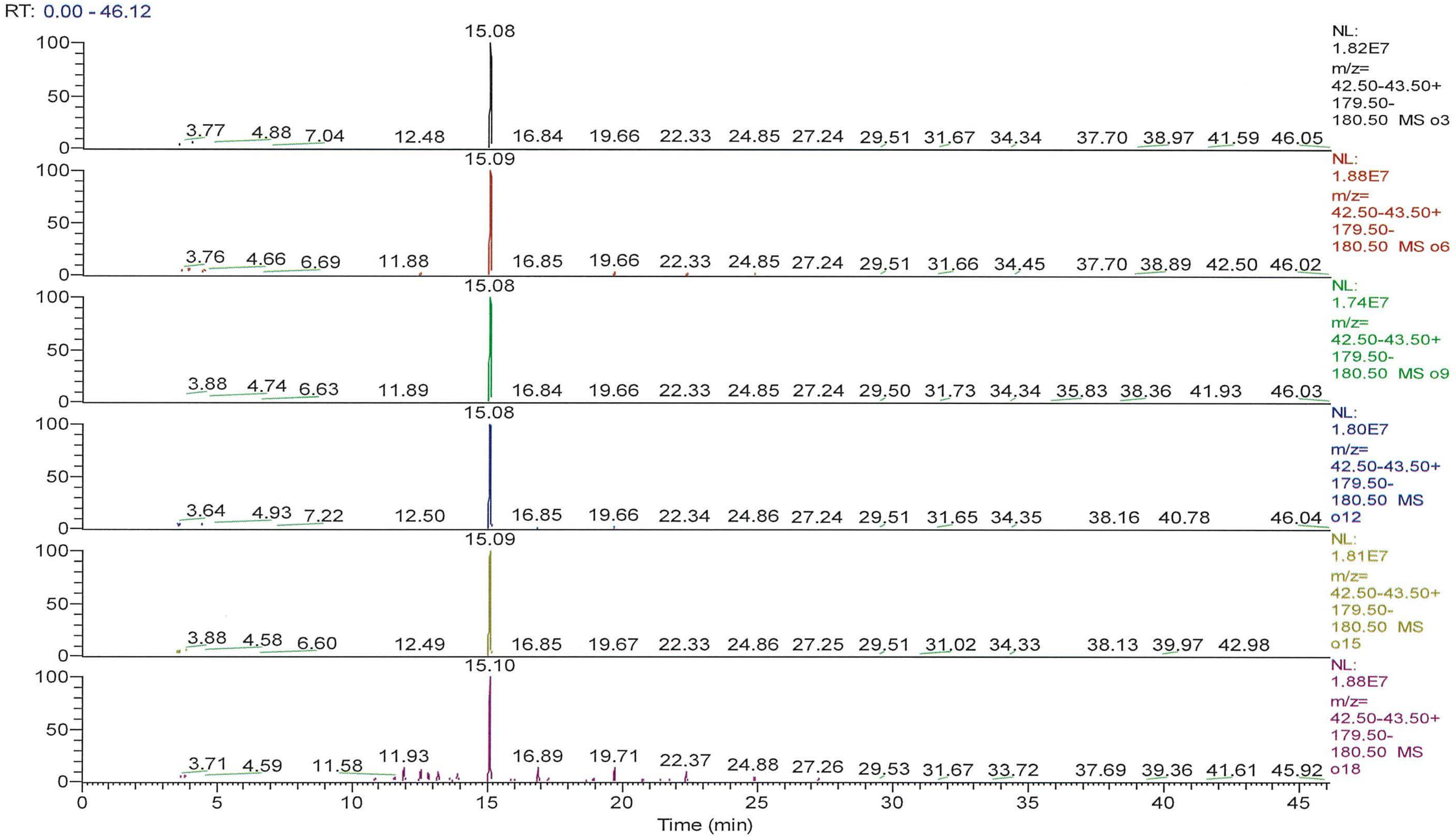

Figure 6.16.A Exemplary GC/MS chromatogram obtained from the residue of burned Oak wood samples using kerosene as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M

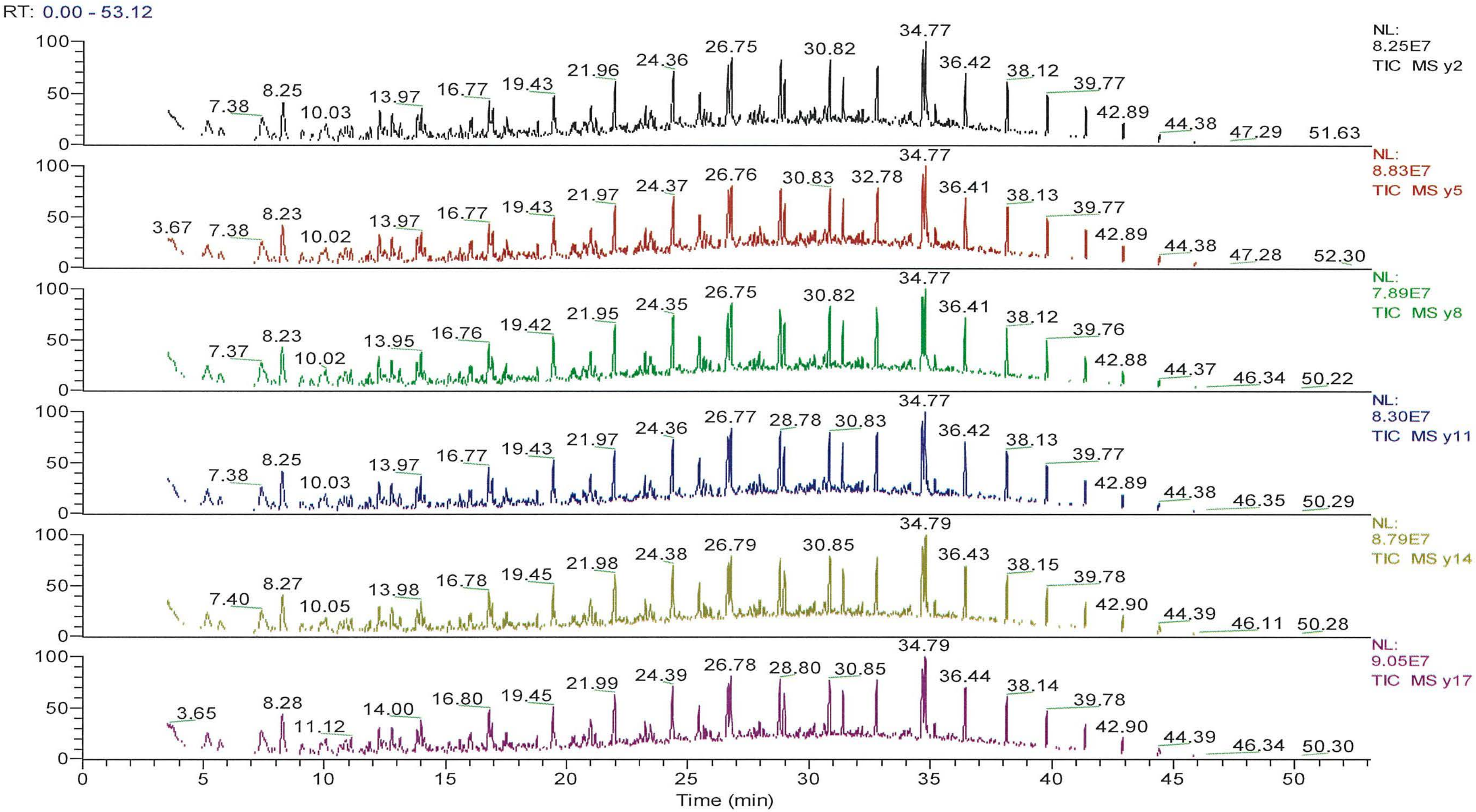

Figure 6.17.A samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M.

