SHORT COMMUNICATION

Rapid Estimation of Peroxide Content of Soybean Oil by Measuring Thermoluminescence

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Thermoluminescence measurements can serve as a simple and rapid procedure for the estimation of peroxide content of soybean oil. The thermoluminescence intensity, measured at 100°C, increases in proportion (r = 0.978) to the peroxide value (from 0.5 to 18.0 meq/kg) of soybean oil, without any interference by the tocopherol contents. The emission spectrum had a maximum wavelength at around 440–480 nm, suggesting that excited triplet carbonyls formed during thermal decomposition of hydroperoxides are involved. The thermoluminescence measurement is readily available for the simple and rapid estimation of the peroxide content of soybean oil, with no need for chemical reagents and delicate skills.

KEY WORDS: Lipid peroxidation, peroxide value, soybean oil, thermoluminescence.

There are several indices and methods for estimating deterioration of edible oils, such as peroxide value, carbonyl value, thiobarbituric acid value and detection of volatiles. Among these chemical indices, peroxide value is the most commonly used because of its direct indication of the hydroperoxide content of oils, in spite of the fact that measuring it is time-consuming and requires delicate skills. On the other hand, extra weak photon emission, also termed low-level chemiluminescence, is well known as one of the physicochemical phenomena observed during oil deterioration (1–7). Chemiluminescence generally originates from electrically excited states, such as singlet molecular oxygen and triplet carbonyls, provoked by radical chain reactions in lipid peroxidation (6,8,9). The chemiluminescence method has been applied for estimating the deterioration of edible oils and oily foods (4,5), as well as for shelf-life dating of fish meats (7). However, chemiluminescence is significantly influenced by antioxidants, such as tocopherols, in the oils (4,6,7).

In this study, we examined the applicability of a thermoluminescence-measuring method for the rapid estimation of peroxide content of soybean oil, which served as a typical edible oil. The thermoluminescence intensity was measured at 100°C without any luminescent reagent, and we found that the thermoluminescence intensity is proportional, with good reproducibility, to the peroxide values (ranging from 0.5 to 18.0 meg/kg) without any interference from the tocopherols.

MATERIALS AND METHODS

Materials. Soybean oil was purchased from Nippon Oil & Fats Co. (Tokyo, Japan). The soybean oil was a commercially available oil that had been prepared by refining, bleaching and deodorizing crude soybean oil. The soybean oil was kept at −15°C until used in the experiment. Tocopherols with purity of 99.5% were a gift from Eisai Co. (Tokyo, Japan). Fatty acid compositions (in wt%) of soybean oil were 9.9, 5.2, 19.9, 55.2 and 9.8 for palmitic, stearic, oleic, linoleic and linolenic acids, respectively. Tocopherol contents for soybean oil were 121, <0.1, 1063 and 455 for α-, β-, γ- and δ-tocopherols, respectively.

Autoxidation procedure. Soybean (20 g, peroxide value = 0.5 meq/kg) was placed in an open glass cell (150 mm in diameter) and kept in the dark at 40°C to prepare the oil samples of different peroxide content (peroxide value, 0.5, 2.8, 6.0, 10.0 and 18.0 meq/kg). Peroxide values of the soybean oil samples were determined iodometrically according to the AOCS method (10).

Measurement of soybean oil thermoluminescence. For measuring the thermoluminescence of soybean oil, a CLD-100 chemiluminescence analyzer (Tohoku Electronic Ind. Co., Sendai, Japan) was used. The oil sample (0.2–1.0 g) was placed on a stainless-steel plate (50 mm in diameter and 10 mm in height), and the thermoluminescence intensity was measured in air at 100°C for 500 s (7). The background count of the plate blank at 100°C was 5.7×10^4 counts/500 s. The thermoluminescence intensity was expressed after subtraction of the background count. Emission spectra of soybean oil thermoluminescence at 100°C were measured by a CLD-100 FC filter spectral analyzer (Tohoku Electronic Ind. Co.). Resolution of the spectrometry was 10 nm in the wavelength region between 420 and 600 nm.

