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Applications of Fourier Transform Raman Spectroscopy in Forensic Science

ABSTRACT: A number of possible new applications for the use of Fourier Transform Raman spectroscopy (FT-Raman) in forensic science have been investigated. The evidence materials studied were fragments of broken plastic automobile lenses, paint coatings, paper and others.

Raman spectroscopy was not only able to distinguish between the types of polymers employed in the manufacture of the lenses but, was also found to be sensitive to the thermal history imparted to the item during its production. The detection of these internal stress conditions and their characterization by FT-Raman led to the differentiation of manufacturers of the same products.

When inherent background fluorescence does not interfere (white, yellow, light colors) the Raman spectra of paint coatings supplies complementary information to that of FT-IR about the polymer binder while being a more useful technique for mineral pigment and extender component analyses.

The FT-Raman technique is useful in forensic document examination of paper because of its ability to identify mineral components and some of the minor components which are associated with the origin of the cellulose and technology of paper production.

KEYWORDS: forensic science, Fourier transform, Raman spectroscopy

Raman spectroscopy is a complementary technique to infrared spectroscopy and is reported to have some theoretical advantages over the latter. Until recently the reported applications of Raman Spectroscopy to forensic science studies have been sparse; for example, it has been used for gemstones [1] and antique inorganic paints [2]. The main reasons for this were the high backgrounds encountered in the Raman spectra of most samples due to either impurities or inherent fluorescence, the high cost of instrumentation, the difficult adjustments of sample position and alignment of optics, as well as the length of the experimental procedure. These, along with the more limited collections of library spectra, cause Raman spectroscopy, at present, to be a less attractive technique than the widely used Fourier Transform Infrared Spectroscopy (FTIR).

Recent developments in the Fourier Transform Raman Technique in the near infrared range make it possible to reduce some of these limitations [3] and to add this method, as an accessory, to current commercial FTIR spectrometers.

Experimental

The Raman spectra were measured on a Bruker spectrometer IFS 66 with FT-Raman accessory FRA 106. Scattering was excited by a 350 mW diode pumped Nd-YAG laser (ADLAS) at 1.064 μm. Spectra were recorded in the anti-Stokes $\Delta\nu = -2000$ to -100 and Stokes 100–3500 cm^{-1} ranges using a special liquid nitrogen cooled Germanium detector. Resolution in all cases was 4 cm^{-1} with data treatment by 4P-apodisation. Scattering geometry was 180°. The laser beam spectral bandshape stability (intensity ratio of different modes) in time was controlled by symmetric difference spectra of elastic scattering and Raman bands at the same point of a lens surface. Small bandshifts were also measured using the method of symmetric difference spectra (equal integrals of positive and negative resultant bands). This subtraction of spectrum "N" from a series over reference spectrum "R" ($N - c^*R$) was carried out using a coefficient "c" to keep the equal integrals of the Raman bands of interest. The surface point of a plastic lens for measurement of the reference Raman spectrum was chosen using a polariscopic screening for localization of isotropic area. All the measurements were made at the same laser power of 210 mW on the sample.

The IR spectra were measured on a Bruker spectrometer IFS 45 which was equipped with an infrared microscope incorporating a x15 Cassegranian objective and a liquid nitrogen cooled Mercury-Cadmium-Telluride detector. Spectra were recorded in the range 600–4000 cm^{-1} at 4 cm^{-1} resolution. Samples were prepared using a diamond anvil cell.

Optical anisotropy of the plastic automobile lenses was studied using a "Polariscope-polarimeter PKS-250." Lenses were placed between two large horizontal windows. The optical system in front of the first window produced linearly polarized light. A second window was used as an interference analyzer for large samples, or was replaced by a microscope accessory for small samples.

Automotive samples and the polymer granules used for their production, paint coatings, binders and mineral components, as well as the papers, studied in this project, were from the laboratory's collection.

Results and Discussion

Automotive Lenses

Fragments of broken automotive lenses as well as paint chips or flakes are often encountered in cases connected with traffic accidents and are submitted to the forensic laboratory for analyses. Particles of at least 1 mm in size can be analyzed directly by the FT-Raman technique without the microscope accessory which in turn allows even smaller items to be evaluated.