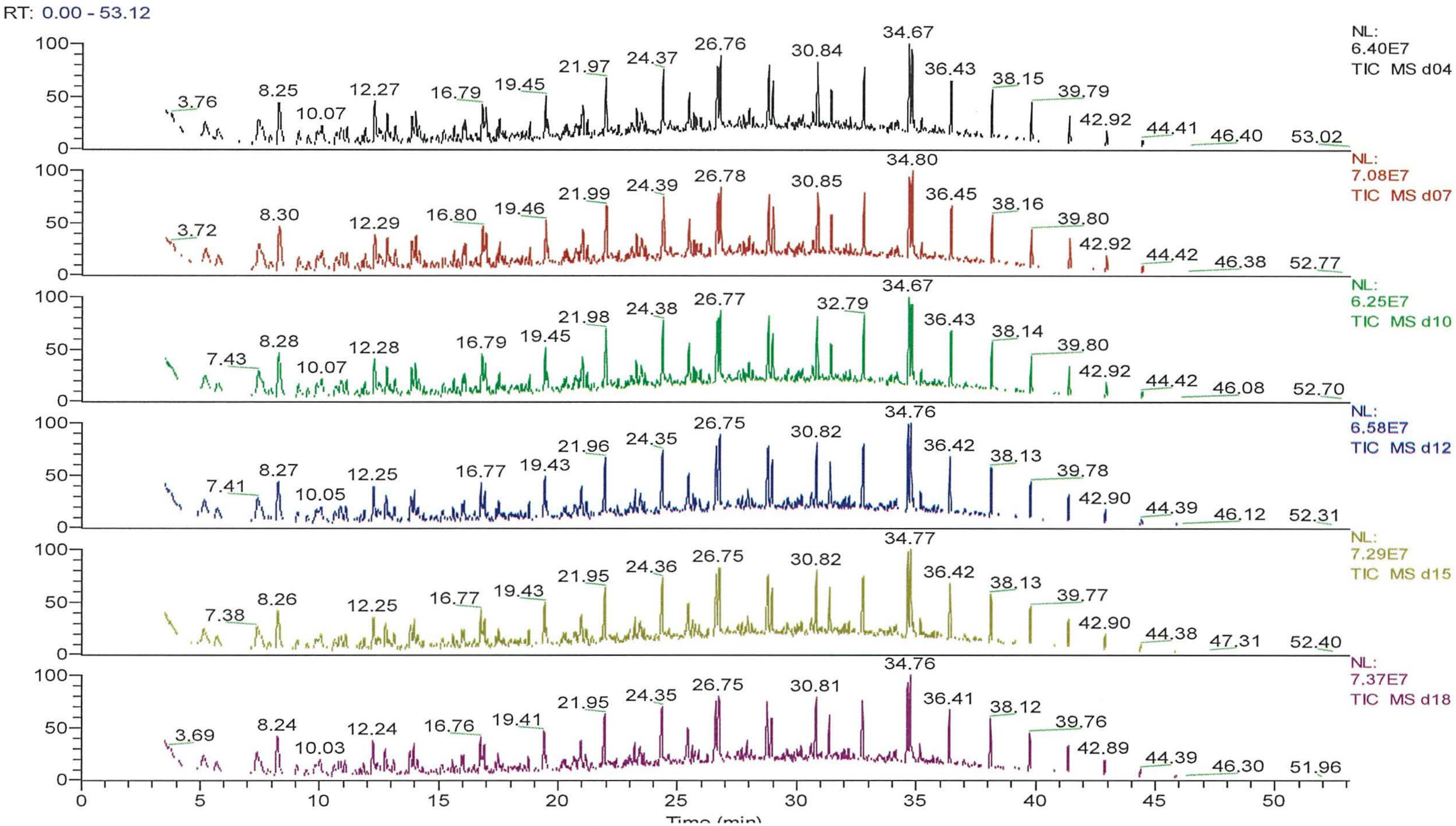

Figure 6.19.A Exemplary GC/MS chromatogram obtained from the residue of unburned Douglas-fir wood samples using diesel as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M.

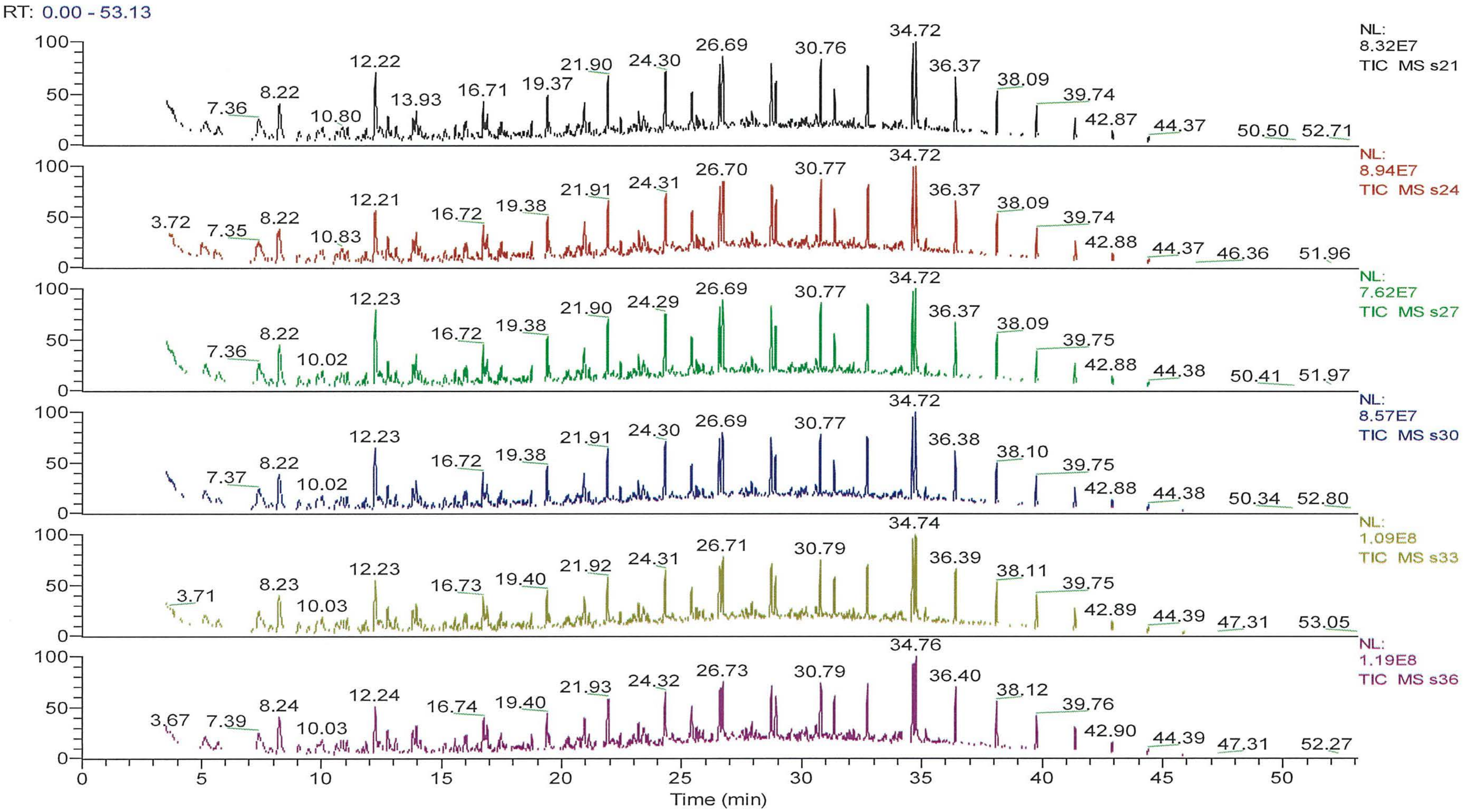

Figure 6.20.A Exemplary GC chromatogram obtained from the residue of unburned Sapele wood samples using diesel as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M

