Determination of aluminum soaps in pitch deposits by gas chromatography

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ABSTRACT: Aluminum soaps can be determined by formation of aluminum-acetylacetonate chelates that are volatile enough to be analyzed by gas chromatography. Application of the technique to pitch deposits containing aluminum soaps entails acid hydrolysis to break down the aluminum soaps, chelation of the aluminum with acetylacetonate at pH >6, and analysis of the aluminum chelates by gas chromatography. The technique offers results that are comparable to those obtained by a traditional, much longer method that requires acid digestion of aluminum soaps and analysis of aluminum content by inductively coupled plasma spectroscopy.

Application: This research will help mills obtain more detailed information on the chemistry of sticky deposits and thus spend wisely and correctly in alleviating the problems.

Several aluminum-containing additives are used in making pulp and paper. Alum, for example, is used for water clarification, as a retention aid, as a sizing anchor in rosin sizing, and as a pitch control agent [1-5]. The flocculating power of alum makes it an ideal agent for these applications. Alum works well as long as it is used in acidic environments, such as conventional newsprint manufacture. In alkaline environments, fatty acids originating from wood resins are ionized and can complex with aluminum ions. The result is a very tacky aluminum soap that sticks to process equipment, causing process upsets during paper manufacture, and on printing machines [6-8]. Certain clay products used as filler also can cause aluminum soaps to form [9,10]. This happens when the products contain tetrasodium pyrophosphate (TSPP) as a dispersant. The TSPP abstracts aluminum ions from the clay matrix, which then complex with fatty acids in an alkaline environment to form aluminum soaps. Deinked paper (DIP) mills that recycle newsprint containing alum often experience deposition problems resulting from the formation of aluminum soaps [11,12]. The alkaline conditions in a DIP plant are ideal for metal soap formation. Quantitative analysis of aluminum soaps in pitch deposits is an important component in solving the problems. For example, the aluminum soaps can be determined by acid hydrolysis and precipitation as aluminum chloride [13]. Unfortunately, the analysis methods are long and require expensive instrumentation, such as inductively coupled plasma (ICP) spectroscopy or energy dispersive spectroscopy, to ascertain the presence of aluminum. More rapid analyses would be ideal.

In this work, we report on the determination of aluminum soaps by gas chromatography (GC). At first glance it might be hard to visualize that aluminum compounds can be analyzed by gas chromatography. However, aluminum ions can chelate with acetylacetonate to form a chelate that is volatile enough to be analyzed by GC [14,15]. We have adapted this process to analyze for aluminum soaps in pitch deposits.

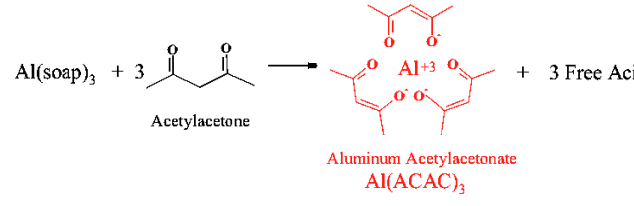
EXPERIMENTAL

Materials

We obtained aluminum tristearate, aluminum trioleate, acetylacetonate, and aluminum acetylacetonate chelate (Al-ACAC) from Sigma-Aldrich and used pitch deposits known to contain aluminum soaps from previous analyses.

Preparation of Al-ACAC

Two procedures were investigated for the preparation of Al-ACAC chelates. The first involved directly obtaining chelates from the Aluminum soaps by refluxing according to the following mechanism:



The procedure we used was as follows:

1. Reflux 0.5 g quantities of aluminum oleate and aluminum stearate standards with 20 mL of ACAC:chloroform (1:1).
2. Quantitatively transfer to a 25 mL volumetric flask (use chloroform for rinsing and make-up volume).
3. Inject 1 µL portion of the refluxed sample into GC.

Subsequently, tetramethyl ammonium hydroxide (TMAH) was added during the reflux process to ascertain whether this could enhance the formation of the Al chelates.

