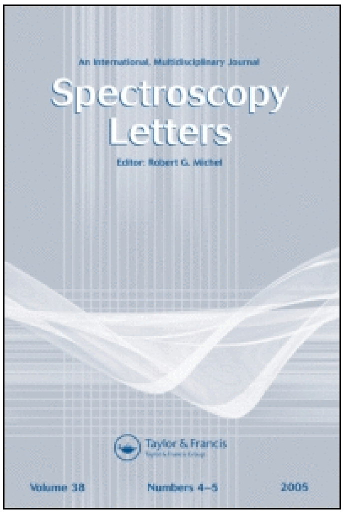

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Carbon as Reference for Normalizing Infrared Photoacoustic Spectra

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CARBON AS REFERENCE FOR NORMALIZING INFRARED PHOTOACOUSTIC SPECTRA

Key Words: Photoacoustic Spectroscopy, Infrared, Carbon, Surface Species

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Photoacoustic spectra of solids[1] are usually "source compensated," i.e., normalized for differences in source emission at different wavelengths, and such compensation is done by comparing the photoacoustic spectrum of a sample to the emission spectrum of the source measured directly with, say, a photocell,[2] power meter,[3] or photodiode,[4] or to the photoacoustic spectrum of "carbon" recorded under the same conditions as that of the sample. A variety of carbons has been used for this purpose, including carbon black on silica,[5] soot from a gas torch,[6] and acetylene-sooted bakelite,[7] such a reference substance being assumed to be a flat black absorber. That assumption appears to be valid, as indicated by the close comparison of photoacoustic spectra of carbons with directly measured spectra of the exciting sources[1,8,9] observed in the visible region, and would also seem to apply to the spectra of Fig. 1.

The top two traces of Fig. 1 are the photoacoustic spectra of granular chars resulting from the vacuum pyrolysis of sucrose, recorded with a Princeton Applied Research Corp. Model 6001 spectrometer, compensated by ratioing against the spectrum of a carbon standard. The signals from the chars were about one fifth as strong as that from the standard, and this difference

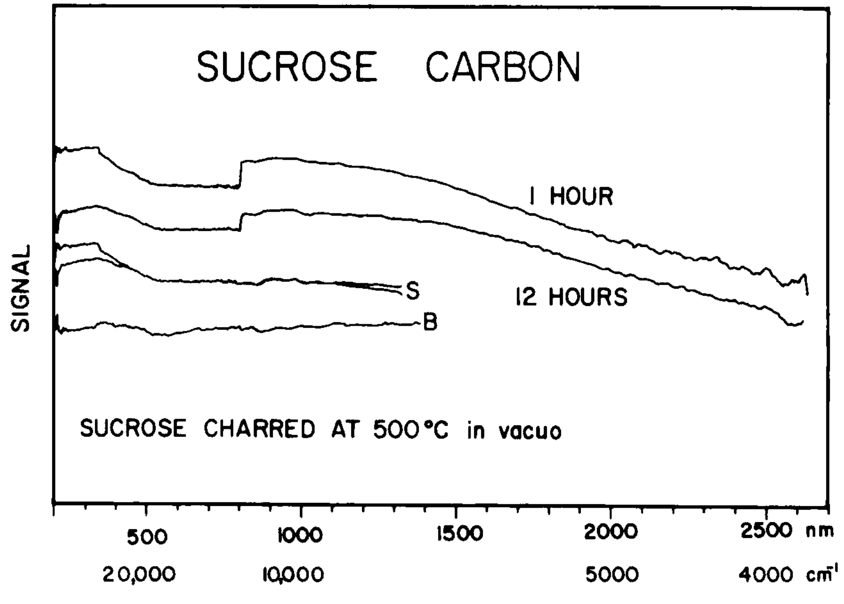

Fig. I. Spectra of carbon obtained by charring sucrose for 1 and 12 hrs, recorded with a P.A.R.C. Model 6001 spectrometer. S, B: see text. The ordinates are displaced.

in signal strength can be attributed to differences in particle size of the solids. The abrupt changes in slope at 800 nm are artifacts caused by the automatic grating change during the scan. If the artifacts are deleted and the segments redrawn so that the traces join at 800 nm, traces S result. Trace B was obtained by ratioing two spectra of the same carbon standard and is useful in indicating the noise level attainable. The spectra of the two chars are "flat" and identical over much of the visible region and would be usuable as reference. The spectra remain essentially featureless but change slightly in slope through the near-IR, but differ substantially at longer wavelengths.

