Determination of rosin sizing agents in paper by pyrolysis–gas chromatography combined with on-line methylation

Yasuyuki Ishida, Hajime Ohtani, Takeshi Kato, Shin Tsuge, and Tatsuya Yano

ABSTRACT: Rosin sizing agents in paper are determined by pyrolysis-gas chromatography combined with on-line methylation technique using tetramethylammonium hydroxide. The methyl esters of the rosin adducts consisting of rosin acids and fumaric acid are used as the key products in the pyrograms of paper samples for determination. The amounts of the rosins retained in paper samples are determined with about 1% relative standard deviation. The results are interpreted in terms of the effect of aluminum sulfate on the retention of the rosin sizing agents in the paper samples.

KEYWORDS: Additives, gas chromatography, methylation, pyrolysis, rosin acids, rosin size, size.

Sizing agents are often added to paper in order to decrease the rate of aqueous fluid penetration into the capillary structures of the paper. This treatment, called sizing, improves the printing and writing qualities of paper. Rosin is one of the most popular and traditional sizing agents. However, the acidic nature of alum [$Al_2(SO_4)_3 \cdot 18H_2O$] added as the fixing agent for the rosin sometimes makes it difficult to preserve the paper for long periods of time. Rosins are chiefly composed of a series of rosin acids, mainly abietic acid, which are obtained mostly from pine trees. Moreover, the mixture called fortified rosin used industrially consists of rosin itself and its adducts prepared by the partial reaction of the rosin with maleic acid or fumaric acid, as shown in **Fig. 1.**

This fortified rosin emulsion and alum added to pulp slurry are partly lost with the white water during paper production. Therefore, it is important to determine the amount of rosin retained in paper samples for quality control. The reliable determination of rosin in paper, however, is very difficult because trace amounts of the rosin are not only physically retained in paper but also chemically bound to some extent in the paper matrix after fixing.

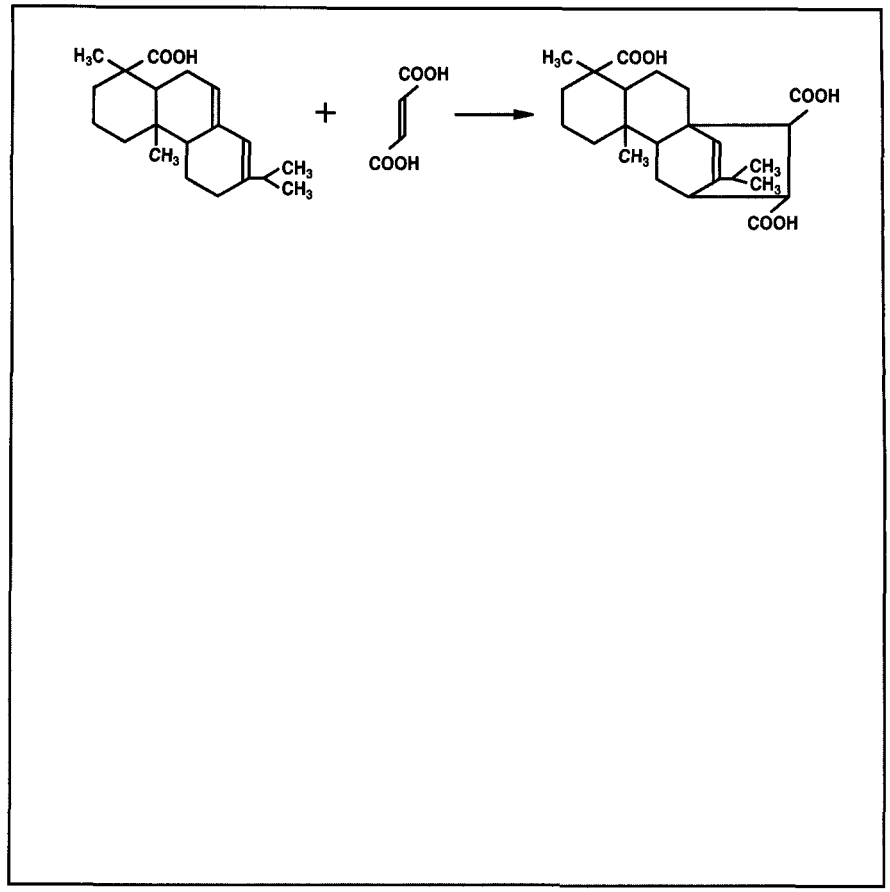
A standard method to determine the rosin sizing agents is described in a TAPPI Method *(1)*. In this method, the rosin compounds in paper are first extracted with acidic alcohol. The alcohol extract is then subjected to the further extraction with chloroform. Thus the rosin content is determined from the weight of the residue after evaporation of the chloroform extract. In addition, the determination of rosin using the absorbance of the extract was also reported *(2)*. But the methods described above not only need laborious extraction of the rosin from paper but also lead to insufficient extraction of the rosin components and the possibility of extracting impurities other than the rosin, which can lead to the unreliable determination of the rosin.