The six types of polymers used in automotive lens production can be easily identified and differentiated by Raman spectroscopy (See Fig. 1). This can also be accomplished by FTIR. The spectra of polymethylmethacrylate (PMMA), polycarbonate (PC), polystyrene (PS) differ remarkably. The copolymers of styrene with acrylonitrile (SAN), methylmethacrylate (MS), and acrylonitrile with methylmethacrylate (MSN) can be identified and differentiated by the presence of the nitrile and ester carbonyl bands. Some Raman bands useful for polymer identification and their tentative assignments are presented in Table 1. More detailed interpretations of vibrational spectra with information about their sensitivity to changes of conformation have been published [4–13]. A large number of automobile models employ each polymer type of certain color, with PS and MS being rarely used. Copolymers of the latter with anhydride units (MSA) are used in foreign models only (for example, Volvo).
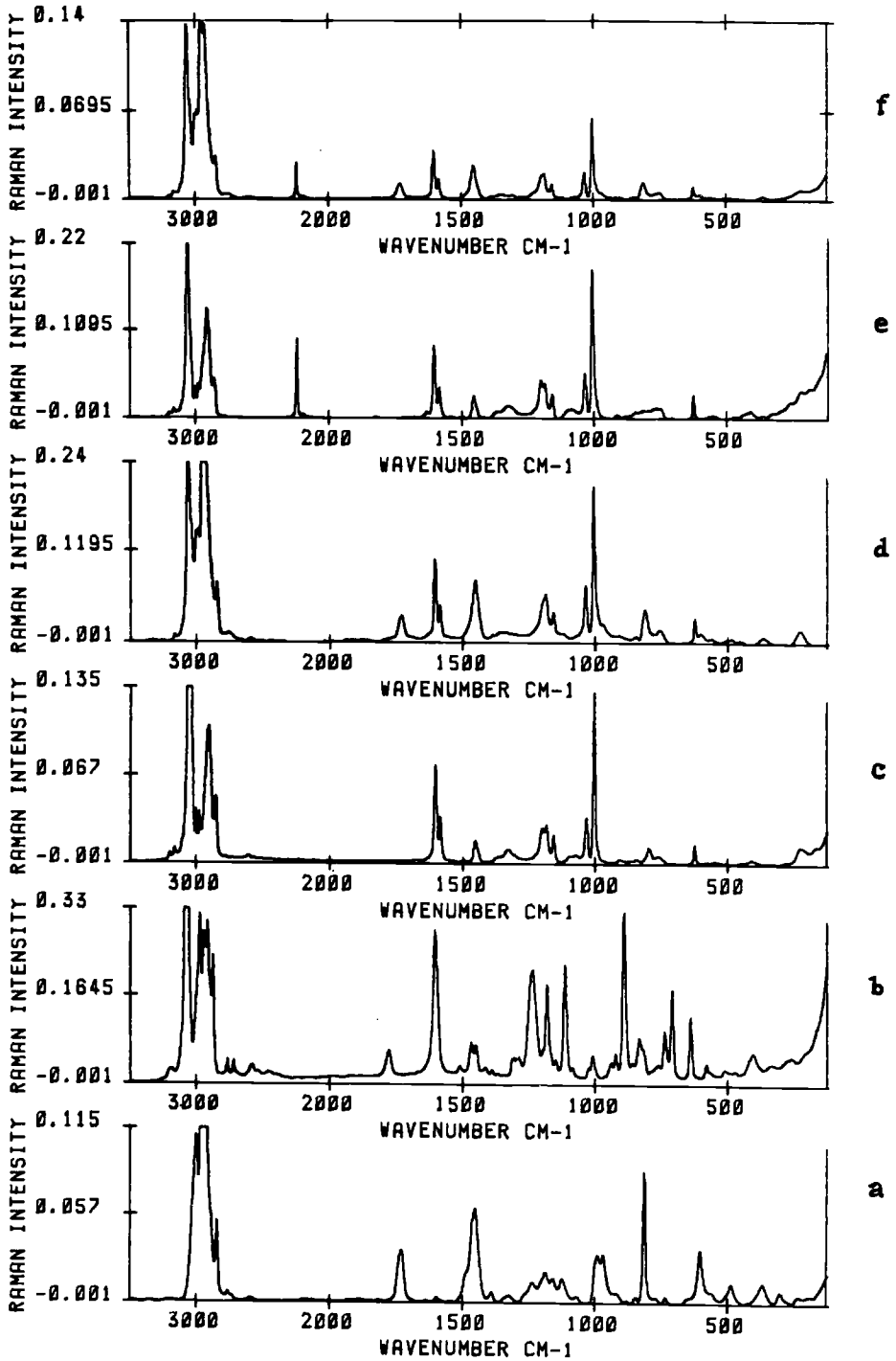
FIG. 1—*The Raman spectra of PMMA* (a), *PC* (b), *PS* (c), *MS* (d), *SAN* (e), *MSN* (f). *Number of scans −500. All the spectra except* (b) *have slight background correction.*

TABLE 1—*Assignment of some polymer lens characteristic Raman bands.*

PMMA	PC	PS	MS	SAN	MSN	MSA	Tentative assignment
. . .	. . .	. . .	. . .	2234	2234	. . .	C≡N stretching
. . .	. . .	. . .	. . .	. . .	. . .	· 1857	C=O sym. str. anhydr.
. . .	. . .	. . .	. . .	. . .	. . .	1780	C=O asym. str. anhydr.
. . .	1774	. . .	. . .	. . .	. . .	. . .	C=O stretching
1728	. . .	. . .	1727	. . .	1726	1726	C=O stretching
. . .	1604	1601	1601	1601	1601	1601	benzene ring mode
. . .	. . .	1580	1580	1580	1582	1580	benzene ring mode
. . .	1112	. . .	. . .	. . .	. . .	. . .	benzene ring mode
. . .	. . .	1001	1000	1001	1001	1002	benzene ring mode

When splinters or fragments of the lens are large enough to identify the type of lens by morphology and physical matching then the number of suspect models is reduced to about 20 or less. The actual number depends on the type of the lens. Some lens types are produced by more than one manufacturer and these manufacturers supply lenses for various models. The actual source can be identified in many cases by characteristic morphological markings found on the lens fragments, allowing further reduction of the number of suspect models.

FT-Raman investigation of lens fragment internal stresses, which reflect thermal history, could be used for source differentiation. Of seven manufacturers of these lenses in the former USSR, two did not use any sub-T_g annealing and one used in only on some lenses. This annealing process at below the glass transition temperature reduces internal stress. Polarized light views of unannealed lenses can reveal residual stresses. This anisotropy is a consequence of internal stresses as well as partial orientation of the polymer chains. The latter is responsible of the continued anisotropy seen after annealing in the vicinity of the inlet point of the liquid polymer into the lens mold. In spite of the partial stress relaxation at the edges of small splinters a characteristic anisotropic picture was observed to be present in large fragments (those of few centimeters).

