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1. Introduction

1.1 This laboratory analytical procedure covers the determination of acidic content of bio-oils using potentiometric titration with automatic end point detection. Acids in bio-oils contribute to corrosion of materials used during storage and handling. Reduction of acids is one important aspect of oil upgrading, which can be monitored using this methodology.

1.2 This methodology is based on the ASTM standard method D664, test method B for determination of acid content of petroleum products [1]. Modifications to the standard method have been made to improve detection of phenolic content of bio-oils. The modifications are the replacement of potassium hydroxide titrant with tetrabutyl ammonium hydroxide (TBAOH) and replacement of the lithium chloride electrolyte solution with tetraethyl ammonium bromide (TEABr). This combination of titrant and electrolyte has been found to improve detection of phenolics over the standard methodology [2].

2. Scope

2.1 This procedure is developed for the determination of both carboxylic acid numbers (CAN) and total acid numbers (TAN) of bio-oils. Total acid number includes carboxylic acids as well as weaker acidic compounds such as phenolics. As such, the results of this procedure can be used to differentiate carboxylic acids from other acidic components such as phenolics.

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 *End Point* – The point of inflection in a titration curve (plot of pH vs titrant volume) recorded by automatic titrator software. The point of inflection can be determined from the derivative of the titration curve.

3.3 *Carboxylic acid number (CAN)* – The portion of acidic content of bio-oil that can be attributed to carboxylic acids expressed as mg KOH/g of sample.

3.4 *Total acid number (TAN)* – The total amount of acidic content of a bio-oil determined by titration, expressed as mg KOH/g of sample.

4. Interferences

4.1 Bio-oils can coat the pH electrode used to monitor the progress of titration. It is imperative that the pH probe be cleaned thoroughly between titrations to maintain adequate signal for analysis.

4.2 Bio-oils are known to degrade over time when exposed to oxygen and heat. Samples that have aged may not be representative of the original bio-oil product.

4.3 Identification of the second endpoint (TAN) can be troublesome for some bio-oils. Limiting TAN identification to a specific pH window is necessary for a reliable analysis using this method. This pH window is defined below for an oak-derived raw pyrolysis bio-oil.

5. Apparatus

5.1 Analytical balance accurate to 0.1 mg

5.2 Ultrasonic bath (Branson 3510 or equivalent)

5.3 Automatic titration instrument including stirring plate and automatic burette (Metrohm Titrando 809 or equivalent)

5.4 Combination pH electrode (Metrohm 6.0229.010 Solvotrode or equivalent)

6. Reagents and Materials Needed

6.1 Reagents

6.1.1 Isopropyl alcohol (VWR BDH20880 or equivalent)

6.1.2 Tetrabutyl ammonium hydroxide (TBAOH), 0.1 M in 10:1 (v/v) isopropyl alcohol/methanol (Sigma-Aldrich 86891)

6.1.3 Tetraethyl ammonium bromide, 0.4 M in ethylene glycol (Metrohm 6.2320.000 or equivalent)

6.1.4 Potassium hydrogen phthalate (KHP) (Sigma-Aldrich 179922 or equivalent). Dried for a minimum of 2 hours at 120 °C.

6.1.5 Deionized (DI) water, 18.2 MΩ

6.1.6 Phenol (Sigma-Aldrich P5566 or equivalent)

6.1.7 Glacial acetic acid (Sigma-Aldrich 320099 or equivalent)

6.1.8 pH 4 buffer (Metrohm 6.2307.100 or equivalent)

6.1.9 pH 7 buffer (Metrohm 6.2307.110 or equivalent)

6.1.10 pH 9 buffer (Metrohm 6.2307.120 or equivalent)

6.2 Materials

6.2.1 Glass jars, 120 mL (VWR 16151-622 or equivalent)

6.2.2 Disposable plastic beakers, 120 mL

6.2.3 Teflon lined stir bars

6.2.4 Volumetric flask, 50 mL (Class A)

7. ES&H Considerations and Hazards

7.1 Isopropyl alcohol is extremely flammable

7.2 Acetic acid is corrosive and flammable

7.3 Tetrabutyl ammonium hydroxide is corrosive

7.4 Phenol is a significant health hazard

7.5 Follow all applicable chemical handling procedures

8. Sampling, Test Specimens and Test Units

8.1 Bio-oil should be allowed to reach room temperature and thoroughly homogenized to obtain a representative sample.

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

9. Analytical Procedure

9.1 pH calibration

9.1.1 Following the instrument manufacturer's instructions to calibrate the pH range of the pH probe using the pH 4, 7, and 9 buffers.

