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Industrial Applications of Accelerator-Based Infrared Sources Analysis Using Infrared Microspectroscopy

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Industrial applications of accelerator-based infrared sources
Analysis using infrared microspectroscopy

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ABSTRACT

Infrared Microspectroscopy, using a globar source, is now widely employed in the industrial environment, for the analysis of various materials. Since synchrotron radiation is a much brighter source, an enhancement of an order of magnitude in lateral resolution can be achieved. Thus, the combination of IR microspectroscopy and synchrotron radiation provides a powerful tool enabling sample regions only few microns size to be studied. This opens up the potential for analyzing small particles. Some examples for hair, bitumen and polymer are presented.

Keywords: infrared microspectroscopy, synchrotron, hair, bitumen, polymer

1. INTRODUCTION

Mid-IR spectroscopy (between 4000 and 650 cm^{-1}) is widely employed for the identification of molecular systems because of its high chemical specificity. To characterize samples at the microscopic level, however, a molecular microprobe device is desirable. At the end of the 80's infrared spectrometers were coupled with optical microscopes to allow infrared microspectroscopy measurements to be made[1]. Such systems have now been developed to the point where they are now widely used for industrial applications[2].

Whereas conventional visible light microscopy is useful for identifying physical microstructure, IR microspectroscopy provides chemical imaging of the sample.

Infrared imaging is achieved by raster scanning the sample across the microfocused IR beam, taking a complete spectrum at each point. From these data a map of the integrated absorbance of a specific frequency is built up. In an IR microscope, the lateral resolution of such an image is imposed by the projected size of the aperture, which itself is limited by the brightness of the IR source. Indeed, for mapping experiments, a conventional infrared source (typically a 1200K blackbody) does not possess sufficient brightness to achieve acceptable signal-to-noise (S/N) ratios and reasonable scanning times when the size of the beam on the sample is less than 30 x 30 microns. In order to improve the lateral resolution, herefore, a brighter source is needed. Infrared light produced as synchrotron radiation has been found to be 2 to 3 orders of magnitude brighter than conventional sources[3]. Since 1994 at the NSLS, Brookhaven, an infrared microspectrometer has been coupled to a synchrotron infrared light source[4]. This has allowed mapping experiments with an acceptable S/N (-Root Mean Square-RMS (T%) =5 x 10^{-3}) with a beam size of only 6 x 6 microns. Further improvements are possible, depending on the absorbance and thickness of the material.

The present work was done at the National Synchrotron Light Source (Brookhaven National Laboratory) at the IR micro spectroscopy beamline in the frame of collaboration with the Elf Aquitaine Company.

In this paper, we focuse first on the comparison between conventional and synchrotron sources. Then, we also report results of chemical imaging characterization obtained in different fields of interest of the chemical industry. In cosmetics, results obtained on the microstructural characterization of hair are presented. Bitumen and polymers infrared imaging characterizations are also reported.

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2. SYNCHROTRON INFRARED SPECTROSCOPY

A commercial IR microspectrometer (a Spectra –Tech "Irμs"^{tm}) is installed at beamline U2B[3, 4] of the NSLS. The Irus system consists of an integated FTIR spectrometer and microscope optical module. The spectrometer contains a rapid-scan Michelson interferometer with a germanium coated KBr beam splitter. Spectral resolution can selected from 2 to 16 cm^{-1}. It is equipped with a MCT (HgCdTe) detector which allows experiments between 4000 to 600 cm^{-1}. The microscope optics used was a 32x, 0.65 NA, objective lens. The condenser used for the transmission experiments was a 10X, 0.71 NA. Both objective and condenser were Schwarzschild reflecting designs. A two dimensional motorized stage was used for the raster scanning. A schematic of the Irμs microspectrometer is shown in figure 1.

