

An improved method for analyzing resin acid in wood, pulp, process water, and effluent samples

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RESIN ACIDS ARE MAJOR COMPONENTS of softwood extractives. The eight common resin acids identified in Fig. 1 are dominant contributors to the toxicity of pulp mill effluents toward fish and aquatic life (1–6). Fish that have been exposed to pulp mill effluents show trace amounts of resin acids in blood plasma, liver, kidney, heart, intestine, gill, skin, brain, spleen, and red and white muscle (7–13). Resin acids are known to have serious toxicological and physiological effects on fish (7, 8, 10, 11, 14–19).

In addition, resin acids can cause problems in papermaking, and these can be particularly severe in the case of mechanical pulps. Deposition of resin acids on the paper machine can lead to reduced production or increased costs for pitch control. If the deposits are retained in the pulp, they can affect such properties as absorbency and strength (20–23).

This work (a) reviews the current analytical procedures for measuring resin acids and (b) proposes a rapid method for quantitative measurement of resin acids in wood, pulp, process water, and effluent samples. The proposed method can be used for routine monitoring on site.

BACKGROUND—CONVENTIONAL TECHNIQUES

GC separation

Gas chromatography (GC) is the most widely used technique for analyzing resin acids (24–38). Separation of many of the resin-acid iso-

mers on packed columns has been achieved using polar stationary phases (27). It is clear that highly polar liquid phases are useful in the GC separation of resin acids, especially for palustric and levopimaric acids, which are particularly difficult to separate. However no single liquid phase in a packed column provides sufficient separation among the common resin acids for adequate resolution of all components. Thus, a complete separation of the various resin acids requires GC on several different packed columns.

On the other hand, resolution of all the common resin acids can be achieved on a single capillary column, and this was first done by Holmbom (26). Since then, many of the high-resolution capillary GC column (6, 35–39) have been used to separate and detect resin acids. The capillary columns are coated so that the phases are covalently bonded, both in the form of crosslinks within the polymer as well as bonds from the phase to the silica surface. These columns are highly stable and perform well at high temperatures, thus allowing a reduction in analysis time.

The column used in this work was a very polar fused-silica capillary column (coated with a modified polycyanopropylsiloxane phase). This column provided better separation and improved resolution for eight common resin acids—especially levopimaric and palustric acids—compared with results previously reported in the literature.

ABSTRACT

This work proposes a simple, rapid, and accurate method for identifying and quantifying individual resin acids in wood, pulp, process water, and effluent. Test results showed that a mixture of common solvents provided the best extraction and recovery of resin acids in both solid and aqueous samples. Further tests identified a methylating agent (Methyl-8) that simplified the sample-handling procedure while quantitatively converting resin acids for analysis by gas chromatography (GC). Finally, the results show that a very polar fused-silica capillary column can provide adequate separation and resolution for eight common resin acids.

