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AN IMPROVED SOLVENT-EXTRACTION BASED PROCEDURE FOR THE GAS CHROMATOGRAPHIC ANALYSIS OF RESIN AND FATTY ACIDS IN PULP MILL EFFLUENTS

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SUMMARY

An analytical procedure for the determination of resin and fatty acids in pulp mill effluents is described. The procedure involves isolation of the resin and fatty acids from the effluent sample by solvent extraction with an equal volume of methyl *tert.*-butyl ether under alkaline (pH 9) conditions, derivatization of the extract with diazomethane, and subsequent analysis of the methylated extracts by gas chromatography on a 25 m × 0.20 mm I.D. OV-17 fused-silica capillary column using a flame ionization detector. The method of isolation, that is, extraction of the effluent sample at pH 9 with an equal volume of solvent, is a key feature of the new analytical procedure. These conditions overcome many of the major problems commonly associated with the application of a solvent extraction isolation technique to pulp mill effluents, such as emulsion formation, lignin precipitation, and resin acid isomerization.

INTRODUCTION

Extensive research over the past ten years, particularly that done by British Columbia Research in Canada, has established that resin acids and, to a lesser extent, unsaturated fatty acids are major contributors to the toxicity of softwood pulp and paper mill effluents to fish[1–5] as determined from acute lethal bioassays using salmonoid fish species (trout and salmon). Consequently, the availability of analytical methods for determining resin and fatty acids (RFA) is essential for controlling the discharge of these compounds to the environment and assessing their biological effect.

Although analytical methods utilizing high-performance liquid chromatography show some promise for determining RFA in pulp mill effluents[6–8], analysis by gas chromatography (GC) still remains the method of choice for a detailed characterization of the RFA constituents in pulp and paper mill effluents. Almost all GC

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procedures in use today for RFA analysis in pulp mill effluents have evolved from two distinct methods which were first developed in the early 1970s, one by the National Council of the Paper Industry for Air and Stream Improvement (NCA-SI)[9,10] in the U.S.A. and the other by British Columbia Research (BCR)[11,12] in Canada. The fundamental difference between the NCASI and BCR procedures was the method of isolation. The NCASI procedure used solvent extraction of the acid-ified (pH 2–3) effluent with diethyl ether, whereas, the BCR procedure removed the RFA from the effluent under alkaline (pH 9–10) conditions by adsorption onto a porous polymeric resin (XAD-2). In both cases, the final step of the analysis involved packed column GC of the methyl ester derivatives of the isolated RFA which were prepared by reaction with diazomethane. Over the past ten years, the analytical methods for RFA determination in pulp mill effluents have been improved or modi-fied, principally by incorporating many of the latest developments in analytical in-strumentation for chromatographic separation and detection such as high-resolution capillary GC[13–16] and combined GC–mass spectrometry (MS)[17–19]. However, the methods used to isolate the RFA from the effluent samples have essentially remained the same, that is, diethyl ether extraction or XAD-2 resin sorption.

The isolation method chosen for a given analysis is important as it defines the maximum recovery of the analytes of interest, as well as possible co-extractives that may interfere with the quantitative analytical step. If the isolastion methods used in the BCR and NCASI procedures gave equivalent results, then either would be an acceptable component of an analytical procedure designed for RFA analysis. How-ever, it is this aspect of the procedures which has become a major source of disa-greement among analysts involved with the determination of RFA in pulp mill ef-fluents.

Rogers and Mahood[20] and Claeys and Owens[21] evaluated the use of XAD resins for the analysis of RFA in pulp mill effluents. Both groups reached similar conclusions, namely, that the NCASI solvent extraction technique should be used for routine quantitative determinations of RFA in pulp mill effluents. The use of XAD resins was recommended for qualitative analyses of effluents and for environ-mental studies involving the processing of large sample volumes such as highly dilute samples of receiving waters or pulp mill effluents from which toxicants are to be recovered.

