

ANALYSIS OF RESIN AND FATTY ACIDS ENRICHED IN PAPERMAKING PROCESS WATERS

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The applicability of a special pilot-scale installation (Short Circulation Device) was studied for demonstrating the enrichment of selected resin and fatty acids in process waters when increasing water reuse during the manufacture of paper. The traditional gas chromatography with flame ionization detection (GC-FID), turbidity, and online sample enrichment (solid phase extraction, SPE) for atmospheric pressure chemical ionization-mass spectrometry (APCI-MS) measurements were used for the analysis of the resin and fatty acids. The data from all the measurements with unbleached thermomechanical pulp (TMP) process waters were in a good agreement, and correlation coefficients (R^2) > 0.9 were obtained in each case. Rapid information about the levels of wood extractives in papermaking process waters is of great importance, and it offers a suitable way to predict oncoming pitch problems. It was concluded that the routine control of the extractives level in papermaking process waters is possible by all these methods.

Keywords: Atmospheric pressure chemical ionization; Fatty acids; Mass spectrometry; Papermaking; Pitch; Process waters; Resin acids; Short circulation device

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INTRODUCTION

The papermaking industry is closing water circulations for environmental and economic reasons (Latorre et al. 2005). Due to the many roles of water usage in papermaking, its reduction is not a simple procedure. Typically, water is used in paper mills for the papermaking process, cleaning, washing, sealing, and cooling (Gavrilescu et al. 2008). Decreasing the fresh water consumption in paper mills increases also the recirculation of the process waters, e.g., white waters of the paper machine. Process waters and effluents from closed-cycle water circuit paper mills are enriched with a large number of harmful substances, mainly organic materials, which interfere with the papermaking system (Holmberg 1999). These substances also cause considerable damage to the receiving waters if they are not treated before discharge. Effective waste water treatment enables the recycling of these waters back to the paper mill, thus replacing fresh water.

Dissolved and colloidal substances (DCS) (1-5 % of the wood material) can accumulate in process waters, especially during mechanical pulping processes, and have a tendency to form deposits as well as increase the problems of the paper machine, particularly in the wet end (Holmberg 1999). The enrichment of certain pitch components

also increases the anionic charge of the papermaking stock and greatly impacts the quality of the final product (Pelton et al. 1980; Sundberg et al. 2000). The main substance group in the deposits has been identified as wood extractives, composed mainly of free fatty (~6 %) and resin acids (~10 %), sterols, steryl esters, and triglycerides (Qin et al. 2003). Of these constituents, the presence of slightly soluble resin and fatty acids, their esters, and in some cases especially their salt derivatives, form the main reason for negative effects on papermaking. The resin and fatty acids are also a major concern because they are responsible, for example, for effluent toxicity and process problems (Mörck et al. 2000; Makris and Banerjee 2002; Lacorte et al. 2003). The extractive content is also considered an important quality parameter for papermaking, especially for pulp production (Alén 2000). The formation of extractives-derived pitch deposits is an unavoidable occurrence, and a series of procedures have been developed to reduce this problem. The pitch problems are not limited only to the manufacturing of wood fibers, because various pitch precipitations are also found in the production of non-wood fibers (Gutiérrez and del Río 2005). They can effectively be diminished, for example, by debarking, seasoning, and adding controlling agents. In addition, new biotechnological techniques, such as fungal and bacterial pre-treatments, have been developed for this purpose (Kallioinen et al. 2003; Gutiérrez et al. 2006; van Beek et al. 2007; Widsten and Kandelbauer 2008).

Previously, methods that measure the summative parameters (e.g., the determination of total organic carbon and total extractives) of process waters have dominated analysis procedures (Holmbom 1999), even though these methods provide little information about the individual components of the process waters. A correlation between the amount of wood resin and turbidity in the solution has also been found (Mosbye et al. 2003; Saarimaa et al. 2006). In practice, the simple and easy to perform turbidity measurement has been used to evaluate the DCS in process streams in paper mills where the usability of more sophisticated methods is limited. Although various kinds of chromatographic procedures has been presented in wet-end chemistry (Holmbom 1999; Knuutinen and Alén 2007), there are only a few reports on the use of alternative methods to traditional solvent extraction and gas chromatography (GC) (Örså and Holmbom 1994) for the analysis of wood extractives. One of these alternative methods is high performance liquid chromatography (HPLC) combined with mass spectrometry (MS) (Lacorte et al. 2003; Rigol et al. 2003a,b). Also, the use of one or two resin acids as a marker for the total content of resin acids (Serreqi et al. 2000) and online sample enrichment with APCI-MS technique without multistage sample pretreatment (shorter analysis time compared to that of traditional GC-FID analysis) is reported for the rapid analysis of certain common resin and fatty acids (Valto et al. 2007, 2008, 2009).

