# A rapid spectrophotometric procedure for the determination of total resin and fatty acids in pulp and paper matrices

B. Bruce Sitholé

*ABSTRACT: Current techniques for the determination of fatty and resin acids in pulp and paper matrices are long and require sophisticated instrumentation not available in most mills. The industry needs rapid techniques for monitoring these compounds, for example, to ascertain their buildup in closed whitewater systems, or to monitor the efficiency of effluent treatment systems. A rapid colorimetric procedure used for monitoring free fatty acids in vegetable oils has been adapted for the determination of total free fatty and resin acids in extractives obtained from pulp and paper samples. The fatty and resin acids in the extractives are made to complex with cupric ions. The complexes are extracted into a solvent, and their concentrations are determined colorimetrically. This paper demonstrates the use of this procedure with pitch deposits, wood chips, whitewaters, and effluents.*

*KEYWORDS: Effluents, extractives, fatty acids, photometry, pitch, resin acids, spectroscopy, test methods, white water, wood.*

Wood extractives, important components of wood, comprise about 3–6% of the weight of the wood, depending on the species *(1–4)*. Residual amounts of the extractives, which are found in a variety of pulp and paper matrices, are important in several ways: they are major contributors to the toxicity of untreated pulp and paper mill effluents *(5–7)*; they commonly cause pitch deposition problems *(8–10)*; they are a valuable by-product in the form of tall-oil in kraft pulping *(11)*; they can impart desirable water repellency properties, hence sizing in some pulps, or affect water absorption properties of mechanical fluff pulps *(12)*. Thus it is often important to determine their concentrations in various pulp and paper matrices.

Conventional procedures for their determination generally involve some kind of extraction. Typically, the extractives are separated from the matrices by solvent extraction *(13–16)* or solid phase extraction *(17–20)* to yield the total extractives content after evaporation of the solvent. The value of the total extractives can include items such as oils (from defoamers or lubricants), sizing agents, and other solvent-soluble additives used in pulping and papermaking which do not originate from the wood. Accurate chemical characterization of the extractives' content can be done by further analysis of the extractives using gas or liquid chromatographic procedures *(21–23)*. These procedures can be time consuming and they require sophisticated instrumentation not commonly available in mills.

Because the industry badly needs rapid methods for the measurement of extractives our institute has embarked on research in this area *(24, 25)*. This report describes a spectrophotometric procedure for the determination of total free fatty and resin acids in pulp and paper matrices. The procedure is faster than current chromatographic procedures and is an adaptation of a method that is used to monitor free fatty acids in vegetable

**Sitholé is group leader, process chemistry with the Pulp and Paper Research Institute of Canada, 570 St. John's Boulevard, Pointe Claire, PQ, Canada H9R 3J9.**

oils *(26, 27)*. The steps involved are as follows: obtain extractives from pulp and paper matrices, complex the free fatty and resin acids in the extractives with copper ions to yield blue complexes, extract the complexes into a solvent, and measure the absorbance of the complexes on a spectrophotometer at 680 nm. Shown below are examples of the application of the procedure to extractives obtained from wood, pitch deposits, effluent, and whitewater samples.

## Experimental

### Materials and solutions

Stock solutions of resin and fatty acids (RFAs) were prepared in high purity acetone or chloroform. The copper ions were in the form of a 5% solution of cupric acetate in distilled water

### Spectrophotometric procedure

The original method consisted of dissolving an aliquot of vegetable oil in benzene, followed by the addition of 2 mL of the cupric acetate solution, and by shaking vigorously for about a minute before measuring the absorbance of the benzene layer at 630 nm *(26)*. Our procedure was as follows: extractives in a suitable solvent, typically 1 mL of acetone, were mixed with 2 mL of the cupric acetate solution in a separatory funnel, followed by the addition of 5 mL of hexane and by shaking vigorously for about a minute before the absorbance of the hexane layer was measured at 680 nm. We decided not to use benzene because of its carcinogenic properties. A calibration curve was prepared using oleic acid as the standard. Total resin and fatty acids in pulp and paper matrices were quantified using the calibration curve.