Recently, the authors have reported that pyrolysis-gas chromatography (Py-GC) is potentially useful for the analysis of trace agents in paper, such as wet-strength resin *(3)* and neutral sizing agents *(4)*. In particular, Py-GC enabled precise and quantitative determination of the neutral sizing agents such as alkylketene dimers which, in turn, clarified the mechanism of sizing *(4)*.

Ishida, Ohtani, Kato, and Tsuge are, respectively, graduate student, assistant professor, undergraduate student, and professor, Department of Applied Chemistry, School of Engineering, Nagoya University, Fro-cho, Chikusa-ku, Nagoya 464-01, Japan. Yano is researcher with the Laboratory of Japan PMC Corp., Ichihara-shi, Chiba 290, Japan.

However, conventional Py-GC does not necessarily provide satisfactory results for the determination of rosin sizing agents because of their extremely high polarities due to one or more carboxyl groups existing in the components, some of which are too polar to be eluted even by the best capillary columns. On the other hand, pyrolysis in the presence of an alkylating reagent such as tetramethylammonium hydroxide (TMAH) [$(CH_3)_4NOH$], which converted the compositional acids and phenols in polyesters into their methyl derivatives, enabled the precise determination of the polyesters *(5, 6)*. Therefore in this work, Py-GC combined with the on-line methylation technique was applied to the determination of the rosin sizing agents in paper samples. The effect of alum on the retention of rosin in paper samples was also studied.

1. Formation of fortified rosin



Results and discussion

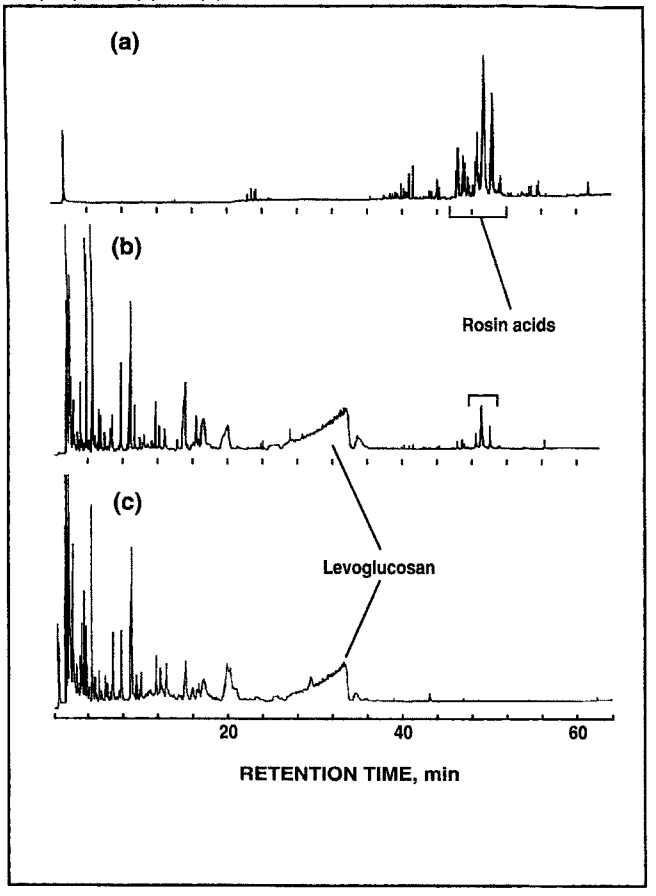
Pyrolysis in the presence of TMAH

Figure 2 shows the pyrograms of the rosin sizing agent alone (a), an actual paper sample P-3.0(2.0) containing both rosin and alum (b) and the control paper sample P-0(0) (c) at 450°C observed without adding TMAH. In the pyrogram of Fig. 2(a), a series of rosin acids such as abietic acid, which is the main component of rosin, evaporated from the sample cup eluted between 44 and 52 min. These peaks, however, are weak and broad to some extent. Furthermore, no chromatographic peaks are observed for the extremely polar rosin adducts. In the pyrogram of the control paper P-0(0) [Fig. 2(c)], pyrolysates of cellulose, the chief component of paper, show a complex peak pattern. In particular, the big leading peak between 28 and 33 min was identified as levoglucosan, which is known to be the major product of the pyrolysis of cellulose *(4)*. On the other hand, in the pyrogram of P-3.0(2.0) [Fig. 2(b)], the peaks of the rosin acids were separated from those of the paper components. The peaks of the rosin acids, however, were broad and those of the rosin adducts gave no chromatographic peaks on the pyrogram because of their high polarity. In addition, the peak intensities of the rosin acids do not always reflect the exact amount of the rosin sizing agents retained in the paper sample because the rosin acids, including abietic acid, might exist to some extent even in the original pulp material. Therefore, the reliable determination of rosin in the paper samples cannot be made on the basis of these peaks.

