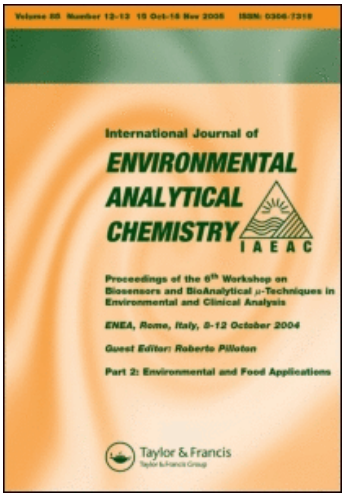

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Resin acids are considered to be significant contributors to the toxicity of pulp mill effluents. Traditionally, the analysis of these acids is performed by liquid–liquid extraction followed by gas chromatography. This paper describes a method suitable for monitoring the relative concentration levels of the main resin acid component, dehydroabietic acid (DHAA), in process waters by atmospheric pressure chemical ionisation-mass spectrometry (APCI-MS). This method was further improved, first by testing different precolumns for on-line sample clean-up and then by developing the APCI-MS analysis of the analytes trapped in the precolumn (i.e., solid-phase extraction column). The external standard, internal standard, and response factor methods were compared. The curve profiles of the results obtained with the above determinations were very similar to each other. This finding suggested that the rapid APCI-MS method, using a selected ion monitoring (SIM) technique, is a potential tool for monitoring relative concentration levels of DHAA. The technique is also recommended for rapid and simple monitoring of DHAA as well as of other resin acids, and their derivatives, such as their chlorinated analogues, in various aquatic environmental samples.

Keywords: resin acids; effluents; solid-phase extraction; mass spectrometry; paper industry; wood extractives

1. Introduction

The pulp and paper industry is among the six largest polluters in the world [1], although in recent years discharges have been significantly decreased. Mainly due to this pollution problem, the papermaking industry is gradually moving towards more closed water circulation systems to reduce both the consumption of fresh water and discharges into the environment. However, the water closure systems will increase the levels of dissolved and colloidal substances (DCS) in process waters. These compounds are known to be released during mechanical pulping, and high levels of DCS are associated with different process problems, such as the formation of pitch deposits and effluent toxicity [2,3]. Resin acids, a DCS group of tricyclic diterpenoid acids which exist naturally in conifers, are toxic to

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fish [4–7], and are thought to be the main contributors to effluent toxicity in softwood pulping effluents. In addition, the problems concerning the toxicity of resin acids will extend beyond pulp and paper mills [8–12].

In aqueous pulping discharges, the most commonly monitored resin acids are abietic, dehydroabietic (DHAA), neoabietic, pimaric, and isopimaric acids. Resin acids can easily undergo isomerisation and more stable isomers are gradually obtained, the most abundant of these isomers being DHAA [9,13]. In general, due to a rather stable carbon skeleton, these acids and their isomerisation products can easily survive in the papermaking process and thus exist in pulp and paper mill effluents at concentrations as high as 40 mg L^{-1} [1]. However, due their toxicity, it is necessary to reduce the amount of resin acids in effluents before discharge. This can be done, for example, by using either aerobic or anaerobic biodegradation in a wastewater treatment plant [14–16], although in this case, several problems are encountered since resin acids are toxic to the anaerobic bacteria in the treatment system. Studies have focused in particular on the degradation of DHAA, as it is the most abundant resin acid in wood industry effluents and also causes operating problems to anaerobic reactors [17,18].

Rigol *et al.* [19] have published a comprehensive review of the methods used to analyse resin acids in papermaking process waters and effluents. They found the most commonly used technique to be gas chromatographic (GC) analysis after liquid–liquid extraction (LLE) with organic solvent, but high-performance liquid chromatography (HPLC) has also been used [8,20–24]. However, both these methods are rather time-consuming as they include more or less complicated pretreatment steps. Only a few studies have dealt with the fast analysis of resin acids. In this connection, it has been shown [25,26] that the solid-phase extraction (SPE) procedure can replace the established LLE method. Serreqi *et al.* [27] have used one or two resin acids as a marker for the total content of resin acid. HPLC has also been combined with mass spectrometry (MS) for the determination of resin and fatty acids [28,29]. The MS technique offers major advantages due to its high sensitivity and selectivity. With this technique samples can be analysed without sample pretreatment (e.g., derivatisation) and the problem of the decomposition of the silylated sample during storage prior to the GC analysis can be avoided. Unfortunately, some problems were observed concerning the simultaneous separation of all the structural resin acid isomers such as abietic, isopimaric, and pimaric acids [30]. However, this is not a real problem as in practice the quality of the process waters can be estimated on the basis of the total amount of resin acids as well.

