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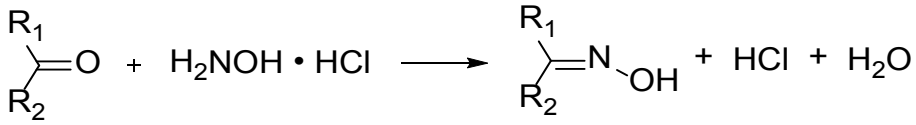
1. Introduction

1.1 While pyrolysis bio-oils are comprised of a large variety of compounds and chemical functional groups, quantification of carbonyl groups is especially important. Carbonyls are known to be responsible for the instability of bio-oil during both storage and processing. The titration method presented here is a simple technique which can reliably quantify the total carbonyl content of bio-oils.

1.2 For analysis of bio-oils, quantification of carbonyl groups by titration has traditionally been accomplished using the method of Nicolaides [1]. This is a simple procedure where carbonyls are converted to the corresponding oxime (see Scheme 1). The liberated HCl reacts with pyridine to force the equilibrium to completion. The conjugate acid of pyridine is titrated with a known amount of NaOH (base titrant). The number of equivalents of NaOH used is stoichiometrically equivalent to the moles of carbonyl present in the bio-oil.

Scheme 1:



1.3 The Nicolaides method, however, has several limitations. It can require reaction times in excess of 48 hours to reach completion. This severely limits sample throughput. It utilizes pyridine, which is toxic. Sample weights of 1 to 2 g are required. Sample weight used is dependent on the amount of hydroxylamine HCl present and the carbonyl content of the sample. If initial estimates of the sample weight used are incorrect, the titration has to be repeated. Furthermore, it has recently been shown that the Nicolaides method significantly underestimates carbonyl content of bio-oils [3].

1.4 Faix, et al. [2] developed a method that has been modified here to address the issues of the Nicolaides method. The reaction is carried out at 80 °C for 2 hours, thereby increasing sample throughput. Pyridine has been replaced with triethanolamine which is a less toxic chemical. The sample size can be reduced to 100 to 150 mg. The triethanolamine consumes the liberated HCl, driving the reaction to completion and the unconsumed triethanolamine is titrated directly. A secondary titration of the hydroxylamine is unnecessary. An in-depth comparison of both of these carbonyl titration methods has recently been published [3].

2. Scope

2.1 The method described here has been modified from the original method [2] to be more applicable to the analysis of pyrolysis bio-oils. This method was developed for the analysis of raw pyrolysis bio-oils, but it has been successfully applied to other types of

biomass-derived oils, including hydrotreated bio-oils. Additionally, this method has been used to monitor changes in carbonyl content during both aging and upgrading.

3. Terminology

3.1 *Bio-oil* – The crude liquid product of converting solid biomass into a liquid via fast pyrolysis or other thermochemical conversion process.

3.2 *Carbonyl* – the chemical functional group consisting of a carbon-oxygen double bond, C=O. For this method, this includes all aldehydes and ketones, but does not include carboxylic or lactone groups.

4. Interferences

4.1 The selectivity of the method was tested by using 1-butanol, 1-pentanol, tertiary butanol, 2-propanol, ethyl acetate, acetic acid, xylose and glucose as model compounds, representing alcohol, ester, carboxylic acid and carbohydrates in the bio-oil.

4.2 No interferences were seen for ethyl acetate or acetic acid. Monosaccharides are measured using this method. Addition of alcohols cause interferences but it is dependent on chain length. The reason is as yet undetermined but may be related to solvent properties of the alcohol.

5. Apparatus

5.1 Analytical balance accurate to 0.1 mg

5.2 Dry block heater with magnetic stirrer or hot water bath with magnetic stirrer

5.3 Automatic titration instrument (Metrohm Titrando 809 or equivalent)

6. Reagents and Materials Needed

6.1 Reagents

6.1.1 Deionized water

6.1.2 Ethanol (reagent grade) (CAS # 64-17-5)

6.1.3 Hydroxylamine hydrochloride (CAS # 5470-11-1)

6.1.4 Triethanolamine (CAS #102-71-6)

6.1.5 Hydrochloric acid (37%) (CAS # 7647-01-0)

6.1.6 Sodium Carbonate (primary standard) (CAS # 497-19-8)

6.1.7 4-(benzyloxy)benzaldehyde (CAS # 4397-53-9)

6.1.8 Dimethyl sulfoxide (CAS # 67-68-5)

6.2 Materials

6.2.1 5 mL glass Reacti-vials (Thermoscientific TS-13223) with solid lid

6.2.2 Teflon spinvane for 5 ml Reacti-vial

6.2.3 200 mL volumetric flask

6.2.4 Volumetric or mechanical pipettes

6.3 Reagent solutions

6.3.1 *Hydroxylamine hydrochloride solution (Solution A)*: Add 7.7 g of hydroxylamine hydrochloride and 50 mL of deionized water to a 250 mL volumetric flask. Swirl till all solids are dissolved, then dilute up to the mark with ethanol.