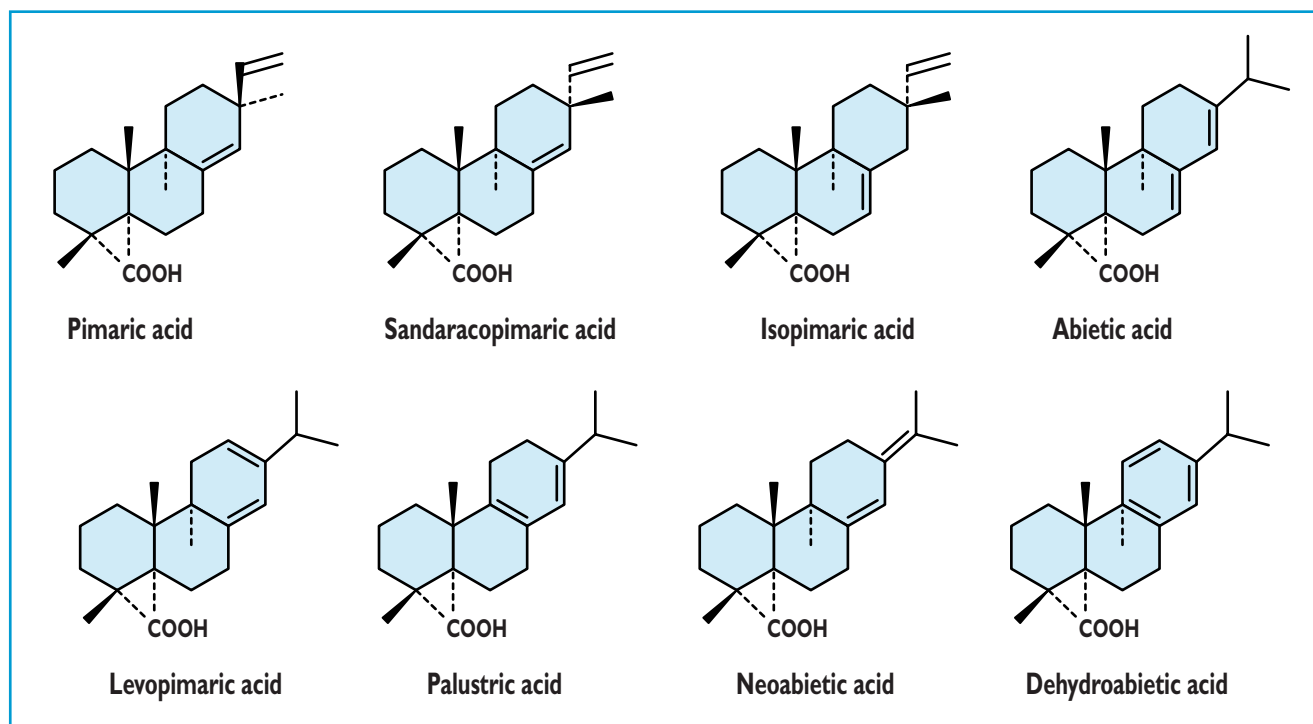
Application:

A simple, fast, and accurate method for measuring resin acids in aqueous and solid samples.

Extraction of wood and pulp samples

Resin acids are a components of softwood resin. The quantity of these extractives can be determined only after isolation, which is usually performed by extraction with a neutral solvent mixture and/or sequentially with a single solvent. Typically, these solvents are ether, acetone, benzene, ethanol, dichloromethane, or a mixture of these solvents.

The applicable TAPPI test method (T 204 om-88) (40) recommends that dichloromethane is a suitable solvent for the measurement of extractives such as waxes, fats, resins, photosterols, and nonvolatile hydrocarbons. Acetone has also been used to measure extractives in wood and paper samples (41–46). In other cases, diethyl ether (29, 38, 47–50), methanol-acetone (46), and acetone-petroleum ether (51) have been used for extraction of resin acids. It is difficult to conclude from the literature which solvent or sol-



1. Structures of eight common resin acids

vent mixture provides the best extraction of resin acids.

A mixture of dichloromethane, acetone, and methanol in equal proportions was used as the extraction solvent in this work. This mixture has shown a very high recovery of resin acids from wood and pulp samples.

Extraction of effluent samples

The main procedures for isolating resin acids from aqueous samples (such as pulp mill effluents) have been developed by the National Council of the Paper Industry for Air and Stream Improvement (NCASI) (52, 53) and by British Columbia Research (BCR) (54). The BCR procedure removes the resin acids from the effluent under alkaline (pH 9–10) conditions by adsorption onto a porous polymeric resin (XAD-2), whereas the NCASI procedure uses solvent extraction of the acidified (pH 2–3) effluent with diethyl ether. The use of other extraction solvents has also been reported, including dichloromethane (34, 35, 55, 56), petroleum-acetone-methanol (55), methyl tert butyl ether (34), and hexane-methanol (28).

