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Improved Spectrophotometric Analysis of Fullerenes C_{60} and C_{70} in High-solubility Organic Solvents

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Fullerenes are among a number of recently discovered carbon allotropes that exhibit unique and versatile properties. The analysis of these materials is of great importance and interest. We present previously unreported spectroscopic data for C_{60} and C_{70} fullerenes in high-solubility solvents, including error bounds, so as to allow reliable colorimetric analysis of these materials. The Beer–Lambert–Bouguer law is found to be valid at all wavelengths. The measured data were highly reproducible, and yielded high-precision molar absorbance coefficients for C_{60} and C_{70} in *o*-xylene and *o*-dichlorobenzene, which both exhibit a high solubility for these fullerenes, and offer the prospect of improved extraction efficiency. A photometric method for a C_{60}/C_{70} mixture analysis was validated with standard mixtures, and subsequently improved for real samples by correcting for light scattering, using a power-law fit. The method was successfully applied to the analysis of C_{60}/C_{70} mixtures extracted from fullerene soot.

Keywords Fullerene, C_{60}, C_{70}, UV/Vis, molar-absorption coefficient, light scattering, *o*-xylene, *o*-dichlorobenzene

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Introduction

The discovery and study of new allotropes of carbon, starting with the spherically structured Buckminsterfullerene (C_{60}) in 1985, is a burgeoning field which has driven a revolution in modern nanotechnology.[1,2] Carbon-based materials with cage-like (fullerenes), cylindrical (carbon nanotubes) and sheet (graphene) structures can be synthesised by a wide range of methods, although the mechanisms of formation are not all fully understood. They exhibit a variety of unique and tunable optical, electronic, mechanical, structural, thermal and chemical properties, offering the prospect of applications in photovoltaics, nanoelectronics, medicine, sensors, display technology, nanocomposites, simulated photosynthesis, batteries and supercapacitors. This has generated great interest in analysis, especially in the quantification of fullerenes from synthetic and environmental sources.[3-5] For this, the fullerenes are extracted with organic solvents, and often analyzed with UV/Vis-spectrometry or liquid chromatography (*e.g.* LC/UV).[3-6] The distinct absorbance features of the most abundant fullerenes, C_{60} and C_{70}, has made UV/Vis-spectroscopy a powerful analysis tool, since it is a fast, cheap and reliable detection method and this even for C_{60}/C_{70}-mixtures from direct soot extraction.[3,4,7,8] The accuracy of such colorimetric mixture analyses rely on the extraction efficiency and the reliability of molar-absorption coefficients used, the values of which vary with the solvent type. Well-established solvents for fullerene extraction are the aromatic solvents *o*-xylene, toluene and *o*-dichlorobenzene (DCB).[4,9,10] However, there is very little spectrophotometric data reported for *o*-xylene and *o*-DCB, for example, there is no

reported data on molar-absorption coefficients for C_{70} in these solvents. For the limited data that does exist in the literature, there are inconsistencies in the molar-absorption coefficients presented, and no indication of uncertainty or errors is provided.[6,7,11,12]

Here, we characterize C_{60} and C_{70} in *o*-xylene and *o*-DCB with UV/Vis-spectrometry at 320 to 800 nm, demonstrate the validity of the Beer–Lambert–Bouguer law and determine accurate molar-absorption coefficients with confidence limits. By closing the literature gap, we give researchers the means to determine mixtures of C_{60} and C_{70} in either *o*-xylene or *o*-DCB spectroscopically. These solvents exhibit higher C_{60} and C_{70} solubility than observed for toluene,[9] and therefore offer the prospect of improved extraction efficiency. This is of potential importance for the analysis of samples containing only trace levels of fullerenes, such as un-degraded environmental samples. The validity of colorimetric mixture analysis is confirmed by measuring known mixtures containing C_{60} and C_{70} and analyzing the data with the newly determined molar-absorption coefficients. Additionally, the reliability of analyzing C_{60}/C_{70}-mixtures from real soot samples is investigated.

