

Quantitative Determination of Hydroperoxides by Fourier Transform Infrared Spectroscopy with a Disposable Infrared Card

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ABSTRACT: Disposable polyethylene infrared cards (3M IR cards) were investigated for their suitability for the quantitative determination of peroxide value (PV) in edible oils relative to a conventional transmission flow cell. The analysis is based on the stoichiometric reaction of triphenylphosphine (TPP) with hydroperoxides to produce triphenylphosphine oxide (TPPO). Preliminary work indicated that the cards, although relatively consistent in their pathlength ($\pm 1\%$), had an overall effective pathlength variation of $\pm 5\%$, caused by variability in loading of the oil onto the cards. This loading variability was reduced to $<0.5\%$ by developing a normalization protocol that is based on the peak height of the ester linkage carbonyl overtone band at 3475 cm^{-1} , which allowed one to obtain consistent and reproducible spectra. The standard PV calibration approach, based on the TPPO peak height at 542 cm^{-1} , failed because of unanticipated card fringing in the region where the measurements were being made. However, the development of a partial-least-squares (PLS) calibration provided a means of eliminating the interfering effect of the fringes and allowed the TPPO band to be measured accurately. An alternate approach to the standardized addition of TPP reagent to the oil was also investigated by impregnating the 3M IR cards with TPP, thus allowing the reaction to take place *in situ*. The spectral analysis protocols developed (normalization/calibration) were programmed to automate the PV analysis completely. The 3M card-based Fourier transform infrared PV methods developed were validated by analyzing oxidized oils and comparing the PV predictions obtained to those obtained in a $100\text{-}\mu\text{m}$ KCl flow cell. Both card methods performed well in their ability to predict PV. The TPP-impregnated 3M card method reproduced the flow cell PV data to within ± 1.12 PV, whereas the method with an unimpregnated card was accurate to ± 0.92 PV over the calibrated range (0–25 PV). Our results indicate that, with spectral normalization and the use of a PLS calibration, quantitative PV data, comparable to those obtained with a flow cell, can be provided by the 3M IR card. With the analytical protocol preprogrammed, the disposable 3M card provides a simple, rapid and convenient means of carrying out PV analyses, suitable for quality control laboratories, taking about 2–3 min per analysis. *JAOCS* 75, 1095–1101 (1998).

KEY WORDS: Edible oils, Fourier transform infrared spectroscopy,

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FTIR, lipid oxidation, oil analysis, peroxide value, polyethylene, PV, triphenylphosphine, triphenylphosphine oxide, 3M IR card.

Fourier transform infrared (FTIR) spectroscopy is rapidly becoming an important analytical technique in the edible oils industry (1). FTIR spectrometers have dramatically improved the quality of IR spectra, minimized the time required to obtain data, and, through the use of computers and advanced chemometrics, evolved from a largely qualitative tool into a viable quantitative analytical tool (2). Oils are commonly analyzed in a simple transmission cell, usually composed of two salt windows (e.g., KBr, NaCl) plus a spacer to provide a defined pathlength, mounted in a cell holder. Although standard IR cells are relatively simple, they can be somewhat awkward to work with for oil analysis unless specially designed for this purpose (2). Convenience, simplicity, and speed of analysis are all desirable elements in any quality control (QC) analysis method. From a sample handling perspective, an alternative to flow cells would be welcomed in many situations. One of the most viable alternatives to date is the attenuated total reflectance (ATR) cell, which allows one simply to apply a sample onto an exposed crystal surface and obtain a spectrum (3). Selected organic polymers, such as polyethylene and Teflon films, can also serve as IR-transparent substrates (4,5) and are employed as such in single-use, disposable IR cards developed by the 3M Co. (St. Paul, MN). These cards, which fit into a standard IR cell holder, consist of a stretched IR-transparent polymer film sandwiched between two layers of stiff cardboard, leaving a circular aperture (12 mm diameter) for sample application onto the polymer film (Fig. 1). The 3M cards are available in two pathlengths, 10 and $100\text{ }\mu\text{m}$; these two formats were designed for qualitative and quantitative analysis, respectively. The latter contains a porous polyethylene (PE) or polytetrafluoroethylene (PTFE) film, which has microcrystalline pores capable of absorbing liquids into the polymer matrix by capillary action. Theoretically, with the film thickness and porosity adequately controlled, the sample volume would be constant, and the card could effectively behave much like a constant-pathlength cell. Based on literature obtained from 3M (6), some of the suggested uses for the quantitative (“quant”) IR cards include the analysis of edible oils, fuel oils, lubricants, engine oils, and oil in wastewater, but no details regarding any specific applica-

