The conclusion is then that the use of N_2 at 77 K (or hydrocarbons such as benzene at 298 K) should be complemented with the adsorption of CO_2 at 273 K in order to obtain a better knowledge of the whole porosity range of the activated carbons.

IR Spectrophotometric Method for the Measurement of Toluene Adsorptivity in Activated Carbon[†]

David D. Saperstein

IBM, San Jose, California 95193

IR spectra of toluene adsorbed to high surface area (activated) carbons show downward shifts for both the ring and C–H out-of-plane modes. The band shapes are consistent with the adsorbate in two distinct environments—monolayer and liquidlike. Progress has now been made toward developing an estimate of carbon adsorptivity based on IR measurement of retained toluene (3–30 w/w %). IR intensity correlates directly (±15%) with uptake and highlights surface area differences among four types of activated carbon.

Introduction

Activated carbon readily adsorbs toluene and other organics because of its very high internal surface area[1-4] consisting of micropores (less than 2-nm channels), mesopores (2–50-nm channels), and macropores (greater than 50-nm channels). In general, most of the surface is associated with the micropores. IR spectra of activated carbons show a very weak and characteristic band at approximately 1580 cm^{-1} due to residual graphitic structure[5] (Figure 1B). Other features in the 3200–2800 cm^{-1} (C—H stretches), 1720 cm^{-1} (C=O stretch), and 1220 cm^{-1} (C—O stretch) may not be observed in all carbons.[5,6] Likewise, low-frequency bands in the region 800 cm^{-1} and below may be due to metal–oxygen modes from impurities or arise from ring motions.[7] Unlike the carbon spectrum, toluene adsorbed to activated carbon (Figure 1A) shows two prominent peaks (Figure 1C) in the 600–4000-cm^{-1} region which arise from the C–H (approximately 726 cm^{-1}) and ring (approximately 692 cm^{-1}) out-of-plane modes.[8] The corresponding peaks in liquid toluene, observed at 730 and 695 cm^{-1}, indicate that the toluene is physically adsorbed to the carbon[8] as expected.[1] Each of the toluene peaks in the adsorbed sample is composed of two overlapping bands separated by about 8 cm^{-1}. The more intense bands in each peak are consistent with IR absorption by toluene in multilayer environments; the low-energy shoulders are consistent with IR absorption by the first adsorbed monolayer. Other toluene bands can be observed;[8] however, they exhibit lower signal to noise. When benzene is used instead of toluene, its out-of-plane C–H vibration can be observed[8] at 673–675 cm^{-1}, which is red-shifted from the liquid frequency of 677 cm^{-1}.

Activated carbon is physically and chemically heterogeneous,[3,4] and therefore, the preparation of carbon samples for reproducible, quantitative IR measurement is not straightforward.[5,6,9] Typical adsorbents such as fiber and powder samples are very different in shape and thus may show apparent differences in their carbon and adsorbate

IR spectra. We previously reported[8] that IR spectra of adsorbed toluene gas in high-area carbons might be used to estimate adsorbate quantities. That report, however, was based only on the analysis of one type of carbon. Because we wish to determine whether adsorptivity of activated carbon can be quantified spectroscopically, the desorption of toluene from three different kinds of powder and one fiber has now been investigated. Initial results show that with IR techniques an estimate of the carbon area (>100 m^2/g) covered by adsorbed toluene can be obtained on nonuniform samples.

Experimental Section

IR spectra were obtained in transmission with an IBM Instruments IR/85 FT-IR (Fourier transform infrared spectrometer, f/4.2 optics) equipped with an MCT detector (low-frequency cutoff, ca. 550 cm^{-1}) at 2-cm^{-1} resolution. No special accessory optics were used to collect the scattered light from the samples. Before the start of data collection each day, the detector was allowed to settle for approximately 90 min to equilibrate the MCT element to the liquid nitrogen temperature. A wire screen was

