SANDIA REPORT
SAND2001-0131
Unlimited Release
Printed February 2001

The Thermal History of Charred Materials by Raman Spectroscopy

David R. Tallant and Regina L. Simpson

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia is a multiprogram laboratory operated by Sandia Corporation,
a Lockheed Martin Company, for the United States Department of
Energy under Contract DE-AC04-94AL85000.

Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

Available to DOE and DOE contractors from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865)576-8401
Facsimile: (865)576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: http://www.doe.gov/bridge

Available to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd
Springfield, VA 22161

Telephone: (800)553-6847
Facsimile: (703)605-6900
E-Mail: orders@ntis.fedworld.gov
Online order: http://www.ntis.gov/ordering.htm

SAND2001-0131
Unlimited Release
Printed February 2001

The Thermal History of Charred Materials by Raman Spectroscopy

David R. Tallant and Regina L. Simpson
Materials Characterization Department
Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185-1411

Abstract

We investigated whether Raman spectroscopy, using a common set of calibration spectra, can be used to determine the temperature exposure of charred materials from diverse sources. This type of capability is expected to be useful in the investigation of fire scenes and in research into fire causes and fire dynamics. We charred pieces from a set of six materials (a pine 2-by-4, plywood, OSB, PVC pipe, nylon carpet and Formica) at temperatures from 235°C to 1140°C. Raman spectra were obtained of the charred materials. We analyzed the Raman spectra using multivariate Partial Least Squares (PLS) analysis to see if the trends in the Raman spectra correlated to their heat treatment temperatures. For five of the six materials (all except Formica) we found a high correlation between changes in the Raman spectra and their heat treatment temperatures. Raman spectra from the five types of charred materials with a high correlation were then analyzed by PLS as a combined set. The Raman spectra in this combined set are likewise highly correlated to exposure temperature and provide a common "calibration graph" from which exposure temperatures of char from the five materials can be determined with an average error of about 60 °C. These results are encouraging and suggest that Raman spectroscopy can be used to determine exposure temperatures of the diverse collection of charred materials expected to occur at a fire scene.

Contents

Figures

Table

The Thermal History of Charred Materials by Raman Spectroscopy

Introduction

In a fire where localized oxygen depletion occurs, organic materials are only partially converted to combustion gases. In a process known as pyrolysis, the organic material loses hydrogen and oxygen, leaving behind a solid material referred to as char, charcoal or soot (Figure 1). Char has the same basic structure as graphite, being composed of small, nanoscale sheets of fused, graphene (six-membered aromatic) rings, but graphite has extended (microscale and above) structures of stacked sheets of graphene rings. Char can be converted progressively and irreversibly to graphite by thermal treatment .

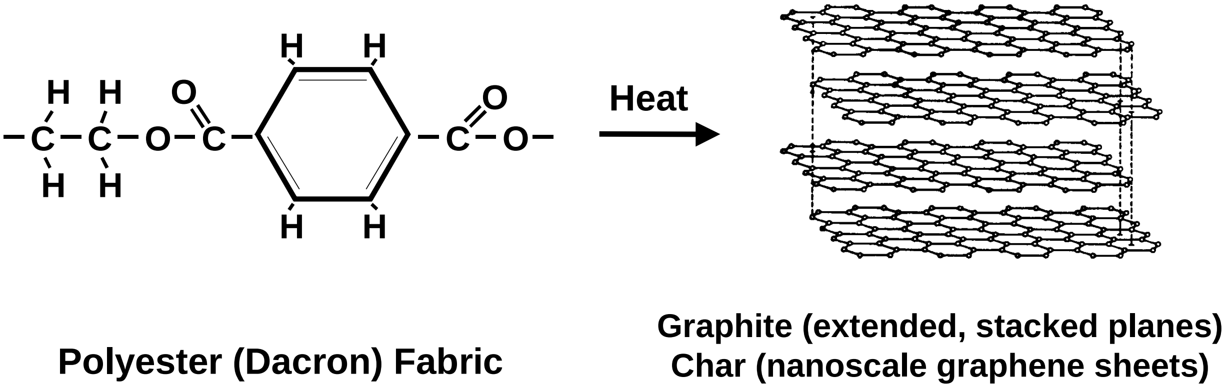

Figure 1. The charring process – an organic material, heated with insufficient oxygen for complete combustion to volatile products, pyrolyzes to graphite-like structures.

Raman spectroscopy, an inelastic scattering technique using optical photons, is sensitive to the char-to-graphite structural evolution with temperature (Tuinstra and Koenig, 1970; Nakamizo et al., 1974; Tallant et al., 1995). Raman spectra vary subtly, but consistently, as a function of the maximum temperature to which the charred material was exposed. We have used Raman spectra to determine thermal exposure temperatures from 500°C to greater than 2000°C in char pyrolyzed by atmospheric re-entry (Tallant et al., 1995), by missile exhaust gases (Tallant, 2000) and by a fire in a microcircuit fabrication facility (Tallant, 1987). This previous work established the correlation between Raman spectra of a specific material and its char temperatures, but the question remained whether the charring of different organic materials (wood, plastics, etc.) proceeded similarly enough to yield comparable Raman spectra. In this investigation we concentrated on exploring the generality of the correlation between Raman spectra of char and its thermal exposure. We sought to determine if char from different starting materials is similar enough in its structure that Raman spectra from different charred materials can be combined into a single "calibration" set, which can then be used to determine thermal exposures of the broad range of charred materials typically present at a fire scene.