6.3.2 *Triethanolamine solution (Solution B)*: Add 17.4 mL of triethanolamine to a 250 mL volumetric flask, then dilute up to the mark with ethanol.

6.3.3 *Hydrochloric acid solution*: Either purchase 0.1N solution or prepare using 10 ml concentrated HCl and 1 L water.

7. ES&H Considerations and Hazards

7.1 Ethyl alcohol is flammable.

7.2 Follow all applicable chemical handling procedures.

7.3 Follow all applicable waste disposable and handling procedures.

8. Sampling, Test Specimens and Test Units

8.1 Make sure the oil sample is at room temperature prior to withdrawing a sample. Bio-oil should be thoroughly homogenized to obtain a representative sample.

8.2 The test specimen should consist of 100 to 150 milligrams of bio-oil.

8.3 Exposure to oxygen and heat should be minimized to prevent sample degradation prior to analysis.

9. Analytical Procedure

9.1 Standardization of the base solution.

9.1.1 Prepare primary standard sodium carbonate using standard methods.

9.1.2 Weigh 100 to 150mg of sodium carbonate to a titration vessel, record the actual weight, add a stir bar and add appropriate amount of D.I. water.

9.1.3 Quantitatively transfer the sample to a titration vessel and titrate with the acid solution using an automatic titrator, and record the endpoint.

9.1.4 Repeat the process twice, to obtain three points.

9.1.5 Use the average value as the normality of the acid solution.

9.2 Preparation of titration blanks

9.2.1 Blank A: add 1 mL dimethyl sulfoxide (DMSO) to 5 ml Reacti-vial with spinvane.

9.2.2 Add 2 mL hydroxylamine hydrochloride solution (solution A).

9.2.3 Add 2 ml triethanolamine solution (solution B).

9.2.4 Cap tightly, place in preheated (80 °C) heater block or water bath and stir for 2 hours.

9.2.5 Titrate with acid solution using an automatic titrator and record endpoint.

9.2.6 Blank B: If mineral acid is suspected to be present in sample, add 1 mL DMSO to 5 mL Reacti-vial with spin vane.

9.2.7 Add 2 mL triethanolamine solution (solution B).

9.2.8 Cap tightly and stir at 80 °C for 2 hours.

9.2.9 Quantitatively transfer the sample to a titration vessel and titrate with acid solution and record endpoint.

9.2.10 Repeat process three times to obtain three points.

9.3 Validation of the method using a known carbonyl.

9.3.1 Weigh ~ 100mg of 4-(benzyloxy)benzaldehyde (4-BBA) to a Reacti-vial, record the actual weight, add a spinvane.

9.3.2 Add 1 mL DMSO.

9.3.3 Dissolve the sample in 2 mL hydroxylamine hydrochloride solution (solution A).

9.3.4 Add 2 ml triethanolamine solution (solution B).

9.3.5 Close lid tightly and stir at 80 °C for 2 hours.

9.3.6 Quantitatively transfer the sample to a titration vessel with ethanol and water to make a solution of 80% ethanol and titrate with the acid solution using an automatic titrator, and record the endpoint.

9.3.7 Repeat the process three times, to obtain three points.

9.4 Analysis of bio-oil using the method

9.4.1 Weigh close to 100 mg of the bio-oil to Reacti-vial, record the actual weight and add a spinvane.

9.4.2 Add 1 mL DMSO.

9.4.3 Dissolve the sample in 2 mL hydroxylamine hydrochloride solution (solution A).

9.4.4 Add 2 ml triethanolamine solution (solution B).

9.4.5 Close lid tightly and stir at 80 °C for 2 hours.

9.4.6 Quantitatively transfer the sample to a titration vessel with ethanol and water to make a solution of 80% ethanol and titrate with the acid solution using an automatic titrator, and record the endpoint.

9.4.7 Repeat the process three times, to obtain three points.

9.4.8 Blank C: If mineral acid is suspected to be present in sample, Weigh close to 100 mg of the bio-oil into a Reacti-vial, record weight and add a spinvane.

9.4.9 Add 1 mL DMSO.

9.4.10 Add 2 mL triethanolamine solution (solution B).

9.4.11 Cap tightly and stir at 80 °C for 2 hours.

9.4.12 Quantitately transfer the sample to a titration vessel with ethanol and water to make a solution of 80% ethanol and titrate with acid solution and record endpoint.

9.4.13 Repeat process three times to obtain three points.

9.5 Other considerations

9.5.1 Blanks B and C are unnecessary if only organic acids are present in the bio-oil sample.

9.5.2 4-(benzyloxy)benzaldehyde (4-BBA) has a sufficiently high molecular weight to use approximately the same amount as a bio-oil sample. Other models may be used.

9.5.3 An 80% solution of ethanol is not necessary for the transfer of the sample to the titration vessel. Only a final volume of 80% ethanol is needed.