Figure 2 shows the photoacoustic spectra of the same chars recorded with a single-beam dispersive spectrometer[10] in the IR range. The spectra were normalized by ratioing against the spectra of graphite, (powder scraped from a high-purity electrode from Ultra-Carbon Inc.) and show substantial structure. For example, the top trace clearly indicates the presence of O-H and C-H absorptions and other features below 2000 cm^{-1}. Substantial changes occur upon further pyrolysis (lower trace); these will be discussed elsewhere. Obviously, materials which are "black" in the visible are not necessarily so in the IR. More significant is the observation that the IR spectra of the chars continue to change and faint structure

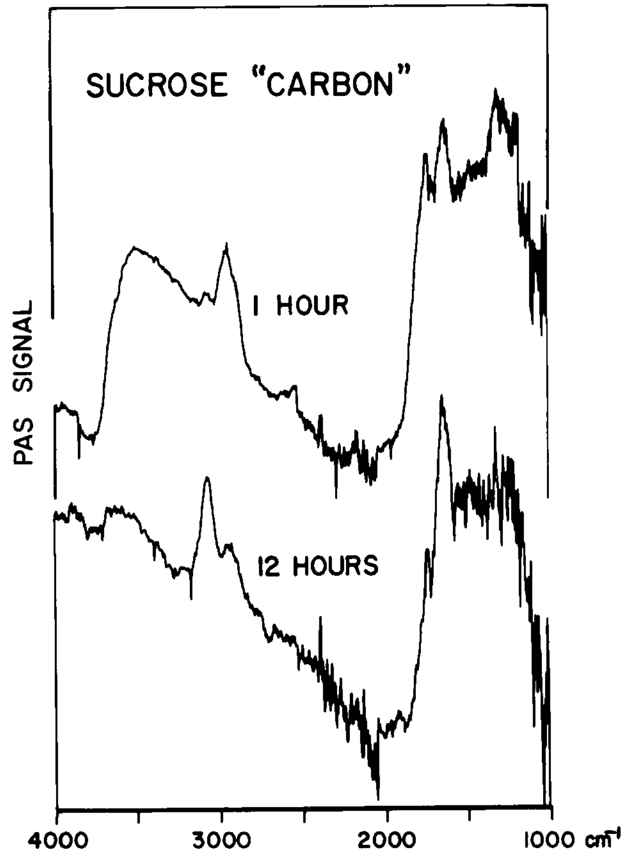

Fig. II. IR spectra of the samples of Fig. 1. The ordinates are displaced.

persists even after heating at 900°C, when the spectra of the chars approach the spectrum of the reference graphite. However, so do the spectra of other blacks.

Figure 3 shows scale-expanded segments of spectra of other carbons (which might very well be used as standards) ratioed against the spectrum of the reference graphite. The spectra

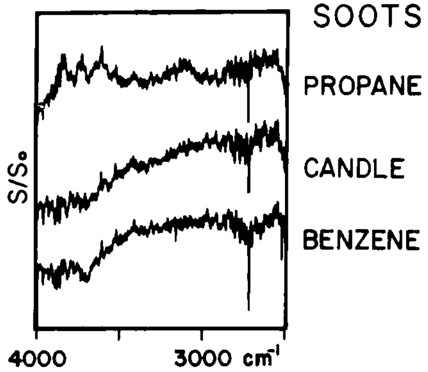

Fig. III. IR spectra of soots. The ordinates are displaced.

show small differences, but these are artifacts: the compensated spectrum of each carbon, including that of the reference graphite, changes when one of the other three carbons is used as reference. It is thus not at all clear what the "correct" spectrum is or might be. Consequently, some care must be taken in choosing a reference, and the need for caution becomes more stringent if carbon-like materials are examined, especially when studying molecular species on the surfaces of such materials. The need for an adequate compensation method is apparent. However, the use of carbon is questionable.

It is well-known that the chemical and physical properties of finely-divided carbons--precisely the type of material which would seem to be desirable to use for compensation--are greatly dependent on the method of preparation and treatment; there are many different carbons. Of these, most and perhaps all would be suitable as reference for compensating spectra showing relatively strong discrete absorptions but a weak background, e.g.[10-12], and it might be possible to choose one particular carbon reference material by common consent. However, the capacity of carbons for chemisorption and physical adsorption is notorious, so that it seems likely that, even if a single material were chosen, different results would be obtained in different laboratories, and possibly in the same laboratory at different times, because of changes of the reference brought about by sorption and desorption effects. It would thus seem better to avoid carbon and use direct measurements of the exciting source to compensate spectra.

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