Although BCR workers reported optimum recovery by XAD resin when the pH of the effluent sample was adjusted to about[9,11,13,14], Claeys and Owens[21] and Rogers and Mahood[20] reported that the best results were achieved with XAD resins when processing acidified (pH 3) samples. Claeys and Owens[21] found an average efficiency of only 23% for the XAD-2 extraction of resin acids from a sample of biologically treated kraft mill effluent at adsorption pH values of 6.4–10. Upon aci-dification of the sample to pH 3 the efficiency improved to about 90%. Claeys' find-ings with respect to the effect of pH were consistent with the results reported earlier by Junk et al.[22] who found that a mixture of organic acids, including oleic acid, at the 10–50 μg/l level could be quantitatively recovered from distilled water provided that the sample was acidified (5 ml of hydrochloric acid per liter of sample). Other-wise, a low recovery (e.g., 32% for oleic acid) was observed.

From a recent evaluation of the applicability of solvent extraction and XAD-2 adsorption for the isolation of resin acids from thermo-mechanical pulp (TMP) ef-

fluent before and after treatment by an activated sludge process, Richardson and Bloom[23] found that XAD-2 adsorption gave the best recovery. In addition, like BCR, they observed that a pH > 7 was required for the optimum recovery of resin acids from untreated TMP effluent by XAD-2 adsorption. Curiously, a pH of 5 was found to give the best recovery for the treated effluent samples.

Recently BCR and NCASI participated in a split-sample program of analysis of pulp mill effluents for the purpose of comparing the results obtained by their respective analytical procedures[19]. The BCR resin sorption procedure gave 20–40% lower results for resin acid constituents than the NCASI solvent extraction procedure. In general, the BCR procedure provided higher concentrations of fatty acids. In contrast, in an earlier study[14] BCR had found that the recovery of RFA from a sample of softwood bleached kraft pulp mill effluent by the resin sorption method was approximately twice that obtained by ethyl ether extraction. The poor agreement found between the two methods in the recent cooperative study[19] cannot, however, be attributed solely to the different isolation procedures (*i.e.*, XAD-2 adsorption and solvent extraction). There were other procedural differences in the methods particularly with respect to sample preservation and separation–measurement methods which could have influenced the results. After sample preparation, the BCR method used capillary GC with flame ionization detection (FID) for the subsequent analysis, whereas, the NCASI procedure used packed column GC and MS as detection system. The NCASI report[19] from this interlaboratory study recommended that further development and improvement of the analytical methodologies was necessary in order to provide more reliable analytical results.

In principle, solvent extraction should provide a simpler and faster method of isolation for wastewater samples. However, the solvent extraction method has its problems. Direct solvent extraction of pulp mill effluent samples produces foaming emulsions[10,12,14,17–19,23] which can make the sample work-up step more difficult (*e.g.*, by requiring centrifugation to break the emulsion) and can result in low recoveries and poor precision for the RFA analysis. In fact, the absence of emulsion problems is one of the major arguments in favour of using resin sorption methodology in place of solvent extraction procedures for the analysis of organic compounds in wastewaters[24]. Emulsion problems can be reduced by making the effluent very acidic (pH 2–3) prior to extraction[10] as in the NCASI procedure[9,10,16,17,19], however, this can lead to additional problems such as isomerization of some of the resin acid constituents[19,23], particularly levopimaric acid, and precipitation of lignin residues which can impede the recovery of the RFA from the effluent samples. McMahon[25] recently reported the application of a petroleum ether–acetone–methanol (PAM) extraction procedure for the analysis of the RFA in kraft mill internal process streams. Emulsions can be more severe for process streams where the lignin content is relatively high. Using the PAM solvent system, McMahon was able to eliminate emulsions in the extraction of acidified process effluents. Claeys *et al.*[19] applied McMahon's procedure to the analysis of biologically treated pulp mill effluents and found that it did not provide a significant improvement in RFA recovery compared to the NCASI diethyl ether extraction procedure. A similar approach, using the solvent system hexane–acetone–methanol, has been developed at our institute[26] for the analysis of acidic and neutral extractives in sulphite-mechanical pulps and process streams. This approach, however, requires repetitive extraction which results in extended sample

preparation time particularly when applied to very dilute effluent streams.

This paper describes a solvent-extraction based GC procedure for the determination of RFA in pulp mill effluents. This new procedure overcomes many of the major problems commonly associated with the application of this isolation technique to pulp mill effluents such as emulsion formation, lignin residue precipitation and resin acid isomerization.

