

OVERVIEW OF ANALYTICAL PROCEDURES FOR FATTY AND RESIN ACIDS IN THE PAPERMAKING PROCESS

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This review describes the role of wood extractives, especially fatty and resin acids, in papermaking, as well as the importance of their removal from process waters. One of the main aims is also to illustrate versatile analysis methods for this purpose and highlight recent developments in corresponding applications. Most of the current methods require time-consuming and laborious sample pretreatment procedures prior to gas chromatography coupled either with flame ionization or mass selective detection. However, some faster, even online techniques with minimum sample pretreatment, are also available, mainly including high performance liquid chromatography coupled with mass spectrometry. The advantages and disadvantages of all analytical procedures are briefly discussed.

Keywords: Fatty acids; GC; HPLC; MSD; Pitch; Resin acids; Wood extractives

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INTRODUCTION

The pulp and paper industry is responsible for a large amount of water usage throughout the world. Environmental legislation has been leading to reduced usage of fresh water; this reduction has been achieved by multiple reuse of process water within paper machine systems (Ali and Sreekrishnan 2001; Latorre *et al.* 2005). Paper mills have answered new, tighter regulations by upgrading or replacing facilities. For example, they can replace bleaching facilities with elemental chlorine-free (ECF) bleaching or can add extended delignification in pulping. The emission of various oxygen-demanding substances has been reduced, and the use of highly chlorinated substances has been eliminated. Although water usage is essential to papermaking, ideas for reducing fresh water use and more extensive recycling of effluents have been presented (Gavrilescu *et al.* 2008). It has been suggested that the non-process elements (NPEs) entering the pulp mill with the wood are potential air and water contaminants and they possibly contribute to solid waste.

Due to water circulation closure, the papermaking industry has encountered new challenges caused by the build-up of concentrations of harmful substances, such as wood resin constituents, in water circulation (Lacorte *et al.* 2003). Fatty and resin acids are some of the most important wood resin constituents because of their important role in major process problems, such as lower pulp quality, foaming, odor, and effluent toxicity (Holmbom 1999a; Sitholé 2007). To prevent these compounds from causing pitch deposits, one possible solution is to bind soaps formed by fatty and resin acids to the mechanically pulped fibers by adding complex-forming additives, thus binding pitch droplets to the fiber surface through the presence of the complex.

The role of analytical chemistry in resolving problems caused by wood extractives is also vital. Monitoring resin acids during storage time, for example, plays an important role in the success of the papermaking process. The most common method for the analysis of fatty and resin acids in papermaking process waters is gas chromatography (GC) with a flame ionization detector (FID) (Örså and Holmbom 1994). This technique and many other currently used methods are rather time-consuming and include complicated pretreatments, such as solvent extraction and derivatization of the evaporated samples, before actual chromatographic analysis. The use of high performance liquid chromatography (HPLC) with mass spectrometric detection (MSD) provides a useful alternative with excellent repeatability and without complicated sample pretreatment steps, thus ensuring faster analysis with almost real-time results for process control.

The important role of wood extractives and their removal from the papermaking process are well recognized in the industry. However, most of the current analytical methods for these compounds are rather laborious and the urgent need for faster analytical procedures is evident. This review highlights the relevant aspects of selected wood-derived extractives as well as the need for their removal from the process. The aim is also to introduce the current analytical techniques and some recent developments in corresponding applications.

WOOD EXTRACTIVES

Wood extractives can be defined as lipophilic compounds that are soluble in neutral organic solvents (Sjöström 1993; Back and Ekman 2000). Water-insoluble lipophilic extractives are also called wood resin or pitch and are mainly comprised of free fatty acids, resin acids, waxes, fatty alcohols, steryl esters, sterols, glycerides, ketones, and other oxygen-containing compounds. The composition and the content of wood extractives in the tree vary, depending on the different parts of the tree (heartwood and sapwood), the wood species, age, growth conditions, and environmental factors (Levitin 1970; Hillis 1971; Alén 2000a).

Extractives are considered to be a major characteristic of wood composition, although they constitute, depending on the wood species, only 2 to 5% of the total dry matter (Sjöström 1993; Sjöström and Westermarck 1999; Alén 2000a). Resin acids occur only in softwoods, and the composition of individual resin acids depends on the species (Holmbom 1999a; Back and Ekman 2000). The composition of fatty acids also differs significantly according to the wood species and climate. Trees in warm climates produce a higher amount of saturated fatty acids but show less seasonal variability. In addition, wood extractives affect the wood's odor, color, and physical properties and play a significant role in the protection of wood from biological attack. Extractives have an important role in pulping and papermaking because they can produce negative effects, such as process problems and lower paper quality. However, they can also be useful raw materials as by-products, for example, in the form of tall oil (mainly fatty and resin acids) in kraft pulping and as a source of the further production of conventional rosin products and biodiesel fuel (Holmbom 1977, 2011; Quinde and Paszner 1991; Sitholé 1993; Lee *et al.* 2006).

Wood Extractives in Papermaking

The increasing recirculation of process waters (for example, white waters of the paper machine) is leading to an accumulation of a large number of harmful substances, mainly organic materials, called dissolved and colloidal substances (DCS) that interfere with the papermaking system (Ricketts 1994; Holmberg 1999b; Holmbom and Sundberg 2003; Latorre *et al.* 2005; Gavrilescu *et al.* 2008). These substances are anionic and can often disturb the function of papermaking chemicals. DCSs are released especially during mechanical, chemi-mechanical, and sulfite pulping (Dorado *et al.* 2000), and high DCS levels are associated with different process problems, such as the formation of pitch deposits (Laubach and Greer 1991; Back 2000a) and effluent toxicity (Holmbom 1999a; Ali and Sreekrishnan 2001; Lacorte *et al.* 2003; van Beek *et al.* 2007). The papermaking process itself results in the accumulation of organic compounds (Fig. 1). The substances present in the papermaking process depend greatly on the raw materials, additives, and energy sources used.

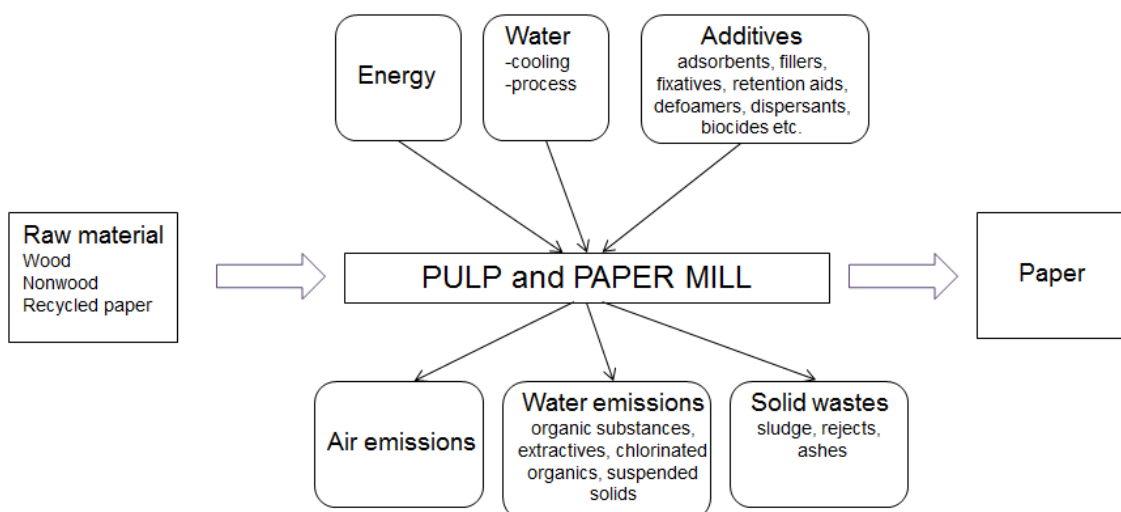


Fig. 1. Overview of the papermaking process mass stream (Lacorte *et al.* 2003)

In general, most studies have focused on wood extractives and their role and effect on effluents (Koistinen *et al.* 1998; Latorre *et al.* 2005). Due to modern wastewater treatment technology, a major part of these compounds can be removed from effluent waters. However, even at low concentration levels, they can have negative effects on aquatic life and on rats, when accumulating in liver, bile, and plasma (Fåhræus-Van Ree and Payne 1999; Kostamo and Kukkonen 2003; Rana *et al.* 2004). An effective effluent-treatment system enables the recycling of these waters back to the paper mill, thus decreasing fresh water usage (Gavrilescu *et al.* 2008).

