

BEST PRACTICE FOR DETERMINING LOW FREE FORMALDEHYDE LEVELS IN PHENOL FORMALDEHYDE RESIN (RESOLES) USING EN 11402:2004-MODIFIED

Based on the results of a series of round robin test carried out in April 2016 and analytical tests performed by members of the European Phenolic Resins Association Regulatory and Safety Committee, the following procedure is recommended for the determination of low level free formaldehyde (< 0.2 wt%) in Phenol Formaldehyde Resole Resins, based on a modified version of UNI EN ISO 11402:2004 (Resole resins in water or methanol/water solvent).

1. Test temperature

All tests should be carried out at 23°C +/- 1 °C

2. Test sample preparation

Weight a test sample (+/-0.1 mg) of resole resin of sufficient mass to achieve a titration difference of $V_1 - V_0$ (see below) of more than 3 ml. Add the test sample to a 250 ml titration flask.

Note: If the titration difference is <3 ml the weight of the test sample should be increased appropriately.

3. Analytical Procedure

3.1 Test Sample Titration

(a) Add 50 ml of solvent^{*1} to the titration flask containing the test sample and place a magnetic stirring bar in the flask. Place on a magnetic stirrer and stir until the resin has dissolved and the temperature has stabilized at 23°C +/- 1 °C.

^{*1} *Recommended solvent:*

- *Aldehyde and ketene free Methanol, or*
- *IPA/water - 3 volumes of aldehyde and ketenes free propan-2-ol and 1 volume of water.*

Note: The accuracy of the formaldehyde determination depends on accurate pH measurement and therefore a minimum water content of 10 wt% is required in the system. Default solvent for this method is Methanol, however for Resole Resins with a low water content the use of the IPA/water solvent is highly recommended.

(b) Using a pH-meter adjust the pH of the resin/solvent solution to 3.5 using 0.1 mol/l hydrochloric acid for neutralized resin, or 1 mol/l hydrochloric acid for highly alkaline resins.

(c) Using a pipette, add approx. 25 ml of hydroxylamine hydrochloride solution at 23°C +/- 1 °C, and stir for 10mins +/- 1 min.

(d) Titrate quickly to pH 3.5 using 0.1 mol/l hydrochloric acid. Record the titration volume as V_1 .

3.2 Blank Titration

Carry out a blank titration in parallel to the test sample titration following the same procedure as above, but omitting the test portion. Record the titration volume as V_0 .

4. Calculation of Results

Calculate the free formaldehyde content as a percentage by mass using the equation:

$$\text{Free formaldehyde} = 0.3002 * (V_1 - V_0) / \text{mass}$$

Where:

- V_0 = titration volume of sodium hydroxide in ml from the blank titration
- V_1 = titration volume of sodium hydroxide in ml from the test titration.
- Mass = mass of the test portion in grams

Notes:

- (i) All measurements of free formaldehyde should be carried out in duplicate.
- (ii) All test equipment should be calibrated and checked prior to use.
- (iii) All tests should be performed quickly, continuously and without interruption.

5. Analytical Sensitivity

The minimum quantity of free formaldehyde measurable using this technique:

0.029 wt%

6. Analytical Repeatability

The analytical repeatability of the technique with a confidence level of 95 % (2x STD) is:

0.007 wt% (as Free Formaldehyde) in water

0.021 wt% (as Free Formaldehyde) in resole

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