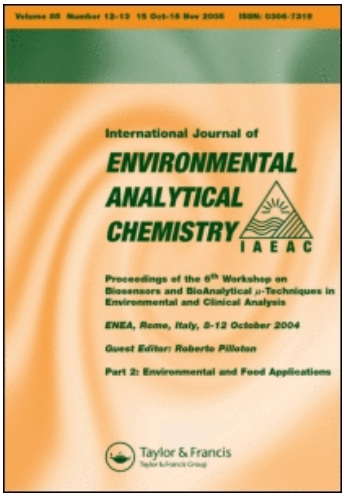

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Resin and fatty-acid analysis by solid-phase extraction coupled to atmospheric pressure chemical ionization-mass spectrometry

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Resin and fatty-acid analysis by solid-phase extraction coupled to atmospheric pressure chemical ionization–mass spectrometry

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Using gas-chromatographic analysis, the suitability of liquid–liquid extraction and solid-phase extraction (SPE) methods was studied for the rapid separation of resin and fatty-acid fractions from papermaking process waters. In the second phase of this study, a novel procedure (correlation coefficient >0.99 and repeatability RSD <8%) for on-line monitoring of selected individual acid components (limits of detection 11–78 $\mu g\,L^{-1}$) by SPE combined with atmospheric pressure chemical ionization–mass spectrometry was developed. The suitability of this technique for quality control of papermaking process waters was tested by means of industrial samples. The method was also found suitable for the analysis of resin and fatty acids in receiving waters of pulp and paper mills.

Keywords: Resin acids; Fatty acids; Solid-phase extraction; Mass spectrometry; Process waters; On-line measurement

1. Introduction

The papermaking industry is moving towards a more closed water-circulation system, which increases the formation and accumulation of interfering substances in process waters. The main environmental issues are discharges to the effluents, which can also contain compounds showing toxic effects on aquatic organisms [1]. The wood extractives comprise one of the most important groups of interfering substances, consisting mainly of resin acids, esters of fatty acids (mainly triglycerides), free fatty acids, triterpenoids, sterols, and phenolic compounds. The extractives disperse in process waters during mechanical defibration and cause detrimental effects in papermaking including the formation of sticky deposits on paper machines together with various runnability problems [2, 3].

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In addition, some detrimental extractives-based substances, such as resin acids, which have a rather stable chemical structure under these process conditions, are considered to be the major contributors to the toxicity of paper mill effluents [4–7]. These compounds can be detected at levels as high as $mg\,L^{-1}$ in waste waters, and problems caused by these acids can be seen in the receiving ecosystems beyond paper mills, for example, in sediments, waters, and fish. In contrast, the esters of fatty acids can be at least partly hydrolysed resulting in the formation of free acids and alcohols (mainly glycerol). Thus, 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 [8]. Based on these facts, it was concluded that a simple and rapid method for detecting these acids from different process waters will be of benefit to the further control of this process.

Lacorte *et al*. [9] have reviewed several analytical methods for determining interfering substances in papermaking process waters. Most of these methods require liquid–liquid extraction (LLE) and a subsequent derivatization step prior to the final gas-chromatographic analysis. Chow and Shepard [10] have reported many different analytical methods including high-performance liquid chromatography (HPLC) particularly for resin acids, but also for fatty acids. In addition, they have successfully used a direct injection HPLC analysis for resin acids in pulp-mill effluents. This rapid method provides information about the effluent toxicity, thus predicting possible problems because of the high content of resin acids. However, in general, only a few studies are available on the analysis of these acids by HPLC using mass-selective detection (HPLC–MSD) and either electrospray ionization (ESI) or atmospheric-pressure chemical ionization (APCI) [11–13].

Recently, several methods based on solid-phase extraction (SPE) have been developed to isolate resin and fatty acids from papermaking process waters and effluents [14–16]. Various solvents, such as methanol, hexane, acetone, and dichloromethane, have been used as such or as mixtures for eluting the acids adsorbed on the SPE catridge. Carbon chain (C18) packing has proved to be useful for this application. Clear advantages of using SPE include short analysis time, low solvent need, and possibility of connecting it on-line with different chromatographic techniques such as HPLC–MSD. This type of connection has already been realized in many commercial on-line SPE–HPLC apparatus or can be readily made by using switching valves [17, 18].