### Extraction of RFAs from pulp and paper matrices

The RFAs were obtained in the form of total extractives by Soxtec extraction of solid samples using acetone *(28)*. In effluent and whitewater samples, the compounds were obtained by solvent extraction using two methods. In the first method, 250 mL of samples were extracted using the Saltsman procedure *(14)*; the samples were acidified to pH less than 1 and extracted with a mixture of acetone-methanol-petroleum ether (250:60:200) followed by a second extraction with 200 mL of petroleum ether. In the second method, the samples were extracted using a procedure outlined by Voss and Rapsomatiotis *(13)*: the samples were made alkaline before extraction with an equal volume of methyl *t*-butyl ether. The extracts were reduced to about 10 mL on a rotary evaporator and then to about 1 mL under a gentle stream of nitrogen before being analyzed by the spectrophotometric procedure. Other extraction procedures were investigated for effluents and whitewater samples, such as the use of solid-phase extraction tubes and adsorption onto XAD resin sorbents.

### Determination of bound RFAs

The spectrophotometric procedure measures only free fatty and resin acids. Compounds containing RFAs such as glycerides and metal salts do not react with cupric ion, but can be freed to do so by hydrolysis. Thus, the amount of bound RFAs can be determined by the difference between the total RFA values obtained before and after the hydrolysis of the extractives. The hydrolysis was done by refluxing the extractives or pitch deposits with acidified acetone (25 mL acetone +0.1 mL 10 *M* HCl) for about 30 min. The solvent was reduced to 2 mL and 1 mL of the extract was analyzed by the spectrophotometric procedure.

### Apparatus

All the absorbance measurements were done on a HP8452 diode array spectrophotometer using a glass cuvette with a path length of 1 cm.

### Accuracy of the spectrophotometric procedure

A mixture of 10 ppm each of linoleic, dehydroabietic, and abietic acids in acetone was analyzed by the spectrophotometric procedure and by capillary gas chromatography of methylated acids. An aqueous mixture containing the same mixture was extracted with solvent, and the extracts were also analyzed by the two methods. The amounts of RFAs in the samples were expressed as equivalent amounts of oleic acid.

## Results

### Behavior of various fatty and resin acids

For equal amounts, resin and fatty acids yielded the same extinction coefficient, within experimental error, at 680 nm. This is different from the original procedure where the complexes of palmitic and stearic acids were found to be insoluble in benzene. Oleic acid was arbitrarily selected as the standard to use in determining the concentrations of total resin and fatty acids. A typical absorbance spectrum for 0.2 ppm of oleic acid, as in **Fig. 1**, shows that the absorption maximum occurred at 680 nm, and not at 630 nm, as reported in the original method. Perhaps the absorbance maximum is dependent on the extraction solvent used.

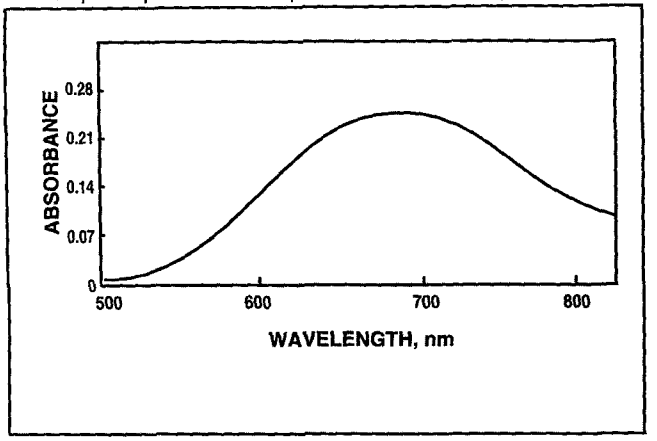
### Interference from non-RFAs

A test of a variety of compounds commonly found in pulping and papermaking systems showed that only benzoic acid was able to complex with the cupric acetate. However, the complex is not soluble in hexane and thus is not expected to interfere in the determination of total free fatty and resin acids.