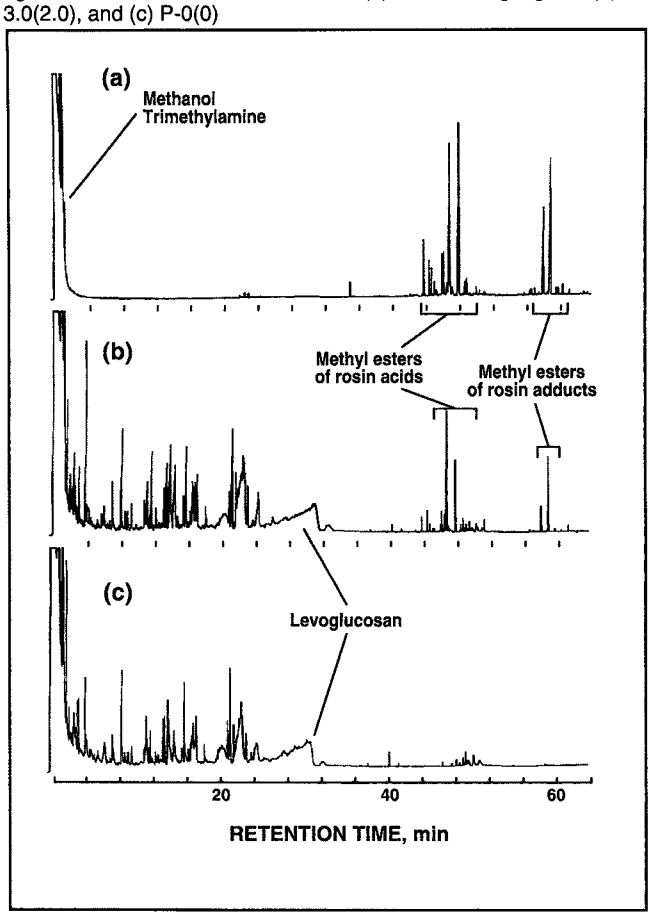
Figure 3 shows the pyrograms of the rosin sizing agent alone (a), the paper sample P-3.0(2.0) (b) and the control paper sample P-0(0) (c) at 450°C in the presence of TMAH. As shown in the pyrogram of the sizing agent alone [Fig. 3(a)], a series of sharp peaks including two large peaks *A* and *B* at 47.1 and 48.6 min, respectively, were observed after the elution of trimethylamine and methanol formed from TMAH and the solvent. The ion of abietic acid methyl ester (m/z = 316) was observed in the mass spectrum by gas chromatography-mass spectrometry (GC-MS) measurement for peak *A* as its molecular ion peak. The molecular weight of the peak *B* component was determined to be 318 by GC-MS, which corresponds to the methyl ester of dihydroabietic acid. These peaks were identified as methyl esters of the rosin acids derived from the pyrolysis with TMAH.

Furthermore, two additional sharp peaks *C* and *D* assigned to the methyl esters of the rosin adducts were observed at about 58.3 and 59.3 min, respectively. In both mass spectra for *C* and *D* peaks, the same molecular ions (m/z = 460) for the methyl esters of the adducts between abietic acid and fumaric acid were observed together

2. Pyrograms of paper samples containing rosin and rosin sizing agents alone without TMAH at 450°C: (a) rosin sizing agent, (b) P-3.0(2.0), and (c) P-0(0)



3. Pyrograms of paper samples containing rosin and rosin sizing agents alone with TMAH at 450°C: (a) rosin sizing agent, (b) P-3.0(2.0), and (c) P-0(0)



with fragment peaks related to the methyl ester of abietic acid at m/z = 316 and that of fumaric acid at m/z = 144. Therefore, the two peaks *C* and *D* might be assigned to the stereoisomers of the adducts. Thus the pyrolysis of the rosin sizing agents in the presence of TMAH made it possible to detect the rosin adduct components as well as those of the rosin acids on the resulting pyrograms as sharp peaks.