The main components of DCS are hemicelluloses, wood extractives, and lignin-related substances. They are roughly classified by their lipophilic and hydrophilic properties (Table 1). This means that the compounds can be in their protonated or salt forms depending on the pH of the solution. In addition, resin acids, for example, can be classified as amphiphilic (amphipathic) molecules including both hydrophilic and hydrophobic structural units. The extent of the problems caused by these DCS compounds depends greatly on the wood species, the pulping process, and the degree of

water circulation closure. These substances also cause considerable damage to the receiving waters if they are not treated before discharge.

Table 1. The Lipophilic and Hydrophilic DCSs (Holmberg 1999b)

	Lipophilic/Hydrophobic	Hydrophilic
Fatty acids	X	
Flavonoids		X
Phenols		X
Resin acids	X	
Salts		X
Sterols	X	
Steryl ester	X	
Sugars		X
Tannins		X
Triglycerides	X	

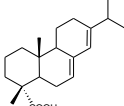
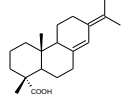
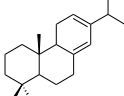
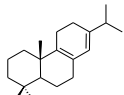
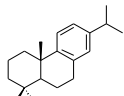
Fatty and Resin Acids in Papermaking

The role of fatty and resin acids in papermaking process waters has been studied extensively (Ali and Sreekrishnan 2001; Lacorte *et al.* 2003). These compounds originate from raw materials and from additives such as surfactants. The papermaking process releases these compounds during debarking, pulping, bleaching, washing, and with the final product, paper. Each paper manufacturing process is a unique combination of these different steps; the levels of fatty and resin acids in the process depend on the process performance. In particular, the pH of the process strongly affects the behavior of fatty and resin acids (Ström 2000). At high pH values, these acids dissociate and dissolve in water, depending on the temperature and the metal ion concentration. The metal soaps formed can either form soluble aggregates or precipitate as metal salts. Therefore, the pK_a values of fatty and resin acids play an important role in predicting and resolving possible problems caused by these compounds (McLean *et al.* 2005).

The most commonly found resin acids in the papermaking process waters are divided into two compound groups: the abietanes (abietic, levopimaric, palustric, and neoabietic acids along with dehydroabietic acid) and the pimaranes (pimaric, isopimaric, and sandaracopimaric acids) (Sjöström 1993; Ekman and Holmbom 2000; Serreji *et al.* 2000). Due to their chemical structure that comprises a combination of a hydrophobic skeleton and a hydrophilic carboxyl group, they work as good solubilizing agents. Dehydroabietic acid is the most common and stable (the aromatic nature of ring in structure) resin acid found in the papermaking process waters and effluents (Chow and Shepard 1996). It also accounts for the majority of wastewater toxicity because it can be transformed into more toxic compounds such as retene (Fig. 2) (Judd *et al.* 1996; Liss *et al.* 1997; Hewitt *et al.* 2006). Detrimental effects to fish caused by dehydroabietic acid have also been reported (Bogdanova and Nikinmaa 1998; Peng and Roberts 2000a). In addition, dehydroabietic acid is the most soluble acid among the resin acids, whereas pimaric type acids are the least soluble (Peng and Roberts 2000a).

present in papermaking process waters. The determinations of so-called colloidal pK_a values were made at 50 °C (normally 20 °C), which is a temperature representative of the actual papermaking process (McLean *et al.* 2005).

Table 2. The Most Common Fatty and Resin Acids in Pine and Spruce, and Their Colloidal pK_a Values (Alén 2000a; Back and Ekman 2000; Ström 2000)

Name	Formula	Molar mass (g mol ⁻¹)	pK_a
Fatty acids			
Palmitic	C ₁₅ H ₃₁ COOH	256.42	5.1 ^a , 8.6 ^c
Linolenic	C ₁₇ H ₂₉ COOH	278.43	8.3 ^b , 6.3 ^c
Linoleic	C ₁₇ H ₃₁ COOH	280.45	9.2 ^b , 7.8 ^c
Oleic	C ₁₇ H ₃₃ COOH	282.46	5.0 ^a , 9.9 ^b , 8.3 ^c
Stearic	C ₁₇ H ₃₅ COOH	284.48	10.1 ^b , 9.3 ^c
Resin acids			
	Structure		
Abietic		302.45	6.4 ^a , 6.2 ^c
Neoabietic		302.45	6.2 ^c
Levopimaric		302.45	-
Palustric		302.45	-
Dehydroabietic		300.44	5.7 ^a , 6.2 ^c

a = Ström 2000; b = Kanicky and Shah 2002; c = McLean *et al.* 2005

Problems Caused by Wood Extractives

The extent of the pitch problems and environmental issues depends greatly on the pulp (chemical or mechanical) manufacturing process and the degree of water circulation closure (Holmberg 1999a; Manner *et al.* 1999; Allen 2000). Paper mills with integrated pulp mills have more problems because a fraction of the DCS originating from the pulping and bleaching processes will be passed along to the subsequent processing of the pulp. In the alkaline process, the total wood extractives content may not be as relevant as the composition of these extractives (Dunlop-Jones *et al.* 1991). Saponification of fats and waxes is involved in the process, and fatty and resin acids create soluble soaps that are removed in an early segment of the cooking stage (Alén 2000b). Sterols and some waxes do not form a soluble soap under alkaline conditions and therefore have a tendency to deposit and cause pitch problems, whereas in neutral and acidic processes such as mechanical pulping (~ pH 5) it is difficult to remove lipophilic extractives. In addition, extractives that are not retained in the wet web will accumulate in the white water system and finally end up in the final effluent, thus giving rise to possible toxicity problems (Peng and Roberts 2000a; Rigol *et al.* 2004).

The aim of the thermomechanical pulping (TMP) process is to separate the fibers from the wood matrix with minimum damage through high temperature and pressure. The beneficial TMP process also preserves the lignin, hemicelluloses, and wood extractives in the fibers and fines produced (Kangas and Kleen 2004). This makes it possible to keep material losses at a low level (1 to 5%). The composition of the pulp in the TMP process differs only slightly from that of the original wood (Manner *et al.* 1999; Sundholm 1999). Compared to other pulping methods, such as chemical pulping, a high yield up to 97 to 98% can be achieved, and more paper can be produced from limited wood resources. However, during the TMP process, the harmful lipophilic extractives in the parenchyma cells and softwood resin canals are released and accumulate in the papermaking water system because mechanical pulp is not usually washed (Ekman *et al.* 1990; Laubach and Greer 1991). For example, in the bleaching stage, which consists of several intermediate washing cycles using oxygen and various chemicals such as hydrogen peroxide and ozone, the importance of pulp washing must be considered because removal of the wood resin components and metal salts is not efficient in the closed bleaching process, *i.e.*, recycling the bleaching effluents (Basta *et al.* 1998). TMP pulping also causes dissolution of high-charge-density pectic acids in the waters, thus constituting a major part of the anionic charge in waters, consuming the cationic retention chemicals and forming aggregates with cations such as sodium (Na^+), magnesium (Mg^{2+}), and calcium (Ca^{2+}) (Bertaud *et al.* 2002; Saarimaa *et al.* 2007).

Pitch deposition results in low-quality pulp and can cause a shutdown of mill operations (Pelton *et al.* 1980; Sundberg *et al.* 2000). Economic losses associated with pitch problems in kraft mills often amount to 1 to 2% of sales. The main cost components of pitch in pulp mills are the losses as a result of contaminated pulp, lost production, and the cost of pitch control additives. Pitch present in contaminated pulp can be the source of problems in paper machine operations such as spots and holes in the paper, sheet breaks, and technical shutdowns (Allen 2000). The main substance group in pitch deposits has been identified as hydrophobic wood extractives, composed mainly of free fatty (~6%) and resin acids (~10%), sterols, steryl esters, and triglycerides (Qin *et al.* 2003).

Due to their stable structure (tricyclic diterpenoid acids), resin acids resist chemical degradation and easily survive the pulping and whole papermaking process, thus tending to form pitch deposits in white waters (Dethlefs and Stan 1996) and ending up in industrial sediments (Leppänen *et al.* 2000; Lahdelma and Oikari 2005; Rämänen *et al.* 2010). This might also lead to resin acid being transformed into resin-acid-derived base neutrals such as dehydroabietin and tetrahydroretene that in turn accumulate in fish and freshwater mussels (Tavendale *et al.* 1997). The impacts of the fatty and resin acids are summarized in Table 3.