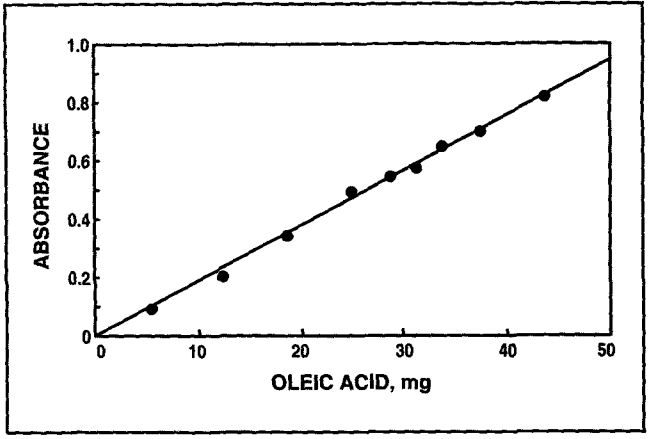
### Calibration curve and defection limit

Linear calibration curves were obtained over the range of 1 mg to 45 mg of oleic acid, as shown in *Fig. 2*. The reproducibility of the method was very good and yielded a coefficient of variation of 1.5%. The detection limit, an absorbance reading of 0.02, for oleic acid spiked in distilled water was ascertained to be 5 ppm in 250 mL of water and could be lowered to 1.25

1. Absorption spectrum of a cupric ion-oleic acid complex in hexane




2. Calibration curve for oleic acid using the spectrophotometric procedure




ppm in 1 L of water (because the RFAs will be concentrated from a four times bigger volume). For practical purposes, it is best to work with 250 mL as it is easier to handle a 250-mL separatory funnel than a 1 L one.

### Accuracy of the spectrophotometric procedure

Analysis of a 10-ppm mixture of 3 RFAs in distilled water by the spectrophotometric procedure gave a total RFA value of 27 ppm oleic acid, whereas analysis of the same mixture by gas chromatography gave a value of 28.2 ppm oleic acid. Thus, our spectrophotometric result agrees well with that from gas chromatography.

The results indicate that the hexane extraction efficiency was about 96%; this agrees very well with literature reports *(13, 18)*.

A plot of the results from the analysis of a RFAs mixture (in a solvent) at various concentrations by both procedures gave a correlation of 0.998. This is further proof of the accuracy of the spectrophotometric procedure.

## Application of the spectrophotometric procedure

### Pitch deposits

The analysis of pitch deposits usually entails solvent extraction with acetone to yield a wood resin and oil fraction, followed by extraction of the residual matter with chloroform to yield a fraction containing complexes of multivalent metals and fatty and resin acids, and by further extraction of the residual matter with toluene to yield a defoamer component (amide) fraction. The wood resin/oil fraction can be further segregated into wood resin and oil fractions by column chromatography *(29)*. The spectrophotometric procedure was used to measure the total RFAs in the acetone extractives. **Figure 3** shows the amounts of total acetone extractives and RFAs determined in pitch deposits from a mechanical pulp mill. The results, besides showing that there was very good reproducibility in duplicate samples, indicate a significant component of the extractives was due to nonfatty and resin acid material (the total RFAs in the extractives were 30% and 15% in the two deposits). In fact, this component was determined (by column chromatography) to be chiefly due to oil which most probably originated from the oil-based defoamer being used at the mill. The metal complexes of RFAs in the deposits were determined to be 0.9% and 0.3% in the deposits. These values agreed well with those obtained by the solvent extraction procedure (0.8% and 0.4%, respectively).

### Wood chips

The extractives content and total RFAs of wood chips from several wood species are shown in **Fig. 4**. The figure shows there is a correlation between the acetone extractives content and the total RFAs; in general, the greater the extractives content, the more resin and fatty acids in the wood chips. Aspen does not follow the trend, however, because aspen extractives contain less fatty acids and more nonfatty acid compounds such as steryl esters and cholesteric materials *(30)*. Thus, the total extractives content of this species is largely comprised of compounds which are not free fatty acids (hardwoods do not contain resin acids), as has been reported before *(30)*.

