Determination of Phenolic Antioxidant DBPC and DBP Levels in Electrical Insulating Oil

Agilent 5500, 4500, and Cary 630 FTIR Spectrometers

Application Note

Authors

Dipak Mainali and Frank Higgins

Agilent Technologies, Inc.

Introduction

The phenolic antioxidants 2,6-ditertiary-butyl paracresol (DBPC) (also known as butylated hydroxytoluene (BHT)) and 2,6-ditertiary-butyl phenol (DBP) are the two most common oxidation inhibitors added to the electrical insulating (transformer) oil and mineral oil based lubricants. The typical recommended value of DBPC and DBP in fresh electrical insulating oil is approximately 0.3% by weight. These inhibitors prevent electrical insulating oil from oxidative degradation, and prolong the life of the oil. It is essential to maintain the optimum concentration level of inhibitors to ensure the proper functioning of mineral oil used in transformer units as an insulating or cooling agent. The depletion rate of the inhibitors in the oil is dependent on various factors such as the amount of oxygen available, soluble contaminants, catalytic agents, and temperature. Therefore, regular testing of the inhibitors in electrical insulating oil is necessary to ensure its reliable operation in high value assets such as transformer units.

ASTM 2668 and IEC 60666 are the standard test methods, using infrared spectroscopy (IR) technology to monitor the concentrations of DBPC and DBP in electrical insulating oil. These test methods are used to determine if the new electrical insulating oil meets the specification for oxidation inhibitor initial concentration levels. They also monitor the concentration of inhibitors in the used oil. If the inhibitors have been depleted to a critical level, additional inhibitor can be added. Therefore, the standard test methods are essential for manufacturing control, specification acceptance, and to periodically monitor the level of inhibitors in used oils.

This application note describes the methods developed following ASTM 2668 and IEC 60666 to measure the concentration level of DBPC and DBP in electrical insulating oil. The methods described are suitable for all mineral oil base stocks [1], including turbine oils, hydraulic oils, gear oils, compressor oils, and crankcase oils. The ASTM and IEC methods described in this application note are able to measure up to 1 wt.% DBPC and 0.8 wt.% DBP concentration in new or used mineral oil, which is higher than the amount covered by ASTM 2668 or IEC 60666 test methods, which only cover up to 0.5 wt.%. The methods are developed using the high performing Agilent 5500, Agilent 4500, or Agilent Cary 630 FTIR spectrometers, and the measurements using these methods are quick, easy, and can be performed on-site with the mobile 5500 and fully portable 4500 FTIR.

Methods and Materials

To develop the ASTM 2668 method, the calibration samples were prepared from an uninhibited standard mineral base oil without phenolic antioxidants. The standard mineral oil was obtained as Base 20 and Base 76 from SPEX standards. The calibration samples in the range of 0–1.0% DBPC by weight were prepared by dissolving DBPC in standard mineral oil using a high precision analytical balance. The samples were measured on 5500, 4500, and Cary 630 FTIR spectrometers with the TumblIR or DialPath transmission cell set at a pathlength of 100 µm (0.1 mm). Each spectrum was collected at 8 cm^{-1} resolution with 128 co-added scans, yielding the approximate measurement time of 30 seconds.

To develop the IEC 60666 method, the calibration standards in the range of 0–0.8% DBPC by weight were prepared by adding DBPC in uninhibited Base 20 mineral oil obtained from SPEX standards using a high precision analytical balance. The calibration samples were measured using a TumblIR and a DialPath transmission cell at three different pathlengths (200 µm, 500 µm, and 1,000 µm). Each spectrum was collected at 4 cm^{-1} resolution with 64 co-added scans.

A **B**

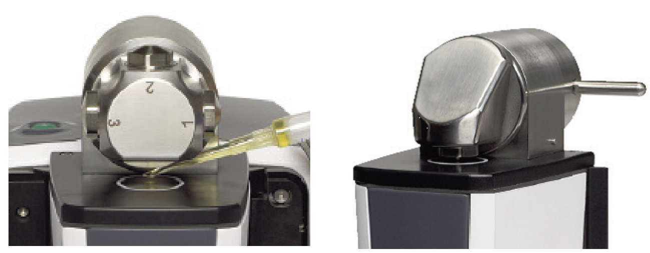

Figure 1. A) DialPath and (B) TumblIR accessories.

Results and Discussion

For both ASTM and IEC method calibrations, the region of the FTIR spectra used to determine the DBPC concentration is the phenolic OH stretch at 3,650 cm^{-1} (Figure 2). FTIR spectra indicated no interfering differences in the oils with different viscosities in the region of interest for measurement of the phenolic OH stretch at 3,650 cm^{-1}.