This paper presents a pilot-scale study to demonstrate the enrichment of wood extractives in papermaking process waters when increasing water reuse and/or recycling. The process water samples were achieved from the experiments performed by the Short Circulation Device (VTT Technical Research Centre of Finland, Jyväskylä). This pilot-scale installation enabled us to study the chemical state of papermaking processes under well-controlled conditions. The installation was used to demonstrate the actual water circulation of the paper machine, in which the white waters are usually recycled. For this reason, it was possible to conduct a wide range of investigations from the analysis of

headbox flow dynamics to the clarification of web phenomena and paper properties. The process water samples were analyzed by using GC-FID, online sample enrichment APCI-MS, and turbidity measurements. In general, turbidity is a useful indicator of the colloidal material in mechanical pulp filtrates and used especially as an indicator of colloidal wood pitch (Sundberg et al. 1996). Therefore turbidity measurements were included as one of the analytical techniques. Further goals of our study were, on the one hand, to compare the results from chromatographic and turbidity measurements and, on the other hand, to identify a correlation between analytical data and the fraction of resin and fatty acids. This kind of approach is of benefit when predicting possible future pitch problems.

EXPERIMENTAL

Water Samples

The most suitable softwood species due to its favorable fiber properties for mechanical pulping is spruce, in which the extractives content varies between 0.5 and 2% (Alén 2000). Therefore, unbleached thermomechanical pulp (TMP) from a mill in Finland using spruce was used to enrich the process waters and five representative water samples were taken from a Short Circulation Device (Fig. 1).

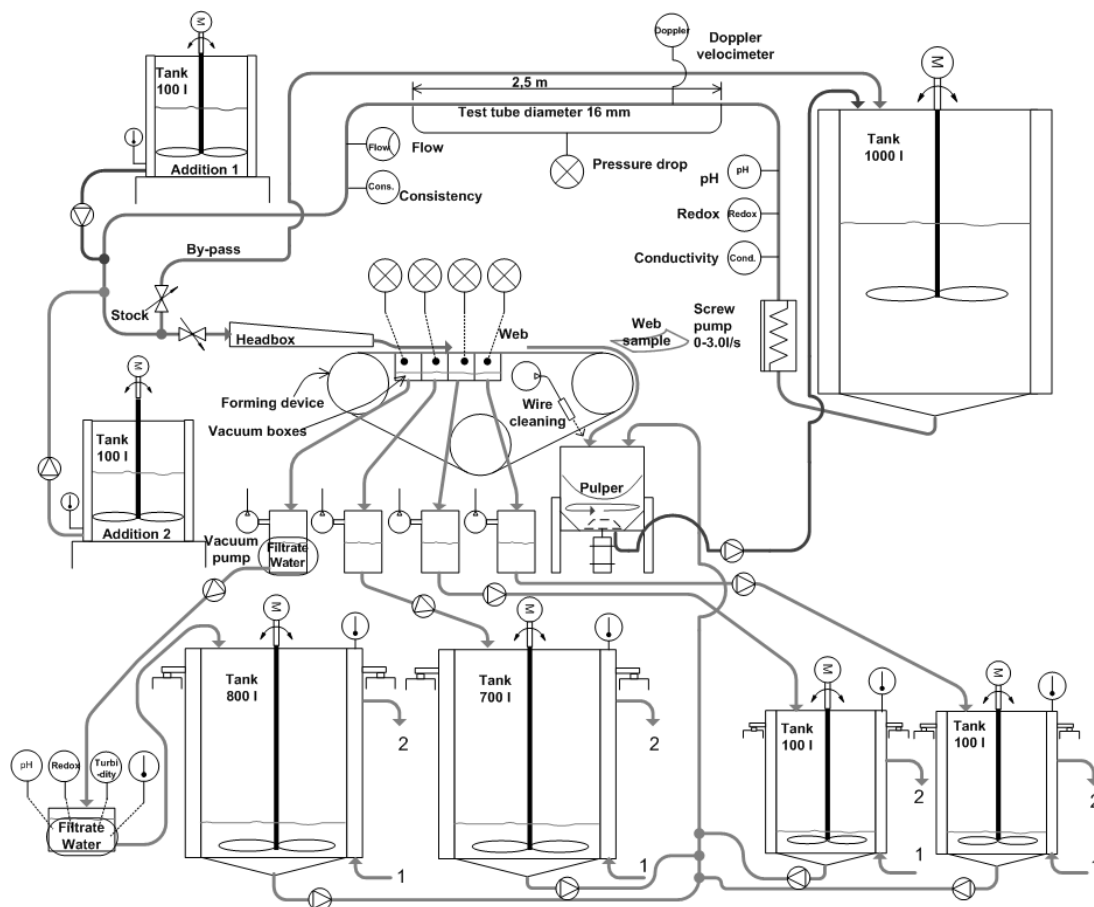


Fig. 1. Scheme of the Short Circulation Device

This installation consisted of a combination of a headbox and a fourdrinier device. The dewatering unit contained a controllable wire section with four adjustable vacuum boxes. The feeding tank volume was 1 m³, and volumes of the white water tanks varied from 0.1 m³ to 0.8 m³. The temperature range was between 20 °C and 60 °C. The installation also had a retention agent and a filler feed system. The chemical state of the process was characterized by online pH, conductivity, redox, turbidity, and temperature measurements. Conductivity was measured before the headbox, whereas solid content and pH were measured in samples collected from the first white water tank.

