

Using multi-method analysis to identify challenging paper machine deposits and defects

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ABSTRACT: Based on its speed and versatility, Fourier transform infrared (FTIR) spectroscopy is the industry's common starting point for analysis of a paper machine deposit or defect sample. However, certain contaminants and papermaking process additives cannot be precisely identified solely by infrared spectral interpretation. This lack of specificity could lead to a misinterpretation of the composition of the deposit or defect.

A multi-method analysis uses data from two or more analytical techniques, including FTIR spectroscopy, microbiological staining/phase contrast microscopy, pyrolysis-gas chromatography/mass spectrometry (Pyro-GC/MS), and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX), to produce a more specific assessment of a sample's composition. This paper discusses the use of a multi-method analysis in deposit and defect analysis and presents several case studies that demonstrate how this comprehensive approach can often produce an interpretation result of greater conviction and value to the papermaker.

Application: This paper discusses how the use of multiple analytical techniques can work in concert to help troubleshoot challenging paper machine deposits and defects.

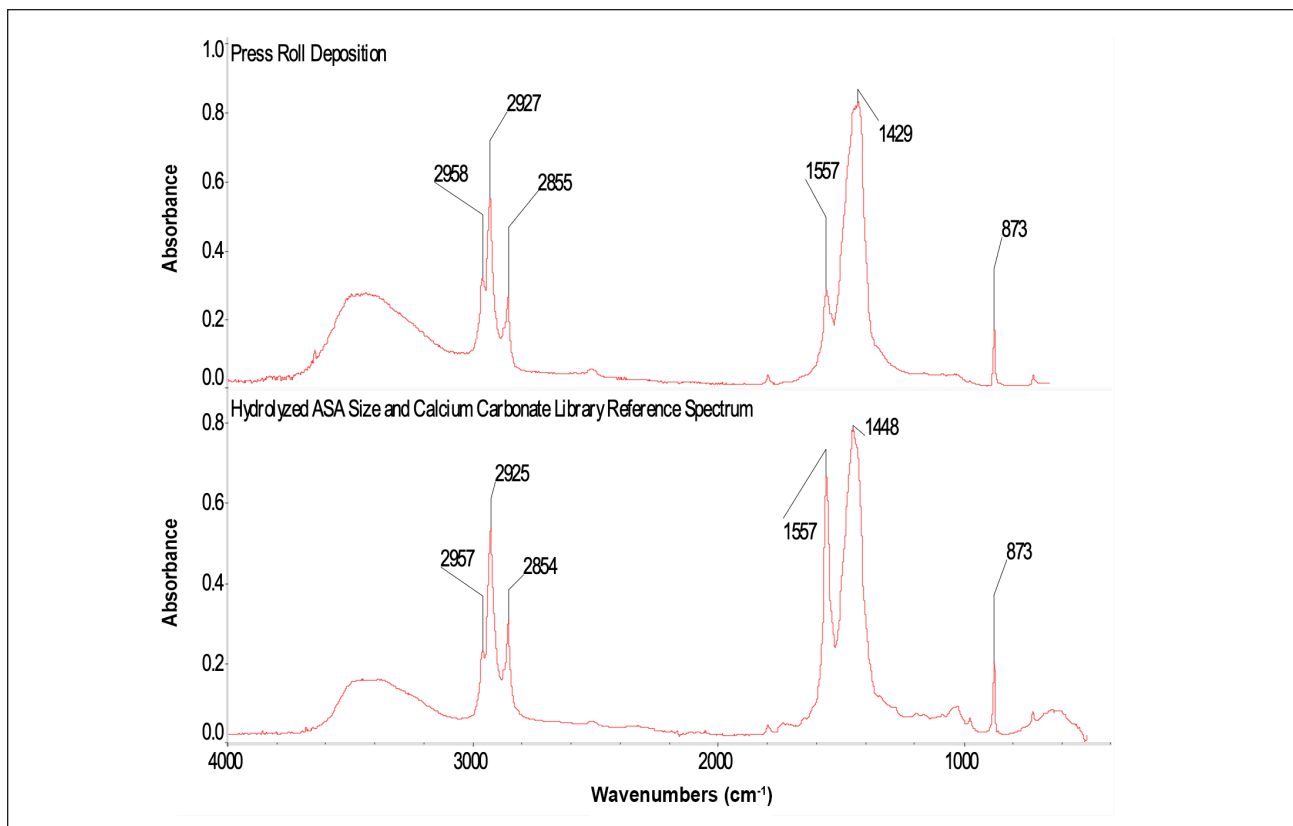
A Fourier transform infrared (FTIR) spectroscopic analysis is almost universally considered to be the starting point in an analytical troubleshooting effort to determine the composition of a machine deposit or defect sample. The FTIR spectroscopic analysis holds this preeminent position thanks to its speed of analysis (approximately 20 min or less, including sample preparation); its flexibility regarding sample type (deposits or defects); and its focus on functional group identification, which can be used to confirm or rule out the presence of various organic and inorganic process additives or contaminants [1,2]. In many circumstances, the initial IR analysis of a sample and the subsequent interpretation of the resulting spectrum are very fast and straightforward, effectively validating the use of an FTIR spectroscopic analysis as a starting point for investigations [3]. For example, a tacky deposition on a paper machine wire may be readily identified by a library search as strongly matching a "lab-curated" library reference spectrum of a bale label adhesive that was inadvertently repulped. In another example, a quick IR analysis of a fresh tote of a process additive can be compared against a standard to rule out the presence of contamination. Yet, although FTIR analysis has clearly demonstrated strengths, in other circumstances determining the connection between the interpretation of the IR spectrum and the ultimate source of a deposit or defect can be challenging. Consequently, analysts can sometimes reach differing conclusions about the composition or source of the deposit. When runnability issues are causing costly downtime and unsellable paper, the lack of a clear understanding of

the cause of the problem and the best solution can be not only distressing but also expensive.

INFRARED SPECTRAL INTERPRETATION: MANUAL AND AUTOMATED LIBRARY SEARCHING

Most IR spectral data are interpreted through a combination of a manual (human) process that is based on an individual's accumulated training and experience and a computerized, automated library search. This library search is based on a collection, potentially well into the tens of thousands, of commercial library reference spectra and "lab-curated" spectra of known process additives and previously analyzed deposit samples. Even the automated search ultimately requires a human component because it is the analyst who chooses to accept or reject the automated search results. And, although individuals with decades of experience may rarely use the automated library search, analysts with less experience may initially rely more heavily on automated library searches as they gain experience.

Regardless of an analyst's experience level with IR spectral interpretation, linking the interpretation of the data to the ultimate source can be challenging for several reasons. One reason is the complexity of the IR spectrum. Deposits and defects frequently are comprised of mixtures of various materials, including fiber, inorganic fillers, various process additives, and contaminants. Consequently, the resulting infrared spectrum will exhibit individual peaks that could readily be associated with several different materials. For example, both wood pitch steryl/triterpenyl esters and vari-



1. Infrared spectra of press roll deposition and a “lab-curated” spectrum confirmed to consist of hydrolyzed alkenyl succinic anhydride (ASA) size in its diacid calcium (di-calcium) soap form and calcium carbonate.