RESULTS AND DISCUSSION

The time course of the thermoluminescence of soybean oil measured at 100°C is shown in Figure 1. The thermoluminescence intensities of soybean oil showed a proportional increase with the peroxide values (Fig. 1A) and with the oil weights submitted to the measurement (Fig. 1B). Figure 2 shows the linearity of the thermoluminescence intensity with peroxide value of soybean oil (Fig. 2A and 2B) and with sample weight (Fig. 2C and 2D). The correlation coefficients for the thermoluminescence intensity and the peroxide value were 0.978 (0.2 g of soybean oil) and 0.971 (1.0 g of soybean oil). The thermoluminescence intensity was not affected by γ-tocopherol contents (Table 1), at least up to 0.5% (w/w) in the oil.

To investigate the light-emitting species, a filter spectroscopic analysis was carried out. The emission spectrum of thermoluminescence observed at 100°C of soybean oil (peroxide value, 0.5–18 meq/kg, 1 g) showed a broad emission line with maximum wavelength regions at about 430–480 nm (Fig. 3). The emission spectra of the soybean oil suggested that the excited triplet carbonyls, provoked by thermal decomposition of lipid hydroperoxide, are

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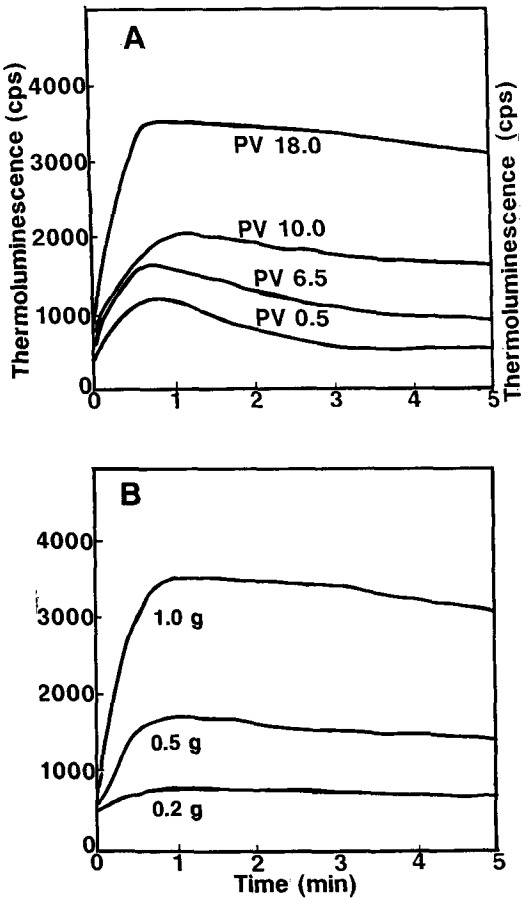

FIG. 1. Time course of soybean oil thermoluminescence measured at 100°C. A, Thermoluminescence of 1.0 g of soybean oil [peroxide value (PV), 0.5, 6.5, 10.0 and 18.0 meq/kg]; B, thermoluminescence of 0.2, 0.5 and 1.0 g of soybean oil (PV = 18.0 meq/kg); cps, counts per second.

TABLE 1

Effect of γ-Tocopherol on Thermoluminescence Intensities of Soybean Oil at 100°C

	Peroxide value[a] (meq/kg)	
Oil sample	0.5	10.0
Soybean oil (0.2/g)	120 ± 4	242 ± 15
Soybean oil (0.2/g) + γ-Tocopherol (0.2/mg)	121 ± 4	244 ± 10
Soybean oil (0.2/g) + γ-Tocopherol (1.0/mg)	119 ± 9	243 ± 17

[a]Thermoluminescence (× 10^3 count/500 s). Values are means ± SE of five determinations.

involved in soybean oil thermoluminescence (11). When the thermoluminescence was measured at 150°C, the light emission observed was unstable and not reproducible.

