

Near-infrared spectrophotometric determination of compositions of fullerene samples

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Abstract

A novel method has been developed for the sensitive and accurate determination of compositions of fullerene samples. The method is based on the synergistic use of spectrophotometric measurements and partial least square method. The method is not only simple, inexpensive and fast but also is non-destructive. Compositions of various fullerene samples including fullerite which is the precursor to C_{60} and C_{70} , can be directly and non-destructively determined by this method without any time-consuming separation step as in the HPLC method or destruction as in the MS method.

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1. Introduction

Fullerenes are the subject of wide and intense study in many disciplines including chemistry, physics, and materials science [1–4]. Fullerenes were first found in the laser desorption mass spectroscopy of carbon in 1985 [1]. However, it was not until the discovery of mass production of fullerenes by Kertchmer et al. in 1990 that the field is opened to a large number of new workers interested in this class of materials [2]. Macroscopic amount of C_{60} and C_{70} and higher-order fullerenes can now be prepared by arc heating of graphite under about 13 KPa He condition [2–4]. Crude products are then extracted from the carbon soot by aromatic solvent such as benzene or dichlorobenzene. The extractant usually contains a mixture of C_{60} , C_{70} and higher-order fullerenes. However, number and identity of components in the extracted mixture are not known until they are separated by HPLC and identified by MS [2–5]. Because the number of components and their relative concentrations in the mixture are dependent on experimental conditions, it is desirable to have a method

that can directly determine composition of the extracted mixture.

Fullerenes are known to absorb light in the red region because of their unique molecular structures [1–5]. The red region of the spectrum is known to be relatively quiet as background absorption in this region is much lower than those in the other visible and UV region. As a consequence, it may be possible to use spectrophotometric method for the determination of fullerenes in extracted mixture. However, to date such use has not been realized. This is rather unfortunate considering the ease, simplicity but effectiveness of the method. The limitation is probably due to the fact that C_{60} , C_{70} and other fullerenes have extensive overlapped spectra in this region. As a consequence, it is not possible to use a single wavelength for the determination of components of fullerene samples. It may be possible, however, to use the multivariate method of analysis (e.g., partial least square regression (PLS) method), a full spectrum chemometric method, for the determination of components of fullerene samples. The aim of this study is to develop a novel, simple and effective method for the determination of components of fullerene samples. The method is based on absorption spectrophotometric measurements of samples in the red region for the subsequent data analysis

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using partial least square regression method. Results on the method development and evaluation of its effectiveness will be reported in this paper.

2. Experimental

Fullerenes C₆₀ (99.5%) and C₇₀ (99%) were purchased from MER Co., Tucson, AZ, and used as received. Absorption spectra were taken on the Shimadzu UV 2501 absorption spectrophotometer. Multivariate analysis of data was performed using Unscrambler version 9.0 (Camo ASA) similar to procedures previously reported [6–9].

3. Results and discussion

Fullerenes are known to have relatively low solubility, especially in polar solvents. Limited amounts of fullerenes can, however, be dissolved in aromatic solvents. Shown in Fig. 1 are the absorption spectra of solutions of C₆₀ (1.0 mg/mL) and C₇₀ (0.1 mg/mL) in dichlorobenzene. As illustrated, the spectrum of C₆₀ solution (solid line) is rather broad and contains several overlapped bands with maxima at about 540 and 600 nm. C₇₀ also absorbs in this region (dashed line) but its absorption maximum is shifted towards shorter wavelength (470 nm). As expected, these spectra agree well with those reported in literature [5].

As depicted in Fig. 1, there are considerable amounts of overlaps between absorption spectra of these two fullerenes. As a consequence, it is difficult to use univariate method to determine compositions of each component in a mixture of fullerenes. Accordingly, multivariate method of analysis

Table 1

Set of 31 solutions containing mixtures of C₆₀ and C₇₀ used to prepare calibration models

Sample	C ₆₀	C ₇₀
1	0	100
2	2	98
3	4	96
4	6	94
5	8	92
6	10	90
7	12	88
8	15	85
9	18	82
10	20	80
11	25	75
12	30	70
13	35	65
14	40	60
15	45	55
16	50	50
17	55	45
18	60	40
19	65	35
20	70	30
21	75	25
22	80	20
23	82	18
24	85	15
25	88	12
26	90	10
27	92	8
28	94	6
29	96	4
30	98	2
31	100	0

These solutions have the same total concentration of 100 μM but different concentrations of each fullerenes.

