Low-temperature Electronic Paramagnetic Resonance Measurements of TEMPO and 4-Hydroxy-TEMPO Benzoate for Purity Analyses by the Effective Magnetic-moment Method

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The purities of two high-purity organic compounds with a nitroxyl radical moiety were quantified based on their free-radical content using the effective magnetic-moment method. Magnetic moments were measured and X-band electron paramagnetic resonance (EPR) spectra were obtained using a superconducting quantum interference device and X-band EPR spectrometer, respectively, over a wide temperature range of near-room temperature to near-liquid-helium temperature. Concerning measurements of effective g-values using an EPR spectrometer, both the sweep direction and sweep speed were taken into account to obtain accurate g-values. The purities of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) and 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl benzoate (4-hydroxy-TEMPO benzoate) were close to 1 kg kg⁻¹ with relative uncertainties of 1%, which represented improved values compared to those obtained by us previously. These results show a possibility for both compounds to act as reference materials in providing reliable quantification of free radicals per unit mass using this analytical method.

Keywords Quantitative analysis of free radical, primary direct method for amount of substance, paramagnetism, diamagnetism, magnetometer, electronic paramagnetic resonance, nitroxyl radical, purity as free radical

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Introduction

The purity of a chemical is a fundamental parameter that assesses its quality in many cases. Potential primary direct methods of measurement, such as gravimetry, coulometry, and the freezing point depression method, can directly measure the fraction or concentration of various chemicals in a sample. These primary direct methods can measure the fraction of unknown substances without reference to a standard. However, these methods cannot always directly analyze the purities of chemicals. In such cases, the purities have been conventionally estimated using the "subtraction method" or "area normalization method." In the subtraction method, the purity or concentration, xᵢ, as a function of k impurities with mass fractions, yᵢ, is conventionally given as xᵢ = 1 - ∑ᵢ yᵢ. Each xᵢ is generally measured by a quantitative analytical method using an empirical measurement equation. In the area normalization method, xᵢ is given as xᵢ = yᵢf(yᵢ + ∑ᵢ yᵢ), where yᵢ is the peak area owing to the major component, and the yᵢ is the peak area owing to the impurity. A common problem in both the subtraction and peak normalization methods is that all impurities cannot be detected and quantified.

We have proposed a quantitative analytical method, the effective magnetic-moment method, which is based on combining the Curie-Weiss law and the fundamental equation of electron paramagnetic resonance (EPR) spectroscopy. The effective magnetic moment is the magnetic moment of a mini magnet originating from unpaired electrons (free quantum spins). This value can be experimentally obtained from the quantum spin number, S, the Bohr magneton, and the g-value measured by continuous wave (CW)-EPR measurements. This effective magnetic-moment method can calculate the number of atoms (quantum spins) with unpaired electrons, of which the atoms exist in a diamagnetic matrix, utilizing the difference between the temperature dependence of the magnetic moment of unpaired electrons and that of electrons in closed-shell structures. The magnetic moment of unpaired electrons, obeying the Curie-Weiss law, is proportional to the inverse of the temperature corrected by the Weiss temperature, while closed-shell electrons show a temperature-independent weak diamagnetic moment according to the Langevin theory of diamagnetism.

An example of species containing unpaired electrons/quantum spins is an organic free radical. In a previous paper, the number of free radicals in each of three high-purity organic compounds in powder forms was attempted to be quantified using the effective magnetic moment method. The determined number of free radicals was converted into purity as a mass fraction, assuming that one molecule of each compound possessed one free radical. The results of the purities were (0.998 ± 0.064) kg kg⁻¹ for 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, C₆H₁₄NO), (1.019 ± 0.040) kg kg⁻¹ for 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, C₆H₁₄NO), and (1.001 ± 0.048) kg kg⁻¹ for 4-hydroxy-2,2,6,6-tetramethyl-
piperidine 1-oxyl benzoate (4-hydroxy-TEMPO benzoate, 4HTB, C₈H₆N₂O₄). The relative expanded uncertainty (coverage factor k = 2) for each compound was 4 - 6%. The purity of TEMPOL was 2% higher than 100%, while the purities for TEMPO and 4HTB were close to 100%.

