AN EVALUATION OF REFLECTANCE-ABSORPTION INFRA RED SPECTROSCOPY FOR IN SITU INVESTIGATION OF ORGANIC COATINGS ON CORRODED METALS

S. C. BOYATZIS[1*], V. ARGYROPOULOS[1], A. SIATOU[1], K. POLIKRETI[1], D. CHARALAMBOUS[1] and A. M. DOUVAS[2]

[1] TEI of Athens, Dept. of Conservation of Antiquities & Works of Art, Egaleo 12210, Greece

[2] Institute of Microelectronics, NCSR "Demokritos", 15310 Aghia Paraskevi, Greece

Introduction

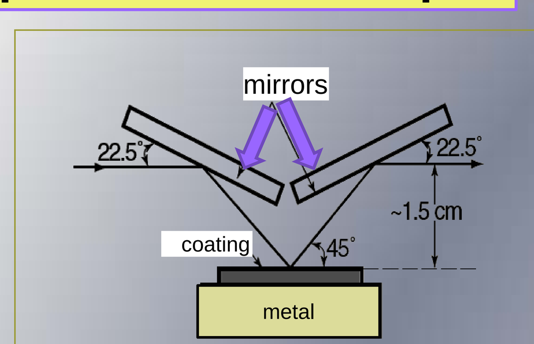
Reflection-Absorption Infra Red Spectrometry (RAIRS) along with Attenuated Total Reflectance spectroscopy (ATR) have been widely used as characterization and monitoring tools that can be used to evaluate the effectiveness of coatings on metal[1]. Increasingly, these techniques are being applied to test coatings for cultural property made of metals, such as outdoor bronze monuments [2]. The advantage is that the RAIRS technique can carry out an in-depth characterization of layers from the bulk coating to the metal surface analyzing changes in the chemical bonds.

This work evaluates the application of RAIRS to investigate Paraloid®B-72 and Poligen® ES 91009® coatings of variable thickness on corroded iron and copper alloy coupons under the auspices of the EC project PROMET. Furthermore, it highlights how a simple FTIR system (PE Spectrum GX) can be adapted to carry out reflectance measurements coupling with a reflectance accessory (PE, 12.5˚ fixed angle) at a relatively low cost. Such adaptability makes it attractive for conservation research, since most Conservation facilities, such as ours have a simple FTIR system.

For an accurate interpretation of the spectra throughout the coating layers, the following properties are significant: *thickness* and *uniformity* of the coating, *glossiness* of its surface, and the *nature* of the metal surface. In conservation research, the effectiveness of coatings often needs to be evaluated on corroded metals which are far from being considered as ideal cases.

The Reflection-Absorption FTIR Technique

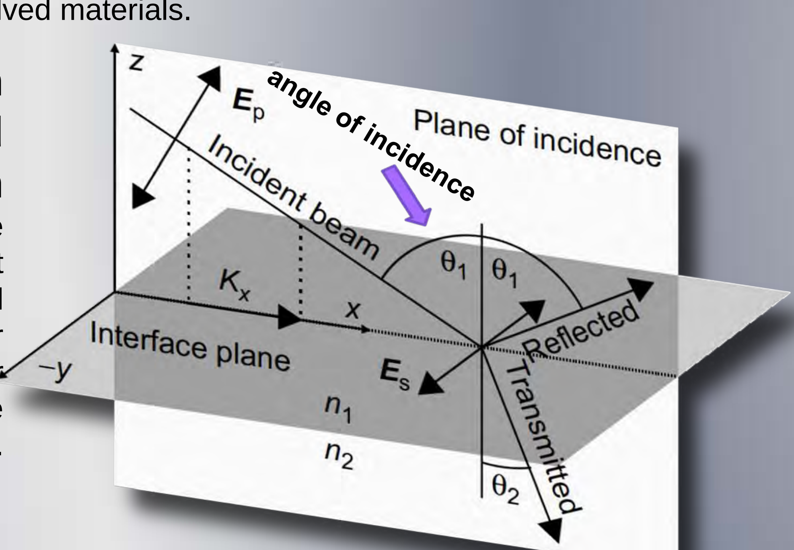
IR beam geometry
during the reflectance-absorption technique