The isolation method chosen for a given analysis is important, since it

defines the maximum recovery of the sample as well as possible coextractives that can interfere with the quantitative analysis. Several workers have evaluated the use of XAD-2 resin for analysis of resin acids in pulp mill effluents (36, 54, 57). The XAD-2 resin has been recommended for qualitative analysis of effluents where large sample volumes are required. Nevertheless, solvent extraction should, in principle, provide a simpler and faster method of isolation for effluent samples. However, the solvent-extraction method has various problems. Direct solvent extraction of pulp mill effluents often causes foaming emulsions, which can make sample handling more difficult, resulting in low recoveries and poor precision (34, 36). Although emulsion problems can be reduced by making the effluent sample very acidic prior to extraction, this can introduce errors caused by, for example, the isomerization of some of the resin-acid constituents (particularly levopimaric acid) as well as the precipitation of lignin residues that can impede the recovery of resin acids (36, 53). Many attempts have been made to overcome these problems (34, 36, 58, 59). The general conclu-

sion is that the effluent pH plays a very important role in both solvent extraction and XAD-2 resin adsorption, and it must be optimized for each sample type.

Solid-phase extraction techniques are a more recent innovation. An 18 carbon chain (C_{18}) solid-phase packing has proved to be suitable for the separation of extractives (23, 60–62). Different solvents—methanol, chloroform, hexane, acetone, dichloromethane, ethanol, and/or combined solvents—have been used to give the appropriate fractions (23, 60, 61), and emulsion problems can be minimized or even eliminated through judicious choice of solid-phase adsorbent, solvent, sample pretreatment, and post-column analytical techniques (63). Moreover, solid-phase extraction is faster and consumes lower sample amounts and solvent volumes than other traditional extraction procedures.

The method proposed in this work uses a solids-extraction technique in combination with a solvent mixture that was shown to provide the highest recovery of resin acids from liquid samples. The same solvent mixture was used for

the solvent extraction of solid samples to avoid the potential of introducing errors from a change in the extraction system.

RESULTS AND DISCUSSION

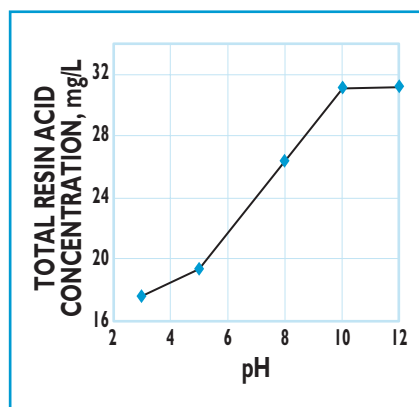
The general procedure used in the proposed method—as in existing methods of resin-acid analysis—consists of three steps:

1. Extraction (isolation of the resin acids from wood, pulp, process water, or effluent samples)
2. Derivatization
3. GC analysis (identification and quantification)

Extraction

Resin acids from process water and effluent samples were isolated using a solid-phase extraction column with a carefully selected solvent mixture. The results showed very good recovery while almost eliminating the foaming problems and lignin precipitation that have always been associated with extraction procedures for liquid samples (34, 36, 53). The solvent mixture that was used for extraction of process water and effluent samples was also used in the extraction of wood and pulp samples. This was done to avoid errors that might be introduced by changing the extraction procedure.

Recovery of resin acids from known standard solutions (1 mg/L) using a solid-phase extraction column was carried out in an effort to select a suitable eluting solvent. In a series of experiments, dichloromethane, acetone, diethyl ether, ethanol, methanol, and mixtures in different combinations were used as eluting solvents. The quantity of resin acids isolated from known standard solutions was measured by GC. The results showed that mixed solvents generally give better resin-acid recovery than single solvents in solid-phase extraction. A mixture of dichloromethane, acetone, and methanol in equal proportions (by volume) gave the best recovery. The

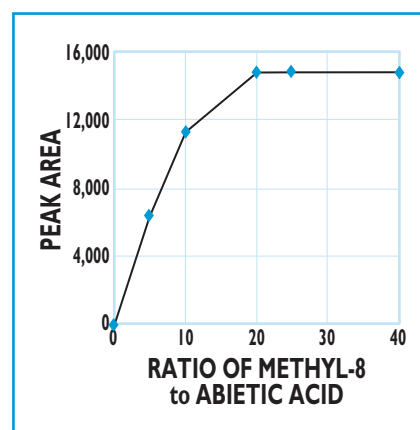


2. Effect of sample pH on the recovery of resin acids using solid extraction

recovery efficiency for the solid-phase extraction of a liquid sample was $97.3 \pm 2.4\%$, and efficiency for Soxhlet extraction of a solid sample was $96.5 \pm 3.1\%$.