All of these results described above were based on measurements of the magnetic moment using superconducting quantum interference device (SQUID) measurements and CW-EPR using X-band microwave, in a temperature range of 80 K to around/near room temperature. Using the effective magnetic moment method, the g-value obtained by EPR measurements should be the same as that obtained from magnetic moment measurements using SQUID in the same temperature range. In previous work, measurements using the SQUID were carried out from 300 K (or 260 K) to near-liquid-helium temperature. However, the EPR measurements used in our previous work were performed only over a temperature region higher than the liquid-N₂ temperature. Then, results of both the SQUID and EPR measurements obtained at temperatures higher than 80 K were considered for estimating the analytical purity values. The magnetic moment obeying the Curie-Weiss law increased rapidly with a decrease in the temperature in the low-temperature region. Temperature-independent g-values and the dataset of the magnetic moment and the temperature from near-liquid-He temperature to near room temperature might help us to estimate purity more accurately with much smaller uncertainty.

To improve the uncertainties of purities, a constant g-value must be confirmed at temperatures lower than 80 K, and the purity must be estimated using experimental SQUID and CW-EPR data over a much wider temperature range. TEMPOL is well-used starting material for preparing standard solutions for the calibration of EPR equipment. In the preparation, powder of the high-purity free radical is diluted by an appropriate solvent (for example, water, or, benzene). In general, it is said that quantitative free-radical analyses using EPR in the field of bioscience have a precision of 3 to 5%. If the uncertainty of the purity values based on the effective magnetic-moment method will be much smaller than 4 - 6%, the uncertainty can be almost ignored in comparison with the precision of EPR, and the high-purity chemicals with the purity determined by the effective magnetic moment will be for practical use on the preparation. However, the magnetic susceptibility of TEMPOL deviates from the Curie-Weiss law at temperatures lower than 80 K, and it is difficult to be quantified with greater accuracy based on the effective magnetic moment method. On the other hand, both TEMPO and 4HTB still show the Curie-Weiss behavior at temperatures lower than 80 K, and thus their purities can be determined with more precision by this analytical method. In particular, handling of 4HTB is easier than TEMPO, since it can be stored at room temperature and it is easy to introduce the 4HTB powder into a reagent bottle using a spatula, while the TEMPO powder aggregates and becomes hard clusters when stored in a refrigerator. Paramagnetic resonance results of 4HTB near temperatures of liquid-He temperature have not reported within our knowledge, although 4HTB has been used as a spin probe for studies of concerning the formation mechanism of mesoporous materials. For TEMPO and TEMPOL, some researchers had reported magnetic resonance behaviors until near-liquid-He temperature for TEMPO and TEMPOL. However, it has not been clear whether the effective g-values for TEMPO from liquid-N₂ temperature to near-liquid-He temperature is temperature-independent.

In this study, the X-band EPR measurements in a temperature region lower than 80 K was performed by using liquid He as the cryogen. The purities and their uncertainties were dependent on the temperature range. Determination of the range was also discussed. The experimental g-values obtained from the spectra were carefully determined in consideration of the direction and speed of the sweep field, and were used for estimating purities with higher accuracy.