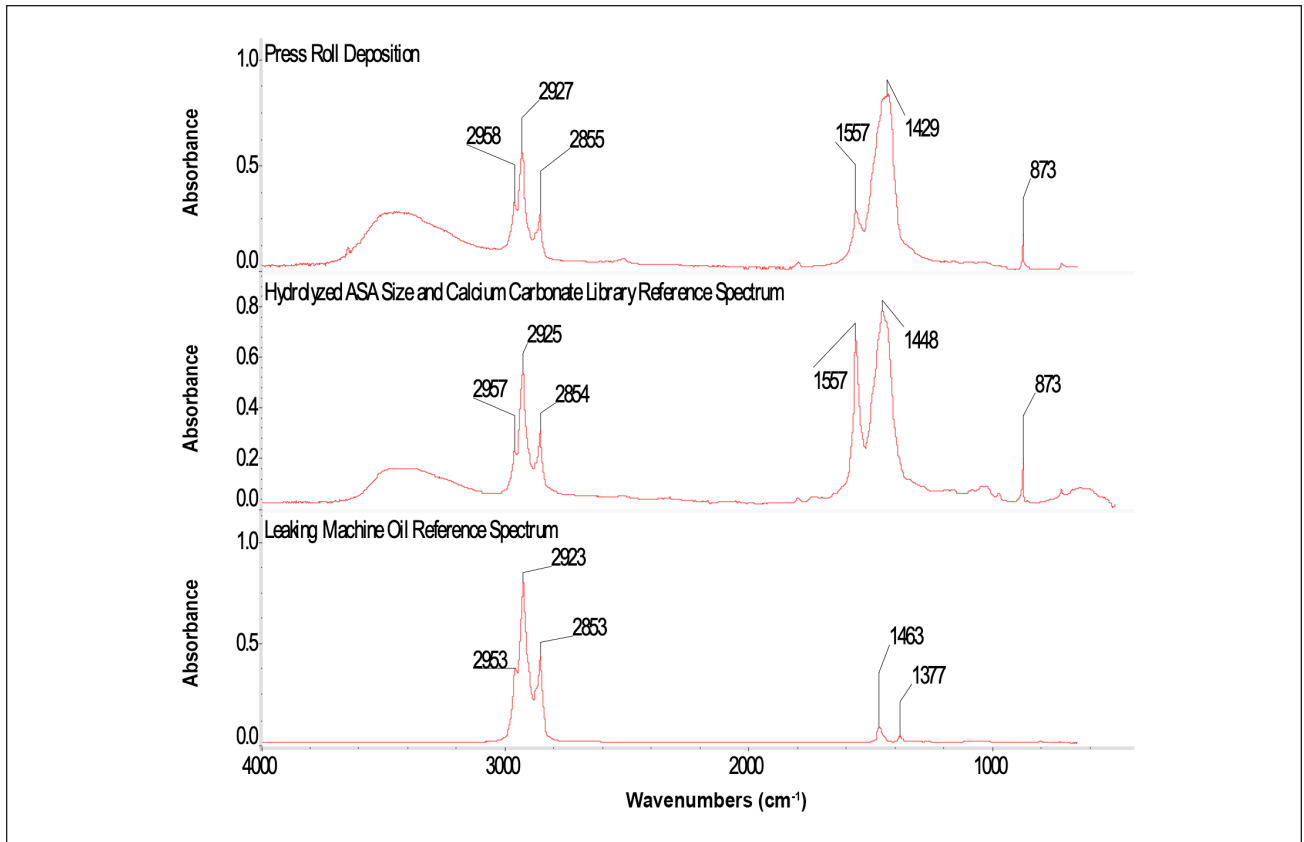
ous acrylate-based adhesives from recycled fiber can produce an IR spectral peak between 1737–1732 cm^{-1} , reflective of an ester-based functional group. A scenario where two different functional groups — for example, a wood pitch carboxylic acid functional group and a hydrolyzed alkyl ketene dimer (AKD) size ketone-based functional group — may both be observed at or around 1715 cm^{-1} to 1705 cm^{-1} . A second reason reflects the tendencies of the automated library search algorithm to favor certain regions of the infrared spectrum, particularly in situations with prominent peaks between 3000 and 2800 cm^{-1} for aliphatic hydrocarbon functional groups. A third reason revolves around the difficulty of resolving structural similarities between certain types of materials that can be present with the papermaking system, such as polyamide-based wet strength resins and polyamide-based microbiological activity. An example involving a press roll deposition highlights each of these factors.

A mill was facing significant press roll deposition that led to frequent sheet breaks. An IR spectrum of the deposition was acquired by the mill’s laboratory and is shown in **Fig. 1**, along with a lab-curated library reference spectrum of a previously analyzed deposit that had been confirmed to contain hydrolyzed alkenyl succinic anhydride (ASA) size and calcium carbonate. The automated spectral library search identified that particular reference spectrum

as the top search result.

A comparison of the IR spectra, which shows their numerous similarities, quickly reveals why the automated library search identified the library reference spectrum of hydrolyzed ASA size and calcium carbonate as the top search result. Peaks in the reference spectrum at or near 2957, 2925, 2854, 1557, and 971 cm^{-1} for the hydrolyzed ASA size and at or near 1448 and 873 cm^{-1} for calcium carbonate are all accounted for in the spectrum of the press roll deposition. Based on the quality of the spectral match, the analyst concluded that the deposition primarily was due to hydrolyzed ASA size. However, a subsequent quality analysis of the ASA emulsion by particle size distribution and IR analysis indicated no irregularities in terms of particle size or hydrolysis. As multiple variables could ultimately lead to size hydrolysis including, but not limited to, product quality, emulsion particle size, wet-end charge, and fines retention, the IR and particle size analysis results alone certainly do not rule out other potential contributors to size hydrolysis. While hydrolyzed ASA size is confirmed in the deposit per the IR spectral interpretation, it is also possible that the observed hydrolyzed ASA size could be present in relatively minor quantities, and that it is being aggregated by another material(s), which is actually driving the observed deposition.

During a mill troubleshooting exercise, a process engineer revealed that a significant process leak of machine oil



2. Infrared spectra of press roll deposition, a “lab-cured” reference spectrum confirmed to consist of hydrolyzed ASA size in its di-calcium soap form and calcium carbonate, and the confirmed leaking hydrocarbon oil.

had recently occurred. Adding the reference spectrum of the machine oil into the comparison, as shown in **Fig. 2**, further explains why a spectral interpretation, either manual or automated, could easily fail to identify the oil as a source of the deposition.

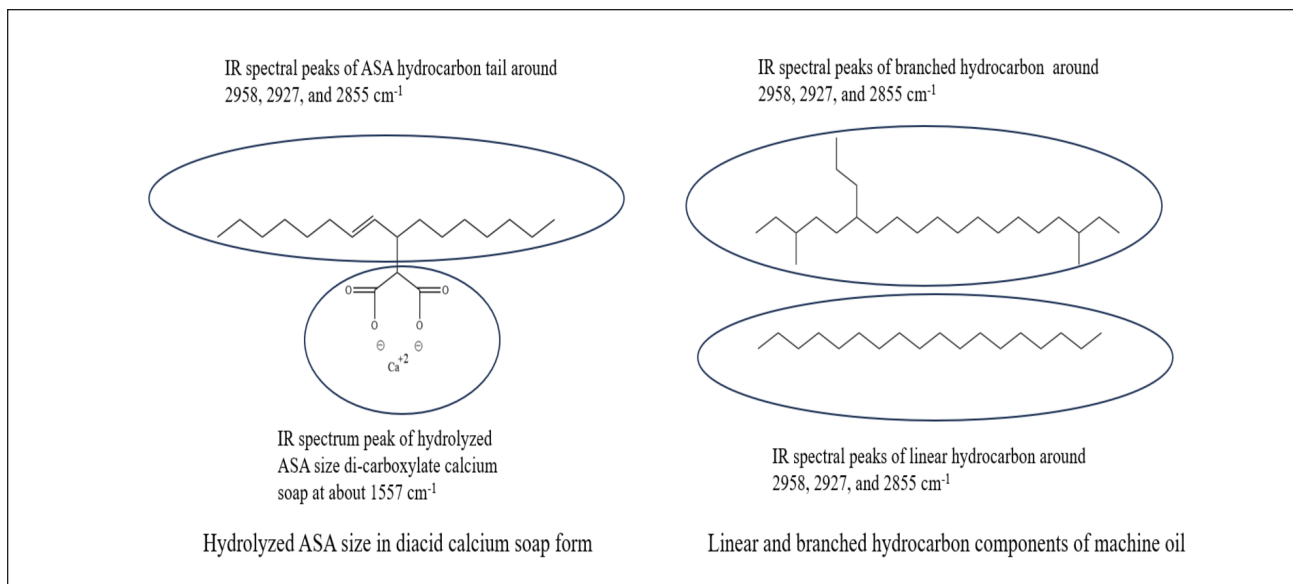
Figure 2 shows significant overlap of the peaks of the oil-based reference spectrum at 2953, 2923, and 2853 cm^{-1} with the peaks of the ASA reference spectrum at 2957, 2925, and 2854 cm^{-1} . This peak overlap is due to chemical structure-based similarities between the long hydrocarbon-based tail of the ASA size and the long linear and branched hydrocarbon chain components prevalent in the industrial oil. A structural comparison of the calcium soap of hydrolyzed ASA size and various linear and branched hydrocarbons typically observed within a machine oil sample is displayed in **Fig. 3**, along with the assigned IR spectral peak frequencies as observed in Fig. 2. Note the structural similarities between the hydrocarbon tail portion of the ASA size and the linear and branched hydrocarbon components of a machine oil. In both cases, the hydrocarbon tails are represented by peaks at approximately 2958, 2927, and 2855 cm^{-1} , while the dicarboxylate calcium soap of hydrolyzed ASA size is represented by a peak at 1557 cm^{-1} .

The two peaks at 1463 and 1377 cm^{-1} are hidden by the presence of the broad carbonate peak at 1448 cm^{-1} ; however, these two peaks are consistent with general hydro-

carbon tails present in both oils and ASA hydrocarbon. This significant overlap explains why an interpretation of the press roll deposition spectrum could potentially overlook the presence of the hydrocarbon oil.