The study reported here is a part of a larger project with the aim of developing fast monitoring methods for use by the papermaking industry. This report continued our earlier research [26], in which an on-line SPE-HPLC-MS method was developed and tested by means of pure standards and only a limited amount of real process waters. The main purpose of this study was to develop further a fast method based on an on-line sample enrichment technique suitable for the separation of DHAA followed by its detection with atmospheric pressure chemical ionisation-mass spectrometry (APCI-MS). In principle, the method developed is a flow injection analysis (FIA) where the sample is introduced to analysis without passing through a separation column. Altogether four precolumns were tested for the sample clean-up and in each case quality parameters were determined. In addition, the method was tested for industrial samples from papermaking process waters.

2. Experimental

2.1 *Samples and chemicals*

The process water samples were taken from different stages of the papermaking process from a paper mill in southern Finland: samples 1–3 and 5 from different places in the grinding zone of a pulping plant and sample 4 from a paper machine. Samples were stored at 4°C until analysed. Prior to analysis, each sample was allowed to warm up to room temperature and was mixed by hand. The sample pH was not adjusted before analysis, because the method has been shown [26] to be independent on pH. Sample dilutions were made with Milli-Q water (Millipore, Bedford, MA, USA). Samples were analysed without any prefiltration or samples with high fibre content were filtered with 0.45 or 1.2 μm filters. HPLC grade methanol was obtained from Rathburn (Walkerburn, Scotland). DHAA was purchased from ICN (Plainview, NY, USA) and it was of analytical grade (purity > 98%). Margaric acid with a purity of 97% was obtained from Aldrich-Europe (Beerse, Belgium).

2.2 *Standard solutions*

Stock solutions of standard compounds, DHAA ($C_{20}H_{28}O_2$, mol wt 300.4 g mol^{-1}) and margaric acid ($C_{17}H_{34}O_2$, mol wt 270.5 g mol^{-1}), (1 mg mL^{-1}) were prepared by dissolving an accurate amount of pure standard in methanol. Working solutions were prepared by diluting the stock solution with Milli-Q water. Standard solutions were stored in the dark at 4°C for up to 1 month. Margaric acid (a long chain fatty acid) was selected as the ISTD since it would be rare to find it in papermaking water samples [29]. However, the absence of this compound should be always checked before embarking on the analysis.

2.3 *Instrumentation*

An HP 1100 liquid chromatography-mass spectrometer from Hewlett Packard (Palo Alto, CA, USA) including a binary pump, a vacuum degasser, and a thermostatted column compartment with a six-port switching valve were used (Figure 1). Four different precolumns were tested: Hypersil ODS 5 μm (Agilent Technologies, Santa Clara, CA, USA), Atlantis dC 18 5 μm 4.6 * 20 mm (Waters, Milford, MA, USA), Guard-Pak RCSS CN 10 μm, 125 Å (Waters, Milford, MA, USA), and Guard-Pak μBondapak NH_2 10 μm 125 Å (Waters, Milford, MA, USA).

The sample was introduced by a Waters 501 pump (pump 1, Waters, Milford, MA, USA) and a HP 1100 pump (pump 2) was used to deliver the mobile phase (methanol) at a flow rate of 0.5 mL min^{-1}. Before analysis the precolumn was flushed with mobile phase at the same flow rate as used in the analysis. The sample was enriched for one minute and the sample flow was turned into the waste with a six-port switching valve (valve 1, HP 1100 thermostatted column compartment). The sample flow rate was 0.2 mL min^{-1}, thus giving a sample volume of 0.2 mL. The analytes trapped in the precolumn were flushed in the backflush mode and transferred on-line to the MSD. A Waters column switching valve (valve 2, Milford, MA, USA) controlled by a HP 35900E Interface (Palo Alto, CA, USA) was used to switch the flow coming from pump either to the waste (sample clean-up) or to the MS. The flow was turned into the waste after 2.5 minutes to prevent any particles from precolumn or organic material from sample coming to the ionisation chamber, thus keeping the MS clean.