Experimental

The fullerenes C_{60} and C_{70}, the fullerene soot and the two solvents were supplied by Sigma-Aldrich, UK and used without further purification. The purity of C_{60} was quoted as 99.9%, the purity of C_{70} as 98.6% and the approximate content of fullerenes in the soot as 6.4% by weight (including ~78.6% C_{60}, ~19.2% C_{70}, balance higher-order fullerenes). The solvents *o*-xylene and *o*-DCB were of GC grade with purities ≥99%. The physicochemical constants of the solvents were taken from Furniss *et al.*[13] and solubility data for fullerenes from a previous study.[9]

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Absorption measurements were made with a Shimadzu UV-Vis 1601 and recorded with the appending software UV Probe V.2.21. The device was used as a single-beam instrument at a scan speed of 260 nm/min, a 2.0 nm slit width and a 1.0 nm wavelength interval. Each sample and solvent blank was measured five times from 800 to 320 nm with quartz cells of 1, 2 and 10 mm (± 0.02 mm each), manufactured by Starna Scientific Ltd. Additionally, the UV-Vis spectrophotometer was combined with a thermostat (Grant GR 150) and set at $20 \pm 0.01°$C for all measurements.

For determining the molar-absorption coefficients, 10 standard solutions per solvent were prepared in the concentration range of 1 μM to 1.4 mM fullerene. All stock solutions and dilutions were measured by mass with an analytical balance (5 figure, Mettler AT201) to ensure very high accuracy of the standard solution concentration. Stock solutions of C_{60} and C_{70} (1 g/L) were sonicated for 5 min each, using a sonicator bath (QH Kerry Ultrasonic Limited, f = 50 Hz). C_{60}-standards with low concentrations were measured in 2 and 10 mm cells, and high concentrations were measured in 1 and 2 mm cells. Since C_{70} absorbs much more strongly than C_{60} at all wavelengths, low concentrations were only measured in a 2 mm cell. Standards were produced in triplicate for each solvent, stored while being protected from light and measured within one week. All measured data were highly reproducible across all replicate preparations and measurements. This gave sufficient data to create calibration curves with up to 56 calibration points to evaluate the molar-absorption coefficients (ε) and their errors using the Beer–Lambert–Bouguer law. The molar-absorption coefficients were derived from the gradient of the line of best fit to the calibration data at each wavelength analysed and standard errors were derived from the linear regression errors.

The Beer–Lambert–Bouguer law can be used for the analysis of mixtures. If there is no interaction between the various species present, such that each does not affect the absorption profile or solubility of the other species, then the absorbance of all species will be additive, see:

$$A = \sum_{i}^{n} \varepsilon_i l c_i, \tag{1}$$

where, at a given wavelength, A is the sample absorbance, l is the sample pathlength and ε_i and c_i are the molar-absorption coefficient and concentration respectively for each species present. For the colorimetric analysis of binary mixtures, two wavelengths are generally used (dual-wavelength analysis). Normally, wavelengths are selected to be at maxima for each species, respectively, but also at a point where there is a large difference between the absorption spectra. Here, in order to increase the accuracy of the determination, a wide range of wavelengths were used simultaneously to fit the data (multi-wavelength analysis). Model spectra were calculated by minimizing the sum of the errors squared (*via* Solver in Microsoft® Excel®), so that they closely overlapped each sample spectrum over a wide range of wavelengths (400 to 650 nm).

The standard mixture samples were measured in 2 mm cells within one week of preparation. Vials with 20 mg of fullerene soot and 10 mL solvent were sealed and incubated at room temperature (protected from light) for either one, two, three or four weeks. The solids were filtered, with the filter paper and solids then being thoroughly rinsed with further solvent, after which the united solution was diluted to a set volume. This solution was then filtered through a 3.0 μm PTFE-syringe filter (Bibby-AZLON-Sterilin Ltd.) and measured in a 2 mm cell. The preparation of all standards and samples was designed so as to ensure that the fullerene concentrations were well within the solubility limits.[9]

Light scattering in the C_{60}/C_{70}-soot mixtures was corrected using the power-law,

$$A_S(\lambda) = \alpha \lambda^{-\beta}, \tag{2}$$

suggested by the literature to correct for Mie scattering by small particles.[14-22] Here, $A_S(\lambda)$ is the apparent absorbance arising from scatting of light by particulates in the sample at a specific wavelength, λ; the scattering exponent, β, is a function of the particulate size and α is a particulate size and concentration dependant scaling factor. The scattering equation (Eq. 2) is fit to data points from 700 – 800 nm, where the fullerenes are known to not absorb light. The absorbance of scattered light is then extrapolated over the whole wavelength range and subtracted from the original absorbance spectrum.

