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Short Communication: Analysis method

# A methodology free of pyridine for measuring hydroxyl value in polymers and oils

Edson Fernandes [a], Jéssica Vicente [a], Rogério Cruz [a,b], Márcio Nele [a,*],
Érika Nunes [a], Rodrigo Costa-Félix [b]

[a] Departamento de Engenharia Química, Escola de Química, Universidade Federal do Rio de Janeiro, Cidade Universitária, CP 68502, Rio de Janeiro 21945-970, RJ, Brazil
[b] Laboratório de Ultra-Som, Diavi/Dimci/INMETRO, Duque de Caxias, RJ, Brazil

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ABSTRACT

This paper presents a new methodology, free of pyridine (PY), for measuring the hydroxyl value ($I_{OH}$). Solid catalysts and solvents of lower toxicity than PY were tested. Imidazole (IMID) provided an $I_{OH}$ measurement comparable to the standard method. The relative standard deviation of the proposed method in relation to the standard method was less than 1% in most of the twenty-three samples tested. The new method is presented as a safer, reliable and inexpensive alternative to determine the $I_{OH}$ in different compounds.

## 1. Introduction

The hydroxyl value ($I_{OH}$) is the amount of potassium hydroxide (KOH), expressed in milligrams, required to neutralize the acid formed by acetylation of the hydroxyl groups present in 1 g of a sample [1,2]. Its determination has as the main objective the characterization of the crosslinking efficiency in polymer synthesis, and quality control of raw materials such as polyols, vegetable oils and polyurethanes with free hydroxyl groups [3].

The methods used to determine the $I_{OH}$ value can be divided into chemical and spectroscopic methods. The spectroscopic determinations require expensive equipment, specialized technicians and certified standards to correlate the sample spectra to hydroxyl concentration using multivariate calibration approaches. In nuclear magnetic resonance analysis, the overlapping of chemical shifts can make integration difficult [4], and thus provide inaccurate values. Likewise, when using infrared spectroscopy, the regions of the deformation of O–H may overlap with others, such as C–H and N–H [5], which causes uncertainty in the measurement of the selected band.

Chemical methods are based on derivatization to hydroxyl groups using excess anhydride, most commonly acetic and phthalic anhydrides, in the presence of amine bases, acids (organic or mineral) or oxides of transition metals as catalysts [1,2,6–9]. After the reaction, the acid generated by hydrolysis of the anhydride is titrated with a standardized basic solution and $I_{OH}$ is calculated as the difference between the volumes of KOH used to titrate the blank and the sample. The sample acidity can change the $I_{OH}$ value by consuming more titrant, and corrections are usually necessary.

The main chemical methods use PY as both reaction solvent and catalyst-activator of the acylation reagent [10–12]. This is a complicating factor in the laboratory because of the high toxicity of PY; potentially it can cause several damages to human health and the environment. Furthermore, pyridine

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[*] Corresponding author.
*E-mail address:* nele@eq.ufrj.br (M. Nele).

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does not dissolve completely certain analytes, such as polyurethanes and polyacrylates, which interfere directly with the reliability of the result. Other amine bases, such as 4-dimethylaminopyridine and 4-pyrrolidinopyridine, are also cited in the literature but have not been widely used because of their high cost and the promotion of side reactions detectable by rapid discoloration of the acylation reagent. Although it is possible to find works that employ imidazole and derivatives as catalyst, they still use pyridine as the reaction solvent [10,13].

This work reports a method for determining the $I_{OH}$ value using less toxic reagents and solvents but that allows accurate and reproducible measurements, comparable to the methods of the International Organization for Standardization (ISO), American Oil Chemists' Society (AOCS) and ASTM International.