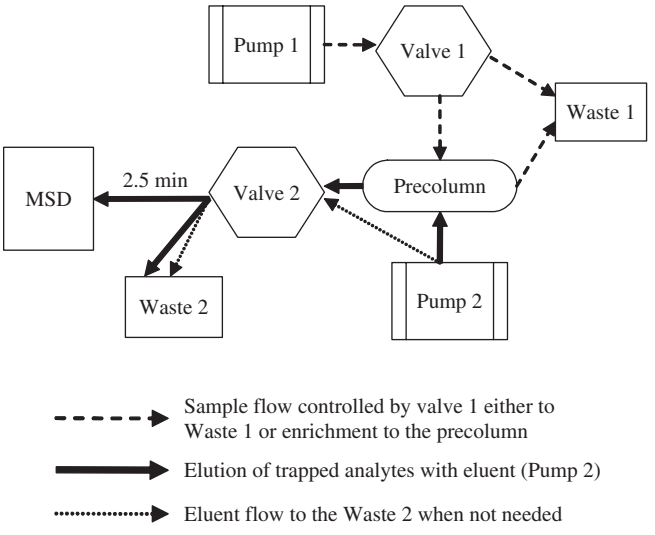

Figure 1. Schematic diagram of the on-line sample clean-up system with APCI-MS.

Detection was carried out using a HP 1100 Series single quadrupole MS (Hewlett Packard, Palo Alto, CA, USA), equipped with an APCI interface in the negative ion mode. The selected ion monitoring (SIM) mode was used to monitor $[M\text{-}H]^-$ for each compound for negative ion analysis with a dwell time of 390 ms. In negative mode only the intensive $[M\text{-}H]^-$ ion is generated with a high yield, as shown in a previous study [30], and these very abundant ions were selected for the present SIM conditions. This result was expected in view of the fact that in the structure of the resin and fatty acids only a carboxylic group susceptible to fragmentation is present. The operating conditions for the APCI were as follows: drying gas (N_2) at a flow rate of 3.0 L min^{-1} and temperature of 350°C, nebuliser pressure 60 psig, vaporiser temperature 325°C, corona current 16 μA, capillary voltage 3500 V, and fragmentor voltage 100 V, lens 1 −3.4 V and lens 2 33 V. The MS was tuned using an APCI calibration solution provided by Agilent (Agilent Technologies, Santa Clara, CA, USA) and thus automatically optimising mass resolution and sensitivity. HP ChemStation software (version A.06.03) was used for instrumental control and data acquisition.

3. Results and discussion

In our study, the method was applied to the analysis of DHAA in process waters at levels commonly measured in papermaking. Several studies have showed that effluents with a resin acid level of mg L^{-1} are toxic to fish [1]. Therefore, the analytical range was kept at the mg L^{-1} level. The toxicity of resin acids is also structure [9] and pH [19] dependent. The pimaric type (pimaric, sandaracopimaric, and isopimaric acids) resin acids are more toxic than abietic type (abietic, levopimaric, palustric, neoabietic, and dehydroabietic acids) (Figure 2), and the decreasing pH increases the toxicity of resin acids. In particular, DHAA is a major concern since it can be anaerobically transformed to retene, which is toxic to aquatic organisms [18]. The retene compounds are derived from DHAA by a decarboxylation-aromatisation process [31,32] and they are more lipophilic than their