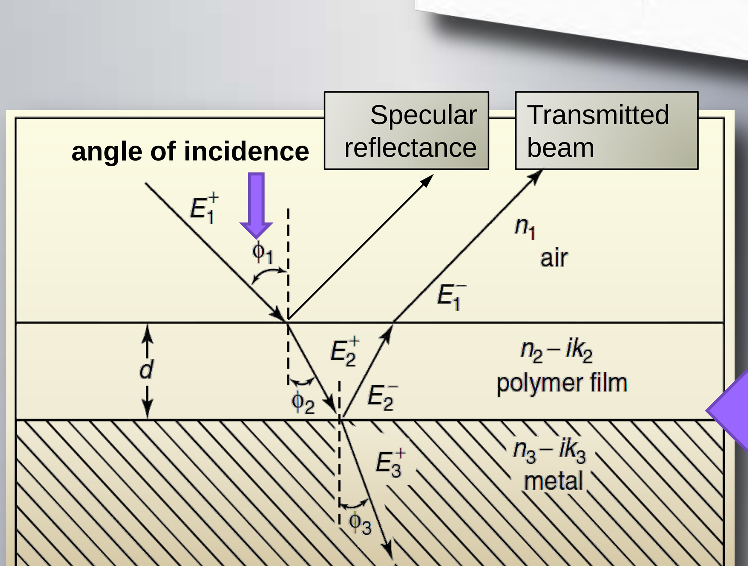


In a typical reflection-absorption FTIR experiment the infra red beam impinges in the coating at a specified angle of incidence. A part of this beam is reflected *on* the coating surface (***specular reflectance***). Another part is transmitted inside the film, accordingly reflects on the metal surface, re-transmits and finally, exits the film travelling to the detector (see figure). This is the ***absorption*** part of the RAIRS technique, recording the average information throughout the entire beam path. Both beam paths are detected within the same experiment: different physical information is recorded in each case, along with the chemical information of the involved materials.

Beam polarization and reflection

Polarization of the electrical IR component can be either parallel (***p*-polarized**) or perpendicular (***s*-polarized**) to the plane normal.





When angle of incidence equals the **Brewster's** angle of the coating material, the p-polarized beam is totally transmitted through the material.

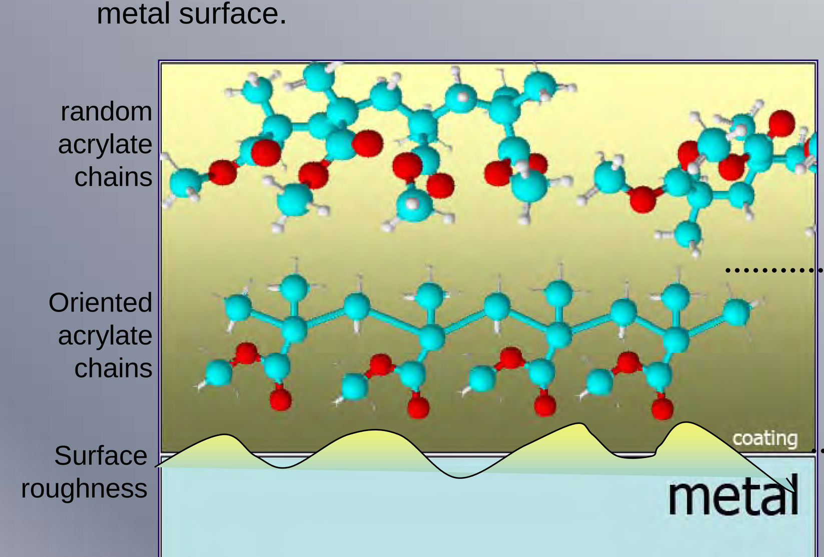
Three-layered system:

layer 1 (air, refr. index n_1)
layer 2 (coating, refr. index n_2)
layer 3 (metal, refr. index n_3)

Reflectance spectroscopy: Thin or thick films?