Results and Discussion

Pure solutions of C_{60} and C_{70} were colored magenta and reddish brown, respectively; this was observed for solutions prepared with both *o*-DCB and *o*-xylene. The absorption spectra for C_{60} are shown Fig. 1 and those for C_{70} are shown Fig. 2. The absorption spectrum of C_{70} in *o*-DCB has not previously been presented in the literature and is hereby reported. The profile of the absorption spectra for C_{60} in *o*-DCB and *o*-xylene and for C_{70} in *o*-xylene agree well with the literature.[6,23] As previously reported for a range of aromatic solvents, the absorption spectra of both fullerenes are nearly independent of solvent type above 450 nm, but deviate more noticeably below 450 nm.[23] Differences between spectra cannot simply be explained by experimental error and represent a real deviation due to solvent effects. It would be reasonable to assert that any differences in the solvent polarity affect electrostatic interactions between fullerenes and the solvent molecules, altering the observed absorbance profile. C_{60} absorbs strongly in the UV region with a major peak around 335 nm and a minor peak around 408 nm. The absorbance then quickly falls off to a weak, but broad, absorption band with maxima at 543 and 598 nm. In contrast, C_{70} absorbs strongly throughout, with major peaks at around 335, 384 and 473 nm. In addition, a minor peak is observed in the UV region at 364 nm and a notable shoulder is observed in the visible region around 535 nm. The region from 700 to 800 nm exhibited zero absorbance across all wavelengths and standards for both fullerenes (data not shown). This region can therefore be used to check the instrumental off-sets, and can act as an indicator for possible errors, such as baseline drift, contamination or light scattering.

Fullerene solutions were tested for photo-degradation, to check that the absorbance measurements were stable and reproducible. Solutions were irradiated by continuously scanning and measuring at 800 to 320 nm over a one hour period, resulting in no change of absorbance for both fullerenes and demonstrating photo-stability over the measurement conditions used throughout (data not shown).