The FT-Raman technique is very powerful for detecting small differences in chemical structure, orientation and conformational isomerism and even the residual internal stresses of solid materials. This is most effectively demonstrated by the use of difference spectral analyses. If the former features of polymer materials are useful in comparative studies, the latter could be used also as technological feature for search information. The high reproducibility and wavenumber accuracy inherent in the Fourier Transform methodology make the detection of these differences with reliability a routine practice. Many of the bands of interest are very strong and or sharp in the Raman spectra while they may be weak and or broad in the IR spectra (the stronger and sharper the band, the smaller bandshift could be detected). Therefore, for some samples Raman has distinct advantages while the use of FTIR and FT-Raman together as complementary techniques has even more to recommend it. The non-destructive nature of the Raman analysis along with the ability to analyze thick and various shape materials at small localized points without any preparation techniques is another decided advantage.

Bandshifts in the vibrational spectra of polymers induced by stress have been previously reported [9–11]. Generally most bands shift to higher frequency from pressure induced stress while shifts to lower frequency are caused by stretching. This reveals the reliable and convenient way of a residual stress studies by means of FT-Raman spectroscopy technique consisting in shift measurements of strong sharp not overlapped bands using as a reference bands of spectrum measured at a nonstressed (isotropic, see Experimental, or solvent relaxed) area of the same plastic lens unit.

In Fig. 2 are displayed a series of Raman spectra collected from the different points along a traverses at a center of annealed lens. A representative Raman spectrum is depicted in 2a while the resultant spectra generated at each scanning point beginning from the inlet point region's spectrum by subtracting a reference spectrum are displayed in Fig. 2b. A view of this lens in polarized light is shown in Fig. 2c, solid line at a center along traverses represents location of analyzed points as well as in Fig. 3b. The left end point of this line (final from the series) is coincided with isotropic area of the lens surface and its spectrum is used as a reference.

The photographs in Fig. 3 show the view in normal (3a) and polarized light (3b) of the same type of PC lens from another manufacturer, which does not perform annealing. The polarscopic technique reveals the residual stresses as concentric "waves" propagating from the mold inlet point in the unannealed lens. A series of 17 symmetric difference spectra (equal integrals of positive and negative sides [10,13], see Experimental) were generated at each scanning point along a traverse at equal distances. Measurements were started from the inlet point region as in Fig. 2a with the final point spectrum used as a reference for subtraction. The generated spectra in the range 620–650 cm^{-1} of the benzene ring are presented in Fig. 3c and 3d. In Fig. 3c spectra in the same scale are displaced along abscissa (wavenumber) axis, while in Fig. 3d they are superimposed in the same axes. In the Fig. 3d it is clearly seen that all effects are caused primarily by the bandshifts but not by the broadening and bandshape changes. Fig. 3c displays the distribution of stress amplitude along the surface (the stronger stress yields the larger bandshift and the greater difference intensity), and shows good correlation with the first three concentric "waves" in Fig. 3b. All the high stress regions of studied plastic lenses were the stresses of surface stretching (low frequency bandshifts) so they have well known tendency to be broken at first in case of impact.
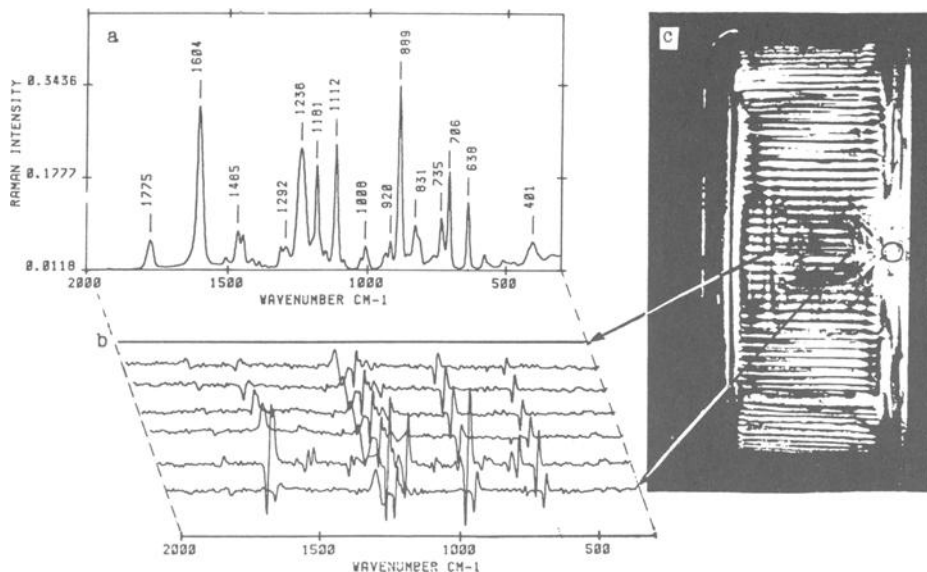