9.1.2 The slope of the calibration must be ≥ 95%.

9.1.3 The difference between the mV reading of the pH 4 and pH 7 buffer must be ≥ 162 mV.

9.1.4 A slope below 95% or reading difference between pH 4 and 7 below 162 mV indicate the pH probe requires maintenance or should be replaced. Follow manufacturer's instructions for cleaning and maintaining the pH probe.

9.2 Prepare KHP solution for titrant standardization

9.2.1 Into 50 mL volumetric flask weigh approximately 100 mg of dried KHP and record weight to 0.1 mg.

9.2.2 Fill volumetric flask with DI water to the graduation mark and record weight of water to 0.1 mg.

9.2.3 Place mixture into ultrasonic bath at 30°C and sonicate until dissolved, approximately 5 minutes.

9.2.4 Alternatively, dried KHP can be titrated directly as in 9.3.2.

9.3 Standardize titrant

9.3.1 Into a 120 mL glass jar weigh approximately 5 g of KHP solution and record weight to 0.1 mg.

9.3.2 Alternatively, into a 120 mL glass jar weight approximately 100 mg dried KHP powder and record weight to 0.1 mg. Add 5 mL DI water and ensure KHP is fully dissolved.

9.3.3 Add 50 mL of DI water to glass jar.

9.3.4 Add stir bar and titrate solution with 0.1 M TBAOH while stirring. A total titrant volume of 2 mL is recommended if titrating the KHP solution as in 9.3.1. A titrant volume of 10 mL is recommended if titrating dried KHP powder as in 9.3.2. Determine the potentiometric end point using the automatic titrator software. Record volume of titrant and determine molarity as in 10.2.

9.3.5 Determine molarity in triplicate. The average value of triplicate determinations should be used to determine acid numbers. The average value should agree ± 0.0005 M of each reading.

9.4 Blank titration

9.4.1 Add 50 mL isopropyl alcohol to a disposable 120 mL beaker and add stir bar.

9.4.2 Titrate solution using 0.1 M TBAOH while stirring. A total titrant volume of 2 mL is recommended. Record titrant volume of potentiometric end point.

9.4.3 Note that the blank may not contain sufficient acidic content to be detected, resulting in an invalid result by the titration software. In this case the blank titration volume is 0 mL.

9.5 Sample titration

9.5.1 Into a disposable 120 mL beaker weigh 200 ±50 mg of sample and record weight to 0.1 mg.

9.5.2 Add 50 mL of isopropyl alcohol and a stir bar.

9.5.3 Titrate solution with 0.1 M TBAOH while stirring. A total titrant volume of 15 mL is recommended. Record titrant volume of potentiometric end points.

9.5.4 For bio-oils containing only carboxylic acids one endpoint will be detected. For bio-oils containing both carboxylic acids and phenolics multiple end points may be detected. The pH reading of carboxylic acids in isopropyl alcohol is in the range of 8 to 11 and for phenolics between 12 and 14. pH readings of individual systems may vary depending on pH calibration, pH probe, and sample size titrated. Individual systems should be checked with model compounds to ensure accurate detection of compound types. Mixtures of acetic acid and phenol have been found to be sufficient for determining pH ranges. Alternatively, multifunctional compounds such as syringic acid (4-Hydroxy-3,5-dimethoxybenzoic acid) or vanillic acid (4-Hydroxy-3-methoxybenzoic acid) can be used.

9.5.5 After each titration, thoroughly rinse the pH probe with isopropyl alcohol to remove any residue. After isopropyl alcohol rinse soak the probe in DI water for at least 3 minutes prior to the next titration.