Experimental

Raman Measurements

The Raman effect (shown schematically for silicon in Figure 2) is an inelastic scattering technique, in which a photon in the beam of monochromatic (single wavelength, or frequency) photons from a laser source interacts with an electron cloud in a bond linking atoms in the material being illuminated. Most of the incident photons rebound elastically (with the same frequency as the incoming photons) as Rayleigh scatter. About one in a million photons scatter inelastically by interacting with the phonons (quanta of vibrational energy) intrinsic to the crystal structure of the material being illuminated. If the photon loses energy due to this interaction, it is said to be (Stokes) Raman-shifted. This energy loss (or “Raman shift”) is measured in frequency units (cm^{-1}) and is the same as the frequency of the atomic vibration with which it interacted. If, as is customary, we plot the intensity of the inelastically scattered photons versus frequency, with the initial laser frequency as 0 cm^{-1}, then the frequency axis is in Raman shift units, and peaks in the spectrum correspond directly to vibrational modes of the atoms in the material being illuminated. Raman spectra look generically similar to infrared absorption spectra, but the same vibrational bands are not necessarily present in both types of spectra.

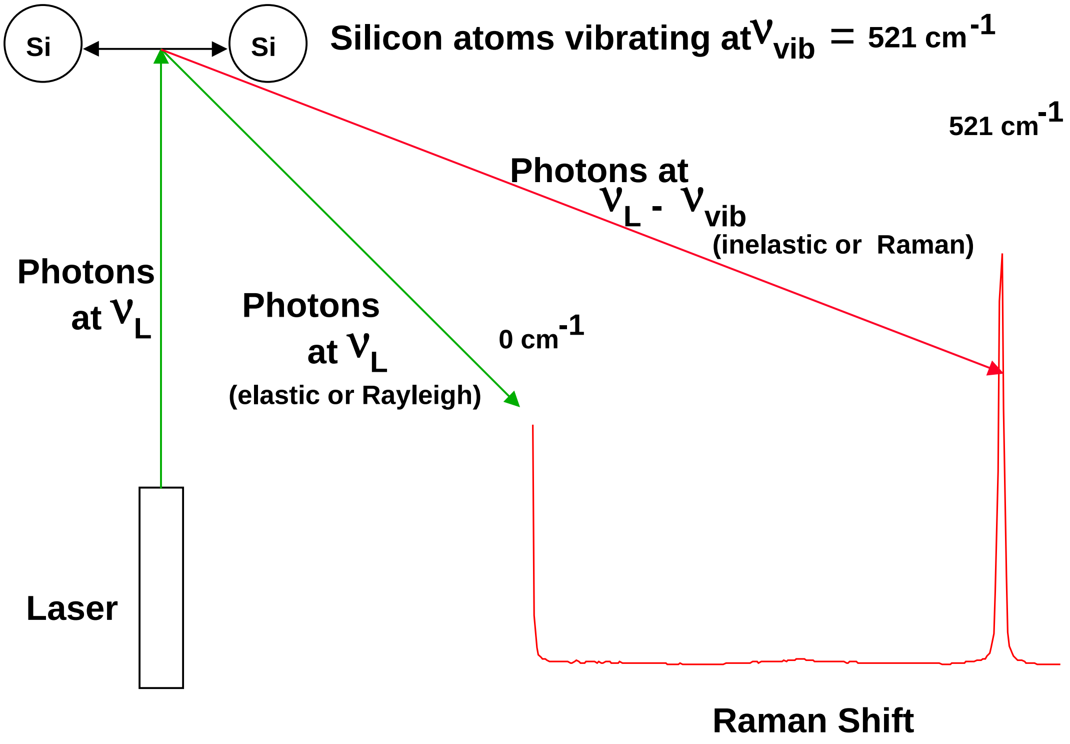

Figure 2.The Raman effect in silicon - interaction of photons with phonons (vibrational quanta) resulting in inelastically scattered photons.

We obtained Raman spectra of the charred materials at room temperature using 458 nm and 514 nm laser wavelengths for excitation and a triple spectrograph with a charge-coupled-device detector for separation and measurement of the inelastically scattered photons. The laser beam used for excitation was focused to an approximately 1 mm by 0.1 mm rectangle on a powdered portion of sample, hand-pressed into a pellet holder. The results using 514 nm excitation generally provided superior differentiation with respect to exposure (charring) temperatures, and these spectra were used in the subsequent analysis. If present, a broad fluorescent background was removed from the spectra, and they were normalized with respect to intensity prior to chemometric analysis. Otherwise, the spectra were analyzed as acquired. We also obtained Raman spectra using a near infrared (785 nm) wavelength for excitation and found interesting variations in luminescence and Raman bands. These variations are too complex to analyze adequately within the limited scope of this project, but they suggest an area for subsequent work.

Starting Materials and Charring Conditions

In consultation with experts National Center for Forensic Science (U. of Central Florida), we selected a set of materials of interest for forensic and fire research applications. The materials which we used in this study are a pine 2-by-4, plywood, OSB (a high-tech plywood-like material), PVC pipe, nylon carpet and Formica (see the Table).