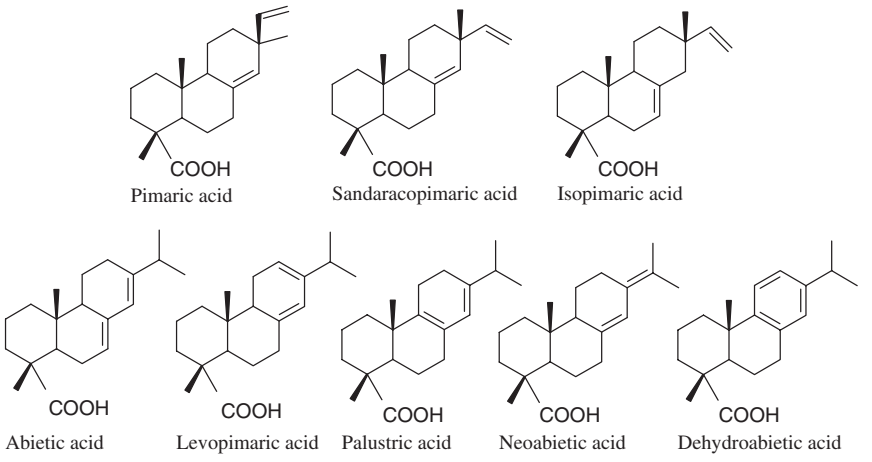

Figure 2. Chemical structures of the most common resin acids.

parent compounds [2]. These retene-based compounds have also been found in sediments downstream of kraft pulp mills.

In this study, the APCI-MS method established earlier [26] was further developed with respect to its validation and the testing of new precolumns. The basic idea was to develop the procedure so as to be able to measure the concentration levels of the compounds of interest directly, rather than determine the absolute concentrations of the analytes in the samples. The performance of the method was first improved by testing four different precolumns for the sample clean-up. An internal standard (ISTD) was also used in the determination of the quality parameters. The performance of each precolumn was tested by determining the quality parameters (i.e., precision, linearity, and accuracy).

3.1 *Precision*

Precision was evaluated for injected concentrations of 1.0 and 4.0 mg L^{-1} and each precolumn was tested through seven replicate injections ($n = 7$) conducted over a period of three days ($n_1 = 3$). An analysis of variance (ANOVA) was performed and intra-day, day-to-day, and intermediate precision were calculated [33]. The area of the analyte was used in the calculations. The results (Table 1) show that at lower concentrations (1.0 mg L^{-1}), in particular, the RSD values were higher and the precolumns did not function sufficiently. The higher RSD values and variations in day-to-day and intermediate precision might be due to the problems related to the first measurement day when stabilisation of the precolumn was not satisfactory causing matrix interference or ion suppression in the MS instrument. However, compared to the other precolumns, the performance of the NH_2 precolumn was considered to be satisfactory, with RSD values $< 3.6\%$ for upper part of the analytical range (4.0 mg L^{-1}).

3.2 *Linearity*

A standard of DHAA was diluted to give six samples at six different concentrations (0.5–5.0 mg L^{-1}). Seven replicates were carried out for each concentration and the average

Table 1. Analysis of intra-day ($n = 7$) and day-to-day ($n_1 = 3$) and intermediate precision of areas.

	RSD (%) Intra-day		RSD (%) Day-to-day		RSD (%) Intermediate precision	
Injected concentration ($mg\,L^{-1}$)	1.0	4.0	1.0	4.0	1.0	4.0
Atlantis	5.5	6.9	14.4	22.3	15.4	23.3
ODS	3.5	6.2	7.8	13.1	8.5	14.6
CN	4.4	4.9	6.6	21.2	7.9	21.7
NH_2	5.5	3.4	15.3	1.3	16.3	3.6

Table 2. Results of the linearity responses of peak area and height.

Precolumn	R^2 Peak area	RSD (%)	R^2 Peak height
Atlantis	0.9935	6.7	0.9903
ODS	0.9928	5.9	0.9990
CN	0.9729	4.7	0.9772
NH_2	0.9982	3.5	0.9953

Table 3. Linear regression and RSD values for the upper concentration on the linear range used in this study.