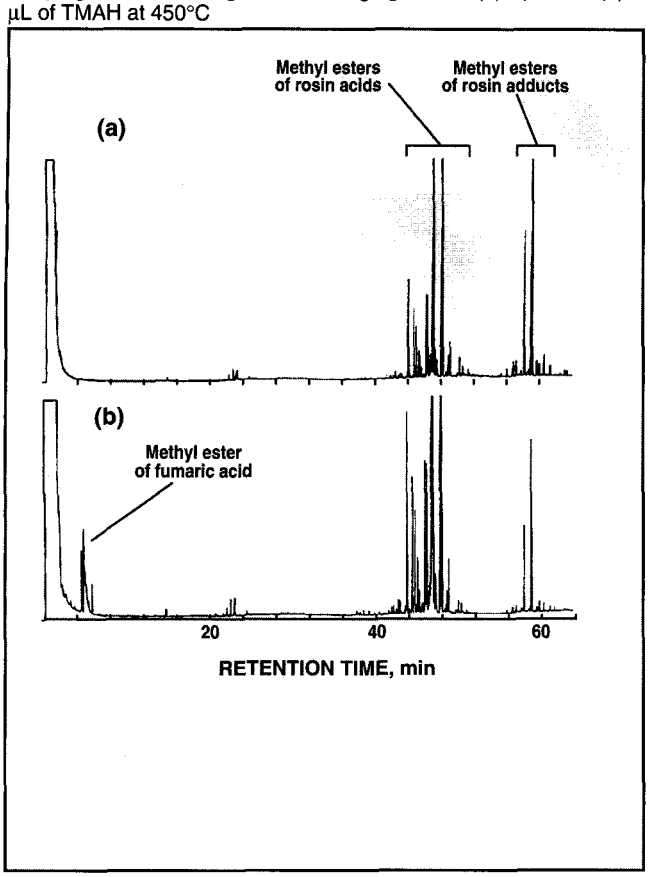
On comparing Fig. 3 with Fig. 2, it is apparent that the addition of TMAH affects not only the pyrolysis of rosin but also that of cellulose in the paper samples. For example, the peaks of levoglucosan in Fig. 3(b) and (c) are smaller than those of Fig. 2(b) and (c), while many additional peaks are observed at earlier retention times in Fig. 3(b) and (c). Moreover, disaccharides such as cellobiosan are eluted at around 50 min as their methyl derivatives in Fig. 3(b) and (c). Here, it should be noted that the peaks of methyl esters of the rosin acids slightly overlap those of disaccharides. Moreover, the pulp material might contain the naturally occurring rosin acids to some extent, as mentioned above. Therefore, the intensities of the two large peaks *C* and *D* of the methyl esters of the rosin adducts were used for the determination of the retained sizing agents in the paper samples.

Effect of pyrolysis temperature

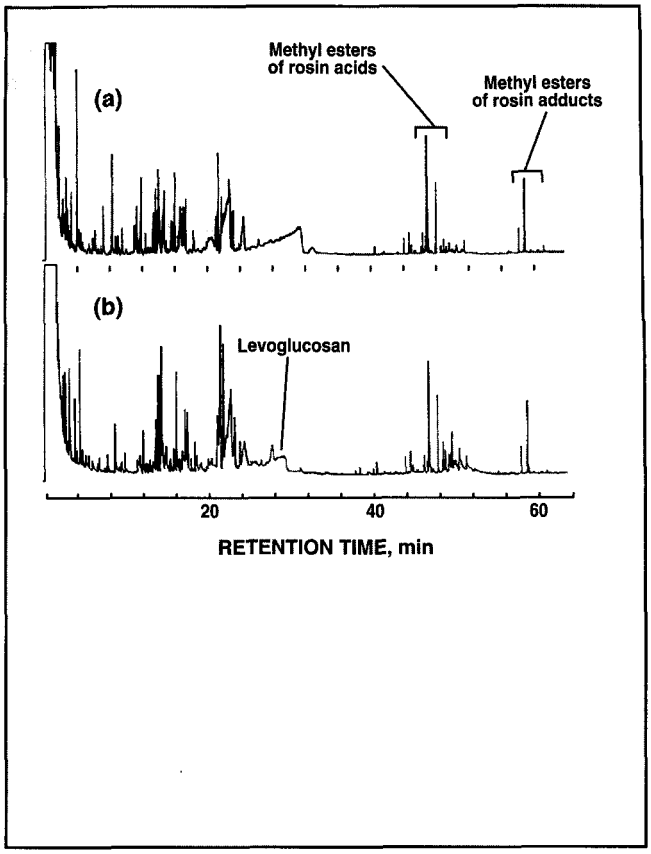
The pyrolysis of rosin samples was carried out at 350°C to 600°C to investigate the effect of the pyrolysis temperature on the intensities of characteristic peaks. Here, a rosin sample weighing about 50 μg was pyrolyzed in the presence of 1 μL of TMAH solution. **Table I** shows the recoveries of the methyl esters of the rosin acids and those of rosin adducts, respectively. The recovery was determined from the peak intensity of α-methylstyrene monomer from an accurately weighed sample of poly-α-methylstyrene (P-α-MSt) through its complete depolymerization at about 500°C *(7, 8)*. First, the absolute sensitivity of flame ionization detector (FID) is calibrated by the peak intensities of α-methylstyrene monomer formed from a known amount of P-α-MSt. The absolute recovery of each component is calculated from the peak intensities of the methyl ester of rosin acid and rosin adduct (weighing about 50 μg) with the absolute sensitivity of FID described above under the same conditions. The equations for the recovery (R_e) are as follows:

$$R_e(\text{rosin acids})(\%) = (8.9 \times 316 \times C_R \times W_{St}) / (19.6 \times 118 \times C_{St} \times W_{Ro} \times 0.59) \times 100 \quad (1)$$

4. Pyrograms of 0.05 mg of rosin sizing agent with (a) 1 μL, and (b) 4 μL of TMAH at 450°C



5. Pyrograms of 0.5 mg of P-3.0(2.0) with (a) 1 μL and (b) 4 μL of TMAH at 450°C



$$R_e(\text{rosin adducts})(\%) = (8.9 \times 460 \times C_{RA} \times W_{St}) / (23.2 \times 118 \times C_{St} \times W_{Ro} \times 0.41) \times 100 \quad (2)$$

Here absolute sensitivity of FID refers to the effective carbon number (ECN) *(9)*. The ECN of α-methylstyrene is 8.9 and those of methyl esters of the rosin acids and the rosin adducts are 19.6 and 23.2, respectively (in this case, abietic acid was expressed as the rosin acid). C_{St}, C_R and C_{RA} represent the peak intensities of α-methylstyrene, the methyl esters of rosin acids and those of rosin adducts, respectively. Here, the peaks of the methyl esters of the rosin acids include all the ones between 44 and 52 min and those of rosin adducts between 55 and 61 min. W_{St} and W_{RO} are the amounts (μg) of poly-α-methylstyrene and the rosin sizing agent, respectively. The ratio of the weight of the rosin acids to the rosin adducts in the sizing agent, 59:41, is used since the molar ratio of the rosin acids to the rosin adducts is determined as 68:32 from the peak intensities on the pyrogram shown in Fig. 3(a). The numbers of 118, 316 and 460 are the molecular weights of α-methylstyrene, the methyl ester of abietic acid, and that of the rosin, respectively.

I. Influence of pyrolysis temperature on the recovery of methyl esters of rosin acids and rosin adducts in the pyrograms of pure rosin sizing agent observed by Py-GC combined with on-line methylation.[a]

Py-temp., °C	*Recovery of methyl esters of rosin acids, %*	*Recovery of methyl esters of rosin adducts, %*
350	58	41
400	71	58
450	55	55
500	55	56
550	67	46
600	91	38

[a] Using all peaks from 44 to 52 min or from 55 to 61 min for rosin acids or rosin adducts, respectively.

As shown in Table I, the recovery of the methyl esters of the rosin adducts becomes highest about 60% at the pyrolysis temperatures between 400°C and 500°C, while it becomes lower at higher or lower temperatures than that in the range between 400°C and 500°C because of insufficient

II. Influence of TMAH on peak intensities of methyl esters of rosin acids and rosin adducts in the pyrograms of pure rosin sizing agent

Amount of TMAH, μL	*Peak intensities[a] of methyl esters of rosin acids, counts/μg*	*Peak intensities[b] of methyl esters of rosin adducts, counts/μg*
1	9890	5180
4	17,500	2440

[a] Using all peaks from 44 to 52 min.
[b] Using all peaks from 55 to 61 min.

III. Influence of TMAH on peak intensities of methyl esters of rosin acids and rosin adducts in the pyrograms of a paper sample prepared by adding 3.0% rosin and 2.0% alum

Amount of TMAH, μL	*Peak intensities[a] of methyl esters of rosin acids, counts/μg*	*Peak intensities[b] of methyl esters of rosin adducts, counts/μg*
1	123	59.3
2	128	63.2
3	127	62.0
4	125	64.9

[a] Using the two large peaks *A* and *B*.
[b] Using the two large peaks *C* and *D*.

methylation and partial decomposition of the rosin adducts, respectively. On the other hand, the recovery of the methyl esters of the rosin acids increases when increasing the pyrolysis temperature above 500°C, which also suggests the decomposition of the rosin adducts into the original rosin acids at elevated pyrolysis temperatures. These results suggest that the rosin adducts are most effectively recovered as their methyl esters between 400°C and 500°C. Therefore, the following determination was carried out at 450°C.