EXPERIMENTAL

Analytical procedure

The effluent sample (50 ml of biotreated effluent or typically 10 ml of untreated effluent diluted to 50 ml with distilled water) was spiked with heptadecanoic acid (50 μl of a 0.208 μg/μl solution in dimethyl sulfoxide). The heptadecanoic acid was included as a surrogate for RFA and served as an indicator of potential problems with respect to recovery and/or derivatization. Then, after adjusting the pH of the effluent sample to pH 9 using 0.5 M sodium hydroxide, the sample was extracted once with an equal volume (*i.e.*, 50 ml) of methyl *tert.*-butyl ether (MTBE) (Burdick & Jackson, distilled-in-glass) in a 125-ml separatory funnel. The solvent extract was transferred to a 50-ml round-bottomed flask having a graduated conical tip[22] and concentrated to approximately 0.3 ml using a vacuum rotary evaporator at 25–30°C. To the concentrate were added 100 μl of methanol (which served as a catalyst for the subsequent esterification step[27]) containing 22.6 μg of propyl dehydroabietate as an internal standard and approximately 0.6 ml of diethyl ether. The resulting mixture was methylated by bubbling continuously generated diazomethane through the solution (using a diazomethane generating system similar to that described by Levitt[28]) until the yellow colour of excess diazomethane persisted for at least 5 min. Finally, the methylated extract was concentrated to 0.2 ml using a gentle stream of nitrogen, and a 2-μl aliquot was analyzed by split capillary GC with FID.

Chromatographic analyses were made using a Hewlett-Packard Model 5880A gas chromatograph and a 25 m × 0.20 mm I.D. fused-silica capillary column (Hewlett-Packard) wall-coated with cross-linked 50% phenylmethyl silicone (OV-17 type) phase of 0.17-μm film thickness. The GC conditions were as follows: column temperature was held at 150°C for 1 min then programmed to 200°C at 10°C/min followed immediately by a 2°C/min increase to 260°C; injector, 250°C; detector, 270°C; carrier gas, helium at 173 kPa; split injection (1:13 split ratio). Compound concentrations were estimated on the basis of electronically-integrated GC peak areas relative to the internal standard (propyl dehydroabietate). An assumed relative response factor of 1.0 was used for each RFA. This is consistent with the values near unity which have previously been reported for many of these compounds[9,10,29–31].

Samples

A sample of effluent, collected from the outlet of a (5-day) aerated lagoon treatment system of a softwood bleached kraft mill located in eastern Canada, was used for the development and evaluation of the analytical procedure for RFA determination. Although the level of RFA in this combined bleached kraft mill effluent (BKME) after biological treatment was relatively low (total concentration about 50 μg/l), the background level was further reduced by passing the (pH-unadjusted) ef-

fluent sample through a column containing XAD-2 resin. By using the XAD-treated effluent for method validation, the correction required for background levels was minimized, particularly for RFA at relatively low concentration levels. Yet, at the same time, this approach provided an effluent sample whose matrix was on the whole much the same (particularly with respect to relatively high-molecular-weight lignin residues and inorganic constituents) as the effluent without XAD-2 treatment.

To demonstrate the application of the RFA method, samples of BKME entering and leaving a (5-day) aerated lagoon treatment system were collected from a second softwood bleached kraft pulp mill site in eastern Canada.

Standards

The unsaturated fatty acid standards, oleic (*cis*-9-octadecenoic) and linoleic (9,12-octadecadienoic) acid, were obtained from Alltech (Deerfield, IL, U.S.A.). Standards of the resin acids (and chlorinated resin acids) commonly found in pulp mill effluents were purchased from BCR (Vancouver, Canada) with the exception of pimaric acid which was obtained from Chemicals Procurement Lab. (College Point, NY, U.S.A.). The propyl dehydroabietate internal standard[19] was supplied by courtesy of L. LaFleur (NCASI, Corvalis, OR, U.S.A.).

RESULTS AND DISCUSSION

Method development and evaluation

During the course of exploratory work on the extraction of a sample of BKME with MTBE, we discovered that problematic emulsions could be eliminated provided that a volume of MTBE solvent approximately equal to or greater than the volume of the effluent sample was used. Otherwise, emulsions would form. The benefit of emulsion retardation by extracting with an equal volume of solvent was also observed when extractions were made using diethyl ether.

