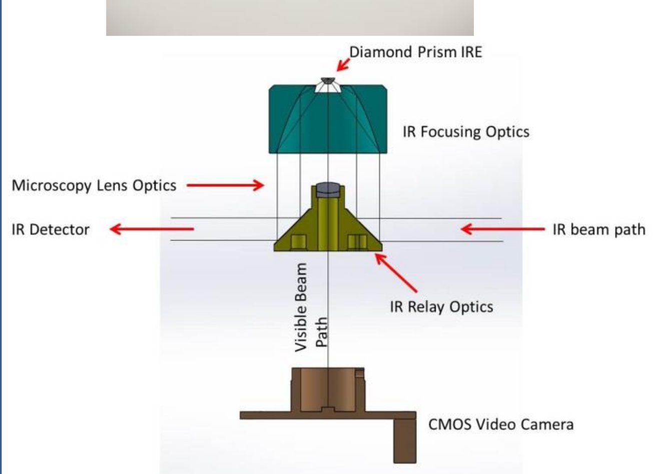
A New Diamond ATR Video Microscopy Accessory – Applications in Surface Analysis (Poster 2300-8P)

David W. Schiering – Czitek, 6 Finance Dr., Danbury, CT 06810 USA

INTRODUCTION – The chemical analysis of surface modifications and surface contamination present special challenges to the analytical chemist. Excising surface located material is not always feasible and is time consuming. Bulk analysis methods are not applicable to microscopic surface features or contamination. Finally, selectively measuring the particle or small area of interest on a surface, minimizing the contribution of the substrate requires special techniques. Infrared (IR) spectroscopy is well suited to characterize materials. Coupling IR spectroscopy with total internal reflection optics allows the selective measurement of surface modifications or contamination by attenuated total reflection (ATR) spectroscopy. Conventional IR ATR spectroscopic methods are not well suited to micro-contamination either because the crystal area is significantly larger than the area of interest or the difficulty in positioning the sample on the internal reflection element (IRE). With conventional ATR accessories, an opaque sample substrate obscures the view of the area of interest on the surface.

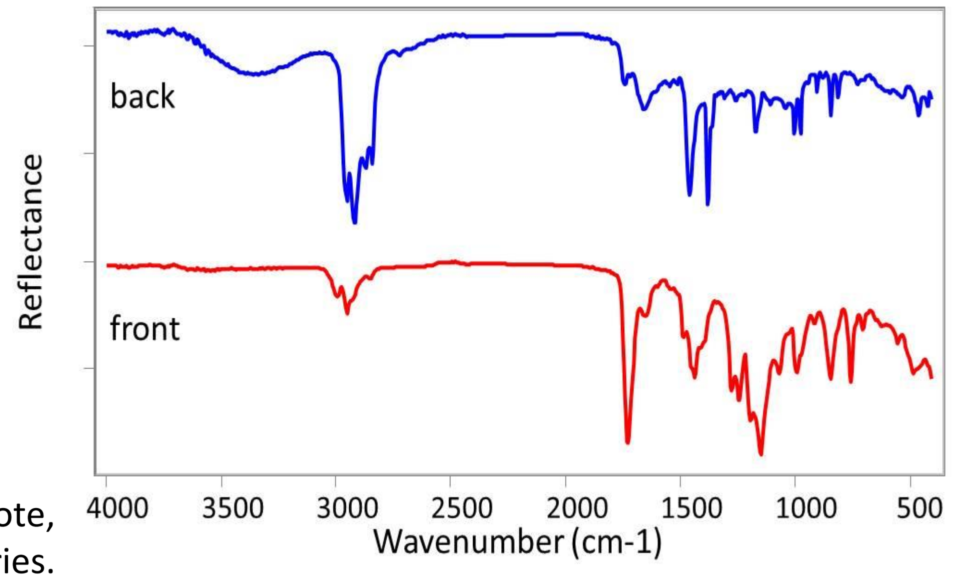
Type IIA diamond is a near perfect material for IR spectroscopy applications. The combination of diamond's IR transmission, hardness, and chemical resistivity are unsurpassed by alternative IR materials. The optical transmission of diamond in the visible range allows the combination of IR spectroscopy with visible imaging of the specimen. This discussion will primarily concern the application of diamond ATR IR spectrometry in combination with video microscopy to measure surface located materials, where "targeting" the sample is difficult with conventional diamond ATR accessories. The applications include the analysis of coatings on different surfaces, and defects.