Resin acids are also thought to be the main contributors to effluent toxicity in softwood pulping effluents (Patoine *et al.* 1997; Peng and Roberts 2000a; Makris and Banerjee 2002; Rigol *et al.* 2004). However, even low concentrations of unsaturated fatty acids and sterols can also have long-term effects (Ali and Sreerkrishnan 2001). For instance, the toxic effects of resin acids together with unsaturated fatty acids occur at a concentration of only $20 \mu\text{g L}^{-1}$ (Kostamo *et al.* 2004). The influence of resin acid toxicity on fish has been studied extensively for decades (Oikari *et al.* 1984, 1985; Meriläinen *et al.* 2007; Hewitt *et al.* 2008). Effluent constituents can accumulate in the fish and affect reproduction. Furthermore, sterols have been reported to affect the development, reproduction, and growth of fish (Nakari and Erkonmaa 2003; Lahdelma and Oikari 2006).

Table 3. The Effects of Fatty and Resin Acids in Papermaking

Component Groups	Effect	Reference
Resin acids	Paper machine runnability, deposits	Holmbom, 1999a; Zhang <i>et al.</i> 1999; Rigol <i>et al.</i> 2003a
	Odor	Tice and Offen 1994; Holmbom 1999a
	Allergic reactions (oxidized products)	Holmbom 1999a
	Effluent and sediment toxicity	Holmbom 1999a; Peng and Roberts 2000a; Ali and Sreekrishnan 2001; Rigol <i>et al.</i> 2003a, 2004; Lahdelma and Oikari 2005; Rämänen <i>et al.</i> 2010
Fatty acids	Paper machine runnability, deposits	Zhang <i>et al.</i> 1999; Holmbom 1999a
	Odor	Blanco <i>et al.</i> 1996; Holmbom 1999a
	Lower sheet strength, friction	Holmbom 1999a; Sundberg 1999; Tay 2001; Kokkonen <i>et al.</i> 2002; Kokko <i>et al.</i> 2004
	Toxicity (unsaturated fatty acids)	Ali and Sreekrishnan 2001; Rigol <i>et al.</i> 2004
Fatty and resin acid soaps	Foaming	Holmbom 1999a
	Deposits	Holmbom 1999a; Rigol <i>et al.</i> 2003a

The metal soaps formed by free fatty and resin acids present in the process waters with metal ions, such as Mg^{2+} , Al^{3+} , or Ca^{2+} , are connected to tackiness problems in papermaking (Allen 1988; Laubach and Greer 1991; Sihvonen *et al.* 1998; Ström 2000; Hubbe *et al.* 2006). However, higher pH values increase the stability of the deposits in a colloidal pitch solution with Al^{3+} (Dai and Ni 2010). High sodium ion concentrations can render some sodium salts of fatty and resin acids, such as sodium oleate and abietate, insoluble, which implies the possible deposition problem of normally water-soluble sodium soaps of wood resin in closed water circulations (Palonen *et al.* 1982). Metal ion concentrations are expected to increase in a closed paper mill because of the usage of different process chemicals in various stages, *e.g.*, bleaching stages, stock preparation, and paper machine operations.

The effect of temperature and pH on wood pitch deposition in the papermaking process depends on the chemistry of the wood compounds and the operating conditions. Unexpected pH changes with temperature changes can destabilize the colloidal pitch, thus causing pitch deposition (Allen 1979; Back 2000a). The polymerization of wood resin components with increasing temperature can form material with low solubility in common solvents or alkali (Raymond *et al.* 1998; Dai and Ni 2010). This pitch polymerization has an important role in promoting pitch deposition, and it is obvious that storage of wood chips could enhance pitch polymerization, whereas storing wood as logs could be beneficial for reducing this phenomenon. Low temperature at neutral pH results in minimal deposition of the resin acid pitch, whereas deposition of the fatty acid pitch

increased significantly under the same conditions (Dreisbach and Michalopoulos 1989; Dai and Ni 2010).

The relationship between pH and pK_a values strongly affects the deposition of acidic lipophilic extractives such as fatty and resin acids. It has been found that due to the low solubility of these compounds in water, they can appear as suspended colloids in the process (Ström 2000; Nylund *et al.* 2007). At a pH near the pK_a values, resin acids especially tend to combine with colloidal particles, whereas at pH values higher than pK_a values, the amounts of these compounds in water can rise to a higher level. The composition of colloidal pitch changes, and less deposition is expected when fatty and resin acids start to dissolve ($pH > 6$). More free acids can work as emulsifiers in the process (Sihvonen *et al.* 1998; Lehmonen *et al.* 2009). This might also influence the adsorption behavior of the wood resin onto a surface. However, in real processes, the presence of Ca^{2+} causes a high tendency toward the formation of insoluble Ca-soaps with free acids (Otero *et al.* 2000).

Solutions to the Pitch Problems

Removal of wood extractives from the process

The extractive content is considered to be an important quality parameter for papermaking, especially for pulp production (Alén 2000a). The formation of extractives-derived pitch deposits is unavoidable, but a series of procedures has been developed to study and reduce this problem (Ekman *et al.* 1990; Laubach and Greer 1991; Fischer 1999; Allen 2000; Alén and Selin 2007; Sitholé *et al.* 2010). Basically, the wood resin components (*i.e.* DCS) need to leave with the final paper product, or the closed water circulation system should have facilities to handle the enrichment/increased concentrations of wood resin compounds in the white waters (*i.e.* internal cleaning) or, finally, in the effluents and discharges (Fig. 4).

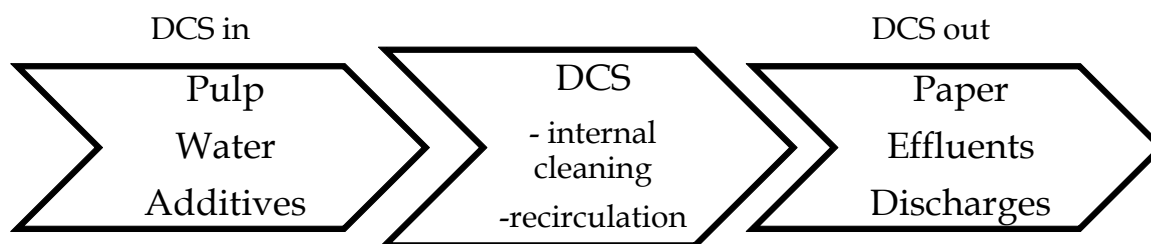


Fig. 4. The schematic flow of DCS in papermaking (Sundberg *et al.* 2000)

Especially in the mechanical pulping process, the variability of process waters parameters (*e.g.* pH, temperature, bleaching type, and process chemicals) could have an influence on the tendency towards pitch deposition (Holmberg 1999a; Alén and Selin 2007; Nylund *et al.* 2007; Gantenbein *et al.* 2010). Process temperature and pH changes have a great impact on wood resin removal during pulping processes (Ekman *et al.* 1990; Allen and Lapointe 2003). For example, increasing white water temperature due to circulation closure can decrease pitch problems because the higher temperature reduces resin viscosity, thus sometimes preventing resins from accumulating on metal surfaces (Allen 2000; Back 2000a). The problems resulting from sudden pH or temperature

changes in the process might be rapid pitch deposition on foils, suction boxes, and press rolls, as well as an increase in the amount of soap anions in white waters.

Traditionally, pitch deposits in pulping processes have been reduced by debarking, seasoning logs, and storage of wood chips (Allen *et al.* 1991; Sjöström 1993; Farrell *et al.* 1997; Allen 2000; Blazey *et al.* 2002). The storage of wood in the form of chips reduces pitch problems considerably because oxidation occurs faster. Wood seasoning and storage are an effective way to reduce wood resin compounds in papermaking systems, especially in mechanical pulping processes (Quinde and Paszner 1991). In practice, the efficiency of seasoning is highly dependent on the weather, *e.g.*, under cold winter conditions, and the rate of hydrolysis decreases with the decreasing temperature. However, wood storage can also produce negative effects, such as reduced pulp yield, a loss of brightness, and a low pulp quality due to the uncontrolled action of microorganisms. Moreover, isomerization of resin acids has been detected (Fig. 2 and 3).