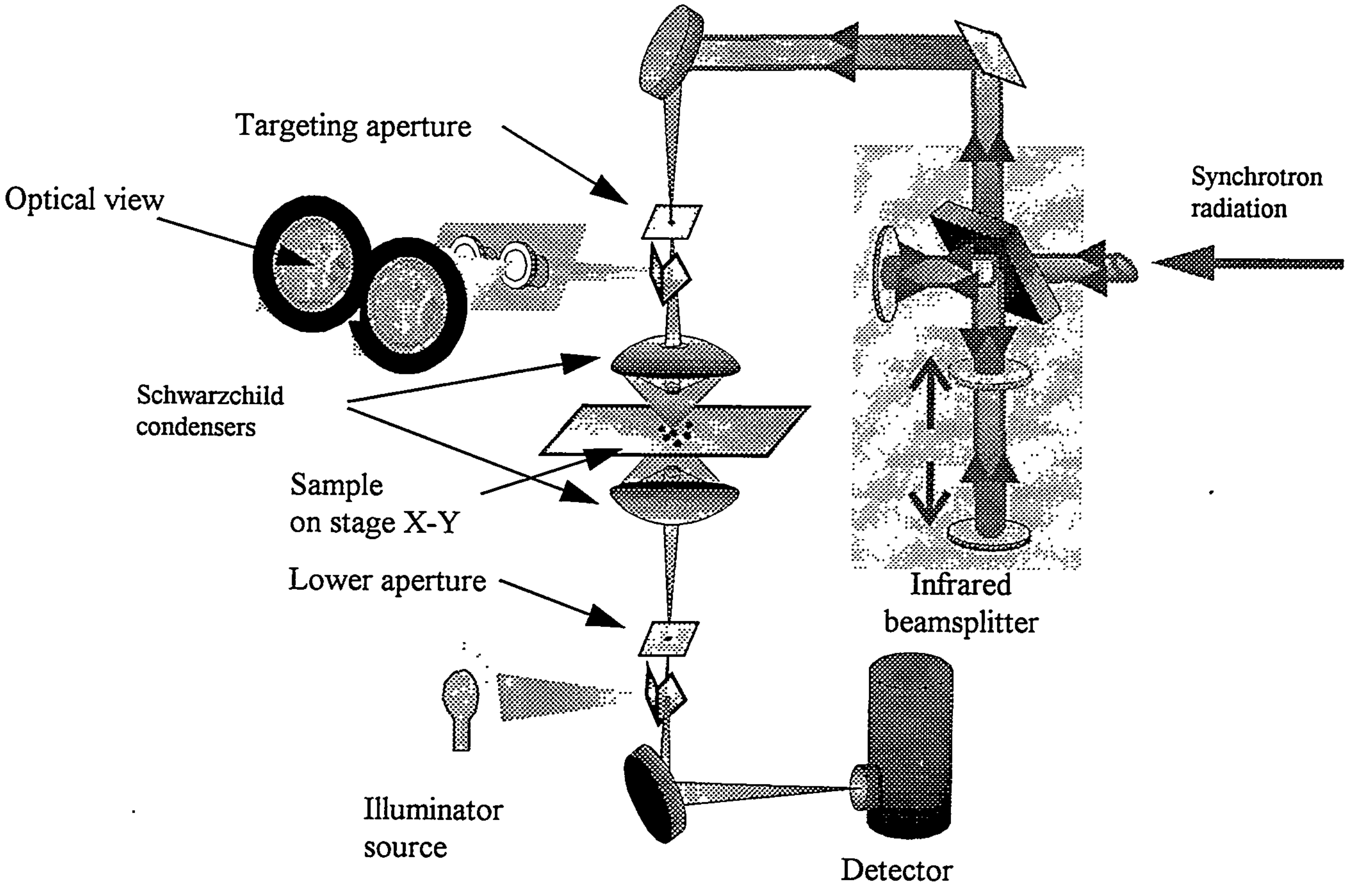

Figure 1: Schematic diagram of the Irμs scanning infrared microspectrometer.