Effect of the amount of TMAH reagent

Stoichiometry tells us that 50 μg of the rosin sizing agent requires 0.03 μL of the TMAH solution and 500 μg of paper sample containing 3% of rosin requires 0.007 μL of the TMAH solution to methylate all the carboxyl groups in rosin components. But in the actual case all the TMAH solution added is not necessarily consumed only for the methylation of the rosin. Moreover, some portion of TMAH should be consumed in the degradation and methylation of cellulose. Therefore, the optimum amounts of TMAH added to the paper sample have to be determined empirically.

Figure 4 shows the pyrograms of 50 μg of rosin sizing agent at 450°C with addition of (a) 1.0 μL and (b) 4.0 μL of TMAH solution, respectively. **Table II** shows the variation of the peak intensities per unit sample weight of the methyl ester of the rosin acids and the rosin adducts. Here, the peaks of the methyl esters of the rosin acids include all the ones between 44 and 52 min and those of the rosin adducts between 55 and 61 min. The relative peak intensities of the rosin adducts decrease while those of the rosin acids increase as the amount of TMAH solution increases. In addition, the methyl ester of fumaric acid was clearly observed in the pyrogram of Fig. 4(b). These results suggest that TMAH is first consumed for the methylation of carboxyl groups of the rosin components while the excess TMAH decomposes the rosin adducts to the corresponding rosin acids and fumaric acid.

The methylation efficiency of the rosin components in paper samples was examined subsequently. **Figure 5** shows the pyrograms of a paper sample, P3.0(2.0) at 450°C with addition of (a) 1.0 μL, and (b) 4.0 μL of TMAH, respectively. **Table III** shows the variation of the peak intensities per unit sample weight with addition of 1.0 to 4.0 μL of TMAH. Here, the large two peaks *A* and *B* were regarded to be those of the methyl esters of the rosin acids, and the peaks *C* and *D* to be those of the rosin adducts. The amounts of TMAH solution do not significantly affect the peak intensities of the rosin acids and the rosin adducts although they affect the peak pattern of cellulose as shown in the two pyrograms in Fig. 5. These results suggest that TMAH is first consumed in the methylation of the rosin components, and further in the reactive decomposition of cellulose. The excess TMAH does not cause the decomposition of the rosin adducts because the decomposition of cellulose consumes the excess TMAH solution. Thus, the added amounts of TMAH between 1.0 μL and 4.0 μL do not cause any significant differences in the determination of the rosin components in the paper samples. Therefore, the determination was carried out with the addition of 1 μL of TMAH solution.

Effect of alum on decomposition of rosin

Metal sulfates including alum act as solid acid catalysts *(10, 11)*. The alum, as the fixing reagent for the rosin, may affect the pyrolysis of the components in the paper samples. Therefore, it is necessary to know how the catalytic effect of alum affects the de-

composition of the rosin components in the paper samples.

Figure 6 shows the relationship between the addition of rosin to the standard paper samples, S-0.48(2) to S-2.83(2), and the peak intensities of the methyl esters of the rosin adducts in the pyrograms (peaks *C* and *D*) per unit weight of the standard samples. These standard samples were prepared by adding 2% of alum and 0.48% to 2.83% of rosin to a filter paper. In this case, all of the alum and the rosin added are contained in the paper sample. Intensities of the characteristic peak *C* and *D* are proportional to the amount of rosin content in the paper sample when the amount of alum is held constant.

Next, the peak intensities of the methyl esters of the rosin adducts (peaks *C* and *D*) were examined for the five standard samples, S-1(0) to S-1(1.87), containing various amounts of alum. These samples contain 1% of rosin and alum ranging from 0 to 1.87%. **Figure 7** shows the relationship between the intensities of peaks *C* and *D* per unit weight of the sample and the amount of alum. The peak intensities of *C* and *D* decrease linearly with increase in the amounts of alum up to 1.4% in spite of the presence of a constant amount of rosin (1%).

These results suggest that alum has a catalytic effect on the decomposition of the rosin adducts into rosin acids and fumaric acid as a function of its amount. However, this catalytic effect becomes constant above 1.4% of alum. Therefore, the determination of rosin in the paper sample should be carried out by considering this catalytic effect of alum. Once the amount of alum contained in the paper samples are determined by AAS (atomic absorption spectrometry), the relationship shown in Fig. 7 gives the correction factor for the determination of the rosin content in the paper samples based on the observed pyrograms taken in the presence of TMAH.