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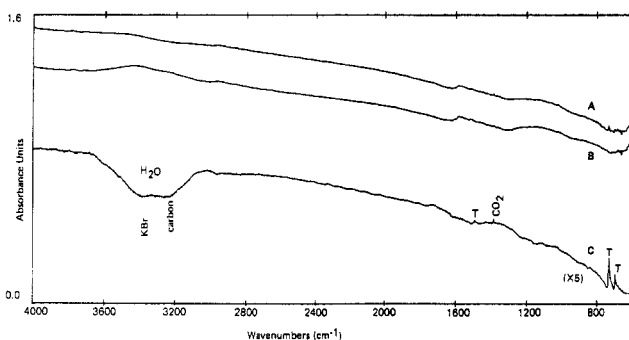
Figure 1. Plots of the carbon (Engelhard) extinction from 4000 to 600 cm^{-1} at 2-cm^{-1} resolution: (A) 14% toluene uptake; (B) no added toluene; (C) difference spectrum, (A) – (B), ×5. T = adsorbed toluene in carbon; CO_2 = adsorbed carbon dioxide in the KBr support.

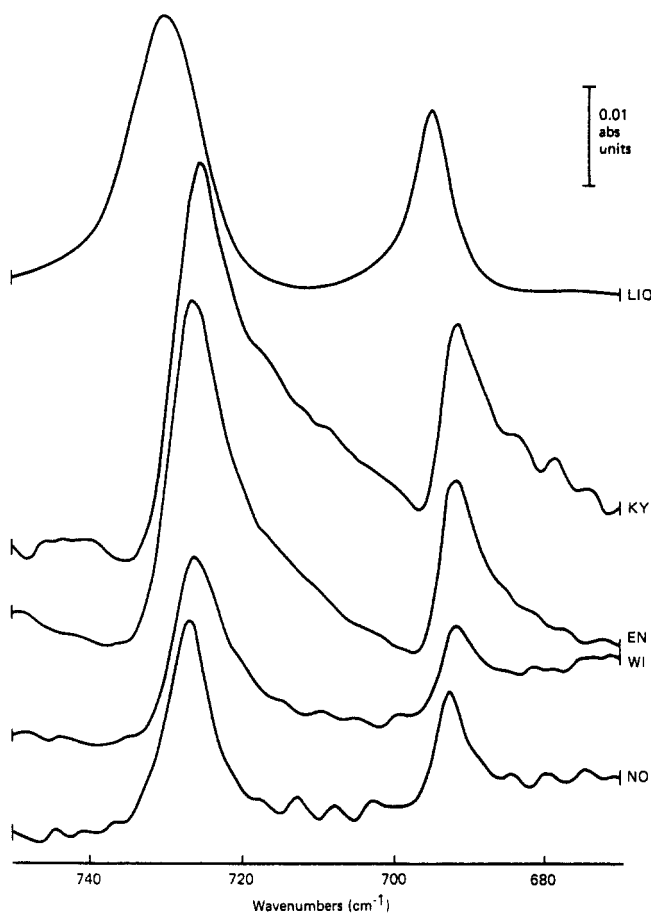**Figure 2.** LIQ: FT-IR spectra of liquid toluene, 750–670 cm^{-1}; resolution, 2 cm^{-1}. Heated for 1 h at 67 °C: KY, toluene retained by Kynol ACN-210; EN, toluene retained by Engelhard CG-5; WI, toluene retained by Witco 965; NO, toluene retained by Norit RB1.

permanently mounted in the optical path to lower the incident flux so the detector would respond linearly. The ratioed spectra, Figure 2, 750–670 cm^{-1}, represent the difference of carbon samples with and without added toluene.

Four kinds of carbon, activated for gas adsorption, were used in the experiment: Witco 965, Norit RB-1, Engelhard CG-5, and Kynol ACN-210. These carbons have nitrogen BET surface areas ranging from 1000 to 1500 m^2/g;[10] see Table III. Although the physical appearances of the Witco, Norit, and Engelhard carbons differ somewhat, they grind to a powder of 10-20-μm particles. The Engelhard CG-5 contains 0.5 w/w % palladium which is not

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(10) EN, Engelhard Catalysts (Newark, NJ); KY, American Kynol (New York, NY); NO, American Norit (Jacksonville, FL); and WI, Witco Chemical Co. (New York, NY).