The recovery of RFA from an effluent sample by a single extraction with an equal volume of MTBE and the influence of effluent pH on the recovery were examined in subsequent experiments. For these studies, an XAD-2 treated lagoon outlet sample (see Experimental) spiked with known amounts of a mixture of RFA was used. The stock spiking solution prepared in dimethyl sulfoxide contained two unsaturated fatty acids, oleic and linoleic acid, and two representative resin acids, isopimaric acid and dehydroabietic acid (Fig. 1).
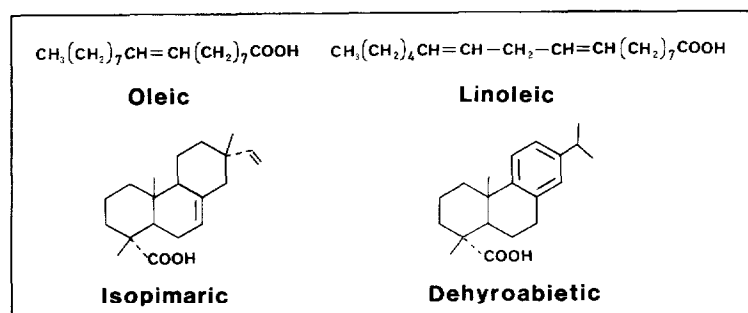

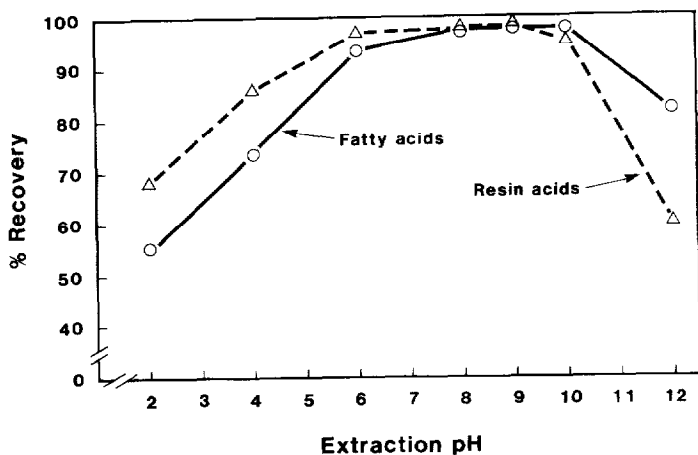Fig. 1. Structures of representative RFA constituents of softwood pulp mill effluents.

Fig. 2. Influence of effluent sample pH on the recovery of resin acids (isopimaric + dehydroabietic) and fatty acids (oleic + linoleic) from a spiked effluent sample by a single extraction with an equal volume of MTBE.

A series of spiked effluent samples, adjusted to various pH values, were extracted twice with a volume of solvent (MTBE) equal to the effluent volume (50 ml). The two extracts were worked up and analyzed separately for RFA. Percent recovery was then calculated from the ratio of the amount of RFA found from the first extraction to the sum of the amounts from the first and second extractions. The results from a study of the influence of effluent pH on the recovery of RFA in the range of pH 2–12 revealed, as shown in Fig. 2, that a maximum recovery (98%) of RFA was obtained at approximately pH 8–9. Interestingly, BCR had observed a similar optimum pH for the recovery of RFA by the resin sorption isolation technique[11,14]. Our results indicated that the recovery by solvent extraction fell off appreciably at effluent pH values less than about pH 6 and greater than approximately pH 10. At low pH, such as pH 2, the recovery of resin acids was poor (*ca.* 68%) although somewhat better than for fatty acids (*ca.* 55%). Conversely, at relatively high pH, such as pH 12, the recovery of the fatty acids (*ca.* 81%) was higher than for the resin acids (*ca.* 60%). The low pH results are consistent with the observation by NCASI that their diethyl ether extraction procedure (at pH 2) appeared to give low recoveries for the fatty acids[19].