The molar-absorption coefficients were evaluated at wavelengths of 320 to 650 nm in 1 nm intervals from calibration curves containing between 19 and 56 calibration points for C_{60} and C_{70}, having between 17 to 44 calibration points. This variation in the number of calibration points is due to the removal of data points with an absorbance over 1.5. This analysis resulted in narrow 95% confidence intervals ($\pm$3% of the molar-absorption coefficient magnitude or less) and excellent
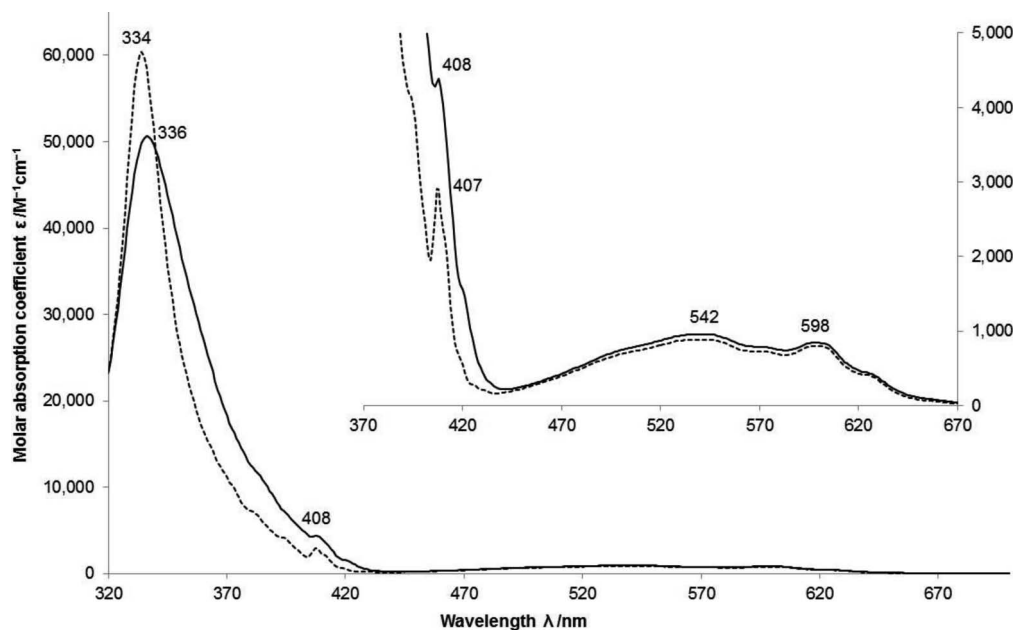
Fig. 1   Molar-absorption coefficients of C_{60} *vs.* wavelength in *o*-DCB (dashed line), in *o*-xylene (solid line); the inset shows the 370 – 670 nm region in more detail.
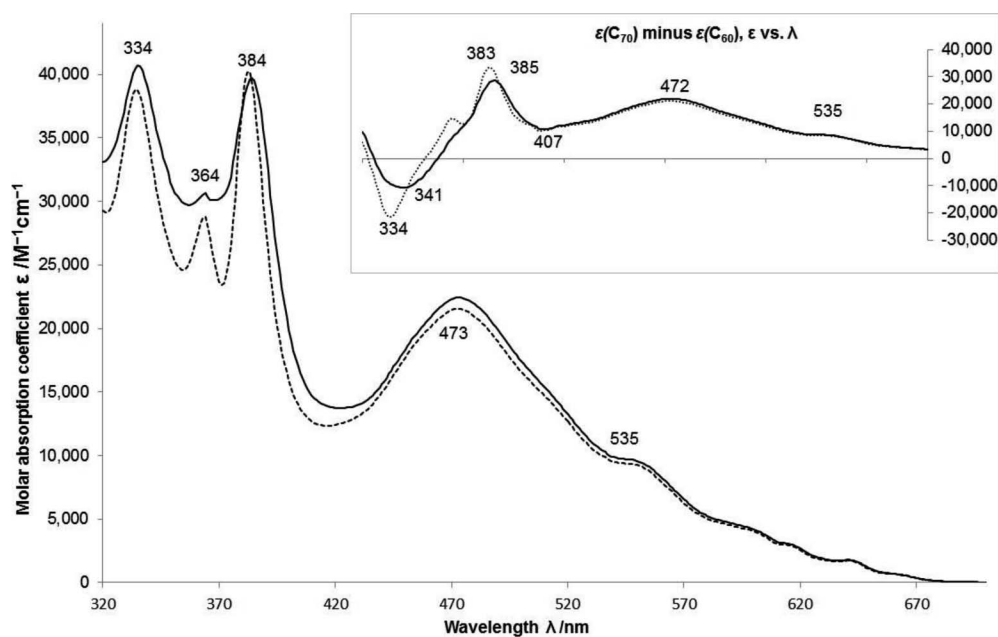

Fig. 2   Molar-absorption coefficients of C_{70} *vs.* wavelength in *o*-DCB (dashed line), in *o*-xylene (solid line); the inset shows difference between C_{70} and C_{60}.

determination coefficients (R^2 >0.999) for linear lines of best fit. As such, the Beer–Lambert–Bouguer law is found to be valid for both fullerenes in both solvents at all wavelengths examined. This is in contrast to a previous study, which suggested that the Beer–Lambert–Bouguer law is not obeyed for C_{60} in *o*-DCB.[12] The explanation offered in this previous work was that deviations from the Beer–Lambert–Bouguer law were caused by fullerene aggregation.[12] It is possible that we have avoided such deviations by careful consideration of solubility limits and careful control of the temperature, to which fullerene solubility can be very sensitive.[9] A summary of the important molar-absorption

coefficient values with confidence intervals are shown in Table 1. Values for all wavelengths, as plotted in Figs. 1 and 2, are also provided online in Table S1 (Supporting Information). No literature values exist for C_{70} in *o*-xylene and *o*-DCB, and are hereby reported. Molar-absorption coefficients for C_{60} found in the literature are compared with measured values in Table 2.[6,7,11,12] The previously reported data is scarce, and deviates from our values. These literature values might be considered to be less reliable due to the fact that either fewer or only single calibration points were used; the fullerenes used were not equally pure; the pathlength was not varied; the

dilution reliability was possibly not as accurately analyzed and corrected for by mass; the fullerene solubility limits where not carefully considered and/or the sample temperature was not controlled. The previous work also fails to report any error bounds. The experimental approach used here addresses all of these issues, resulting in a highly reliable and comprehensive data set.