Table I. Relation between Carbon Weight and Pellet Optical Extinction, log (SBS$_0$/SBS)

weight of Kynol carbon, mg	weight of KBr, mg	log (SBS$_0$/SBS), abs units	log (SBS$_0$/SBS) divided by the weight of carbon
0.630	161.6	0.440	0.698
1.168	178.7	0.799	0.684
1.442	201.6	1.066	0.739
1.661	209.1	1.212	0.729
			av 0.713 ± 3%

expected to affect the physical adsorption results appreciably. The Kynol sample is a fiber of approximately 10 μm in diameter that grinds with only some difficulty to small rods 10–50 μm long.

The carbon was prepared for infrared measurement by grinding in the presence of reagent grade chloroform and then allowing the excess chloroform to evaporate before oven drying at approximately 100 °C. After heating for more than 1 h, there was no spectral evidence of any adsorbed chloroform at 750 cm^{-1} and there was no change to the weak carbon bands in the 850–650-cm^{-1} region. Weight measurements, before the addition and after the removal of the chloroform, changed less than 0.5%. Liquid toluene (spectrograde) was added to the carbon powder dropwise, without grinding, to produce a visibly wet sample. The powder was air dried at room temperature, ca. 22 °C, and then further heated at either 67 or 108 °C for approximately 1 h (60 ± 6 min) in an open aluminum pan. The oven temperatures and times were selected to produce a range of adsorbed weights. The carbon was weighed before the toluene addition and after heating to obtain the weight fraction retained. The sample was mixed with a preweighed amount of KBr until a uniform grey color was obtained. Most samples contained 0.5–1.5 mg of carbon in 200–300 mg of KBr. The powder was pressed into a 13-mm-diameter pellet which transmitted between 2% and 10% of the light—corresponding to log (SBS$_0$/SBS) values of 1.7–1.0, respectively; see below. Transmission values less than 2% or much more than 10% were associated with higher noise and possibly less accurate measurements.

Examination under a visible light microscope showed that the grey color of the pellets was due to well-dispersed black particles—granules or fibers. In order to be sure the pellets were accurately measured and to compensate for as much as 1–2% nonuniformity in absorption when the pellets were rotated, the samples were usually measured 4 times (2000 scans each) at 0°, 90°, 180°, and 270° with respect to an arbitrary point on the pellet. Results from the separate measurements were averaged. After storage for a month at 67 °C in air, the pellets were reexamined by FT-IR spectroscopy within the spectral region 750–650 cm^{-1}. No significant changes were observed after the time lapse.

The spectrum of activated carbon, with or without toluene, has a complex background due to scattering, a sizeable offset from zero due to bulk absorption and some weak molecular absorption features superimposed.[5] The scattering and absorption are properties of the size and shape of the particles with respect to the wavelength of light and are quite complex because of particle irregularity.[5,6] The usual method for normalizing an IR spectrum, dividing the absorbance values by the sample weight, does not account sufficiently for changes in spectral phenomena when different carbons are compared. For example, 0.6 mg of the Engelhard CG5 is sufficient to produce the same light extincition as 1.1 mg of the Kynol ACN-210 in 200 mg of KBr when made into a 13-mm pellet. To estimate the amount of toluene in activated carbon from its IR spectrum, we have ratioed the toluene absorption intensities to the total optical extinction of the sample rather than to the weight of the carbon in the sample. This method is equivalent to determining relative toluene peak areas by normalizing with an appropriate band of the adsorbent. In the case of carbon, there are not any bands and we used the entire spectrum instead.

An estimate of the sample extinction, log (SBS$_0$/SBS), can be obtained by comparing the peak intensity of the carbon interferogram, SBS, with the peak intensity of the interferogram, SBS$_0$, collected without carbon. The correlation of log (SBS$_0$/SBS) with carbon weight for any one type of carbon can be demonstrated by measuring the IR spectra of pellets with different sample weights. Table I shows measured carbon and KBr weights and

