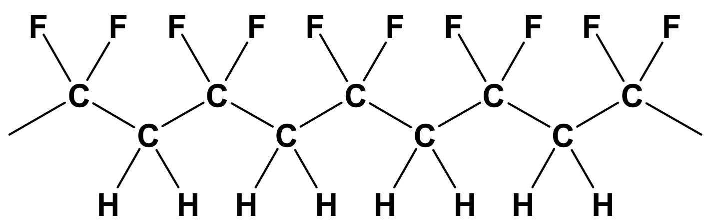
70% PVDF Coatings for Highly Weatherable Architectural Coatings

Kurt Wood, Akira Tanaka, Min Zheng, and Dana Garcia
Atofina Chemicals, Inc.
900 First Avenue
King of Prussia PA 19406 USA

Fluoropolymers have been used in a multitude of high performance coating applications for over thirty five years[1]. Poly(vinylidene fluoride) (PVDF) has been used especially in architectural applications, where both excellent appearance and substrate protection must be maintained over a very long period of time[2]. PVDF is preferred among the fluoropolymers for these applications, because it has enough solvency in ester and ketone solvents to be able to be formulated into solvent dispersion coatings. These coatings can be applied by conventional coil or spray coating techniques, and baked at temperatures of 230-250 ºC.



Poly(vinylidene fluoride) (PVDF)

Figure 1. PVDF structure.

Commercial PVDF coating commonly include some acrylic resin, such as poly(methyl methacrylate) (PMMA), in the formulation. The particular acrylic resins that are used are thermodynamically miscible with PVDF. Although the acrylics are used in relatively small quantities—typically 20-30 weight percent on polymer solids—they can contain functional groups which improve pigment wetting and coating adhesion. In this way, the acrylic properties complement the highly inert PVDF.

The microscopic phase structure that is formed in PVDF coatings is very complicated[3]. PVDF is a semi-crystalline polymer. Pure PVDF homopolymer has a crystalline phase with a typical melting point in the 160-170 ºC range, and an amorphous phase with a glass transition temperature of approximately –40 ºC. In a PVDF dispersion coating, during baking the PVDF crystallites melt, and a high temperature miscible alloy of the PVDF resin and acrylic is formed. Upon cooling, some of the PVDF reforms into crystallites, and the remaining PVDF plus the acrylic form a second amorphous, miscible alloy phase. This combination of crystalline and amorphous phases gives PVDF coatings many of their superior properties, such as flexibility combined with solvent resistance.

The Advantages of 70% PVDF Coating Compositions

As might easily be imagined, the microscopic structure of PVDF/acrylic blends is very sensitive to the ratio of the PVDF and the acrylic used. The amount of crystallinity in PVDF blends drops dramatically when the level of PVDF drops below 70 weight percent[4] (Figure 2). Since the PVDF crystallites give mechanical reinforcement and barrier properties to the coating, this means that certain paint performance properties, like methyl ethyl ketone (MEK) resistance, will be much worse for 50% PVDF coatings, as compared to 70-80% PVDF coatings.

