Determination of Microstickies in Recycled Whitewater by Headspace Gas Chromatography

X.-S. Chai¹,²,*, J.C. Samp¹, Q.F. Yang², H.N., Song², and J.Y. Zhu³

¹Institute of Paper Science and Technology, Georgia Institute of Technology
Atlanta, GA30332, USA
²School of Light Industrial and Food Engineering, Guangxi University
Nanning, Guangxi 530004, China
³USDA Forest Service, Forest Products Laboratory, Madison, WI, 53726, USA

ABSTRACT

This study proposed a novel headspace gas chromatographic (HS-GC) method for determination of adhesive contaminants (microstickies) in recycled whitewater, a fiber-containing process stream in the paper mill. The method is based on the adsorption behavior of toluene (as a tracer) on the hydrophobic surface of microstickies, which affects the apparent vapor-liquid equilibration partitioning of toluene. It was found that the equilibrium concentration of toluene in the vapor phase is inversely proportional to the apparent effective surface area of microstickies that remain in the corresponding solution. Thus, the amount of microsticky materials in the recycled whitewater can be quantified by HS-GC via indirect measurement of the toluene content in the vapor phase of the sample without any pretreatment. The presented method is simple, rapid, and automated.

Key words: Headspace; Gas chromatography; Toluene; Vapor-liquid equilibrium (VLE); Papermaking; Whitewater; Adsorption; Microstickies; Recycling; Recovered paper; Fiber.

INTRODUCTION

With the increased use of recycled paper, the removal and control of adhesive contaminants (stickies) becomes a more important issue as these adhesive materials, synthetic polymers, can seriously affect not only the paper quality but also the paper machine runability during papermaking process [1]. Microstickies, defined as adhesive material able to pass through a laboratory-screening device with 0.15 mm slots, are unpredictable contaminants. They are relatively benign as long as they stay in colloidal form, but they can agglomerate to form macrostickies at mill process conditions. The accumulation of microstickies in the whitewater may cause the stickies to eventually precipitate from the suspension and cause a deposition problem on the machine, which may lead to paper web breaks and impart holes or spots to the paper sheet [2-3]. The threshold for agglomeration is mill-specific and depends upon the paper produced, the process, and the chemistries employed.

The paper industry has long sought an analytical method that can measure the microstickies’ levels in the process whitewater so that preventive action could be taken if their levels were to rise. The analytical methods proposed to date for macrostickies measurement have usually involved deposition on a surface or a wire, but these tests are too time-consuming to be useful for the process applications. Other methods use solvent extraction, which will also detect other extraneous material and will not always dissolve the critical synthetic polymers. All these methods have been summarized and reviewed in the literature [4].

The Institute of Paper Science and Technology (IPST) method, the only technique for microsticky measurement, has been recently proposed [5]. It was based on measuring the total organic carbon (TOC) content of a sample filtered through a 3,000–10,000 Dalton cut-off membrane, in which it assumes that the
high molecular-weight (MW) compounds within this range are the microstickies. A typical preparation of the sample fraction for TOC measurement in IPST method [5] is illustrated in Figure 1.

Obviously, the MW cut-off margins in this approach are empirical, and the materials other than stickies (e.g., starch) that all have high MW in process stream will also be collected in this way and contribute to TOC counts as the sticky materials in this method. Therefore, the results from the IPST method do not accurately represent the amount of microstickies in process stream and will provide a poor correlation to the paper-machine runability in many cases, especially for the process stream with a significant amount of starch.

Headspace gas chromatography (HS-GC) is a powerful technique for analysis of volatile species in the samples having a complex matrix. The headspace technique also provides the opportunities for conducting sample pretreatment and conditioning during the testing, e.g., to convert non-volatile species to a volatile one that can be analyzed by gas chromatography (GC) [6-8] and sample heating and shaking for mixing. Recently, we have developed a HS-GC technique for measuring solubility of inorganic salts in aqueous solution. This technique uses methanol as a tracer [9], based on a salting effect on the methanol vapor-liquid equilibrium (VLE) behavior observed previously [10]. It is known that the problem caused by the microstickies is due to their hydrophobic surface property of tacky particles in aqueous system. We believe that the surface hydrophobic property of stickies can affect the VLE behavior of toluene; thus, a correlation between the amount of stickies in the liquid sample and content of toluene in the vapor phase can be developed.