The TMP process water (tap water, pH ~8) was recycled through the Short Circulation Device demonstrating the paper machine water circulation. The samples were taken from the filtrate water flow of the first vacuum box with the following recycling times: reference sample (RF), 1 hour (S1), 2 hours (S2), 3 hours (S3), and 4 hours (S4). The RF was taken immediately when the enrichment process was balanced. After the first sampling, the process water was enriched for one hour by continuously recycling it through the headbox and forming device. After the second sampling, the recycled stock batch was replaced with a new batch of unbleached TMP. The same process water was once again enriched for one hour by recycling it through the headbox and forming device prior to sampling. The procedure was repeated four times. The turbidity measurements with a sample volume of 30 mL were made with a Hach 2100 AN IS device (Hach, Loveland, CO, USA). The samples were filtered with an 8 µm ceramic filter and stored at -20 °C until analyzed. For the GC and APCI-MS analyses, the sample was allowed to warm to room temperature.

Chemicals and Standard Solutions

Methyl *tert*-butyl ether (MTBE) and HPLC grade methanol were obtained from Labscan (Dublin, Ireland) and J. T. Baker (Deventer, Netherlands), respectively. Compounds that were used as standards were obtained with purity between 97% and 99%. Dehydroabietic acid (DHAA) was purchased from Helix Biotech (Richmond, BC, Canada), margaric acid from Aldrich-Europe (Beerse, Belgium), and betulinol, 1,3-dipalmitoyl-2-oleyl-glycerol, and linoleic acid were from Sigma (St. Louis, MO, USA). Cholesteryl heptadecanoate were from TCI (Zwijndrecht, Belgium) and palmitic and stearic acids were from Fluka (Buchs SG, Switzerland). The silylation reagents, bis(trimethylsilyl)-rifluoroacetamide (BSTFA), and trimethylchlorosilane (TMCS) were obtained from Regis Technologies Inc. (Morton Grove, IL, USA).

Stock solutions of standard compounds were prepared by dissolving an accurate amount of pure standard in a solvent. All solutions for the GC analysis were made with MTBE. For APCI-MS analysis, the stock solutions were made in methanol, and all working solutions were prepared by diluting the stock solution with Milli-Q water (Millipore, Bedford, MA, USA). Standard solutions were stored in the dark at 4 °C for up to 1 month.

Instrumentation

Gas chromatography (GC)

The preparation of the process water samples for GC analysis has been described in detail elsewhere (Örså and Holmbom 1994; Valto et al. 2007). This analytical procedure was applied with the following minor change: Margaric acid was used ($C_{17}H_{34}O_2$, molecular mass (MM) 270.5 g mol^{-1}) as an internal standard (ISTD) because it is rarely present in papermaking water samples (Rigol et al. 2003b), and it can be used in both analytical methods (GC-FID and APCI-MS).

The wood extractives were analyzed for their component groups by GC-FID analysis as described earlier (Örså and Holmbom 1994; Valto et al. 2007). The following analytical procedure was performed to acquire detailed information on individual resin and fatty acids (GC-FID, individual). The analyses were carried out on an Agilent 6850 Series device. A Supelco Equity-5 (30 m * 0.32 mm I.D. with a film thickness of 0.25 μm) column was used with nitrogen as the carrier gas. The temperature of the injector was 290 °C. The detector temperature was 300 °C. The temperature program was 1.5 min at 100 °C, followed by 6 °C min^{-1} to 180 °C (10 min), and then 4 °C min^{-1} to 290 °C (20 min).

Online sample enrichment atmospheric pressure chemical ionization-mass spectrometry (APCI-MS)

The samples were analyzed using an HP Series 1100 binary pump, a vacuum degasser, and a thermostatted column compartment with a six-port switching valve (Hewlett-Packard, Palo Alto, CA, USA). Margaric acid was used as an ISTD, and there was no need to adjust the sample pH (Valto et al. 2007). However, the filtration (an 8 μm filter) was important for the analytical procedure to prevent any organic, solid fine material in the sample from entering into the ionization chamber. This was essential, especially in the case of multi-component process water samples.

The filtered water sample was introduced to the analytical system using a Waters 501 pump at a flow rate of 0.2 mL min^{-1} (Waters, Milford, MA, USA), and an HP 1100 pump was used to deliver the mobile phase (methanol) at a flow rate of 0.5 mL min^{-1} (Valto et al. 2009). A standard precolumn Fusion-RP 4*2.0 mm (Phenomenex, Torrance, CA, USA) was used as a SPE enrichment column, and before analysis the precolumn was flushed with methanol at the flow rate used in the analysis. The sample was enriched for 1-2 minutes, and the sample flow was switched into the waste. In addition, a Waters column switching valve (Milford, MA, USA), controlled by an HP 35900E Interface (Palo Alto, CA, USA), was used to switch the flow coming from the pump either to the waste (sample enrichment) or to the MS. An HP 1100 Series single quadrupole mass-selective detector (MSD) with an atmospheric pressure chemical ionization (APCI) interface detecting ions (M-H) in the negative ion and selected ion monitoring (SIM) mode was used. Data collection and processing were handled by HPChemStation (A06.03) software. The MS parameters and analytical procedure were optimized earlier (Valto et al. 2007, 2008).