In kraft pulping processes, pulp washing plays an important role in pitch deposition behavior (Laubach and Greer 1991; Fleet and Breuil 1998; Back 2000b; Ström 2000). Good washing of unbleached pulp will decrease the amount of wood resin in the bleaching and paper manufacturing stages. However, closing water circulation will increase concentrations of wood resin and metal ions, thus resulting in poor pulp washing (Ström *et al.* 1990). Besides pulp washing, the stock system purification has a positive influence on preventing pitch deposition (Holmberg 1999b; Allen 2000). During bleaching, deresination can be achieved by removing the desorbed resin from fibers by dissolving it with bleaching liquors, followed by removal by proper washing, especially under alkaline conditions or oxidation of resin into more water-soluble forms. The bleaching technique used also has an influence on the wood resin components. For example, ozone significantly decreases the amount of sterols in *Eucalyptus* pulp (Freire *et al.* 2006). On the other hand, the peroxide bleaching stage effectively oxidizes the resin, thus producing complex oxidized products (Holmbom *et al.* 1991; Bergelin and Holmbom 2003).

The formation of pitch deposits is also connected to the disturbances in colloidal stability and aggregation of pitch droplets (Dreisbach and Michalopoulos 1989; Hubbe *et al.* 2006). In unbleached TMP process waters, colloidal extractives are usually sterically and electrostatically stabilized, which inhibits aggregation even with high concentrations of electrolytes (Sundberg *et al.* 1994). However, resin droplets are usually only electrostatically stabilized in bleached TMP. Therefore, aggregation with electrolytes is possible (Willför *et al.* 2000).

The importance of polysaccharides to the deposition problems in the form of complexes of anionic polysaccharides and cationic polymers is also evident because both polysaccharides and wood extractives are released during mechanical pulping. These water-soluble polysaccharides in mechanical pulping have also been considered as a source of bioactive polymers (Willför *et al.* 2005) or barrier film production (Persson *et al.* 2007). Many researchers have shown that a small amount of galactoglucomannans decreased the deposition tendency and affected the stability and character of the colloidal pitch and had a positive effect on paper strength (Sundberg *et al.* 1993, 2000; Sihvonen *et al.* 1998; Otero *et al.* 2000; Johnsen *et al.* 2004; Alén and Selin 2007).

Process additives have been used for pitch control (Allen 2000; Hubbe *et al.* 2006). Alén and Selin (2007) categorized deposit control according to the chemicals needed to solve the problem: adsorbents, fixatives, retention aids, dispersants, surfactants, chelants, solvents, and enzymes. For example, talc has been used to stabilize DCS and to

avoid agglomeration through the reactions of talc's hydrophobic surface with the hydrophobic surface of the tacky material, thus reducing its potential to form deposits (Monte *et al.* 2004; Guéra *et al.* 2005; Gantenbein *et al.* 2010). Kaolin affects the stability of DCS, resulting in a decrease in the amount of lipophilic extractive droplets in the dispersion (Nylund *et al.* 2007). In addition, retention aids, such as cationic polymers, have been used to make wood extractives substantive to fibers, solving precipitation problems and reducing rates of accumulation of these compounds on the papermaking equipment (Sundberg 1999; Allen 2000; Hubbe *et al.* 2009).

The degradation of wood extractives has been conducted with enzymes and microorganisms in the water phase as well as in the wood chips or pulp by wood-inhabiting fungi, to eliminate the possibility of lipophilic extractives leaching into process waters (Farrell *et al.* 1997; Burnes *et al.* 2000; Dorado *et al.* 2001; Kallioinen *et al.* 2003; Gutiérrez *et al.* 2006, 2009; van Beek *et al.* 2007; Dubé *et al.* 2008; Widsten and Kandelbauer 2008). Such treatment can take from several hours to several days; the degradation of the extractives with enzymes/microorganisms is a very selective reaction when DCS is to be eliminated. These biotechnological products have been successfully used for the selective removal of pitch problems caused by sterols, triglycerides, and resin acids (Gutiérrez *et al.* 2001b). So-called bio-pulping, *i.e.*, wood chip pretreatment with white-rot fungi capable of selectively degrading lignin and some extractives, also enables cost savings in the form of lower energy consumption in mechanical pulp production. Especially promising results have been achieved by using a novel surfactant (non-ionic alkyl diethanolamide) with a lipase enzyme treatment that can reduce a wide range of wood extractive compounds in pulp and process waters (Dubé *et al.* 2008).

The ozonation process can be used to prevent the accumulation of wood extractive compounds in TMP circulation waters; this approach can improve product quality and functionality of the paper machine (Laari *et al.* 1999). Ozonation is based on the sensitivity of lipophilic wood extractives to oxidation. However, a relatively high dose of ozone is needed to reach complete degradation, which makes the cost of the treatment relatively high. It has also been found that ozone selectively oxidizes resin acids, decreasing total resin acid concentration by over 90% (Korhonen and Tuhkanen 2000; Ledakowicz *et al.* 2006). Therefore, it is beneficial to use ozone in the posttreatment process of white waters (before the actual treatment process) in order to reduce the amount of organic compounds, chemical oxygen demand (COD), and toxicity (Latorre *et al.* 2007). The high oxidizability of pimarane-type resin acids was also achieved, rather than in the abietane type, as had been expected. Ozone selectively affects the toxicity of the effluents. Ozone treatment also increases the toxicity of resin acids because more toxic intermediates are formed. However, an overall decrease in the toxicity of fatty acids was achieved (Gamal El-Din *et al.* 2006).

Removal of Wood Extractives in Wastewater Treatment

The papermaking industry is one of the largest water consumers in the world. Its consumption depends greatly on the type of paper being produced and the degree of recycling in the process (Thompson *et al.* 2001; Garvilescu *et al.* 2008). Debarking and bleaching are the main sources of wood extractives in pulp and paper mill wastewater. Wastewater treatment processes have become more intensive and important due to the water circulation closure trend (Latorre *et al.* 2005). A huge amount of solid waste, including sludge, mud, ash, and wood processing residuals, is also generated from papermaking (Monte *et al.* 2009). Paper mills have started attempting to lower water

consumption and discharge to the environment for both environmental and economic reasons. However, it must be pointed out that reduced water use would likely lead to higher concentrations of extractives in papermaking waters and to more pitchy wet end. The characteristic properties of wastewaters depend greatly on the type of papermaking process, wood materials, recirculation degree of the waters and effluents, and the process technology applied to the papermaking and wastewater treatment. New and efficient wastewater treatment techniques are being constantly developed. In addition, economic and social aspects need to be taken into account (Burkhard *et al.* 2000; El-Ashtoukhy *et al.* 2009). There are several categories of wastewater treatment methods; Table 4 breaks down the most widely used techniques for wastewater treatment in papermaking.

Table 4. Different Technologies for Waste Water Treatment (Pokhrel and Viraraghavan 2004)

Physicochemical	Biological
Air flotation	Activated sludge process
Ion exchange	Aerobic biological reactors
Adsorption	Anaerobic treatment
Membrane filtration	Fungal and enzymes treatments
Chemical oxidation	
Ozonation	
Sedimentation	

Physicochemical processes are in general quite expensive but achieve the beneficial removal of high molecular mass lignins, color, toxicants, suspended solids, and COD. On the other hand, wastewaters after biological treatments still contain lignin, color, and some COD. To attain optimal biological temperature and pH conditions, biological treatment systems may also require rather extensive modifications of the environmental conditions, such as cooling (Latorre *et al.* 2005). Different kinds of solutions have been tested to overcome these problems, for example, separating the white water and effluent treatments. However, these solutions have not been sufficient to solve all the problems. While secondary wastewater treatments have successfully decreased the toxicity of the effluent, these effluents still have a negative effect on aquatic organisms (Kovacs and Voss 1992; Pokhrel and Viraraghavan 2004). Activated sludge treatment removes up to 90% of wood extractives. However, the transformation of resin acids to more persistent forms, such as retenes, will create new challenges to the environment in the form of new toxic compounds in the sediments (Kostamo *et al.* 2004). Chemical pulping effluents are especially problematic for the environment, since they may contain, even after biotreatment, compounds that are resistant to biological treatment and can thus cause changes in the physiology and biochemistry of fish.