The objective of this study was to develop a novel HS-GC method that can determine microstickies in the recycled whitewater. The effects of other major coexisting materials in the process stream were also evaluated.

EXPERIMENTAL

Materials

Four commercial brands (Carbtec, Avery acrylic, HYCAR 26288, and PAS) of sticky polymers commonly used in paper-related products were received from mills. The polymers are mainly polyacrylates such as polymethylmethacrylate (PMMA) and their copolymers, and hot melts, e.g., polyvinyl acetate (PVA). However, the exact compositions in these samples are confidential. The average particle sizes of these polymers are around 0.7 µm.

Apparatus and Operation

All measurements were carried out using an HP-7694 Automatic Headspace Sampler and Model HP-6890 capillary gas chromatograph equipped with a flame ionization detector (Hewlett-Packard, now Agilent Technologies, Palo Alto, CA, USA.). Gas chromatography conditions were as follows: capillary column (HP-5, Agilent Technologies) with an ID = 0.32 mm, film thickness of 0.25 µm, and a length of 30 m at a constant temperature (30 °C), and helium carrier gas flow rate of 3.1 mL/min. The GC running time is 4 min.

Headspace sampler operating conditions were as follows: oven temperature of 32 °C; 10 min strong shaking of the sample; vial pressurized by helium and pressurization time of 0.2 min; sample-loop fill time of 0.2 min; loop equilibration time of 0.05 min; vial equilibration time of 0.5 min; and loop fill time of 1.0 min.

A custom-built compressed air cooling conduit was introduced into the sampler system, in which the cooling conduit is inserted directly into the oven (from the ceiling). By continuously blowing the compressed air, it can bring the temperature down to 32°C.

The sample preparation and measurement procedures were as follows: 5 mL sample solution was added into a 20 mL headspace testing vial (Agilent Technologies, Santa Clara, CA) and sealed by septum. Then, a 10 µL of standard toluene-methanol solution (85 ppm toluene, on volume/volume basis) was injected into the vial that contains 5 mL sample solution, thus the toluene concentration in the tested sample solution is 170 ppb. The vial was placed in the headspace sampler tray for automatic HS-GC measurements.
Particle size distributions were measured with a Malvern Zetasizer 3000 (Malvern Instruments Ltd, Malvern, UK) based on a quasi-elastic light-scattering technique. The sample solution is placed in a 250 mL beaker for particle-size measurement, the sample dilution may be required if the amount of microstickies is high.

RESULTS AND DISCUSSIONS

Principle

The VLE partitioning coefficient for a volatile organic solute in an aqueous solution is defined as

$$K = \frac{C_g}{C_l}$$  \hspace{1cm} (1)

All symbols are defined in Table 1.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K$</td>
<td>vapor-liquid equilibrium partitioning coefficient</td>
</tr>
<tr>
<td>$C_g$</td>
<td>concentration of the solute in vapor phase</td>
</tr>
<tr>
<td>$C_l$</td>
<td>concentration of the solute in liquid phase</td>
</tr>
<tr>
<td>$C_l^0$</td>
<td>initial concentration of solute in the solution</td>
</tr>
<tr>
<td>$C_s$</td>
<td>concentration of the solute adsorbed by the adhesive substance in the solution</td>
</tr>
<tr>
<td>$k_1$</td>
<td>adsorptivity of the solute on the polymer substances</td>
</tr>
<tr>
<td>$A$</td>
<td>GC peak area</td>
</tr>
<tr>
<td>$k_2$</td>
<td>GC response factor</td>
</tr>
<tr>
<td>$S$</td>
<td>apparent effective surface area</td>
</tr>
<tr>
<td>$d$</td>
<td>average diameter of microstickeys</td>
</tr>
<tr>
<td>$k_v$</td>
<td>ratio factor of volume-to-mass of sticky material</td>
</tr>
<tr>
<td>$k$</td>
<td>hydrophobic characterization coefficient of the polymers</td>
</tr>
<tr>
<td>$a$</td>
<td>intercept</td>
</tr>
<tr>
<td>$b$</td>
<td>slope</td>
</tr>
</tbody>
</table>