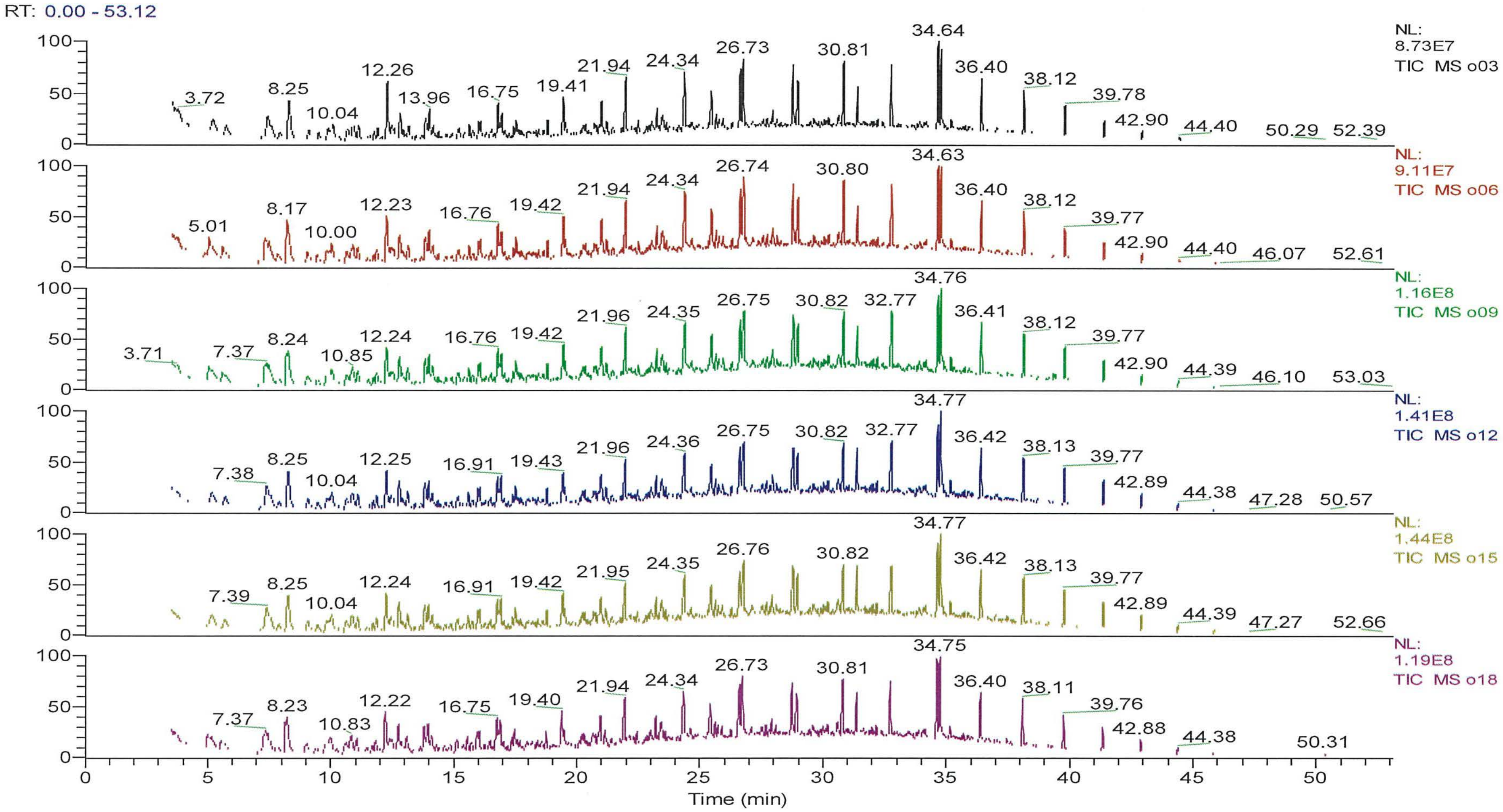

Figure 6.21.A Exemplary GC/MS chromatogram obtained from the residue of unburned Oak wood samples using diesel as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M

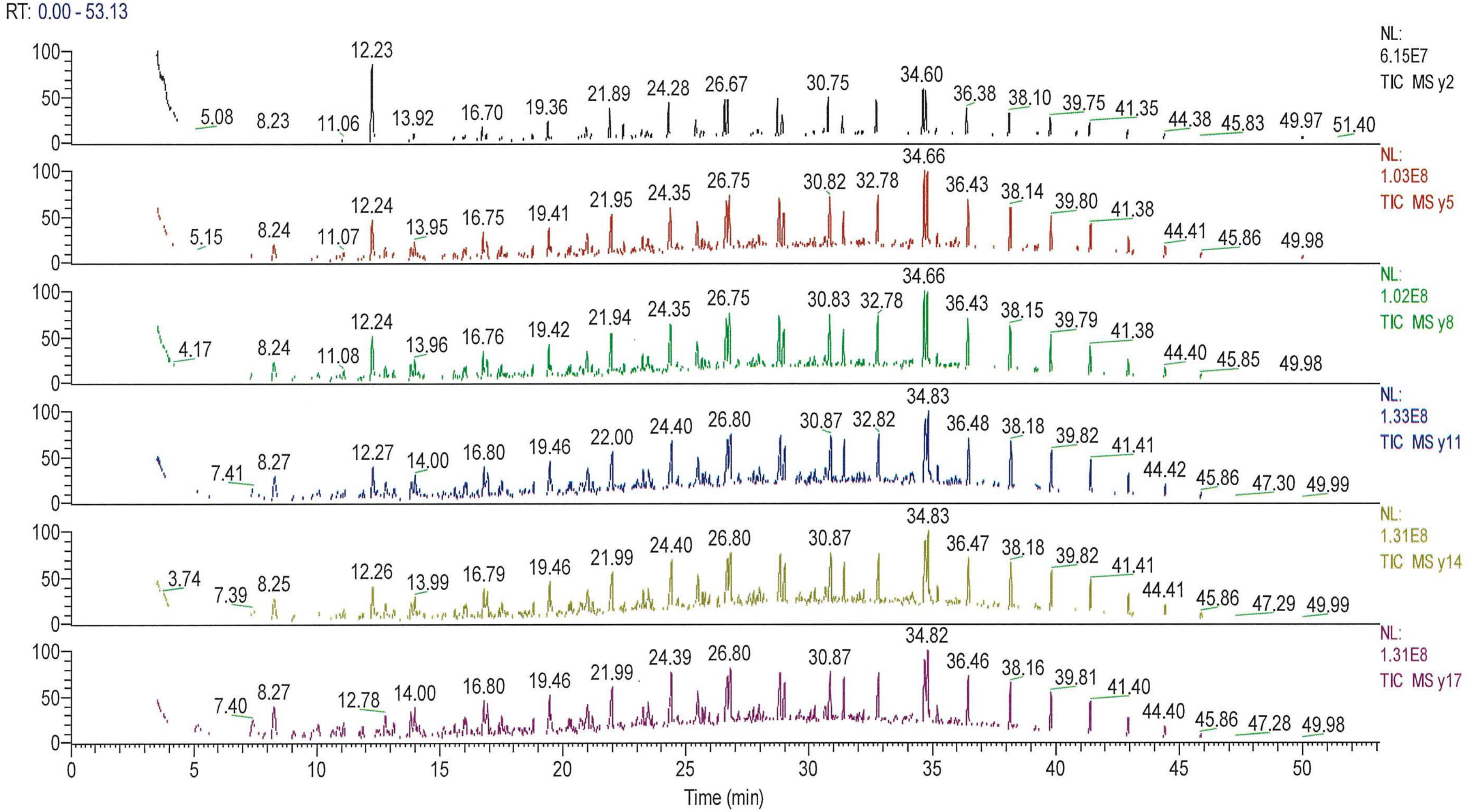

Figure 6.22.A Exemplary GC chromatogram obtained from the residue of burned Yellow pine wood samples using diesel as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M.

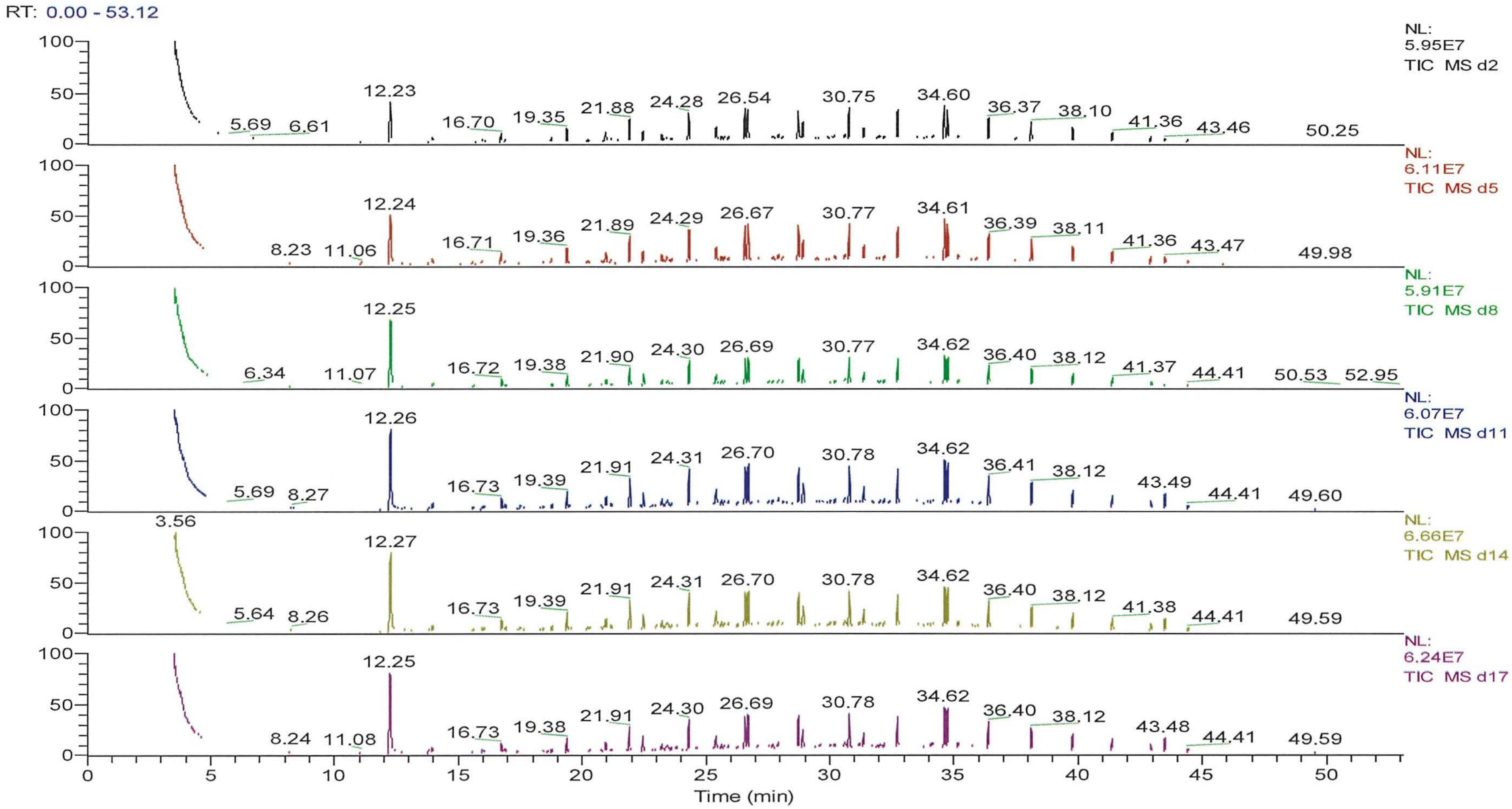

Figure 6.23.A Exemplary GC/MS chromatogram obtained from the residue of burned Douglas-fir wood samples using diesel as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M.