Intuitively, one might have expected an optimum recovery of the acidic RFA compounds at low pH and this presumably is a reason, along with reduced emulsion formation[10], that strongly acidic conditions have been chosen in the past for RFA isolation from pulp mill effluents by solvent concentration. Yet, in contrast, our results (Fig. 2) reveal that poor RFA recovery will be obtained under strongly acidic conditions. One possible explanation for the decreased recovery of RFA from pulp mill effluents by solvent extraction under acidic conditions is that the RFA compounds become bound to the relatively high-molecular-weight lignin residues in the effluent, much in the same manner that various authors have shown that hydrophobic pollutants can bind to dissolved humic materials (*e.g.*, see Landrum *et al.*[32] and references cited therein). For example, Hassett and Anderson[33] have observed that

the recovery of cholesterol from water samples by liquid–liquid extraction was lower in the presence of dissolved humic materials. Carter and Suffet[34] recently found that the binding of DDT by humic materials increases at lower pH levels. Their explanation for the pH effect was that the humic polymer becomes less hydrophilic and consequently more able to bind hydrophobic compounds as its charge becomes neutralized with decreasing pH. Similarly, one can speculate that at lower pH the possibility of binding of RFA by dissolved lignin material in pulp mill effluents can be enhanced because of increases in the hydrophobic character of both the lignin material and the RFA constituents. Our finding, from additional experiments, that RFA compounds were quantitatively recovered when spiked into distilled water and extracted in the range of pH 2 to 7, lends support to the above hypothesis.

Regardless of the mechanisms responsible for the pH effects observed, this study does illustrate the importance of establishing the recovery of an analytical method by using an actual sample of the type to which the analysis is subsequently to be applied. Otherwise, possible matrix effects which can interfere with the analyte recovery may go undetected as, for example, when distilled water[18] is used to assess recovery.

An additional benefit of extracting the effluent samples at pH 9, instead of at pH 2 as in the NCASI procedure, is that the amount of extraneous (often non-volatile) organic material extracted from the effluent sample is very much reduced. Thus, the effluent extracts obtained from the pH 9 extractions can probably be analyzed by splitless capillary GC without additional clean-up such as by silica gel chromatography[16,25].

The procedure presented in this report can also be modified to incorporate the ethylation procedure recently described by LaFleur et al.[16] which uses triethyloxonium tetrafluoroborate.

The precision of the analytical method was determined by performing five replicate analyses of (XAD-2 treated) BKME lagoon outlet effluent spiked with our four-component RFA mixture at two different concentration levels, 200 ppb* and 20 ppb of each RFA constituent.

The precision (percent relative standard deviation) of analysis was found to be ±5% and ±2% for the fatty acids and resin acids, respectively, at the high (200 ppb) concentration level and ±10% and ±3%, respectively, at the low (20 ppb) concentration level.

The detection limit of the method was determined to be approximately 5 ppb by performing split capillary GC–FID analysis of a series of solutions corresponding to concentrations of 20, 10, 5, 2.5 and 1.25 ppb of each of the four RFA used for spiking.

If required, a lower detection limit can be attained by extracting larger volumes of sample and/or by using the splitless GC injection technique in place of the split injection mode.

Method application

Fig. 3 illustrates the application of the analytical method described in this paper to the determination of the RFA content of combined pulp mill effluent en-