The optimum pH at which resin acids and other acidic compounds are adsorbed from a liquid sample during the extraction stage is a subject of some controversy (40, 64–66). In order to investigate the influence of sample pH on the recovery of resin acids using a solid extraction column, a sample of TMP process water was taken and divided into five portions that were adjusted to pH 3, 5, 8, 10, and 12 using either dilute sodium hydroxide or dilute hydrochloric acid. Each sample was then extracted and analyzed. The results in Fig. 2 show that the concentration of total resin acids increased with increasing pH of the sample. Maximum recovery of resin acids from process water was obtained when the extraction pH was 10 or higher.

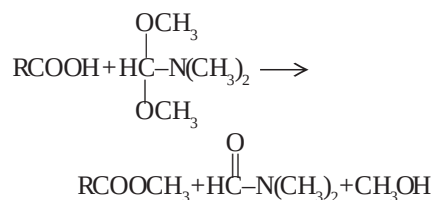
The effect of solvent pH on the recovery of resin acids from wood samples using Soxhlet extraction was also examined. These samples were ground and extracted at different pH, but there was no obvious effect of pH on the recovery of resin acids. For ground samples, the particle size and extraction time were the only variables that affected the precision of the extraction method. In a series of experiments, it was found that a 6-hour extraction time was needed for samples with a maximum particle size of $1 \times 2 \times 2$ mm.



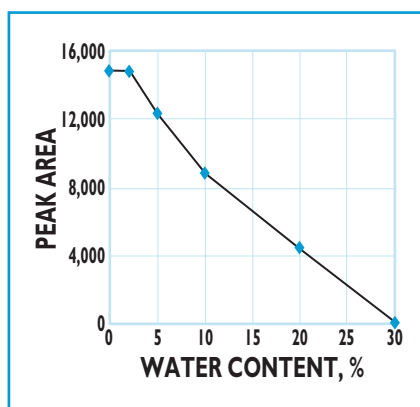
3. Effect of amount of Methyl-8 reagent on formation of abietic-acid methyl ester

Derivatization

To facilitate GC analysis of resin acids, their methyl esters are usually prepared by derivatization. Most methods of forming methyl esters require the use of diazomethane, which is highly toxic and difficult to use. In this work, the use of a methylating agent (Methyl-8, Pierce, USA) simplified the sample-handling procedure and gave quantitative conversion of resin acids for GC analysis. The mechanism of the reaction is believed to involve the carboxylate ion and an alkoxy-carbonium ion from the methylating reagent (67).



An important consideration in an esterification reaction is to have a sufficient excess of reagent to ensure that quantitative conversion to the ester occurs at all sample concentrations. An experiment in which 1 mg of abietic acid was reacted with different amounts of reagent was designed to assess the quantitative formation of resin-acid methyl esters. The results in Fig. 3 show that the peak area of abietic-acid methyl ester increased dramatically at first as the amount of excess methylating reagent was increased. When the excess reached 20 times, the peak area reached a maximum and remained unchanged as higher levels of reagent were added. Therefore, a 20-



4. Effect of water content on formation of abietic-acid methyl ester

fold excess of reagent was considered to be sufficient to ensure quantitative derivatization.

During the course of this investigation, the derivatization of resin acids in the extraction samples from wood, pulp, process water, and effluent was not the same as the derivatization of pure resin acids. This is because the extraction samples contained resin acids along with other organic acids, alcohols, carbohydrates, etc., all of which contain functional groups that can be methylated. The presence of these extra constituents increases the amount of derivatization reagent required. The sample size involved in either solid or liquid sample handling gave extractives in the range of 10–20 mg. In the presence of this level of extractives, 200 μ L of Methyl-8 reagent was sufficient to form quantitative amounts of the resin-acid methyl esters.