Table – Summary of Materials and Heat Treatment

Starting Materials	Char Temperature (Air, °C)	Heat Treatment Temperatures (Argon, °C)
Pine 2-by-4	300	400 - 1140
Plywood	300	400 - 1140
OSB	235	400 – 1140
PVC pipe	300	400 – 1140
Nylon carpet	300	400 – 1140
Formica	300	400 – 1140

Documents available at the web site of the Building and Fire Research Laboratory of the National Institute of Standards and Technology (e.g., Walton et al., 1996) indicate that the range of temperatures generally encountered in structure fires is from about 200°C to about 1200°C. Samples of the pine 2-by-4, plywood, OSB, PVC pipe, nylon carpet and Formica were initially pyrolyzed in a muffle furnace in an air atmosphere. All but the OSB were pyrolyzed (to char) at 300°C for half an hour. The OSB ignited at temperatures greater than 250°C, so it was pyrolyzed at 235°C. In air above 300°C, the char was largely oxidized to volatile products. Heat treatment above 300°C was, therefore, carried out in a tube furnace in an argon atmosphere. Different samples of the charred products of the pyrolysis were heat treated for half an hour at

100°C intervals from 400°C to 1000°C and at 1140°C (the maximum temperature of the tube furnace). We believe that these pyrolysis and heat treatment procedures mimic reasonably what occurs in a structure fire, since little or no char would survive temperatures above 300°C in an oxygen-rich environment. The heat treatment temperatures are believed to be accurate to ±10°C.

Raman Spectra of Char

Figure 3 shows selected Raman spectra of char from the pine 2-by-4. Heat treatment temperatures are indicated in the figure. These spectra are generally characteristic of char from any organic source, showing two relatively broad bands, one peaking near 1350 cm^{-1} and the other peaking near 1600 cm^{-1}. The band peaking near 1600 cm^{-1} is due to a fundamental vibration of the graphite structure, and it is expected to be Raman active from a symmetry analysis of that structure. The other band, peaking near 1350 cm^{-1}, has been referred to as the “disorder” band. It is absent, or of very low intensity, in highly oriented graphite with large crystalline domains, but its intensity increases as the domain size of graphite decreases, becoming a major feature in the char regime of nanoscale crystalline domains. The 1350 cm^{-1} band is believed to be a vibrational mode which becomes Raman-active at the edges of the graphitic domains and so increases in intensity when domain size decreases and the edges become a larger fraction of the crystalline structure (Wang et al., 1990). In the range of temperatures used in this study, the peak height of the 1350 cm^{-1} band increases with heat treatment temperature, suggesting that the char structure is beginning to form the stacked plane structure characteristic of graphite but that graphite-like crystalline domains are not significantly increasing in size. We will use this variation in the relative intensities and shapes of the 1350 and 1600 cm^{-1} Raman bands to discriminate between char samples heat treated at different temperatures.

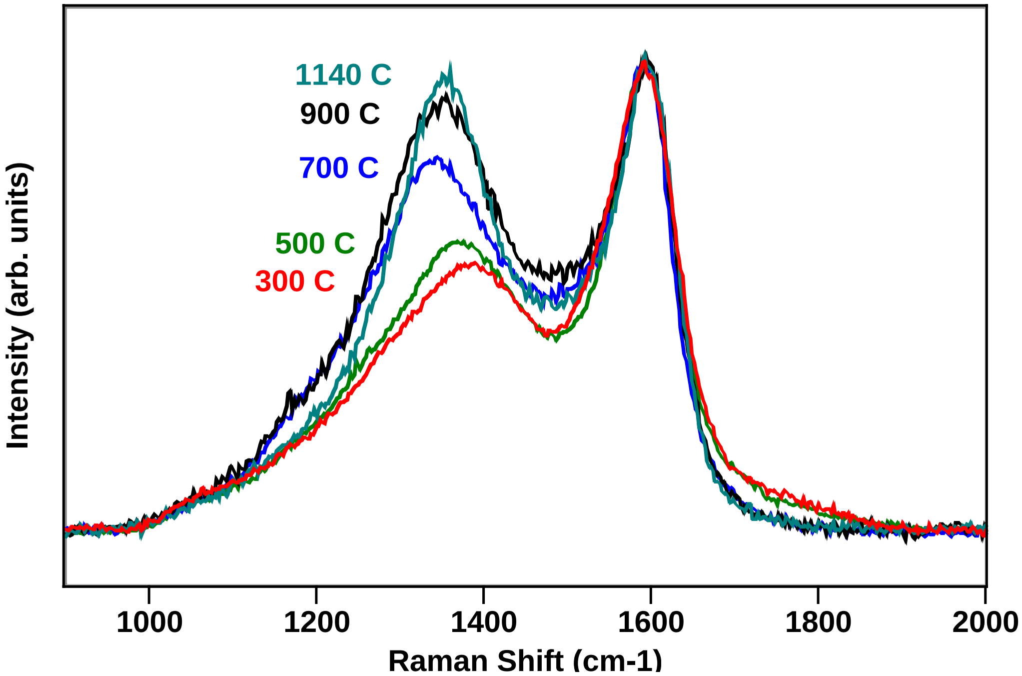

Figure 3. Raman spectra of pine 2-by-4 charred at different temperatures. Spectra have been scaled in intensity to the peak at 1600 cm^{-1}.