## 2. Experimental

### 2.1. Materials

Ethyl acetate, *n*-Amyl acetate, benzoic acid, ethanol 95% v/v, anhydride acetic, *i*-propanol, phenolphthalein, KOH (85% purity), imidazole, morpholine, N,N-dimethylformamide, phosphorus pentoxide, pyridine and quinoline were purchased from Vetec Química (Rio de Janeiro, Brazil). 1,4-butanediol (>99% purity) was purchased from Sigma–Aldrich (São Paulo, Brazil). Trimethylolpropane was purchased from Arinos (São Paulo, Brazil). Cordaflex® (UC125, SC980 and SC1752) were purchased from Scandiflex (São Paulo, Brazil). PPG1000 and Voranol® 2110, 450N and 4730N were purchased from Dow Chemical (São Paulo, Brazil). Lupraphen® VP9000 and 8020 were purchased from BASF (São Paulo, Brazil). YF® 210, 304 and 330 were purchased from Nantong Yifeng (China). Dehydol K28B was purchased from Cognis (São Paulo, Brazil). Renex® 300, Ultramona® RH400 and ULTROL® CE200F were purchased from Oxiteno (São Paulo, Brazil). Castor oil was purchased from Campestre Óleos Vegetais (São Paulo, Brazil). Polyurethanes were purchased from Polink (Rio de Janeiro, Brazil) and Comercial Stall (Pinhais, Paraná). BYK® 330 was purchased from Bandeirante Brazmo (São Paulo, Brazil). All reagents and solvents were used as received except benzoic acid, which was dried for 24 h in a desiccator containing phosphorus pentoxide.

### 2.2. Methods

Acetylation solutions (100 ml) containing 15 mmols of catalyst (morpholine or quinoline) and 25 mL of anhydride acetic ($Ac_2O$) were prepared in N,N-dimethylformamide. Similar solutions were prepared containing IMID, but in different solvents (N,N-dimethylformamide, ethyl acetate and *n*-amyl acetate). These acetylation solutions were compared to the standard acetylation solution composed of pyridine and acetic anhydride (1:3 v/v). The titration solution, a 0.5 M KOH solution in EtOH 95% v/v, was standardized against benzoic acid. All solutions were stored in dark bottles in a refrigerator and used within two weeks.

The prescribed amounts of the acetylation solution and sample were added to a round bottom flask according to the $I_{OH}$ expected (Table 1) [1,2]. The mixture was refluxed using an oil bath for 1 h. When the reaction medium viscosity did not allow proper reflux conditions to be reached, an extra amount of 25 ml of N,N-dimethylformamide was added to the flask. After 1 h, 10 ml of distilled water was added to the flask and the reflux maintained for 10 min.

**Table 1**
Amounts of sample and acetylating solution used.

| $I_{OH}$ expected | Sample (g) | Acetylation solution (mL) |
|---|---|---|
| 0–20 | 10 | 5[a] |
| 20–50 | 5 | 5[a] |
| 50–100 | 3 | 5 |
| 100–200 | 2 | 5 |
| 200–250 | 1 | 5 |
| 250–350 | 0.5 | 10 |
| 350–700 | <0.5 | 10 |
| >700 | <0.5 | 15 |

[a] 25 ml of DMF was further added to reduce reaction medium viscosity.

Finally, the heating was removed and the system was allowed to cool to room temperature. The condenser and the sides of flask were washed with 15 mL of *i*-propanol previously neutralized and containing 1 ml of phenolphthalein solution (1% w/v in EtOH). The mixture in the flask was titrated with the 0.5N ethanolic KOH solution and the $I_{OH}$ was calculated using Equation (1):

$$I_{OH} = \frac{(B-S)\cdot N\cdot 56,11}{W} \quad (1)$$

where $B$ and $S$ are the volumes in ml of KOH solution consumed by the blank and sample, $N$ is the normality of the KOH solution and $W$ is the sample weight (g) added to the acetylation.

## 3. Results and discussion

The absence of toxic fumes and unpleasant odor from chemical reagents is beneficial to the analysis. Among the substances normally used in determining the $I_{OH}$, PY is the one that has the highest toxicity and also a pungent odor. The main objective of this work is to replace it with amine bases of lower toxicity.

Initially, a polyol (PPG1000) was used to evaluate the effectiveness of the proposed acetylation solutions, the measured $I_{OH}$ mean values (in triplicate) are showed in Table 2. It can be observed that different results were obtained for each amine base. The measured $I_{OH}$ value using PY and IMID are similar and within the range prescribed by the manufacturer. Quinoline, despite having a $pK_b$ value close to PY, provided very low values, indicating

**Table 2**
$I_{OH}$ values measured with the alternative bases and manufacturer specification range ($I_{OH}$ theoretical).

| Bases | $pK_b$ | $I_{OH\ theoretical}$ | $I_{OH}$ |
|---|---|---|---|
| Pyridine | 8.75 | 107–115 | 108.07 |
| Imidazole | 7.05 | | 107.64 |
| Morpholine | 5.50 | | 57.57 |
| Quinoline | 9.50 | | 7.03 |