To determine graphically the largest differences between the absorbance properties of C_{60} and C_{70}, the absorption coefficients have been subtracted from one another (Fig. 2 inset). This is useful for choosing the most appropriate wavelengths for dual-wavelength analysis; these are optimal when located at absorbance maxima and at the same time the difference in absorbance is large. As such, wavelengths of 542 and 473 nm are proposed for dual-wavelength analysis of C_{60} and C_{70} mixtures; the molar-absorption coefficients for these wavelengths are reported in Table 1.

A range of standard C_{60}/C_{70} mixtures with known concentrations were prepared and measured in order to validate the use of colorimetric analysis for these systems. The measured spectra were analyzed by fitting the model spectra to all wavelengths from 400 to 650 nm, using Eq. 1 and the newly determined molar-absorption coefficients. The model spectra closely overlapped the measured data; examples are shown in Figs. S1 and S2 (Supporting Information), and resulted in fullerene concentrations in good agreement with the expected values. Around twenty mixtures with a range of C_{60}/C_{70} ratios were prepared and analyzed for each solvent; typical examples are shown in Table 3. There was no significant difference

between the prepared and measured concentrations at the 99% confidence level ($P = 0.01$), as demonstrated by paired t-tests for each fullerene/solvent combination across all mixtures. As such, the absorbance of C_{60} and C_{70} is indeed additive for binary mixtures in o-xylene and o-DCB. It was demonstrated previously that the absorbance of C_{60} and C_{70} is additive for binary mixtures prepared in o-DCB. However, the method did not use molar-absorption coefficients, but instead used a large set of calibration spectra from mixtures of standard samples, cross-validating them with the sample spectrum.[3] The evaluation of the data for the standard mixtures was also tested by the dual-wavelength approach, which yielded comparable results (not shown). However, as will be indicated later, this approach is more susceptible to errors (*e.g.* contamination) for real samples, since fewer data points are used and possible errors from difficulties, such as light scattering would be less apparent.

This newly validated method was also utilized for the analysis of real fullerene soot samples. The extraction of fullerenes from the soot was straight forward, only requiring simple incubation at room temperature. This is in contrast to more complicated methods, such as those that employ the Soxhlet apparatus or similar. The extracted fullerene mixtures yielded brownish solutions with reproducible spectra. An example spectrum measured after one-week of extraction is shown in Fig. 3, along with the corresponding model fit. The measured spectra were again analyzed by fitting model spectra to all wavelengths from 400 to 650 nm, using Eq. 1 and the newly determined molar-absorption coefficients. The model spectra exhibited a very poor fit to the measured spectra, with large deviations between the measured data points and the lines of best fit (as exemplified in Fig. 3), indicating that the model is not appropriate for

Table 1   Important molar-absorption coefficients for C_{60} and C_{70}; peak positions in bold; C_{70} shoulder at 535 nm

λ/nm	Molar absorption coefficients ε ($\pm$95% CI)/M^{-1} cm^{-1}			
	C_{60}		C_{70}	
	o-xylene	o-DCB	o-xylene	o-DCB
334	49840 ± 405	**60370 ± 612**	40520 ± 485	**38820 ± 465**
336	**50630 ± 408**	58560 ± 601	**40610 ± 477**	38320 ± 467
383	11640 ± 137	6273 ± 44	39570 ± 465	**40260 ± 484**
384	11280 ± 133	6404 ± 40	**39720 ± 460**	39550 ± 482
407	4344 ± 71	**2914 ± 18**	15570 ± 172	13160 ± 100
408	**4384 ± 72**	2903 ± 18	15230 ± 170	12960 ± 98
472	447 ± 9	414 ± 5	22420 ± 241	**21560 ± 177**
473	458 ± 9	424 ± 4	**22440 ± 243**	21560 ± 178
535	952 ± 16	882 ± 7	10400 ± 106	9959 ± 66
542	**955 ± 16**	**885 ± 6**	9786 ± 107	9421 ± 64
598	**841 ± 14**	**792 ± 6**	4322 ± 41	4150 ± 24

