Easy Detection of Adulterated Cooking Oil

This study demonstrates that electron spin resonance (ESR), with its unique ability to detect and quantify lipid free radicals rapidly, provides a convenient and straightforward tool for ensuring plant-based cooking oils' authenticity.

Introduction

The adulteration of food products for commercial gain is a growing problem. A common means of consumer deception to increase profit margins is to bulk up the genuine product with cheaper alternatives. Disreputable retailers adopting this practice use inaccurate labeling to gain full price for inferior products. Such fraudulent activity is detrimental to consumer satisfaction and the reputations and livelihoods of honest producers. Furthermore, in some cases, the adulteration may also carry the risk of harming human health.

This is exemplified by the mixing of plant-based cooking oils, such as rapeseed oil, sunflower oil, corn oil, and olive oil, with similar oils that have already been used. These polyunsaturated oils have become increasingly popular as healthier alternatives for frying. However, plant oils with high amounts of unsaturated fatty acids are highly susceptible to thermal oxidation[1]. The species resulting from such oxidation during frying can include polymers, trans-fatty acids, and compounds with oxygen-containing groups, many of which are detrimental to health[2].

The associated health risks of such devious practice are well known, and edible oil manufacture is strictly regulated to protect consumer health. However, efficient and reliable detection of adulteration in commonly used vegetable oils remains a challenge. Although a variety of methods are available for the detection of the products of oxidation, they tend to be labor-intensive, require time-consuming sample preparation and of insufficient sensitivity. Nuclear magnetic resonance, which provides rapid analysis with minimal sample preparation, has been used to identify adulteration of edible vegetable oils, but the limits of detection for many different oils were high[3].

ESR is recognized as a valuable tool for the detection and quantification of lipid-free radicals due to the unique magnetic properties of radicals with unpaired electrons. The steady-state concentration of lipid-free radicals in adulterated vegetable oil, however, is typically below the limit of detection using this technique. The sensitivity can be increased using a diamagnetic compound that enables the formation of more stable species that can accumulate to detectable concentrations[4]. Such ESR spin-trapping methodologies have been widely used to study the oxidative stability of lipids in food[5,6]. The most commonly used spin trap for lipid analysis of foodstuffs is α-phenyl-N-tert-butylnitrone (PBN) due to its high lipophilic and reactivity characteristics.

This study used the ESR spin-trapping technique to analyze plant-based cooking oils to identify contamination with used plant-based oils[7].

Experimental

Materials and Sample Preparation

Pure samples of commercially available rapeseed oil, soybean oil, peanut oil, corn oil, and olive oil were purchased from local markets. Used frying oil was obtained from fast food outlets and was mainly rapeseed oil. The used frying oil was added to the five commercial oil samples at varying concentrations ranging from 1% to 80%. Samples of 100% used frying oil as well as each of the pure vegetable oils were analyzed as controls.

An aliquot of 100 µL of each of the oil samples was mixed with 20 µL PBN in toluene in 4 mm quartz tubes to achieve a final PBN concentration of 25 mM. The PBN was used as a spin trap to stabilize any free radicals produced to detect contamination with used frying oil.

Instrumentation

Each sample was analyzed by ESR at 140°C using a Bruker EMXplus-10/12 spectrometer operating at 9.85 GHz and fitted with the Bruker variable temperature control unit.

The tubes were only inserted into the resonant cavity when a temperature of 140°C was reached. ESR spectra were recorded every 2 minutes without the presence of light.

Statistical Analysis

The g value and hyperfine coupling constants for each sample were calculated using Bruker's Xenon software after optimizing signal-to-noise ratios. The precision in the ESR parameters is about 3%. Initial signal intensities and adulteration proportions underwent linear regression for quantitative analysis.

Acid values and peroxide values were determined using the AOCS official method[4].

Results

Peroxide values were considerably higher in the used frying oil than in the pure commercial oils, indicating that the used frying oil contained much greater levels of hydroperoxides. Acid values in the pure edible oils were initially very low but increased during heating. The proportion of polar compounds, which includes the products of oxidation, polymerization, and hydrolysis, was around 2% in the pure oils but 24% in the used frying oil.

Oxidation of the pure oils at high temperature would be greater in the samples adulterated with used frying oil. This would be reflected in higher signal intensities of spin adducts. The higher the signal intensity observed, the greater the contamination with used frying oil.

The initial signal intensities of the ESR analysis and the rate at which they increased were both higher in the used frying oil than in the pure commercial oils. The edible oils adulterated with high proportions of used frying oil showed increases in signal intensities after 2 minutes. This was the result of thermal oxidation products present in the used frying oil. However, some of the increases thereafter were canceled out by an increase in decay rates as heating continued.

Comparison of signal intensities at 2 minutes provided an accurate indication of the degree of adulteration (Figure 1). In each of the five oils tested, the initial signal intensities observed at 2 minutes increased with increasing amounts of added used frying oil. The initial signal intensities of the samples with adulteration proportions below 50% increased faster than those of the samples containing more than 50% used frying oil.

The prooxidant content of the vegetable oils increased proportionately with the amount of used vegetable oil added, making it possible to determine the amount of adulterant present from the ESR signal intensity at 2 minutes (Figure 2).

Figure 1

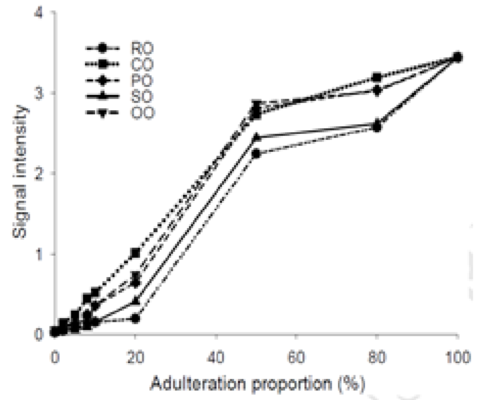

Figure 1. ESR signal intensity at 2 minutes for edible oils with varying proportions of adulteration with used frying oil

Figure 2

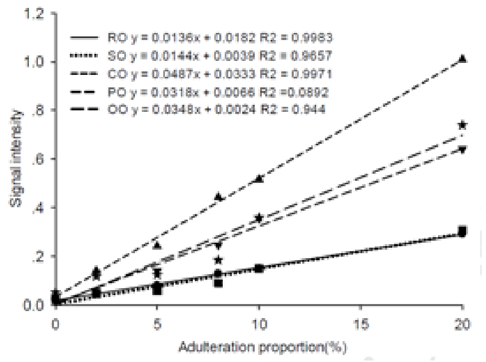

Figure 2. Relationship between signal intensity at 2 minutes and level of adulteration with used frying oil

RO, rapeseed oil; CO, corn oil; PO, peanut oil; SO, soybean oil; OO, olive oil

Conclusion

This paper demonstrates a highly sensitive and reliable electron spin resonance spin-trapping technique for effective detection and quantification of vegetable oil adulteration with used frying oil.

Since ESR is a convenient and straightforward analysis that can be easily used to provide objective results quickly, it represents a valuable new tool for the screening of vegetable oils for adulteration with oils that have been previously used.

The proposed ESR spin-trapping technique could be applied to screen vegetable oils for adulteration and protect consumers from hidden health risks.

References

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Bruker BioSpin

info@bruker.com
www.bruker.com