The higher brightness of the synchrotron source compared to the globar in the mid-IR region has been quantified at the NSLS for the U2B beamline[3], the U2/globar ratio being about 10^2 at 1000 cm^{-1}. This enhancement of the brightness allows regions smaller than 10 μm to be probed with acceptable S/N values. We quantified the S/N of the microspectrometer with the synchrotron source and the globar source by ratioing two nominally identical spectra (128 scans / 4 cm^{-1}) through a 2mm thick BaF_2 pellet. The plots of the ratios (versus frequency) produces a line around 100 %, the deviations from 100 % giving the lack of reproducibility, or noise. The RMS value of the "noise" was evaluated in 500 cm^{-1} intervals from 4000 cm^{-1} to the lowest frequency usable. With a beam size of 6 x 6 microns for both sources, the synchrotron/globar noise ratio is about 10^{-2} between 3000 and 2500 cm-^{1}, which is in agreement with the brightness calculations. Addressing practical limitations of the spatial resolution, however, we show another comparison of the noise as a function of the frequency in Fig. 2 below. On the left are data for a globar using aperture sizes of 22 x 22 microns, which is the practical limit with a conventional source, and on the right, data for the synchrotron with aperture sizes of 6 x 6 microns. The RMS (%) is below 5 x 10^{-3} between 4000 and 1300 cm^{-1} for both sources. The lost of signal below 1700 cm^{-1} is mainly due to the combination of diffraction effect and refractive index variation for this frequency range, the latter being the most important. However , an adequate retuning of the condenser could increase significantly the signal to noise ratio in this specific frequency range. If attention has to be paid in this region, less dispersive substrates like KBr would be better.

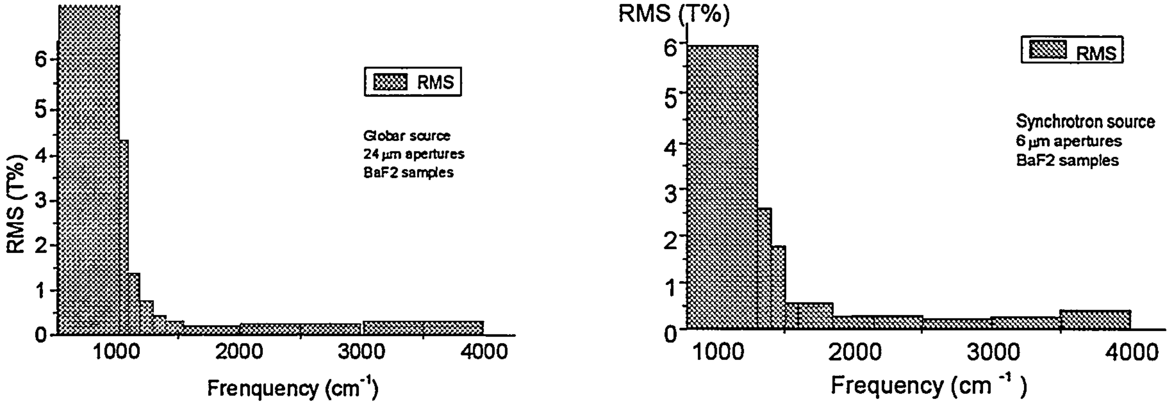

Figure 2 : Noise as a function of frequency for synchrotron and globar infrared sources (note the aperture sizes are different).

3. CHEMICAL IMAGING OF A HAIR

The ultimate goal of these experiments which map the chemical microstructure of hair is to study the interaction of chemical reagents. Initially, and as a control, a characterization of hair free from any chemical treatments is also needed and those results are presented here. This work is being done in collaboration with the Yves Rocher company.

From the morphological point of view, the human hair shaft structure consists of three main components (figure 4). The hair is typically composed of an inner core, the **medulla** (~10 µm diameter), which is surrounded by the **cortex** which constitutes the main part of the bulk of the fiber. The outer layer, which is exposed to the environment, is the **cuticle** with an average thickness of 5-10 µm.

Chemically, hair mainly consists of keratin, a protein highly cross-linked by the amino acid cystine. The infrared frequencies characteristic of the intramolecular vibrations of this protein[5.] in the mid-IR (4000 – 1000 cm^{-1}) are given in table 1 and agree well with those seen in a spectrum of hair.(figure 3).