Table II. Summary of IR Absorption and Carbon Adsorption Data for Toluene

spec no.[a]	carbon wt in pellet, mg	log (SBS_0/SBS)	toluene uptake, w/w %	out-of-plane[b] C–H wag			out-of-plane[b] sextant ring bend		
				peak freq	peak height	peak area[c]	peak freq	peak height	peak area[d]
liquid[e]				730	0.0730	1[f]	694.5	0.0460	0.33
EN R	0.85	1.22	30.2	726	0.0310	0.335	692	0.0151	0.102
KY L	1.56	1.57	21.2	725.5	0.0239	0.287	692	0.0116	0.085
WI L	1.26	1.46	14.6	726.5	0.0223	0.201	692	0.0104	0.074
EN L	0.85	1.26	13.7	726	0.0270	0.304	692	0.0131	0.097
WI L	0.96	0.97	13.7	726.5	0.0182	0.151	692	0.0075	0.044
EN L	0.68	1.13	13.0	725.5	0.0245	0.244	691.5	0.0122	0.084
NO L	1.07	1.36	11.7	727	0.0147	0.102	692.5	0.0075	0.038
KY H	1.51	1.52	5.6	725.5	0.0110	0.121	691	0.0051	0.037
EN H	0.82	1.05	4.0	726	0.0100	0.099	691.5	0.0043	0.033
KY H	1.66	1.20	3.8	725	0.0040	0.035	690	0.0018	0.011
NO H	1.15	1.48	2.9	727	0.0053	0.045	693	0.0024	0.014
WI H	1.15	1.33	2.8	726	0.0050	0.039	692	0.0026	0.014
EN H	0.68	1.07	2.8	726.5	0.0085	0.087	691	0.0038	0.022
WI G		0.80	34.0	726	0.0098	0.126	692.5	0.0053	0.047
WI G		0.80	4.3	726	0.0040	0.054	693	0.0025	0.020

[a] KY, American Kynol ACN-210, WI, Witco 965; NO, Norit RB1; EN, Engelhard CG-5 0.5% Pd on carbon; H, toluene desorbed at 108 °C; L, desorbed at 67 °C; R, desorbed at room temperature; and G, carbon powder on KBr for gas adsorption. [b] Reference 7, frequency in cm^{-1}, intensity in absorption units and area in cm^{-1}. [c] Integration limits 740–710 cm^{-1} with a linear base line. [d] Integration limits 700–675 cm^{-1} with a linear base line. [e] Neat liquid between KBr plates. [f] Peak heights and the area of the 695-cm^{-1} band are normalized with respect to the area of the 730-cm^{-1} band.

Table III. Correlation[a] between Weight Retained and IR Band Intensity for Toluene Adsorbed to Activated Charcoal[b]

IR intens	726 band				692 band			
	slope	intercept	av error	corr. coef.	slope	intercept	av error	corr. coef.
height	1.1×10^{-1}	4.1×10^{-3}	13.3	0.92	5.2×10^{-2}	1.8×10^{-3}	13.5	0.91
area	1.2	3.0×10^{-2}	14.9	0.90	3.6×10^{-1}	1.1×10^{-2}	16.7	0.88

[a] IR intensity = (slope)(carbon weight) + intercept. [b] Witco 965, Norit RB1, American Kynol ACN 210, and Engelhard CG-5 powder.

optical extinctions for four samples of Kynol ACN-210. The right most column shows that the log (SBS_0/SBS) values track (±3%) the threefold change in concentration even when the extinction is greater than 1. Thus, when toluene adsorption is measured spectroscopically for only one type of carbon sample, either log (SBS_0/SBS) or carbon weights can be used to normalize the toluene intensities with satisfactory results, ±5% average error between toluene uptake and IR intensities. However, normalization with log (SBS_0/SBS) rather than with the amount of carbon in the sample can improve the overall correlation between the weight of retained toluene and the IR intensity by nearly a factor of 2 when different kinds of carbon are compared: ±22% compared to ±13% average error. If the carbon weight is unavailable or unreliable, IR transmission values can provide a crude estimate of the weight (1 ± 0.5 absorption unit/mg for all the carbons measured in the 13-mm-diameter pellets) and the spectral normalization. log (SBS_0/SBS) can now be used to normalize the toluene gas adsorption results,[8] facilitating comparison with the liquid desorption results below.

log (SBS_0/SBS) is approximately equivalent to the average absorbance of the entire spectrum, 550 (detector cutoff)–5500 cm^{-1} (germanium cutoff), and is quite insensitive to spectral noise and the small toluene absorptions at 726 and 692 cm^{-1}. Because the background is usually higher at the higher wavenumbers, it would seem likely that log (SBS_0/SBS) would overestimate the background absorption in the 750–650-cm^{-1} region. However, when the average background absorbance values for the 750–650-cm^{-1} region were measured and used to normalize the toluene band absorbances, no change was observed in the estimated error of the fit.