The effects of temperature and reaction time on resin-acid derivatization were also investigated. A 1-mg sample of abietic acid was reacted with 200 μ L of methylating reagent at different temperatures and for different reaction times. Esterification for the purified acid was completed very shortly after dissolution. Subsequent GC analysis showed that heating the reaction mixture or lengthening the reaction time had no further effect on the conversion. However, samples from wood, pulp, process water, and effluent showed a different response. Apparently, the extraction of colloidal materials

along with the resin acids affected the dissolution of resin acids in the methylating reagent, and heating the reaction mixture was then found to be necessary. Esterification of the extraction samples was shown to be complete after 30 min at 60°C. Higher temperatures and increased heating times had no further effect on the conversion, as indicated by GC analysis. Thus 30 min at 60°C was chosen as the best condition for esterification of the extraction samples.

Extraction of liquid samples using a solid-phase extraction column resulted in the elution of traces of water along with the resin acids and other organic materials. Traces of water in the reaction mixture influenced the methylation reaction, giving rise to an abnormally shaped GC peak. The effect of water content on resin-acid derivatization was therefore examined by adding known amounts of water to the reaction mixture and measuring the peak area. The results in Fig. 4 show that water contents of less than 2% had no effect on the GC analysis. As the water content increased above this level, the peak areas of abietic-acid methyl ester decreased rapidly. Figure 4 shows that the peak area approaches zero when the water content reaches 30%. Therefore, great care was taken to dry the solid-phase extraction column by drawing air through it for at least half an hour after all aqueous solution had passed through. Dry solvents and nitrogen gas were then used throughout.

GC separation

The aim of the chromatography experiments was to select a suitable column that was capable of separating all of the eight common resin acids (Fig. 1) on a single column. Although this problem has already been overcome by using a wall-coated open tubular (WCOT) capillary column coated with 1,4-butanediol succinate (BDS) (26), this is not

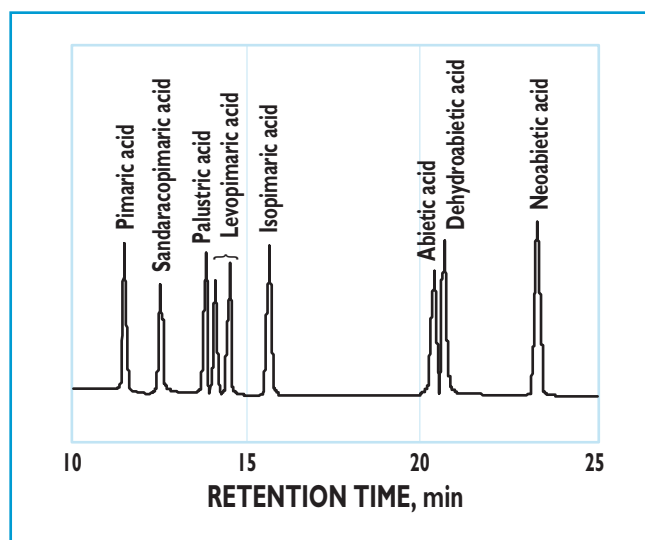
readily available nowadays. In experiments designed for column selection, a very polar fused-silica capillary column (see Experimental section) gave baseline resolutions for all eight resin acids, as seen in Fig. 5.

It is interesting to note that, when using this column, the analysis of a supposedly pure sample of levopimaric acid gave rise to two peaks. Figure 6 shows the two peaks with retention times of 14.06 and 14.44 min and area percentages of 42% and 58%, respectively. This is a positive indication that there are two substances present, but it has not been possible to identify them. Further research is required to establish their identity, but for the purpose of this investigation, both peaks were used for calibration.