	ν (cm-1)	comments
νNH	3290	Amide A
νNH	3063	Amide B
νCH	3000-2800	
νC=O	1650	Amide I
νCN and δNH	1540	Amide 2

Table 1: vibration of the melanin protein[5.]

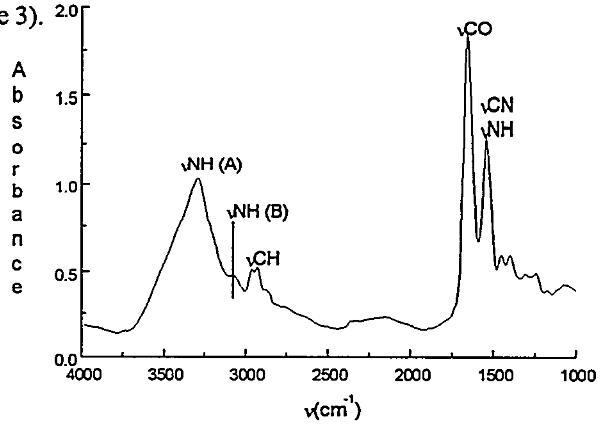

Figure 3 : IR spectrum of a hair

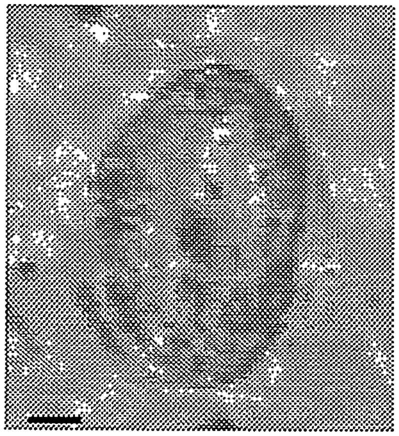

Figure 4: cross-section of the hair (optical image)

Samples were prepared by embedding hairs in polymer blocks and afterwards slicing with a microtome. The cross-sectioned cuts were on the order of 6 μm thick (figure 4). The polymer was chosen to have vibrational features away from those of the hair sample.

The hair section shown in figure 3 was spectroscopically mapped with a lateral resolution of 6 μm. The integrated absorbance of the amide A band (3290 cm^{-1}) was then extracted and a contour map showing the absorbance of this band as a function of position in the sample is shown in figure 5. Since this band is present throughout the hair, but at differing concentrations in the various components, the cuticle, cortex and medulla are all revealed in this map. The variations in absorbance which give the contrast are consistent with the differences in protein composition between these components[5]. The next step of this work will be to study the influence of dyes and cosmetic reagents on the structure of hair samples.

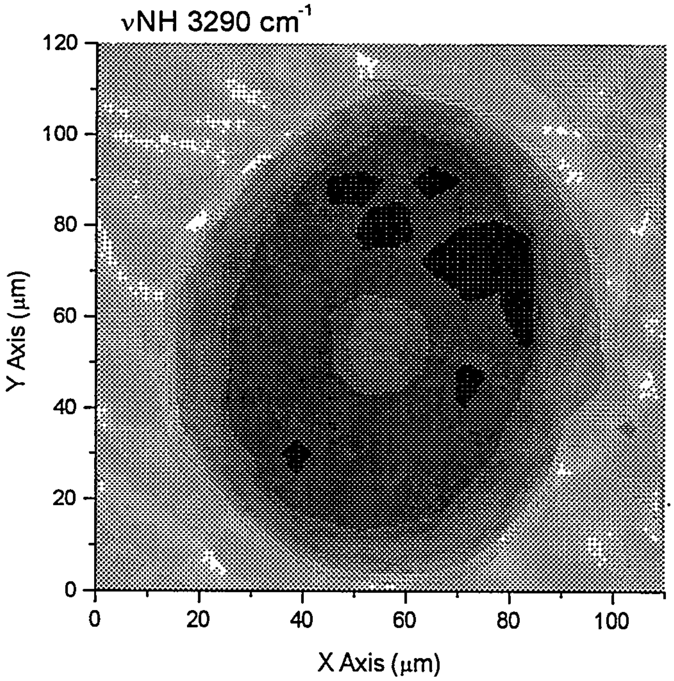

Figure 5 : Absorbance contour map of a hair for the amide A band (3290 cm^{-1}). Darker region represent lower absorbance.