Now, with the knowledge of the unaccounted-for oil and a significant amount of IR interpretation experience, it is easier to see that the ratio of the intensity of the ASA peak at 1557 cm^{-1} for the carboxylic acid salt and the peaks at 2957, 2925, and 2854 cm^{-1} for both the ASA hydrocarbon and the oil are different between the spectra of the press roll deposition and the library reference spectrum. In other words, the presence of the machine oil in the spectrum of the press roll deposit increased the intensity of the hydrocarbon chain peaks at 2957, 2925, and 2854 cm^{-1} , as these peaks are found in both materials and are therefore additive in observed intensity. However, it did not affect the ASA carboxylic acid salt peak at 1557 cm^{-1} that is observed only in the hydrolyzed ASA soaps. During a follow-up meeting with the troubleshooting team, the consensus was that the significant oil leak was causing the deposition.

In this example, the presence of the leaking machine oil was missed — understandably so — by the initial IR analysis. Fortunately, a process engineer’s comment about the unaccounted-for oil was a critical revelation at a key moment. However, in many troubleshooting efforts, such a critical clue may not be uncovered in a timely manner and



3. Structural comparison of hydrolyzed ASA size in its di-calcium soap form and linear/branched hydrocarbon components observed in a machine oil. Note the structural similarities between the hydrocarbon tail portion of the ASA size and the linear and branched hydrocarbon components of a machine oil. In both cases, the hydrocarbon tails are represented by peaks at approximately 2958, 2927, and 2855 cm^{-1} , while the di-carboxylate calcium soap of hydrolyzed ASA size is represented by a peak at 1557 cm^{-1} .

thus could remain unaccounted for during an IR analysis. Consequently, the true cause of the runnability issue could remain hidden.

USING A MULTI-METHOD APPROACH TO TROUBLESHOOT MACHINE DEPOSITS AND DEFECTS

When, as in the previous example, conducting only an initial IR analysis could miss a key clue as to the cause of the deposition or defect, a multi-method approach to troubleshooting should then be employed following the initial IR analysis. The multi-method approach incorporates data from multiple analytical techniques to provide complementary data to the initial IR analysis. The additional analytical techniques can be performed concurrently alongside the initial IR analysis. This complementary data can then be used to differentiate between multiple potential outcomes to uncover possibilities that otherwise likely would have been missed. The result of using this approach is a body of credible evidence that supports the analyst's interpretation and provides mill personnel with information needed to implement the necessary and appropriate corrective action.

The additional analytical techniques that can be employed include photomicroscopy, microbiological staining/assessment, pyrolysis-gas chromatography/mass spectrometry (Pyro-GC/MS), and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX). It is important to note that there is no preferential order for employing the various analytical techniques. They can be, and often are, run in parallel with each other, or the testing can be arranged in a fashion that is best for an individual lab's workflow, with the data being collected and examined as things progress, as well as

at the conclusion of all the testing. Also, in some cases, a microbiological assessment may only be performed if other testing results suggest that organic material is present. The benefits of the data provided by each of these techniques are summarized in the following sections. While an exhaustive description of each technique is beyond the scope of this paper, references are listed for each technique. One natural question that arises from the use of the multi-method strategy is the length of time needed to perform this testing in aggregate. Depending on the urgency of the request and lab circumstances, such as sample load and instrument availability, data from each technique can be collected independently within two business days. The data can then be reviewed in totality to arrive at a conclusion about the likely source of the runnability issue. Case studies included in this research paper effectively demonstrate how the complementary data from the multi-method approach can help solve challenging runnability issues of interest to papermakers.

Photomicroscopy

The act of examining a sample under a stereoscope and taking photos can be a very valuable, and overlooked, aspect of an analysis [4]. Many troubleshooting efforts that have reached an impasse subsequently have been resolved by a passing comment made during a viewing of a simple photograph. While analytical techniques often require experience in interpretation, the potential evidence within an image can reveal itself to anyone who sees it — from the experienced mill manager to the first-day-on-the-job process engineer novice. Invariably, these visual cues require human intervention because they cannot be captured or interpreted by sophisticated analytical instruments.

PROCESS ANALYSIS

Microbiological staining/assessment

Microscopic analyses can be performed to assess the presence and relative quantity of microbiological activity in machine deposits and defects. Standard best practices involve sample preparation, staining, and microbial identification to determine sample composition [5]. High resolution wet mounts of the sample aid in determining the presence of microbiological activity, while the stains provide insight into the structural detail of microorganisms and therefore the relative amounts of biological vs. non-biological material.

Pyrolysis-gas chromatograph/mass spectrometry

Pyrolysis-gas chromatography/mass spectrometry (Pyro-GC/MS) has strengths that complement the potential shortcomings of IR analysis in determining the organic components within an unknown sample [6]. Pyrolysis can volatilize materials that chromatography can separate, and then mass spectroscopy can definitively identify them as being unique to a specific material. This analysis can help identify or rule out a connection to a very specific material source. The increased specificity of the source of the deposit naturally leads to a more specific corrective action with a comparatively greater probability of solving the runnability issue.

Scanning electron microscopy-energy dispersive X-ray spectroscopy

Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) can be used to determine the elemental composition of a machine deposit by combining SEM imaging with EDX elemental analysis [7]. This technique can provide quantitative data for each element identified on the surface of a thin layer of sample within seconds. Parameters such as spot size and magnification can be adjusted using SEM to focus on specific areas of a sample. Accelerating voltage can be adjusted within the software to improve resolution, charging, or differentiation between lightweight and heavy elements. Results from SEM-EDX testing can be independently used to help identify unknown compounds in pure samples. However, interpreting results of mixed samples using SEM-EDX alone can be challenging. When SEM-EDX results are compared with results from other analytical techniques such as IR and microscopy, greater confidence is gained in positively identifying the composition of a sample.

EXPERIMENTAL

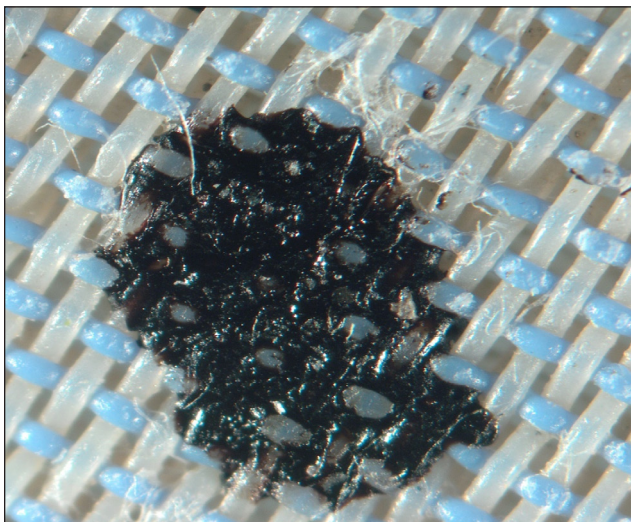
The FTIR spectroscopic analyses were conducted using a Thermo Scientific Nicolet iS50 FTIR spectrometer (Thermo Fisher Scientific; Waltham, MA, USA) equipped with a DuraScope attenuated total reflectance (ATR) accessory from Smiths Detection. All infrared spectra were collected on an as-is basis using samples dried overnight at 50°C. Infrared spectral library searches discussed in the paper

were conducted using a combination of commercial and homemade libraries of reference infrared spectra of both pure materials and deposit samples of confirmed composition. The IR analysis can be useful in identifying both organic and inorganic materials present in deposits or defects. One limitation with respect to IR analysis of inorganic compounds is the potential difficulty in providing elemental analysis (e.g., aluminum, calcium, barium, sulfur, phosphorous, etc.) that other analytical techniques such as SEM-EDX may readily provide.

The Pyro-GC/MS analyses were conducted using a JPS-700 curie point pyrolyzer (Japan Analytical Industry Co. Ltd.; Tokyo) connected to an Agilent 7890A gas chromatograph coupled to an Agilent 5975C triple axis mass selective detector (Agilent Technologies; Santa Clara, CA, USA). An Agilent DB-5MS capillary column (30 m x 0.250 mm x 0.25 μ m) was used with the following temperature ramp profile: 40°C for 1 min, followed by a 10°C/min ramp to a final temperature of 325°C with a 20-min hold. All samples underwent a single step pyrolysis at 650°C for 7 s with a GC inlet temperature of 300°C, and helium was used as the carrier gas with a 100:1 split ratio. Pyro-GC/MS analysis is primarily applicable to the analysis of organic compounds, which will frequently volatilize at varying pyrolysis temperatures to permit detection by mass spectrometry. Inorganic compounds will likely not volatilize, outside of the potential evolution of simple gases such as carbon dioxide (CO₂), and a quantitative/qualitative elemental profile cannot be obtained to positively identify the presence of inorganic compounds such as magnesium silicate-based talc, for example.