Precolumn	R^2 confidence interval	Intercept confidence interval	RSD (%) confidence interval
Atlantis	0.9746; 0.9987	−0.084; 0.083	6.9; 8.0
ODS	0.9671; 0.9926	−0.111: 0.087	6.4; 9.3
CN	0.9658; 0.9748	−0.143; 0.143	4.4; 6.6
NH_2	0.9916; 0.9971	−0.067; 0.067	1.6; 2.6

of the peak areas was used to evaluate the linearity of the response. This was calculated by plotting the peak area and peak height corresponding to the DHAA standard against its injected concentration. The data were analysed by linear regression. As shown in Table 2, the linearity was >0.99 for all the precolumns except CN (R^2 0.9729). The RSD (%) of the peak area was calculated by averaging the RSD (%) values for each sample, and it ranged from 3.5 to 6.7%. The best overall linearity (3.5%) was achieved with the NH_2 precolumn (Table 2).

The linearity of the method was also evaluated by plotting the concentrations obtained against the introduced concentration. The analysis was performed through seven replicates over three days and the correlation coefficient R^2, intercept, and RSD% were calculated for each measurement. For all the precolumns, the analytical range used was 0.5–5.0 $mg\,L^{-1}$. As shown in Table 3, precolumn NH_2 gave the most satisfactory results in all cases.

Table 4. Accuracy of injected and measured concentrations (samples 1.0 and 5.0 mg L^{-1}).

Precolumn	Measured concentration (1.0/5.0 mg L^{-1})	Recovery (%) (1.0/5.0 mg L^{-1})	RSD (%) (1.0/5.0 mg L^{-1})
Atlantis	0.975/4.805	98/96	7.0/8.0
ODS	1.045/5.590	105/112	3.2/9.3
CN	1.055/4.355	106/87	4.4/6.6
NH_2	0.990/5.075	99/101	2.2/4.2

3.3 *Accuracy*

The accuracy of the precolumns was determined by analysing samples at two different concentrations: in the lower (1.0 mg L^{-1}) and in the upper (4.0 mg L^{-1}) part of the analytical range. Each sample was analysed through seven replicate injections and the averages of the areas were used to calculate the concentration with calibration curves obtained with the external standard method. All the precolumns gave satisfactory results, all recoveries being between 87% and 112% (RSD 2.2 and 9.3%). Precolumn NH_2 again gave the most accurate results with a recovery rate between 99% and 101% (RSD 2.2% and 4.2%, respectively) (Table 4).

Earlier results showed that the use of a commercially available NH_2-type SPE cartridge in sample clean-up improves a GC performance significantly [34]. According to this information and our above-described results, precolumn NH_2 was used in the analysis of the real samples of process waters. In all the quality parameter measurements, the RSD% values seemed to be higher than those recommended by the normal method validation regulations. This might be partly due to the absence of sample pretreatment, which can cause matrix interferences in the ionisation process.

3.4 *Internal standard*

An ISTD (margaric acid) was tested to improve the recovery and precision of the method. In order to measure the linearity range of margaric acid, a series of samples in the range of 0.25–5.0 mg L^{-1} was analysed, and the analytical range was determined to be between 0.25 and 1.0 mg L^{-1}. A series of DHAA standards in the range 1.0–5.0 mg L^{-1} containing ISTD in the range 0.25–1.0 mg L^{-1} was measured to obtain the calibration curves. These samples were analysed by using precolumn NH_2 for sample clean-up. All the standards (1.0–5.0 mg L^{-1}) were analysed through seven replicate injections and the average of the areas was used in the calculations of the response factors (RFs). The correlation coefficients were also calculated: R^2 was 0.96 without ISTD and 0.98 with ISTD. The RFs for analysis were measured relative to ISTD by comparing the peak areas of ISTD to that of the analyte. The RFs were calculated for all the injections and the mean value was used in the calculations. The values ranged between 2.9 and 3.4, depending on the measurement day. The results showed that the use of ISTD and RF values distinctly improve the results.