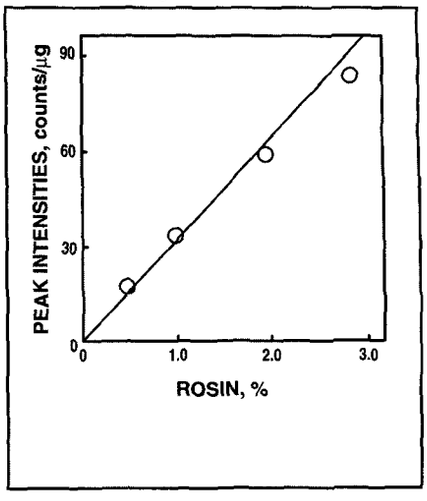
Effect of alum on the amount of rosin retained in paper samples

Finally, the determination of rosin in an actual paper sample was carried out for the P-series samples. **Figure 8** shows the relationship between the amount of alum added to the pulp slurry and the amount of alum retained as estimated by AAS. The broken line refers to the hypothetical relationship for complete retention (100%). The observed results suggest that about 80% of the alum fed to the paper sample is retained up to about 1.3% dosage under the given conditions for the paper preparation. However, above 1.3% dosage the amount retained levels off at about 0.95% irrespective of the dosage of alum.

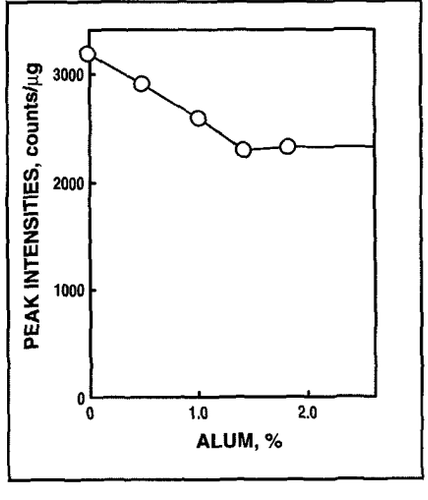
Figure 9 shows the relationship between the amount of rosin added to the paper samples and the amount of rosin retained, as estimated by Py-GC considering the amount of alum retained in paper and the relationships shown in Figs. 6–8.

The reproducibility of this method was about 1% of relative standard derivation by three measurements for the P-3.0(2.0) paper sample. All the observed data fall under the broken line, which represents complete retention (100%) because a part of the rosin added into the pulp slurry is lost with the white water. The amount of alum added into the pulp slurry significantly affects the amounts of rosin retained in the paper samples. Only about 20% of the rosin added is retained in the paper samples prepared with 0.75% of alum, while about 60% or 80% of the rosin is retained when 1.0% or 1.25% of alum is added to the pulp slurry, respectively. However, the amounts of rosin retained in the paper sample become almost constant (80%) above 1.3% of alum added chiefly because the amount of alum retained in the paper sample starts to level off above 1.3% of alum added to the pulp slurry, as shown in Fig. 8. Under the given conditions for the paper preparation, 1.3% of alum in the pulp slurry might be sufficient to attain maximum retention of the added rosin components to the paper samples.

6. Relationship between addition of rosin in standard samples containing 2% alum and peak intensities of methyl ester of rosin adducts in the pyrograms of standard samples



7. Relationship between addition of alum in standard samples containing 1% rosin and peak intensities of methyl ester of rosin adducts in the pyrograms of standard samples



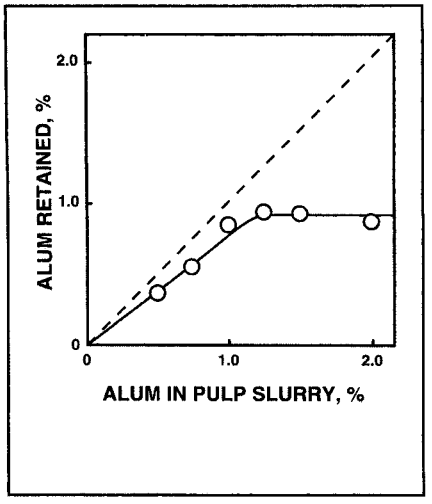
The results demonstrate that the high resolution of Py-GC combined with on-line methylation is a powerful method for the rapid, convenient and precise determination of the rosin components in paper samples.

Experimental procedures

Materials

Two series of paper samples were prepared. Thirty-two paper samples, named the P-group, were prepared with 0–3.0% of rosin and 0–2.0% of

8. Relationship between addition of alum into the pulp slurry and alum retained in paper samples, estimated by atomic absorption spectrometry.



alum added to the pulp slurry under conditions similar to those for commercial paper production. Here, P-3.0(2.0), for example, represents a paper sample prepared from the pulp slurry by adding 3.0% of rosin and 2.0% of alum. P-0(0) represents a control paper prepared without adding any rosin or alum. The actual amounts of rosin and alum retained in the paper samples should be lower than those added to the pulp slurry because they are partly lost in the white water during paper production.