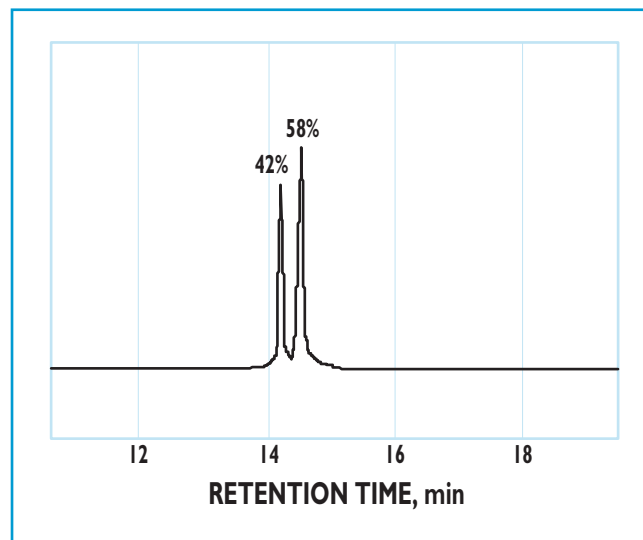
Heptadecanoic acid was chosen as the internal standard. Comparison of its retention time with those of derivatized extracts from a spruce and pine mixture showed that heptadecanoic acid does not occur in spruce or pine. Further, by spiking the samples, it was clear that heptadecanoic acid could also be separated completely on the column. Table I gives the relative response factor (RRF) of each resin acid using heptadecanoic acid as the internal standard on the column.

It is essential that the calibration be carried out correctly. Great care was taken during handling the pure resin acids and the internal standard. The calibration procedure was repeated many times to obtain the average values in Table I, which shows a large difference between the response factors of abietic and levopimaric acid as compared with other resin acids. The results indicate that abietic and levopimaric acids produced much weaker intensity signals at the detector than the other resin acids. Isopimaric acid gave the signal with the strongest intensity.

Most existing methods of resin-acid analysis are based on the as-



5. Gas chromatogram showing separation of eight resin acids



6. Gas chromatogram of levopimaric acid

Methyl ester of resin acid	RRF
Pimaric acid	1.24
Sandaracopimaric acid	1.30
Palustric acid	1.16
Levopimaric acid	2.40
Isopimaric acid	0.83
Abietic acid	5.31
Dehydroabietic acid	1.15
Neoabietic acid	1.41

I. Relative response factor (RRF) of resin-acid methyl esters

Resin acids	MDQ, mg	MDC*	
		Liquid, µg/L	Solid, µg/g
Pimaric acid	0.5	0.5	0.5
Sandaracopimaric acid	1.3	1.3	1.3
Palustric acid	1.1	1.1	1.1
Levopimaric acid	2.4	2.4	2.4
Isopimaric acid	0.4	0.4	0.4
Abietic acid	5.0	5.0	5.0
Dehydroabietic acid	0.7	0.7	0.7
Neoabietic acid	1.8	1.8	1.8

* Based on 1-L liquid sample or 1-g solid sample

II. Minimum detectable quantity (MDQ) and minimum detectable concentration (MDC) of resin acids

sumption that all resin acids have the same response to the detector. This is particularly true of work published before 1980, when pure resin-acid samples were not so readily available. However, the present work shows that the relative response factors of individual resin acids are very different and, therefore, must be determined individually.

The detection limit is always a great concern in GC analysis, particularly because the concentration of resin acids in wood, pulp, process water, and effluent may be very low. The minimum detectable quantity (MDQ) and minimum detectable concentration (MDC) are usually used to evaluate a trace analysis method. In this work, the MDQ was determined for each resin-acid methyl ester diluted with pyridine to different levels and analyzed by GC. The results are given in Table II.

There is a linear relationship between the peak area and the absolute amount injected. The minimum detectable amount of resin acids when reacted with 200 µL Methyl-8 reagent (using a 0.2-µL injection size and a 1:100 split ratio) was in the range 0.5–5 mg. It is possible to lower this limit by reducing the split ratio or increasing the injection amount, but this may lead to changes in the linearity of the response and the relative response factor.

Apart from the MDQ, the MDC ultimately depends on the sample size. The MDC data listed in Table II are based on a sample size of (a) 1000 mL for process water or effluent and (b) 1 g (dry wt.) for wood or pulp samples. The minimum detectable concentration is in the range 0.5–5

µg/L (liquid samples) and 0.5–5 µg/g (solid samples). Of course, the minimum detectable concentration could be made much smaller by increasing the sample size.