Chemometric Data Analysis

The Raman spectra of the char samples were analyzed using multivariate Partial Least Squares (PLS) techniques. Haaland (1990) has shown how PLS techniques can be applied to the Raman spectra of char. In PLS analysis a set of Raman spectra are decomposed into a number of component-like spectra. The component spectra are derived from the complete set of Raman spectra such that, properly scaled and summed, they can reproduce any spectrum in the original set. The component spectra are common to the whole set of Raman spectra, but the scaling factors are different for each spectrum. The component spectra derived from the set of charred pine 2-by-4 spectra are shown in Figure 4. The first component is usually an average of the spectra in the set. Higher numbered components are scaled and added to or subtracted from the first component to reproduce any spectrum in the set. When the factors used to scale the component spectra are regressed against some parameter, in this case the heat treatment temperature, it is possible to determine how strong the correlation is between that parameter and changes in the spectra.

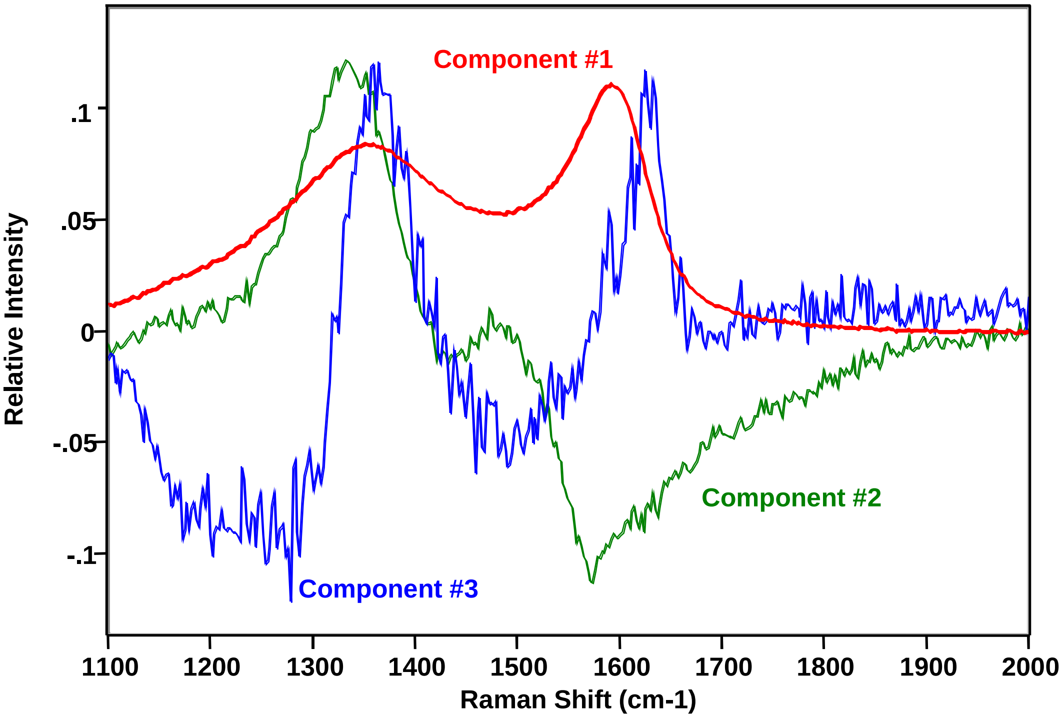

Figure 4. Component spectra from PLS analysis of 2-by-4 pine

Cross-Validation of the Raman Spectra of the Char

Cross-validation is a PLS technique used to gauge the correlation between, in our case, heat treatment temperature and changes in the char Raman spectra. In cross-validation, one spectrum is removed from the set of spectra, and its temperature is “predicted” using the remaining spectra in the set and their associated “actual” temperatures (as measured in the heat treatment furnace), in conjunction with the components and scaling factors generated by PLS. This procedure is repeated for all the spectra in the set. Then the “predicted” temperature for each char spectrum is plotted against its “actual” temperature. This plot provides a measure of the correlation between the Raman spectra and the heat treatment temperature and also provides an estimate of the predictive accuracy of the set of Raman spectra. An “ideal” correlation between the predicted and actual temperatures would have all the data points on a 45° line passing through the point of origin (0,0) and would yield a correlation coefficient (R^2) of 1.0 (i.e., each predicted temperature would be exactly the same as its actual temperature). Another indication of measurement accuracy is the Standard Error of Cross-Validation (SECV), which is the average error in the predicted temperatures. In effect, cross-validation estimates how accurately of the set of spectra, when used as a calibration set, will measure heat treatment temperatures of “unknown” samples.

Initially we treated the char Raman spectra from each type of organic material as a separate set and performed individual cross-validation analyses for spectra from the pine 2-by-4, plywood, OSB, PVC pipe, nylon carpet and Formica char samples. The plots of predicted versus actual temperatures resulting from these cross-validation analyses are shown in Figures 5 through 10.