9.6 Standard mixture for system check

9.6.1 Into a 50 mL volumetric flask weigh approximately 400 mg of phenol and 400 mg acetic acid and record weights to 0.1 mg. Fill flask to the graduation mark with isopropyl alcohol and record weight to 0.1 mg. Invert flask a minimum of 3 times to mix. If phenol is not fully dissolved approximately 1 minute of sonication should complete dissolution.

9.6.2 Into a 120 mL glass jar weigh approximately 1 g of standard mixture. Add stir bar and titrate following procedure used for bio-oils.

9.6.3 Alternatively, multifunctional compounds such as syringic acid or vanillic acid can be weighed individually and titrated to check the system.

9.6.4 Compare measured carboxylic acid and phenol concentrations in mmol/g to known values. Measured values should not differ from actual by greater than 5 % for carboxylic acid and 10 % for phenol.

10. Calculations

10.1 KHP solution:

$$KHP_{mmol/g} = (KHP_g * 1000)/[204.23_{g/mol} * (KHP_{\ g} + water_g)]$$

10.2 Titrant molarity:

If titrating KHP solution as in 9.3.1:

$$M = \frac{\left(KHP\ Solution_{g} * KHP_{\frac{mmol}{g}}\right)}{titrant\ volume_{mL}}$$

If titrating dried KHP powder as in 9.3.2:

$$M = \frac{(KHP_g)}{(titrant\ volume_{mL} * 204.23_{g/mol})}$$

10.3 Standard mixture:

$$Acetic\ acid_{\frac{mmol}{g}} = \frac{Acetic\ acid_g * 1000}{60.05_{\frac{g}{mol}} * total\ weight_g}$$

$$Phenol_{mmol/g} = (Phenol_g * 1000)/(94.11_{\frac{g}{mol}} * total\ weight_g)$$

10.4 Acid number:

$$AN_{mg\ KOH/g} = \frac{(V_T - V_b) * M * 56.1_{g/mol}}{W}$$

Where:
V_T = Titrant volume to generate end point in mL
V_b = Titrant volume for solvent blank in mL
M = Titrant molarity in mol/L
W = Sample weight in grams

10.5 % Relative Standard Deviation (%RSD)

$$\%RSD = \left(\frac{\sigma}{mean}\right) * 100$$

Where:
σ = the standard deviation of concentration from replicate analyses
mean = the average concentration determined from replicate analyses

11. Report Format

11.1 Report CAN and TAN as mg KOH/g of sample.

12. Precision and Bias

12.1 In 2015, an inter-laboratory study was performed on a raw pyrolysis bio-oil using the method as described here [3]. The first endpoint, CAN, had very low inter-laboratory variabilities (less than 5% RSD). In the round robin study, only three of the five labs were able to successfully identify the TAN endpoint. While the TAN variability was low between the three reporting labs (less than 2% RSD), the results showed that TAN identification can be problematic. Due to these difficulties, it is critical that the user follow all instructions carefully to obtain reliable results, including the pH windows for the identification of CAN and TAN endpoints.

13. Quality Control

13.1 The 0.1 M TBAOH titrant should be standardized weekly to monitor for any changes in titrant concentration due to reaction with carbon dioxide. When not in use the titrant should be stored in the dark in a closed container. Exposure to carbon dioxide should be avoided to prevent degradation.

13.2 It is recommended that a representative bio-oil or standard solution containing acetic acid and phenol be analyzed with each sample set to provide a daily check standard. Results of this standard should be tracked to monitor for out of control results.

13.3 A minimum of 1 sample per sample set should be analyzed in triplicate. % RSD of CAN should not exceed 5 % and TAN should not exceed 10 %.

14. References

[1] ASTM D664-11a, *Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration*. 2011, ASTM International: West Conshohocken, PA.

[2] Christensen, E., G. M. Chupka, J. Luecke, T. Smurthwaite, T. L. Alleman, K. Iisa, J. A. Franz, D. C, Elliott, and R. L. McCormick, *Analysis of Oxygenated Compounds in Hydrotreated Biomass Fast Pyrolysis Oil Distillate Fractions*. Energy & Fuels, 2011. 25(11): p. 5462-5471.

[3] 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.