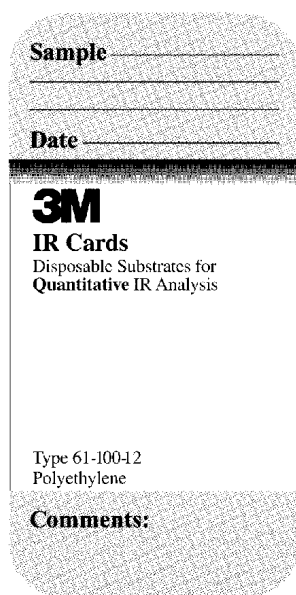


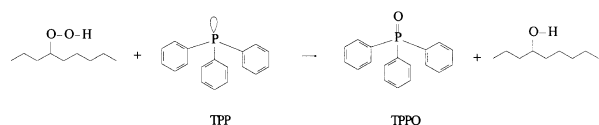
FIG. 1. Typical 3M IR card, illustrating its cardboard frame, the polymer aperture, and the defined central loading area within the polymer aperture.

tion that has been implemented are cited, nor is there any information available in the literature regarding the use of these “quant” cards in quantitative analysis.

The McGill IR Group has focused on the development of rapid, quantitative analytical methodologies for the analysis of edible oils and has developed a variety of automated methods based on mid-IR transmission spectroscopy, including methods for the determination of peroxide value (PV), anisidine value, iodine value, *cis* and *trans* content, and solid fat index (7–10). An integral part of the automated methods developed has been the use of a custom-designed heated transmission flow cell to facilitate sample handling and analyses (Dwight Analytical, Toronto, Canada). For applications in which only a limited number of samples are to be analyzed and heating is not required, the ability to utilize a disposable IR card rather than a transmission flow cell could be advantageous for QC applications if adequate quantitative accuracy could be ensured. However, to date, no publications have appeared regarding quantitative applications for edible oils with the 3M IR card.

Of the IR methods developed by the McGill IR Group, the determination of PV is one of the simplest, as it is based on the stoichiometric reaction of triphenylphosphine (TPP) with hydroperoxides to produce triphenylphosphine oxide (TPPO) and the corresponding hydroperoxide alcohols (7), as shown in Scheme 1.

The TPPO formed produces an intense band at 542 cm^{-1} in the mid-IR spectrum. The intensity of this band is readily



SCHEME 1

measured and related to the PV of the sample. The simplicity of the mid-FTIR PV method makes it an ideal candidate for evaluating whether the 3M card could be a suitable vehicle for the quantitative determination of edible oil quality parameters. This paper describes the considerations involved in adapting the FTIR PV method for use with the 3M card and presents an assessment of the performance characteristics of the 3M IR card for the determination of PV in edible oils relative to the performance of a standard transmission flow cell.

MATERIALS AND METHODS

Materials. Reagent-grade triphenylphosphine (TPP, >99%), triphenylphosphine oxide (TPPO, >99%), *tert*-butyl hydroperoxide, isooctane, chloroform, and hexanol were obtained from Aldrich Chemicals (Milwaukee, WI). Canola oil was obtained at a local retail outlet; prior to use, the oil was heated to 200°C under vacuum for 1 h to destroy any residual hydroperoxides and low-molecular-weight aldehydes and was then passed through a column of activated silica gel to remove any remaining polar compounds that might be present. The cleaned canola oil was analyzed for its PV by the standard AOCS method (11), and the oil was considered clean if the PV was <0.10 .

Instrumentation. The spectrometers used for this work were a PC-controlled Bomem FTIR spectrometer (Hartmann & Braun, MB Series, Bomem, Inc., Quebec, Canada), run under Windows-based Bomem-Grams/386 software (Galactic Industries Co., Salem, NH), as well as a Nicolet Magna 550, also PC-controlled and running under Omnic software (Nicolet Instrument, Madison, WI). The optical compartment and sample-handling system of both instruments were continuously purged with CO_2 -free dry air, supplied by a Balston dryer (Balston, Lexington, MA), to minimize water vapor and carbon dioxide interferences. The Bomem spectrometer was selected for the spectral analysis of the 3M cards because of its accessible, open-architecture sample compartment, the purge being maintained by two telescoping tubes that enclose the sample holder. The Nicolet spectrometer was equipped with a custom-designed oil analysis flow cell accessory (Dwight Analytical) described in detail in a previous publication (9); the insert was a $100\text{-}\mu\text{m}$ pathlength KCl cell. Spectra were collected by scanning for 1 min over the range of $4000\text{--}400\text{ cm}^{-1}$ (16 co-added scans on the Bomem and 64 co-added scans on the Nicolet); all spectra were collected at a resolution of 4 cm^{-1} with triangular apodization. For both the transmission cell and the card, the single-beam spectrum of the sample was ratioed against a single-beam spectrum recorded with an open beam to produce a conventional absorbance spectrum. These absorbance spectra were stored to disk for subsequent analysis or spectral data processing.