9.5.4 Titration of the sample following oximation should be done within 2 to 8 hours. Triethanolamine can form triethanolamine•HCl which will result in an error in the measurement.

9.5.5 Faix, et al. [2] mix the triethanolamine and hydroxylamine hydrochloride solutions to make a stock solution. This leads to the formation of triethanolamine•HCl which will result in a measurement error.

10. Results

10.1 The following Tables can be used as a guide to record the data.

10.2 Standardize the base solution:

Purity of Na_2CO_3		%
	Na_2CO_3 weight (g)	Endpoint (mL)
Run #1		
Run #2		
Run #3		

10.3 Blank endpoint volume. Repeat as necessary for all blanks:

	Endpoint (mL)
Run #1	
Run #2	
Run #3	

10.4 Validation of the method using 4-(benzyloxy)benzaldehyde (4-BBA):

Purity of 4-BBA		%
	4-BBA (g)	EP(mL)
Run #1		
Run #2		
Run #3		

10.5 Analysis of bio-oils:

	Bio-oil weight (g)	Endpoint (mL)
Run #1		
Run #2		
Run #3		

10.5.1 A typical titration curve consists of single endpoint.

10.5.2 If the software in incapable of detecting the endpoint, the 1st derivative of the titration curve can be constructed using a standard graphing program.

11. Calculations

11.1 Standardization of the base solution.

11.1.1 If the weight of the dry sodium carbonate in grams is w1, the purity (written as a fraction, i.e., 99% is 0.99), and the endpoint in mL, the concentration of the acid solution (mol/L) is given by:

$$[acid] = (1000 * w_1 * purity\ of\ \mathrm{Na2CO3})/(105.9885 * endpoint)$$

11.2 Validation of the method using a known carbonyl.

11.2.1 If the weight of the 4BBA in grams is w2, the purity (written as a fraction, i.e., 99% is 0.99) is known, the concentration of the acid solution is [acid], triethanolamine/hydroxylamine•HCl blank is EP_{BA} (the average value of three blanks, in mL) and the endpoint is EP (in mL); the concentration of 4BBA (mol/L) in the sample is given by:

$$[4BBA] = \left(\frac{(EP_{BA} - EP)}{w_2}\right) * [acid]$$

11.3 Analysis of bio-oil

11.3.1 If the weight of the bio-oil in grams is w3, the concentration of the acid solution is [acid], triethanolamine/hydroxylamine•HCl blank is EP_{BA} (the average value of three blanks in mL) and the endpoint is EP (in mL); the concentration of carbonyls in bio-oils [CO] (mmol/g-bio oil) is given by:

$$[CO] = \left(\frac{(\mathrm{EP}_{BA} - EP)}{w_3}\right) * [acid]$$

11.4 Acid correction

11.4.1 The presence of mineral acids or organic acids with pKa < 2 can cause artificially low carbonyl values due to the reaction of the acid with triethanolamine. If this is suspected, blanks detailed in sections 9.2.6 and 9.4.8 should be performed. The weight of bio-oil in the sample in grams is w_3, EP is the endpoint of the sample and EP_{BA} is the triethanolamine/hydroxylamine blank. EP_{BB} is the endpoint of Blank B, EP_{BC} is endpoint of Blank C and the weight (g) of oil used in Blank C is w_{BC}:

$$[CO_{corrected},] = \left(\frac{(EP_{BA} - EP)}{w_3} - \frac{EP_{BB} - EP_{BC}}{w_{BC}}\right) * [acid]$$

For bio-oil samples that contain mostly acetic acid, this is an unnecessary step.

12. Report Format

12.1 Report the concentration of carbonyls in bio-oils as mmol of CO per gram of bio-oil. The standard deviation may also be reported.

13. Precision and Bias

13.1 In 2015, an inter-laboratory study was performed on a raw pyrolysis bio-oil using the method as described here [4]. It was found that the Faix carbonyl method presented here was especially reliable, with < 5% RSD variability between all participating laboratories.

14. Quality Control

14.1 To ensure proper operation, validation with a known carbonyl (9.3) should be performed periodically.

14.2 Replicates: Run all samples in triplicate.

15. References

[1] Nicolaides, G. M. (1984). *The chemical characterization of pyrolytic oils*. MASc Thesis, Dept. of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada, (1984)

[2] Faix, O., B. Andersons and G. Zakis, *Determination of Carbonyl Groups of Six Round Robin Lignins*. Holzforschung, 1998. 52: p. 268-272

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[4] Ferrell, J.R. III; Olarte, M.V; Christensen, E.D.; Padmaperuma, A.B.; Connatser, R.M.; Stankovikj, F.; Meier, D.; Paasikallio, V. *Standardization of Chemical Analytical Techniques for Pyrolysis Bio-oil: History, Challenges, and Current Status of Methods*. Biofuels, Bioproducts & Biorefining 2015, submitted.