RESULTS AND DISCUSSION

The chemical state of the process was measured by online solids content, pH, and conductivity measurements, whereas the turbidity measurements were made offline (after filtration) in order to achieve representative results with other analytical techniques (GC-FID and APCI-MS). According to the results shown in Table 1, turbidity increased linearly ($R^2 = 0.99$) except for the RF. The reason for a higher turbidity value for RF was probably due to the dissolution of colloidal material of the filtrate water during the first enrichment process. The solids content that increased within each enrichment process was still at a quite low level. Correspondingly, pH decreased almost linearly after the first enrichment process; differences between these waters and typical TMP water values resulted from the tap water (pH~8) used. At this pH level, the relative amounts of released resin acids from wood are higher than at pH of below 5 (Örså et al. 1997). Conductivity increased after each recycling, thus indicating an increase in anionic trash in the process.

Table 1. Some Characteristics of the Water Samples

Sample	Recycling time (h)	Turbidity (NTU)	Solid content (%)	pH	Conductivity ($\mu\text{S cm}^{-1}$)
RF	-	81	0.024	8.68	248
S1	1	63	0.028	9.18	421
S2	2	124	0.035	9.11	552
S3	3	195	0.045	9.02	700
S4	4	277	0.074	8.87	837

GC Analysis

Various kinds of resin and fatty acids can be found in papermaking process waters. Figure 2 presents the structures and molecular masses of compounds identified in this study. The GC-FID results of detected individual fatty (linoleic, oleic, and stearic) and resin (pimaric, isopimaric, palustric, abietic, neoabietic, and DHA), acids as well as the GC-FID analysis of these fatty and resin acids as their component groups were compared (Fig. 3). These results showed that the total amount of resin acids was comparable ($R^2 = 0.9936$) to the sum of the individual resin acid compounds. On the other hand, in the case of fatty acids, the corresponding correlation was $R^2 = 0.7692$.

The enrichment of the individual resin acids is shown in Fig. 4. The sample (S1) was obviously taken before any enrichment of resin acids had occurred. The enrichment of the main resin acid component, DHAA, could be easily detected. The enrichment profiles of other resin acids (pimaric, isopimaric, palustric, abietic, and neoabietic acids) found in the process waters were also quite similar. Unfortunately, the levels or the profiles of structural resin acid isomers, such as abietic, pimaric, and isopimaric acids, could not be measured with the APCI-MS technique because of their equal molecular masses. However, when monitoring the ion m/z 301 (M-H), the total amount or concentration level of all abietic acid isomers could be estimated.

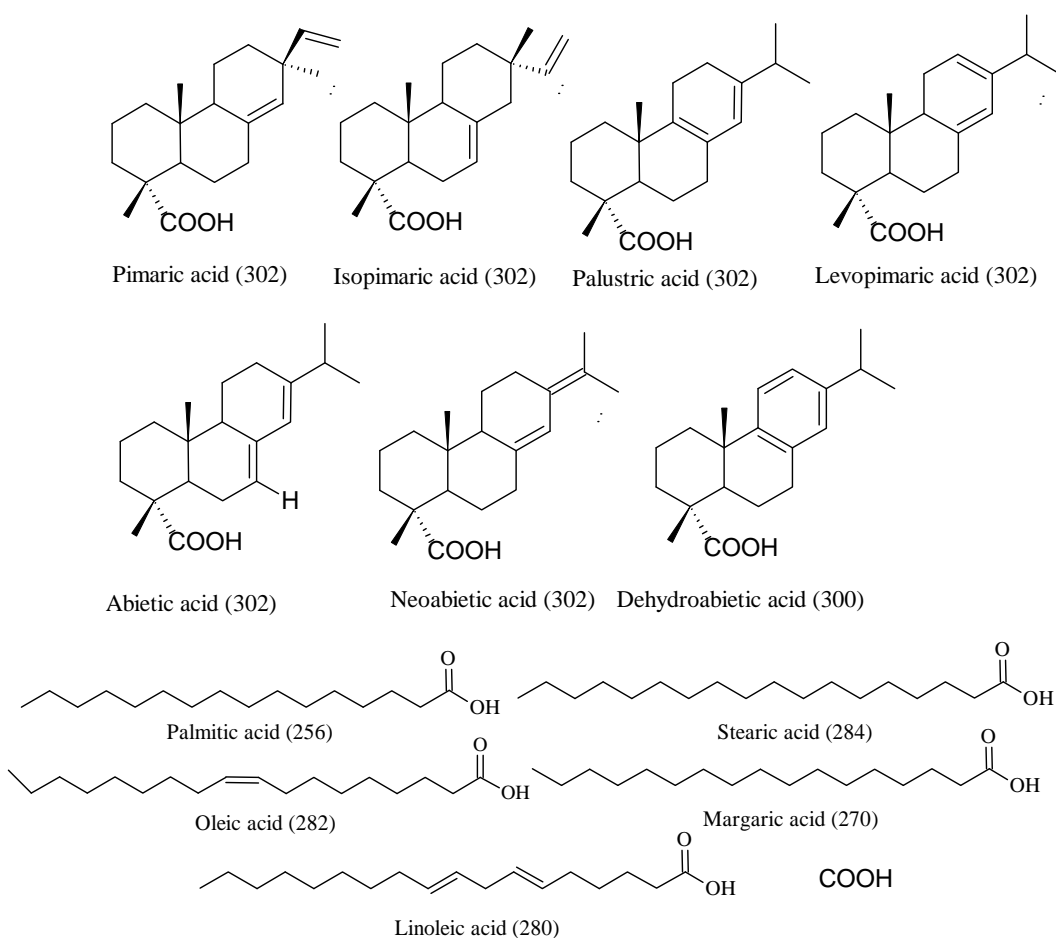


Fig. 2. The structures and MM (in parenthesis as g mol^{-1}) of the compounds analyzed