IR cards/sample application. The 3M IR cards (61-100-12) were made of PE film with a nominal pathlength of $100\text{ }\mu\text{m}$ and a circular microporous sample application region 12 mm in diameter, holding up to $12.5\text{ }\mu\text{L}$ of a nonvolatile liquid. Oil was applied onto the cards by various means, including: (a) a piston applicator designed for the 3M card (Pike Technologies, Madison, WI); (b) a micropipette, with removal of any excess oil by absorbing it onto an absorbent tis-

sue; (c) a micropipette, with vacuum applied to the card placed on a porous support; and (d) dilution of the oil in isooctane and delivery of this solution in sequential stages with a micropipette, the solvent being evaporated between applications in a stream of dry nitrogen. Method (d) was found to be the simplest and most convenient method for obtaining a relatively uniform application of oil onto the card and was used for the validation portion of this study.

Calibration and validation. Hydroperoxide calibration standards were prepared by gravimetrically adding a 30% solution of TPPO in hexanol to peroxide-free canola oil to provide TPPO concentrations that represented PV from 0 to 25. For the cards, the calibration standards were applied to the card and scanned, and the spectra were subsequently normalized by using the peak height of the carbonyl overtone band, measured at 3475 cm^{-1} , relative to two baseline points at 3512 and 3417 cm^{-1} . A partial-least-squares (PLS) calibration was developed for the card by using the region of $570\text{--}520\text{ cm}^{-1}$ with Omnic TQAnalyst (Nicolet Instrument). The standard analytical protocol (7) for the 3M card was first to add TPP/hexanol reagent to the oils to be analyzed, to shake the sample for 30 s and then to apply reacted sample to the card and measure the TPPO formed. An alternative procedure investigated was to prepare TPP-impregnated 3M IR cards by applying $30\text{ }\mu\text{L}$ of 1% TPP/chloroform solution onto the porous PE sample application region of the card and letting the card dry. Sufficient TPP was incorporated into the card to react with all hydroperoxide groups in an oil sample with a PV of ~ 150 . For method validation, fresh canola oil was heated with aeration until it reached a PV of ~ 100 and diluted with PV-free canola oil to produce samples covering a wide range of PV. These samples were analyzed by the two card methods. The PV predictions obtained were compared with those obtained with the flow cell.

RESULTS

IR card issues. In considering the 3M card as a vehicle for carrying out a PV analysis, the main concerns are the inherent pathlength variability of the cards themselves as well as sample loading consistency. The spectrum of a $100\text{-}\mu\text{m}$ PE card (Fig. 2A) is relatively clear, except for strong, sharp CH stretch absorptions in the $3000\text{--}2800\text{ cm}^{-1}$ region, as well as some minor CH bands at lower frequencies. The spectrum of the card (when no sample has been applied) has a substantial baseline tilt, which is due to light scatter caused by the microcrystalline nature of the porous PE membrane; the baseline tilt largely disappears once a sample is applied. Figure 2B illustrates a spectrum of canola oil applied to the card, which appears similar to the spectrum one obtains from a $100\text{-}\mu\text{m}$ KCl flow cell (Fig. 2C). The sharp CH stretching bands of the card blend into the broad off-scale CH bands produced by the oil.

Examination of the pathlength of the cards by measurement of the height of the 1475 cm^{-1} band of PE, relative to two baseline points at 1575 and 1375 cm^{-1} , in spectra recorded prior to application of sample, indicated that the pathlength variability was on the order of $\sim 1\%$. However, when cards were loaded

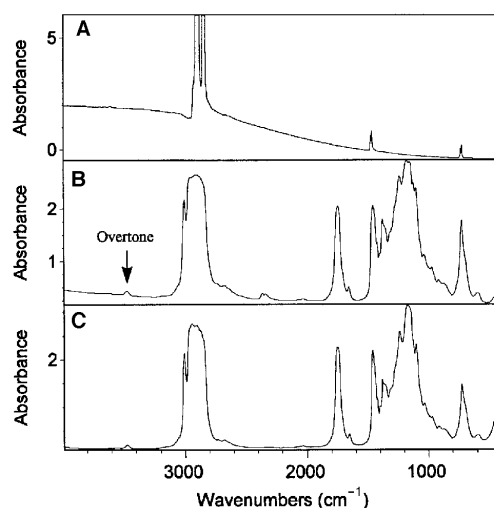


FIG. 2. (A) Spectrum of a $100\text{-}\mu\text{m}$ polyethylene (PE) IR card, (B) spectrum of a card loaded with canola oil, and (C) spectrum of canola oil in a $100\text{-}\mu\text{m}$ KCl flow cell.