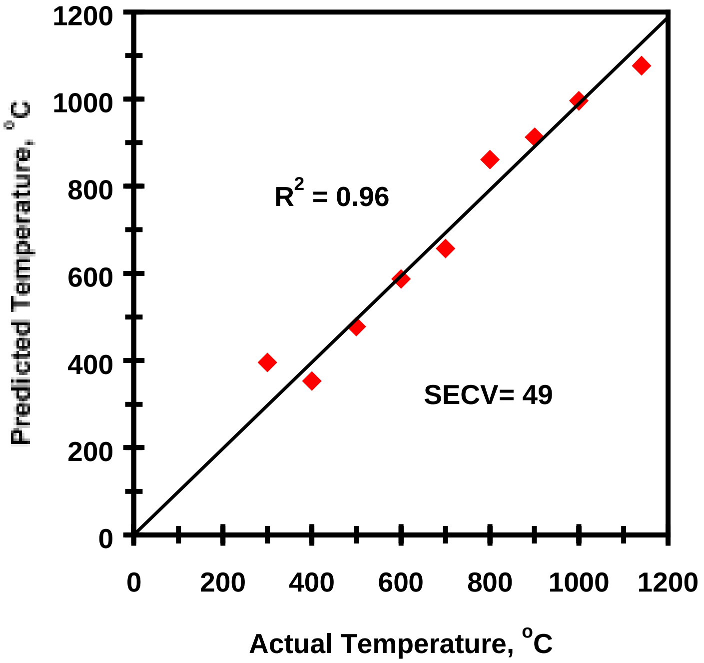

Figure 5. PLS cross-validation results – Raman spectra of charred pine 2-by-4.

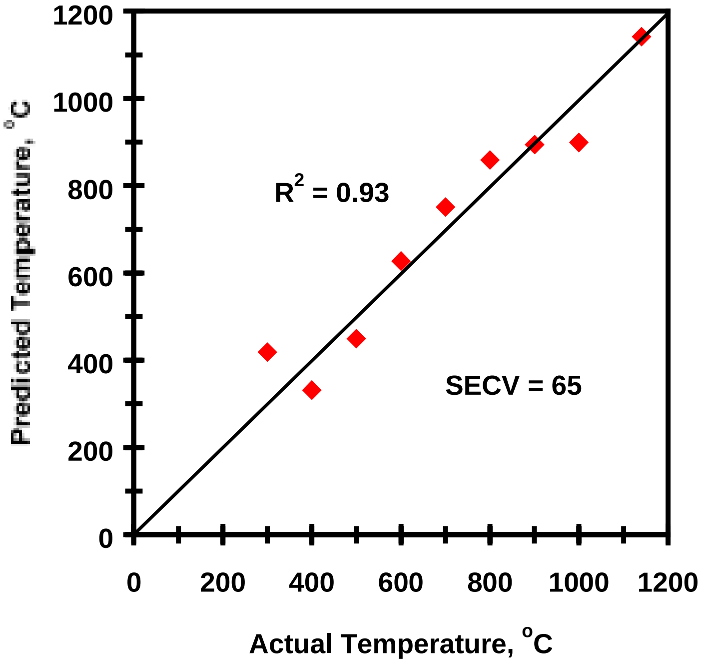

Figure 6. PLS cross-validation results – Raman spectra of charred plywood.

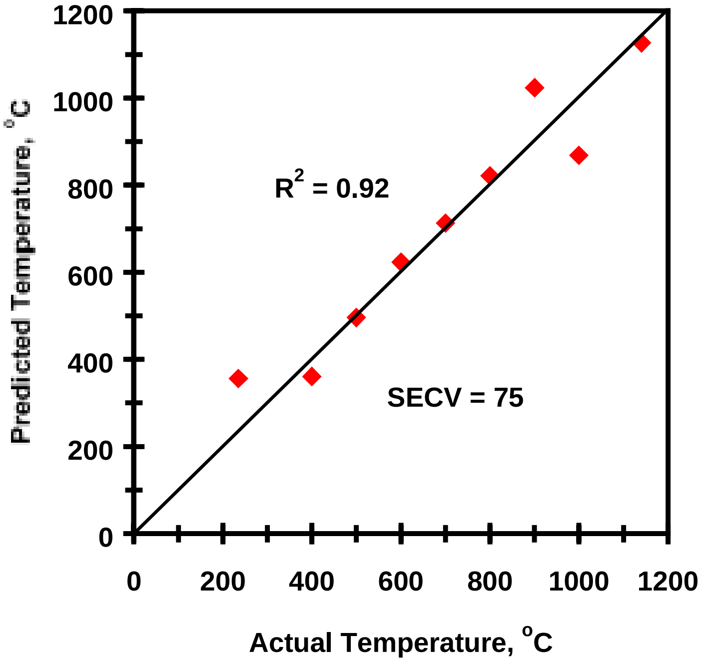

Figure 7. PLS cross-validation results – Raman spectra of charred OSB.