3.5 *Analysis of process waters*

The APCI-MS method was applied to the analysis of the concentration levels of DHAA in papermaking process water samples 1 to 5 and the results were obtained using the external

standard calibration (ESTD), ISTD, and RF methods (Figure 3a). These results were compared with those obtained with the conventional GC-FID method (DHAA and total resin acids calculated) (Figure 3b) [35]. The relative concentrations of the results obtained with the different calculations were very similar, indicating that DHAA was a good marker for total resin acid content. The ISTD method with determined RF gave results similar or quite close to those of the GC-FID method. In the case of significant changes in the concentrations levels, the traditional GC-FID analysis [35] or HPLC [22,24] could be used to verify the results. Using the HPLC method the analysis time, including pretreatment, was about one hour/sample, whereas the use of APCI-MS reduced the analysis time substantially (analysis time 10 to 15 minutes). The monitoring of the levels of DHAA give information about the process conditions, and on the basis of our experiences, the change

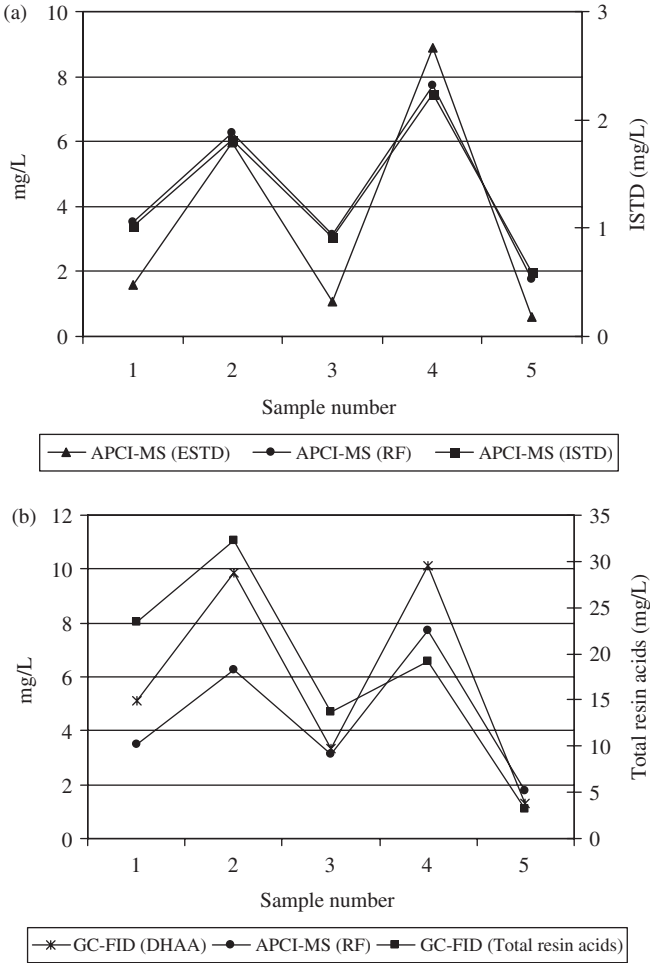

Figure 3. The profiles of results obtained by different methods and calculations.
Notes: ESTD = external standard calibration; ISTD = internal standard calibration; RF = response factor.

in these levels should give enough information about possible impending problems in the papermaking process. The variability between the different calculations and methods (GC-FID *versus* APCI-MS) may have been caused by the high resin acid content of some samples (i.e., sample 2) or the sample pretreatment, for example, in the GC-FID analysis the sample pH was adjusted to 3.5.

In the present study, the samples were also analysed with both filtration and dilution, and without any pretreatment before analysis. It was concluded that these sample pretreatment steps did not improve or only slightly improved the repeatability of the analysis. The results also indicated that differences in papermaking conditions also clearly have a great impact on the concentration levels of the compounds analysed in this study. Although samples 2 and 5 were taken from the same sampling site, the process conditions were different. As can be seen in Figure 3, the change in concentration levels was significant.

4. Conclusions

The results clearly indicated that the on-line enrichment method with APCI-MS detection and without the time-consuming sample pretreatment step is a potential tool for monitoring the concentration levels of DHAA in process waters from papermaking. The method is also a potential tool in research on environmental pollutants, for example, in receiving waters. However, if accurate concentrations of individual resin acids are required, the use of GC and HPLC is necessary. In addition, it was noted that the use of ISTD and RFs further increased the feasibility of this method.

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