with canola oil by means of the recommended piston applicator, the peak heights of selected bands of the oil varied by 4–5%, indicating that additional loading variability was superimposed onto the inherent variability of the pathlength of the cards. Careful analysis of this variability led to the conclusion that, although the card pathlength is fairly constant, the “apparent” effective pathlength of the card is dictated by the amount of sample incorporated into the polymer matrix. If the polymer micropores are saturated with oil, with excess oil on the surface, the effective pathlength exceeds the nominal $100\text{-}\mu\text{m}$ pathlength, while if the pores are underloaded, the apparent pathlength is less than the rated $100\text{ }\mu\text{m}$. This was determined by adding the oil, diluted 50:50 with isooctane, to cards in stages, evaporating the solvent after each addition, slowly building up the concentration within the polymer matrix, and following the process spectrally. Ideally, one would obtain a reproducible spectral profile by applying a constant volume; however, this is not the situation in practice. A variety of approaches were assessed to determine whether a uniform loading of the card could be obtained (piston applicator, direct pipetting, vacuum loading, as well as diluting with solvent and loading in stages). None of these approaches provided results significantly more consistent than the others, and the overall inherent pathlength variability that one has to contend with is on the order of 4–5%.

Pathlength normalization. A pathlength variability of 4–5% was considered problematic for good quantitative work, and the development of a normalization protocol was investigated to determine whether the pathlength variability could be reduced to a more acceptable level. Normalization requires that one find a relatively invariant absorption band that can be used as a reference peak and set to an arbitrarily fixed value in terms of height or area. With this technique, the linear spectral variations caused by apparent pathlength changes due to variable sample loading are corrected, and the

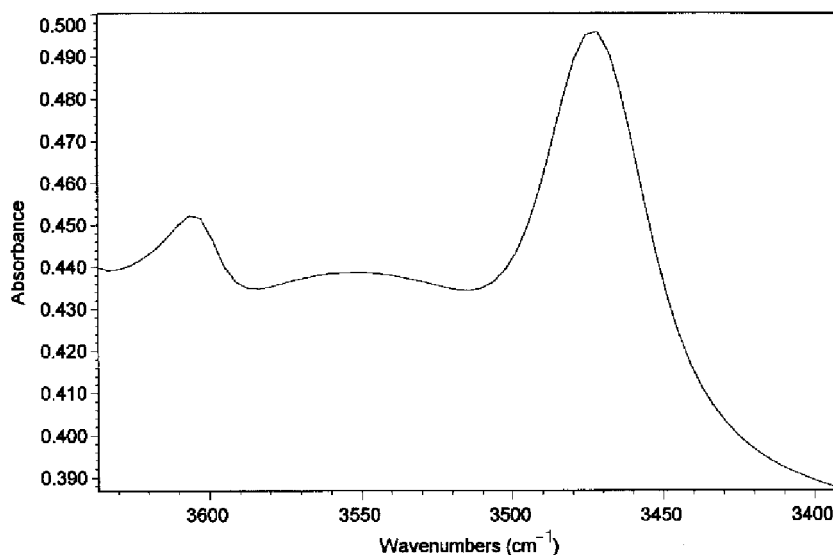


FIG. 3. Expanded view of the 3660–3400 cm^{-1} region in the spectrum of an oil spiked with hexanol and water. The triglyceride ester linkage carbonyl overtone band (3475 cm^{-1}) was employed for spectral normalization. In the normalization procedure, the peak height of the overtone band was measured relative to a baseline drawn between 3512 and 3417 cm^{-1} to compensate for the apparent overlap of the OH absorptions of alcohols and water with the overtone band.

spectra reflect a constant pathlength. Edible oil spectra recorded with a 100- μm pathlength do not provide any ideal, invariant bands that can be used for normalization, because most bands are off-scale or are strongly oil-type dependent. One of the few on-scale bands is the triglyceride ester linkage carbonyl overtone band at 3475 cm^{-1} . Normalizing the spectra obtained from various loadings of clean canola oil on the 3M card by using either the height or the area of the overtone band allows one to bring spectra of divergent loadings to a consistent spectral profile and eliminates the 4–5% variability in peak height originally obtained without normalization. A drawback to the use of the carbonyl overtone band for normalization is that its intensity is related to the weight-average molecular weight or saponification number of an oil. This is not a major concern when analyzing most common vegetable oils (rapeseed, corn, soybean, etc.) because the saponification number does not vary much between oils. However, for oils of distinctly different saponification number, such as palm oil, using this generalized correction will cause an offset in the PV determinations.