FIG. 2—*The difference Raman spectra of annealed PC automobile lens at different points on the surface over the last point spectrum with steps of 2.5 mm along a traverse at the center. Number of acquisitions (scans) for all the spectra –500. Spectra were slightly background corrected before subtraction of the last spectrum. A circle on the photo of the lens in polarized light represents an inlet point location.*
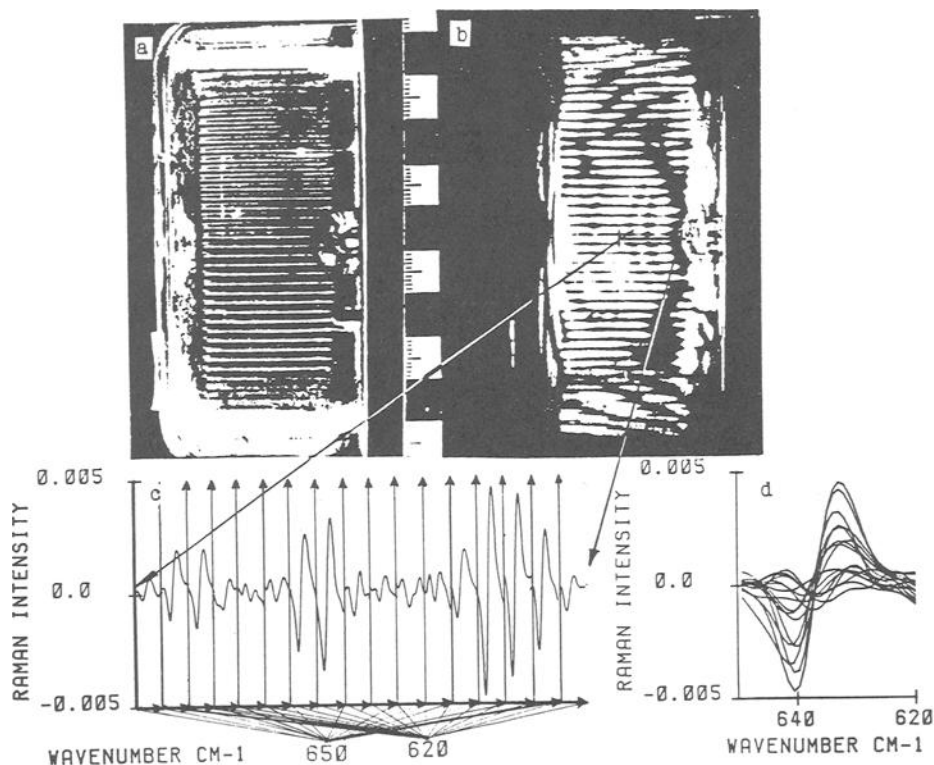
FIG. 3—*Correlation of series of symmetric difference spectra over the last spectrum with steps of 1 mm along a central traverse (c, d) with an image of internal stress in polarized light (b). View of the lens in normal light (a). Each difference spectrum is compressed and shifted along abscissa axis (c) and superimposed in the same axes (d). Number of scans for all spectra −300.*

Precise measurements of small bandshifts can be made from symmetric difference spectra according to the formula [10]:

$$\Delta \nu = \Delta \vartheta * \Delta I / c * I$$

where $\Delta \nu$ is bandshift value, $\Delta \vartheta$ is the peak to peak wavenumber difference (wavenumber distance between positive and negative *extrema*), ΔI is a full amplitude of the peak to peak intensity difference, I is the intensity of a band in the maximum, and C is a factor supplied as 51 for Lorentzian band profile shapes or 84 for Gaussian band profiles.

The wavenumber shifts for the benzene vibration at approximately 638 cm^{-1} were studied at different points along two separate unannealed PC lenses and two additional annealed PC lenses of different manufacturers. Assuming a Lorentzian profile model for annealed lenses the shifts did not exceed 0.03 cm^{-1}, while studies of two unannealed lenses reveal shifts of approximately 0.05 cm^{-1} and 0.04 cm^{-1} (two first waves in Fig. 3c exceed this threshold). The accuracy of measurements for this band was better than 0.01 cm^{-1}. Therefore, it appears if one sets a threshold of 0.03 cm^{-1} for bands shifts at 638 cm^{-1} obtained when measuring across a lens surface then one can determine if a lens belongs to the non annealed groups. Further experimentation and data collection along with statistical evaluation may lead to a lowering of the above threshold value. It

should be kept in mind that to some extent polymer viscosity, lens shape and thickness as well as other factors may play a role in determination of a threshold value and these factors remain to be fully evaluated.

The correlation of the areas of the lens exhibiting birefringence when viewed with polarized light with the Raman intensity profile differences is good, especially coinciding when the anisotropy is a consequence of stress. Therefore, it is apparent that the two techniques are complementary and that polarscopic screening of samples may be useful for locating the areas of high stress for subsequent FT-Raman measurements. The resulting more quantitative data and stress type determination (pressure or stretching) may be more powerful for forensic identification, characterization, and comparison purposes.

The Raman spectra of polystyrene and its copolymers also reveal the presence of a number of sharp bands due to benzene vibrations, especially the distinct and intense band at 1002 cm^{-1}. These would be appropriate for the study of stress induced shifts during the characterization of particles originating from these polymers (see Fig. 1).

In Fig. 2 the consistent shifting direction of the benzene ring peaks observed for the general vibrational bands are noted while the conformationally sensitive vibrations ($\nu_{c=o}$, ν_{c-o} and others) cause both negative and positive band dislocations which confirm the conformational heterogeneity of the polymer at different lens points. The intensity ratios of the bands ascribed to low and high energy conformations have been reported to reflect the thermal history of various polymers. This has been observed in PMMA [12] and studied in detail for PS [13] by differential FTIR spectroscopy. However thermodynamical studies of similar detail of PC by vibrational spectroscopy techniques were not found in literature. The observed large conformational heterogeneity of unannealed lenses may also be used as a method to differentiate lenses with different thermal history.

In a view of these studies it seems to be acceptable to attempt to establish the common origin of fragments of a lens (especially those of symmetric construction as in Figs. 2 and 3), using difference spectra profiles arising from stress fields or conformational heterogeneity when no common edges have been established.

Paints

FTIR spectroscopy has been widely used for the identification and comparison of paint binders, fillers and pigments in forensic science investigations. The technique has some limitations due to the limitation of the low frequency range to about 400 cm^{-1} in most cases.

In distinction the FT-Raman study of automotive and other paint materials can extend the vibrational spectral study to the low frequency area near 100 cm^{-1}. In addition some paint component bands overlapping in IR do not overlap in Raman. In Fig. 4 are displayed a number of inorganic materials commonly employed as fillers and extenders. The utility of the extended range of FT-Raman below 600 cm^{-1} is clearly seen. The Raman bands tend to be sharper and assignment of the band frequency more accurate and precise [14]. The ability to identify some inorganic materials in the presence of the binding polymer is evident from study of the sample spectra found in Fig. 5.