When considering the analytical methods needed to fulfil all the requirements for a rapid analysis of resin and fatty acids, it is obvious that the present methods for determining these compounds in aqueous samples are still rather tedious and time-consuming. Owing to the toxicological evidence related to resin acids in aquatic system, the need for faster analysis methods will be emphasized in the future. For this reason, the study reported here had two main objectives: first, to compare the efficiency of the LLE and SPE techniques for the isolation of resin and fatty acids from papermaking process waters, and second, to connect SPE directly to MSD. However, because of technical interface obstacles, in our present study SPE could not be directly linked to MSD, and in practice we had to use an SPE–HPLC–MSD arrangement without any HPLC column for this purpose. This study is a part of a larger project aimed at developing more useful off-line analytical methods and/or on-line monitoring methods for the determination of resin and fatty acids for environmental purposes.

2. Experimental

2.1 *Chemicals*

For chromatographic analysis, analytical-grade acetone was purchased from Riedel de Haën (Seelze, Germany), MTBE from Lab-Scan (Dublin, Ireland), and HPLC-grade dichloromethane and methanol from Rathburn (Walkerburn, UK). Water was obtained from a Milli-Q water system (Millipore, Bedford, MA). Compounds used as standards were obtained (except abietic acid, purity 85%) with purity between 98.0 and 99.5%. Abietic acid, betulinol, heneicosanoic acid, and cholesteryl heptadecanoate were from Sigma (St. Louis, MO), dehydroabietic acid from ICN (Costa Mesa, CA), and palmitic and stearic acids from Fluka (Buchs SG, Switzerland). Disposable SPE columns (Discovery DSC-18 and DPA 6S) were purchased from Supelco (Bellefonte, PA). The silylation reagents bis(trimethylsilyl)trifluoroacetamide (BSTFA) and trimethylchlorosilane (TMCS) were obtained from Regis Technologies (Morton Grove, IL).

2.2 *Industrial process samples*

The process water samples were originated from a TMP mill integrated with a paper mill. Samples 1–4 were taken at different sampling times from the grinding zone of a grinding plant. Sample 5 was from the pulp section of a paper mill. Samples 6–8 were modified TMP model waters from a chemical supplier. All samples were immediately centrifuged (1500 rpm for 30 min) and stored as such at $-20^{\circ}C$ prior to analysis.

2.3 *LLE and SPE*

Samples (pH adjusted to 3.5) were extracted (i.e. LLE technique) with the well-known MTBE extraction method described elsewhere [19]. The sample quantity was 4–20 mL, depending on the sample origin. Compounds used as internal standards (betulinol, heneicosanoic acid, and cholesteryl heptadecanoate) for the subsequent GC analysis were added (100 μL, $1\,g\,L^{-1}$). At least two or three repeated extractions were carried out.

The disposable SPE columns filled with a sorbent (Discovery DSC-18, a polymerically bonded octadecyl (18% C) reversed phase sorbent) were used with a vacuum manifold system. At least two or three repeated extractions were made for each sample. In some cases, a DPA-6S (polyamide resin) reversed-phase sorbent was also tested. The column was not allowed to dry before sample was eluted. Sorbent drying caused a low recovery and variable repeatability. After the column was preconditioned with the eluent (6 mL) and MQ-water (6 mL), the samples were passed through the column. The sample quantity was 5–20 mL, depending on the sample origin. The columns were then allowed to dry under a low vacuum for 30–60 min. Compounds used as internal standards (heneicosanoic acid and betulinol) in GC analysis were added (750 μL, $0.1\,g\,L^{-1}$), and extractives were eluted with a small amount (4–10 mL) of methanol or mixture of dichloromethane, acetone, and methanol (1 : 1 : 1). The extracts were evaporated to dryness with a gentle stream of nitrogen. The sample was stored at $-20^{\circ}C$ before silylation and the subsequent GC analysis.