Results and Discussion

a. Toluene Desorption Measurements. Figure 2 shows typical toluene spectra for the four kinds of activated carbon used in these experiments. The spectrum of liquid toluene "LIQ" is included for reference purposes. Although the positions of the out-of-plane bands are sim-

ilar, small reproducible differences can be observed in peak position and width. To ascertain whether or not these differences reflect adsorptivity properties of the carbons, 13 samples were prepared that contained 2.8–30% toluene (g/g of carbon). Table II summarizes the carbon data: type, preparation method, weight, total optical extinction [log (SBS_0/SBS)], toluene adsorption weight, peak frequency, height, and area for both the C–H and ring out-of-plane modes. The peak heights and areas are normalized by the log (SBS_0/SBS) values. The bandwidths, which range from 7 to 14 cm^{-1}, can be calculated directly by dividing the area by the height. The samples are listed by the amount of retained toluene except the two gas adsorption samples, which were prepared differently[8] and are listed separately.

Figure 3 shows the amount of scatter in the plot comparing the log (SBS_0/SBS) normalized heights of the 726-cm^{-1} bands and the toluene adsorption weights. It is typical of the other plots (not shown) which compare the normalized areas and/or the 692-cm^{-1} band with uptake. The straight line is the best-least-squares fit to the experimental data—the origin point is included in the calculation, but the line is not forced through it.[11] Correlations between retained weight and the intensity of the 726 and 692-cm^{-1} bands are summarized in Table III. In general, the amount of toluene uptake can be estimated (±15%) from the IR band areas or peak heights. The large error is not unexpected considering that the carbons come from different vendors and are designed for different applications.[10] For both bands peak heights, and not areas, correlate slightly better with toluene weights. This relationship was unexpected because the fused shoulder in
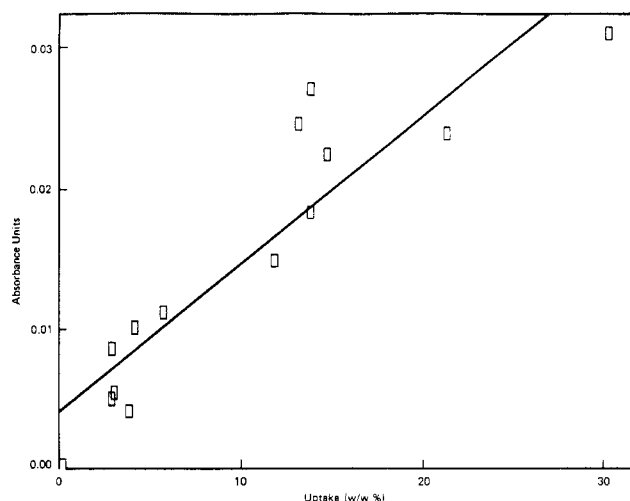
(11) IBM Instruments, Inc. (Danbury, CT).

Figure 3. Plot of the least-squares fit (—) to the comparison of the toluene peak heights (726 cm^{-1}) with weight retained by the Kynol, Engelhard, Witco, and Norit carbons. Correlation data are listed in Table III.

Table IV. Summary of the Toluene Adsorptivity Features by the Carbons Tested

carbon	peak shift from liquid value, cm^{-1}	approx area in shoulders	BET surface area,[9] m^2/g	toluene[a] retentivity (67 °C, 1 h), m^2/g
EN-CG5	4	35–45%	1000	420
KY-210	3.5	35–45%	1500	400
WI-965	3	25%	1300	260
NO-RB1	2	5–10%	1000	180

[a] ± 100 m^2/g.