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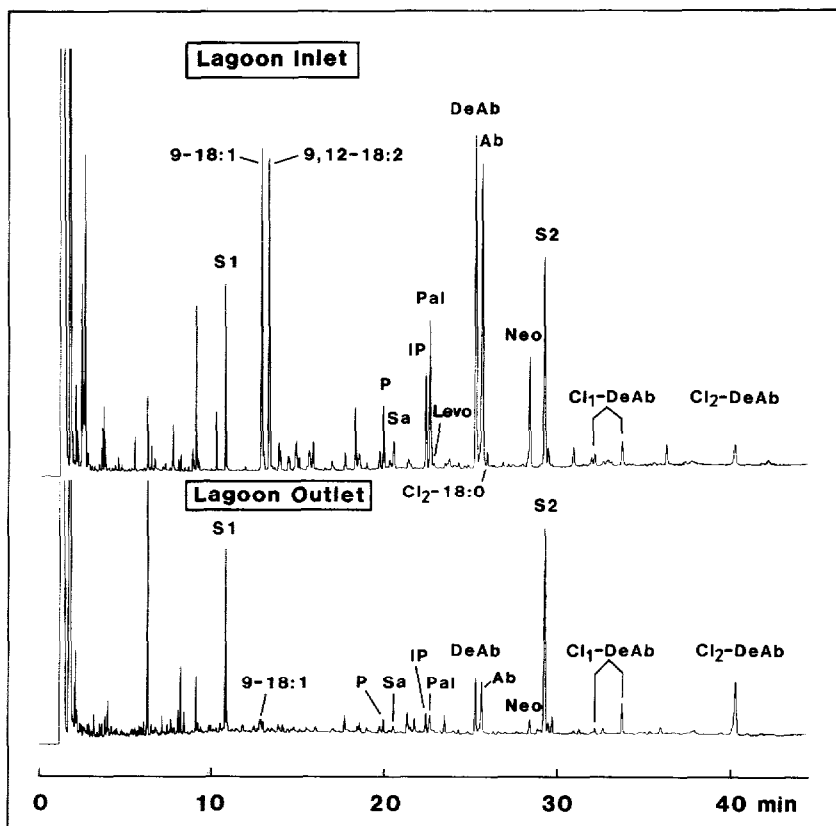* The American billion (10^9) is used throughout the article.

Fig. 3. Capillary GC–FID chromatograms of methylated extracts of combined bleached kraft mill effluent going into and coming out of an aerated lagoon treatment system. (RFA abbreviated notations as in Table I; S1 = surrogate compound, heptadecanoic acid; S2 = internal standard, propyl dehydroabietate).

tering and leaving the (5-day) aerated lagoon treatment system of a softwood bleached kraft pulp mill. In comparing the GC profiles for the lagoon inlet and outlet samples, it should be kept in mind that five times less sample was taken for analysis of the inlet sample. As shown, all of the major RFA constituents in the effluent samples were adequately resolved on the OV-17 type fused-silica capillary column. Of particular interest is the separation of the methyl esters of palustric and levopimaric acid. The resolution of this pair of acids has not been possible on non-polar (methyl silicone) type columns (e.g., SE-30, OV-101, SE-54)[30,31,35] except at relatively low column temperatures[30] which would make the analysis impractical because of the increased analysis time. Using a glass capillary column coated with 1,4-butanediol succinate (BDS), Holmbom[15,35] has been able to satisfactorily resolve all of the major RFA components including the levopimaric–palustric pair. However, this column does not seem to be appropriate for the analysis of both non-chlorinated and chlorinated resin acids (i.e., monochloro- and dichlorodehydroabietic acids) because of the excessively long retention time of the latter compounds on the BDS column.

TABLE I

CONCENTRATIONS OF RESIN AND FATTY ACIDS FOUND IN SOFTWOOD BLEACHED KRAFT MILL EFFLUENT ENTERING AND LEAVING A 5-DAY AERATED LAGOON TREATMENT SYSTEM

Acid	Concentration ($\mu g/l$)	
	Inlet	Outlet
Fatty acids		
Oleic (9-18:1)*	2450	21
Linoleic (9,12-18:1)	2890	—***
9,10-Dichlorostearic (Cl_2-18:0)	34	—
Resin Acids		
Pimaric (P)	612	25
Sandaracopimaric (Sa)	322	19
Isopimaric (IP)	977	39
Palustric (Pal)	1510	54
Levopimaric (Lev)	71	6
Dehydroabietic (DeAb)	3860	126
Abietic (Ab)	3650	114
Neoabietic (Neo)	1300	36
Monochlorodehydroabietic** (Cl_1-DeAb)	477	89
12,14-Dichlorodehydroabietic (Cl_2-DeAb)	339	188
Total	18 492	719

* Shorthand notation for unchlorinated RFA as in ref. 35.

** Sum of two isomers, 12- and 14-chlorodehydroabietic acid.

*** Not detected.

The quantitative results given in Table I indicate that this aerated lagoon's removal efficiency for RFA compounds was approximately 96%. RFA removal efficiencies of > 90% are not uncommon for well-operated aerated lagoons[13,14,36,37].

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