2.4 *GC*

Dry samples were silylated with a mixture of BFSTA (99%) and TMCS (1%) (350 μL), and analysed by GC-FID [19]. Analyses were carried out on a Hewlett Packard HP 5890 Series II Plus System equipped with a HP 7673 injector and a Programmable Cool On-Column Inlet. A HP-1 (7.5 m × 0.53 mm i.d. with a film thickness of 0.15 μm) column was used with nitrogen as carrier gas. The temperature of the injector was 90°C, and after the injection it was raised to 320°C at a rate of 200°C min^{-1}. The detector temperature was 290°C. The temperature programme was 1 min at 90°C, followed by 12°C min^{-1} to 320°C, and 10 min at 320°C.

2.5 *SPE–APCI–MSD*

A sample-enrichment SPE technique [18, 20] was applied with a six-port switching valve and HP 1100 liquid chromatography–mass spectrometry equipment (Hewlett Packard, Palo Alto, CA). An HP Series 1100 binary pump, vacuum degasser, and thermostatted column compartment with a six-port switching valve were used. A standard C18 precolumn (Waters, Resolve C18, 10 μm, 90 Å) was utilized as an SPE enrichment column. Before analysis the SPE column was flushed with methanol for 10 min at a flow rate of 0.5 mL min^{-1}. Sample was introduced by a Waters 501 pump at a flow rate of 0.2 mL min^{-1} and a HP 1100 pump was used to introduce the eluent (methanol) at a flow rate of 0.5 mL min^{-1}. The sample was preconcentrated at a flow rate of 0.2 mL min^{-1} and the analytes trapped on the SPE column were flushed in the backflush mode and transferred on-line to MSD. Sample was enriched for one minute and with the help of a six-port switching valve the sample flow was then turned into the waste.

Detection was carried out using an HP 1100 mass-selective detector (Hewlett Packard, Palo Alto, CA), equipped with the APCI interface. MSD was operated in the selected ion monitoring (SIM) mode to monitor each compound $[M–H]^-$ for the negative-ion analysis. The operation conditions were obtained by maximizing a monitored signal by testing different settings for the highest sensitivity. The nebulizer and vaporizer temperatures were 350 and 325°C, respectively. The nebulizer pressure was 60 psig, and the drying-gas (N_2) flow rate was 3 L min^{-1}. The corona current was adjusted to 16 μA, capillary voltage to 3500 V, and fragmentor voltage to 100 V. MSD was tuned using the APCI calibration solution (Agilent Technologies, Santa Clara, CA) to maximize mass resolution and sensitivity. The LC/MSD ChemStation software (version A.06.03) was used for instrumental control and data acquisition.

Quantitative analysis was performed using the external standard calibration method. In this method, stock solutions of calibration standards (1 mg mL^{-1}) were first prepared in methanol, and final solutions (0.1, 0.2, 0.3, and 0.4 mg L^{-1}) were then prepared by diluting stock solutions with Milli-Q water. All standard solutions were stored at 4°C.

Calibration curves were made for each standard with five consecutive injections, and the SPE column was flushed 5 min with methanol between these injections. The average areas were used in calculations. The data were analysed by linear regression, and the repeatability (RSD%) of the SPE-APCI-MSD method was evaluated by seven consecutive injections (0.48, 1.2, and 2.4 mg L^{-1} standard solution of dehydroabietic acid). In addition, the repeatability together with the quality parameters of the

measurements was evaluated for each compound by five consecutive injections of a $0.2\,mg\,L^{-1}$ standard solution. Preliminary repeatability tests were also made with spiked (dehydroabietic acid, $0.1\,mg\,mL^{-1}$) process water sample. The LOD values using the SIM mode were calculated from the calibration curves according to Miller and Miller [21].