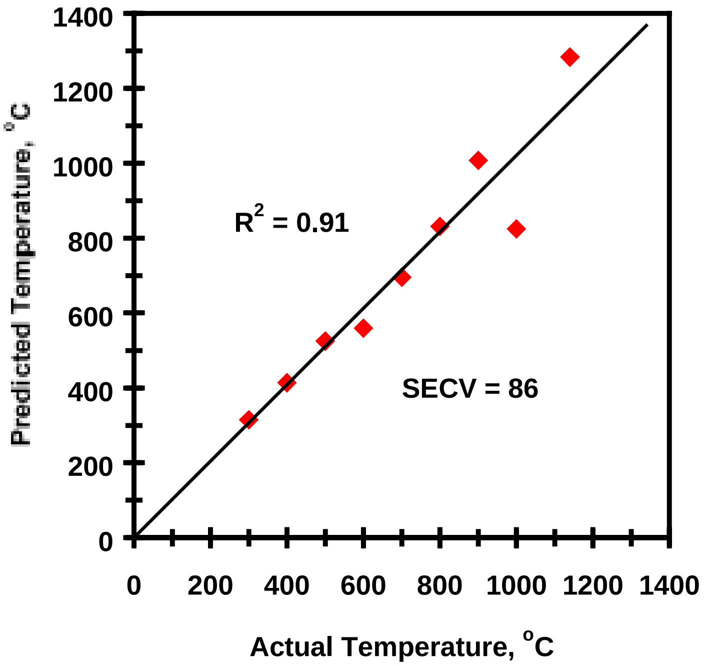

Figure 8. PLS cross-validation results – Raman spectra of charred PVC pipe.

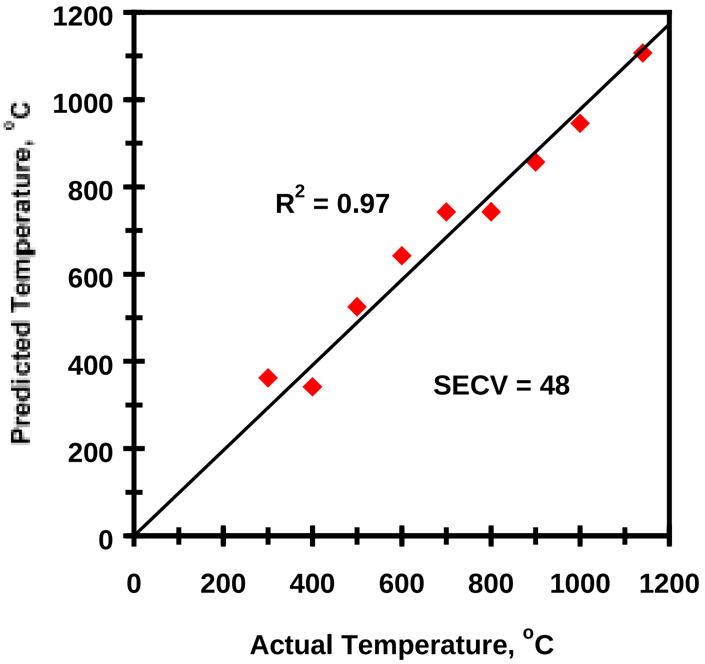

Figure 9. PLS cross-validation results – Raman spectra of charred nylon carpet.

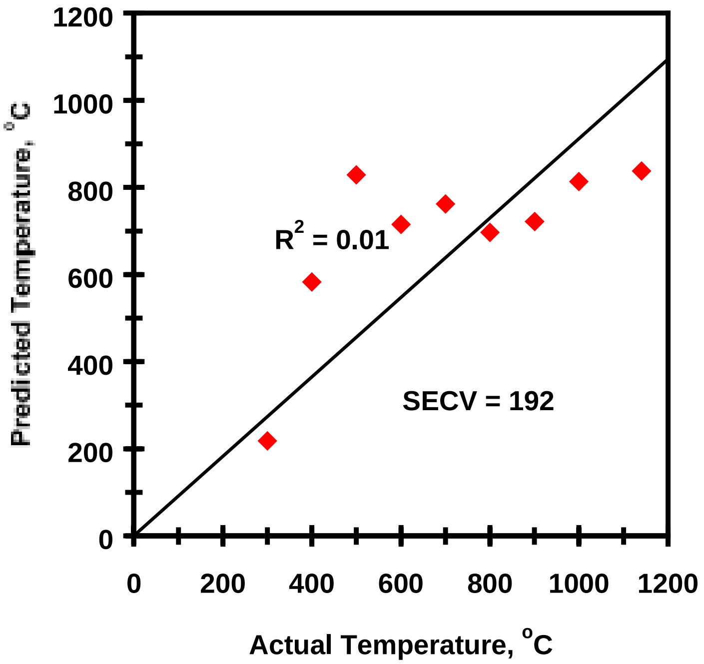

Figure 10. PLS cross-validation results – Raman spectra of charred Formica.

For five of the six organic starting materials, Figures 5 through 9 show a strong correlation between the Raman spectra of their char and heat treatment temperatures. The predicted-versus-actual data points closely bracket the trend line. The correlation coefficients (R^2) range from 0.91 to 0.97 (strong correlations), and the average errors in the predicted points (SECV) range from 43°C to 86°C. For these materials, the pine 2-by-4, plywood, OSB, PVC pipe and nylon carpet, calibration sets derived from the Raman spectra of their char will determine the maximum thermal exposure temperature of like materials, with reasonable accuracy, over the temperature range from about 300°C to 1200°C. Only the Raman spectra from charred Formica (Figure 10) did not show a strong correlation with heat treatment temperature (R^2 = 0.01, SECV = 192°C). The charring of Formica is probably strongly influenced by the presence of inorganic filler materials, with which this composite is heavily loaded.