The VLE partitioning coefficient is constant; that is, it agrees with Henry’s Law if the concentration of the solute is very low, in which the molecular interactions between solutes themselves are negligible. When the aqueous solution system contains solid phase (particle substances) that have the hydrophobic surface, it can adsorb hydrophobic solutes, such as toluene. As a result, the solutes are partitioned between both vapor-liquid and liquid-solid phases. With the presence of hydrophobic solid phase, the solute concentration in liquid phase can be written as

$$C_l = C_l^0 - C_s$$  \hspace{1cm} (2)

According to Eqs. (1) and (2), the relationship between the solute concentrations in vapor phase and in solid phase at the equilibrium can be expressed as

$$C_g = K(C_l^0 - C_s)$$  \hspace{1cm} (3)

For a given amount of solute, its concentration absorbed in solid phase, $C_s$, is proportional to the apparent effective surface area

$$C_s = k_1 S$$  \hspace{1cm} (4)

According to Eqs. (3) and (4), we can develop a relationship between $C_g$ and $S$. 
\[ C_g = KC_i^0 - Kk_iS \]  
(5)

Since GC peak area is proportional to the solute concentration in the vapor phase,

\[ C_g = k_2A \]  
(6)

we can build up the relationship between the GC signal and apparent effective surface area of polymer substances

\[ A = \frac{1}{k_2} \left( KC_i^0 - Kk_iS \right) = a - K_2S \]  
(7)

where the both intercept (a) and slope (K_2) are constants, which can be obtained through calibration.

Since the relationship of the apparent effective surface and the amount of sticky particles can be written as

\[ S = k k_2 \frac{X_s}{d} \]  
(8)

according to Eqs. (7) and (8), we can obtain

\[ A = a - K_2 kk_2 \frac{X_s}{d} = a - bX_s \]  
(9)

Therefore, if the particle size information is available, the amount of polymer substances can be quantified based on headspace GC method using a volatile organic compound species as the tracer.

**Microsticky particle size distribution in the recycled whitewater.**

In a previous work [11], the particle-size distribution of microstickies in the simulated recycled whitewater was investigated. Similar to the industrial process, the recycled paper needs to be dispersed in the aqueous medium to release the fibers, and it can be achieved in a high-speed homogenizer. However, this process also generates microstickies from the macrostickies. In this work, the suspension of microstickies was generated based on the dried adhesive polymer through a high-speed homogenizer. It was found that the particle size generated by this way is below 4 \( \mu \)m, in which the most portions of particles are located around the size of 0.7 \( \mu \)m.

**Tracer and its concentration introduced in the testing solution**

In this work, toluene was chosen as a tracer because it has not only a reasonable hydrophobicity and solubility in water, but also a shorter retention time (3.1 min) in the GC measurement.

As reported [11], the amounts of microstickies in paper mill recycling stream after passing through 0.15 mm slots are varied from 100 to 1,000 ppm. Therefore, the proper tracer concentration introduced into the tested solution is important to achieve relatively large decreases in the vapor toluene concentration. Although higher toluene concentration should lead to higher GC signal, it is more difficult to see small changes in the amount of toluene adsorbed if the total toluene concentration is very high. According to Eq. (2), if the initial concentration (\( C_i^0 \)) of tracer in the testing solution is too high, the portion of toluene adsorbed by sticky particle will be relatively low. Thus, it leads to a lower detecting sensitivity on the microstickies measurement as shown in Fig. 2. On the other hand, a high tracer concentration may also create a multiple layer adsorption on the particle surface, which may result in a non-linear relationship between the vapor content of the tracer in
the headspace and amount of the microstickies in the sample. Our experiment showed that a concentration of about 170 ppb (in the testing solutions) is proper in the testing. Since 170 ppb is much lower than the solubility of toluene in water at a testing temperature [12], it can be quickly dissolved in the aqueous solution. The standard toluene solution (85 ppm) can be easily prepared by adding small amount of pure toluene (by microsyringe) into a given volume of pure methanol. In the microstickies testing, a very small volume (10 µl) of the standard toluene-methanol solution is added into the sample solution, in which the concentration of methanol in the testing solution is about 2000 ppm (v/v). Since the nature of methanol is very close to that of water, a small amount of methanol in the testing solution does not affect the adsorption behavior of toluene on the sticky substances.