each peak (ca. 718 and 684 cm^{-1}) is measured more accurately by the area than by the peak height. Because there is substantial error to the fits, it is possible that the better correlation is not significant. An examination of the spectra can lead to an alternative explanation as follows: there is a consistent peak shape (bandwidth) difference among the four carbons which is quite reproducible and persists in both low (2–5%) and high (12–30%) loadings. The Kynol fiber and Engelhard CG-5 consistently have 35–45% of the total area in the shoulders, 718 and 684 cm^{-1}, whereas the Norit samples have much less, approximately 5–10%. The Witco samples show intermediate values—approximately 25%. In addition to this trend, there appears to be a band shape difference between the sample spectra for toluene gas adsorption and for liquid desorption. For example, at low loadings after gas adsorption by the Witco 965 carbon,[8] the 718-cm^{-1} shoulder is as prominent as the 726-cm^{-1} peak, indicating equivalent peak heights for each band in the fused peak. However, the typical liquid desorption spectrum for the same Witco carbon, Figure 2, indicates a 2:1 ratio. While a tentative explanation for the band shape differences is offered in the next section, it is apparent that the differences can lead to poor area determinations and hence to the better correlation of uptake with peak heights. Accompanying the band shape differences in the spectra are very small differences in the main peak positions. The Kynol samples have the largest red shift (4 cm^{-1}) from the recorded peak frequencies of the liquid, the Norit samples have the smallest shift (2 cm^{-1}), and the Engelhard (3.5 cm^{-1}) and Witco (3 cm^{-1}) samples show intermediate values. It is intriguing that the orders of these shifts are paired with the relative magnitude of the areas in the 718- and 684-cm^{-1} bands, see Table IV.

Table II includes two gas-phase adsorption results with areas normalized by their log (SBS$_0$/SBS) values—these are recomputed from spectra a and c of Figure 1 in ref 8. While the intensities corresponding to the lower loading, 4.3 w/w %, are within the experimental error for the liquid desorption measurements, the intensities corresponding to the high loading are low by a factor of 3. The correspondence of adsorption and desorption results at the low loading reaffirm that a qualitative estimate of the carbon sample size can be obtained from log (SBS$_0$/SBS). The discrepancy at high loading may be due to the crude estimate or to measurement errors deriving from digital

subtraction of the gaseous toluene.[8]

b. Surface Area Comparisons. The weight of the toluene adsorbent can be converted to an upper limit for the surface area assuming the presence of single monolayer coverage and a molecular dimension of 0.3 nm^2/molecule. In the case of toluene adsorbed to the Witco 965 carbon, which shows approximately 45 w/w % uptake at saturation vapor pressure and 25 °C, the upper limit is approximately 900 m^2/g.[8] This approximation is in reasonable agreement with the nominal N2 BET surface area, 1300 m^2/g. In our experiments, saturation coverage was never measured. An assessment of surface areas can be determined from the IR-determined retentivities of the different carbons after heating for a fixed time, e.g., the samples marked "L" in Table II were heated for 1 h at 67 °C. Regardless of whether or not peak heights, areas, or 726- or 692-cm^{-1} bands are examined, a definite ordering of the toluene uptake can be established from absorption intensities. The Kynol and Engelhard carbons retain more than twice as much toluene as the Norit carbon. The Witco samples retain intermediate amounts. By using the derived relationship between IR intensity and recorded weights shown in Table III to predict surface adsorption, IR estimates of an upper limit to the surface area covered by the retained toluene can be obtained. From most to least, these are the Engelhard (420 m^2/g), the Kynol (400 m^2/g), the Witco (260 m^2/g), and the Norit (180 m^2/g) samples. Although the absolute values of these numbers may be of little practical use, the relative ordering indicates a more than twofold difference in surface adsorption not shown by the carbon weights. The simplest way to account for these results, which are compared in Table IV, is that upon desorption there is less material retained in the Norit micropores. The lower apparent retention might be due to a significantly different pore size distribution or pore shape[12] compared to the other carbons. While completely speculative, this hypothesis would account for low retentivity by nominally similar BET surface area carbons, for the correlation of weight retained with peak height, and for the lack of intensity in the Norit 718- and 684-cm^{-1} bands which show the amount of toluene physically adsorbed to the carbon surface.[8] This hypothesis is also consistent with the trend in the small shifts of the main peak positions among the four kinds of carbon. The carbon with the largest micropore radius would have the smallest frequency shift because the carbon surface would exert the least perturbation of the liquid structure. An alternative explanation, an anomalous blue shift of the shoulder bands, is not consistent with the measured toluene peak areas.