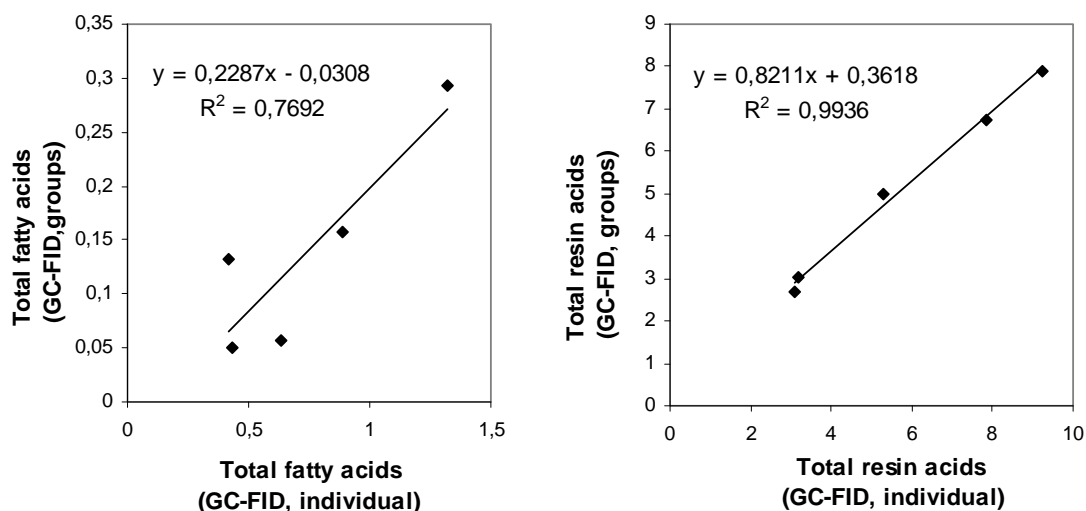


Fig. 3. Correlation of the total fatty acids (GC-FID, groups and GC-FID, individual) and total resin acids (GC-FID, groups and GC-FID, individual) present in the water samples (mg L^{-1}). GC-FID, groups = analysis of the component groups by a 5-7 m column. GC-FID, individual = analysis of individual fatty and resin acid components by a 30 m column.