Temperature effect of toluene adsorption equilibrium on microstickies

Due to a lower glass transition point for most sticky polymers, a higher temperature (above 50°C) can easily cause the microstickies agglomeration during the sample VLE, in which the uncertainty of particle size distribution will affect the measurement. As shown in Fig. 2, both lower temperature and larger amount of microstickies cause a more significant decreasing in GC signal, which makes the microstickies measurement more sensitive. However, there is no cooling system available in the current headspace sampler (HP-7694), which causes the difficulty to perform an equilibration below ~ 40°C. Therefore, a custom-designed compressed air-blow cooling system as described above was implemented into the headspace sampler, which can bring the temperature down to 32°C.

Equilibration time for toluene adsorption.

For quantification analysis, it is important to achieve a complete equilibration in the present three-phase “wet” system. It was reported that the equilibration time of volatile organic compounds adsorption/desorption in the “dried” system, e.g., the dried polymers [13] or the packaging materials [14–16], are very long, usually takes hours. However, the equilibrations in the “wet” system of adding a solvent as a displacer to the dried polymer [13] or in a polymer latex [17] are much faster. In this work, we found that the toluene adsorption equilibration on the microstickies in the aqueous system is very fast, which can be achieved within 5 min as shown in Fig. 3. In the present work, the equilibration time in all testing is 10 min.

Headspace GC testing on the commercial microstickies.

Fig. 4 shows the results on four sets of microstickey sample solutions with a content level from 0–1,000 ppm. Although the compositions in these sticky samples are different, they basically fall onto the same line, which agrees with Eq. (9); the GC signals linearly decrease with the amount of microstickies in the solutions. Thus, the present headspace GC technique can be used for the quantification of the microstickies in the recycled whitewater if there is no significant interference from the coexisting species. Obviously, the present method is much simpler and faster because it avoids the complicated and time-consuming procedures such as filtration and ultra-filtration as reported in the previous method [5]. The results also showed that the hydrophobic properties of these sticky polymers commonly used in paper industry are quite similar, which makes the calibration procedure easier.

The agglomeration of microstickies to form macrostickies during the papermaking process is the major cause that affects paper machine runability. Such an agglomeration is related to the nature of the sticky materials, mainly their hydrophobicity. Therefore, we believe that the apparent effective surface (S) as we defined in Eq. (8), instead of the amount of the microstickies, is a more proper parameter to evaluate their impact to the process. Presently, however, the paper industry uses the amount of the sticky substances to correlate to their process performance.

Effects of the other coexisting materials

There are many sorts of the suspended substances such as cellulose fines, fillers (e.g., clay) and retention aid agent (typically the cationic starch) remaining in the clarified recycle whitewater. Therefore, the effect of these coexisted species on the toluene measurement should also be investigated. As shown in Table 2, all these
major coexisting suspended species have no significant effect on the toluene VLE behavior; we believe that is probably due to the hydrophilic nature of these substances. In order to confirm this, a water-soluble polymer, polyvinyl alcohol (PVOH) was used in the testing. The results showed that the addition of PVOH does not affect the toluene VLE behavior. Our testing also showed that there is no significant salting effect on toluene VLE behavior observed at an ionic strength range of 0–0.1 mol/L, as met in the recycled whitewater. Since the coexisting species in the recycled whitewater are diluted, it could be also one of the reasons that their effects on toluene VLE are not significant.

Table 2. Effect of the major coexisting species on toluene VLE behaviors.

<table>
<thead>
<tr>
<th>Content (ppm)</th>
<th>GC signal</th>
<th>Content (ppm)</th>
<th>GC signal</th>
<th>Content (ppm)</th>
<th>GC signal</th>
<th>Content (mol/L)</th>
<th>GC signal</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>99.9</td>
<td>0</td>
<td>100.4</td>
<td>0</td>
<td>100.8</td>
<td>0</td>
<td>100.8</td>
</tr>
<tr>
<td>200</td>
<td>100.1</td>
<td>40</td>
<td>99.0</td>
<td>200</td>
<td>100.4</td>
<td>0.02</td>
<td>100.4</td>
</tr>
<tr>
<td>400</td>
<td>99.9</td>
<td>80</td>
<td>100.9</td>
<td>400</td>
<td>99.5</td>
<td>0.04</td>
<td>99.5</td>
</tr>
<tr>
<td>600</td>
<td>98.9</td>
<td>120</td>
<td>100.7</td>
<td>600</td>
<td>101.0</td>
<td>0.06</td>
<td>101</td>
</tr>
<tr>
<td>800</td>
<td>99.7</td>
<td>200</td>
<td>101.4</td>
<td>800</td>
<td>100.6</td>
<td>0.08</td>
<td>100.6</td>
</tr>
<tr>
<td>1,000</td>
<td>98.3</td>
<td>300</td>
<td>99.6</td>
<td>1,000</td>
<td>101.4</td>
<td>0.1</td>
<td>101.4</td>
</tr>
</tbody>
</table>

