

Humic Acid Analysis

1. Scope:

This method may be used for solid samples containing at least 0.5% humic acid, and for liquids containing at least 0.05% humic acid.

2. Principle:

Humic acids are dissolved using 0.5N sodium hydroxide and are then precipitated with hydrochloric acid.

Samples are prepared according to RA-SP-SMPL-PREP.

3. Safety

Read all SDS before proceeding with analysis. Hydrochloric acid and sodium hydroxide are corrosive and will cause severe skin burns and serious eye damage. They shall be used in a fume hood. Proper PPE (gloves, safety glasses, lab coat, etc.) shall be worn when handling these items.

4. Apparatus and Equipment:

- 4.1. Centrifuge
- 4.2. 100mL centrifuge bottles with screw caps
- 4.3. 100-110°C drying oven
- 4.4. Mechanical shaker

5. Reagents and Supplies:

- 5.1. 0.5N NaOH (20g NaOH in 1L H₂O)
- 5.2. 1% NaOH (10g NaOH in 1L H₂O)
- 5.3. HCl, concentrated (37%)

6. Analysis:

- 6.1. Prepare 3.7% HCl by combining 100mL concentrated HCl in 1L H₂O.
- 6.2. Mix dry samples thoroughly by rotating the jar and liquid samples by shaking the container.
- 6.3. Prepare a QC sample by weighing ~1g of a laboratory control sample (LCS) and subject it to the same process as the samples.

- 6.4. Verify the analytical balance.
- 6.5. Weigh 1-5g of sample (based on guarantee) into a 100ml wide mouth screw top centrifuge bottle. Lower sample weights can be taken for samples with higher guarantees.
- 6.6. Add 50mL 0.5N NaOH and seal tightly.
- 6.7. Shake on mechanical shaker for at least 1 hour.
- 6.8. Rinse the cap with 5-10mL 1% NaOH (ensuring all the sample has been rinsed off) and centrifuge for ~20 minutes at ~2000 rpm.
- 6.9. Decant supernatant liquid into a second, previously weighed centrifuge bottle.
- 6.10. Rinse the precipitate at the bottom of the bottle by adding 5-10mL 1% NaOH (based on the amount of precipitate) to first bottle, shake vigorously, and centrifuge.
- 6.11. Again, decant the supernatant into the second bottle. Discard the first bottle with the precipitate.
- 6.12. Add enough HCl (~10mL) to the combined extracts in the second bottle to lower the pH to < 1.
- 6.13. Centrifuge the sample for ~20 minutes at ~2000 rpm.
- 6.14. Carefully decant and discard the liquid.
- 6.15. Add 25mL of 3.7% HCl (prepared in step 6.1) to the bottle, cap and shake vigorously to free all precipitate from the bottom, and centrifuge again.
- 6.16. Carefully decant and discard the liquid.
- 6.17. Repeat steps 6.15 and 6.16.
- 6.18. Dry the bottle with humic acid overnight at 100-110°C.
- 6.19. Cool in a desiccator 2-3 hours and weigh.

7. Calculations:

$$\% \text{ Humic Acid} = \frac{\text{Weight of Dried Residue}}{\text{Sample Weight}} \times 100$$

8. QA/QC:

Run a reference material obtained from the International Humic Substances Society or a well-characterized humic acid sample as an LCS. For the International Humic Substances Society Reference Material, an acceptable recovery is $\geq 90\%$. For a well characterized humic acid sample, an acceptable recovery is $\pm 10\%$ of the average value (based on a minimum of 10 results).

If a sample result fails below the guarantee, the results should be verified by rerunning with differing amounts of sample. A suggested scheme is to rerun using sample weights within the range of 0.5g – 25g. If the results are higher with the higher weight samples than the original, continue running higher levels until the guarantee is met or the results come back at a consistent level.

The minimum reporting limit for solid samples is 0.5%, and for liquid samples is 0.05%.

9. References:

- 9.1. John Husler, Univ. of New Mexico, Dept of Geology, Albuquerque, New Mexico, A.L. Page, Methods of Soil Analysis, Part 2, American Society of Agronomy, Inc., Madison, Wisconsin. 1982
- 9.2. R.S. Swift, Methods of Soil Analysis Part 3, American Society of Agronomy, Inc., Madison, Wisconsin. 1996.

California Department of Food and Agriculture
Center for Analytical Chemistry
Regulatory Analysis Laboratory
3292 Meadowview Road
Sacramento, CA 95832

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Approvals:

Revised By:

Chugiao Tu
Chugiao Tu
Senior Environmental Scientist (Specialist)

8/5/21
Date

Approved By:

Stacy Aylesworth
Stacy Aylesworth
Senior Environmental Scientist (Supervisor)

8/5/21
Date

Maryam Khosravifard
Maryam Khosravifard
Environmental Program Manager I

8/5/21
Date

Sarva Balachandra
Sarva Balachandra
Quality Assurance Officer

8/19/21
Date

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