Often the broad overlapping IR bands of quartz, kaolinite, calcite, baryte and other fillers obscure regions of the spectra useful for binder identification. This is not necessarily the case in Raman where many bands do not overlap and are very sharp and intense.

Styrene modification of alkyds (alkyd Raman bands assignment has been reported in [3]) is not readily discerned in the presence of rutile by FTIR while in Raman styrene and ortho-substituted benzene of alkyds are manifested by sharp bands respectively at 1001 and 1042 cm^{-1} (see Figs. 1 and 5). Mixtures of alkyd and urea-formaldehyde (the latter has a Raman inactive amide II IR band at 1550 cm^{-1}) resins used in truck coatings
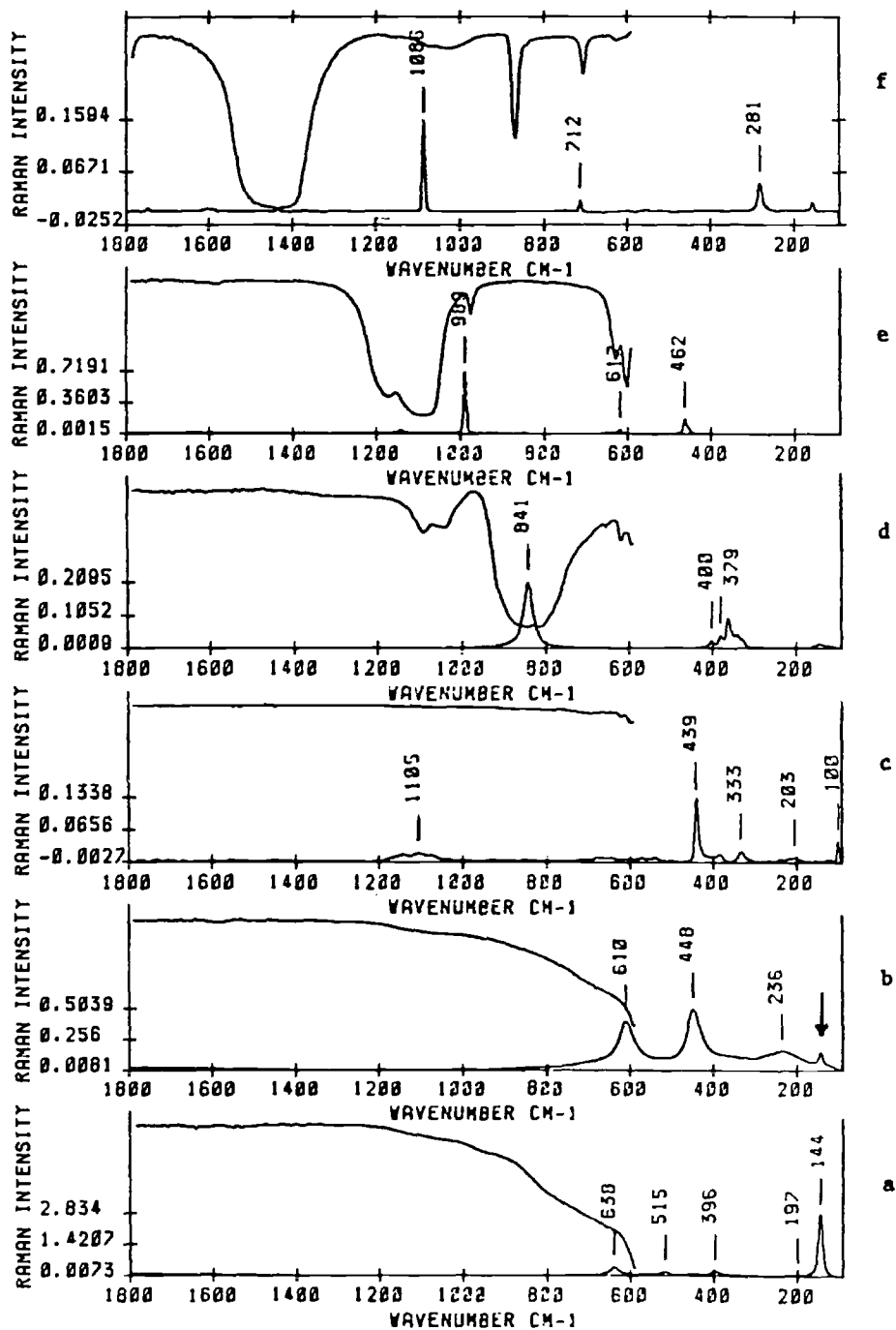
FIG. 4—*The infrared (no transmittance scale) and Raman spectra of commonly used mineral components of automobile paints: anatase (a), rutile (b), ZnO (c), PbCrO₄ (d), BaSO₄ (e), CaCO₃ (f). Number of scans for all the IR spectra –50, Raman –300. Arrow shows anatase band.*
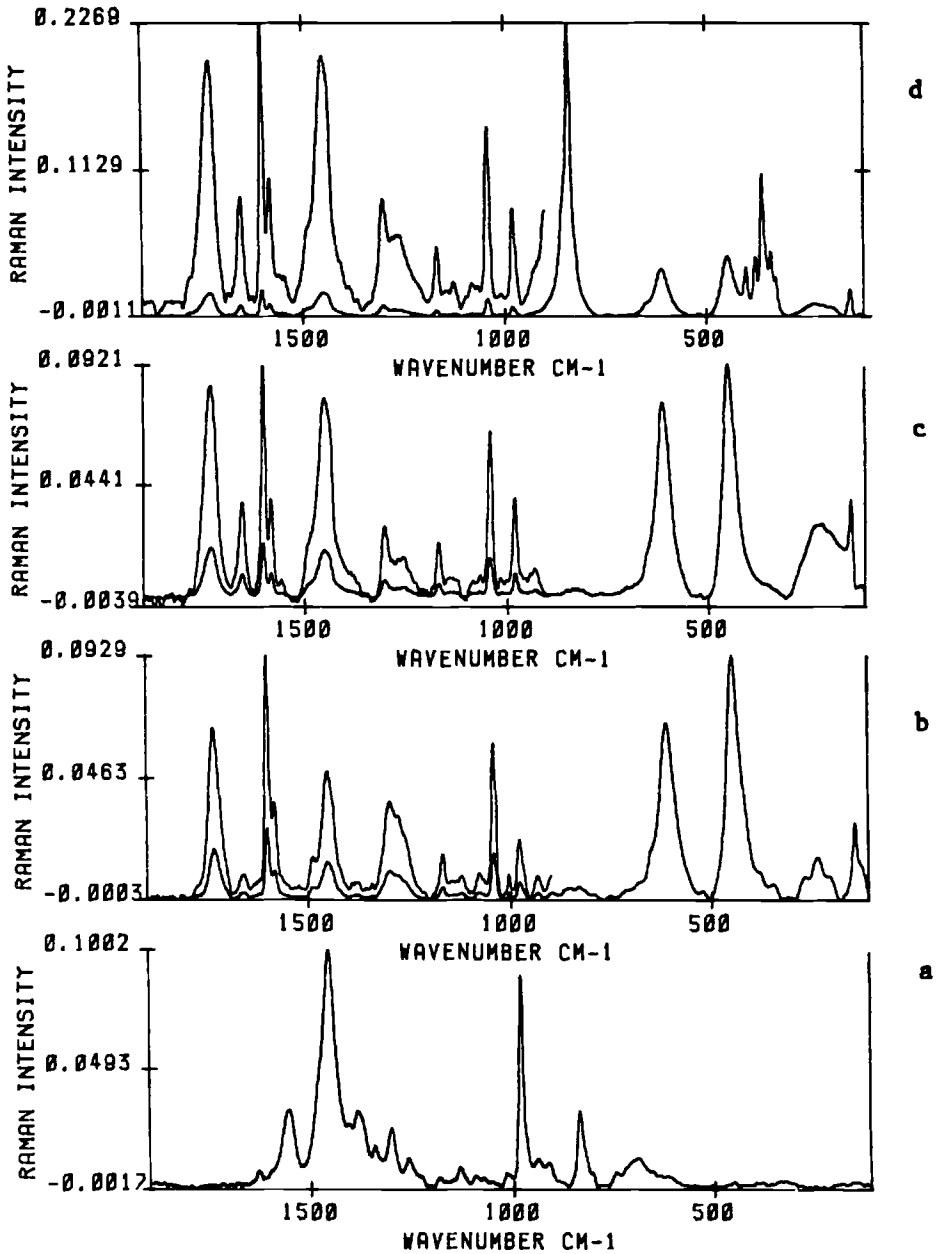
FIG. 5—*The Raman spectra of automobile paints: melamine-formaldehyde resin* (a), *melamine-alkyd binder and rutile of "Duga," Yugoslavia, top coating* (b), *melamine-alkyd binder and rutile of home made top coating* (c), *melamine-alkyd ML-12, TiO_2:$PbCrO_4$ = 1:1 of factory laboratory made coating* (d). *Number of scans − about 500. Spectra are background corrected. Intensity scales are expanded to a most intensive bands of organic (top spectra, intensity scales not shown) and inorganic components.*