4. CHARACTERIZATION OF BITUMEN-POLYMER MIXTURES

Bitumens are the heavy organic fraction of petroleum products. The main industrial application of this material is road surfaces. For this application, polymers are added to the bitumen to improve the mechanical properties. These in turn depend on the homogeneity of the mixture. Two ways of preparing the mixture can be used:

-One where the polymer is only mechanically mixed with the matrix of bitumen;

-a second one where the polymer chemically reacted with the bitumen.

The concentration of the polymer in the bitumen (5 %) is identical for both mixtures.

We have characterized the relative distribution of the polymers in the bitumen matrix for the two different preparations.

For sampling, the bitumen-polymer mixture is first heated in a oven at 353K and then spread on a BaF_2 pellet of 2 mm thick. We obtain a film of which thickness is hardly under accurate control.

The mapping experiments were made in transmission mode with 2 cm^{-1} resolution and 128 accumulations per spectrum with a lateral resolution of 8 microns. Figure 6 shows the IR spectrum of the mecanically mixed Bitumen-polymer. The 1377 cm^{-1} band is a signature for the bitumen and the 967 cm^{-1} band is assigned to the polymer. After mapping, the integrated absorbance (IA) of both bands has been calculated as a function of the position. As the thickness of the sample is not homogeneous, the ratios of these values (IA 967 cm^{-1} / IA 1377 cm^{-1}) was calculated for each position.

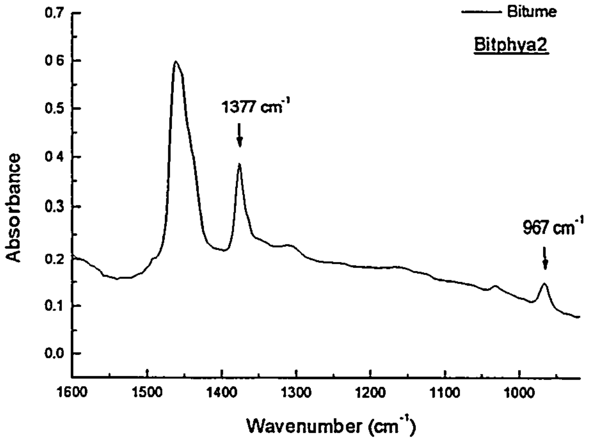

Figure 6 : IR spectrum of the mecanically mixed Bitumen-polymer

The image obtained is shown figure 7. The colors represent increments of 1.1 % variation of relative concentration of polymer in the matrix of bitumen. The spatial resolution is limited by the diffraction limit of the wavelength of the polymer band at 10.3 microns. Therefore we are able to observe heterogeneity of the relative concentration of the polymer of 9 % in the bitumen for the mechanically mixed sample. This scale of heterogeneity (order 10 microns) is impossible to observe by using a conventional source.