The second method was to obtain Al-ACAC chelates from $AlCl_3$ formed after hydrolysis of the aluminum soaps. In this

case, the aluminum soaps are hydrolyzed to form aluminum chloride, which will complex with ACAC according to the following mechanism:

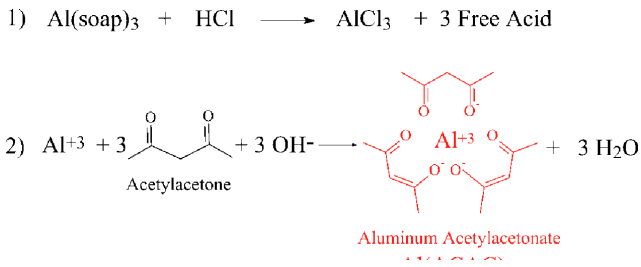
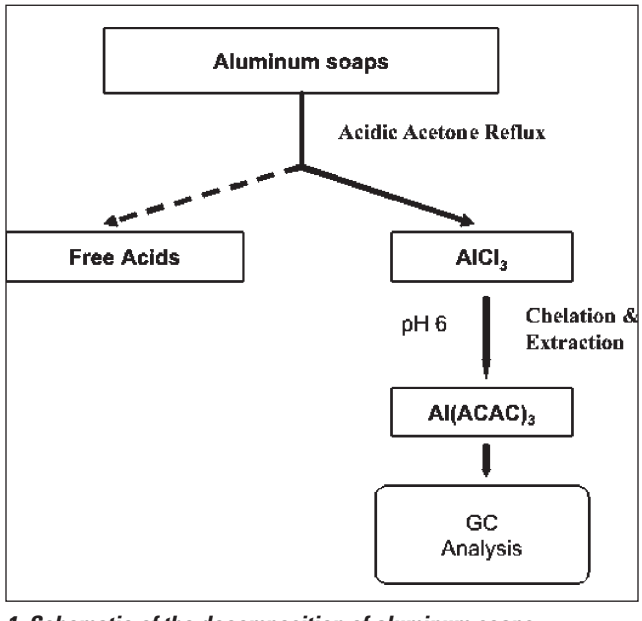
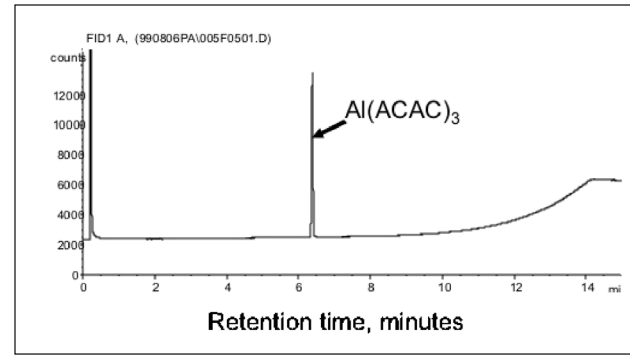


Figure 1 shows a schematic of the hydrolysis procedure, summarized as follows:

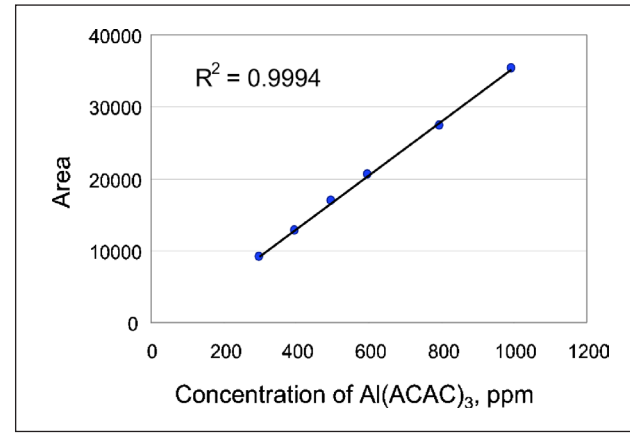
1. Break down approximately 0.5 g aluminum soaps to form aluminum chloride [13]: hydrolyze aluminum soap in standards or in deposits with acidic acetone and collect the aqueous fraction containing aluminum chloride.
2. Evaporate down to about 5 mL and transfer, quantitatively, to a 50 mL beaker (the final volume of the sample should not exceed 30 mL).
3. Adjust pH of sample to 6.0 with 0.5 N sodium hydroxide and transfer to a 100 mL separator funnel.
4. Extract with three successive equal volumes of a solution made up of acetylacetonate and chloroform (1:1). The volume of the organic solvent and water should be about the same to prevent emulsion problems.
5. Combine and wash the organic extracts with an equal volume of distilled water.
6. Collect the organic layer at the bottom and remove the solvent by evaporation using a rotary evaporator.



1. Schematic of the decomposition of aluminum soaps.



2. Chromatogram illustrating the elution of the aluminum acetylacetonate chelate (Al-ACAC) complex.



3. Calibration curve for Al-ACAC complex.

7. Quantitatively transfer sample to a 10 mL volumetric flask (use chloroform for rinsing or make-up solution). Inject 1 µL of the solvent into a GC column.
8. Prepare a series of standard samples containing 300–1000 ppm commercial Al-ACAC and inject into the GC.