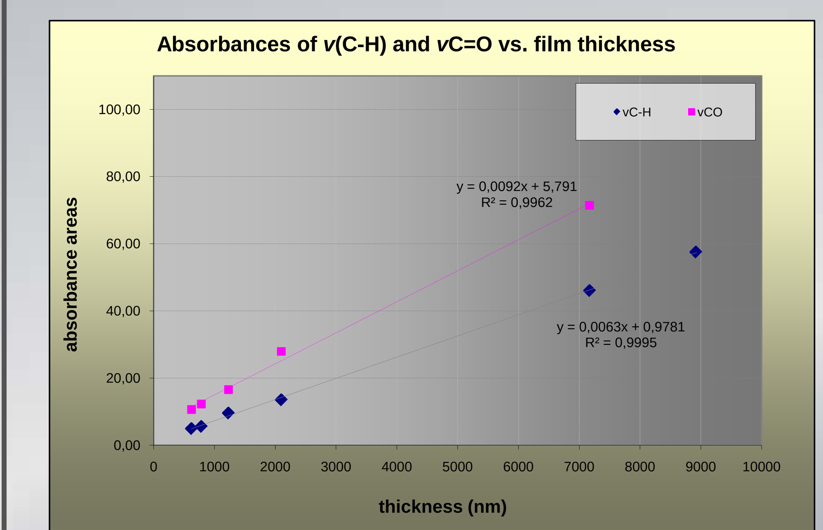
This question illustrates the geometrical aspects of a coating, basically controlled by the film application practice. The effectiveness of metal protection as well as the chemical information acquired spectroscopically is dependent on the film thickness, as this controls reactive species migration, light penetration, etc. The chemical spectroscopic information is averaged through the IR beam path in thin or thick films and reflects the behavior of polymeric coating chains and their functional groups with the metal and/or, if present, corrosion products.

In ***thin*** films the transmitted beam carries basically chemical information through the small path of a few nanometers, as it records orientational phenomena of polymeric chains towards the metal surface. Orientation is lost in thicker films, as chains tend to be more "random", away from the metal surface.



Physical information can be dominant in IR reflectance in ***thick*** films, where anomalous dispersion of refractive index is important. This results in numerous distortions of the recorded chemical peaks, depending on the nature of coating medium (i.e. refractive index), the film thickness, surface smoothness, IR beam polarization and the angle of incidence. Predicting these distortions can lead to a spectrum with "pure" chemical information.

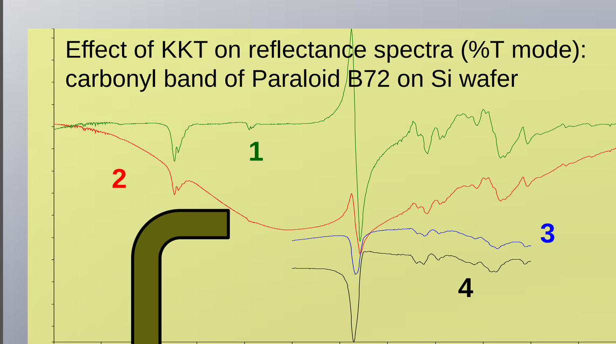
Paraloid® B-72 Transmittance and RAIR spectra



Transmittance spectra

The carbonyl band and the methyl/methylene stretch are markers for chemical alterations of organic coatings.

Reliable absorbance measurements of bands v(C-H) and v(C=O) for Paraloid B72 can be taken for films up to 8-9 μm where linearity in absorbance vs. thickness is obeyed.