**Experimental**

TEMPO (manufacture’s stated purity: 99.5 wt%, estimated by the subtraction method using gas chromatography (GC) and the Karl-Fisher titration method, which provided a 0.13% water content) and 4HTB (98.5%, estimated by the area normalization method using GC with a flame ionization detector) were purchased from Alfa Aesar (UK) and Wako Chemical, Ltd. (Japan), respectively. They were in the powder form. The experimental conditions of magnetic moment measurements were the same as that in a previous work. A SQUID magnetometer (Quantum Design, MPMS-5 DC) with the Reciprocating Sampling Option was used for the measurements. The powder sample was packed into a cellulose capsule (Matsuya, MP capsule, No. 4, diameter: 5 mm, length: 12 mm), and then approximately 20 mg of cotton infill was inserted into the capsule to prevent movement of the sample within the capsule. A drinking straw was used as the sample holder. The mass of the sample filled into the capsule, W, was measured using an analytical balance capable of measuring masses as small as 0.01 mg. The values of W for TEMPO and 4HTB were 18.45 ± 0.07 and 20.93 ± 0.07 mg, respectively. The magnetic field was set to a constant value of 795.7 kA/m. The magnetic moments were successively measured 10 times from 80 to 300 K in 10 K steps, from 30 to 80 K in 5 K steps, and from 4 to 30 K in 2 K steps. An EPR spectrometer (Bruker, E500) was used with a cryostat (Oxford Instruments, ESR900) with a temperature controller for X-band. Liquid He was used as a cryogen for cooling the sample. A liquid-He outlet and the spectrometer were connected by a stainless transfer tube. He gas vaporized from the spectrometer flowed to a large facility for liquefier of the vaporized He to liquid He. For X-band measurements, approx. 1 mg of the powder sample was sealed in an evacuated quartz-Pyrex tube (Agri, ST-X-4-5, diameter: 2 mm, length: 100 mm). High-purity He gas with much lower pressure than atmospheric pressure was also introduced into the tubes, to ensure good thermal conductivity in the gas phase and rapid stabilization of the sample temperature.

**Results and Discussion**

**X-band EPR measurements**

Figure 1 shows the EPR spectra obtained at representative temperatures for each sample. For both compounds, a large single first-derivative peak has been detected in each spectrum. The spectra 4HTB at all temperatures for qualitatively showed almost the same pattern and symmetrical peaks. On the other hand, qualitative differences were observed in the spectra TEMPO at around 345 mT between the symmetrical peaks at >70 K and asymmetrical and non-smoothing line shapes at <50 K. The non-smoothing line shapes will be discussed later. EPR measurements have not been performed at <10 K because of the difficulty of temperature control in that regime.

Figure 2 shows the effective g-values, gₑₑ, in the temperature range of 10 K to room temperature. The gₑₑ is an experimental value obtained from the magnetic field B₀ when EPR occurs and a microwave frequency ν, in accordance with the fundamental
equation of EPR spectroscopy. For TEMPO, the $g_{\text{eff}}$ values were plotted when the sweep field direction was up or down with a sweep field speed of 38.13 mT s$^{-1}$. The differences between the $g_{\text{eff}}$ values for different directions had a similar value. For 4HTB, $g_{\text{eff}}$ at each temperature except for 293 K was measured for only the up direction, with a sweep field speed of 38.13 mT s$^{-1}$.

As shown in Fig. 3, the differences between the $g_{\text{eff}}$ for up and down directions, $\Delta g_{\text{eff}}$, for 4HTB at 293 K were measured at various sweep field speeds from 76.34 to 1.19 mT s$^{-1}$. These speeds were realized by fixing the sweep field to 40.0 mT and setting the sweep times in the range of 5.24 – 335.534 s on a software connected to the ESR spectrometer. The $g_{\text{eff}}$ value obtained at 76.34 mT s$^{-1}$ was 0.0028. $\Delta g_{\text{eff}}$ decreased with decreasing field sweep speed. Figure 3 also includes the intermediate values, $g_{\text{eff,inter}}$, between $g_{\text{eff,up}}$ and $g_{\text{eff,down}}$, where $g_{\text{eff,inter}} = (g_{\text{eff,up}} + g_{\text{eff,down}})/2$. Those intermediate values were almost constant over the whole speed range, and were not influenced by the speed.