Energy-dispersive X-ray spectroscopy (EDX) analyses were conducted using a Hitachi SU3500 scanning electron microscope (SEM, Hitachi; Tokyo) equipped with a Bruker Quantax EDX system (Bruker; Billerica, MA, USA). As-is or 900°C ash samples were mounted on a stub using carbon tape and evaluated using an accelerating voltage of 20 kV. An SEM-EDX can be utilized for qualitative and quantitative elemental analysis of inorganic compounds to complement the predominantly organic-focused FTIR and Pyro-GC/MS analytical techniques. At the same time, an infrared spectrum of a barium sulfate-based pulp mill scale can be utilized in concert with a quantitative elemental analysis of barium and sulfate using SEM-EDX to link the combined analysis results to ascertain the presence of barium sulfate with increased certainty. Organic compounds, primarily containing carbon and hydrogen, are not readily detected by this technique due to their light atomic weights, which yield comparatively weak X-ray signals for detection.

Microscopic analyses of as-received samples were conducted on an Olympus BX40 light microscope (Olympus; Tokyo) using 10x, 20x, 40x, and 100x phase-contrast objectives. Commercially available stains, such as Lactophenol Cotton Blue, were used to enhance the structures of microorganisms for viewing and identification purposes. This allows for determining if organic components of the deposit



4. Dark, tar-like, tenacious material blinding over a portion of the wire.

or defect identified in the FTIR spectroscopic analysis are microbiological in nature or are abiotic.

CASE STUDIES

An effective multi-method analysis can increase the specificity, accuracy, and confidence in the test results. The following three mill case studies demonstrate how these various ana-

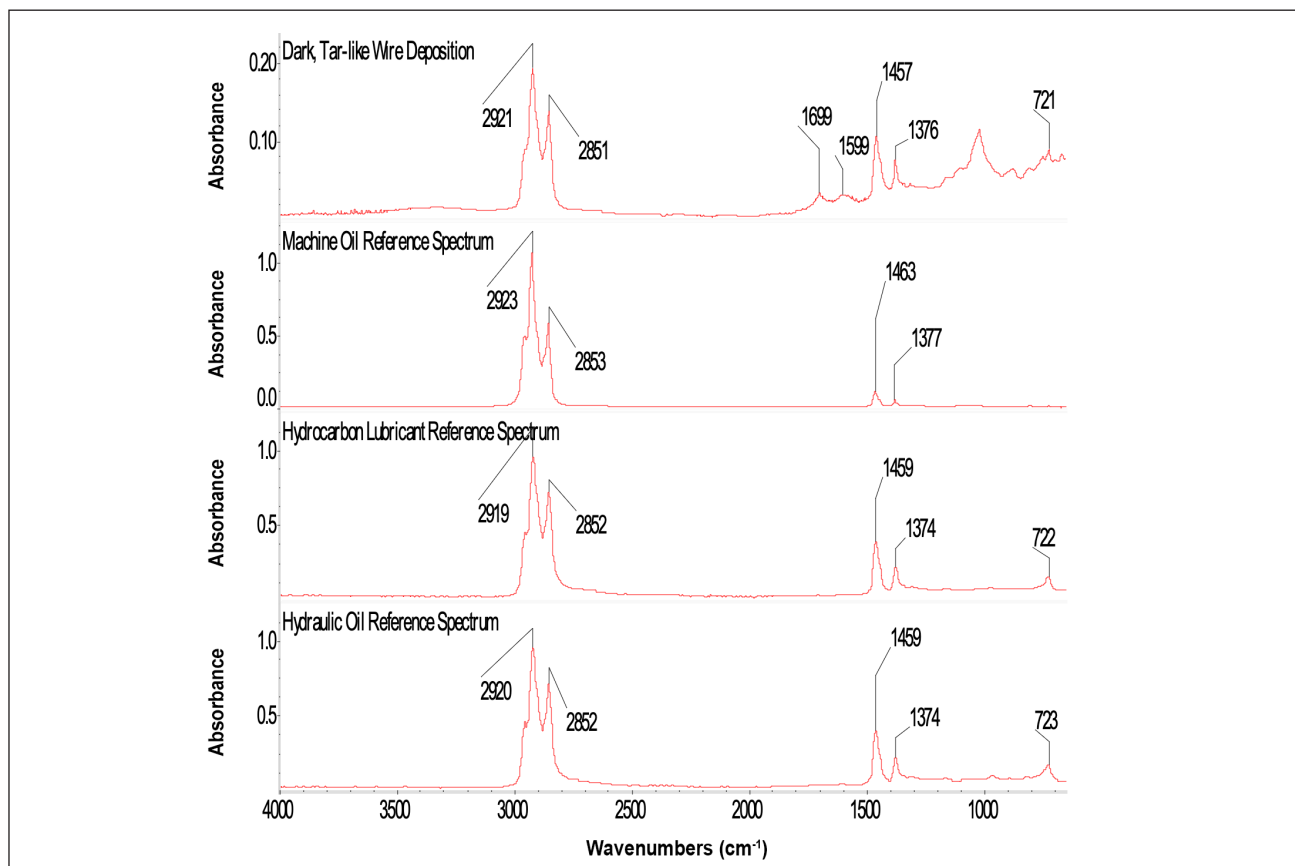
lytical techniques can be applied in concert to more accurately assess the causes of machine deposits and defects.

Case study #1: Machine wire deposition

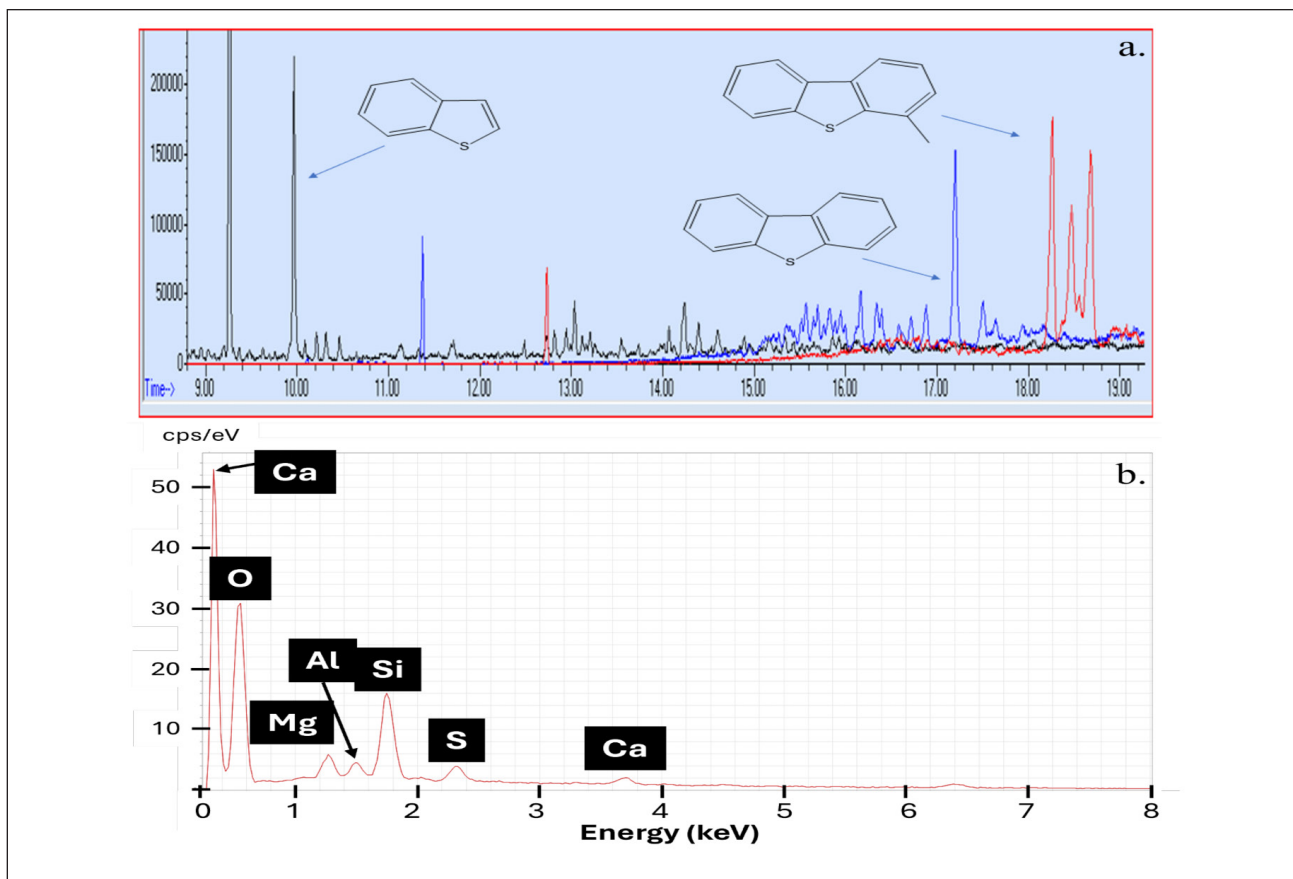
The mill was experiencing severe wire (formally referred to as a forming fabric) deposition across all of its machines, leading to sheet defects and quality complaints. The wire deposition, as shown in **Fig. 4**, appeared as a dark, tar-like material that was clinging tenaciously to the wire.