Another issue of consequence in relation to this normalization procedure is the potential for interferences that affect the overtone band measurement, owing to the proximity of this band to the OH stretching absorptions of hydroperoxides, alcohols, and moisture (12). For the PV method, the hydroperoxide absorptions are not of concern, because all hydroperoxide groups are eliminated by reaction with TPP. However, the alcohol absorptions are a potential source of interference, because TPP is added in a hexanol carrier and the hydroperoxides being analyzed are converted to alcohols by the analytical reaction. Although there are apparent band

overlaps in the spectra of an oil spiked with an alcohol and moisture (Fig. 3), with proper selection of baseline points (3512 and 3417 cm^{-1}), the spectra of canola oil samples deliberately contaminated with alcohols and moisture could be normalized to a similar degree of accuracy as obtained for the clean oil.

PV calibration. Having succeeded in resolving some of the key issues associated with the loading variability of the cards, a conventional peak height PV calibration was attempted. The cards were loaded with canola oil/TPPO calibration standards and scanned. After ratioing against an open-beam background spectrum, the spectra were normalized, and the peak height at 542 cm^{-1} was measured relative to a single-point baseline at 530 cm^{-1} . The calibration plots of peak height vs. TPPO concentration (expressed in terms of PV) were poor and irreproducible (Fig. 4) whereas the same calibration standards produced excellent linear calibration plots for the flow cell.

Comparison of the card calibration spectra with the flow cell spectra indicated that a residual fringing pattern from the polyethylene film was superimposed on the TPPO absorption band (Fig. 5). This fringing pattern affects the TPPO peak height measurement by its contributions to the absorbance measured at the peak maximum (542 cm^{-1}) as well as that measured at the baseline point (530 cm^{-1}). The fringe pattern, although small in absolute absorbance units (2–3 mA), is substantial relative to the intensity of the TPPO band (~ 1 mA/PV unit), and based on these observations, it became clear that a peak height calibration would be unworkable for the cards. An alternative means of calibrating under these problematic circumstances is to make use of PLS regression, a powerful chemometric technique that allows one to make quantitative

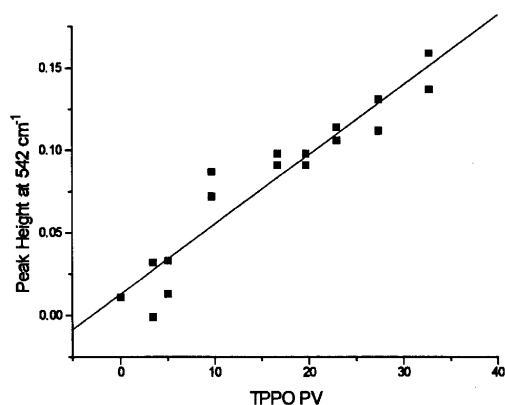


FIG. 4. Absorbance at 542 cm^{-1} in the normalized spectra of the calibration standards on the 3M cards vs. triphenylphosphine oxide (TPPO) concentration of the standards [expressed in terms of equivalent peroxide value (PV)]. The linear regression equation for the plot is $y = 0.012 + 0.0042x$; $r = 0.95$, $\text{SD} = 0.015$.

measurements when interfering or overlapping bands, such as the interference fringes produced by the card, are present in the region of interest (13). By providing PLS with TPPO concentration information, as well as spectral information encompass-

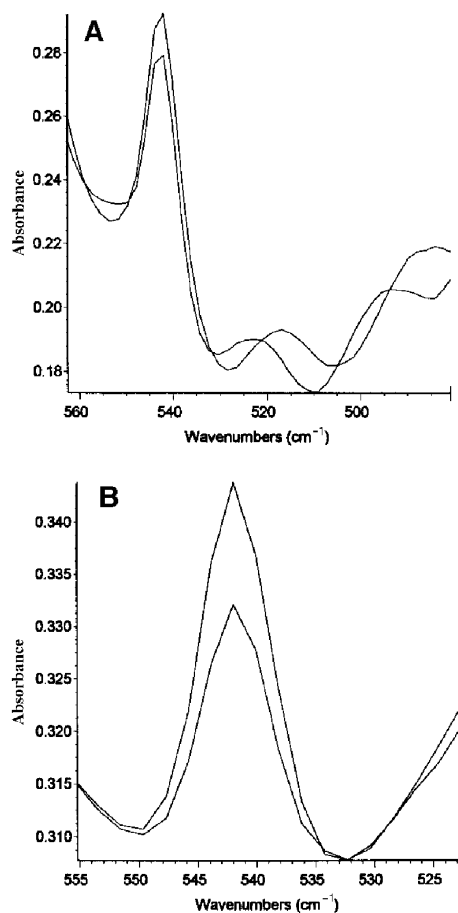


FIG. 5. Spectra of two TPPO/canola oil calibration standards recorded from the 3M card (A) and from a $100\text{-}\mu\text{m}$ KCl cell (B), illustrating the superimposition of fringes contributed by the polymer matrix of the card.