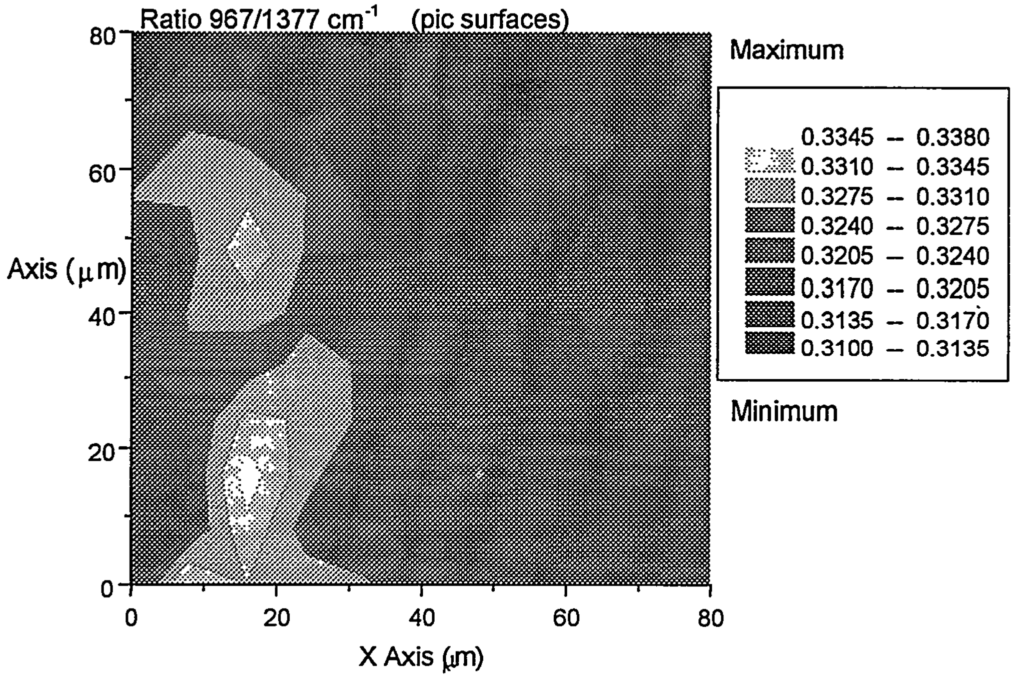

Figure 7: Absorbance contour map of a mecanically prepared bitume-polymer mixture for the ratio of the 967 cm^{-1} band (polymer) and the 1377 cm^{-1} band (bitumen). Darker region represent lower absorbance.

We have also tried to make a similar map for the mixture made chemically, but the polymer band was weaker due to the chemical process. The intensity of the band is now too weak to allow a quantification of the relative proportion of both phases (figure 8). Nevertheless a linear mapping of this mixture shows that this signature is still present everywhere even if it is weak (figure 9).

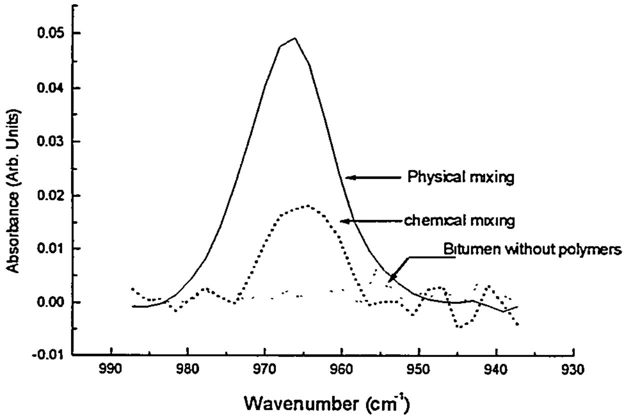

Figure 8 : 967 cm^{-1} band of the polymer in the different mixtures

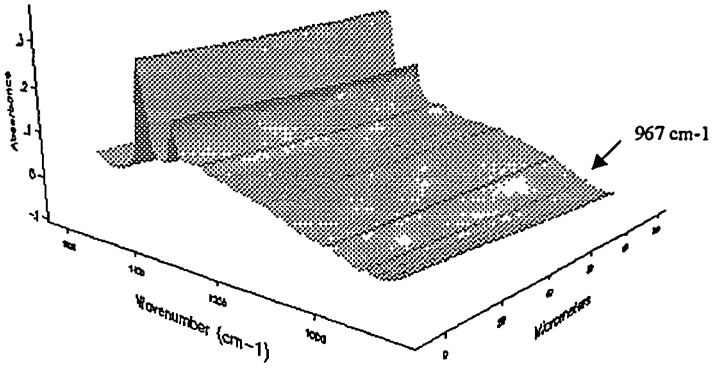

figure 9 : linear mapping of the chemical mixture

5. CHARACTERIZATION OF FLUORINATED POLYMER MULTILAYER

Polymer multilayers are widely used in the chemical industry and building trade. A better knowledge of the polymer structure is essential if their mechanical strengths and longevities are to be improved. We have studied a multilayer comprising a PVDF polymer "sandwiched" with a PVC polymer and with a tie layer. Different industrial process (thermal and mechanical process) are used to prepare the multilayers. Those processes induce different behavior during ageing of the material. The characterization of the interfaces of the different multilayer has been made.