An initial FTIR spectroscopic analysis and subsequent spectral library search of the oven-dried, as-is wire deposition indicated that it was likely hydrocarbon-based; thus, as shown in **Fig. 5**, various oils and lubricants dominated the top results of the spectral library software search.

The presence of commonly observed hydrocarbon-based peaks at approximately 2920, 2852, 1458, 1374, and 723 cm^{-1} are observed in the spectrum of the wire deposition and in a variety of reference oils and lubricants, making precise identification potentially challenging. While some additional peaks at 1699 and 1599 cm^{-1} are also present, they may or may not be associated with the hydrocarbon-based peaks and might be representative of other independent materials present within the deposit. Given the hydrophobicity and obvious tackiness of the deposit, it is easy to see how it serves as an aggregator of other material present within the papermaking system. Based on this



5. Infrared spectra of a dark, tar-like wire deposition and the automated library search results for machine oil, lubricant, and hydraulic oil.



6. (a) Extracted ion chromatogram of wire deposition displaying the presence of asphaltene-related benzothiophenes and polycyclic aromatic sulfur heterocyclic compounds present in the pyrolysis-gas chromatography/mass spectrometry (Pyro-GC/MS) analysis of the wire deposition. **(b)** Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX) data for the wire deposition indicating the presence of calcium (Ca), magnesium (Mg), sulfur (S), aluminum (Al), and silicon (Si).

initial IR assessment of oils and lubricants, mill personnel conducted investigations, but they documented no evidence of oil leaks or any loss of oil. In addition, multiple samples of various oils were also analyzed by IR spectroscopy; however, no single oil was differentiated as being the source of the deposition because of the significant similarities of the IR spectra between various oil samples.

As shown in **Fig. 6a**, analysis of the wire deposition by Pyro-GC/MS found the presence of benzothiophenes and polycyclic aromatic sulfur heterocyclic compounds consistent with asphalt [8]. The presence of these materials within the extracted ion chromatogram suggests that the source of the tar-like wire deposition could be related more specifically to an asphalt-based material. An SEM-EDX analysis also confirmed the presence of sulfur within the wire deposition, as shown in Fig. 6b.

The presence of calcium carbonate (CaCO_3), kaolin clay ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), and talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) could account for the observed calcium, magnesium, aluminum, and silicon elements. In addition, the presence of the sulfur would be consistent with the benzothiophenes and polycyclic aromatic sulfur heterocyclic compounds identified by the Pyro-GC/MS analysis. The sulfur content of asphaltenes

typically ranges from between 0.05% and 7% weight of asphaltene [9]. While the SEM-EDX data is not conclusive in and of itself as to the presence of asphaltene in the wire deposition, the presence of sulfur serves to further support the data collected by IR spectroscopy and Pyro-GC/MS.

Based on the body of analytical evidence, a lengthy, mill-wide search for potential asphalt contamination was initiated. The increased confidence in the likelihood of asphalt-based contamination generated by the multi-method approach was very important, because the search took a significant amount of time and arrived at a few apparent dead ends before the asphalt contamination source was identified. Had the multi-method analysis approach not been employed, the troubleshooting task force may have lacked the conviction throughout the extended investigative process to stay the course, continue the search, and proceed with the appropriate corrective action. Ultimately, when an eroding asphalt-paved road was identified within proximity of openings within the mill's water reservoir, the open routes of entry within the water reservoir were sealed off, and the wire deposition ceased to occur after the reservoir cleaning. As a final post-mortem of this deposition analysis, given that both asphalt and machine



7. Doctor blade debris collected during a mill outage.

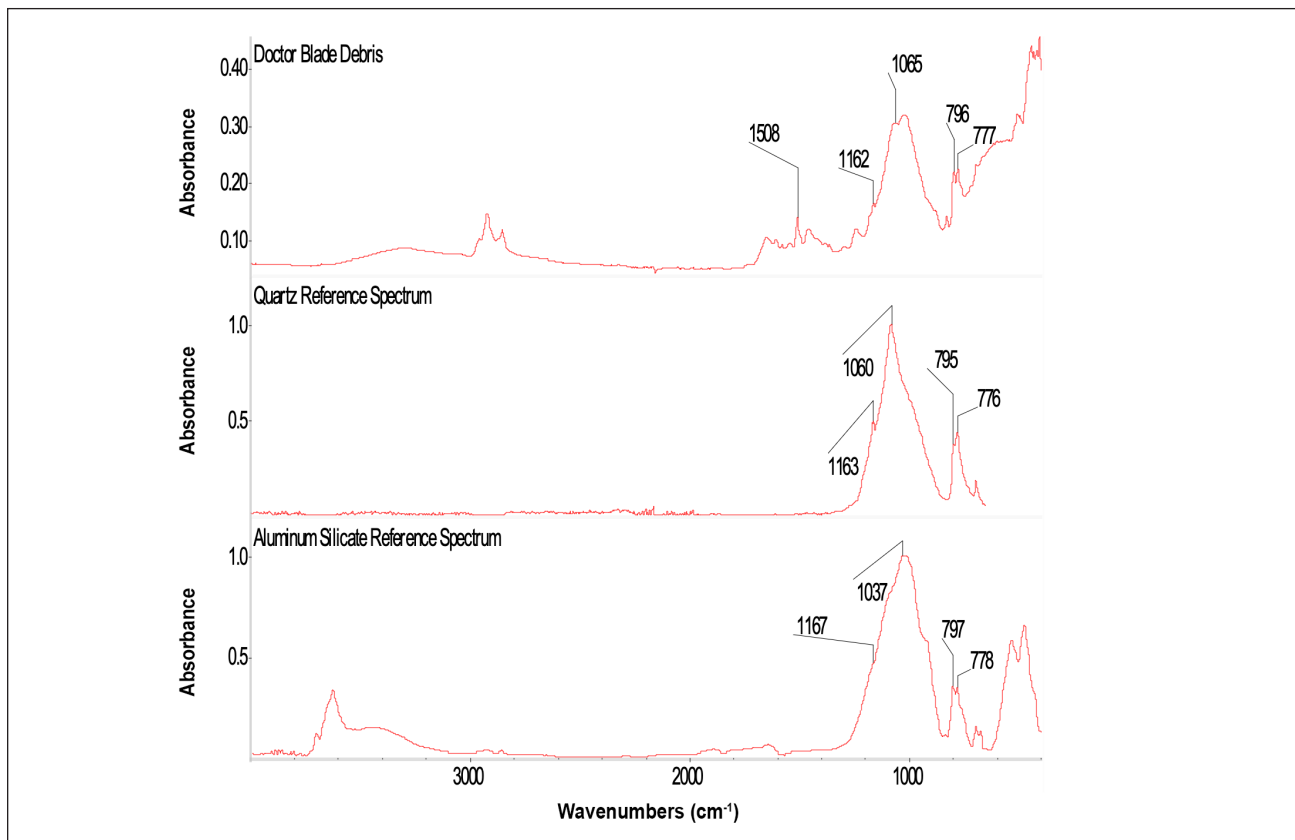
oils/lubricants are derived from petroleum, it is not surprising that the initial IR analysis struggled to specify asphalt as the source of the wire deposition. However, the

complementary techniques employed within the multi-method analyses more than compensated for this initial difficulty, ultimately leading to a differentiated analysis conclusion.