Optical Diagram (bottom) and photograph (top) of MicromATR™ Vision

METHODS – The optical layout of MicromATR single reflection ATR accessory is shown in the left inset. For the work described here, a diamond prism internal reflection element (IRE) was used at a nominal angle of incidence of 49°. All optics are pinned-in-place and kinematically mounted. The diamond IRE is mechanically fixed into a 316 stainless steel disk. Visible observation of samples is accomplished with a microscope lens that is focused on center through the diamond prism rooftop, imaging the specimen plane onto a megapixel CMOS camera. An integrated LED, powered by USB +5 VDC, provides illumination of the specimen in a reflected light geometry. eSpot™ video capture software was to record all video micrograph images. Measurements in external reflectance were made with external reflectance optics with a nominal incidence angle of 45°. All spectra were recorded at 4 cm-1 resolution with a DTGS detector.

Document Analysis - Currency

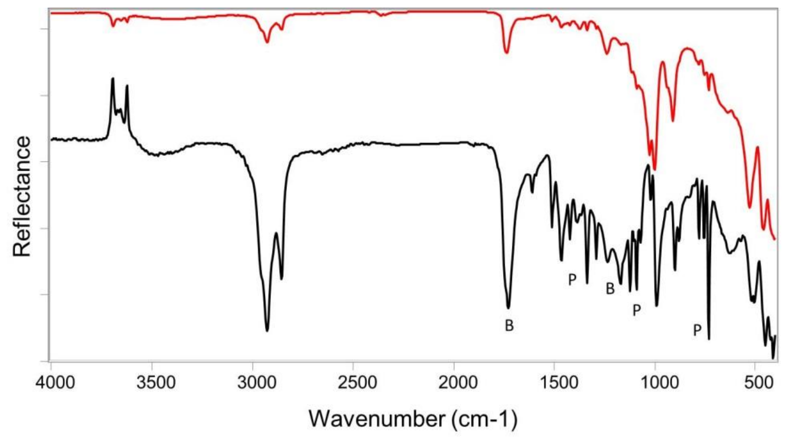


Canadian $20 bank note, the 2012 Frontier Series. **Top** – front of bill; **Bottom**, back of bill.

To thwart counterfeiters, new authentication technologies are being implemented in products, labeling, and documents. The new, polymer based Canadian currency is a good example of the implementation of these authentication technologies. **Right, top** – IR spectrum of unprinted, clear portion on the back of the bill, measured using single reflection, diamond ATR . The spectrum is dominated by the contribution of polypropylene film with the presence of other materials. **Right, bottom** – IR spectrum of a clear, unprinted area on the front of the bill, measured with single reflection diamond ATR. The spectrum corresponds to polymethyl methacrylate. The surface selectivity of the ATR measurement is noted – No contribution from the polypropylene base layer is observed.

Analysis of Printing on Coated Paperboard

Video Micrograph of printed Paperboard

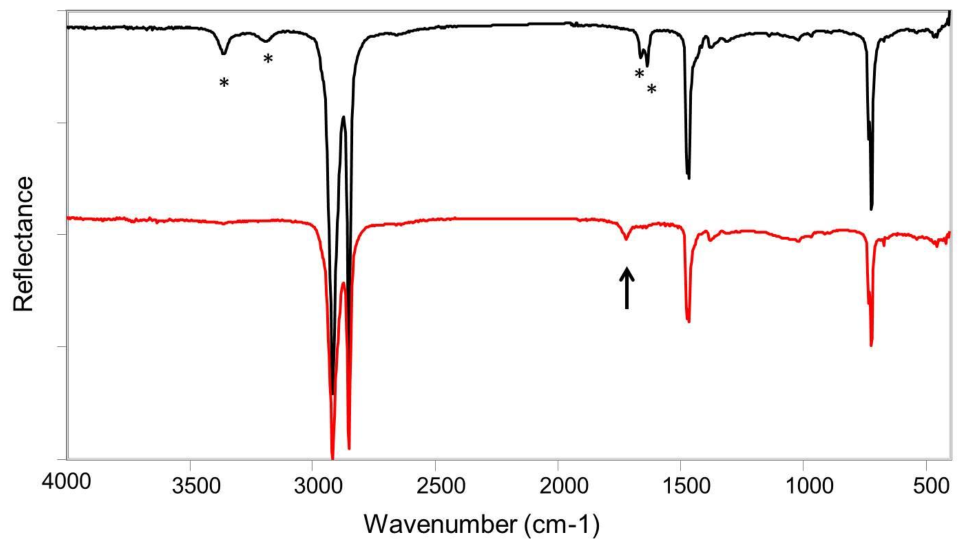


Right, top - unprinted, coated paperboard. Dominated by the pigment in the coating, kaolin and the binder. A triplet of νOH bands at 3690, 3650, and 3620 cm^{-1} and strong Si-O and Al-O bands in the 1000-800 cm-1 range are indicative of the kaolin. Bands at 1736 (νC=O) and 1238 cm^{-1} (νC-O) are consistent with a polyester binder.