For the ASTM 2668 method, the calibration constants were obtained by performing the linear regression plot of the peak area (at 3,650 cm^{-1}) with dual baseline against DBPC concentration, as shown in Figure 3. The calibration curve has excellent linearity, with $R^2 = 1.00$, and provides the repeatability and reproducibility of the predicted results much better than the ASTM-specified 0.04 wt.% limits.

As shown in the validation results in Table 1, the maximum variance in this method is 0.01 wt.%, and 0.02 wt.% for the standards measured in the range of 0–0.5 wt.% and 0.5–1 wt.%, respectively. The second measurement range of 0.5–1 wt.% is above the range covered in ASTM 2668 procedure, but still exceeds its performance criteria. Therefore, the ASTM 2668 method developed using 5500, 4500, or Cary 630 spectrometers covers the measurement of DBPC up to 1 wt.%, and provides the quantitative measurement of DBPC with excellent repeatability and reproducibility.

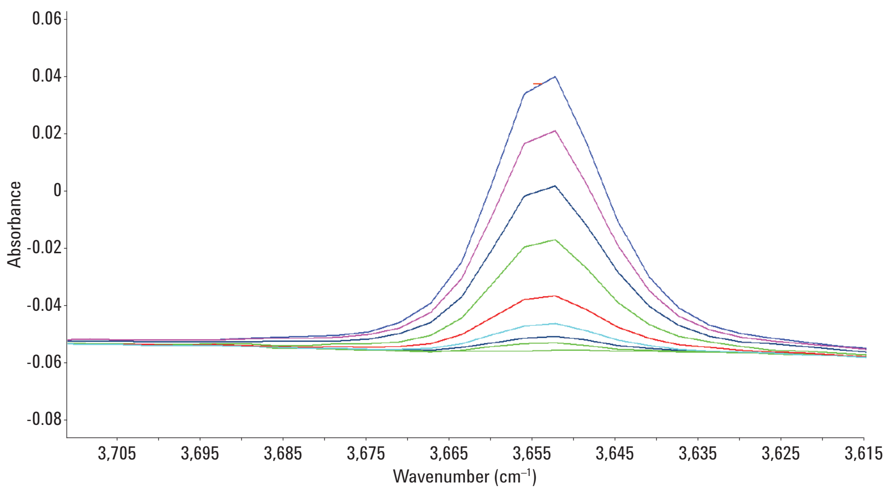

Figure 2. The IR spectral overlay of the absorbance band for phenolic OH stretch of DBPC in mineral oil (0–1 wt.%).

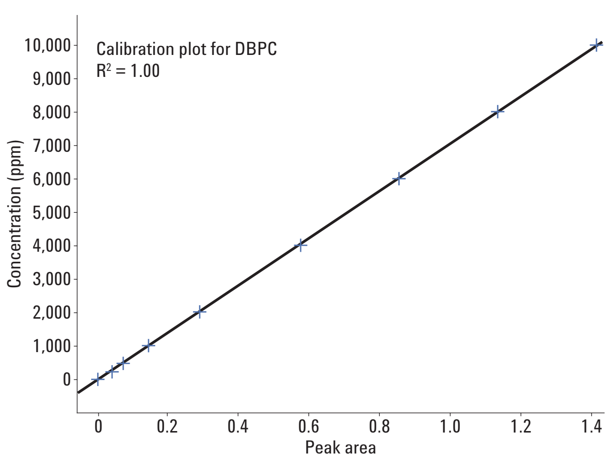

Figure 3. The calibration plot for DBPC (aka BHT) in mineral base stock in ppm units, multiply ppm by 0.0001 for weight% values.

Table 1. Predicted Versus Actual Values for the Calibration Data Set Using the ASTM 2668 Method

ASTM 2668 method

	DBPC concentration weight%	
Sample no.	**Actual**	**Predicted[1]**
1	0	0 ± 0
2	0.03	0.03 ± 0
3	0.05	0.05 ± 0
4	0.1	0.10 ± 0
5	0.2	0.20 ± 0
6	0.4	0.40 ± 0.010
7	0.6	0.60 ± 0.016
8	0.8	0.80 ± 0.016
9	1	1.0 ± 0.02

[1] Average of four values measured in four different instruments ± two standard deviations

Figure 4 shows that, for the IEC 60666 method, a calibration curve for the standards measured at a 1,000 µm pathlength was obtained by plotting absorbance at 3,650 cm^{-1} against the DBPC weight percent values. The calibration has excellent linearity, with $R^2 = 0.999$. The calibration curves looked similar for the samples measured at 200 µm and 500 µm pathlengths.

