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Facile electrochemical method and corresponding automated instrument for the detection of furfural in insulation oil

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ABSTRACT

Determining the concentration of furfural contained in the insulation oil of a transformer has been established as a method to evaluate the health status of the transformer. However, the detection of furfural involves the employment of expensive instruments and/or time-consuming laboratorial operations. In this paper, we proposed a convenient electrochemical method to make the detection. The quantification of furfural was realized by extraction of furfural from oil phase to aqueous phase followed by reductive detection of furfural with differential pulse voltammetry (DPV) at a mercury electrode. This method is very sensitive and the limit of detection, corresponding to furfural contained in oil, is estimated to be 0.03 μg g^{-1}. Furthermore, excellent linearity can be obtained in the range of 0–10 μg g^{-1}. These features make the method very suitable for the determination of furfural in real situation. A fully automated instrument that can perform the operations of extraction and detection was developed, and this instrument enables the whole measurement to be finished within eight minutes. The methodology and the instrument were tested with real samples, and very favorable agreement between results obtained with this instrument and HPLC indicates that the proposed method along with instrument can be employed as a facile tool to diagnose the health status of aged transformers.

1. Introduction

Power transformers are essential equipments in power system. Transformer failures whilst in service, which can result in significant economic loss for the power supplier or even severe injury or death of human beings, have occurred in the past. Thus, regular diagnosing of the health status of transformer is critical important, especially for the aged transformers. A typical transformer incorporates coils of conducting wire which is wrapped around a core and covered with a paper-based insulator. The system is immersed in insulation oil, which can serve as insulating and heat dissipation function. Investigations indicate that most transformer failures are caused by the degradation of the insulation condition. Many diagnostic techniques, as summarized in a well written review [1], have been developed in the past to assess the insulation condition.

Among these techniques, furfural detection is a widely accepted and intensively explored method. This is because furfural is the major degradation product of cellulose insulation paper [2], and it can serve as the chemical indicator for the insulation condition [3–8]. High performance liquid chromatography (HPLC) is the most-frequently-used technique for furfural detection [3,4]. Although HPLC has a very low limit of detection, it is time consuming and labor intensive. The literature reported furfural detection methods besides HPLC are mainly spectrometric methods, such as spectrophotometry [5], fluorescence [6], and infrared detection [7]. These methods also require a specialized operator working in a laboratory remote from the transformer, and involve the use of a bench-top spectrophotometer together with toxic chemicals [8].

Electroanalytical techniques are characterized by their high sensitivity, simple instrument and easy of minimization etc. It may be a good choice for furfural detection. Theoretically, any compounds that can be oxidized or reduced have the possibility to be analyzed with electroanalytical techniques. There is an aldehyde group and a furan ring in the chemical structure of furfural, which implies that electro-oxidation or electro-reduction of furfural is possible [9]. Unfortunately, only very a few literature reports can be found to detect furfural by means of electrochemical methods. Saini et al. reported a pulsed amperometric furfural detection method, with a linear range of 0–10 μg ml^{-1} and limit of detection of 2 μg ml^{-1} [10]. Since potential pulse always generates very large current spike in acidic or alkaline solutions, the recorded current response was always noisy and thus degraded the reproducibility. Furthermore, the limit of detection is too high that makes the method not suitable for most real samples detection.

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Contrary to experiments carried out by Saini where furfural was oxidized, Shamsipur and Kumbhat independently reported the reduction of furfural with mercury electrode at a very negative potential [11,12]. The limit of detection was in the very favorable sub-ppm range. The method developed by Shamsipur can even simultaneously detect furfural and 5-hydroxymethyl-2-furaldehyde, which is another degradation product of cellulose and always coexist with furfural [11].

However, reductive determination of furfural described above was realized in aqueous solution, and it is difficult to directly detect the furfural contained in the insulation oil due to the large viscosity of the oil. Fortunately, the solubility of furfural in water is always better than that of in insulation oil, which implies that furfural can be extracted from oil phase to water phase. Investigation carried out by us indicates that the extraction was an easy and time saving process. Conditions for the extraction process were moderate. In no more than three minutes, a large proportion of furfural could be transferred to the extraction solution. Subsequently, differential pulse voltammetry was carried out with the extraction solutions. The original concentration of furfural in oil phase could be calculated by the concentration obtained with the extraction solution and the ratio of extraction. With the above procedures, the concentration of furfural contained in insulation oils could be quickly and conveniently determined. Thus the diagnosis of the health status of aged transformers can be realized.