Right, bottom - difference spectrum : unprinted area subtracted from blue area. The pigment is attributed to a metal phthalocyanine, most probably copper phthalocyanine. Significant IR absorption bands at 1507, 1334, 1120, 1090, 780, 754, and 730 cm^{-1}, attributable to the metal phthalocyanine are labeled "P". The binder is identified as poly(butyl acrylate). Major characteristic absorption bands of the poly(butyl acrylate) are observed at 1728 (νC=O), 1234 (νC-O) and 1165 cm^{-1} (νC-O) and are labeled "B" in the Figure.

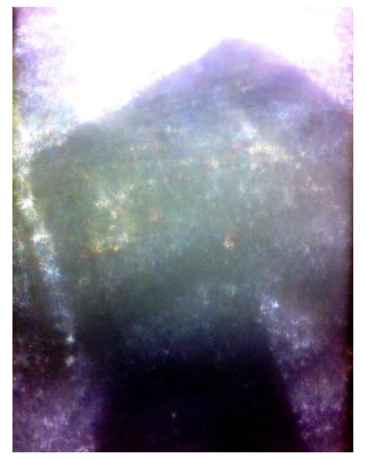
Surface Defect on Polymer Bag Substrate

Video micrograph of defect , characterized by striations across the field of view

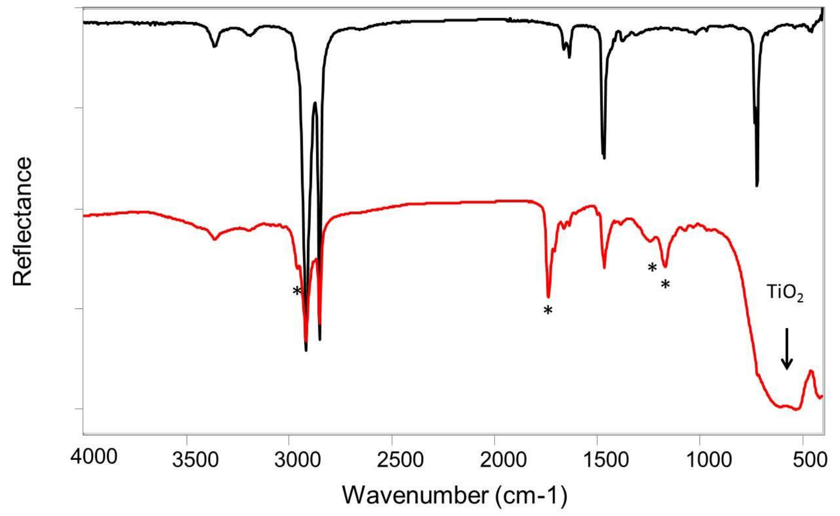


Right, top – spectrum of polyethylene bag measured with diamond ATR. This area of the bag exhibited no apparent defect or quality problem. Absorption bands indicated with an asterisk (*) at 3363, 3186, 1659, and 1632 cm^{-1} are due to oleamide, a long chain amide slip agent used in the manufacture of the bag. Slip agents function to keep adjacent layers of the polymer film from sticking together and lowering the coefficient of friction. **Right, bottom** – IR spectrum of defect area above, left measured with single reflection diamond ATR. The data is consistent with a loss of the oleamide slip agent as the aforementioned bands are no longer observed. A carbonyl absorption band at 1718 cm^{-1}, indicated with an arrow, is indicative of oxidation and presence of carboxylic acid functionality. The defect appears to be due to thermal degradation of the polyethylene.