Case study #2: Doctor blade debris collected during outage

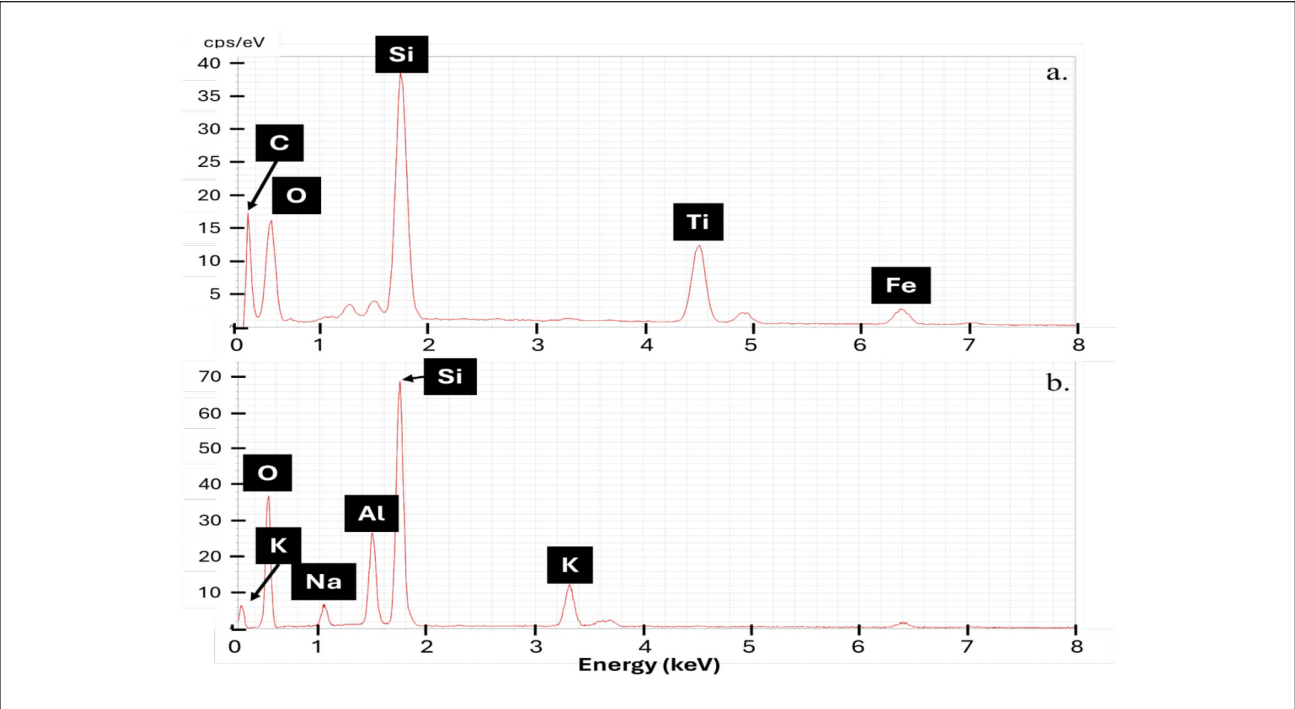
Doctor blade debris was collected from the mill's primary machine during an unscheduled outage. The mill had previously experienced a temporary, but severe, stickies outbreak, and the machine superintendent wanted to determine whether the current deposition was related to a stickies re-occurrence or something else. A digital image of the doctor blade debris was acquired and is displayed in **Fig. 7**.

The collected as-is IR spectrum of the oven-dried doctor blade debris is shown in **Fig. 8**, along with reference spectra of quartz and an aluminum silicate-based material. The initial IR analysis search results suggest that, while a silica or silicate-based material might well be present, significant ambiguity may still remain about its potential source. Clay-based papermaking additives, natural river water contaminants such as feldspar, and degrading water treatment silica beds are all potential sources of silica or silicate-based materials, and differentiating between them solely on the basis of the IR analysis can be very difficult. One shortcom-

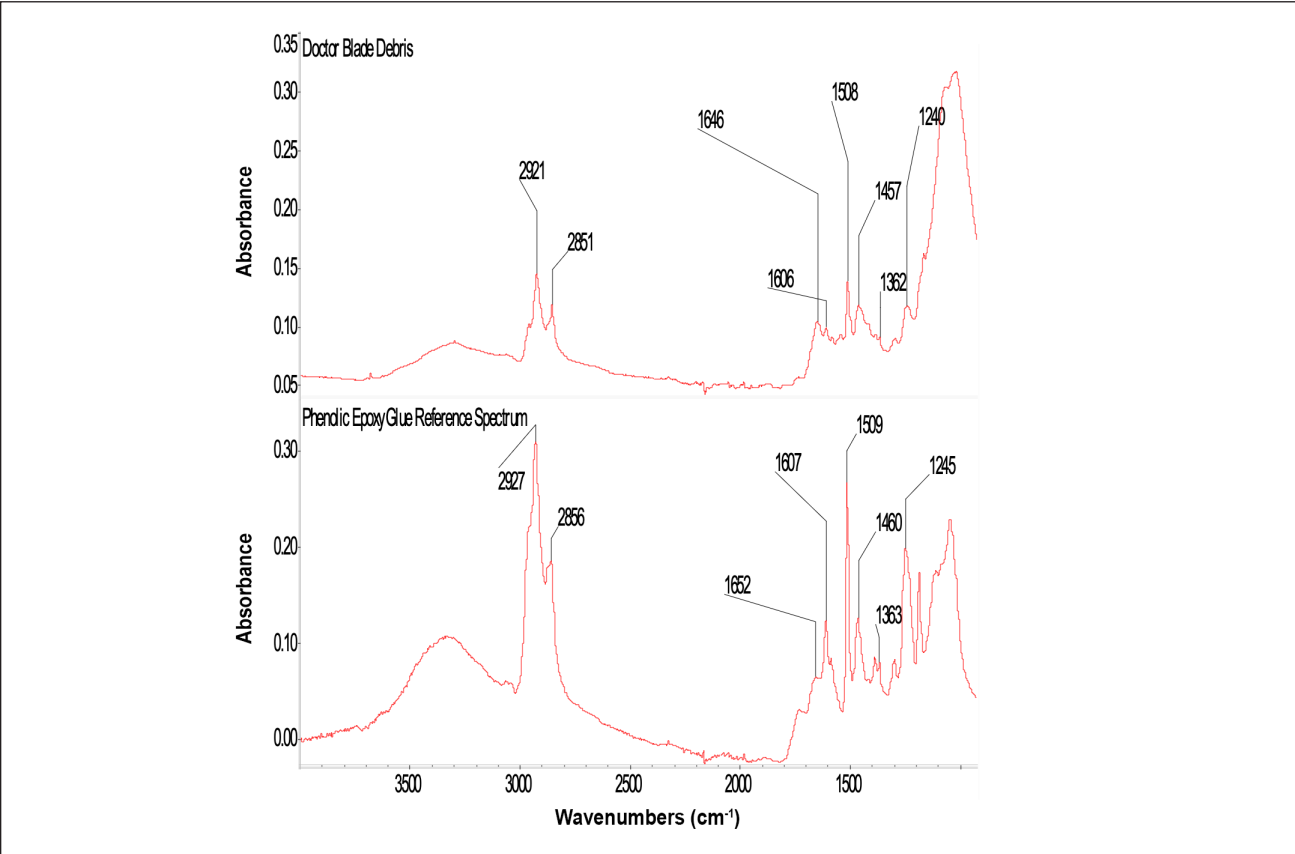


8. Infrared spectrum of doctor blade debris collected during outage and reference spectra of quartz and an aluminum silicate-based material.

PROCESS ANALYSIS



9. (a) SEM-EDX data for the doctor blade debris indicating the predominant presence of silicon (Si) along with lesser quantities of titanium (Ti) and iron (Fe). (b) SEM-EDX data for a tectosilicate-based feldspar sheet contaminant highlighting the presence of aluminum (Al), sodium (Na), and potassium (K) cations in addition to silicon.



10. Infrared spectrum of doctor blade debris collected during outage and a reference spectrum of a phenolic epoxy glue.



11. Gelatinous deposition found during the cleaning of a whitewater chest.

ing of standalone IR analysis is that it does not easily differentiate between a silica — i.e., silica (SiO_2)-based material such as quartz — and an inorganic silicate containing one or more cations (e.g., aluminum, sodium, calcium, and potassium) that an IR analysis alone may not identify. In general, the infrared spectra of both silicas and silicates exhibit a broad, very strong peak between 1100 and 1000 cm^{-1} , consistent with silicon-oxygen vibrations. Consequently, a multi-method analysis including the use of SEM-EDX can be helpful in identifying these cations. An analysis of the SEM-EDX data of the debris, shown in **Fig. 9a**, indicates that SiO_2 is likely the dominant inorganic component of the deposit.

The SEM-EDX elemental data shows that the dominant peak is consistent with silicon. The absence of traditionally observed cations, such as aluminum, potassium, sodium, and calcium, may suggest that silica rather than a silicate is present. To further demonstrate the comparative differences between silicas and silicates, a reference SEM-EDX analysis of a naturally occurring water-based feldspar, a tectosilicate-based contaminant from a previously analyzed sheet defect, is shown in Fig. 9b.

The SEM-EDX data for the feldspar contaminant shows the presence of several cations, namely sodium, aluminum, and potassium. This composition is consistent with an inorganic silicate. The SEM-EDX spectrum of the doctor blade debris, however, exhibits primarily silicon followed by a moderate amount of titanium. This composition is more consistent with that of quartz, which is primarily silica with minimal evidence of associated cations. While being able to differentiate between a silica and a silicate is helpful, this analysis alone will not determine a definitive source of the predominantly silica-based material found in the doctor blade debris.

A subsequent search of the right side of the initial IR spectrum, excluding the primarily confirmed quartz silica-based peaks, yielded search results consistent with a phenolic epoxy glue, as shown in **Fig. 10**.