2. Methods and procedures

2.1. Chemicals

Furfural was purchased from TCI Company (Shanghai, China). Ammonium solution was obtained from Chinasun Specialty Products Co., Ltd. Ammonium chloride was purchased from Tianjin Damao Chemical reagent Factory. Fresh and aged transformer oil was obtained from Electric Power Research Institute of Guangdong Power Grid Corporation and used as received. NH_3–NH_4Cl buffer solution with a concentration of 0.25 M was used as the supporting electrolyte for voltammetric detection as well as furfural extraction. The water and oil phase stock solutions (1000 $\mu g\ g^{-1}$) were prepared by dissolving suitable amount of furfural in NH_3–NH_4Cl buffer solution with optimum pH and in the fresh transformer oil, respectively. All other reagents were of analytical grade and water used in the experiments was doubly distilled.

2.2. Laboratorial experiments

All laboratorial electrochemical experiments were carried out with a CHI660D electrochemical workstation and with a three-electrode configuration. Mercury electrode was employed as the working electrode, with a saturated calomel electrode (SCE) and a platinum wire as the reference electrode and counter electrode, respectively. All potential values in this paper were with respect to this reference electrode unless otherwise specified. Before the experiments, the glassy carbon electrode was polished with 0.05 μm aluminum oxide power and ultrasonically cleaned with alcohol and doubly distilled water to obtain a renewed electrode surface. An Agilent1100 high performance liquid chromatography (HPLC) was also used to validate the results obtained with the proposed electrochemical technique.

2.2.1. Determination of furfural in water phase

The pre-treated glassy carbon electrode was inversely fixed in a cylinder voltammetric cell. After that, 1 mL of the prepared 0.02 M $Hg(NO_3)_2$ (with 0.1 M HNO_3) was injected into the cell. Then, the electro-deposition of the mercury ion to the surface of the glassy carbon electrode was carried out at -0.4 V for 240 s. A compact and thin mercury film was obtained through the above process. Finally, the working electrode was kept still for two minutes before the following experiments to guarantee the stability of the newly formed mercury electrode.

In order to characterize the electrochemical properties of furfural, cyclic voltammetry and DPV were carried out with water solution [13]. The potential sweep ranges for CVs and DPVs were respectively -0.3 to -1.6 V, and -1.15 to -1.55 V. Additional experiments were carried out in order to determine the optimum detection conditions. According to Saffron, the pH of the solution has some impacts on the detection [14]. We carried out a series of experiments with pH varied from 8.5 to 10.0. Other quantificational experiments were carried out with the optimum pH (9.26).

2.2.2. Extraction of furfural from the oil phase to water phase

Extraction of furfural from the oil phase to water phase was performed by adding certain amount of NH_3–NH_4Cl buffer solution to 50 mL insulation oil, and making the mixture be fully stirred at 400 rpm for a certain time. Then the mixture was transferred to a separating funnel where the phase separation process occurs. After the phase separation, the lower (water phase solution) layer was collected. The collected solution was divided to two parts, and the first part was transferred to the cylinder electrochemical cell. DPV was taken to determine the concentration of furfural in the water phase solution, with the same experiment conditions shown in Section 2.2.1. The second part was subjected to HPLC measurement.

Importantly, the quantification of furfural in oil phase can only be realized on the basis of being aware of the extraction ratio. Theoretically, under equilibrium conditions, the extraction ratio is a thermodynamic constant that is determined by the inherent nature of the involved chemicals and the extraction temperature. In order to evaluate the influence of extraction time, extraction temperature, and the water/oil volume ratio on the obtained extraction ratio, a series of experiments were carried out with each parameters independently controlled. The extraction time was varied from 0.5 min to 4.5 min, the extraction temperature was varied from 25 °C to 80 °C, and the water/oil volume ratio was varied from 1:1 to 1:5.

2.2.3. Determination of furfural in real samples

With the understanding of the optimum detection conditions and the extraction ratio in the previous two stages, the proposed methodology was further checked with real samples [15]. Various aged insulation oil samples were collected from different transformer substations within Guangdong Province. Most aged insulation oil and fresh oil differ greatly in color. However, no extra pretreatment was performed with the aged oils and the oils were tested with the procedure as described in the above sections. Since the content of furfural in some real samples was too low to be detected, furfural equivalent to 0.1 $\mu g\ g^{-1}$ was intentionally spiked to the oil samples in this case. HPLC tests were also carried out for the same processed solutions. Results got from electrochemical method and HPLC were compared with each other.

2.3. Automated instrument

The ultimate goal of this research is to establish a facile and reliable diagnostic tool that can be used in real situation. Thus, we specially developed a fully automated instrument [16]. The whole instrument is controlled by the combination of an industry standard Human Machine Interface (HMI) and a homemade mainboard which performs electrochemical detection and pumps/stirrer control. However, the details about the electronics and firmware/software will not be discussed in this paper. We only focus