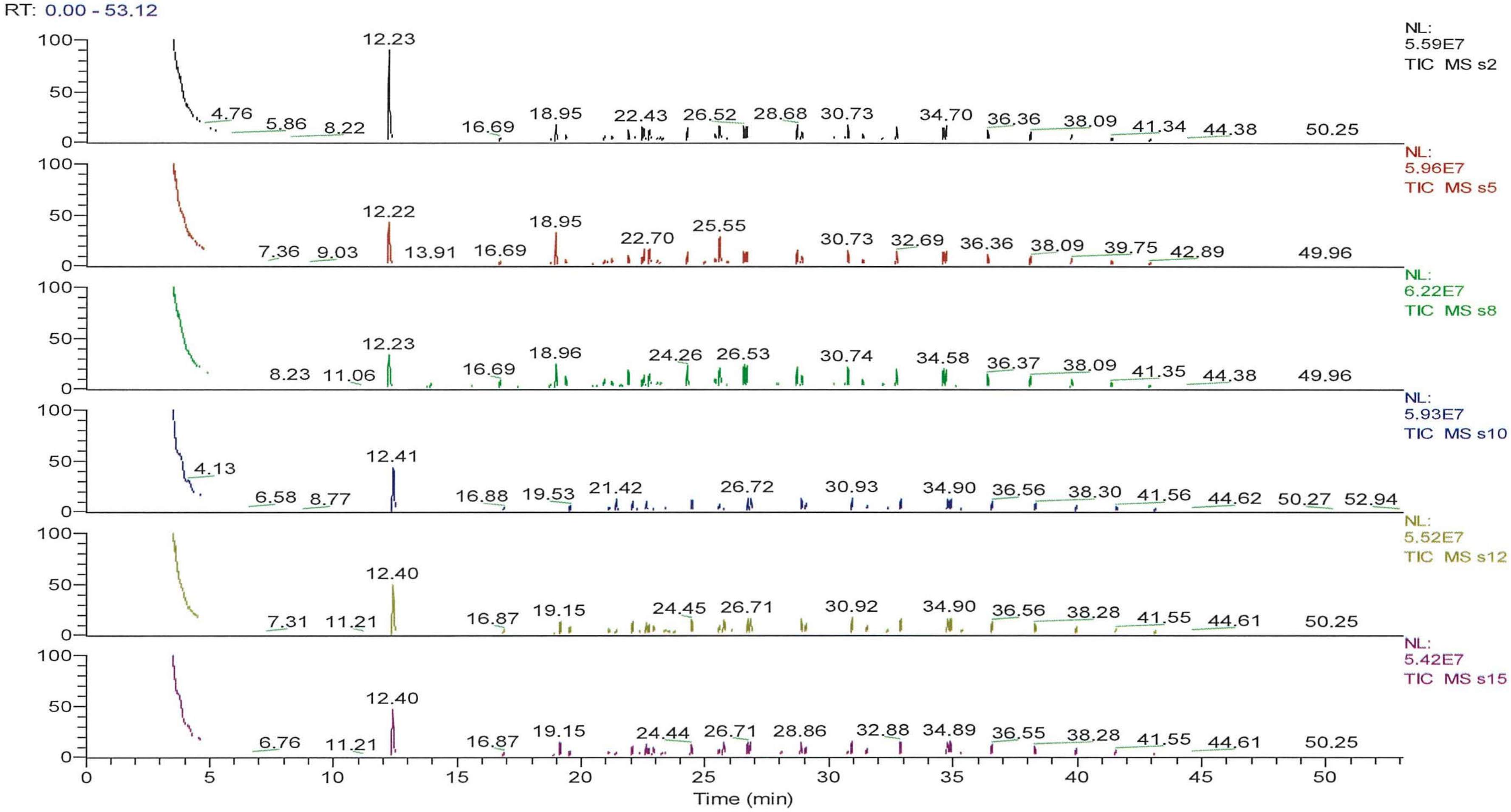

Figure 6.24.A Exemplary GC/MS chromatogram obtained from the residue of burned Sapele wood samples using diesel as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M

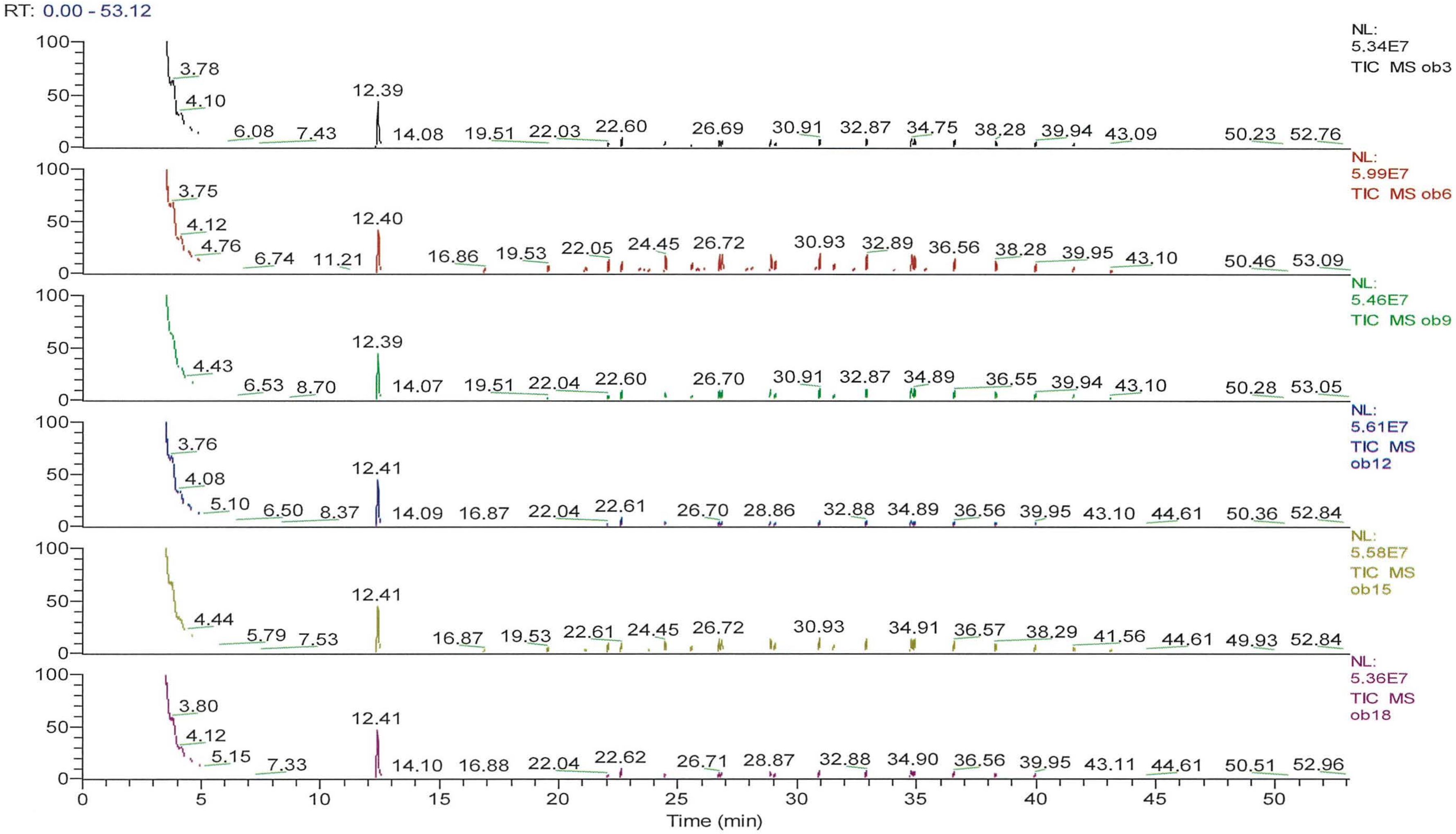

Figure 6.25.A Exemplary GC chromatogram obtained from the residue of burned Oak wood samples using diesel as an accelerant. The wood samples were treated with different concentrations of boric acid; (1) control sample; (2) solvent (distilled water); (3) 0.1 M; (4) 0.2 M; (5) 0.3 M; and (6) 0.4 M.

