

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

Based on the results of a series of round robin test carried out in 2020-21 and analytical tests performed by members of the European Phenolic Resins Association Regulatory and Safety Committee, the University of Santiago (ES), the following procedure is recommended for the determination of low level free formaldehyde (< 0.2 wt%) in Phenol Urea Formaldehyde Resole Resins (with more than 1 % of urea), 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 10 °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 methanol, or 50 ml of 3 volumes of propan-2-ol and 1 volume of water, 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 10°C +/- 1 °C.

*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 10 °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:

0.01 wt%

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