CONCLUSIONS

A simple, fast, and accurate method for measuring resin acids in aqueous and solid samples was proposed.

1. **Extraction.** Isolation of resin acids from aqueous samples using a solid-phase extraction column with a carefully selected solvent mixture was shown to achieve very good recovery. The same solvent mixture was used to extract solid samples, since this avoids potential errors associated with a change in the extraction procedure.

2. **Derivatization.** The use of Methyl-8 reagent simplified the sample preparation step and gave a quantitative conversion for GC analysis. However, derivatization of pure resin acids did not adequately predict the behavior of extraction samples from wood, pulp, process water, and effluent. Extra Methyl-8 reagent and heating were necessary for the real-world samples. The presence of trace water in the reaction mixture also affected the methylation reaction.

3. **GC analysis.** A very polar fused-silica capillary column was found to be capable of separating all of the eight common resin acids present in softwood. Heptadecanoic acid was shown to be a suitable internal standard for analysis of the resin acids present in spruce and pine samples. The relative response factors (RRF) were different for individual resin acids, and the minimum detectable amount of resin acids was within the range 0.5–5 µg.

EXPERIMENTAL

Extraction

Solid samples (wood or pulp).

The amount of solid sample used for extraction was 0.5–1 g (dry wt.). All samples were oven dried, ground, and placed into a Soxhlet extraction thimble (40). Each sample was then extracted under reflux with a solvent mixture of dichloromethane, acetone, and methanol in equal proportions (by volume) for 6 hours. After extraction and cooling, the solvent was removed by evaporation under vacuum at 40°C. The same solvent mixture (3 mL) was then used to wash the extraction flask and transferred to a light-protected vial (reacti-vial) with heptadecanoic acid (0.5–1 mg) as an internal standard. Finally, the solvent was removed under a gentle stream of dry nitrogen.

Aqueous solutions (process water or effluent).

The volume of the liquid samples for extraction was 100–1000 mL. Sample pH was adjusted to 10 with dilute sodium hydroxide. The sample was then successively filtered through a mesh filter cloth, a Whatman 541 filter paper, and a Whatman GF/A filter paper. The C₁₈-octadecyl bond Elut solid-phase extraction column (Varian, USA) was conditioned by rinsing with 5 mL of solvent mixture (dichloromethane, acetone, and methanol in equal proportions by volume) and 5 mL of water. The aqueous liquid sample was then pulled through the extraction column under vacuum, thus fixing the resin-acid salts to the column. After this, dilute hydrochloric acid (the same amount and concentration as the dilute sodium hydroxide) was used to readjust the pH of the extraction column, and water (10 mL) was used to wash the extraction column. Excess water was removed from the extraction column by applying vacuum for at least half an hour after all of the liquid sample had passed through. The adsorbed resin acids and other organic acids could then be eluted into a light-protected vial by adding 3 mL of solvent mixture with heptadecanoic acid (0.5–1 mg) as an internal standard. Solvent was then removed under a gentle stream of dry nitrogen. The eluting process was repeated twice more to ensure that all the resin acids had been removed from the extraction column.

Derivatization

After finishing the extraction, the esterification reaction was performed in a light-protected vial by adding 200 µL of Methyl-8 reagent (Pierce, USA). The vial was sealed and heated at 60°C for 30 min.

GC separation

A gas chromatograph (PE Nelson 1022 Autosystem) equipped with a flame-ionization detector (FID) was

used for analysis of the resins. Both the injection port and detector were maintained at 300°C.

The column was 50 m long with an inside diameter (ID) of 0.22 mm. The fused-silica capillary column (SGE, Australia) was coated with a modified polycyanopropylsiloxane phase. Column temperature was kept at 200°C. Helium was used as a carrier gas, with a linear velocity of 20.9 cm/s.

The identification of the peaks was based primarily on retention times of standard pure resin-acid samples (Helix Biotech, Canada). Calibration was performed using heptadecanoic acid (Aldrich, UK) as the internal standard. Standard samples were prepared by placing a known quantity of resin acid and heptadecanoic acid in a light-protected vial before addition of the Methyl-8 reagent. **TJ**

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