3. Results and discussion

3.1 *LLE and SPE*

The LLE technique is the most widely used procedure [19] for separating resin and fatty acids from papermaking process waters, and at first our work was also focused on this traditional method. In addition, it was generally found that sample handling and storage had a significant influence on the result. Thus, because of the further reactions of certain acid components [22], only the recoveries of 40 and 29% for resin and fatty acids were respectively obtained when, for example, Sample 8 was analysed in detail by LLE–GC after 2 months' storage.

In the first phase of the SPE experiments with Sample 1, two sorbent types (i.e. DSC-18 and DPA-6S) and the different combinations of sorbent amounts (i.e. 50, 100, 250, and 500 mg), column volumes (i.e. 1, 3, and 6 mL), and eluents were tested, and the results obtained were compared with those of the LLE experiments with the same sample. In the case of DPA-6S, the detected concentrations of resin and fatty acids increased almost linearly as the sorbent amount increased, although, compared with the LLE results, clearly lower recoveries for resin acids and higher recoveries for fatty acids were achieved (figure 1). However, for the most interesting substance group, resin acids, the use of DSC-18 resulted, compared with that of DPA-6S, in a better recovery which was also almost similar to that obtained with LLE. In addition, in the separate experiments with DSC-18, it was found that the use of more than 500 mg of sorbent resulted in somewhat higher recoveries, but problems with the repeatability of the results (RSD >20%) and, because of varying amounts of fines and some colloidal extractives in our Samples 1–8, column plugging were simultaneously obtained. For this reason, as indicated earlier [23], also in our application, the overall efficiency of SPE was shown to be highly dependent on the type and amount of sorbent and the column size. Thus, based on these tests, the DSC-18 column (500 mg per 6 mL) gave the best results (RSD <15%), compared with LLE, and this system was selected for the further experiments.

In the previous research on SPE [14], any washing between separations was made to remove the interfering substances possibly retained in the column during the elution of the compounds adsorbed. Since there was no clear indication, whether this washing step is needed for obtaining repeatable results, we also separately performed some washing experiments with DSC-18 and Sample 2 by using different washing solvents (i.e. water, water–methanol (1 : 1), and water–acetone (1 : 1)). The preliminary results suggested that, with respect to resin and fatty acids, no such washing is necessary, although this can be technically achieved without difficulty.

In the last phase of the off-line SPE experiments, the total concentrations of resin and fatty acids were compared in the cases of LLE (i.e. MTBE extraction) and SPE