Appendix (B)

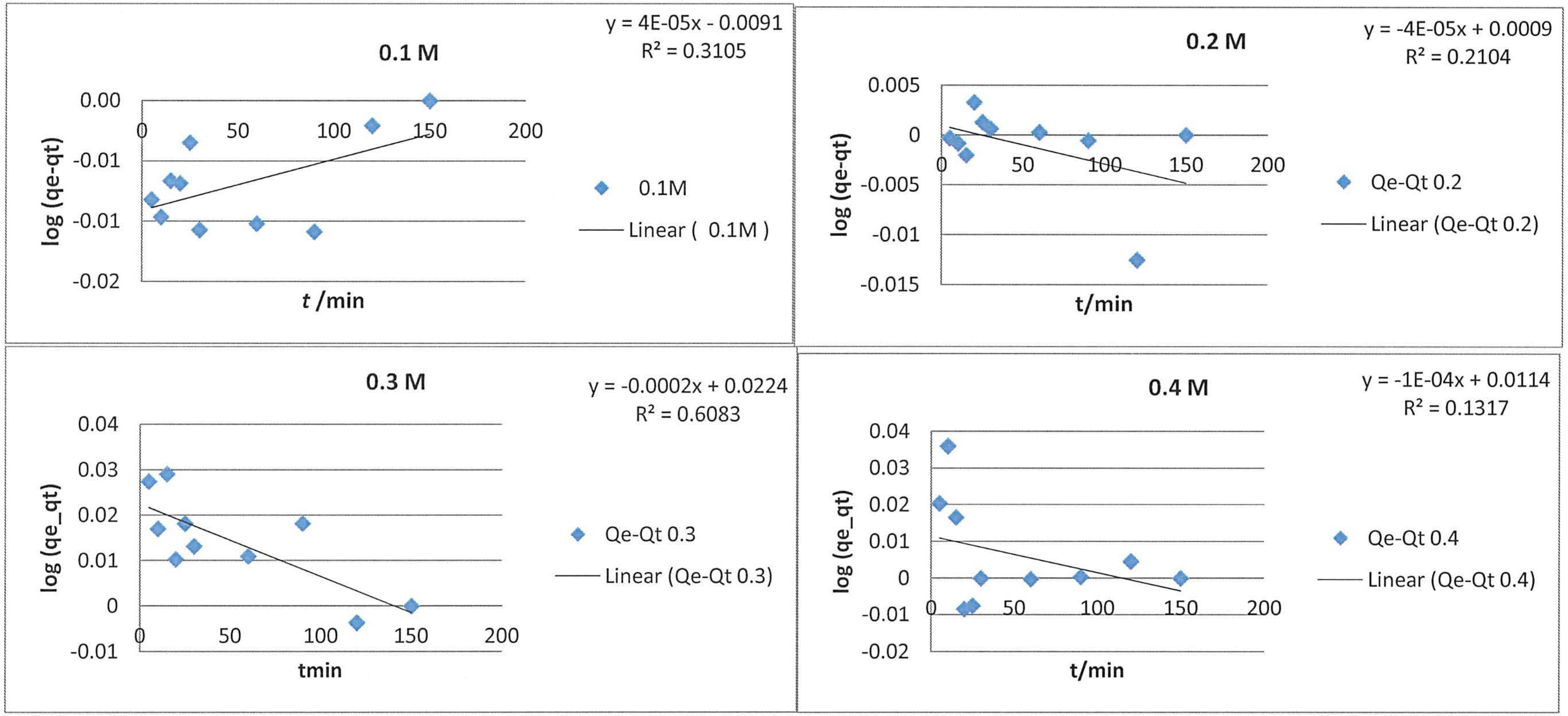

Figure 6.26.B Plots of pseudo first–order reaction for boron adsorption on Yellow pine wood treated with different concentrations of boric acid (0.1, 0.2, 0.3 and 0.4 B Ml).

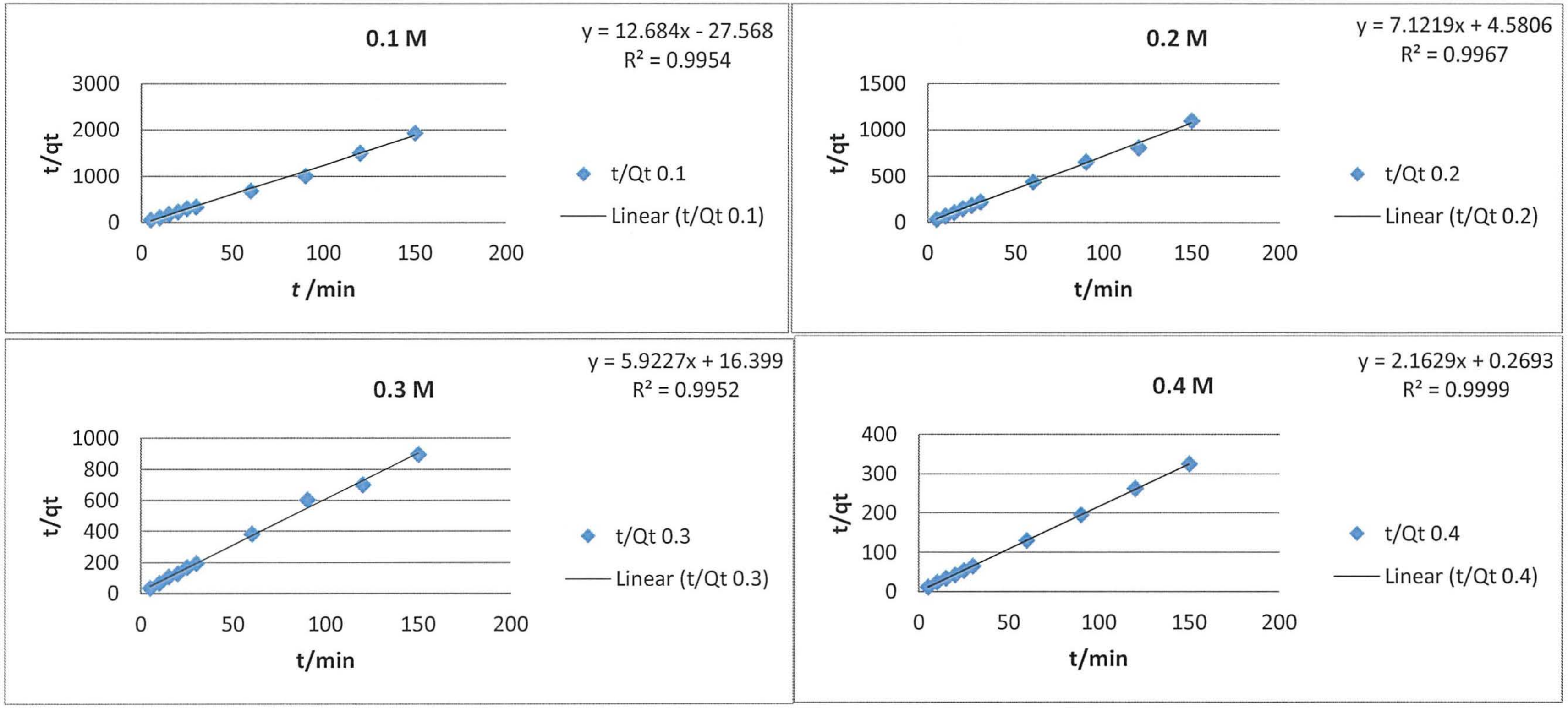

Figure 6.27.B Plots of pseudo second–order reaction for boron adsorption on Yellow pine wood treated with different concentrations of boric acid (0.1, 0.2, 0.3 and 0.4 B Ml).