Table 3 Comparison of measured concentrations (full-wavelength analysis) of C_{60} and C_{70} mixtures with prepared concentrations

	Concentration/μM							
	o-DCB				o-xylene			
	C_{60}	C_{70}	C_{60}	C_{70}	C_{60}	C_{70}	C_{60}	C_{70}
	Prepared		Measured		Prepared		Measured	
Mixture 1	58.1	9.5	56.8	9.3	56.2	9.0	57.1	8.9
Mixture 2	47.8	19.6	46.4	20.0	42.8	17.0	45.0	17.3
Mixture 3	32.6	33.0	32.6	33.9	34.3	27.1	36.3	27.2
Mixture 4	23.1	39.6	21.6	40.4	22.1	36.1	23.7	36.4
Mixture 5	16.4	44.3	15.1	45.2	11.4	44.9	13.1	45.2
Soot model	52.2	10.3	51.9	10.5	49.4	11.1	50.8	10.9

Table 2   Molar-absorption coefficients of C_{60} compared with literature values

| Molar absorption coefficients ε ($\pm$95% CI) for C_{60}/M^{-1} cm^{-1} at λ/nm								
o-xylene			o-DCB					
Wavelength	Literature	Measured	Wavelength	Literature	Measured	Wavelength	Literature	Measured
332	52640 [12]	47780 ± 407	331	66845 [12]	56270 ± 557	515	1022 [12]	777 ± 6
335	47000 [7]	50390 ± 411	333	54523 [6]	59960 ± 610	520	979 [11]	810 ± 6
399	4040 [12]	5788 ± 91	400	2590 [12]	2692 ± 18	570	938 [12]	724 ± 5
517	957 [12]	852 ± 14	410	3170 [11]	2364 ± 15	580	786 [11]	685 ± 5
570	834 [12]	786 ± 13	470	616 [11]	394 ± 4	600	887 [11]	792 ± 6
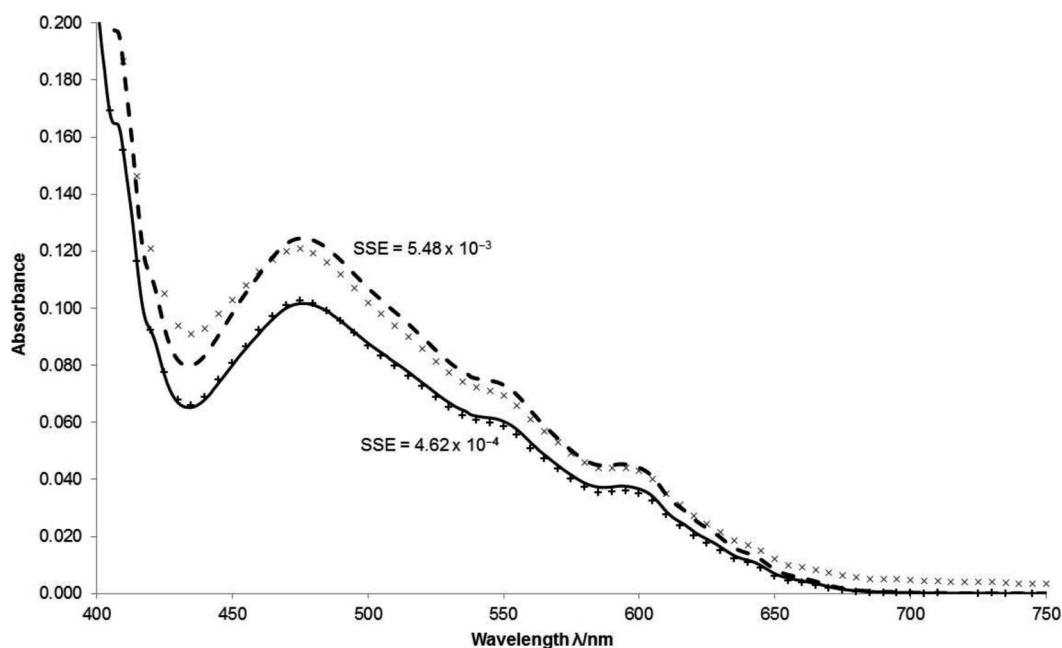
Fig. 3   Comparison of data points measured for a mixture extracted from fullerene soot and model lines of best fit — original spectrum fullerenes extracted with *o*-xylene (×) with a model of the best fit to the original spectrum (dashed line), original spectrum corrected for light scattering (+) with the model of the best fit to this corrected spectrum (solid line); for clarity only every 5th data point is shown; the sum of the squared error (SSE) shows relative goodness of the fit.