Conclusions

It was not obvious to us that IR spectroscopy could be used to estimate adsorption in high area (activated) car-

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bons. The problems that plague the direct IR measurement of the carbon (samples are highly scattering, strongly IR absorbing, and not homogeneous) were expected to obscure the IR spectrum of an adsorbate. To ascertain whether IR can be used to measure uptake, we have attempted to quantify a nonfavorable case: the comparison of different kinds of carbon adsorbents. Our results show that the relative uptake by different carbons for toluene can be estimated with IR spectroscopy to approximately 15% accuracy. When studying the relative uptake of a single type of carbon, we estimate that 5% accuracy can be achieved with IR spectroscopy of adsorbed toluene or

other aromatic hydrocarbon. Finally, when a single sample is studied in situ[8] even greater measurement accuracy can be achieved.

The spectra of toluene adsorbed to the different carbons also highlight the relative contributions of the adsorbate in the first monolayer and the multilayer, revealing significant differences among the carbons tested.

Registry No. C, 7440-44-0; toluene, 108-88-3.

Internal Heating of Multilayered Aerosol Particles by Electromagnetic Radiation

Marek Sitarski

Clarkson University, Potsdam, New York 13676

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Expressions for the heat source function inside an irradiated multilayered spherical particle have been derived. The proposed new algorithm circumvents the typical numerical difficulties with generation of the Riccati–Bessel functions of complex arguments by reformulation of the series expansions of the electromagnetic fields and the corresponding systems of complex algebraic equations for the coefficients of the expansions. The developed computer code appears to be stable in a wide range of size parameters. The results of the test computations for homogeneous coal spheres, two-layered coal–water and water–coal spheres, and three-layered coal–vapor–water concentric spheres prove the correctness of the derived equations as well as the computer code. The computations for the two- and three-layered particles simulate optical properties of an explosively boiling colloidal coal–water droplet exposed to high-intensity infrared radiation.

Introduction

Layered particles have been found in many man-made and natural systems. Ultrafine coal particles wetted by water or liquid fuels in combustors, soot and fly ash particles coated by water in the polluted atmosphere, metallic fine particles covered by oxides, and multilayered combustion aerosols resulting from fast multicomponent nucleation and subsequent condensation are typical examples. None of them are perfect concentric spheres; however, an understanding of their basic radiative properties can be obtained by studying the simple geometry of multilayered concentric spheres. Internal radiant heating of layered particles causes a number of interesting phenomena such as linear photophoresis, nonlinear photophoresis, and explosive evaporation of two-phase droplets.[1-3] Numerical difficulties in computations of the internal fields have restricted the studied systems to relatively small size parameters. The expressions for electromagnetic fields evaluated by Aden and Kerker[4] for two concentric spheres involve expansion series whose terms contain Riccati–Bessel functions and their derivatives of complex arguments and first and second derivatives of the Legendre polynomials. The most serious obstacle in writing a computer program for an arbitrary layered sphere is that the expressions for the fields have to be put in a form that avoids the computation of excessively small or large numbers beyond the limits of the computer employed.

Accordingly, Bohren and Huffman[5] call such a program "explosion-proof". On the other hand, the values of internal fields inside large and absorbing particles can become excessively small on physical grounds. To cope with these and other numerical problems, we first reformulate the derived expressions to avoid generation of the Riccati–Bessel functions of complex arguments. This approach makes the program explosion-proof within certain limits, and then we apply the published experience in Mie scattering computations of Toon and Ackerman,[6] Wiscombe,[7] and Bohren and Huffman.[5]

The purpose of this paper is threefold: (1) to present a very brief derivation of the working expressions for the heat source function for irradiated multilayered spheres; (2) to construct an algorithm for computations of the heat source function applicable to large (in terms of size parameter) and absorbing multilayered spheres; and (3) to perform test calculations for one-, two-, and three-layered spheres checking correctness of the derived equations, algorithm, and computer code. The particular systems chosen for test computations are coal–water particles irradiated by infrared unpolarized light. Results of the computations can be related to the absorption properties of the colloidal coal–water ultrafine slurry droplets exposed

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