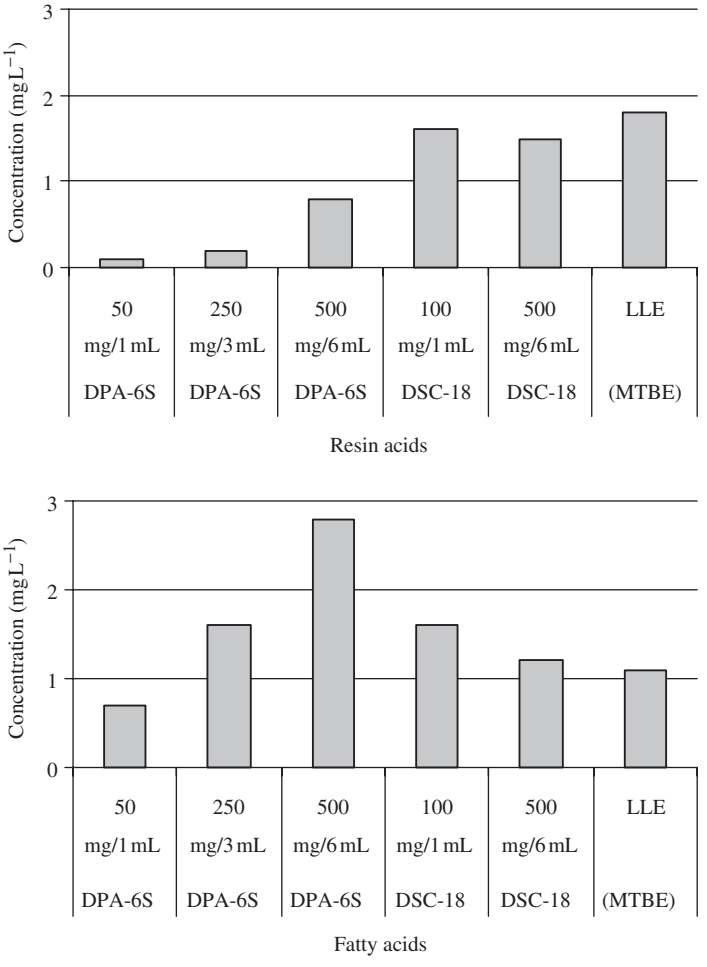


Figure 1. Detected total concentrations (mean, number of replications = 2 or 3) of resin and fatty acids in the SPE and LLE experiments with Sample 1. In SPE, two sorbent types (DPA-6S and DSC-18) at varying amounts (mg) and column volumes (mL) were tested.

(i.e. DSC-18 column under the selected conditions) methods for Samples 3, 6, and 7 (figure 2) to clarify the further need of sample pretreatment. The recoveries of the methods have been determined earlier, and these varied between 73 and 94 (pH 5, RSD 5%) and between 69 and 99 (pH 3.5 and 9, RSD 15%) for SPE and LLE, correspondingly [15]. In LLEs, the pH of these samples was adjusted to 3.5 according to the conventional extraction procedure [19] applied. In contrast, SPEs (made with methanol) were performed without pH adjustment (initial pHs in the range 4–6), and the repeatability of these separations varied between 0.2 and 15 RSD%. The effect of sample pH has been investigated earlier [15, 17, 18] in similar applications with somewhat conflicting results. However, for example, for model white water, the recovery of extractives (73–94%) and the reproducibility of the results have been even better for the sample without pH adjustment [15], which also supported our approach to analyse the samples at their original pHs. In general, both LLE and SPE gave rather similar concentrations of resin and fatty acids in the samples investigated. Thus, it could

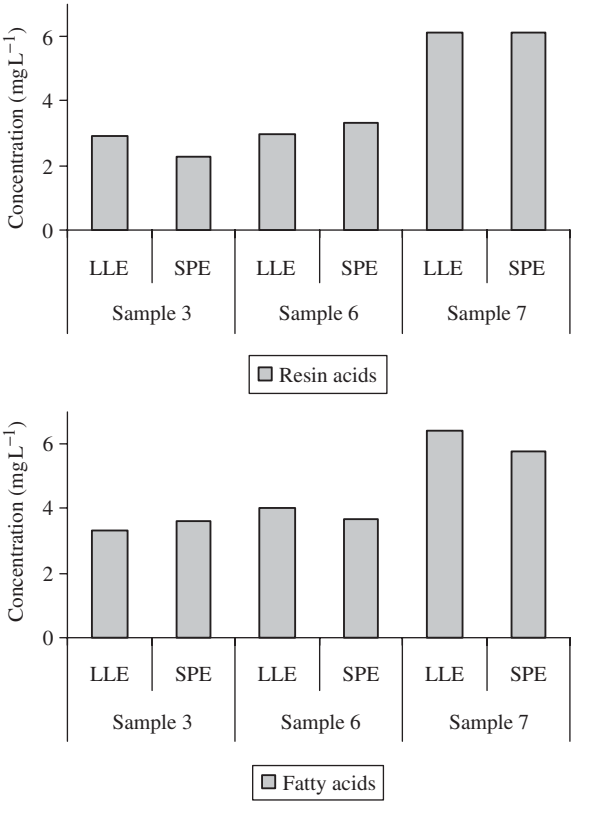


Figure 2. Comparison of LLE with SPE for determining the total concentrations (mean, number of replications = 2 or 3) of resin and fatty acids in Samples 3, 6, and 7.

be concluded that these methods are equally effective for separating a substantial amount of aliphatic carboxylic acids from papermaking process waters, although the most significant advantages of SPE over LLE are a short separation time and a low solvent consumption. In addition, as a rapid and simple enrichment technique, SPE can be readily connected to a proper detection system, as already indicated by earlier studies [15, 16].