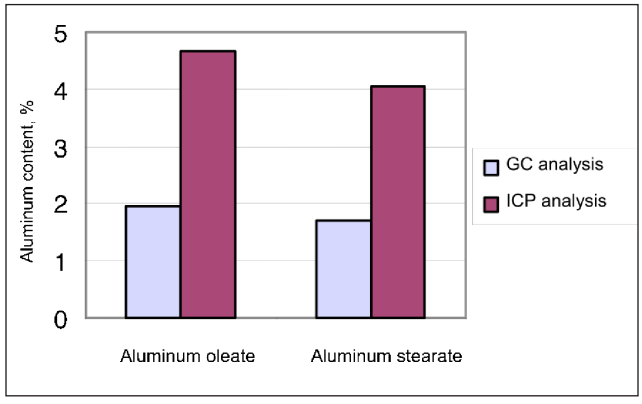
Effect of pH on the extraction recovery of Al-ACAC

The effect of pH on the formation of the Al-ACAC chelates was studied in the following steps:

1. Prepare a stock solution of aluminum nitrate in water.
2. Adjust pH of aluminum nitrate solution to 3.0, 4.5, 6.0, and 9.0.
3. Prepare Al-ACAC chelates, as previously described.

The accuracy of all analyses was determined by comparing the data with those obtained by ICP spectroscopy. The amounts of Al determined were then used to compute aluminum soap concentrations in the deposits by assuming a 3:1 aluminum: fatty acid ratio [16].

To analyze the Al-ACAC complexes, we used gas chromatography-flame ionization detector (GC-FID) and confirmatory runs on a few samples by gas chromatography-mass spectroscopy (GC-MS). GC was conducted using a temperature sequence of 50°C for 2 min, increasing by 8°C per min to



4. Determination of aluminum ion in aluminum soaps by refluxing with tetramethyl ammonium hydroxide (TMAH).

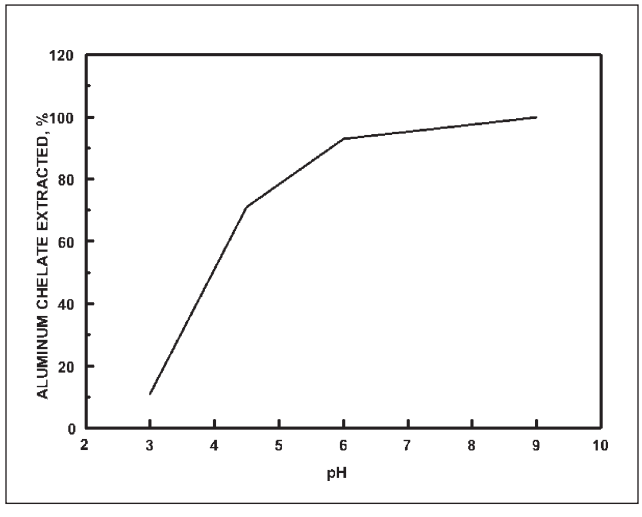
310°C, then held for 0.5 min. MS was conducted using an interface temperature of 320°C and an m/z scan range of 50-650.

RESULTS AND DISCUSSIONS

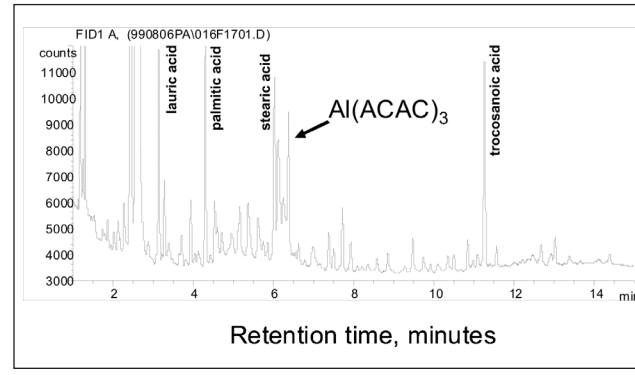
Preparation of Al-ACAC chelates from Al-nitrate yielded an Al-chelate that, under the GC conditions used, elutes at 6.43 min (**Fig. 2**). A linear calibration curve was obtained for Al-ACAC standards (**Fig. 3**). The presence of Al-ACAC was confirmed by GC-MS analysis.