After reviewing the spectral comparison, we determined that the presence of mutually appearing peaks at about

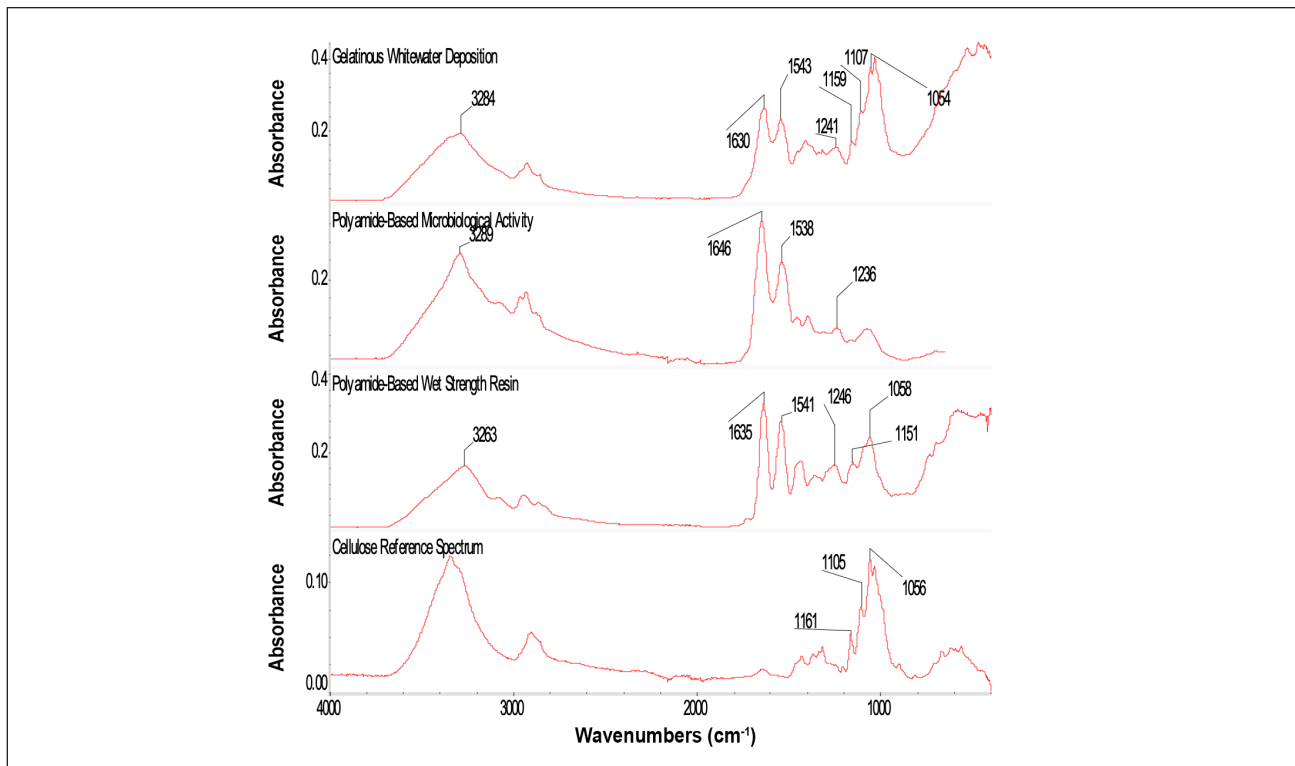
2921, 2851, 1646, 1606, 1508, 1457, 1362, and 1240 cm^{-1} suggested that the epoxy glue may well be present. The combined findings of an epoxy glue and quartz could possibly suggest construction-related debris. In this particular example, a final decisive piece of the puzzle originated from a simple but often overlooked source, the image of the debris itself. After revisiting the photo of the debris with the knowledge of the IR and SEM-EDX data, we concluded that the doctor blade debris likely was related to grout chunks from the inner surface tiling of machine tanks/chests. Interestingly, the presence of titanium within the SEM-EDX spectrum of the doctor blade debris could potentially originate from titanium dioxide, a common industrial filler in epoxy-based composites.

During a discussion, mill operators indicated that substantial construction work had recently been performed by some contractors, and the grout doctor blade debris was acknowledged as likely being a residual of that work.

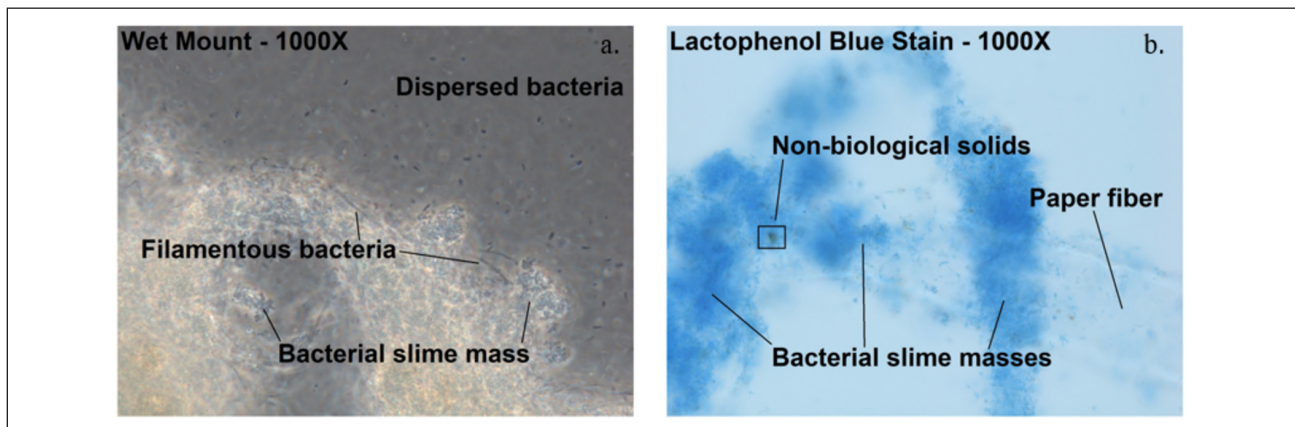
Case study #3: Whitewater deposition in board mill

Our final case study involves gelatinous, amber-colored deposition that was found in a whitewater chest and was believed to be the cause of recent sheet breaks. Whether the deposition was related to microbiological activity or whether it was related to a wet-strength resin trial the mill had recently run was unknown. A digital image of the deposition was acquired and is shown in **Fig. 11**. The initial as-is IR analysis results of the oven dried whitewater deposition are displayed in **Fig. 12**, along with reference spectra of polyamide-based microbiological activity, polyamide-based wet strength resin, and cellulose fiber.

As the IR spectral comparison exhibits, peaks consistent with a polyamide-based material at approximately 3284, 1630, 1543, and 1241 cm^{-1} are observed in the spectra of both polyamide-based microbiological activity and the polyamide-based wet strength resin. This makes differentiation between microbiological and wet-strength materials difficult by either automated spectral library searching or by human interpretation. The structural polyamide similarities between polyamide epichlorohydrin (PAE)-based wet strength resins and microbial proteins readily account for the virtually indistinguishable pair of peaks between 1680–1630 cm^{-1} and 1570–1515 cm^{-1} . While it is true that there are other differentiated functional groups also present within microbial proteins and PAE-based wet strength resins, the frequent presence of cellulose peaks between 1200 and 1000 cm^{-1} in deposit and defect infrared spectra can hide these additional differentiated peaks, leaving only the aforementioned peaks between 1680–1630 cm^{-1} and 1570–1515 cm^{-1} to attempt to differentiate between the two materials. Consequently, in using an automated library searching program, a mixture of microbiological and wet strength resin-based library spectra is typically reported back as high-quality search results with little conviction



12. Infrared spectra of gelatinous whitewater deposition, polyamide-based microbiological activity, polyamide-based wet-strength resin, and cellulose fiber are shown, highlighting the presence of cellulose peaks at about 1161, 1105, and 1056 cm⁻¹ in the spectrum of the deposition.