3.2 *SPE–APCI–MSD*

The main purpose of the second phase of this study was to connect the SPE (i.e. DSC-18 column) enrichment technique to APCI–MSD for the on-line detection of certain individual acids. The APCI conditions were optimized with respect to sensitivity and selectivity, and in each case the intensive deprotonated molecular ion $[M-H]^-$ was used for the quantification of the selected resin acids (dehydroabietic and abietic acids) and fatty acids (palmitic and stearic acids) (table 1). The ions were verified by extracting the corresponding chromatographic profiles from each total ion current (TIC) chromatogram.

Two different measurement series were made to evaluate the repeatability of the APCI–MSD results. First, the intra-day precision (i.e. repeatability) was calculated by

Table 1. Compounds detected by APCI–MSD in this study.

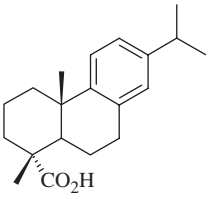
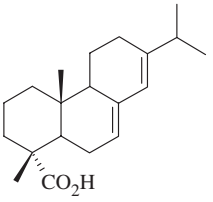
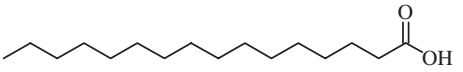
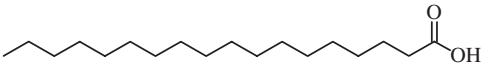
Compound	Structure	Molecular mass
Dehydroabietic acid		300
Abietic acid		302
Palmitic acid		256
Stearic acid		284

Table 2. Repeatability (as RSD%, $n = 7$) of the SPE–APCI–MSD method tested by an aqueous dehydroabietic acid solution at different concentrations.

Concentration ($mg\,L^{-1}$)	Injected amount (μg)	RSD (%)
0.5	0.60	4.01
1.2	0.36	5.47
2.4	0.72	4.77

performing seven consecutive injections of dehydroabietic acid at different concentrations during one working day (table 2). These results indicated that RSD% was between 4 and 5%. Second, the performance of this method was evaluated by determining the quality parameters such as repeatability, limits of detection (LOD), and linearity for all four model acid compounds (table 3). In this case, the repeatability of the results was based on five consecutive injections of the acid solution and varied between 1 and 8%. The linearity was investigated in detail with calibration standards, and a linear response was measured in the range of 0.1–0.4 $mg\,L^{-1}$, using in each case a sample amount of 0.2 mL. Of all the calibration curves of the model acid compounds (i.e. dehydroabietic, abietic, palmitic, and stearic acids), the lowest correlation coefficient was obtained for dehydroabietic acid ($R^2 < 0.99$). According to our preliminary results with spiked

Table 3. Quality parameters of the SPE–APCI–MSD method tested by the model acid compounds.[a]

Compound	Dehydroabietic acid	Abietic acid	Palmitic acid	Stearic acid
Repeatability (RSD%, $n=5$)	1.2	4.9	3.8	7.7
LOD (μg)	0.016	0.002	0.008	0.007
LOD ($\mu g\,L^{-1}$)	78	11	38	36
$Y=ax+b$	$948{,}714x+40{,}991$	$140{,}545x+28{,}526$	$558{,}312x-8782$	$1{,}746{,}315x-80{,}819$
R^2	0.9738	0.9994	0.9938	0.9943

[a]The initial concentration of each acid in water (Milli-Q) was $0.2\,mg\,L^{-1}$. For LOD values and linearity, see also section 2.

process water sample, the repeatability of the measurement varied between 0.2 and 2.2% with an R^2 higher than 0.93. The LOD values varied between 0.002 and 0.016 μg (11–78 $\mu g\,L^{-1}$). Since the corresponding values for the simple injection in earlier LC–MSD research [13] have been between 0.5 and 80 $\mu g\,L^{-1}$, our method seemed to represent a rapid and sensitive method for the selected acids.