The use of ozone to treat different types of industrial wastewater was reviewed comprehensively by Rice (1997), who found that ozone bleaching has a strongly positive effect on the plant's water consumption, in that it allows water reuse in bleaching and lowers the cost of wastewater discharge. Basically, ozone is used to enhance the biodegradability of the effluents before further reduction with biological treatment. New techniques having great potential, such as a gas-induced ozone reactor for highly complex industrial wastewater treatment with ozone (Lin and Wang 2003) or an integrated anaerobic bioreactor and ozone treatment system (Chaparro *et al.* 2010) have been developed. Moreover, wet oxidation (WO) (Laari *et al.* 1999; Verenich *et al.* 2004)

has been successfully used to degrade lipophilic wood extractives from TMP wastewaters. In the WO process, the organic matter in the water phase reacts with oxygen at high temperature and pressure to produce carbon dioxide and water (Collyer *et al.* 1997).

The removal of wood extractives in wastewater is a challenging process that also requires the development of faster analysis methods for these compounds. The resin acids are the main contributors to the toxicity of the effluent; their removal by wastewater treatment plays an important role. Biological treatment has been considered the most effective way of removing large amounts of organic matter from wastewaters (Lacorte *et al.* 2003; Latorre *et al.* 2007). It has also been used for removal of resin acids, as have anaerobic reactors (Ali and Sreekrishnan 2001; Kostamo and Kukkonen 2003). In particular, the use of secondary treatment in an aerobic lagoon was found to remove over 90% of the influent resin acids. However, the system does not take into account the possible process variations that can cause effluent biological oxygen demand (BOD), COD, and toxicity values to rise to unacceptable levels. Moreover, pH strongly affects the toxicity and solubility of resin acids in wastewaters (Ali and Sreekrishnan 2001). It must be also noted that a reduction in resin acid levels may not have a direct correlation with the reduction of toxicity or COD values. This is because of the possible modification of these compounds in the water treatment process (Liss *et al.* 1997; Fåhræus-Van Ree and Payne 1999). Fatty acids can be degraded anaerobically, but their concentration levels should be kept low to prevent them from inhibiting the anaerobic bacteria.

ANALYSIS OF EXTRACTIVES

Wood extractives in water samples have been extensively analyzed and studied (Holmbom 1999a, b; Ekman and Holmbom 2000; Holmbom and Stenius 2000; Baeza and Freer 2001; Lacorte *et al.* 2003; Rigol *et al.* 2003a; Douek 2007). The use of component group analysis of wood extractives, including techniques such as extraction and gravimetric determination, has been preferred. However, these analytical methods provide little detailed information about the composition of different wood extractive groups, such as fatty and resin acids. Alternative analysis procedures have also been presented in the literature. For example, somewhat simple turbidity measurements have been used to evaluate DCS levels in process streams in paper mills (Tornberg *et al.* 1993; Sundberg *et al.* 1994; Mosbye *et al.* 2003; Ravnjak *et al.* 2003; Saarimaa *et al.* 2006). In model systems, the correlation between turbidity and colloidal wood pitch seems to be useful. However, in the real process, fibers and fines affect turbidity measurement and disturb this correlation.

A potentially interesting study involves a 5-component analytical system in which typical TMP water constituents such as carbohydrates, extractives, lignans, lignin, and low molecular mass components were measured; the results were controlled by the use of COD or total organic carbon (TOC) measurement (Lenes *et al.* 2001). The results showed that these five components accounted for only 75 to 90% of the COD values measured directly. Traditionally, a simple COD measurement has been used to study organic compounds, *e.g.*, the total concentration of particulate and dissolved components in pulp mills, or to evaluate the efficiency of white water treatment (Latorre *et al.* 2007). Clearly, the analysis of organic compounds (such as wood extractives) in papermaking process

waters must include compromises between simple, less accurate methods and more sophisticated, accurate methods.

Wood extractives have often been isolated from the sample matrix through extraction techniques. The choice of the extraction method is vital for the further success of the analysis (Lacorte *et al.* 2003; Rigol *et al.* 2003a; Latorre *et al.* 2005). To remove harmful matter like suspended solids and particles from process water samples, centrifugation (2000 rpm for 20 min) or filtration through 0.45 μm , 0.7 μm , and 1 μm filters is necessary. Filter extraction is also recommended because apolar compounds in the sample may remain on the filters. Centrifugation is preferred to filtration because dissolved and colloidal particles are taken into account with supernatant, whereas in filtration, an unmeasured amount of lipophilic droplets and colloidal particles may remain on the filter or the fiber mat formed (Örså and Holmbom 1994).

The effect of the sample pH value on extraction efficiency has been studied extensively; pH values varying from 2 to 12 have been used in the analysis. Voss and Rapsomatiotis (1985), followed by several other studies (Lee *et al.* 1990; Dethlefs and Stan 1996; Serreqi *et al.* 2000; Gutiérrez *et al.* 2001a), used a basic pH to prevent isomerization and binding problems of the resin acid. Several researchers have reported extraction with organic solvents with an acidic pH because this reduced the formation of emulsions, and thus microbial growth during sample storage could be achieved (Ekman and Holmbom 1989; Morales *et al.* 1992; Örså and Holmbom 1994). For example, a medium acidic pH increases the isomerization of some resin acids, such as palustric acid, to abietic acid. In addition, low solubility of resin acids in aqueous systems may require higher pH values (*i.e.* above pK_a values). For example, due to structural differences, dehydroabietic acid is the most soluble ($\sim 5 \text{ mg L}^{-1}$) in water at pH 7. It has twice the solubility of other resin acids (Peng and Roberts 2000a). Mosbye *et al.* (2000) preferred the original sample pH value (~ 5), which is representative of the real papermaking process. A better recovery was also observed with the original pH 5 than with the acidic (pH 3) or basic (pH 12) conditions tested.

Most methods use LLE with an organic solvent such as hexane, acetone, dichloromethane, or methyl tert-butyl ether (MTBE). The use of diethyl ether has also been presented by Ekman and Holmbom (1989) in their analytical scheme for extractives in water samples. Extraction studies have shown that a mixture of selected solvents will give better recovery results than will single solvents (Peng and Roberts 2000b). These solvent fractions are collected and dried by evaporation. Prior to chromatographic analysis, the samples are exposed to chemical derivatization with methylation (*i.e.* diazomethane-ether solution), formation of pentafluorobenzyl (PFB) esters, or per(trimethylsilyl)ated (*i.e.* the preparation of trimethylsilyl (TMS) derivatives) with *N,O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) containing trimethylchlorosilane (TMCS).

SPEs have also been used to isolate fatty and resin acids from papermaking process waters and effluents (Richardson *et al.* 1992; Dethlefs and Stan 1996; Mosbye *et al.* 2000; Rigol *et al.* 2003a). SPE uses a solid and a liquid phase to isolate analytes from a solution. Typically, silica-based liquid chromatography type stationary phases with a special functional group, such as hydrocarbon chain, amino groups, sulfonic acid, or carboxyl group resin, are packed in a glass or disposable plastic column with a frit. The samples are passed through these columns, and analytes retained in the stationary phases are flushed with organic solvents (Fritz 1999). Various solvents or combinations, such as hexane, chloroform, and diethylether, were used in these applications, for example, to isolate different groups of lipophilic extractives present in wood and pitch deposits

(Gutiérrez *et al.* 1998). The SPE technique has clear advantages with a short analysis time, low solvent requirement, and possibility to connect online with different chromatographic techniques such as HPLC (Hennion 1999). Compared to LLE, SPE also minimizes the formation of emulsions. However, the overall efficiency of SPE was shown to be highly dependent on the sorbent type, amount, and column size. Chen *et al.* (1994) used the SPE technique to separate different groups of extractives in the fractions; quantitative results were achieved by weighing the fractions.

Gas Chromatography

The most widely used analytical method for wood extractives analysis is GC with high-resolution capillary columns. This method has been used for the analysis of fatty and resin acids present in tall oil since the 1970s (Holmbom 1977). The analysis procedure of wood extractives includes the separation of wood extractives from a sample matrix with extraction, derivatization of the samples, and finally, GC analysis combined with mass spectrometry (MS) or FID (Holmbom 1999b; Knuutinen and Alén 2007). The sensitive and reliable FID detector has a wide linear range and good responses for different organic compounds.

The critical points of analysis have been the choice of extraction method, extraction solvent, and the pH of the water samples. LLE extraction has proven to efficiently extract organic compounds from particulate and dissolved fractions, whereas the SPE may suffer losses of some of the compounds through adsorption (Lacorte *et al.* 2003). Resin acids have also been extracted from TMP effluent by adsorption onto XAD resin with subsequent analysis by GC (Richardson and Bloom 1982). However, this technique is rather time-consuming as it involves long sample preparation and analysis time.