The sample is formed by two layer of PVDF polymer (thickness 25 and 12 microns) and a layer of paste (thickness 12 microns -Polymer P-) on a substrate of PVC. Due to the fact that the interface itself is of interest, the synchrotron is necessary to perform accurate chemical contrast images of this region.

Cross-sections of the multilayered polymers were prepared using a microtome, the samples being 10 microns thick. Linear mapping across the layers of the film was recorded at 3 microns intervals using 6 x 6 microns dual-confocal-apertures. Spectra were collected over a range of 3000-900 cm^{-1} with a resolution of 4 cm^{-1}, and 128 scans were coadded for each spectrum. The chemical contrast image is shown on figure 10. Variations of composition across the layers are detected. More precisely, these results point out that the paste, characterized by the 1731 cm^{-1} band (C=O vibration) diffuses into the PVDF polymer for at least 25 microns. Therefore, the barrier role of the interface of the two layers of PVDF polymer is shown. Due to the presence of a band of additives of the PVC at the same frequency, it is not possible to draw conclusive lines concerning the diffusion of the paste in the PVC. Due to the lack of contrast, this kind of information would have been impossible to get by optical microscopy.

The diffusion of the paste in the PVDF layer has been also observed when the multilayer is prepared by mechanical process. The microscope will now be used to study the influence of ageing on the structure of polymer samples.

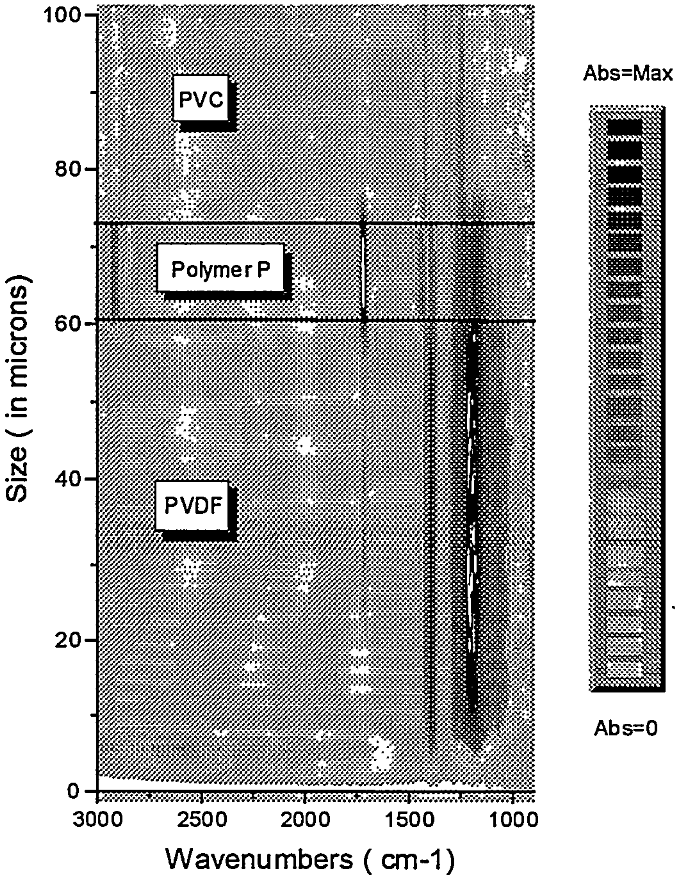

Figure 10 : Absorbance contour linear map of the fluorinated polymer multilayer obtained by mechanical process. Darker region represent higher absorbance.

6. CONCLUSIONS

By improving the spatial resolution of infrared microspectroscopy down to few microns, synchrotron radiation allows structural analysis at this level. Consequently, chemical identification of small samples and defects or composition gradients are possible. Chemical differences in the hair structure is shown, characterization of a polymer-bitumen mixture at several microns resolution is realized and heterogeneity of the mixture is pointed out. Furthermore, a more accurate description of polymer multilayer is demonstrated.

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