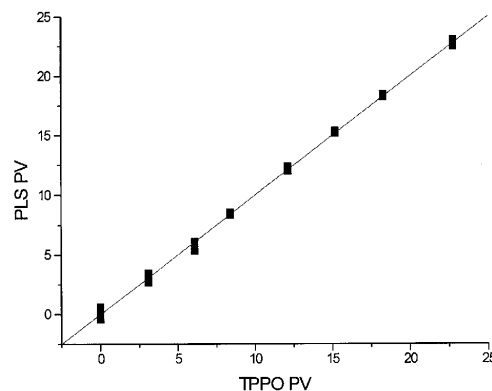


FIG. 6. Partial-least-squares (PLS) calibration plot for the 3M card method. PLS-predicted PV is plotted vs. calculated PV (based on TPPO concentration) for the calibration standards. The linear regression equation for the plot is $y = 0.002 + 0.999x$; $r = 0.999$, $\text{SD} = 0.26$. For abbreviations see Figure 4.

ing the fringes and the TPPO absorption band, a calibration was developed that compensated mathematically for the interference fringes overlapping the TPPO absorption band. Figure 6 presents the PLS calibration plot obtained for the card with normalized spectra. This plot has similar characteristics to the peak height calibration plot obtained in a $100\text{-}\mu\text{m}$ KCl flow cell (Fig. 7), which does not suffer from either pathlength variation or fringing. Although the plots presented in Figures 6 and 7 are not directly comparable because the calibration procedures differ, the PLS calibration has all the desired characteristics of the conventional peak-height calibration, being linear and the intercept passing close to zero. Comparing these calibrations in terms of PV regression SD, the PLS calibration has an SD of 0.26 PV, while the cell calibration has an SD of 0.20 PV. A more realistic estimate of the expected performance of the PLS calibration is obtained by carrying out a cross validation; the SD obtained on this basis is ± 0.35 PV. These results

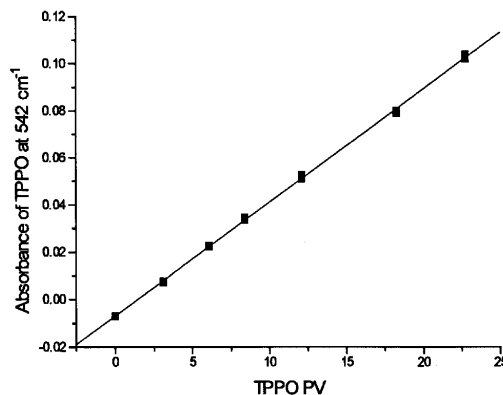


FIG. 7. Peak-height calibration plot for the flow-cell method. Absorbance at 542 cm^{-1} in the spectra of the calibration standards measured in a $100\text{-}\mu\text{m}$ KCl flow cell is plotted vs. TPPO concentration of the standards (expressed in terms of the equivalent PV). The linear regression equation for the plot is $y = -0.0069 + 0.0048x$; $r = 0.999$, $\text{SD} = 0.00096$. For abbreviations see Figure 4.

indicate that PLS provides an effective, alternative means of calibration that can overcome the fringing caused by the card, and that, in effect, the card can be made to behave much like a constant-pathlength cell.

TPP-impregnated card. One of the potential benefits of using the 3M card, other than convenience, is that the card could be impregnated with TPP, thereby eliminating the need to add the TPP/hexanol reagent to the oil. This approach was also investigated by preimpregnating the cards with TPP and investigating the uniformity of application, the oxidative stability of TPP over time while on the card, the effect of light, and the rate of reaction of hydroperoxide-containing oils with the TPP embedded in the card. It was found that TPP-impregnated 3M cards left exposed to air showed clear spectral evidence of significant TPPO formation after several days, regardless of whether they were exposed to light or kept in the dark. TPPO formation could be avoided by storing the impregnated cards in an evacuated desiccator. In terms of reaction time, it was found that after the addition of an oxidized oil onto a TPP-impregnated card, the reaction was ~95% complete within 2 min; however, as the time course was asymptotic, a full 20 min of reaction time was considered necessary to ensure that the reaction had gone to more than 99.9% completion.