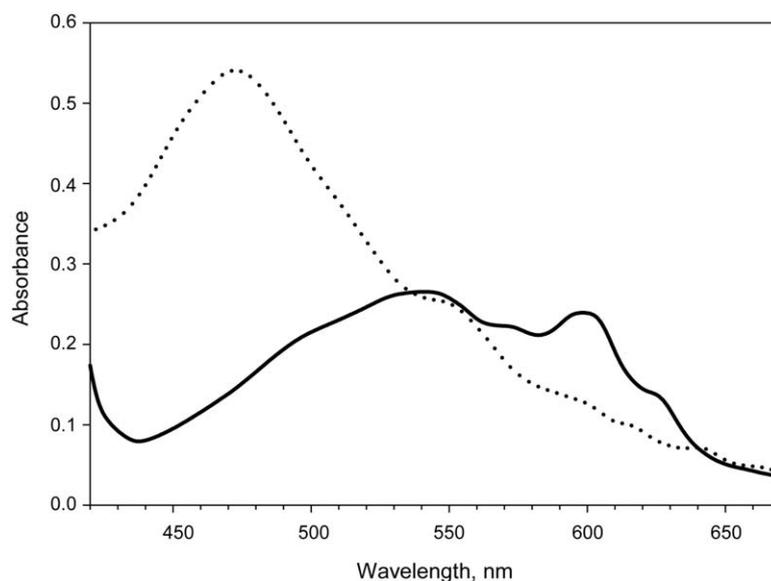


Fig. 1. Absorption spectra of solutions of C₆₀ (1.0 mg/mL) (solid line) and C₇₀ (0.1 mg/mL) (dashed line) in dichlorobenzene.

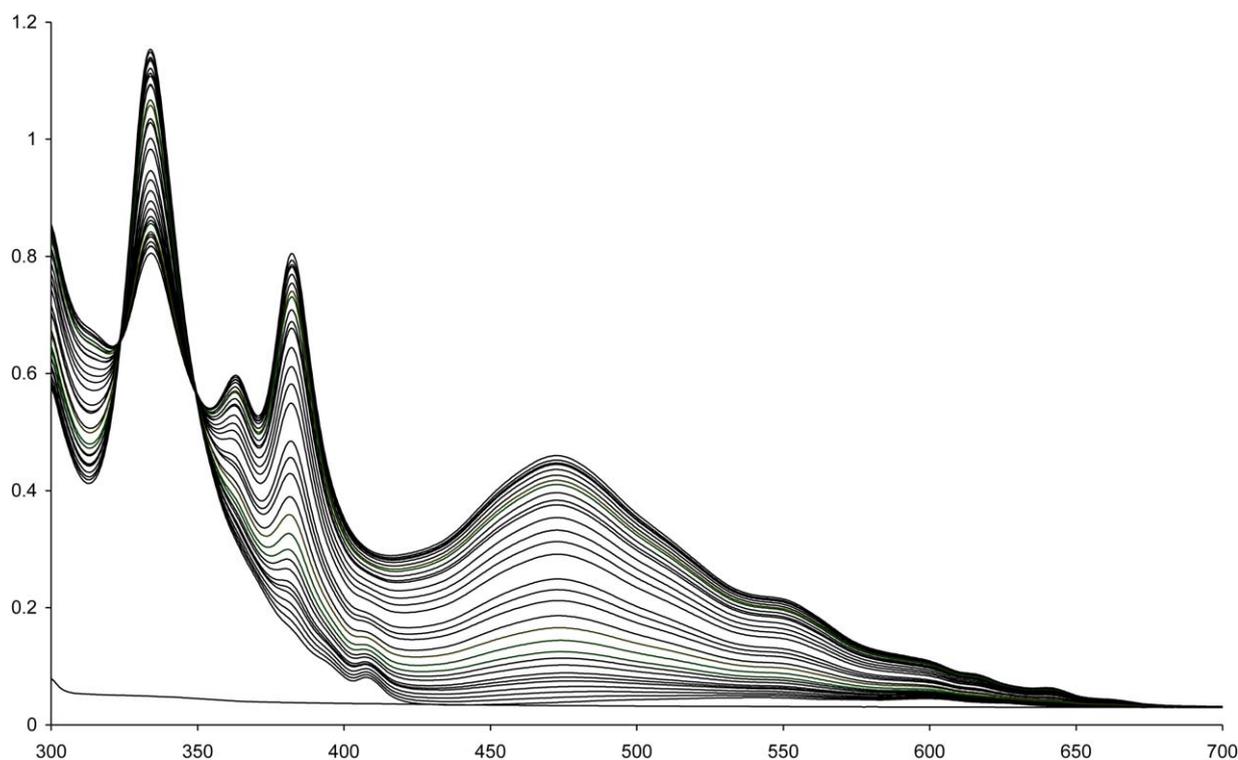
C60 + C70, 100 μ M total in DCB, DCB, calibration, 2 mm

Fig. 2. Absorption spectra of a set of 31 mixtures of C₆₀ and C₇₀ used to prepare calibration models. These mixtures have the same total concentration of 100 μ M but with different concentrations of each fullerene.