Reflux method

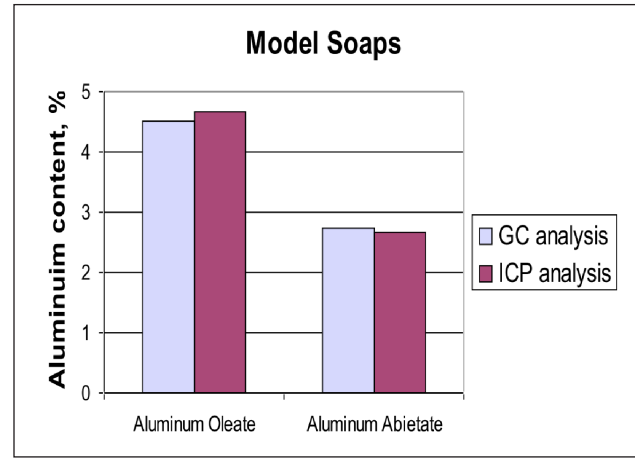
Figure 4 shows the results obtained on model aluminum soaps. The direct reflux method yields results that are lower than those obtained by analysis of aluminum using ICP after acid hydrolysis. Changes in basicity of the mixture during reflux did not improve the results. We anticipated that the addition of TMAH would tie up fatty acids, thus shifting the decomposition equilibrium of the aluminum soaps during refluxing. The reflux method did result in the formation of Al-ACAC chelate, but the reaction was not quantitative.



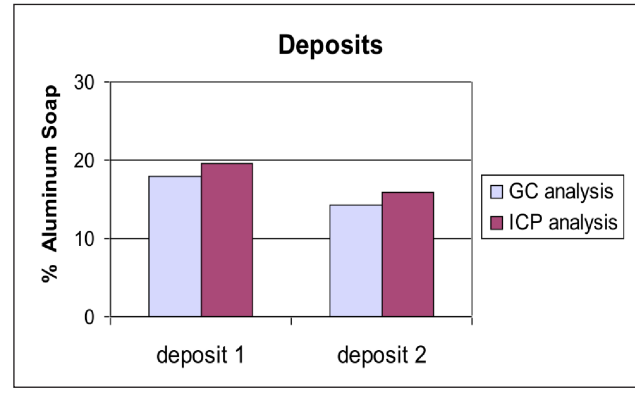
5. Effect of pH on formation of the Al-ACAC complex.



6. Analysis of Al in a deposit sample by formation of the Al-ACAC complex.



7. Comparison of inductively coupled plasma spectroscopy (ICP) and gas chromatography (GC) methodologies for determination of aluminum content in model aluminum soaps.



8. Comparison of ICP and GC methodologies for determination of aluminum content in aluminum soap deposits.

Hydrolysis method

The hydrolysis method proved more successful than the reflux method. The method was optimized by varying the amount of reagent used, the pH of the sample before addition of ACAC, and the extraction time. **Figure 5** demonstrates that pH is an important factor and needs to be above 6.0. **Figures 6-8** show that application of the method to model alu-

minum soaps and pitch deposits containing aluminum soaps was successful. The GC data are very close to those obtained by acid hydrolysis and analysis by ICP.

CONCLUSIONS

Aluminum soaps can be determined by formation of Al-ACAC chelates that are volatile enough to be analyzed by gas chromatography. The technique offers results that are comparable to those obtained by acid digestion of aluminum soaps and analysis of aluminum content by ICP. This is an advantage considering that an ICP instrument is considerably more expensive than a GC instrument. Another advantage of the GC method over the ICP one is that one can obtain information about the chemistry of the fatty acids complexed to the aluminum ions, if so desired. **TJ**

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AUTHOR INSIGHTS

Analysis of pitch deposits is an important aspect of devising effective pitch control measures. This research study offers a faster, as well as accurate, method for the analysis of deposits caused by aluminum soaps.

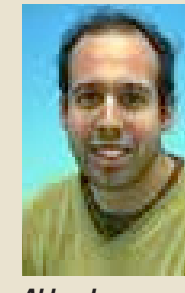
One of the most difficult aspects of this research was finding a method to analyze for metal ions without losing information about the organic moieties bound to the metal ions. Adoption of a method developed in the 1960s to analyze for aluminum ions in water samples worked well on pitch deposits: chelation of the metal ions formed chelated products that could be analyzed by gas chromatography.

We discovered that one could kill two birds with one stone: analyze for aluminum ions and the fatty acids that are bound to the ions to form sticky metaluminum soaps. We did not need to use two different instruments (one for metal ions and the other for the fatty acids).

The presence of aluminum helps pinpoint the source of the problem. Mills can use this information to assess the source of the metal ions (e.g, alum used in the process). Analysis for the fatty acids will help in determining their source (e.g., wood furnish or fatty acids used in the deinking process).

Now mills can have more detailed information on the chemistry of sticky deposits and thus spend wisely and correctly in alleviating the problems. The guesswork is taken out as one is now dealing with concrete data on the chemistry of the problem at hand. In some mills there are arguments about the cause of deposits: virgin pulp or the deinking process? The method described in this study will help settle such arguments.

Sitholé



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