Referring to the results of 4HTB shown in Fig. 3, the $g_{\text{eff,inter}}$ at each temperature for TEMPO in Fig. 2(a) is regarded as the $g$-value at that temperature, assuming that $g_{\text{eff,inter}}$ for TEMPO is also independent on the sweep field. In Fig. 2(a), the $g_{\text{eff}}$ values in the up direction are almost constant from room temperature to 30 K, and then rapidly increase below 30 K. At some temperatures, $g_{\text{eff}}$ for the down direction is not plotted. However, it can be considered that $\Delta g_{\text{eff}}$ is the same as that at other temperatures. The average value of $g$ over a temperature range of 30 K to room temperature was obtained as 2.008, during which the peaks were symmetrically maintained in the temperature range. The effective $g$-values originated from the asymmetrical peaks less than 30 K deviated from the average value at between 30 K and room temperature. The deviation has a maximum of 0.0017 at 10 K. The expanded uncertainty of $g$ with a rectangular distribution based on the difference becomes 0.002, which is $k \times 0.0017/\sqrt{3}$. On the other hand, $g_{\text{eff}}$ of the up direction for 4HTB remained almost constant throughout the whole temperature range. $g_{\text{eff,inter}}$ values from 10 to 150 K were estimated using $g_{\text{eff}}$ at the same speed (38.13 mT s$^{-1}$) like that in Fig. 3. The value of $g_{\text{eff,inter}}$ at each temperature was adopted as $g$ at that temperature. The average value of $g$ in the whole temperature range was 2.0082, with an expanded uncertainty of 0.0008. The uncertainty was evaluated based on the $g_{\text{eff}}$ at 38.13 mT s$^{-1}$ and the standard deviation of $g$ over the temperature range.

Figure 4 shows the temperature dependence of the ratio $W_{\text{pp}}/W_{\text{hh}}$, which is generally a fundamental information obtained from EPR spectra. $W_{\text{pp}}$ is the peak-to-peak distance in the first-derivative spectrum and $W_{\text{hh}}$ is the half-width of the peak in the integrated spectrum. The ratio indicates the rough mixing ratio of the Lorentzian function and Gaussian function in the line shapes of the EPR spectrum. For a general interpretation, if the magnetic field is inhomogeneous and varies over a sample, it is reasonable to guess that the resonance produces Gaussian...
The Lorentzian line shape arises from radicals that freely move as if they are in a solution. $W_{pp}/W_{hh}$ for TEMPO remains almost constant from room temperature to 60 K. The values of $W_{pp}/W_{hh}$ at temperatures lower than 50 K are close to $\sqrt{-2/\pi}$, corresponding to the complete Gaussian function in Fig. 4. For 4HTB, $W_{pp}/W_{hh}$ remained almost constant throughout the temperature range with values close to $1/\sqrt{-3}$, corresponding to the complete Lorentzian function. $W_{pp}/W_{hh}$ for TEMPO was slightly larger than it was for 4HTB and the line shape of the peaks for TEMPO represented a partial Gaussian function.

Temperature dependence of magnetic moment measured using SQUID

In the effective magnetic moment method, the magnetic moment of the sample powder, $m$, under a constant magnetic field strength, $H$, can be theoretically expressed by $m = c_{Curie}(T - \Theta)^{-1} + m_0$. Here, $\Theta$ is the Weiss temperature, $m_0$ is the diamagnetic magnetic moment owing to all closed electrons in both the sample and background, and $c_{Curie} = n\mu_B\mu_{eff}^2H(3k_B)^{-1}$, where $n$ is the number of free radicals in the sample. Each radical has the effective magnetic moment $\mu_{eff} = g[S(S+1)]^{1/2}\mu_B$, where the total spin quantum number, $S$, is $1/2$ and $g$ is determined according to the average value from Fig. 2. $\mu_B$, $\mu_0$, and $k_B$ represent the Bohr magneton, magnetic permeability in free space, and Boltzmann constant, respectively. The experimental values of $c_{Curie}$, $\Theta$, and $m_0$ can be obtained by a non-linear regression analysis for a dataset of $m$ and $T$. The detailed method of the regression analysis is same as that used in our previous work.

Figure 5 shows the $c_{Curie}$ when non-linear regression analysis is carried out in a temperature range of $T_1 - T_2$, where $T_2$ is fixed at 260 K for TEMPO and 300 K for 4HTB. The lower the $T_1$, the smaller is the expanded uncertainty (error bar) of $c_{Curie}$. For 4HTB, the values of $c_{Curie}$ at different $T_1$ values are consistent with each other within their uncertainties. On the other hand, the $c_{Curie}$ for TEMPO apparently increases with decreasing $T$ below 10 K. Thus, one of our research goals was to decide on the analytical temperature range to determine an accurate value for $n$.