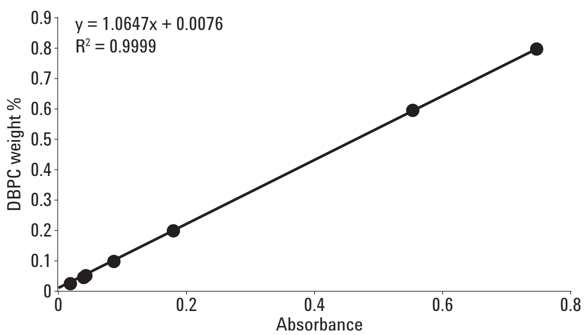

Figure 4. The calibration plot for DBPC in mineral oil measured at a pathlength of 1,000 µm.

Table 2 shows the validation results using the IEC method for the samples measured using the 1,000 µm (1 mm) pathlength. The repeatability and reproducibility were well within the specified limits of the IEC 60666 procedure.

Table 2. Actual Versus Predicted Values for the Calibration Set Using IEC 60666 Method

IEC 60666 method

	DBPC concentration weight%	
Sample no.	**Actual**	**Predicted**
1	0.00	0.00
2	0.10	0.09
3	0.20	0.19
4	0.03	0.03
5	0.05	0.05
6	0.60	0.60
7	0.80	0.82

In the Agilent MicroLab methods for both ASTM and IEC, the user can set threshold limits (Figure 4) as their analysis demands. The final result is displayed in a color code (red, yellow, or green) emphasizing the state of DBPC in the analyzed oil sample (Figure 5). Similarly, the recommendation based on the threshold limit can be described in the MicroLab method, which would be displayed at the end result, prompting the analyst to take an appropriate action (Figure 6). This unique color coding and the recommendation feature of MicroLab software makes it easier for a new operator to understand the result, and take appropriate action.

Conclusion

Both ASTM D2668 and IEC 60666 methods developed using Agilent 5500, Agilent 4500 FTIR, or Agilent Cary 630 spectrometers with TumblIR and DialPath transmission cells provide the sensitive results necessary to assist personnel monitoring the DBPC and DBP levels in electrical insulating oils. The methods are designed to alert the analyst using preset warning levels when the phenolic antioxidants are at or approaching depletion limits. This enables the analyst to maintain the proper level of DBPC or DBP in oil used in high value assets such as transformer units, turbines, and engines.

In addition, the ability of 5500 and 4500 FTIR spectrometers to measure DBPC and DBP on-site eliminates the hassle and cost of sending the samples to an off-site laboratory. The measurements are rapid and minimize the dependency on the skill of the operator due to the intuitive usability of the MicroLab software methods.