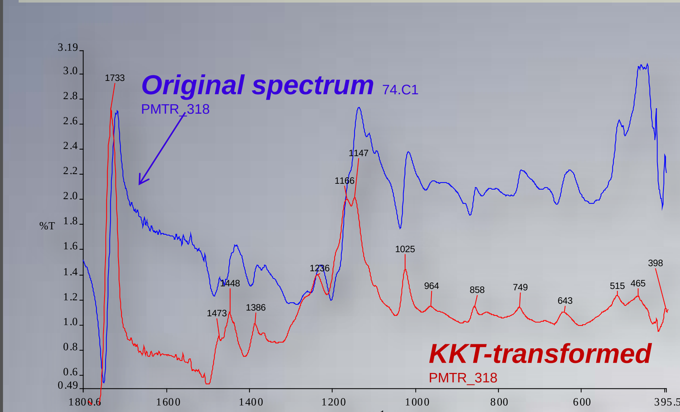


Kramers-Kronig Transformation (KKT)

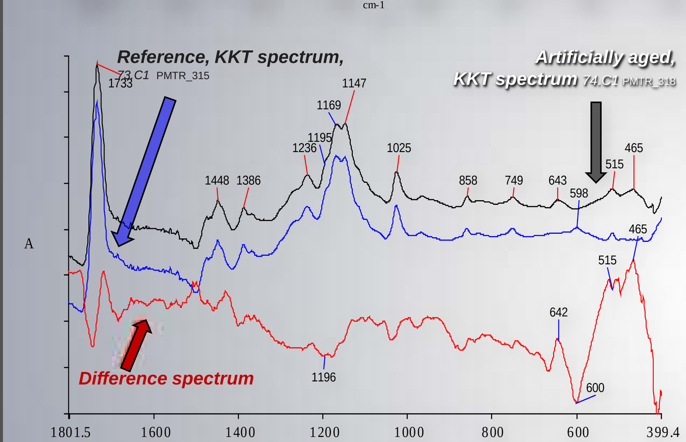
RAIR spectra carry both the *transmittance* and the *specular reflectance* component. When specular reflectance component dominates the spectrum, spectral lines appear with a *derivative-like* distortion

1. Original spectrum exhibiting specular *derivative-like* distortion
2. Baseline-corrected spectrum
3. KKT on original spectrum (in Transmittance mode)
4. KKT on baseline-corrected spectrum (in Transmittance mode)

Application of the *Kramers – Kronig* algorithm transforms the distorted spectral line (1, 2) line to an **absorption spectrum** of the film (3, 4).

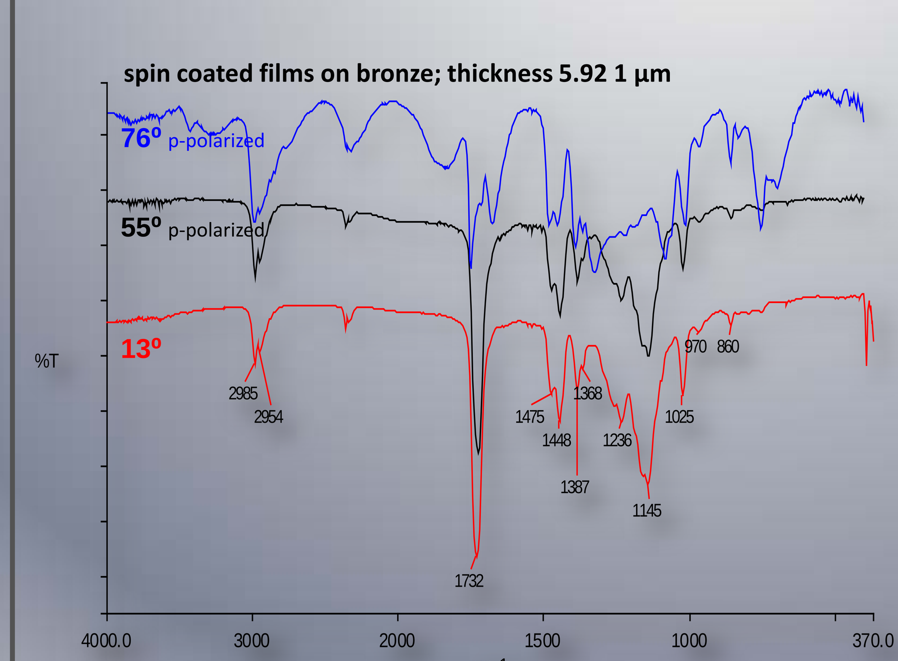


KKT transformation on RAIR spectrum (Absorbance mode) of Paraloid on corroded bronze coupon. The result is a mostly distortionless absorbance spectrum. Comparison in IR peaks of coating and corrosion products may be done in the 1750 – 400 cm-1 region.