Figure 6 shows the temperature dependence of a parameter $S_{res}$ related to the non-linear regression analyses. $S_{res}$ is the residual sum of the weighted squared deviations divided by $(r - q - 1)$, where $q$ is total number of unknown parameters in the equation ($m = c_{Curie}(T - \Theta)^{-1} + m_0$) and $r$ is total number of data points of $m$ and $T$. $S_{res}$ for TEMPO obviously increases below 8 K, similar to the steep increase observed for $c_{Curie}$. However, $S_{res}$ for 4HTB remains roughly constant throughout the temperature range.

Figure 7 shows $(m - m_0)(T - \Theta)$ versus $T$ plots for both compounds, for which $m_0$ and were calculated at $T_1 = 10$ K. This plot is similar to a $\chi T$ versus $T$ plot (where is the magnetic susceptibility) and has an advantage in that inspection of the plot clearly indicates whether the magnetic moment under a...
constant $H$ obeys the Curie-Weiss law. If $m_0$, $\Theta$, and $c_{\text{Curie}}$ have been appropriately calculated by the least-squares method, the value of $(m - m_0)(T - \Theta)$ will be a temperature-independent constant in the range $T_1 - T_2$. For TEMPO, when $T_1$ and $T_2$ are 10 and 260 K, respectively, all values of $(m - m_0)(T - \Theta)$ were consistent within the expanded uncertainty ($k = 2$) of $c_{\text{Curie}}$, and those below 8 K were beyond the uncertainty. It was known that TEMPO showed a maximum peak at around 2 K,\textsuperscript{13,15} originating from an antiferromagnetic transition. The deviation from the Curie-Weiss law below 8 K might be a precursory phenomenon suggesting such an antiferromagnetic transition. Thus, it can be suggested that the magnetic moments for TEMPO obey the Curie-Weiss law at temperatures above 10 K reasonably; $c_{\text{Curie}}$ and its standard uncertainty, $u(c_{\text{Curie}})$, were determined to be $4.700 \times 10^{-4}$ A m$^2$ K and $0.024 \times 10^{-4}$ A m$^2$ K, respectively, on the basis of the data from 10 to 260 K. Although $g$ for TEMPO increased with decreasing temperature below 30 K (Fig. 2), the increase seemed to be negligible compared with the uncertainties of $c_{\text{Curie}}$. On the other hand, for 4HTB, when $T_1$ and $T_2$ are 10 and 300 K, respectively, all values of $(m - m_0)(T - \Theta)$ in the range 4.2–300 K are consistent within the expanded uncertainty of $c_{\text{Curie}}$. The value of $g$ obtained by EPR is also roughly constant from room temperature to 10 K and a Lorentz-type spectrum was observed throughout the temperature range. $c_{\text{Curie}}$ and $u(c_{\text{Curie}})$ for 4HTB were determined to be 2.8749 and 0.0119 $10^{-4}$ A m$^2$ K, respectively.

Purity estimation from both results of SQUID and EPR

The number of free radicals in a sample, $n$, is obtained using the equation $n = 3k_Bc_{\text{Curie}}(\mu g M_r/H)^{1.4}$\textsuperscript{1.4} The purity as free radical, $x_{\text{rad}}$, is obtained using $n$, the molar mass of each compound, the Avogadro number, and the mass of the sample $W$. The results of $x_{\text{rad}}$ and $g$ and $\Theta$ as intrinsic magnetic properties are summarized in Table 1. $\Theta$ for both compounds was non-zero beyond their uncertainties. The values of $x_{\text{rad}}$ for both compounds were close to 1 kg/kg, with relative expanded uncertainties of 1%, which is much better than the value of ~5% obtained previously.\textsuperscript{4} In the case of 4HTB, the uncertainty contributions of $c_{\text{Curie}}$ and $W$ to the standard uncertainty of $x_{\text{rad}}$ were 0.42 and 0.16%, respectively. The other sources of the uncertainty in $x_{\text{rad}}$ were considered to negligible. Further trials to minimize the uncertainty in $x_{\text{rad}}$, i.e., $u(c_{\text{Curie}})$, according to the effective magnetic moment method are required. The reproducibility of the magnetic moment measurement using a SQUID must be improved to decrease the uncertainty in $x_{\text{rad}}$, because this measurement is the main source of uncertainty. It is possible that the distance between the center of the capsule including the powder sample and the central axis of the sensing coil of the SQUID is different every time the capsule is placed inside the sample holder of the SQUID. We presume that the random error introduced by this might cause the poor reproducibility, and still need to consider a countermeasure to address this issue.