Method precision and method validation

The repeatability of the method was conducted by both using a 10 µL toluene–methanol solution in five vials containing 5 mL solution with the microstickies content of 600 ppm. The result shows that the average relative standard deviation (RSD) from 5 measurements is less than 7%.

As mentioned above, the only reported technique (IPST method [5]) for microstickies task lacks the fundamental basis to measure microstickies in recycle whitewater. Therefore, it is not acceptable as a reference method. In this work, the present method was evaluated by a set of synthetic whitewater (containing a certain amount of fines, clay, and starch) with the standard microstickies addition. The samples were then measured by HS-GC. The normalized GC signals (i.e., set the signal for blank testing as one) were used to calculate the content of the microstickies by the following equation

\[
A = 0.996(\pm 0.005) - 1.686 \times 10^{-4} (\pm 8.4 \times 10^{-6}) X_s \tag{10}
\]

which is based on the data presented in Fig. 4.

Table 3 illustrates that the data from HS-GC measurement matched those by the standard addition, indicating that the present method is justifiable. The measurement error (~12%) is acceptable in the paper mill application.

Table 3. Differences between the known amounts of microstickies added and measured by HSGC in the synthetic samples.

| Sample | Microstickies (ppm) | Relative difference (%) |
|-----------------|-----------------|-----------------|-----------------|
| Standard added | HSGC measured | |
| 1 | 200 | 225 | 12.5 |
| 2 | 400 | 360 | – 10.0 |
| 3 | 600 | 620 | 3.3 |
| 4 | 800 | 787 | – 1.6 |
| 5 | 1,000 | 881 | – 11.9 |

The adsorption systems may have only a very narrow linear concentration range [13]. In our previous work, we observed that a methyl methacrylate VLE relationship in an aqueous solution containing more than 1,000–
1,500 ppm of polymethylmethacrylate particles is non-linear [18]. Therefore, we suggest that sample dilution is required in using the present method when microstickies content is greater than 1,000 ppm.

Remarks

As mentioned above, the apparent effective surface area (S) of microstickies, rather than the amount of microstickies, could be a more reasonable parameter that correlates to the microstickies problem in the paper formation process. Clearly, the apparent effective surface area of microstickies is also a function of the process conditions, e.g., temperature. Therefore, further development of the present method is really dependent on the industrial needs and understanding the issue of microstickies to evaluate the microstickies’ effect on the process operations [19]. The present method can definitely provide an effective tool for this purpose for both microstickies quantification and characterization studies.

CONCLUSIONS

We have demonstrated a headspace GC technique for the determination of microstickies in white water. The present method can easily determine the amount of microstickies by measuring the vapor tracer content based on headspace GC, which avoids the complicated and time-consuming procedures such as filtration, ultra-filtration, and solvent extraction methods. The study shows that the other compositions in the recycled white water such as fibers, fines, filler, inorganic ions, and retention aid agent have no significant interference with the microstickies determination in the present method.

ACKNOWLEDGEMENT

This work was partly supported by the Guangxi University Key Program for Science and Technology Research and Chinese National Science Foundation, Contract No. 20576022.

REFERENCES

Figure 1: Sample preparation in the total organic carbon (TOC) based microsticky measurement method [5]

Figure 2: Temperature effect of toluene adsorption on sticky particles.
Figure 3: Equilibration time for the toluene-microstickies aqueous system

Figure 4: Relationship between gas chromatography (GC) signals (normalized) of vapor toluene and the amount of microstickies in the solution.