On the other hand, nine standard paper samples, named the S-group, were used for calibration. In preparing these samples, known amounts of the rosin and alum emulsions were added directly to a filter paper with a microsyringe in order to equalize the sample matrix, and then the paper samples were dried in vacuo. Here, S-1(0) to S-1(1.87) consist of four standard samples containing 1% rosin and 0–1.87% alum, and S-0.48(2) to S-2.83(2) consist of five standard samples containing 2% alum and 0.48–2.83% rosin. The actual amounts of rosin and alum contained in these paper samples are equal to those added because all of the reagents added remain in the paper samples.

The rosin sizing agent used in both groups was an emulsion type (AL-100) produced by Japan PMC Corp., which contains rosin acids and their adducts. The molar ratio of the rosin acids and their adducts was determined to be 68:32 from the Py-GC data, assuming that the recovery efficiencies for all the related components on the pyrogram are the same under the given pyrolysis conditions of 450°C. All the paper samples were cryo-milled into a fine powder by a freezer mill (SPEX 6700) prior to Py-GC measurements in order to homogenize the paper samples.

Conditions for Py-GC

A vertical microfurnace-type pyrolyzer (Yanaco GP1028) was directly attached to a gas chromatograph (Shimadzu GC-7AG) equipped with a flame ionization detector. About 500 μg of the milled paper sample or 50 μg of the rosin sizing agent was placed in a platinum sample cup and then pyrolyzed under the flow of helium carrier gas. A fused silica capillary column (25 m x 0.2 mm ID) coated with dimethylsiloxane (0.33 μm thick), immobilized by chemical crosslinking, was used. The 50 mL/min carrier gas flow rate at the pyrolyzer was reduced to 1.0 mL/min at the capillary column by means of a splitter. The column temperature was initially set at 50°C and then programmed up to 300°C at a rate of 5°C/min. Identification of the peaks on the pyrograms was carried out mainly using a GC-MS system (Shimadzu QP-1000) with an electron impact ionization source to which the pyrolyzer was directly attached.

Methylation with TMAH

Tetramethylammonium hydroxide (TMAH; 25 wt.% solution in methanol; Aldrich) was used as the methylating reagent. A fine powder sample weighing about 500 μg was placed in a platinum sample cup together with 1–4 μL of the TMAH solution and the cup was placed at the top of the pyrolyzer at ambient temperature. Then, after the initial gas chromatographic conditions were attained for the carrier gas pressure and the column oven temperature, the sample cup was dropped into the heated center, where the sample was reactively pyrolyzed, in the presence of TMAH, mainly into the related methyl derivatives of the sample components, which is advantageous for GC measurements.

Determination of aluminum by AAS

The paper samples containing the rosin and alum were cut into *ca.* 2-mm squares. Five mL of concentrated HCl were added to 1 g of the cut paper samples.

The sample suspensions were boiled until their tissues were thoroughly broken followed by filtration after cooling. Distilled water was added to the filtrate to a total volume of 100 mL. Then AAS measurement was carried out on an aliquot of the solution by means of a SEIKO SAS760. The hollow cathode lamp current was 10.0 mA and N_2O-C_2H_2 flame was used. The wavelength for the analysis was set at 309.2 nm for aluminum. ■

Literature cited

1. TAPPI Test Method T 408 om-82, "Rosin in paper and paperboard."
2. Sumikawa, Y., Kishika, Y., and Toda, H., *Japan Tappi J.* 22: 1400(1968).
3. Yano, T., Ohtani, H., Tsuge, S., *et al.*, *Tappi J.* 74: 197(1991).
4. Yano, T., Ohtani, H., Tsuge, S., *et al.*, *Analyst* 117: 849(1992).
5. Challinor, J. M., *J. Anal. Appl. Pyrolysis* 16: 323(1989).
6. Ohtani, H., Fujii, R., and Tsuge, S., *J. High Res. Chromatogr.* 14: 388(1991).
7. Okumoto, T., and Takeuchi, T., *Bull. Chem. Soc. Jpn.* 46: 1717(1973).
8. Nakagawa, H., Tsuge, S., Mohanraj, S., *et al.*, *Macromolecules* 21: 930(1988).
9. Jorgensen, A. W., Picel, K. C., and Stamoudis, V. C., *Anal. Chem.* 62: 683(1990).
10. Tanabe, K., and Aramata, A., *J. Research Inst. Catalysis* 8: 43(1960).
11. Takeshita, K., Ohnishi, R., and Tanabe, K., *Catal. Rev.* 8: 29(1973).

Received for review Dec. 15, 1992.

Accepted April 14, 1993.