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### Table 1 Revised analytical results and magnetic properties for TEMPO and 4HTB according to low-temperature EPR measurement results

| High-purity organic compound | TEMPO | 4HTB |
|-----------------------------|-------|------|
| By EPR measurement          |       |      |
| $g$-value, $g$              | 2.008 ± 0.002 | 2.0082 ± 0.0008 |
| (above 10 K)                 | (above 10 K) |      |
| By SQUID measurement        |       |      |
| Analytical temperature range for magnetic moment | 10 to 260 K | 10 to 300 K |
| Weiss temperature, $\Theta$ | $-2.4 \pm 0.2$ K | $-0.6 \pm 0.2$ K |
| By both SQUID and EPR       |       |      |
| measurements                |       |      |
| Purity as free radical, $x_{\text{rad}}$ | 1.000 ± 0.012 | 1.0029 ± 0.0089 |
| kg kg$^{-1}$                | kg kg$^{-1}$ |      |

Each value of $g$, $\Theta$, and $x_{\text{rad}}$ is accompanied by its expanded uncertainty (with a coverage factor of 2).

### Possibility of application of effective magnetic-moment method to other chemicals

If an organic free radical shows magnetic moments obeying the Curie-Weiss law and has temperature-independent constant effective $g$-value in a wide temperature range, the effective magnetic-moment method will be applicable to the radical. There are many stable nitroxyl radicals other than TEMPO and 4HTB, for example, 4-oxo-2,2,6,6-tetramethylpiperidine 1-oxyl (C$_9$H$_{16}$NO$_2$, TEMPONE), 3-carboxy-2,2,5,5,-tetramethylpyrrolidine 1-oxyl (C$_9$H$_{16}$NO$_3$, 3-carboxy-PROXYL), etc. Karimov and Rozanov\textsuperscript{14} reported that temperature dependence of EPR signal intensity for TEMPO had shown a possibility of Curie-Weiss behavior more than 1 K. 3-Carboxy-PROXYL is expected to show Curie-Weiss behavior more than approximately 13 K, by results of low temperature solid NMR study.\textsuperscript{24} Then, the effective magnetic-moment method has a possibility to give purities as a free radical of both the TEMPO and the 3-carboxy-PROXYL with good accuracy. A nitrogen radical, 2,2-diphenyl-1-picrylhydrazyl (C$_{18}$H$_{12}$N$_5$O$_6$, DPPH) and an oxygen radical, 2,6-di-t-butyl-4-(3,5-di-t-butyl-4-oxocyclohexa-2,5-dienylidenemethyl)-phenoxyl (C$_{29}$H$_{41}$O$_2$, galvinoxyl) are also representative stable radicals and frequently used for EPR measurements.
measurements. In a paper by Fujito,25 the DPPH had shown the Curie-Weiss behavior in a higher temperature region. However, there was a maximum of the magnetic susceptibility at 11 K (≈ Tm), and it decreased at temperatures lower than Tm. The Weiss temperature was ~10 K. Such behaviors was close to those of TEMPOL. The effective magnetic moment method seems to give uncertainty of approximately 6–8% for purity of the DPPH. Mukai, et al.26 reported that the galvinoxyl had shown the maximum of the magnetic susceptibility at 82.5 K. Most manufacturers of galvinoxyl do not officially announce purity values of their high-purity galvinoxyl chemicals, while for the other commercial radicals listed above, the purities by the GC method or the titration method have been given by their manufacturers. Although it might be somewhat difficult to determine the purity of galvinoxyl with good accuracy, purity quantified by the effective magnetic-moment method might be useful information for practitioners of EPR.