Comparison of the KKT- derived spectra (absorbance mode) from Paraloid on bronze coupons, **brown area** (artificially aged and reference). Major changes in Copper oxides and hydroxides (increase in 642, 515 and 465 cm-1 peaks.

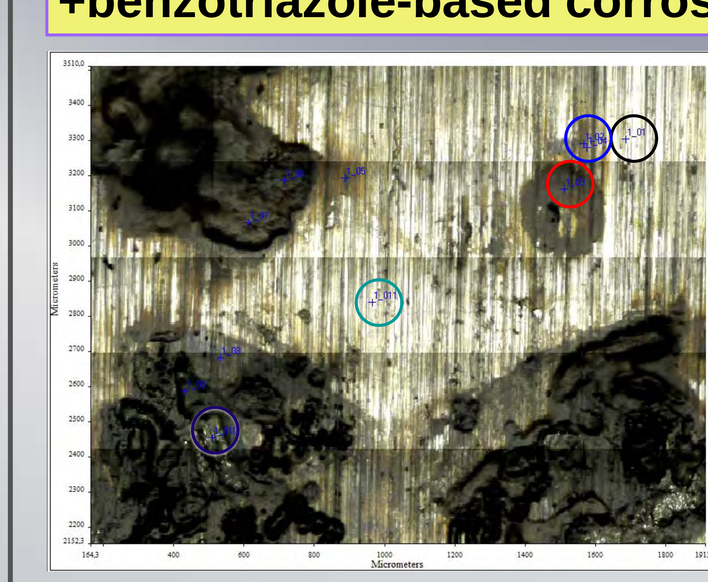
Paraloid® B-72 on bronze and iron

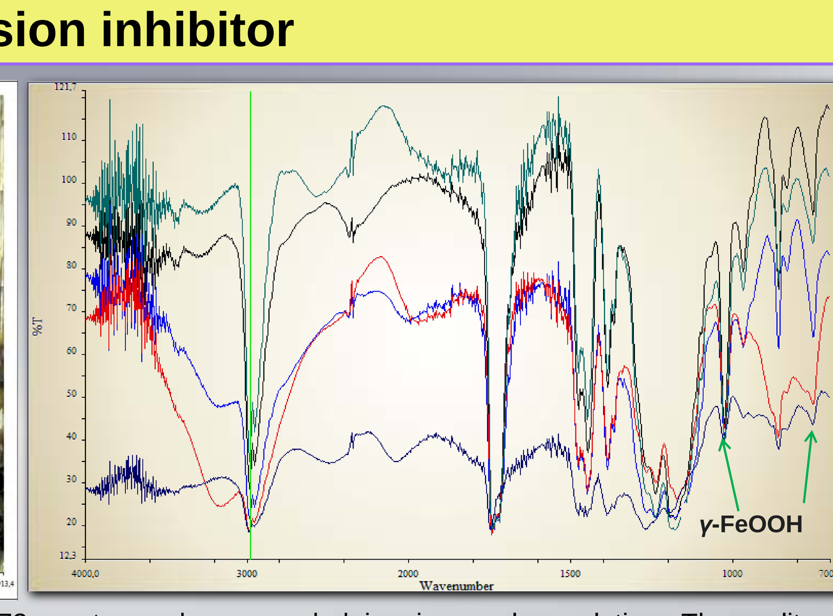


Reflectance spectra: angle of incidence

Linearity fails when reflectance IR bands exhibit *distorted lineshapes* and *saturation* (very high absorbance that does not obey Beer's law), as is commonly the case in thick films.
Band lineshapes can be optimized choosing Brewster's angle (55° for Paraloid) as incidence angle.

