

Wood Chemistry

Wood Chemistry

PSE 406/Chem E 470

Lecture 17

Chemical Isolation and Analysis I

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Class Agenda


- Plant matter analysis
- Sample preparation
- Extractives
- Holocellulose
- Cellulose

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Sample Preparation

- Homogeneous
 - » Sample needs to represent the entire sample to be analyzed
- Sample Size
 - » The sample particle size needs to be small.
 - » Grinding (milling)
 - » Homogeneous particle size
 - Screening of ground material



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Moisture Content

- It is extremely important when analyzing organic material to take into account moisture content.
- The best way to work with material is typically to let the material equilibrate (air dry) and then determine moisture content.
 - » Typical method is to dry material overnight in a 105°C oven.
- Pulp and paper method:
 - » $\%mc_g = (\text{weight}_{\text{wet}} - \text{weight}_{\text{dry}}) / \text{weight}_{\text{wet}}$
- Wood products industry
 - » $\%mc_g = (\text{weight}_{\text{wet}} - \text{weight}_{\text{dry}}) / \text{weight}_{\text{dry}}$

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Extractives

- There are two topics in this lecture under extractives:
 - » Analysis of the amount (and types) of extractives in plant matter.
 - » Removal of extractives prior to analysis for other chemicals.
 - When ever plant material is analyzed for cellulose, hemicelluloses, or lignin, it is necessary to remove the extractive materials.
 - This is because extractive can interfere with the other analysis.

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Extractives


- Not all extractives can be removed using the same system.
 - » Extractives have different solubility's (sp?) and volatilities.
- Most often samples are subjected to 2 or 3 different removal systems if the idea is to rid the sample of extractives.
- I have broken up the extraction techniques into 4 general methods (although there are quite a few other techniques).

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Steam Distillation

- In this procedure, volatile extractives are removed through the action of steam.
- Compounds removed include:
 - » Monoterpenes
 - » Sesquiterpenes
 - » Diterpenes
 - » Triterpenes (not oids)
 - » Tetraterpenes (not oids)
 - » Phenols
 - » Hydrocarbons
 - » Some lignans




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Steam Distillation II

- The volatile compounds removed through steam distillation are cooled thus becoming liquids again.
- These compounds are mostly hydrophobic and thus can be separated (decanted) from the water.



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Ether Extraction

- In this procedure, plant materials are continuously extracted with ethyl ether.
- Think of this procedure as something like dipping a tea bag in a countless number of cups of hot water.
- The picture on the right is of a Soxhlet extractor used to continuously extract samples. There is wood meal in a cellulose thimble (orange tube) being extracted. The dark red solution in the flask is the dissolved extractives.



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9

Ether Extraction II

- Ether is typically used to remove lipophilic materials.
 - » Fats/Oils
 - » Fatty acids
 - » Waxes
 - » Resin Acids
 - » Sterols

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10

Alcohol Extraction

- Ethyl alcohol (typically) or methanol is used in a similar fashion to ether extraction.
- Materials removed:
 - » Tannins
 - » Stilbenes
 - » Flavonoids
 - » Lignans

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11

Water Extraction

- Hot water is used to remove the following:
 - » Carbohydrates
 - » Proteins
 - » Alkaloids
 - » Starch
 - » Pectins
 - » Inorganics

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12



Combinations of Methods

- It is important to note, that there is carry over in the methods. For example, resin acids are better removed by ether but are extracted by alcohol.
- A typical extraction series is:
 - » Four hour extraction with ethanol-toluene (1:2)
 - » Four hour ethanol extraction
 - » Single extraction with boiling water.
- Other solvents can be used include acetone (good), dichloromethane, and mixtures of all of the above.



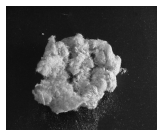
Holocellulose

- Holocellulose is the term which describes the mixture of cellulose and hemicelluloses produced when lignin is removed.
 - » Lignin can be removed through the action of chlorine followed by alcohol extraction.
 - » Another procedure (I like this one) is delignification with acidified solutions of sodium chlorite.
 - » There are a significantly large number of other possible procedures which have been published.
- What is left from these procedures is a very white material which contains a little lignin and has lost a little bit of the carbohydrates.



Holocellulose II

- The idea behind this procedure is that the treatments are very selective to lignin (they attack only the lignin and leave the carbohydrates alone)
- The lignin dissolves in the solution leaving the carbohydrates.
- The truth with these procedures is that you are balancing lignin removal with carbohydrate loss.



Cellulose

- There are three ways to determine the amount of cellulose in plant matter:
 - » Separate the cellulose from hemicelluloses in holocellulose
 - » Separate the cellulose directly from plant matter.
 - » Hydrolyze the plant matter and determine the sugar contents of the solutions



Cellulose Isolation

- A Tappi Standard procedure for cellulose isolation from holocellulose is as follows:
 - » Extract holocellulose with 5% and then 24% KOH to remove hemicelluloses. The remaining material is termed alpha-cellulose
 - This results in cellulose of reduced molecular weight and some yield loss. Typical recoveries are 40-60%
 - » Neutralization of the KOH precipitates beta-cellulose.
 - » The remaining soluble material is gamma-cellulose.



Direct Cellulose Isolation

- It is possible to directly isolate cellulose from plant matter.
 - » Digestion of material in nitric acid and ethanol.
 - » Refluxing material in acetyl-acetone and dioxane acidified with HCl
 - » Treatment of material with chlorine and nitrogen dioxide in DMSO
- These, and other, procedures give high purity but also highly degraded cellulose.



Cellulose Hydrolysis

- Since glycosidic bonds are susceptible to acid hydrolysis, it is possible to hydrolyze wood and analyze the resulting sugars.
- It is necessary to take into account the yield of glucose obtained from the hydrolysis of glucomannans



Cellulose Properties

- There are many procedures used to determine the molecular weight of cellulose and the degree of polymerization.
 - » These procedures deal with procedures which solubilize the cellulose.
 - » I am not actually going to cover these.....just know they exist.
- There are also wet chemistry procedures which are used to determine the presence of functional groups such as carboxyl groups.