(i.e., partial least-squares method (PLS)) was used to develop calibration models for subsequent determination of compositions of unknown mixtures of fullerenes. Table 1 lists the compositions of a set of 31 samples containing C₆₀ and C₇₀ with different concentrations used for calibration model. Calibrations were performed on absorption spectra of these standard samples (spectra shown in Fig. 2) using the partial least-

squares analysis and the full cross-validation method with the Unscrambler chemometric software package (version 9.0). Results from the PLS cross-validation show that calibrations for 31 models require a relatively small number of factors for optimal performance: only 1 for C₆₀ as well as for C₇₀. The root mean standard error of prediction (R.M.S.E.P.) values are 0.185191 and 0.193261 for C₆₀ and C₇₀, while the standard

Table 2
Actual and predicted compositions of solutions of mixtures containing C₆₀ and C₇₀

Sample	C ₆₀		C ₇₀	
	Actual concentration (μ M)	Calculated concentration (μ M)	Actual concentration (μ M)	Calculated concentration (μ M)
1	3.0	3.0 (0.0%)	97.0	97.0 (0.0%)
2	10.0	10.2 (2.0%)	90.0	90.0 (0.0%)
3	14.0	13.8 (1.4%)	86.0	86.0 (0.0%)
4	28.0	27.8 (0.7%)	72.0	72.5 (0.7%)
5	32.0	31.7 (0.9%)	68.0	68.2 (0.3%)
6	48.0	47.5 (1.0%)	52.0	52.2 (0.4%)
7	53.0	52.9 (0.2%)	47.0	47.0 (0.0%)
8	68.0	67.8 (0.3)	32.0	32.2 (0.6%)
9	72.0	72.0 (0.0%)	28.0	28.2 (0.7%)
10	83.0	82.8 (0.2%)	17.0	16.8 (1.1%)
11	95.0	95.0 (0.0%)	5.0	5.1 (2.0%)
12	97.0	97.2 (0.2%)	3.0	3.0 (0.0%)
Fullerite	90.0 ^a	90.0	10.0 ^a	9.9

The numbers in parentheses are relative errors.

^a Quoted by the manufacturer.

error of prediction (S.E.P.) values are 0.191264 and 0.199557 for C₆₀ and C₇₀, respectively. The correlation factors for C₆₀ and C₇₀ are 0.999990 and 0.999989, respectively.

To evaluate the effectiveness of this method, 12 samples containing mixtures of C₆₀ and C₇₀ with different concentrations were prepared and the concentrations of C₆₀ and C₇₀ in each sample were calculated using the calibration models. Results obtained are listed in Table 2. For reference, relative errors are also listed in parentheses in Table 2. It is evident from the table that the method is very effective as the concentrations calculated for all 12 samples agree very well with actual concentrations. Regardless of the relative concentrations of C₆₀ and C₇₀, relative errors between actual and calculated concentrations for all 12 samples are mostly less than 1%. The largest error is only 2.0%.

The method was then used to determine the composition of fullerite. Fullerite is the precursor to C₆₀ and C₇₀. It was obtained from Aldrich Chemicals Corporation and according to the manufacture, based on the analysis using HPLC, it contains 90% of C₆₀ and 10% of C₇₀. As listed in Table 2, the analysis using our method indicates that this sample contains 90% C₆₀ and 9.9% C₇₀ which is in very good agreement with the composition quoted by the manufacture.

Collectively, the results presented clearly demonstrate that a novel method can be developed for the determination of compositions of fullerene samples. The method is based on

the synergistic use of spectrophotometric measurements and partial least square method. The method is not only simple, inexpensive and fast but also non-destructive. Compositions of various fullerene samples including fullerite which is the precursor to C₆₀ and C₇₀ can be accurately, rapidly and non-destructively determined by this method without any time-consuming separation step as in the HPLC method or destruction as in the MS method. Experiments are currently under progress in our laboratory to extend the applications of this method to other nanocomposite materials.

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