μFTIR on corrosion products on iron coated with Paraloid +benzotriazole-based corrosion inhibitor

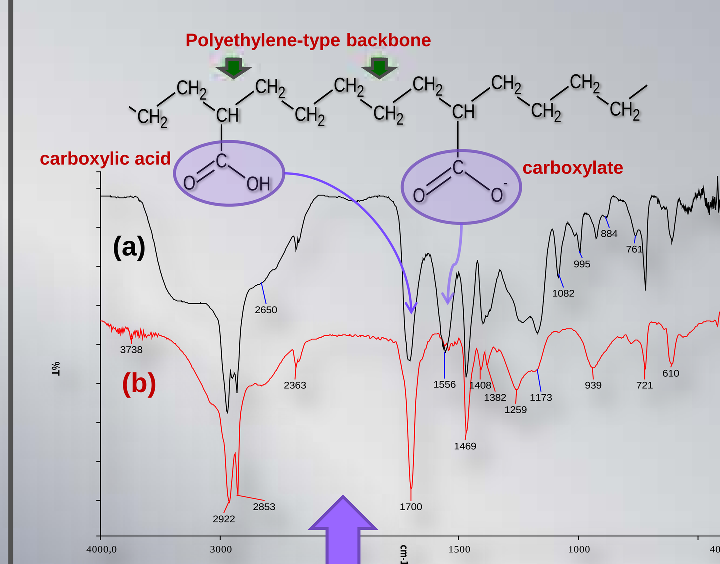




Paraloid B72 spectra are here recorded in micro-scale resolution. The quality of spectra varies between points. Corrosion products are also detected.

BASF Poligen® ES910009 RAIR spectra

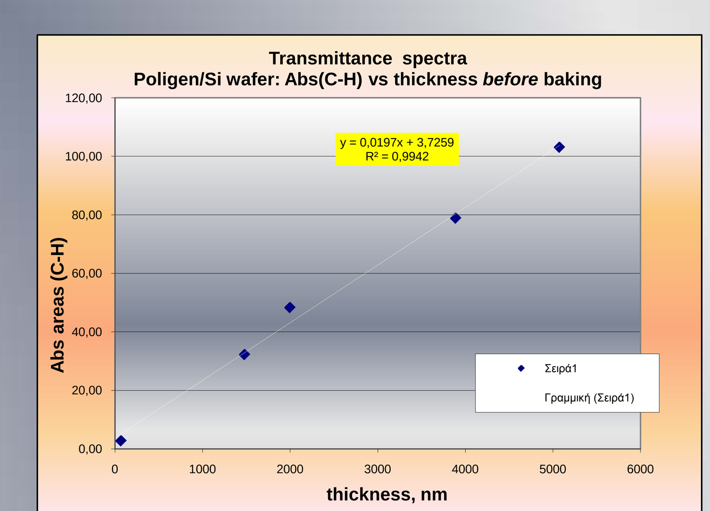
Poligen ES91009 is sold commercially by BASF and reported to be a "*water emulsion prepared from polyethylene wax*". FTIR spectra actually show hydrocarbon-like structure as well as carboxylic acid functionality. RAIR spectra of a film cast from water emulsion on a smooth surface (Si wafer, or metal: bronze, iron) further show carboxylate ion functionality depending upon the water content of the film.



RAIR spectrum of Poligen ES9109 on Si wafer (13° incidence angle).