Bukow *et al.* (12) have reported that chemiluminescence of rancid oil measured by the hypochlorite-activated method is profoundly affected by the tocopherol content. The greatest advantage of the thermoluminescence method described here is that there is no need for any chemical reagents and there is no interference with

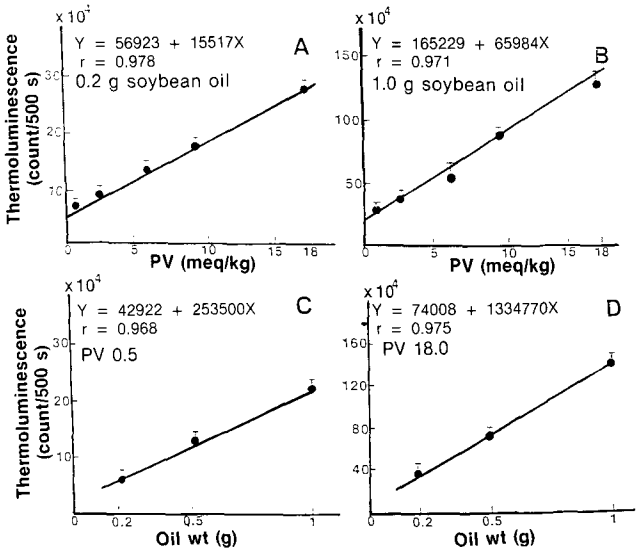

FIG. 2. Proportionality of thermoluminescence intensity vs. peroxide value (PV) and sample soybean oil weights at 100°C. A, Thermoluminescence of 0.2 g of soybean oil (PV = 0.5, 2.5, 6.0, 10.0 and 18.0 meq/kg); B, thermoluminescence of 1.0 g of soybean oil (PV = 0.5, 2.5, 6.0, 10.0 and 18.0 meq/kg); C, thermoluminescence of 0.2, 0.5 and 1.0 g of soybean oil (PV = 0.5 meq/kg); D, thermoluminescence of 0.2, 0.5 and 1.0 g of soybean oil (PV = 18.0 meq/kg). Error bars indicate standard error based on four determinations.

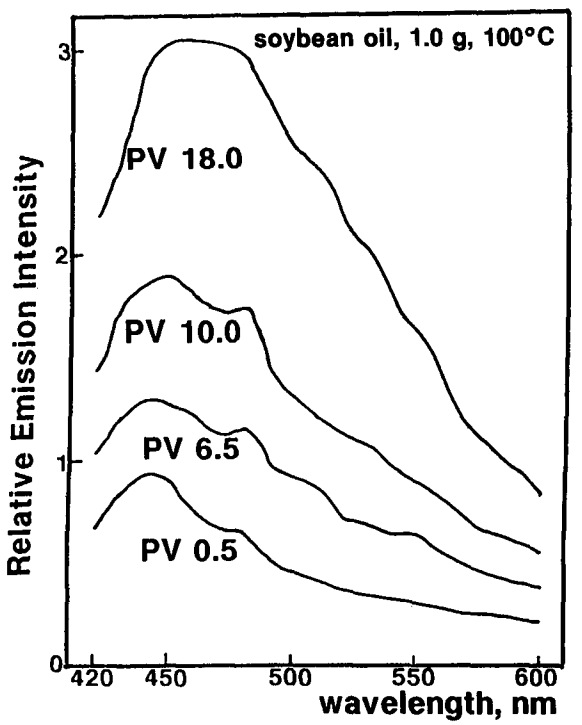

FIG. 3. Emission spectra of soybean oil thermoluminescence at 100°C. Emission spectra of 1.0 g of soybean oil [peroxide value (PV) = 0.5, 6.5, 10.0 and 18.0 meq/kg] were recorded at 100°C.

tocopherols. In conclusion, the thermoluminescence measurement has the advantage of estimating the peroxide value of soybean oil in little time and does not require any special skills.

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[Received July 16, 1993; accepted December 21, 1993]