Encouraged by the strong correlation between the Raman spectra of all but one of the types of charred materials and their heat treatment temperature, we combined all the Raman spectra from the charred wood products (pine 2-by-4, plywood and OSB) into one set and performed PLS cross-validation on the combined set. The results of the cross-validation on the wood product set of char Raman spectra are shown in Figure 11. The high correlation coefficient (R^2 = 0.96) and low average error (SECV = 52°C) indicate that the Raman spectra from all three charred wood products have similar trends as a function of heat treatment temperature, i.e., they can be considered part of the same statistical population. Generally statistical correlation and error parameters are improved by adding data points from the same statistical population; the effect of the more deviant data points tends to be diluted, and a higher statistical confidence is achieved.

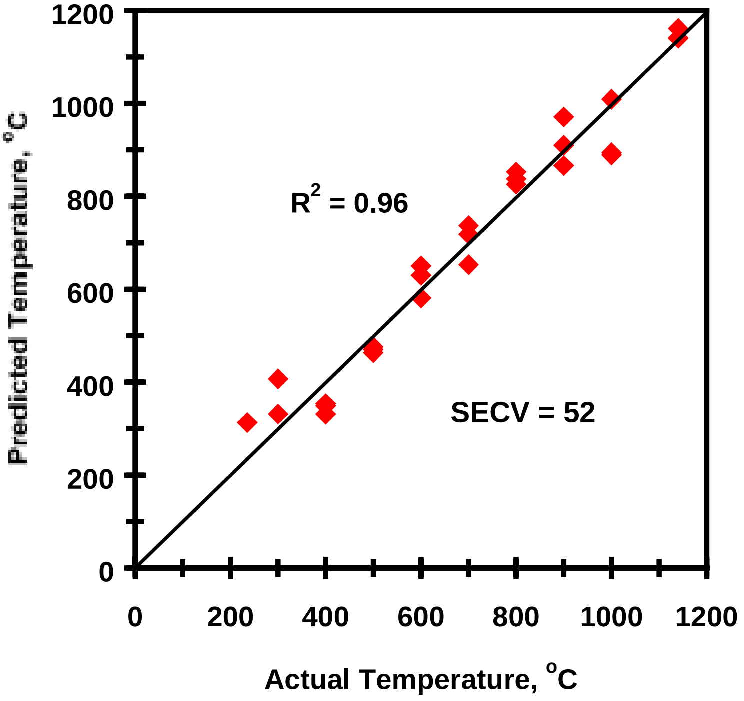

Figure 11. PLS cross-validation results – Raman spectra of charred wood product samples (pine 2-by-4, plywood and OSB)

Finally, we combined, into one set, the spectra from all five materials (2-by-4 pine, plywood, OSB, PVC pipe and nylon carpet) whose char Raman spectra showed a strong correlation to heat treatment temperature. The results of the PLS cross-validation of the combined set from these five materials are shown in Figures 12 and 13. In Figure 12 the data points are plotted in one color, and the trend line, correlation coefficient ($R^2 = 0.95$) and average error (SECV = 63°C) are shown. Figure 13 shows the same data points, but the contributions from the different materials are in different colors. The point of showing the different contributions to the data set in Figure 13 is to demonstrate that no one material has an excessive variance; the Raman spectra from all five materials likely belong to the same population. The high correlation coefficient and moderate average error value indicate that exposure temperatures of unknown samples of any of the five materials could be determined, with reasonable accuracy, from a combined calibration set of Raman spectra from their char.