The derivatization of the sample is commonly recommended in GC analysis to improve separation and ensure quantitative reliability (Lacorte *et al.* 2003; Rigol *et al.* 2003a). Derivatization to methyl esters or PFB derivatives has also been reported (Lee *et al.* 1990), and the formation of TMS ethers has been shown to be beneficial for the analysis procedure (Holmbom 1999b). The main problems with derivitization are caused by the shortened lifespan of the derivatized extract and the possible long-term effects on GC-MS performance. In particular, the TMS derivates are susceptible to hydrolysis, and the analysis time of the derivatized sample is limited to 12-24 hours. The use of internal standards is also preferred in order to improve the quantification of the compounds. Several possible internal standards, such as heptadecanoic acid (Ekman and Holmbom 1989) or heneicosanoic acid (Örså and Holmbom 1994), are available to aid in quantification of the fatty and resin acids.

A detailed method for analysis of wood extractives as groups (free fatty acids, resin acids, lignans, steryl esters, and triglycerides) was introduced by Örså and Holmbom (1994). They used an effective MTBE solvent to separate out both lipophilic extractives and hydrophilic lignans in mechanical pulping process waters. The use of non-split on-column injection is preferred to achieve reliable results, and several different internal standards with different volatilities balanced the possible differences between responses with an FID detector. The analysis of individual free fatty and resin acids, fatty alcohols, and sterols can be conducted by a standard 15 to 30 m long capillary column with different polarities. Fused-silica, non-polar (methyl silicone), phenyl methyl siloxane, and HP-5 columns have been used for this purpose (Holmbom 1999b; Rigol *et al.* 2003a).

GC-MS has also been used for the analysis of fatty and resin acids in waters, sediments, and fish bile samples since the 1970s (Morales *et al.* 1992; Gutiérrez *et al.* 2001a; Rigol *et al.* 2002). MS detection provides the spectra with molecular fragment ions, which provides useful information about the ionized compound and unequivocal peak identification in the complex mixtures as well as good sensitivity and reliability, with excellent LOD values of 3-9 $\mu\text{g L}^{-1}$ (Rigol *et al.* 2002). Compounds can be easily identified by comparing them using databases of spectra involving a wide range of common extractive compounds. The combination of GC-FID analysis with GC-MS provides the best overall component identification.

High-Performance Liquid Chromatography

HPLC provides an important alternative for the difficult analysis of wood extractives with non-volatile requirements for the compounds (Holmbom 1999b; Rigol *et al.* 2003a, b). The method uses high pressure to force solvent through packed columns to provide resolution of the compounds of interest. HPLC can utilize, for example, the reversed-phase (RP) technique, thus providing good separation of wood resin component groups. The size-exclusion (SE) technique can also be used to fractionate the sample for further analysis of individual components (Suckling *et al.* 1990). Mixtures of water and acetonitrile or methanol with an acid modifier are used to elute the compounds. One of the major challenges in the HPLC analysis of resin acids is the difficulty in separating the various resin acid isomers in a mixture by common C8 or C18 columns because of the hydrophobic analyte-column interactions. Recently, ultra-performance liquid chromatography (UPLC), which provides good chromatographic separation with shorter analysis time, has been introduced for water analysis of pharmaceuticals (Nováková *et al.* 2006; Van De Steene and Lambert 2008). The UPLC technique has a beneficial low solvent consumption, and its systems are designed to withstand high system back-pressures. However, this technique has not yet been used to analyze extractives in papermaking process waters.

Ultraviolet (UV) and fluorescence detection have been used to analyze dehydroabiatic acid and total resin acids in effluent samples (Richardson *et al.* 1983, 1992). The analysis of other resin acids, such as abietic acid, through fluorescence detection is not possible because of the non-aromatic structures of these acids. The faster direct injection technique of an untreated effluent sample has shown quite similar results with respect to dehydroabiatic acid. A slightly modified direct injection HPLC method by Chow and Shepard (1996) provided an excellent possibility for using dehydroabiatic acid as an indicator for assessing total resin acid concentration in paper mill effluents. Screening for toxicity in effluents can also be done with this fast detection technique.

The analysis of wood extractives involves a series of limitations, because the detection range must be wide and a large number of different compounds must be analyzed. The limitations of UV detection are based on the absence of chromophores in all resin compounds, whereas the refractive index and infrared detectors are not compatible with gradient elution (Suckling *et al.* 1990). However, light scattering and mass detectors are compatible with gradient elution and thus suitable for analysis of methylated fatty and resin acids as well as partially separated triglycerides.

The derivatization of the extracts in HPLC analysis will also improve the separation of the compounds (Holmbom 1999b). The conversion of resin acids in effluent samples to different types of coumarin esters has been presented by Volkman *et al.* (1993) and Luong *et al.* (1999a, b), who also found that the HPLC method was suitable

for routine monitoring of total resin acids and dehydroabietic acid in process effluents. However, the changes in the composition of individual resin acids in water were better evaluated by the GC-MS method for environmental purposes.

High-Performance Liquid Chromatography-Mass Spectrometry

The use of the HPLC-MS method for the analysis of environmental or pharmaceutical residuals in water samples has been widely published (Zwiener and Frimmel 2004a, b; Petrović *et al.* 2005). However, only limited information on HPLC-MS has been reported regarding the analysis of fatty and resin acids in papermaking waters, effluents, or river water samples (McMartin *et al.* 2002; Latorre *et al.* 2003; Rigol *et al.* 2003b, 2004; Valto *et al.* 2011). Due to the high sensitivity and selectivity of HPLC-MS, the main advantage of analysis is that samples can be directly injected into a column without the need for a derivatization step and that ionization of the compounds takes place in an interface without the need for any post-column addition. Thus, the problem of decomposition of silylated samples during their possible storage, as in GC analysis, could be avoided.

In general, APCI and electrospray ionization (ESI) provide suitable interfaces for analysis. These techniques allow soft ionization in both negative and positive modes, but APCI seems to be the most versatile, in that it provides clear mass spectra with little fragmentation (Willoughby *et al.* 1998; Kostianen and Kauppila 2009). ESI has been used for large biomolecules and for small polar organic compounds, whereas APCI provides a useful choice, especially for non-polar compounds. The benefits of the APCI technique over ESI are that it tolerates higher salt and additive concentrations, polar and non-polar solvents can be used, and the ionization of neutral and less polar compounds is also possible. The selectivity and sensitivity of HPLC-MS analysis depends also upon the HPLC technique. The RP technique is the most commonly used, but ion-change and SE chromatography (SEC) have also been used. The column diameter and solid-phase material affect the HPLC separation efficiency and analysis time. Common solvents consist of mixtures of acetonitrile or methanol and water. The additives must be volatile because non-volatile additives can cause background noise and contamination of the ion source. However, compromises between chromatographic separation and ionization efficiencies must often be made when selecting the eluent composition.

McMartin *et al.* (2002) reported the use of the liquid chromatography-electrospray-mass spectrometric (LC-ESI-MS) method for the analysis of four resin acids in river water. The method used external standard calibration and provided a highly sensitive analysis of dehydroabietic acid and coelution of three structural resin acid isomers (abietic, isopimaric, and pimaric acids). In other studies, LLE has been used for sample preparation, but only the use of direct analysis techniques with sample dilution has been tested (Rigol *et al.* 2003b). C8 and C18 columns have been used in separations of the resin acids with the use of either acetonitrile-water or methanol-water (25 mmol L⁻¹, CH₃COONH₄, pH 7) as the mobile phase. Also, sufficient separation of palmitic, stearic, oleic, linolenic, and dehydroabietic acids was obtained with a Waters Atlantis dC₁₈ column using methanol and aqueous formic acid at pH 2.5 as the mobile phase (Valto *et al.* 2011). Owing to the low polarity of fatty and resin acids, high percentages of organic solvent were necessary for their elution. In addition, the use of acetonitrile caused high background noise, since carbon deposits were produced in the corona of the APCI interface. Dehydroabietic acid was able to separate from the non-aromatic acids that

coeluted in the McMartin *et al.* (2002) study. On the other hand, Rigol *et al.* (2003b) doubled the analysis sensitivity by using APCI and partly separating the coeluting non-aromatic resin acids with a C8 column and adding isopropanol in the mobile phase. The intensive (M-H)⁻ ion was obtained, even with high fragmentor voltage values, for the fatty and resin acids, and identification could be made by means of a single ion by comparing retention time against a standard or a standard addition technique (Lacorte *et al.* 2003).