### Mechanical pulp mill effluents

Solvent extraction is the rate-limiting step in our spectrophotometric procedure. Faster methods for the collection of extractives would be preferable. In recent years, several reports have detailed more rapid extraction procedures for effluents and whitewaters using solid-phase extraction techniques *(17, 18)*. The procedures involve the elution of liquid samples (typically less than 20 mL) through a solid sorbent to trap the extractives; the extractives are subsequently released by elution with a small volume of organic solvent. In this manner, the extractives are preconcentrated to yield concentration levels which are amenable to analysis by chromatographic techniques. These procedures were tested and found unsuitable mainly because the sample volumes used were low and, consequently, did not yield sufficient amounts of extractives to give discernible absorbances in the spectrophotometric procedure. Adsorption onto

XAD resins (ion exchange polymeric beads) was also tested and found to yield inconsistent results. In fact, literature reports indicate that this extraction procedure is very much dependent on the mill effluent: in some cases, the best results are obtained when the samples are first acidified before the adsorption step, whereas in other cases the optimum yields result when the samples are first made alkaline *(19, 20)*.

Conventional solvent extraction procedures offered the best results for the spectrophotometric determination of RFAs in pulp and paper mill process liquids. The method using methyl *t*-butyl ether as the extraction solvent was considered to be the best because it used lower amounts of solvent and it involved fewer steps than the Saltsman procedure.

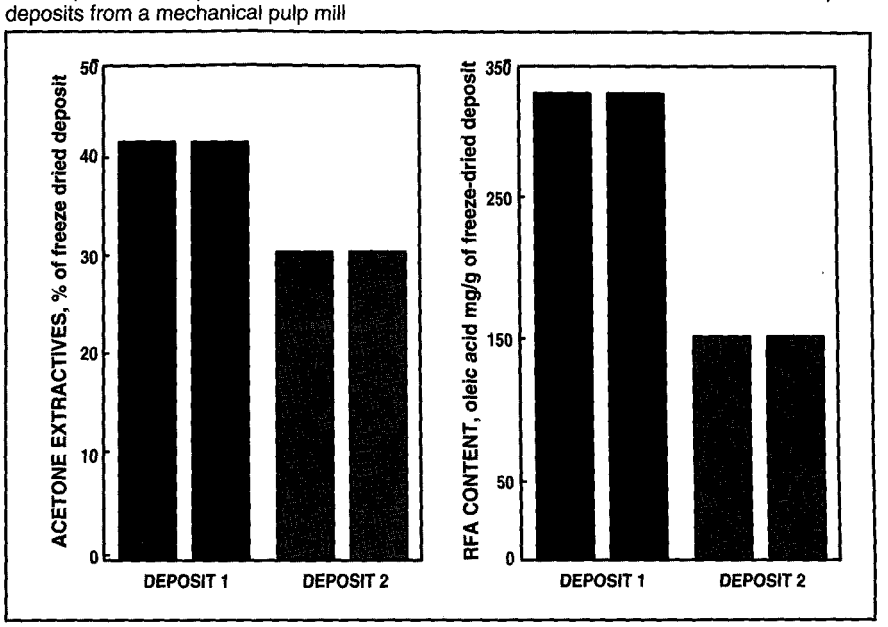
**Figure 5** shows the total RFAs for a CTMP effluent sample which was analyzed after storage for three weeks and for three months at room temperature. The results show that the amounts of resin and fatty acids in the effluent decreased with time, as expected. The reduction could be due to decomposition or transformation of some of the RFAs *(31)*.

### TMP whitewater

The amount of extractives in whitewater can be used as an indicator of potential pitch deposition problems. One measure of this is the concentration of dispersed resin particles which is determined by use of the pitch count technique *(32)*. Nondispersed resin is measured by solvent extraction using the Saltsman procedure *(14)*. Our spectrophotometric procedure was found to be applicable to whitewater samples. Analysis of five replicate samples of a pine TMP whitewater sample from our pilot plant gave total RFA content equivalent to 52.6 ± 0.9 ppm of oleic acid. RFA compounds in the whitewater, namely glycerides, were determined to be equivalent to 20.5 ± 0.9 ppm of oleic acid. The ratio of free RFAs to bound RFAs in the whitewater extractives was found to be 1.1 which was very close to the value of 1.25 found by gas chromatography in the pinewood species *(22)*. Application of the procedure to whitewater samples from cedar and balsam fir species gave total RFAs values of 26.5 and 18.2 ppm of oleic acid, respectively.