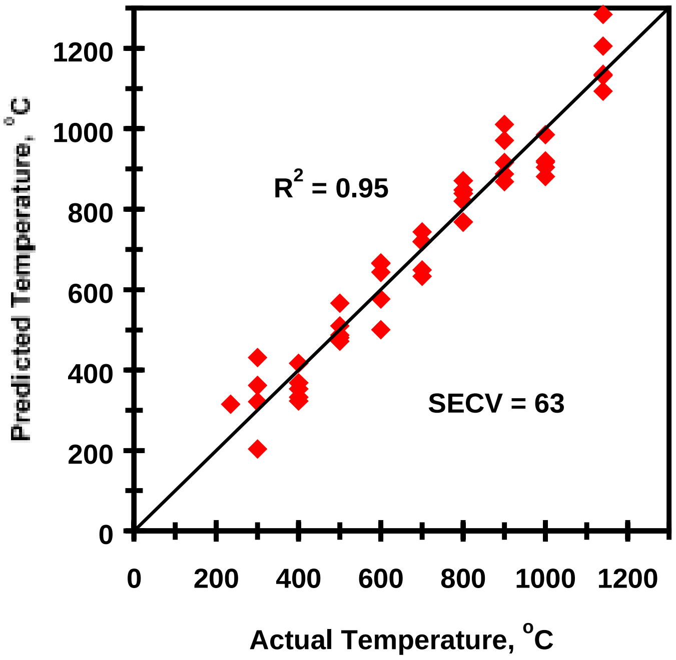

Figure 12. PLS cross-validation – pine 2-by-4, plywood OSB, PVC pipe & nylon

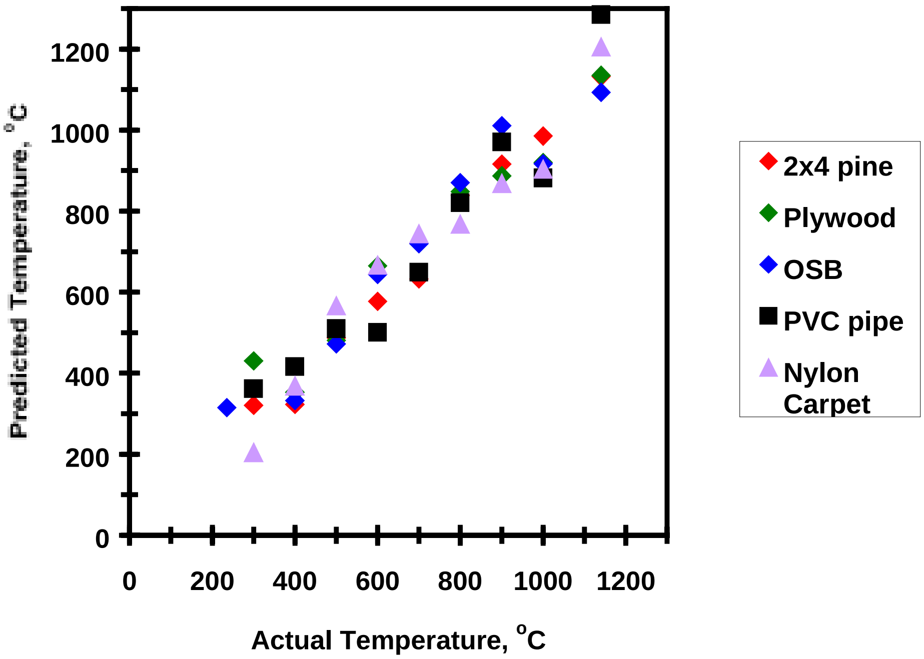

Figure 13. PLS cross-validation – pine 2-by-4, plywood OSB, PVC pipe & nylon

Summary

The results obtained in this study provide encouragement that we may be able to develop a single calibration set of Raman spectra of char samples which can be used to determine exposure temperatures of char from a wide range of organic materials. Raman spectra from char of five of the six materials included in this study (2-by-4 pine, plywood, OSB, PVC pipe and nylon carpet) show, individually and as a combined set, a high correlation to heat treatment temperature and a low-to-moderate error in predicting exposure temperatures. The only material (Formica) not showing such a correlation is a composite heavily loaded with inorganic filler materials. The ability to generally determine thermal exposure temperatures from char means that it should be possible to map the maximum temperatures which occurred at a fire scene after the fact. This capability should provide new and valuable information of use in forensic analysis and in research into fire causes and dynamics. With newer types of compact Raman instrumentation, it should be possible to construct a portable Raman spectrometer capable of performing temperature measurements on char at a fire scene.

Continuation of this work should involve charring and examining by Raman spectroscopy additional organic materials, for example hardwoods and polymers used in clothing and upholstery, to see if a truly generalized calibration set, applicable to nearly all char likely to be at a fire scene, can be developed. The accuracy of the temperature prediction may be improved by adding additional data points over a wider temperature range to the calibration set and by refining the data analysis procedure. Finally, Raman spectra of char obtained using red and near infrared laser excitation wavelengths should also be obtained and analyzed, to see if different forms of laser excitation result in better discrimination of char temperatures.

Acknowledgments

We thank Bob Lagasse for the use of his facilities to heat-treat the char samples.

References

D. M. Haaland, K. L. Higgins and D. R. Tallant, Multivariate Calibration of Carbon Raman Spectra for Quantitative Determination of Peak Temperature History, in *Vibrational Spectroscopy*, vol. 1, pp. 35-40 (1990).

M. Nakamizo, R. Kammereck and P. L. Walker, Jr., Laser Raman Studies on Carbons, in *Carbon*, vol. 12, pp. 259-267, 1974

D. R. Tallant, I. Auerbach and K. L. Higgins, Evaluation and Mapping of Heat-Shield Flight Temperature and Composition with Raman Spectroscopic Techniques, in *Applied Spectroscopy*, vol. 49(5), pp. 598 – 604, 1995.

D. R. Tallant, Sandia National Laboratories internal memorandum, August 24, 1987.

D. R. Tallant, M. J. Garcia and R. L. Simpson, Sandia National Laboratories internal memorandum, June 6, 2000.

F. Tuinstra and J. L. Koenig, Raman Spectrum of Graphite, in *Journal of Chemical Physics*, vol. 53(3), pp.1126-1130, 1970.

W. Walton, A. D. Putorti, Jr., W. H. Twilley and J.C. Albers, Santa Ana Fire Department Experiments at South Bristol Street, in *NISTIR 5776*, February, 1996.

Y. Wang, D. C. Alsmeyer and R.L. McCreery, Raman Spectroscopy of Carbon Materials: Structural Basis of Observed Spectra, in *Chem. Mater.*, vol. 2 pp. 557-563, 1990.

DISTRIBUTION:

1	MS	0185	G. V. Herrera, 01310
1	MS	0188	LDRD, 04000
1	MS	0513	A. D. Romig, 01000
1	MS	0769	D. S. Miyoshi, 05800
1	MS	0782	G. J. Smith, 05861
1	MS	0886	R. P. Goehner, 01822
1	MS	0887	A. K. Hays, 01800
1	MS	1231	R. L. Hagengruber, 05000
1	MS	1411	R. L. Simpson, 01822
10	MS	1411	D. R. Tallant, 01822
1	MS	9018	Central Technical Files, 8945-1
2	MS	0899	Technical Library, 9616
1	MS	0612	Review & Approval Desk, 9612 For DOE/OSTI