Finally, the SPE–APCI–MSD method developed was applied to Sample 4 (i.e. from a grinding plant) and Sample 5 (i.e. from a paper mill). The analysis time was shorter than that of the conventional LLE-based methods and could even be reduced further by decreasing the flushing time between the repeated injections.

In general, dehydroabietic acid is often found [7, 11, 24] to be the most abundant resin acid released from softwoods during mechanical pulping and papermaking. This aromatic-ring-containing acid can be easily identified by negative APCI due to its characteristic $[M-H]^-$ ion (m/z 299) which differs from that ($[M-H]^-$ at m/z 301) typically detected for other common and non-aromatic resin acids, such as abietic acid. For this reason, dehydroabietic acid can be considered a good specific indicator for the total concentration level of resin acids. Correspondingly, palmitic ($[M-H]^-$ at m/z 255) and stearic ($[M-H]^-$ at m/z 283) acids are the typical indicators for the total concentration level of fatty acids, since these acids are common in process waters as well [11, 24]. Thus, changes monitored on-line at both these concentration levels are helpful in predicting the possible oncoming process problems and give, for example, a sampling recommendation for a more detailed chromatographic off-line analysis of extractives. In our experiments, dehydroabietic acid was used as an indicator for the total concentration level of resin acids, for example, in Samples 4 and 5 (figure 3). In this case, no significant differences between the results of the SPE–APCI–MSD method and those of the LLE–GC–FID method could be detected. In addition, the repeatability (RSD%) of the dehydroabietic acid analysis (for Samples 4 and 5, 6.8 and 3.7%, respectively) was determined by injecting each sample repeatedly five times.

4. Conclusion

In this study, a new procedure based on SPE–APCI–MSD, suitable for determining on-line the concentration levels of resin and fatty acids in various papermaking process waters with reasonable accuracy and repeatability, was developed. Compared with the conventional methods used for this purpose, the main benefits of the SPE–APCI–MSD method are rapidity of measurement, simplicity of use, and absence of the need of

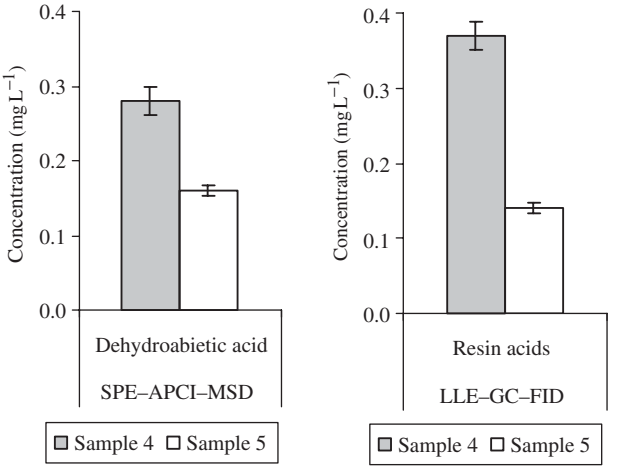


Figure 3. Determination of the concentrations of dehydroabietic acid and resin acids in Samples 4 and 5 by the SPE–APCI–MSD and LLE–GC–FID methods.

multistage sample treatment. Thus, this method is suitable for a rapid monitoring of papermaking by analysing the total concentration of the interfering substance groups (i.e. resin and fatty acids), rather than analysing off-line individual extractives-based compounds in process waters.

Although the results obtained clearly indicated that the SPE–APCI–MSD method developed in this study has a sound basis and seems to have potential for the control of the total concentration levels of resin and fatty acids in papermaking process waters; nonetheless, they were based on rather limited amounts of various process waters. In our forthcoming investigations, the emphasis will be not only on the further development of the method but also on the analysis of process waters with a more versatile chemical composition. This is important, since an increasing current trend to close more effectively the process water circulations aims at a drastic decrease in the wastewater load. It seems that the technique could be modified also for analysing not only resin and fatty acids but also other environmental pollutants.

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