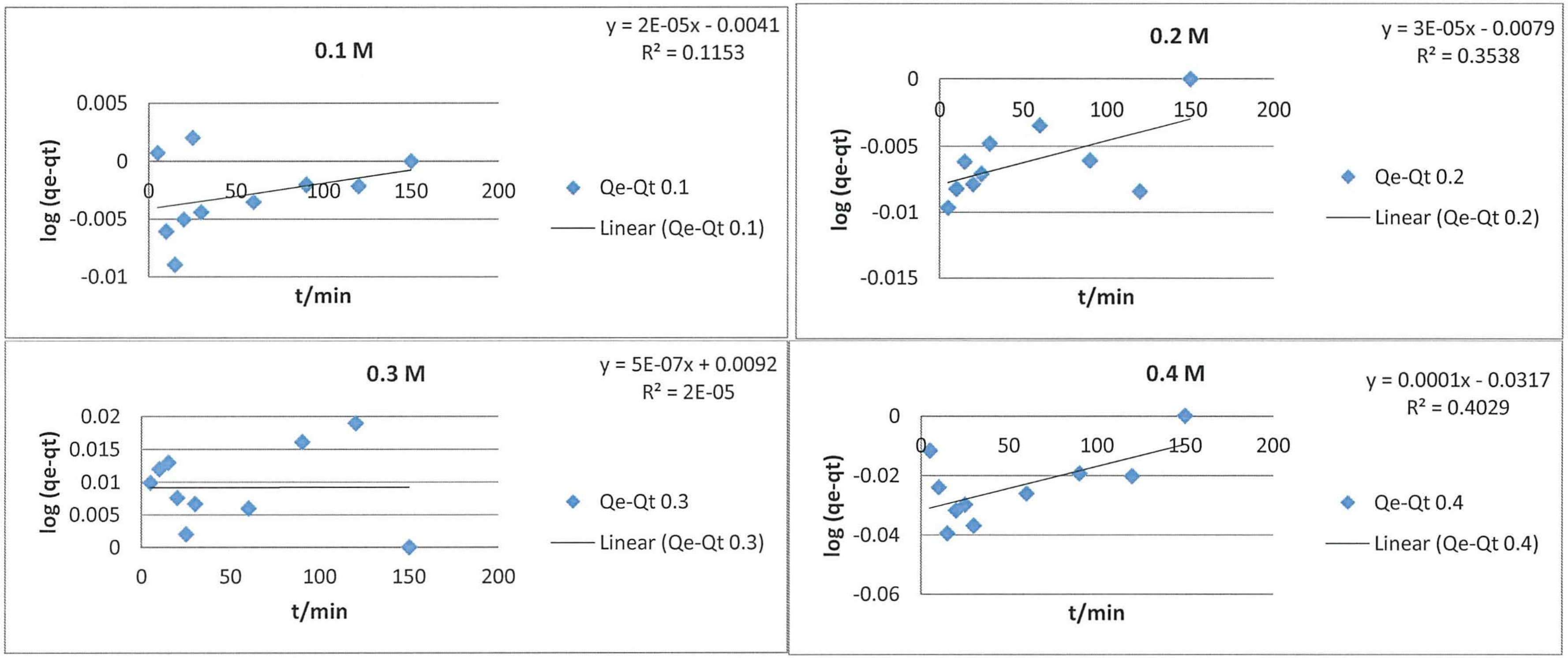

Figure 6.28.B Plots of pseudo first–order reaction for boron adsorption on Douglas–fir wood treated with different concentrations of boric acid (0.1, 0.2, 0.3 and 0.4 B Ml).

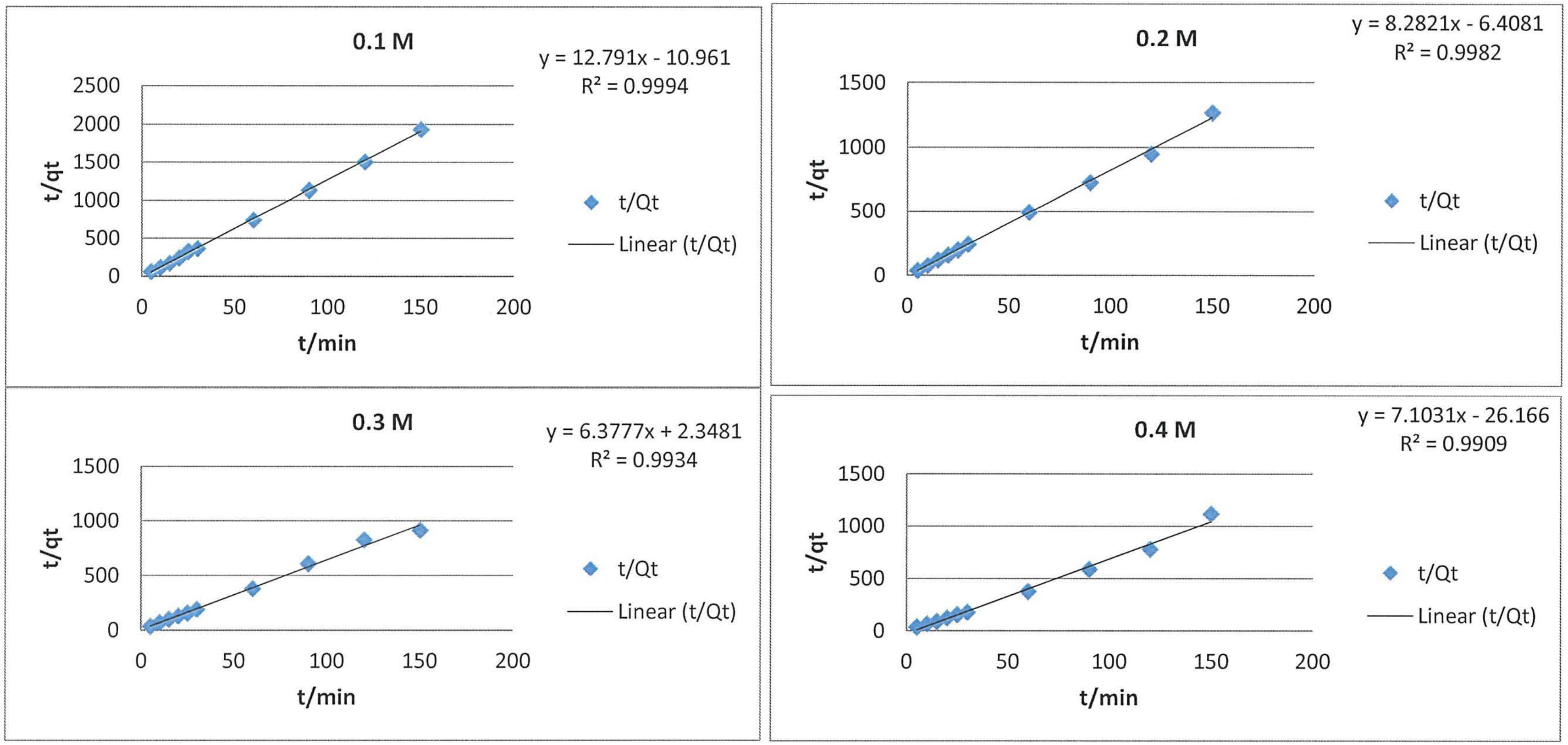

Figure 6.29.B Plots of pseudo second–order reaction for boron adsorption on Douglas–fir wood treated with different concentrations of boric acid (0.1, 0.2, 0.3 and 0.4 B Ml).