The whitewater samples had to be centrifuged and filtered before solvent extraction. We found that the pH of the samples affected the concentration of the extractives in the filtrates. The best results were obtained when the whitewaters were raised to pH 9 before the filtration step. It is not clear why this is so, but similar results have been obtained with the adsorption of wood resin from whitewaters onto solid adsorbents *(18)*.

3. Comparison of duplicate values of the acetone extractives content and total RFAs of pitch deposits from a mechanical pulp mill



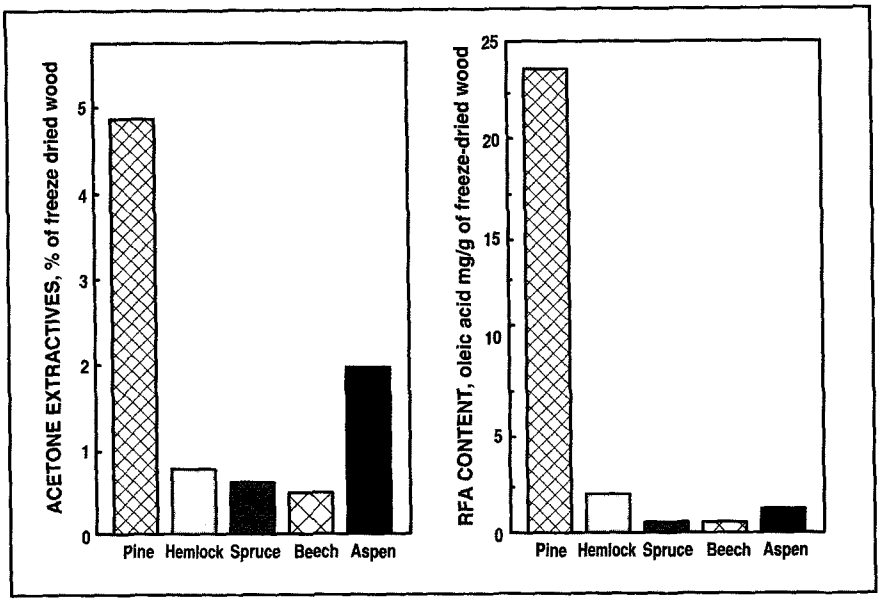

## Conclusions

Spectrophotometric determination of total RFAs in pulp and paper matrices is a simple and rapid procedure which could be used at mills since it does not require sophisticated instrumentation. The procedure yields results which agree very well with those obtained from more sophisticated chromatographic procedures, and it can be used as a rapid procedure to estimate the amount of resin and fatty acids in extractives. It also offers an easy way to estimate the amount of saponifiable matter (esters) in wood chip extractives. A disadvantage of the technique is that it does not detect trace quantities of resin and fatty acids. Also, the procedure requires much larger volumes of liquid samples than those used in chromatographic procedures. ■