The HPLC-MS technique with an RP-178 column attained good linearity, repeatability, and LOD values, with recovery values higher than 70% (Rigol *et al.* 2003b). LOD values of 0.2 to 1.3 µg L⁻¹ and 0.5 to 3.1 µg L⁻¹ were achieved for MTBE extraction and direct sample introduction, respectively. Through the use of the direct injection technique, somewhat higher LOD values were obtained compared to MTBE extraction, but they were still below the levels of the target compounds encountered in the paper industry effluent samples tested. In addition, a faster analytical method without any pre-extraction for fatty and resin acids with a proper method validation process in aqueous and real sample media with internal standard quantitation was reported (Valto *et al.* 2011). The measured quality parameters, such as selectivity, linearity, precision, and accuracy, clearly indicated that compared to traditional GC techniques, the simple method developed provided a faster chromatographic analysis with almost real-time monitoring of these acids.

Applications of the Methods

Examples of the most commonly used methods for the analysis of wood extractives in a water matrix are shown in Table 5. The references were selected on the basis of utility for water analysis related to papermaking. Rigol *et al.* (2003a) have reviewed in detail the analysis of resin acids in process waters; other researchers have also listed various analytical methods for fatty and resin acids (Holmbom 1999b; Peng and Roberts 2000b). Several other studies have been conducted on the analysis of wood extractives in sample matrices such as wood, pulp, black liquors, or wood resin deposits (Sjöström 1990; McGinnis 1998; Holmbom 1999a; Sitholé 2000; Bergelin *et al.* 2003; Hubbe *et al.* 2006; Douek 2007). These analysis procedures utilize the same analytical methods as the water analysis, with the exception of sample pretreatments such as wood grinding or pulp extraction with soxhlet (Holmbom 1999a) or accelerated solvent extraction (ASE) (Thurbide and Hughes 2000).

The most commonly used and most accurate analysis of wood extractives in papermaking process waters is based on traditional LLE extraction with MTBE and GC analysis of the silylated extracts (Örså and Holmbom 1994) (Table 5). The development of a different kind of faster analytical technique has been presented for resin acids in TMP/chemi-thermomechanical pulping (CTMP) process waters (Serreqi *et al.* 2000). GC-FID analysis was used to determine individual and total resin acid content of a series of in-mill process waters, and correlation coefficients of the results were determined. One or two resin acids were used as markers for analysis of total resin acid content, and it was found that abietic and isopimaric acids, but not dehydroabietic acid, were especially useful. However, the opposite results were also obtained in the course of research that found dehydroabietic acid to be a good marker for pulp mill effluent samples (Chow and Shepard 1996). These results showed that the sampling location of the process water plays an important role when using individual resin acids as a marker for total resin content. Also, online sample enrichment using the APCI-MS technique without

multistage sample pretreatment (shorter analysis time compared to traditional GC-FID analysis) was reported for the rapid analysis of certain common fatty and resin acids (Valto *et al.* 2007, 2008, 2009). In addition, Monte *et al.* (2004) developed a procedure in which destabilization of DCS with cationic polymer addition, deposit collection, and quantification with image analysis were used to predict the tendency of the material to form deposits. The applicability of the procedure was tested with adhesives, coated and recycled papers, and deinking soaps. The results showed good reproducibility, and the procedure proved to be suitable for the evaluation of DCS and deposit tendency.

Table 5. Determination of Wood Extractives in Water Matrix

Sample	Sample preparation/ pH	Compounds	Detection Method	Reference
Effluent	Dichloromethane extraction/-	Dehydroabietic acid	LC-UV	Symons 1981
Effluent	Adsorption to XAD resin	Resin acids	GC	Richardson and Bloom 1982
Effluent	Extraction/pH 12	Dehydroabietic acid	HPLC-UV, HPLC-Fluorescence	Richardson <i>et al.</i> 1983
Effluent	MTBE extraction/pH 9	Fatty and resin acids	GC-FID	Voss and Rapsomatiotis 1985
Mechanical pulping waters	Diethyl ether extraction/ pH 3.5	Wood extractives	GC-MS GC-FID	Ekman and Holmbom 1989
Pulp mill effluent	MTBE extraction/pH 8	Fatty and resin acids	GC-MS	Lee <i>et al.</i> 1990
Water	MTBE extraction/ Dichloromethane/pH 5	Fatty and resin acids	GC-MS	Morales <i>et al.</i> 1992
Effluent, water	SPE/pH 9	Total resin acids	HPLC-UV HPLC-Fluorescence	Richardson <i>et al.</i> 1992
Effluents, river waters	SPE/pH 8	Resin acids	GC-MS	Volkman <i>et al.</i> 1993
Process waters, effluents	MTBE extraction/pH 3.5	Wood extractives	GC-FID	Örså and Holmbom 1994
Bleaching effluents	MTBE extraction, SPE/pH 8-9	Resin acids	GC-MS	Dethlefs and Stan 1996
Primary effluent	Dichloromethane extraction SPE/pH 2	Fatty acid esters	GC-MS	Koistinen <i>et al.</i> 1998
TMP circulation water	MTBE extraction/pH 3.5 Hexane extraction	Wood extractives, total relative wood extractives	GC-FID UV-VIS	Laari <i>et al.</i> 1999
Model waters	Model compounds solution	Resin acids	CE-UV HPLC-UV CE-LIF	Luong <i>et al.</i> 1999a, b
White water	MTBE extraction	Total extractives, extractive groups	Gravimetric GC-FID	Zhang <i>et al.</i> 1999

White water	MTBE extraction/pH 3.5, 9 SPE extraction/pH 5	Fatty and resin acids, sterols	GLC-FID	Mosbye <i>et al.</i> 2000
Process water, effluent	SPE (solvent mixture)/pH 10	Resin acids	GC-FID	Peng and Roberts 2000b
Process waters (eucalypt)	Hexane:acetone extraction	Lipophilic extractives	GC GC-MS	Gutiérrez <i>et al.</i> 2001a
Paper-recycling process waters	MTBE extraction/original	Fatty and resin acids	GC-MS	Rigol <i>et al.</i> 2002; Latorre <i>et al.</i> 2003
River water	-/original	Dehydroabietic acid, abietic acid isomers	LC-ESI-MS	McMartin <i>et al.</i> 2002
White waters, effluents, process waters, river water	MTBE extraction, direct injection/pH 6	Fatty and resin acids	LC-APCI-MS	Rigol <i>et al.</i> 2003b, 2004
Wastewater	Hexane:ethanol/original	Wood extractives	GC-MS	Kostamo <i>et al.</i> 2004
Model solution	Trichloromethane-diethyl ether	Resin acids	GC-FID GC-MS	Ledakowicz <i>et al.</i> 2006
White water	MTBE extraction/pH 6	Fatty and resin acids	LC-MS	Latorre <i>et al.</i> 2007
Model water (fish exposure)	Hexane:acetone/pH 3.5	Resin acids	GC-MS	Meriläinen <i>et al.</i> 2007
Process waters	MTBE extraction/- no sample preparation	Fatty and resin acids, Dehydroabietic acid	APCI-MS	Valto <i>et al.</i> 2007, 2008, 2009
Kraft mill effluent	Dichloromethane extraction/pH 9	Sterols	GC-FID	Vidal <i>et al.</i> 2007
Pulp and paper mill wastewater	MTBE extraction/pH 3.5	Wood extractives	GC-MS	Leiviskä <i>et al.</i> 2009
Model TMP water	MTBE extraction/- no sample preparation	Fatty and resin acids	GC-FID, APCI-MS, Turbidity	Valto <i>et al.</i> 2010
Process waters	Dilution methanol	Fatty and resin acids	HPLC-MS	Valto <i>et al.</i> 2011

- = not reported

The other techniques reported for analysis included capillary electrophoresis (CE) and thin layer chromatography (TLC) (Zinkel and Rowe 1964). In general, CE is not preferred for the analysis of resin acids, since these compounds have a relatively apolar structure with low strength chromophores (Rigol *et al.* 2003a). However, Luong *et al.* (1999a, b) successfully used a cyclodextrin-modified CE technique for the analysis of the derivatized resin acids. In this research, methoxycoumarin esters of resin acids were successfully separated with laser-induced fluorescence (LIF) detection with model

compounds. TLC was used for preparative isolation of component groups with silica plates prior to further, more detailed individual component analysis by GC or HPLC (Holmbom 1999a). Quantitative analysis is also possible with the appropriate internal standards for each component group. Moreover, the application of TLC was presented by Yusiasih *et al.* (2003), who used TLC to screen wood extractives by using cellulose TLC plate separation and application directly to bioassays.