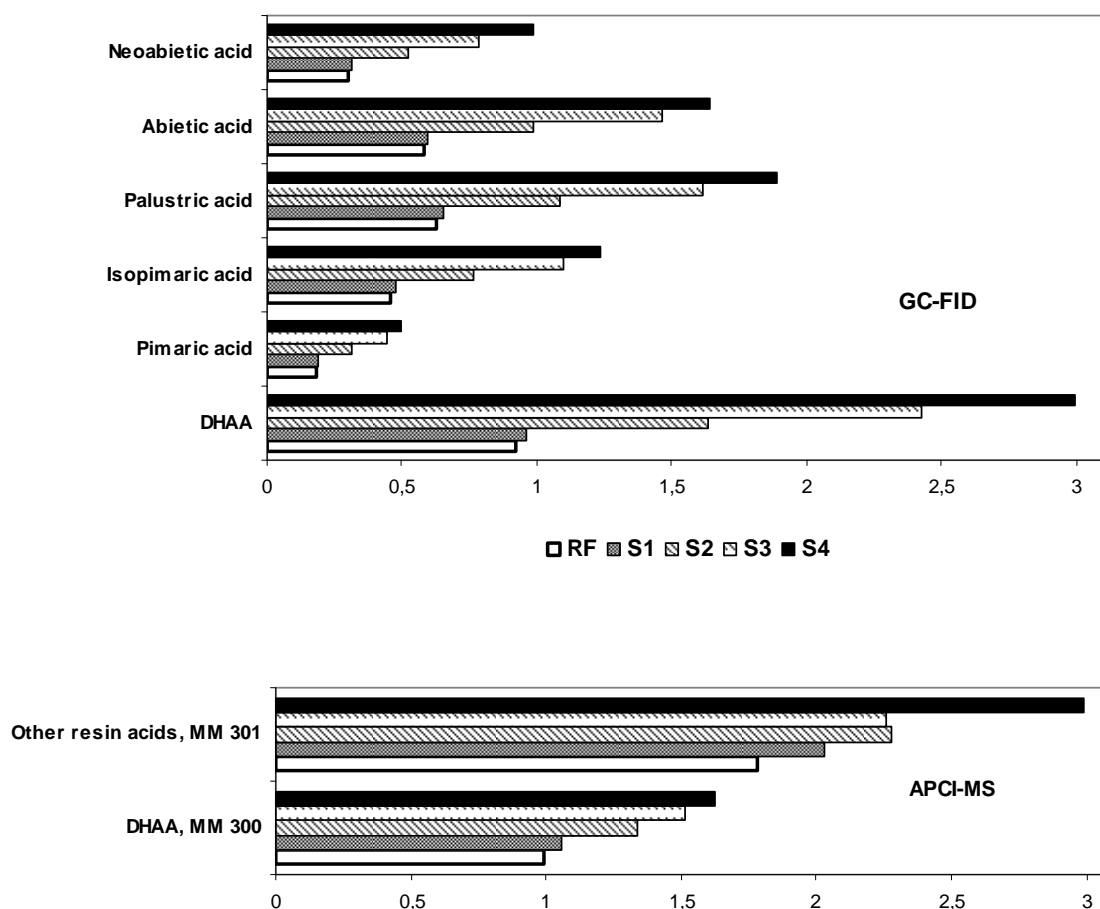


Fig. 4. Enrichment of resin acids (mg L^{-1}) (GC-FID, individual) and comparison with APCI-MS results. GC-FID, individual = analysis of the individual fatty and resin acid components by a 30 m column

Repeatability of the APCI-MS Analysis

With the APCI-MS method, in negative SIM mode, only the intensive $[\text{M-H}]^-$ ion was generated with a high yield, as reported earlier (McMartin et al. 2002; Valto et al. 2007). In order to test the possible matrix effects of the water samples used in this study, all samples were spiked with three different concentrations of selected resin and fatty acids in order to provide three samples at three different concentrations ($0\text{--}59.5 \mu\text{g mL}^{-1}$ for DHAA, $0\text{--}60.6 \mu\text{g mL}^{-1}$ for palmitic acid, and $0\text{--}60.7 \mu\text{g mL}^{-1}$ for stearic acid). Five replicates were carried out for each spiked water sample, and an average of the peak areas was used to evaluate the relative standard deviations (RSD %). The linearity of the response was calculated by plotting the calculated concentrations obtained against the concentrations introduced for each compound. The data were analyzed by linear

regression. The results (Table 2) show that good correlation coefficients ($R^2 > 0.9$) were achieved for all of the samples studied.

Table 2. The Correlation Coefficients R^2 and Relative Standard Deviations (RSD%) of the Repeatability Measurements (APCI-MS)

Sample	RF	S1	S2	S3	S4
Compound					
Dehydroabietic acid	0.9990 (4.3)	1 (3.2)	0.9983 (5.4)	0.9776 (5.8)	0.9790 (4.9)
Palmitic acid	0.9806 (3.9)	0.9903 (4.4)	0.9931 (5.5)	0.9962 (9.8)	0.9976 (2.9)
Stearic acid	0.9819 (2.2)	0.9898 (2.2)	0.9938 (2.9)	0.9971 (3.3)	0.9980 (2.9)

Comparison of the Methods

The APCI-MS method was applied to the analysis of the concentration levels of selected resin acids (abietic acid and DHAA) and fatty acids (palmitic, stearic, and oleic acids) in water samples RF and S1-S4. The results were obtained using the ISTD method. These results were compared to those obtained using the conventional GC-FID method (both individual components and total extractive groups calculated) (Örså and Holmbom 1994; Valto et al. 2007). The profiles of the resin acid results that were obtained using the different calculations, including turbidity measurements, were quite similar (Fig. 5). This indicated that monitoring only DHAA levels in process waters can be used to estimate the total resin acid content. Previously, abietic acid has been found to be a good marker for the in-mill samples, whereas DHAA was found to be a poor marker (Serreji et al. 2000).

The relative concentration levels of selected fatty acids (stearic, palmitic, and oleic acids) were also analyzed using the APCI-MS method. These acids were selected because they are commonly present in paper mill process waters (Rigol et al. 2002). The profiles of the results with APCI-MS, GC-FID, and turbidity values (Fig. 6) were quite similar, indicating that also some information about the quality of process waters could be obtained by following the levels of fatty acids, as well. In most cases, the information on the levels of free fatty acids, which originate mainly from the triglycerides saponified during alkaline kraft cooking, can be used to evaluate the tendency of wood resin to cause pitch problems, because even at high concentrations of these acids, the deposit formation tendency is low (Mörck et al. 2000).

The correlation between the results obtained by the GC-FID and APCI-MS methods has been studied in detail previously (Valto et al. 2007, 2008, 2009). It has been found that DHAA is an especially good marker for a rough evaluation of process water quality. On the other hand, the most appropriate marker for the total resin acid content appears to depend on the site that is being monitored and on the total papermaking process. To ensure the usability of DHAA as a marker, correlations between the GC-FID and the APCI-MS methods were made.