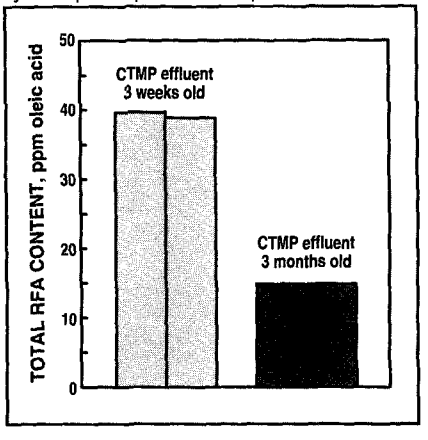
## Literature cited


1. Mutton, D. B., in *Wood Extractives and their Significance to the Pulp and Paper Industries* (W. E. Hillis, Ed.), Academic Press, New York, 1962, Chap. 10.
2. Joint Textbook Committee, *The Pulping of Wood* (R. G. Macdonald & J. N. Franklin, Eds.), McGraw-Hill, New York, 1969, Vol. 1, Chap. 2.
3. Sjostrom, E., *Wood Chemistry: Fundamentals and Applications*, Academic Press, New York, 1981.
4. Rydholm, S. A., *Pulping Processes*, Interscience, New York, 1965, Chap. 4.
5. Leach, J. M. and Thakore, A. N., *J. Fish. Res. Board Can.* 30: 479(1973).
6. McLeay, D., *Aquatic Toxicity of Pulp and Paper Mill Effluent: A Review*, Environment Canada, Environmental Protection Service 4/PF/1, Ottawa, ON, 1987.
7. O'Connor, B. I., Kovacs, T. G., and Voss, R. H., *Environ. Toxicol. Chem.* 11: 1259(1992).
8. Gustafsson, C., Tammela, V., and Kahila, S., *Paper Maker British Paper Trade J.* 124: 38(1952).
9. Back, E., *Svensk Papperstid.* 22: 793(1960).

4. Comparison of the extractives content and total RFAs of several wood species




5. Determination in duplicate of total RFAs in CTMP effluent stored for two different times by the spectrophotometric procedure.





10. Allen, L. H., *Pulp Paper Can.* 76: 70(1975).
11. McSweeney, E. E, Arlt, H. G., and Russell, J., *Tall Oil and Its Uses—II,* Pulp Chemicals Association, Inc., Atlanta, 1987.
12. Malmgren, K. and Spile, N. I., Application Note: Improvement of water absorption properties of mechanical pulp by use of RESINASE™A 2X, Bioindustrial Group, Novo Nordisk, Denmark: A 6130(1991).
13. Voss, R. H. and Rapsomatiotis, A., *J. Chromatogr.* 346: 205(1985).
14. Saltsman, W. and Kuiken, K. A., *Tappi* 42: 873(1959).
15. Claeys, R. R., Natl. Council Paper Ind. Air Improv., Stream Improv. Tech. Bull. No. 281, 1975.
16. Leach, J. M. and Thakore, A. N., Isolation of the Toxic Constituents of Kraft Pulp Mill Effluents, Environmental Protection Service, Environment Canada, Ottawa, CPAR Project Report No. 11-5, 1974.
17. Sweeney, K. M., *Tappi J.* 71: 137(1988).
18. Backa, S., Brolin, A., and Nilvebrant, N-O., *Tappi J.* 72: 139(1989).
19. Richardson, D. E. and Bloom, H., *Appita* 35: 477(1982).
20. Rogers, I. H. and Mahood, H. W., Fish. Mar Serv. Can. Tech. Rep. No. 730, 1977.
21. Holmbolm, B., *Paperi Puu* 62: 523(1980).
22. Nugent, H. M., Allen, L. H., and Bolker, H. I., *Trans. Tech. Sect. CPPA* 3: 103(1977).
23. Richardson, D. E., Bremner, J. B., and O'Grady, B. V., *J. Chromatogr.* 595: 155(1992).
24. Kester, M. D., Horner, J. A., Nicolidakis, H., *et al., Process Cont. Qual.* 2(4): 305(1992).
25. Sitholé, B. B., Sullivan, J. L., and Allen, L. H., *Holzforschung* 45(5): 409(1992).
26. Baker, D., *J. Amer. Oil. Chem. Soc.* 41: 21(1964).
27. Schneider, M. H., *J. Coat. Tech.* 51: 61(1979).
28. Sitholé, B. B., Vollstaedt, P. V., and Allen, L. H., *Tappi J.* 74: 187(1991).
29. Dorris, G. M., Douek, M., and Allen, L. H., *J. Pulp Paper Sci.* 11: J149(1985).
30. Allen, L. H., Sitholé, B. B., MacLeod, J. M., *et al., J. Pulp Paper Sci.* 17: J85(1991).
31. Jansson, M. B., Back, E. L., and Tufvesson, M. I., *Papermaking Raw Materials, 8th Fundamental Research Symposium, Oxford,* (V. Punton, Ed.), Mechanical Engineering Publications Ltd., London, 1985, Vol. 2, p. 729.
32. Allen, L. H., *Trans. Tech. Sect. CPPA* 3: 103(1977).



Technical assistance was provided by Sylvia Wood, a 1992 summer student from the environmental sciences program at McDonald College, McGill University.

Received for review Feb. 17, 1993.

Accepted June 4, 1993.