The importance of analyzing wood extractives in wastewaters and receiving effluent arises in closed water circulations (Stratton *et al.* 2004; Gavrilesco *et al.* 2008). A variety of studies have been conducted concerning wastewater treatment in the pulp and paper industry (Ali and Sreekrishnan 2001; Pokhrel and Viraraghavan 2004). The problems encountered in treatment are often caused by the diversity of the possible ecologically problematic contaminants present, such as bleaching agents, salts, and organics. The analysis of interfering substances, *e.g.*, wood extractives or fatty and resin acids, in wastewaters is basically performed using the same methods as process water analysis. The analysis of resin acids has been used to study and to confirm the efficiency of the wastewater treatment process, as well as the quality of the wastewater (Laari *et al.* 1999; Ledakowicz *et al.* 2006).

Online Analysis and Process Chemistry

The closing of water circulation during the papermaking process will increase the need for sensitive and rapid online measurements. Additionally, increasing consumer demand for product and the use of papermaking additives for paper machines have created a need for real-time monitoring of the wet-end chemistry (Tornberg *et al.* 1993; Holmbom 1999b; Rice 2001; Holmbom and Sundberg 2003). The general understanding and rapid developments in sampling, analytical procedures, miniaturization, and data processing have helped satisfy the need for useful and current information provided by real-time analysis (Workman *et al.* 2003, 2009). In addition, the automation of laborious analytical techniques has improved analytical quality parameters, such as accuracy and reproducibility of the analytical methods.

Particularly, online/real-time chemical measurements are focused on monitoring basic summative parameters with simple and rapid techniques to measure pH, temperature, conductivity, turbidity, and charge (Scott 1996; Boegh *et al.* 2001). The use of COD and total organic carbon (TOC) for the analysis of the total organic compounds in the process waters has been preferred in paper mills (Holmberg 1999a; Manner *et al.* 1999; Knuutinen and Alén 2007). However, these measurements produce little or no information about the chemical behavior of the individual compounds present in the process waters. Also, the optimal consumption of process chemicals in paper production, for example, will be more difficult to control without specific identification techniques, such as chromatographic measurements. Controlling the chemical additives will improve the stability of paper machines and reduce costs. The most promising techniques are based on laboratory chromatographic analytical equipment, such as continuous-flow extraction (Rice *et al.* 1997) and flow cytometry (Vähäsalo *et al.* 2003, 2005). Fourier transform infrared spectroscopy (FTIR) to measure DCS in wet-end with a continuously operating centrifuge separator has also been tested (Tornberg *et al.* 1993). This measurement was compared with COD and measuring of pitch balls and a good correlation was observed. The sensitivity of commercial FTIR equipment was found to be a critical factor in the analysis of online mill trials.

The problems with the sampling system can be considered to be the most challenging task in developing online measurements for process control. Therefore, a lot of research has been concerned with the improving the state of sampling systems (Workman *et al.* 1999, 2005). The main purpose of sampling is to provide a representative sample to a process analyzer. Flow injection analysis (FIA) can be useful for sampling in developing process analytical methods. In this procedure, the sample is treated fluidically through the pumps, valves, and reactors that comprise the flow system. Once sampling occurs, the automated fluid handling, coupled with detection, is the same regardless of the origin of the sampled volume. This useful FIA procedure has been used, for example, in monitoring online COD or kraft pulping liquors (Kuban and Karlberg 2000). Modification of the conventional FIA extraction mode for high-pressure flow extraction has also been studied (Rice *et al.* 1995, 1997). The tangential flow filtration method was developed to remove coarse fibers from pulp slurry. It showed good reliability in mill trials.

Problems arising from automated sampling in the pulp and paper industry have successfully been solved by using CE with UV detection for the analysis of soluble anions (*e.g.* chloride, oxalate, formate, and acetate) in paper mill waters (Sirén *et al.* 2000, 2002; Kokkonen *et al.* 2004). This online procedure has been applied to several process machines at pulp and paper mills. It also enabled the simultaneous separation and determination of the monitored ions, and a good correlation was obtained between changes in process conditions and ion concentrations. Also, the use of a centrifugal pump and a ceramic filter connected to the APCI-MS system with time-controlled column switching valves for the analysis of concentration levels of fatty and resin acids in papermaking process waters has been reported (Valto *et al.* 2009). In addition, Chai *et al.* (2002) have developed an attenuated total reflection (ATR) UV-sensor, which could replace the online automatic titration systems by online monitoring of sulfide, hydroxide, and carbonate ions in kraft pulp white liquors. However, most of the current potential online analytical systems suffer from high maintenance requirements. This has made them unlikely to be suitable for mill applications, and many of these sensors can provide only single-component measurements.

Figure 5 presents the multistage analytical scheme for the analysis of fatty and resin acids in papermaking process waters.

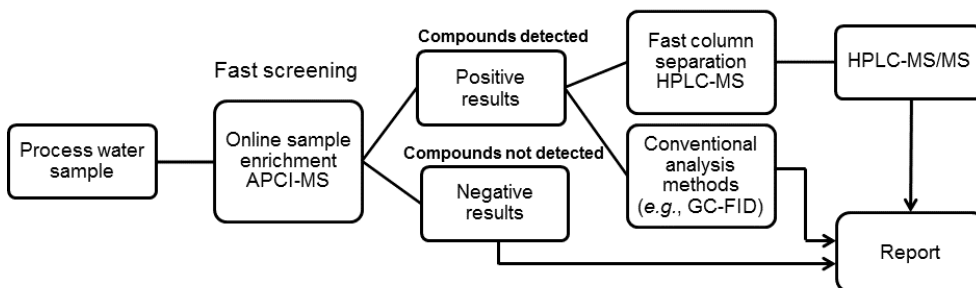


Fig. 5. Proposed scheme of the analytical procedures used for analysis of fatty and resin acids in papermaking process waters

In the first stage, a process water sample can be quickly screened with an online sample enrichment method, and the further analytical procedure can be outlined based on these results (Valto *et al.* 2008, 2009). In the next stage, the procedure utilizes conventional analytical methods such as LLE and GC-FID (Örså and Holmbom 1994). This is necessary if, for example, detailed structural information is needed about all abietic acid isomers. The fast HPLC-MS method is suitable for individual fatty and resin acids (McMartin *et al.* 2002; Valto *et al.* 2011). The possible co-eluting compounds from HPLC-MS analysis can be confirmed by HPLC combined with tandem mass spectrometric detection (MS/MS). The proposed analytical procedure can be used to optimize the sampling by fast screening of the sample and deciding on further analysis based on the positive or negative results.

CONCLUDING REMARKS

In papermaking, there is an urgent need to develop straightforward analytical techniques to clarify problems occurring, for example, as a result of a more intensive closure of water circulations. This closure means an increase in the amounts of wood-derived detrimental substances, such as fatty and resin acids, in papermaking process waters. These acids are present in wood either as free acids or various esters. They are dispersed or dissolved into the process waters during mechanical pulping and carried into the paper machine. Both these compound types can remain as impurities in the final product, causing further problems. In addition, resin acids are mostly responsible for the toxicity of paper mill effluents. However, the development of faster analysis methods for the troubleshooting of process problems is a challenging task. Major current analytical methods require many pretreatment steps, increasing the total analysis time, and therefore they are not suitable for real-time process control.

Several different procedures have been reported for the routine analysis of wood extractives in process waters. The most widely used and basic technique has been sensitive and reliable GC with derivatization and column separation followed by FID or MS detection. LC with derivatization or HPLC techniques coupled to MS with a direct injection technique has also been used. Also, new and interesting modifications, such as direct-injection HPLC analysis of resin acids in pulp mill effluents, HPLC analysis of the total resin acid content using some resin acids as markers, and the analysis of fatty and resin acids in effluents and white waters with HPLC-MS, and online sample enrichment with the APCI-MS technique without multistage sample pretreatment, have been presented. However, more development work is needed to ensure reliability and usability, both in laboratory use and in possible online use in paper mills. The key issue in the use of more sophisticated chromatographic methods, such as HPLC-MS, is also the lack of adequate personnel in paper mill laboratories. In the future, in order to develop more useful online procedures, investigations should focus on the application of these analytical procedures to real process samples and environments.

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