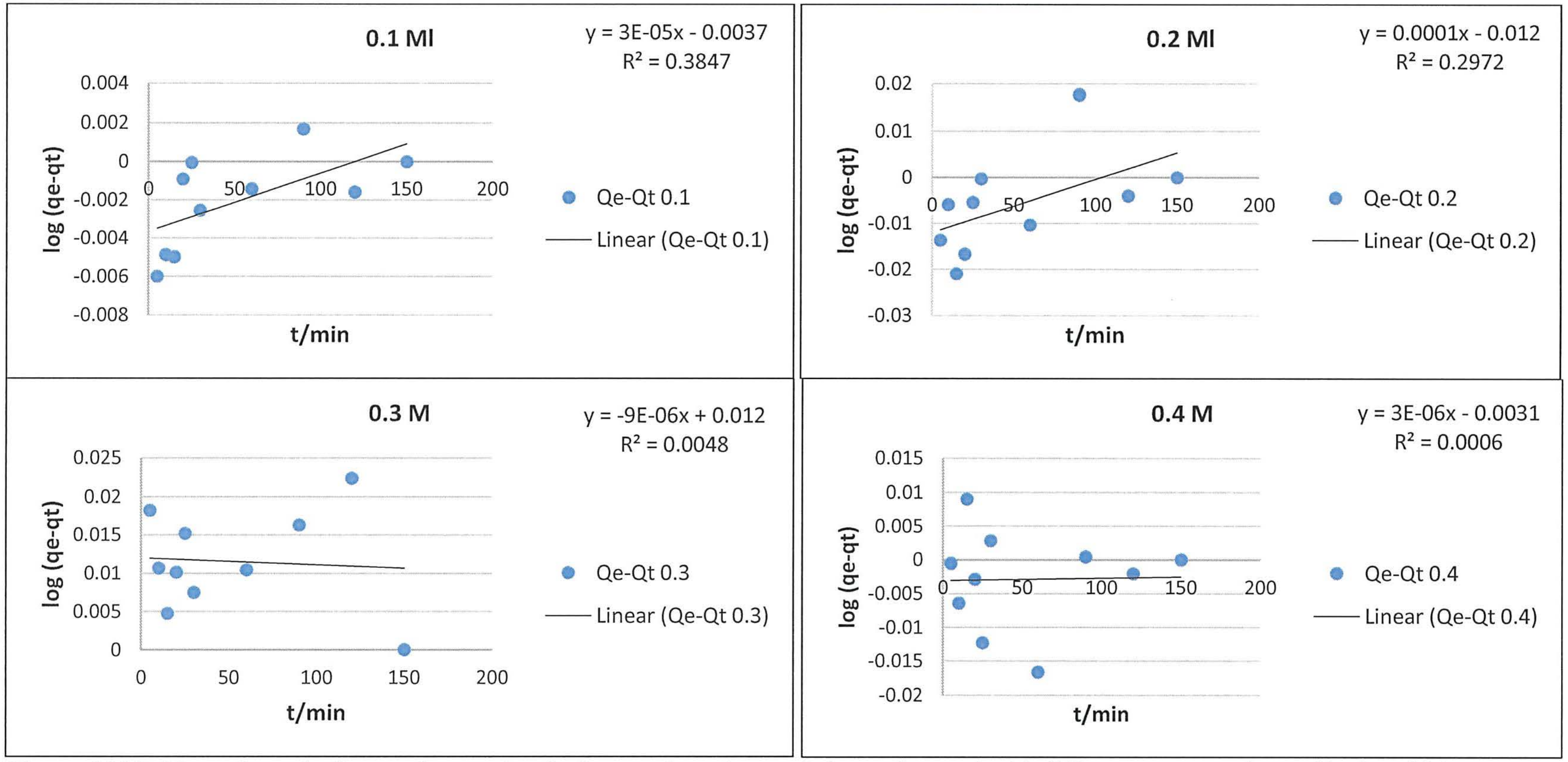

Figure 6.30.B Plots of pseudo first –order reaction for boron adsorption on Oak wood treated with different concentrations of boric acid (0.1, 0.2, 0.3 and 0.4 B Ml).

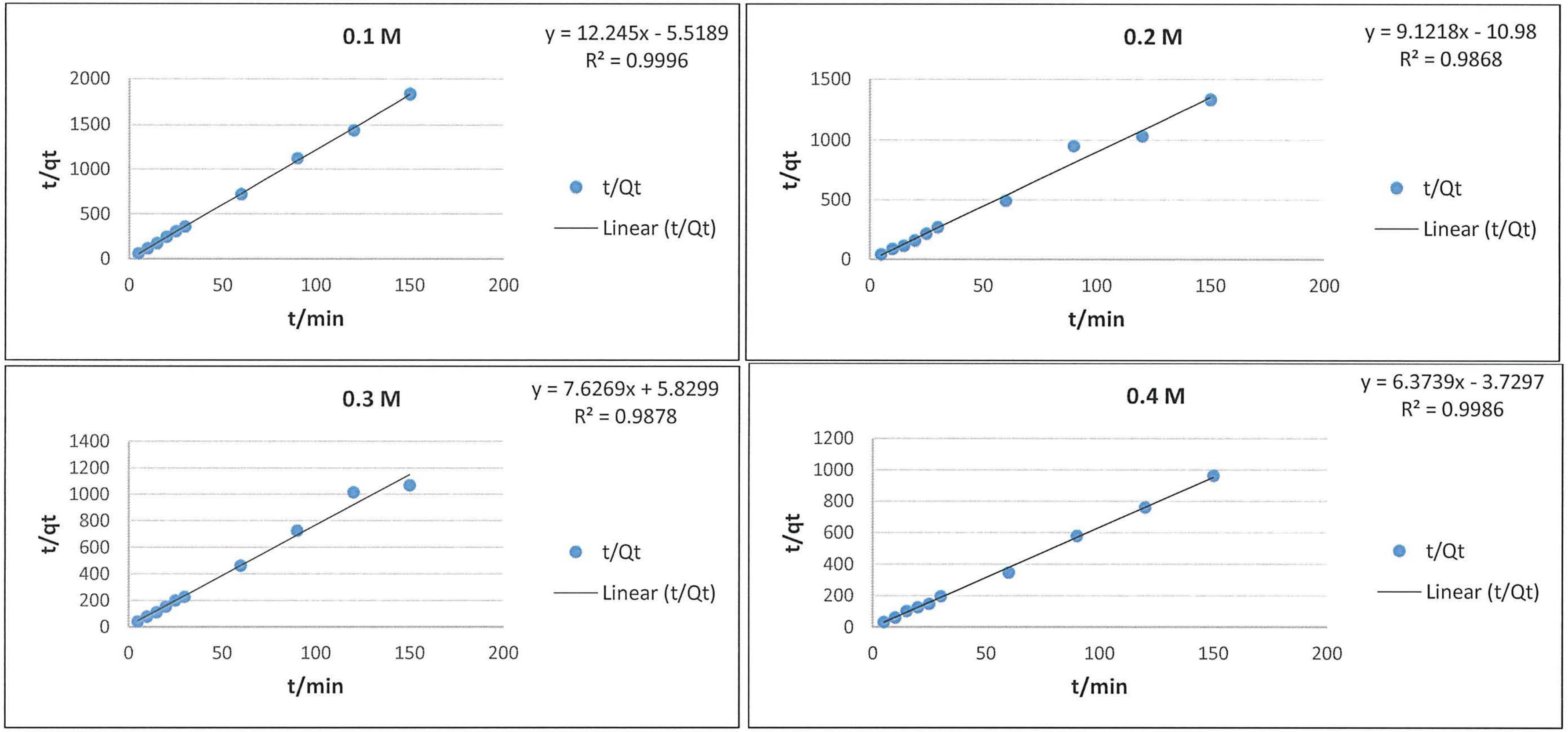

Figure 6.31.B Plots of second–order reaction for boron adsorption on Oak wood treated with different concentrations of boric acid (0.1, 0.2, 0.3 and 0.4 B Ml).

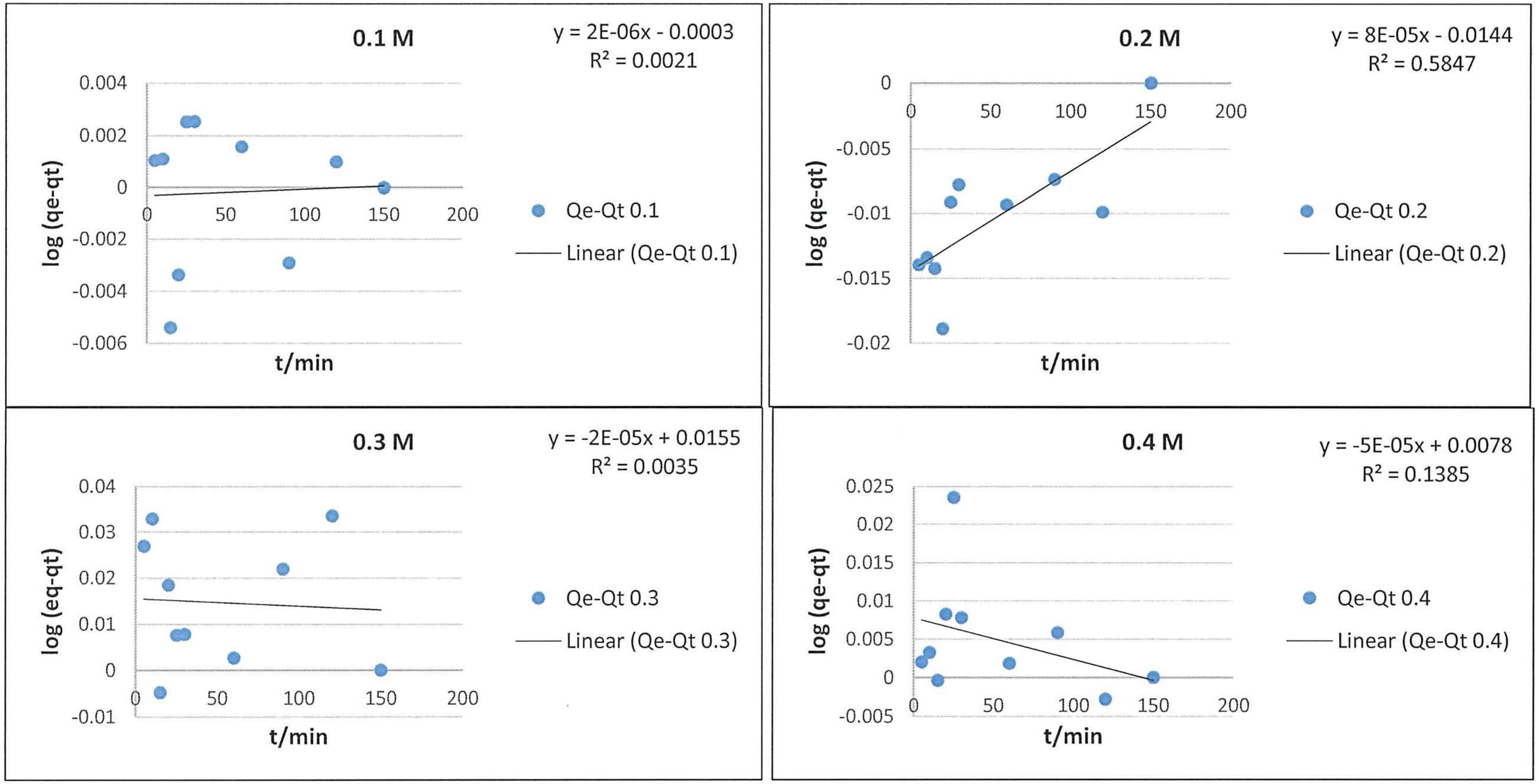

Figure 6.32.B Plots of first –order reaction for boron adsorption on Sapele wood treated with different concentrations of boric acid (0.1, 0.2, 0.3 and 0.4 B Ml).