3400(br) OH (carboxylic acid)
2942(s), 2860(s) vC-H;
2649 (sh) dimeric carboxyls
1706(s) C=O (acidic)
1556(s) C=O (carboxylate)
1468(m-s) δCH₂, 1383(w) δCH₃,
1407(w) δC-O-H
1259 v as C-O-H
1179 v s C-O-C
940(m, br) o.o.p. δ(O-H … O) hydrogen bonded
721 ρCH₂ (long alkyl)

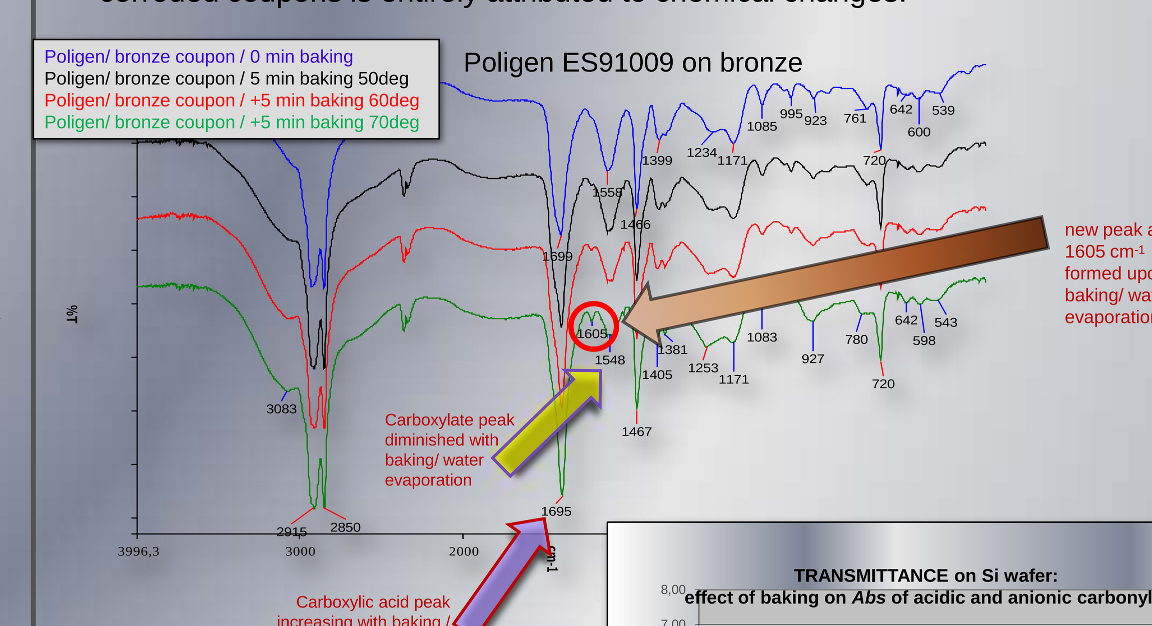
Spectrum **(a)**, recorded after evaporation of most water on cast film, shows both carboxylic acid (1700 cm-1) and carboxylate (1560 cm-1) functionalities as the structure is partly ionized. Spectrum **(b)** recorded one month after film casting ensures "complete" dryness of the film as carboxylate is mostly removed and the polymer is in 'non-ionized' state. This behavior is also confirmed by transmittance spectra of Poligen films on Si wafer.