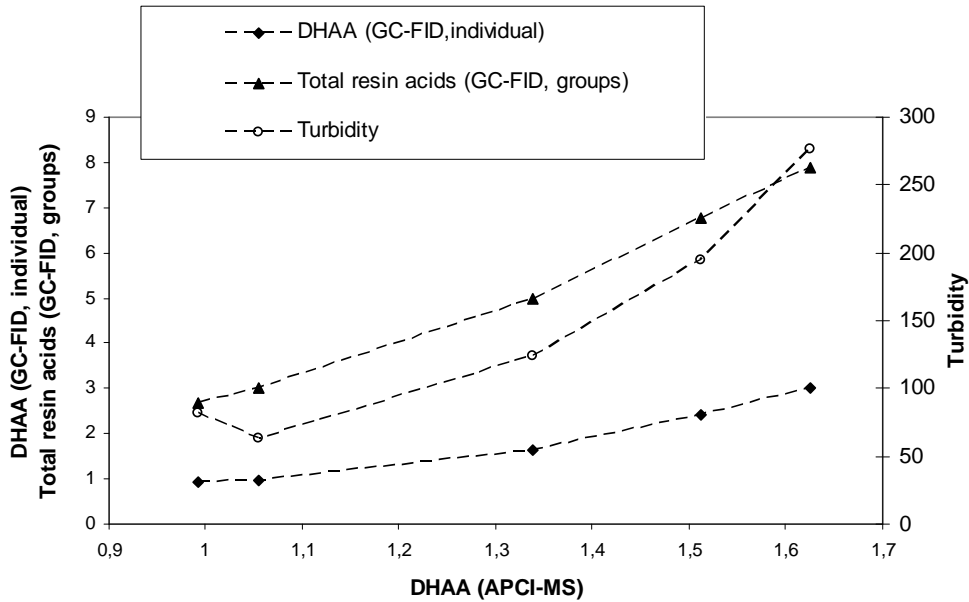


Fig. 5. Correlations of DHAA levels (mg L^{-1}) (analyzed by APCI-MS and GC-FID) and total resin acids (analyzed by GC-FID) and turbidity (NTU) in water samples

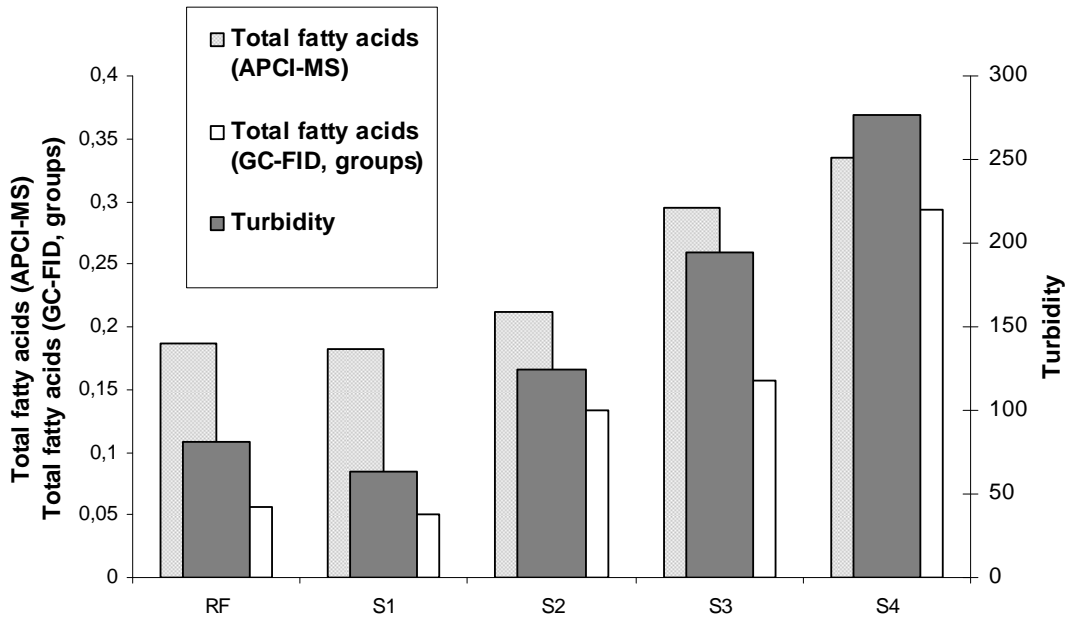


Fig. 6. Profiles of selected fatty acids (palmitic, stearic, and oleic acids) analyzed by APCI-MS and total fatty acid levels (mg L^{-1}) analyzed by GC-FID and turbidity (NTU)

As Fig. 7 shows, the correlations between the individual resin acid component, the DHAA, analysis by GC-FID and APCI-MS, and the total resin acids analyzed by GC-FID, were good ($R^2 > 0.9$). This finding indicated that an approximate evaluation of total resin acids in process waters could be accomplished by analyzing only the DHAA concentration levels using the APCI-MS method.