Method validation. Validation of the 3M card protocols developed was carried out by analyzing a serial dilution of oxidized canola oils with a wide range of PV values by using both the plain and TPP-impregnated 3M cards. The PLS calibration developed was used to predict the PV, and the results were compared with those obtained with the KCl flow cell. For the cell analysis, the oils were analyzed in their neat form. For the card, the samples were diluted 50:50 with isooctane, 2–3 aliquots were sequentially applied to the cards, and the solvent was rapidly evaporated in a stream of nitrogen after each application. The cell analysis was carried out on a Nicolet Magna 550 with an automated PV analytical package developed and described in an earlier paper (7). The card absorbance spectra, collected with the Bomem spectrometer, were processed with a modified version of the PV analytical package, which included the normalization routine as well as the PLS card calibration. The resulting validation plots for the predictions obtained for the two card methods vs. the flow cell predictions for samples within the calibration range were linear and produced the following linear regression equations:

$$\text{CAPV} = -0.917 + 0.975 \text{ CELLPV} \quad R = 0.994 \quad \text{SD} = 0.92 \quad [1]$$

$$\text{ICAPV} = -1.88 + 0.962 \text{ CELLPV} \quad R = 0.991 \quad \text{SD} = 1.12 \quad [2]$$

where CAPV = PV from the plain 3M card method (TPP/hexanol reagent added to the oil) and ICAPV = PV from TPP-impregnated 3M card method (reaction on card).

These results indicate that either card method tracks PV in a manner similar to the flow cell method, although the results obtained from the impregnated card method appear to be somewhat more variable, likely because impregnated cards have more potential sources of variation, including the possibility of an incomplete reaction and possible nonhomogeneity of the

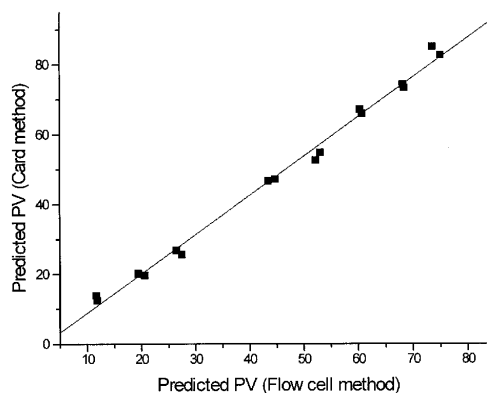


FIG. 8. Plot of PV determined by the TPP-impregnated card method vs. that determined by the flow cell method over the range of 0–100 PV. The linear regression equation for the plot is $y = -2.33 + 1.12x$; $r = 0.996$, $\text{SD} = 2.20$.

TPP distribution on the card. The PLS calibration could be used for the analysis of samples well beyond the calibrated range as illustrated in Figure 8, which compares the predictions obtained for selected samples covering the range of 0–100 PV with the TPP-impregnated card and the flow cell.

DISCUSSION

The results present evidence that the basic PV method, originally devised for a flow cell, can be successfully adapted to the 3M polyethylene IR card, with minor modifications and minimal loss of accuracy. The main source of variability in the card method is not the pathlength of the card *per se*, but the degree of loading, which is difficult to reproduce. The solution to this problem is to normalize the spectra if an appropriate band that can serve as a reference peak can be found. If this is not possible, then spiking with an internal standard may be an alternative. For edible oils, the overtone of the ester linkage carbonyl absorption serves well as a reference peak, but accurate PV values can be obtained only if the saponification number of the oils being analyzed does not vary substantially. This is generally true because most triglyceride oils are predominantly a mixture of C_{16} and C_{18} fatty acids; however, a correction factor may be required for oils that distinctly differ in saponification number. Careful scrutiny is required to select the appropriate baselines for normalization within the overtone region to minimize interferences from alcohols and water; hydroperoxides are not of primary concern because they are transformed to alcohols by TPP. A variety of card loading strategies is available, but our preference is to dilute the oil in isooctane before applying it onto the card with a micropipette. Because dilution lowers oil viscosity, the oil spreads more uniformly, and, when using the TPP-impregnated cards, the oil also appears to react more rapidly if applied in this fashion. With the use of spectral normalization, good results can be obtained, and the reproducibility of the loading technique largely becomes unimportant as long as one covers the application area sufficiently to “wet” the

whole surface uniformly without leaving any irregular bare or dry patches. The impregnated-card procedure is workable but is not recommended, because of the length of time it takes to ensure that the reaction has gone to completion. Further study is needed to determine whether preimpregnated cards would be a viable alternative.