Antiferromagnetic transition and EPR spectra of TEMPO

The antiferromagnetic transition of TEMPO was considered to have originated from a one-dimensional Heisenberg antiferromagnet model, which is a system of quantum spins ordered on a linear chain with nearest neighbor interactions.27 In the case of TEMPO, radicals are linearly arranged due to intermolecular bonding between the H atom and the O atom of the N-O bonding.16 When the molecules are cooled, firstly, short-range ordering of the radicals may occur one-dimensionally, like a “chain”, because of an overlapping of the π electron orbitals. Then, by further cooling, long-range ordering may occur three-dimensionally. Two research groups14,16 reported that Tm of TEMPO was 2.3 or 2.5 K and these values were almost the same. TEMPO of this paper has shown non-Curie-Weiss behavior at temperatures lower than 8 K and is presumed to exhibit such maximum of magnetic susceptibility at temperatures lower than 4 K. The values of Weiss temperature and were –1 K by Yamauchi16 and –2.4 ± 0.2 K by us. These macroscopic magnetic properties may be essentially the same among three research groups. However, the temperature dependence of line-widths of the peak-to-peak (Wpp) were quite different among the two groups and us. An EPR measurement by Yamauchi had shown that the Wpp of TEMPO rapidly increased with the lowering the temperature below Tm, and there was a large increase of ~6 Gauss (0.6 mT) between 2 and ~1.5 K. The Wpp was almost constant from room temperature to 40 K and was gradually increased with lowering temperature from 40 K to Tm. On the other hand, Karimov and Rozantsev34 reported that EPR line-widths decreased with lowering temperature from 296 to 1.4 K. For the TEMPO of this paper, the Wpp slightly decreases from room temperature to 80 K, and then there is a jump of Wpp of 0.72 mT from 80 to 50 K. Wpp is almost constant from 50 to 10 K. The paper by Yamauchi stated that the short-range ordering occurred lower than Tm. For our TEMPO, the jump of Wpp in the temperature range is too far from the low temperature region of non-Curie-Weiss behavior. These different temperature dependences of Wpp among the research groups may depend on the quality of samples, for example, chemical species and their amounts included as impurities in their samples. The non-smooth line-shape of Fig. 1 at temperatures lower than 50 K might also be related to the line-width and be due to such impurity effects. Measurements both before and after some sort of purification for high-purity TEMPO powder synthesized by other some manufacturers may be a method to clarify the intrinsic magnetic resonance properties of this compound.

Conclusions

The effective magnetic-moment method was used to quantify the purities of commercial high-purity TEMPO and 4HTB powders utilizing their free radical contents per unit mass with relative expanded uncertainties (k = 2) of 1%. These results obtained were much better than those obtained previously. The uncertainties are very much dependent on the analytical temperature range of the magnetic moment measured using a SQUID. Both TEMPO and 4HTB obeyed the Curie-Weiss law up to a temperature of around 10 K, as demonstrated by both experimental results of temperature-dependent magnetic moments and temperature-independent g-values. Low-temperature X-band EPR measurements using liquid He, since the cryogen showed that the g-values for both compounds were constant values, from room temperature down to 10 K for 4HTB and to 30 K for TEMPO. These X-band EPR results resulted in the paramagnetic state over a wide temperature range of both compounds. Thus, both 4HTB and TEMPO will be appropriate reference materials for assessing mass fractions of free radicals in organic substrates with sufficiently small uncertainties using this effective magnetic-moment method. The EPR line shapes of 4HTB are closer to Lorentzian ones than those of TEMPO over the whole temperature range and the magnetic moment of 4HTB obeys the Curie-Weiss law even at 10 K.

A field direction dependence and a sweep direction dependence were found from the measurements of effective g-values using the EPR spectrometer. However, the intermediate values between the up and down directions were independent on the sweep field. Effective g-value measurements by both directions or the measurements in several different sweep speeds are good procedures to obtain accurate g-values.

The effective magnetic-moment method has a potential to be a more accurate direct quantitative analytical method for an improvement of the operation of magnetic moment measurements. It is expected that this effective magnetic moment method will clarify accurate purities as free radical for many other stable free radicals.

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