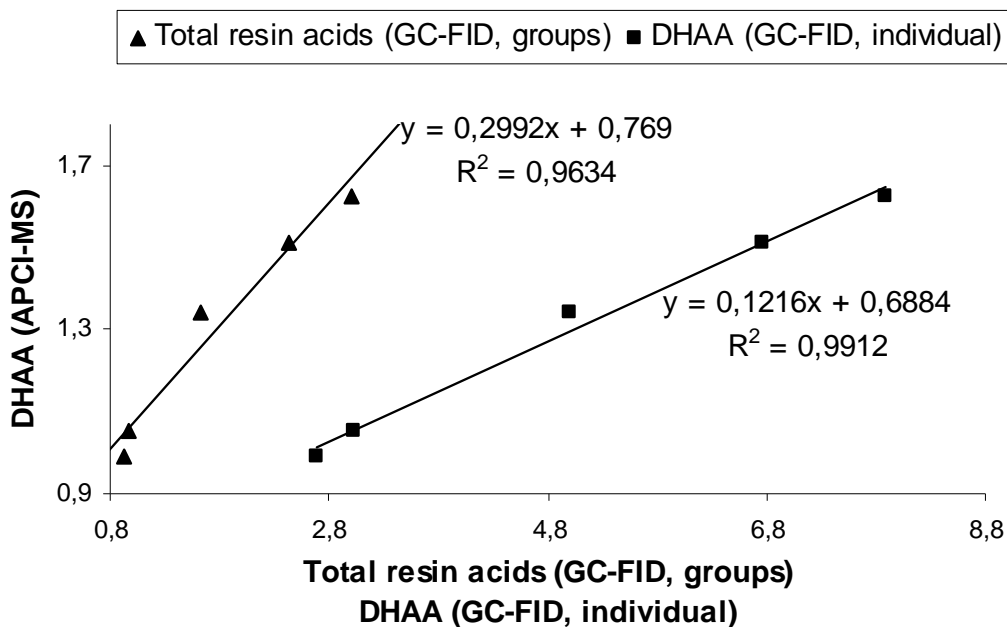
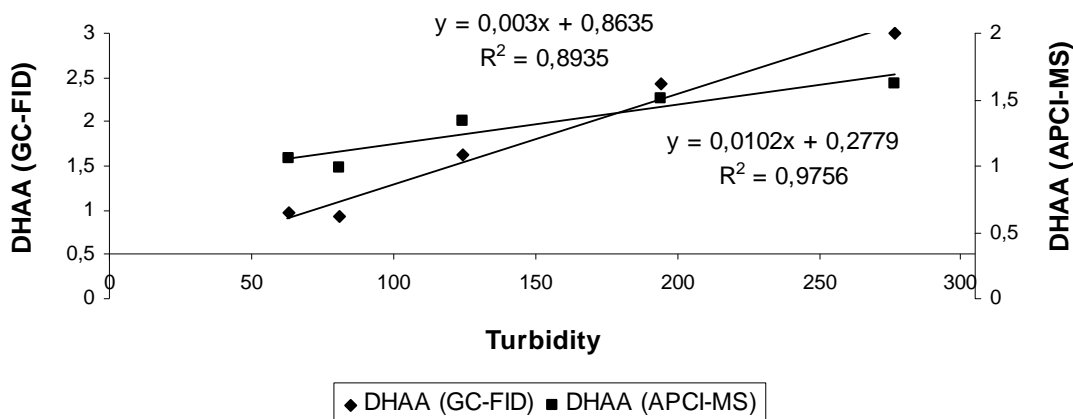


Fig. 7. The correlation of DHAA (mg L^{-1}) analyzed by APCI-MS and GC-FID, and total resin acids compounds (mg L^{-1}) by GC-FID

It is generally known that the turbidity measurement is a suitable method for estimating the total amount of wood resin or DCS in process streams (Ravnjak et al. 2003). In the present study, the different correlations with the turbidity measurements and the results from the analysis of resin and fatty acids using GC-FID or APCI-MS were calculated. Table 3 presents the correlation coefficients (R^2) of turbidity against different measurements of resin and fatty acids. The results showed that, depending on the analytical method used, the correlation coefficients were higher than 0.9, except in cases where abietic acid isomers ($\text{MM } 301 \text{ g mol}^{-1}$) were measured by APCI-MS. The correlation results also show that higher R^2 values were achieved with the correlation of turbidity with DHAA measured by the APCI-MS method than by GC-FID (Fig. 8). The results confirmed the suitability of the turbidity measurement for estimating wood resin in process streams. However, other sophisticated analytical methods are still needed to analyze the amount of the individual wood resin compounds (such as resin and fatty acids) or component groups (such as steryl esters and triglycerides) in the process waters.

Table 3. The Correlation Coefficient (R^2) with Turbidity and Different Methods

	Total fatty acids (GC-FID)	Total fatty acids (APCI-MS)	Total resin acids (APCI-MS)	m/z 301 (APCI-MS)
R^2	0.9551	0.9737	0.9055	0.8329

**Fig. 8.** Correlation of turbidity (NTU) and DHAA (mg L^{-1}) (analyzed by GC-FID and APCI-MS)

CONCLUSIONS

1. An estimation of the wood extractives or selected component groups, such as resin and fatty acids, can be done by using the turbidity measurements, GC-FID, and online sample enrichment APCI-MS methods. Good correlations with $R^2 > 0.9$ were achieved in most cases.
2. The analysis of only one resin or fatty acid level in process waters provided good correlations (R^2) with different results for total component groups (total fatty or resin acids). For example, the total resin acid content can be estimated by analyzing only the DHAA levels in process waters using the online APCI-MS method ($R^2 > 0.9$).
3. All of these methods provide valuable information about the chemistry of the papermaking process. The choice of method depends on the quality of the information needed. The turbidity measurements supported well the results obtained by more sophisticated GC-FID and APCI-MS methods. In many cases, a rapid rough estimation of the resin and fatty acid levels using the online APCI-MS technique is recommended. However, if detailed information about the other wood extractive groups, such as triglycerides, is needed, the use of a traditional solvent extraction method and GC-FID is preferred.
4. The enrichment of wood extractives can also easily be demonstrated in laboratory-scale studies using a Short Circulation Device installation. This allows researchers to conduct different kinds of studies concerning wet-end chemistry and the quality of process waters.

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