Based on the experience we have gained in using the 3M card in this study, it appears that it could serve well for other quantitative applications in the edible oil sector. PV analysis is just one of a variety of routine QC analyses required in the edible oil industry, and based on the positive results obtained, it is likely that *trans* and iodine value analyses (9) could also be performed with the 3M card. One of the additional benefits of methods developed by the McGill IR Group is that they are preprogrammed, precalibrated, and packaged (14) so that they can be implemented directly in the industrial QC laboratory or at line with a minimum of effort; a number of such oil analysis systems have already been implemented in the industry. In terms of FTIR-based spectroscopic analytical techniques for the determination of PV, there are now three methods available: a mid-FTIR method with a flow cell (7), an FT-NIR (near IR) method with glass vials (15), and the mid-FTIR method developed for the 3M card. From the mid-IR perspective, whether one would opt for using the 3M IR card or a heated flow-cell accessory depends on the volume of analyses and the additional analytical flexibility conferred by use of the flow-cell accessory. At present, the flow cell is more versatile because several analyses have been developed for it, and it is capable of handling large numbers of samples more rapidly; however, for low-volume, more occasional analyses, the 3M card would be both cost-effective and convenient. Because the FT-NIR method uses simple glass vials, it is particularly useful for laboratories that deal both with high sample volumes and need a simple, convenient, and foolproof sample handling protocol. These three alternatives provide the edible oil industry with a variety of instrumental alternatives for the measurement of PV, not only providing the benefit of rapid analysis but also avoiding the hidden disposal costs as well as the dangers associated with reagents used in the traditional chemical method.

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REFERENCES

1. van de Voort, F.R., J. Sedman, A.A. Ismail, and S. Dwight, Moving FTIR Spectroscopy into the Quality Control Laboratory. 1. Principles and Development, *Lipid Technol.* 8(July):89–91 (1996).
2. van de Voort, F.R., J. Sedman, A.A. Ismail, and S. Dwight, Moving FTIR Spectroscopy into the Quality Control Laboratory. 2. Applications, *Ibid.* 8(September):117–119 (1996).
3. van de Voort, F.R., and A.A. Ismail, Proximate Analysis of Foods by Mid-FTIR Spectroscopy, *Trends Food Sci. Technol.* 2:13–17 (1991).
4. Sarver, R.W., and W.C. Krueger, Infrared Investigation of the Conformation of Proteins Deposited on Polyethylene Films, *Anal. Biochem.* 212:519–525 (1993).
5. Moeur, H.P., and R.P. Pinnell, Use of the Disposable IR Card in the Organic Chemistry Laboratory, *J. Chem. Educ.* 73:371 (1996).
6. Anon., 3M IR Cards for Quantitative and Qualitative Analysis. Application Notes C-1 and C-2, 3M, St. Paul, MN, 1997.
7. Ma, K., F.R. van de Voort, J. Sedman, and A.A. Ismail, Stoichiometric Determination of Hydroperoxides in Fats and Oils by Fourier Transform Infrared Spectroscopy, *J. Am. Oil Chem. Soc.* 74:897–906 (1997).
8. Dubois, J., F.R. van de Voort, J. Sedman, A.A. Ismail, and H.R. Ramaswamy, Quantitative Fourier Transform Infrared Analysis for Anisidine Value and Aldehydes in Thermally Stressed Oils, *Ibid.* 73:787–794 (1996).
9. van de Voort, F.R., J. Sedman, and A.A. Ismail, A Rapid Automated Method for the Determination of *cis* and *trans* Content of Fats and Oils by FTIR Spectroscopy, *Ibid.* 72:873–880 (1995).
10. van de Voort, F.R., P. Memon, J. Sedman, and A.A. Ismail, Determination of Solid Fat Index by Fourier Transform Infrared Spectroscopy, *Ibid.* 73:411–416 (1996).
11. *Official Methods and Recommended Practices of the American Oil Chemists' Society*, 4th edn., American Oil Chemists' Society, Champaign, 1989, Method Cd 8-53.
12. van de Voort, F.R., A.A. Ismail, J. Sedman, J. Dubois, and T. Nicodemo, The Determination of Peroxide Value by FTIR Spectroscopy, *J. Am. Oil Chem. Soc.* 71:921–926 (1994).
13. Fuller, M.P., G.L. Ritter, and C.S. Draper, Partial-Least-Squares Quantitative Analysis of Infrared Spectroscopic Data. Part I: Algorithm Implementation, *Appl. Spectrosc.* 42:217–227 (1988).
14. van de Voort, F.R., J. Sedman, and A.A. Ismail, Edible Oil Analysis by FTIR Spectroscopy, *Lab. Robotics Automation* 8:205–212 (1996).
15. Dong, J., K. Ma, F.R. van de Voort, and A.A. Ismail, Stoichiometric Determination of Hydroperoxides in Oils by Fourier Transform Near-Infrared Spectroscopy, *J. AOAC Int.* 80:345–353 (1997).

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