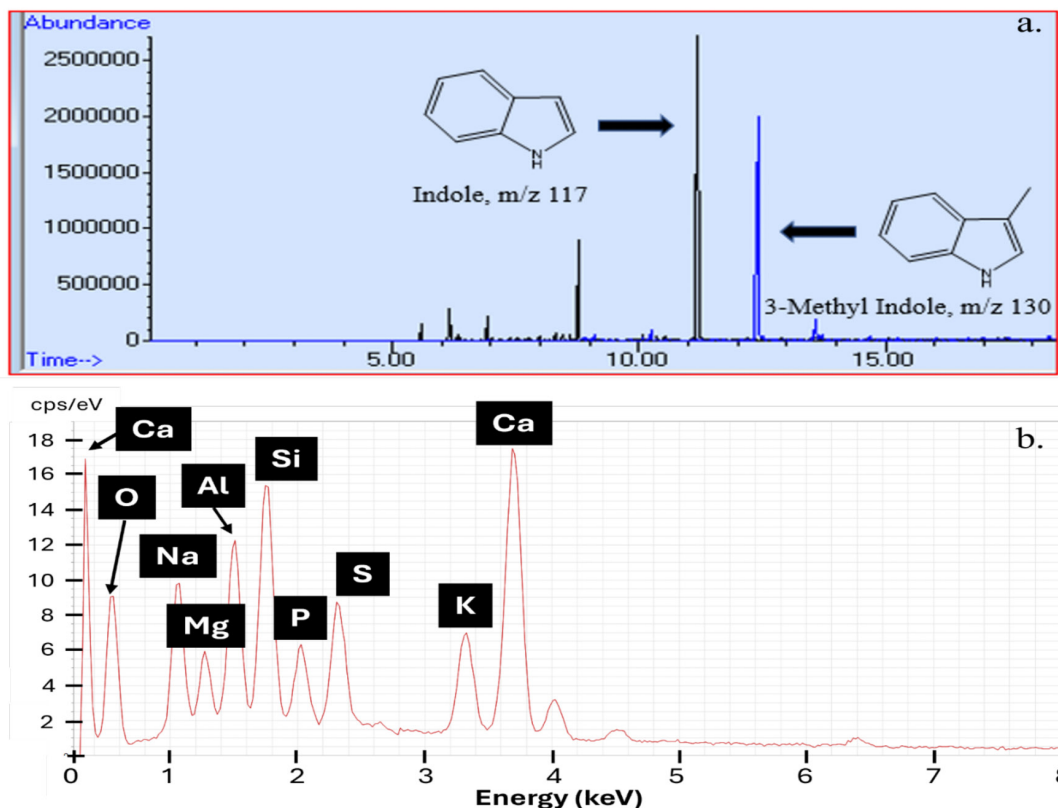
13. (a) Wet mount of whitewater deposit at 1000x magnification, where the higher resolution allows for the identification of individual bacteria cells, bacterial slime, and filamentous bacteria. (b) Lactophenol blue stain of bacterial slime at 1000x magnification, where bacteria cells and slime masses are easily identified by taking up the stain; the paper fiber does not take up the stain, thereby providing contrast.

favoring one versus the other. Due to these challenges of differentiating between these materials by IR spectral interpretation alone, the multi-method analysis approach is well suited to distinguish between these two types of materials.

A microscopic examination of the whitewater deposit showed predominantly bacterial slime masses, dispersed bacteria, and filamentous bacteria, which were estimated to make up approximately 90% of the total deposit. Paper fibers and non-biological solids were also observed but in

smaller amounts. Wet mount and Lactophenol Cotton Blue stained sample photos were captured at 1000x magnification and are displayed in **Fig. 13**.

Next, an analysis of the deposition using Pyro-GC/MS identified fragments associated with indole and methyl indole that were consistent with the presence of proteinaceous microbiological activity [10], as shown in **Fig. 14a**. At the same time, cyclopentanone-based fragments, which would be consistent with the presence of the recently trialed-wet-strength resin, were not observed, thereby further



14. (a) Extracted ion chromatogram displaying the presence of indole and methylindole compounds present in the Pyro-GC/MS analysis of the whitewater deposition. **(b)** SEM-EDX elemental data for the 900°C ash of the whitewater deposition indicating the presence of calcium (Ca), sodium (Na), magnesium (Mg), silicon (Si), phosphorous (P), sulfur (S), and potassium (K).

affirming the results of the microbiological assessment [10]. Lastly, the results of the SEM-EDX analysis of the 900°C ash of whitewater deposition are shown in Fig. 14b.

The SEM-EDX analysis of the whitewater deposit ash indicated a diverse profile of elements, including potassium, magnesium, sodium, calcium, silicon, phosphorous, sulfur, and aluminum, as shown in Fig. 14b. The abundance of each element ranged from 5% to 26% of the ash content. Potassium and magnesium are two of the most abundant metal ions in living cells, followed by sodium, and calcium, all of which were identified in the sample [11]. The detection of potassium, magnesium, sodium, and calcium lends some evidence that the sample may contain biological material, though conclusions cannot be drawn on this information alone.

However, SEM-EDX has been previously used to show the distribution of multiple elements, such as potassium, magnesium, sodium, calcium, silicon, phosphorous, sulfur, chlorine, and manganese, in several known samples of bacteria [7]. All samples tested showed a diverse profile of metal ions; however, the abundance of each metal ion differed depending on the bacterial species tested. For example, *E. coli*, *Salmonella*, and *Chronobacter* all contained potassium, magnesium, sodium, calcium, silicon, phospho-

rous, sulfur, chlorine, and manganese in relatively different amounts, demonstrating the potential for identifying a bacterial species using SEM-EDX when the bacteria species and their respective elemental profiles are known. In comparison, samples that lacked a diverse elemental profile would be less likely to contain microorganisms such as bacteria or more likely to be inorganic in nature.

Although bacteria cannot be identified to a species level in mixed samples, such as the whitewater deposit, using SEM-EDX, the presence of the diverse elemental profile, when combined with the IR, microscopy and Pyro-GC/MS results, provides further evidence that the deposit is microbiological.

When the collective analytical evidence supporting the conclusion that the deposition was microbiological was shared with the mill, their personnel investigated and subsequently determined that the whitewater tank was not being treated with biocide. After the tank was treated with biocide, the deposition was reduced significantly.

CONCLUSION

Identifying the actual “trigger” and source of a deposit or defect issue can potentially be very challenging when using only infrared spectral data, which can point a troubleshoot-

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ing effort in a general direction but may come short of the “last mile” of defining a more precise source. However, employing a multi-method approach in which data is used from a variety of analytical techniques, including photomicroscopy, FTIR spectroscopy, microbiological staining/phase contrast microscopy, Pyro-GC/MS, and SEM-EDX, can help to more accurately frame — and with greater conviction — the specific cause of a runnability issue. The additional individual techniques employed each bring unique advantages. Photomicroscopy appeals to the widest possible audience. Microscopic analysis can be used to identify specific types of microbiological activity and to determine if it is driving the deposition. The Pyro-GC/MS analysis can also be used to detect specific components of otherwise indistinguishable materials based on their IR spectra. And lastly, SEM-EDX can provide insight into the elemental composition of a sample, providing an inorganic perspective that is not available through the other techniques. Moreover, the ability to perform the individual technique analyses simultaneously ensures that the results can be available within a relatively short timeframe, usually within two business days under ideal operating conditions. In a stressful environment when downtime and off-spec product are growing and multiple corrective action pathways are seemingly equally plausible, a proposed solution of high conviction based on a collective body of analytical evidence can help get runnability back on track. **TJ**

LITERATURE CITED

ABOUT THE AUTHORS

We chose this topic to research because we realized that the data from various different analytical techniques “speak” to one another in that they can further support or rule out theories as to what the identity and/or source of the deposit or defect is, and we wanted to share this information with the industry. This study complements previous research that we have done on the use of infrared (IR) spectroscopy in analyzing deposit samples. It also differs from previous research in that it focuses on deposit and defect samples in general rather than just a specific type, i.e., wood pitch or “stickies.”

Through this work, we discovered just how much different sets of analytical data can support or refute each other, as well as the value that provides in finding a clear path forward when you come to a “fork in the road” in a troubleshooting campaign. Finding great, fully resolved case studies was part of highlighting the benefits that this multi-method



Blazey



Gillan



Reichert



Smith

approach can provide in solving runnability issues.

For mills, adopting a multi-method approach to solving issues with deposits and defects is an important way to expedite process corrections moving into the future. In the words of one of our manuscript’s reviewers, “troubleshooting papers are timeless in their relevance and value to papermakers, especially as newer generations take the helm.”

Blazey is senior team leader, Gillan is staff scientist, Reichert is laboratory technician, and Smith is senior staff scientist at Solenis LLC in Wilmington, DE, USA. Email Blazey at mblazey@solenis.com.

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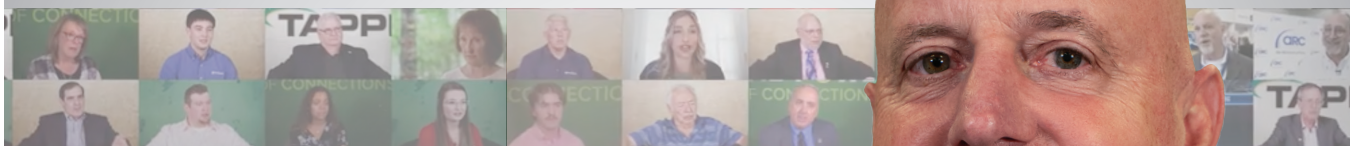
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