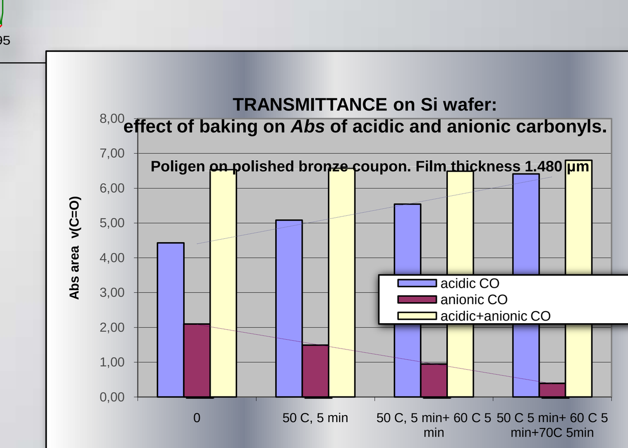


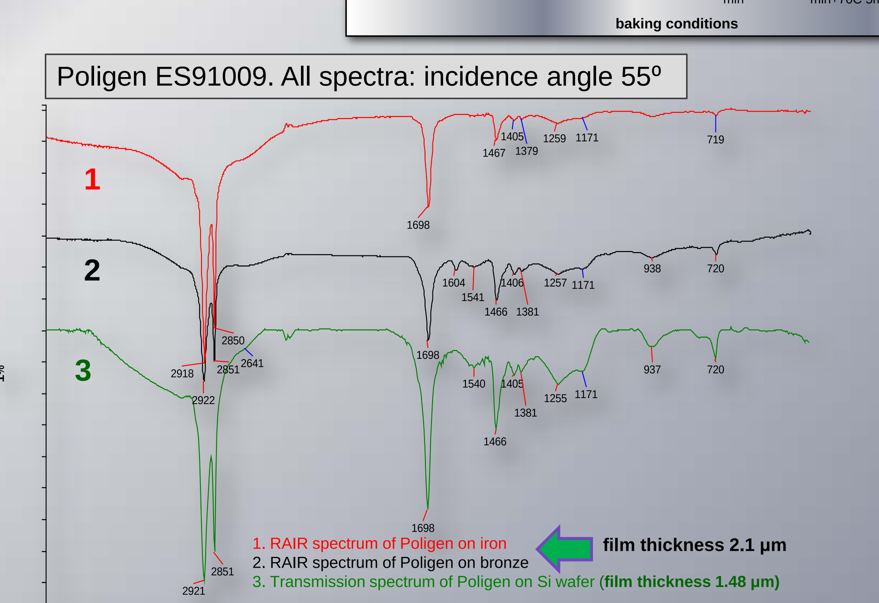
The linear relationship of absorbances (measured as areas) of v(C-H) vs. film thickness assures that quantitative spectra for thick films (at least up to 5 μm) can lead to reliable Transmittance measurements for Poligen . This is crucial esp. for the carbonyl band of acrylics like Paraloid B72, which is a generally accepted marker for chemical alterations.

Poligen® ES910009 on bronze and iron

Significant changes were observed in reflectance mode of Poligen films, most notably the sharp decrease of the original 1535 cm-1 carboxylate band , the increase of the 1700 cm-1 carboxylic acid band and the formation of a new band at 1605 cm-1 (only on bronze), possibly due to a copper-coordinated carboxylate phase. These features were correlated with those in model coupons incorporating the same coating materials with controlled film thicknesses and surface glossiness. Thus, our examination of infra-red RAIRS bands for the coated corroded coupons is entirely attributed to chemical changes.







conclusions

1. Typical application of protective coatings on metal surfaces generally involves non-ideal films of high, non-uniform thickness on non-ideal metal surfaces. RAIR spectra in these cases suffer from band distortions due to anomalous dispersion of refractive index and/or saturation due to high absorbances that fall out of the Beer law regime.
2. In films of low-medium thickness, both the transmitted and reflected beam reach the detector. Optimization involves use of the suitable polarizing angle and angle of incidence, which can eliminate the above problems. Use of p-polarized beam at Brewster's angle, and film thicknesses where linearity in absorbance is obeyed, results in good spectra quality, in which all features carry entirely chemical information.
3. In cases of films so thick, that the transmitted beam is almost zero (because it is fully absorbed in the medium), or with metal surface is so rough that the transmitted beam is poorly reflected, the specular reflectance beam becomes important. In these cases the Kramers-Kronig transformation renders a spectral line that corresponds to an absorption spectrum.

references

1. J. Umemura, Reflection–Absorption Spectroscopy of Thin Films on Metallic Substrates, *Handbook Of Vibrational Spectroscopy*, vol. **2**, John Wiley & Sons Ltd, 2002,1016-1032.
2. L. B. Brostoff, Coating strategies for the protection of outdoor bronze art and ornamentation, Ph.D. dissertation. Netherlands, 2003.
3. V. Argyropoulos et al, Testing of a new wax coating Poligen ES91009 and corrosion inhibitor additives used for improving coatings for historic iron alloys, in: eds., C. Degrigny et al, METAL2007, (2007), 10-15.