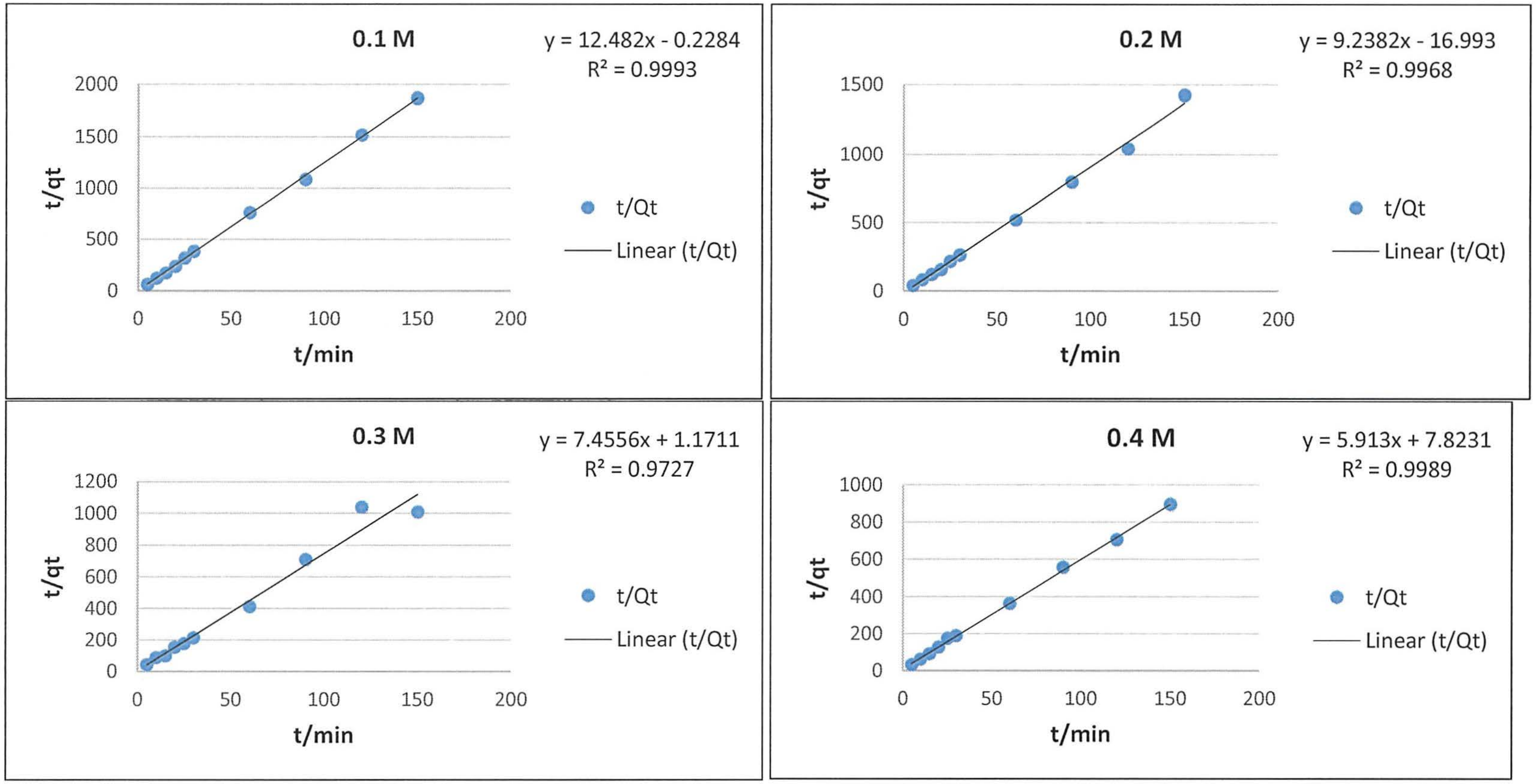

Figure 6.33.B Plots of second–order reaction for boron adsorption on Sapele wood treated with different concentrations of boric acid (0.1, 0.2, 0.3 and 0.4 B Ml).

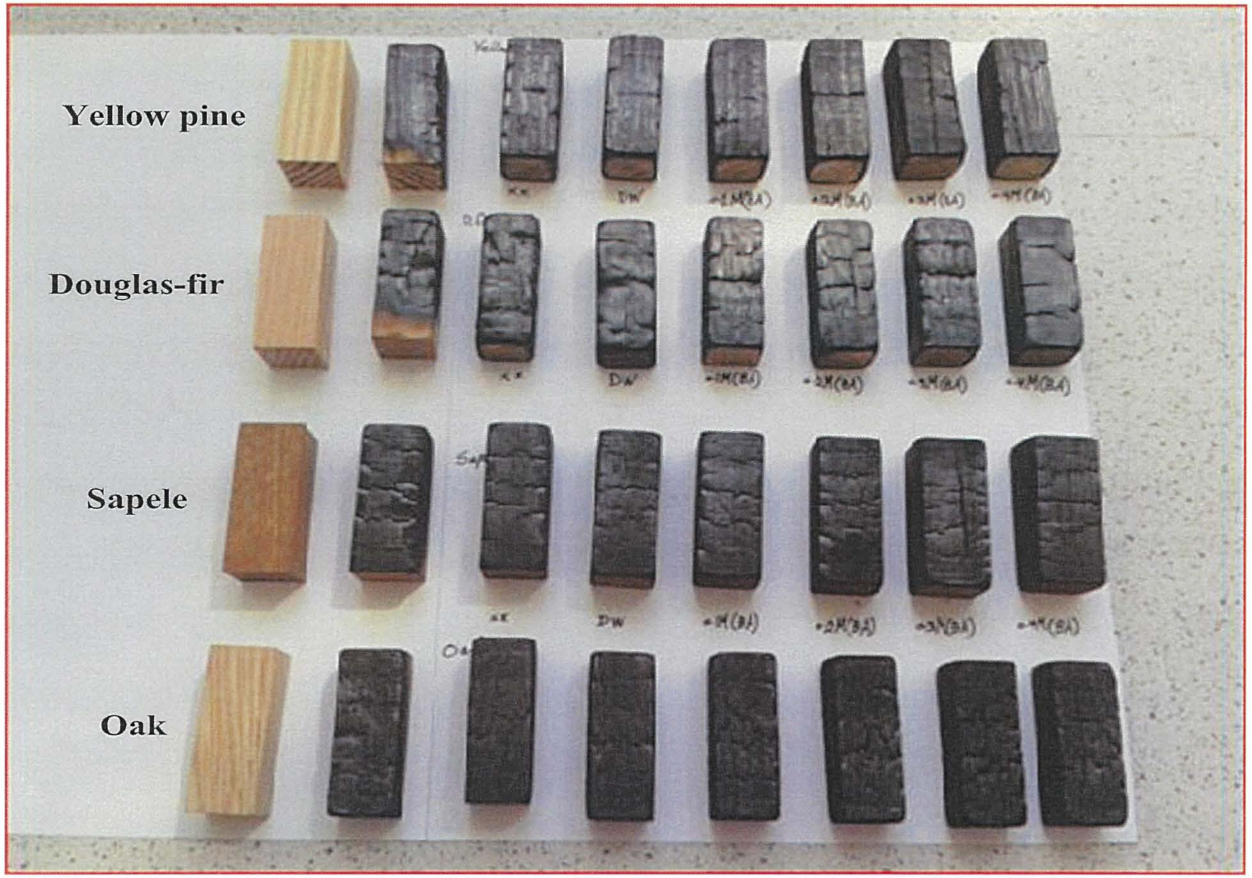

Figure 6.34.B The wood samples were tested against the fire compared with unburned wood samples.