often employ melamine-formaldehyde resins as modifiers. When $PbCrO_4$ is employed as pigment or extender, the melamine polymer bands at 1550 and 814 cm^{-1} of triazine cycle cannot be used for identification. This is due to the overlapping of bands from other components when studied by FT-IR, but triazine is clearly indicated by the intense 978 cm^{-1} Raman band (see Fig. 5).

Modified alkyd binders have various amounts of different drying oils which possess residual C═C bands upon film formation. It is difficult to distinguish these materials employing FT-IR based on the relative intensities of the C═C stretching vibration (about 1640 cm^{-1}) because of its inherent weak absorption. However, the intensity of the Raman band is strong, and these materials may be differentiated. The progressive decrease in the intensity of the Raman band as the film cures, has been observed [3]. The residual C═C bands are indicative of the incomplete linking. The home made top coating from a case study and a laboratory manufactured siccative deficient coating are compared to that of an automotive factory coating in Fig. 5.

The sharp relatively strong band at 144 cm^{-1} in the spectra displayed is evidence that the rutile pigments contain differing amounts of anatase, traces of which could be detected by Raman spectroscopy at 0.1% per rutile weight [15].

Useful Raman spectra can be routinely obtained from light colored paints such as white and yellows but often the technique cannot be employed for some darker paints due to strong backgrounds due to either fluorescence or thermal interferences.

Papers

FT-Raman spectroscopy was also found to be useful in the forensic analyses and comparison of paper. Along with the capability of identifying polymer coatings [16] it can reveal valuable information on white pigments and other mineral components. Easily detectable bands (indicated by filled areas) of widely used calcite ("c") and rarely used talc ("b") are shown in Fig. 6. Commonly used in different papers are pigments and/or fillers such as $BaSO_4$, $CaSO_4$, ZnO, TiO_2 (rutile or anatase), $CaCO_3$, $MgCO_3$ (see Fig. 4 or [14]). Some blends of these and others could be easily observed and identified due to sharpness of their bands. Moreover, comparison of the Raman spectra of papers with that of pure cellulose (Fig. 6a) shows the presence of some minor components at 1600 cm^{-1} (indicated by asterisk) and at 510 cm^{-1}.