Analysis of Printed Area on Polymer Bag Substrate



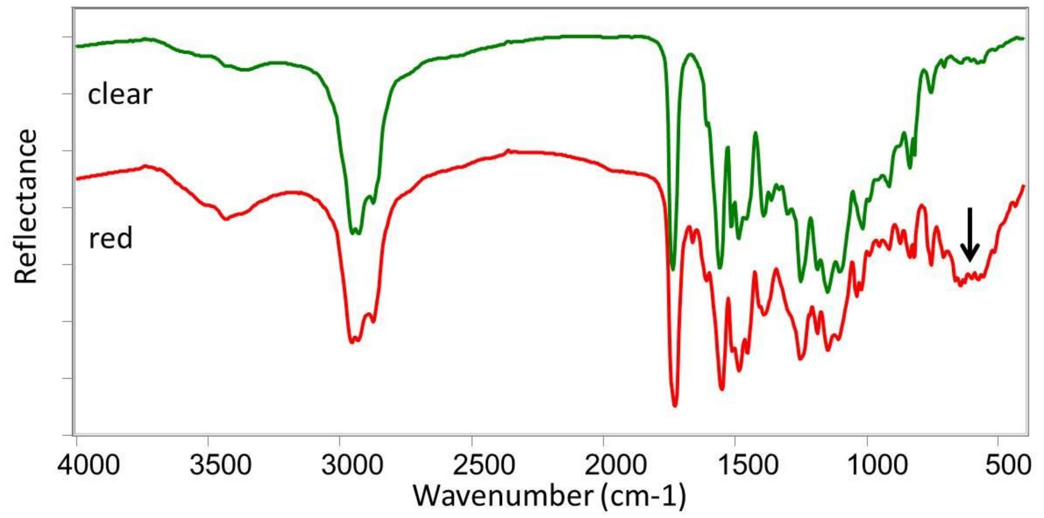
Video micrograph of printing on polyethylene surface



Right, top – spectrum of polyethylene bag from an unprinted area measured with single reflection diamond ATR. As in the example above, absorption bands at 3363, 3186, 1659, and 1632 cm^{-1} are due to oleamide, a long chain amide slip agent used in the manufacture of the bag. **Right, Bottom** – IR spectrum of printed area, shown in the left, in contact with a single reflection diamond ATR prism. The surface contribution to the spectrum is apparent. Major absorption bands due to the printing are noted. The pigment is identified as Anatase TiO_2; bands are observed between 600-500 cm-1. The binder is polyester polybutyl acrylate. Characteristic bands for polybutyl acrylate are noted at 2956 (methyl νC-H, 1734 (ester carbonyl νC=O), 1238 (ester νC-O) and 1167 cm-1 (ester νC-O).

Paint Coating on Aluminum

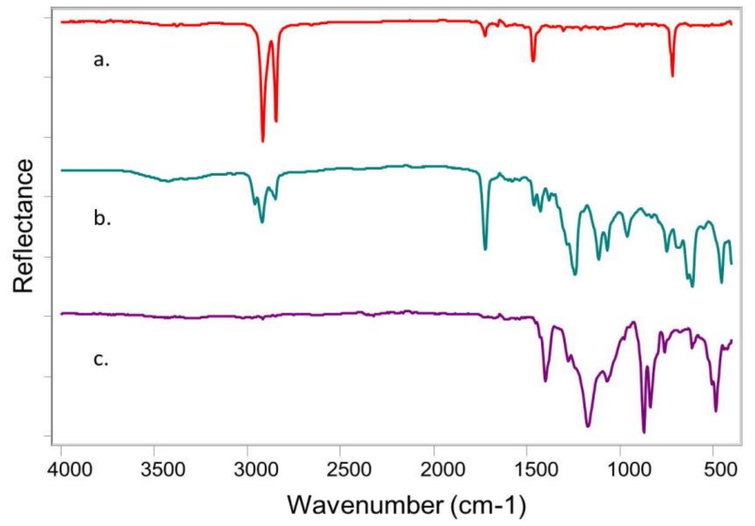
Video micrograph of coating on aluminum substrate.



MicromATR also offers the option of external reflectance optics. Unlike the previous examples, these data were recorded in external reflectance referenced to a gold coated substrate. **Right, top** – IR spectrum of the clear coating, corresponding to the image at the left. The coating is a melamine alkyd polyester characterized by bands at 1736 (polyester, νC=O), 1558 (melamine , triazine ring stretch) and 815 cm^{-1} (melamine, triazine ring bending). **Right, bottom** – IR spectrum of coted, red area corresponding to the image in the left at the bottom. As indicated by an arrow, inorganic pigment is noted by absorption in the 600-500 cm^{-1} region. This region is complicated by spectral overlap but the pigment could be TiO_2. Organic pigment is noted by an absorption band at 1659 cm^{-1} (alkyl, νC=C).

Identification of Insulator Sheathing on Electrical Wires


Electrical Wire Sheathing in contact with diamond ATR prism Left: no pressure. Right: visualization of contact with pressure



Wire insulation sheathing prevents electrical leakage and current from contacting other conductors, and preserves the material integrity of the wire by protecting against environmental threats such as water and heat. Both the safety and effectiveness of the wire depend on its insulation. Sheathing materials are selected based on their electrical and thermal insulation properties and cost. **Right** - IR spectra recorded in ATR mode. a. polyethylene with a small quantity of ester plasticizer. b. Polyvinyl chloride, plasticized with n-alkyl trimellitate. c. polyvinylidene fluoride.