analyzing the extracted mixtures. A simple baseline correction for these samples would have been incorrect because the off-set did not represent a drift in instrumental response, nor a simple baseline error, but rather a physical interference due to the scattering of light by microscopic particles (which depends on the wavelength). As such, the data was corrected for scattering with the use of Eq. 2. This resulted in a greatly improved fit for the model spectra to the data (also shown in Fig. 3). The scattering correction also resulted in zero absorbance above 700 nm, as would be expected, based on the spectra of calibration standards. Furthermore, the improved model fit was found to be more appropriate than that obtained for the uncorrected data, by using the *F*-test, the improvement being statistically significant at the 99% confidence level ($P = 0.01$). This additional step to correct for light scattering has not been used previously for the analysis of fullerene mixtures, and offers a novel route for improving the reliability of the method. Furthermore, if a dual-wavelength analysis had been used, then the light scattering error would not have been highlighted.

The extracts of both solvents showed no increase in the absorbance over a four-week period, indicating that the extractions were complete after one week. The results from the analysis in the two different solvents are in good agreement, and to within the experimental error (see Table 4). The measured values were slightly lower than those quoted by the supplier, also shown in Table 4. However, we cannot comment on whether the observed differences are significant, because the manufacturer did not declare errors in their certificate of analysis. Since the material was not supplied as a calibration standard and no details of the experimental method or design were included, these values are considered to be approximate. It is also possible that the amount of fullerene in the soot varied due to the natural inhomogeneity in the manufactured soot batch. If the presence of higher order fullerenes had made a detectable contribution to the measurements, then the absorbance

Table 4   Comparison of the C_{60} and C_{70} concentrations extracted from fullerene soot with *o*-xylene and *o*-DCB; nominal values from the manufacturer are also shown (*error bounds not provided)

Quantities of fullerenes in the fullerene soot (±95% CI), wt%			
Solvent	Total C_{60}/C_{70}	C_{60}	C_{70}
o-DCB	5.18 ± 0.22	4.26 ± 0.17	0.92 ± 0.06
o-xylene	5.32 ± 0.18	4.44 ± 0.15	0.88 ± 0.03
Toluene (Manufacturer)	6.2*	5.0*	1.2*

levels would have been elevated, and the concentrations obtained would have been higher than the manufacture values, not lower. Finally, the fact that the total analysis from the two different solvents are in such good agreement, shows that the methodology yields reliable and accurate results.

Conclusions

Molar-absorption coefficients for C_{60} and C_{70} have been determined over a wide range UV/Vis wavelengths applicable to spectrophotometric analysis in two solvents with high fullerene solubility. The availability of accurate data for solvents with high fullerene solubility offers the prospect of improving both extraction efficiency and analysis reliability. The differences in the absorption spectra for fullerene C_{60} or C_{70} in solvent *o*-xylene and *o*-DCB are relatively small, but more distinct in the region from 320 to 450 nm. The Beer–Lambert–Bouguer law is valid for all wavelengths, resulting in reliable molar-absorption coefficients derived from a large range of replicate calibration points. The absorbance by C_{60} and C_{70} present in the same

solution was demonstrated to be additive, allowing for colorimetric analysis of these mixtures. The determination of fullerene C_{60} and C_{70} in real soot was straight forward, only requiring a simple solvent extraction, filtration, and subsequent UV/Vis-mixture analysis. The utilisation of a light scattering correction resulted in an excellent fit to the experimental data, which is an important consideration for accurate determinations, and is novel in the field of fullerene spectrophotometric analysis.

Acknowledgements

Supporting Information

A summary of all molar-absorption coefficients and their errors for C_{60} and C_{70} in o-xylene and o-DCB from 320 to 650 nm is provided in Table S1. Example spectra and model fits for standard mixtures of C_{60}/C_{70} in o-DCB and o-xylene are provided in Figs. S1 and S2. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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