In this laboratory about a hundred different samples of wood pulps, pasteboards papers, and celluloses originating from different species of hard and softwoods after sulphate and sulphite processing were analyzed. Representative spectra of some of them, normalized to the most intensive cellulose band at 1096 cm^{-1} are presented in Fig. 7, indicating a large scale of residual lignin and rosin bands (1600 cm^{-1} and 1658 cm^{-1}) intensity variations compared to IR, where the largest of them are an order of magnitude weaker than the cellulose IR bands at 1100–1000 cm^{-1}. It is clearly seen from Fig. 7, that lignin band at 1600 cm^{-1} has an asymmetric and complex contour. Its relative intensity in native woodpulp was shown to be dependent on wood type (hard or soft) [16]. The residual lignin band contour and some other minor component bands was found to be dependent both on wood type and cooking technology (sulphite or sulphate). A paper on this topic is currently in preparation.

In addition to the lignin content, the relative intensity of the band at 510 cm^{-1} was found to vary in the samples of cellulose and paper studied. It was intense in sulphate digested hardwood cellulose, smaller in softwood, and practically non observed in sulphite cellulose (see Fig. 8). An assignment for this Raman band was not found in the literature, but it is known that the sulphate cooking of cellulose results in the formation of some Alkylsulfides and dimethyldisulfide, which are gases and liquid substances. But
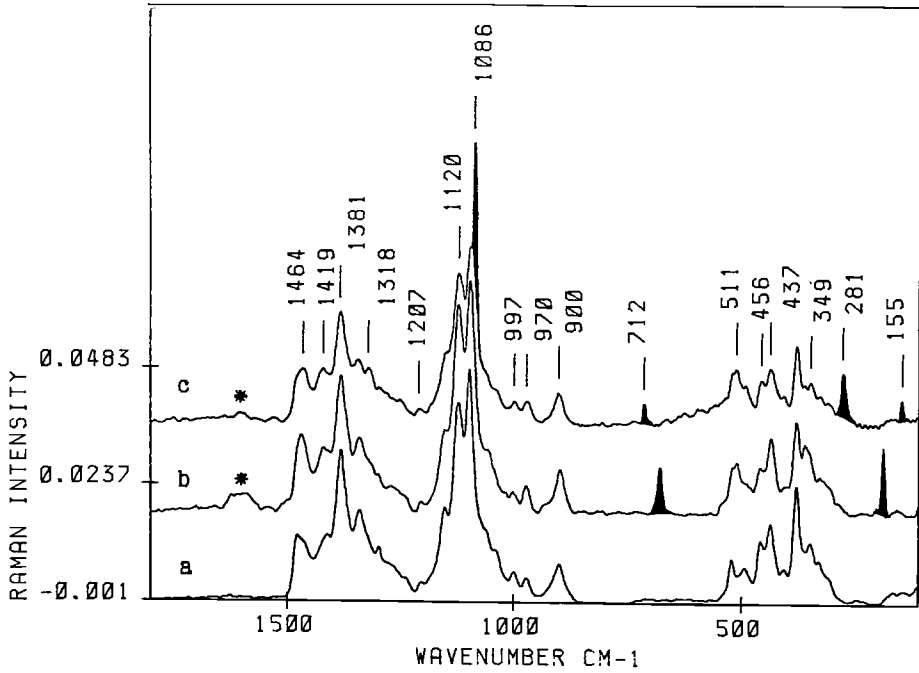
FIG. 6—*FT-Raman spectra of: firwood sulphite cellulose* (a), *notebook sheet* (b), *paper for Bruker printer* (c). *Spectra are background corrected, scans number—about 500.*
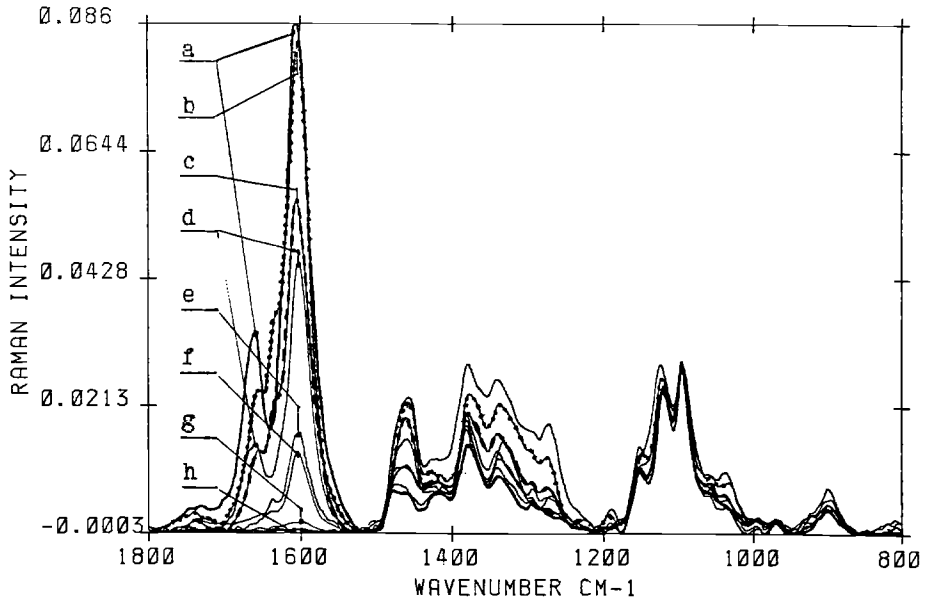