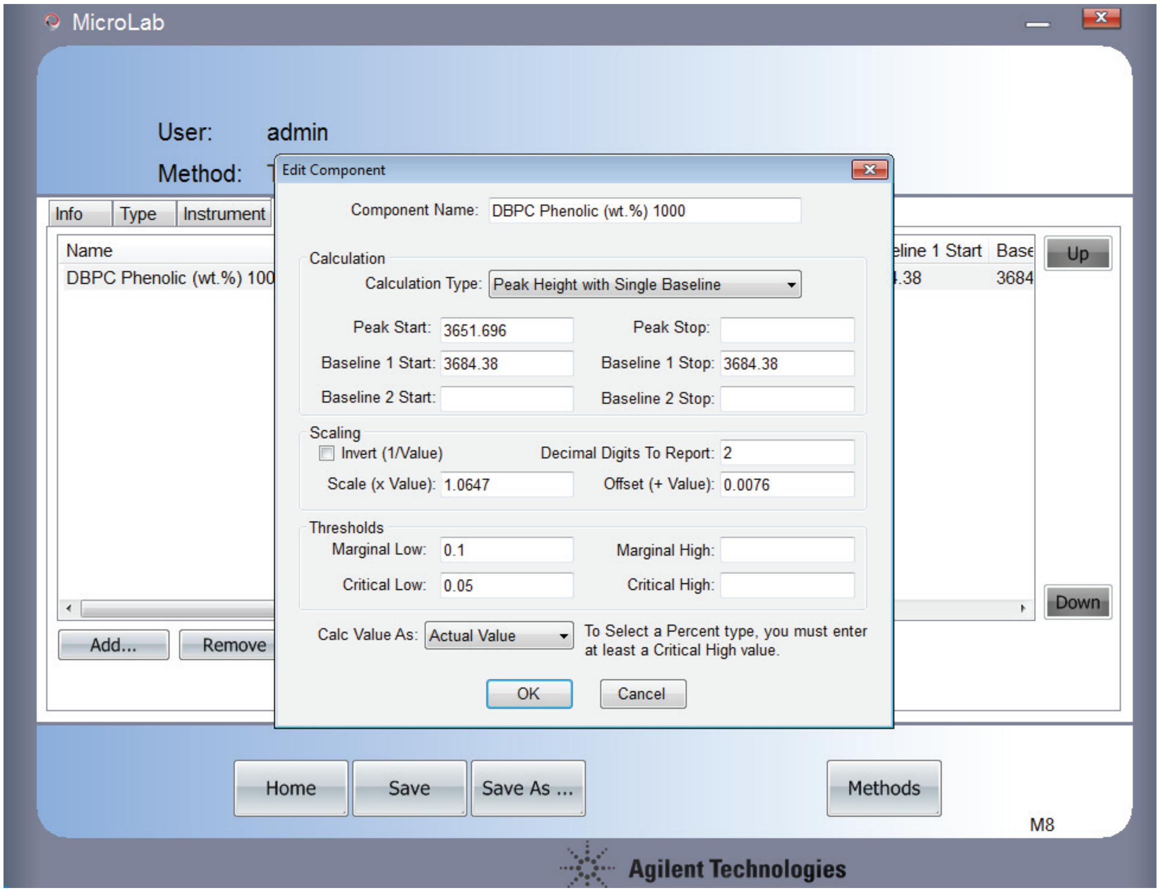

Figure 5. The MicroLab software feature in which the user can define the threshold limit for the DBPC concentration.

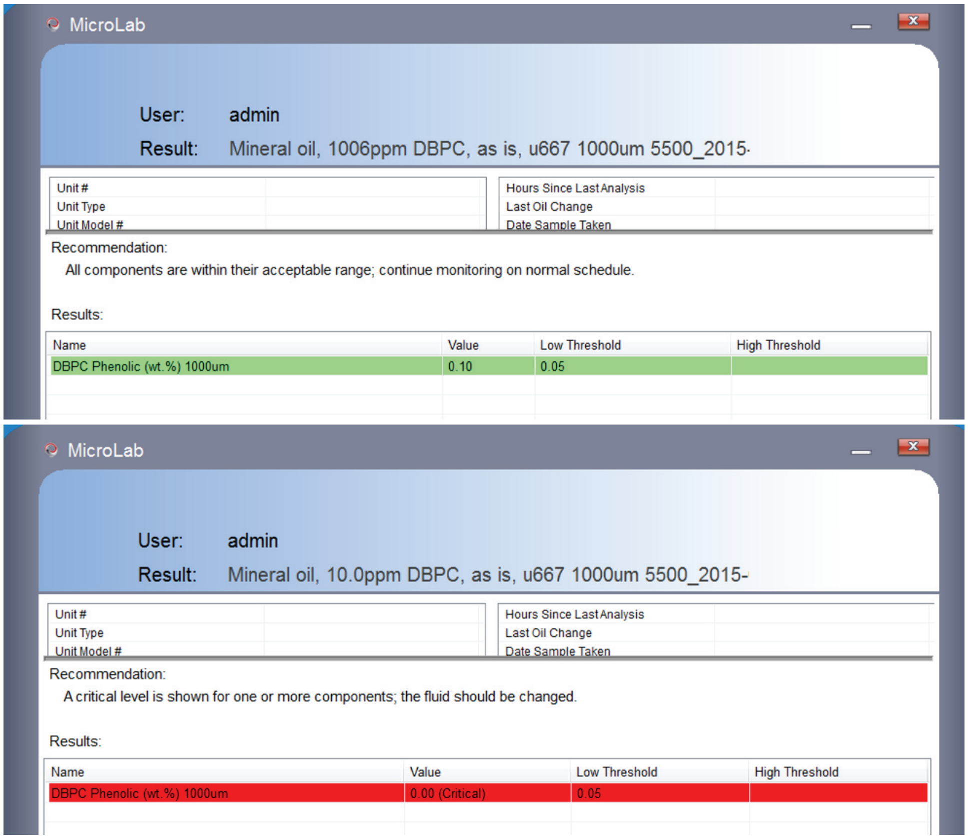

Figure 6. The MicroLab final result screen display where the results are shown color coded, with a recommendation. The green color indicates that the DBPC is at the desired level, whereas the red color indicaties that the DBPC is depleted to the critical level.

Reference

1. F. Higgins, Onsite additive depletion monitoring in turbine oils by FTIR spectroscopy, *Agilent Technologies*, publication number 5990-7801EN (**2011**).

For More Information

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