FIG. 7—*FT-Raman spectra of: firwood pulp* (a), *firwood pulp of different extent sulphate digestion* (b, c), *aspenwood pulp* (d), *firwood sulphite paper* (e), *pine sulphite paper* (f), *birchwood sulphite paper* (g), *aspen wood sulphite cellulose* (h). *Spectra are background corrected, scans number—about 1000.*
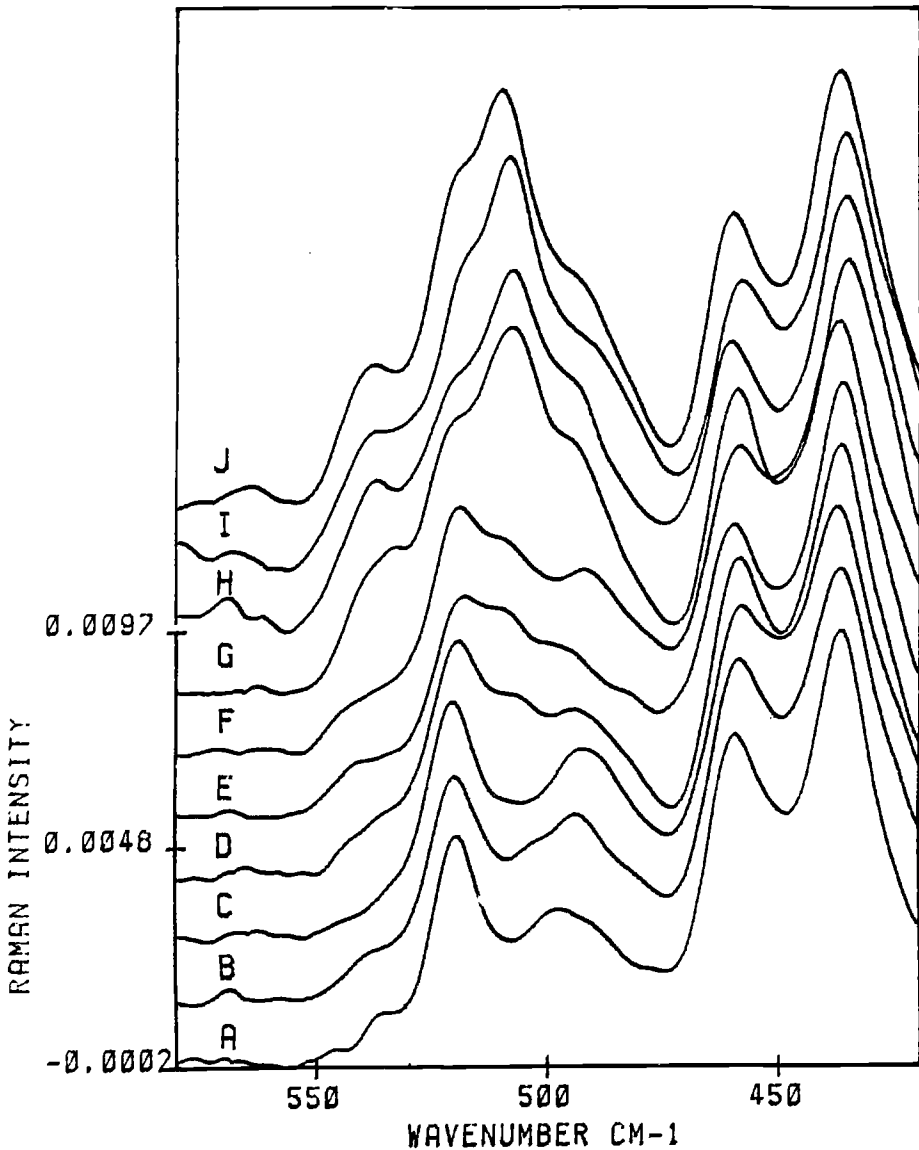
FIG. 8—*FT-Raman spectra of celluloses: birch sulphite* (a), *fir sulphite* (b), *aspen sulphite* (c), *fir sulphate* (d), *pine sulphate* (e), *softwood blend sulphate of Bratsk factory* (f), *birch sulphate* (g), *aspen sulphate* (h), *hardwood blend sulphate of Kotlas factory* (i), *hardwood blend sulphate of Izmail factory* (j). *Number of scans — about 500.*

the observed band in papers was not eliminated upon extraction. Analyses of the difference spectrum of hardwood sulphate over sulphite cellulose and the former at different polarizations (parallel over perpendicular) have shown that difference spectra are similar to the Raman spectra of dialkyldisulfides [17–20], which has a relatively sharp and very strong band at 510 cm^{-1} due to totally symmetric S—S stretching vibrations. Therefore, the 510 and less intense band at 540 cm^{-1} (see Fig. 8) have been tentatively assigned to the S—S stretching vibrations of the disulfide moiety in structures like R—S—S—R.

Analysis by Energy Dispersive X-Ray Spectroscopy indicates the presence of colored coordination disulfide metal complexes [20] to be unlikely. In dialkyldisulfides [17–19] the band at 510 cm^{-1} is attributed to *gauche-90°-gauche* low energy conformation, while the bands at 525 and 540 cm^{-1} to presence of one and two conformations or substitutions.

The ability to investigate these chemical composition features make the FT-Raman technique useful in the forensic analyses of papers.

In a view of these advantages of combined FT-IR and Raman spectroscopy digital libraries of both for different glues have been created in this laboratory.

Conclusion

The data reported herein show that FT-Raman is a very useful technique in automotive paint, coatings, and polymer lens material characterization as well as in paper analyses. The nondestructive and rapid nature of the analysis and, sometimes unique, additional information make the technique valuable not only as a screening routine, but also a powerful discriminating tool.

In addition the data presented speak well for combined FTIR and Raman use for polymer material investigations of forensic science interest. For these applications a FT-IR and Raman spectra digital library of more than two hundred different natural, artificial and synthetic materials including all the main classes of homopolymers and widely used copolymers and blends has been created at our laboratory. Samples of different origin whose IR and Raman spectra are on file is more than 600.

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