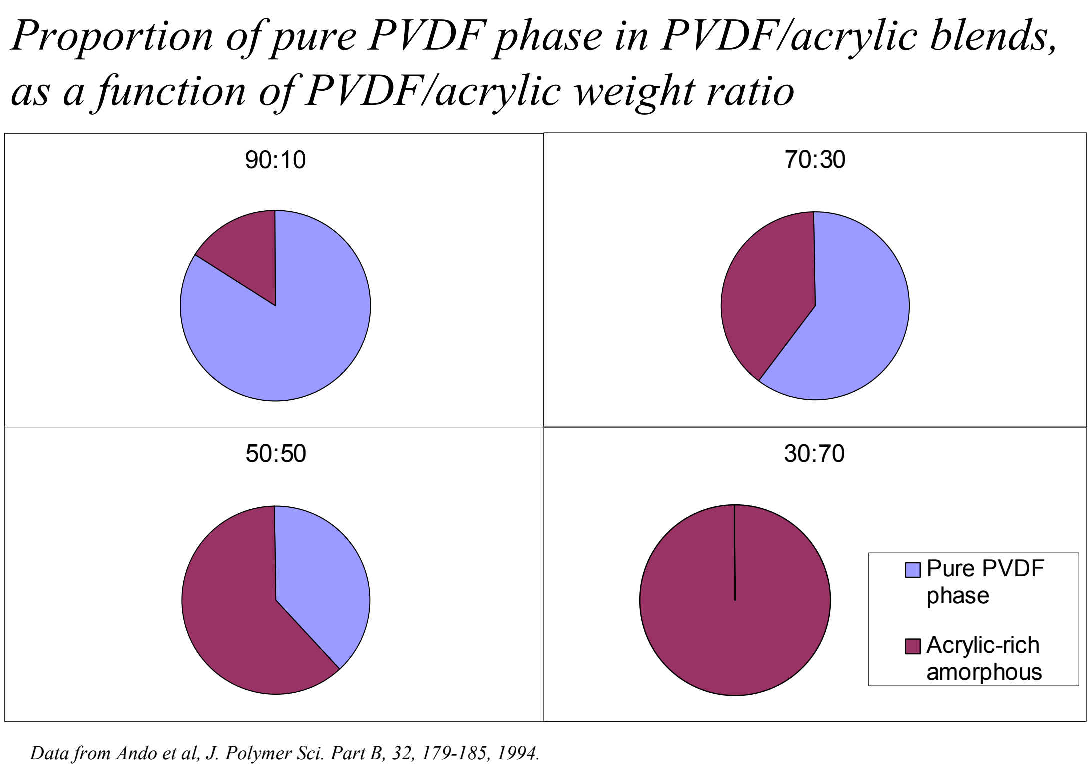


Figure 2. Pie charts showing crystalline content of PVDF/acrylic blends at different blend ratios. From Reference 4.

For some other paint properties, optimum properties are seen for blend compositions in the 70-80% PVDF/20-30% acrylic range. Figure 3 shows how the elongation at break, for instance, has a maximum at 70% PVDF[5].

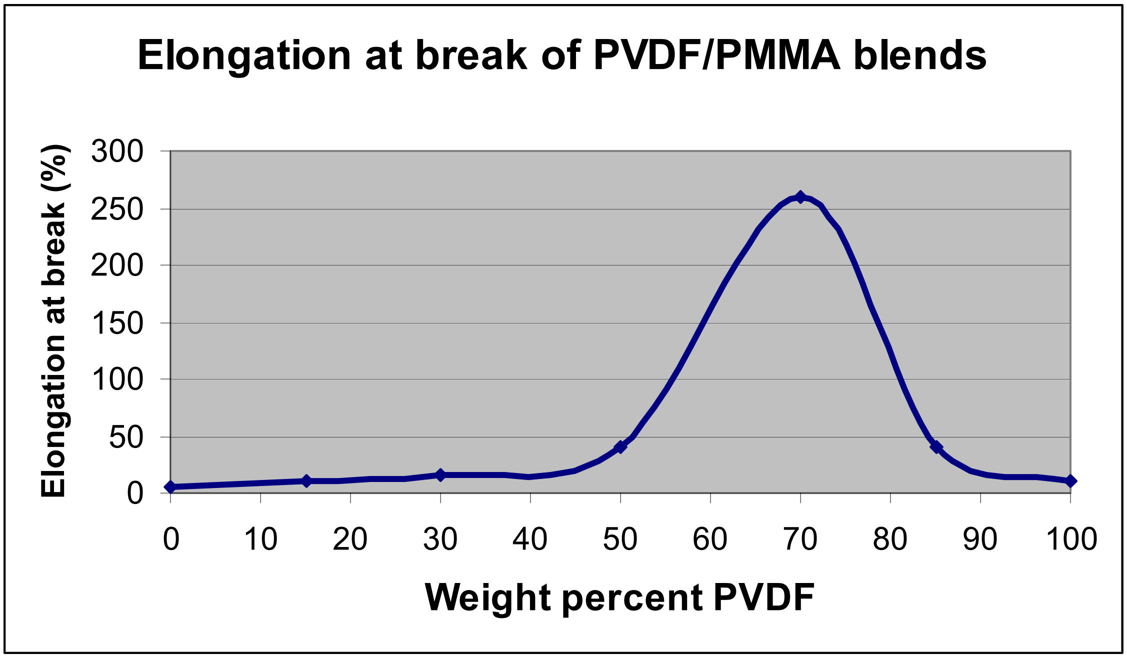


Figure 3. Elongation at break for PVDF/PMMA blends, as a function of phase ratio. From reference 5.

A key paint property that depends on the PVDF:acrylic ratio is weatherability. The PVDF resin itself is highly inert, both chemically and photochemically, due to the high stability and protective effect of the C-F bond. Acrylic resins, on the other hand, contain ester and possibly other functional groups. These groups are more sensitive both to photochemical degradation, and to other degradation processes such as hydrolysis. In the United States, the weatherability of architectural coatings is typically tested in South Florida. The combination of high UV levels and humidity in this sub-tropical location provides a very severe test of coating weatherability.

Figure 4 shows how a number of white coatings have performed after 10 years in Florida. It may be seen that the 70% PVDF coating maintains gloss well. PVDF-based coatings with lower levels of PVDF did not do as well, and lost about half their gloss after 5 years. A polyester coating, by contrast, had less than 20% gloss retention after 5 years. This performance is very typical for polyesters. Based on many field experiments, it appears that even the best polyester paints can survive no more than about four or five years in a humid, sub-tropical environment, before significant gloss loss and chalking occur. This may be due both to the photochemical degradation of the polyester polymer backbone, and to the degradation of the crosslinks[6]. Many of these structural features are also shared by some other kinds of fluoropolymer coatings, such as fluorinated ethylene vinyl ether (FEVE) coatings. However, the PVDF resin does not share these features, and is more highly fluorinated and more inert—which may explain its superior weatherability[7].

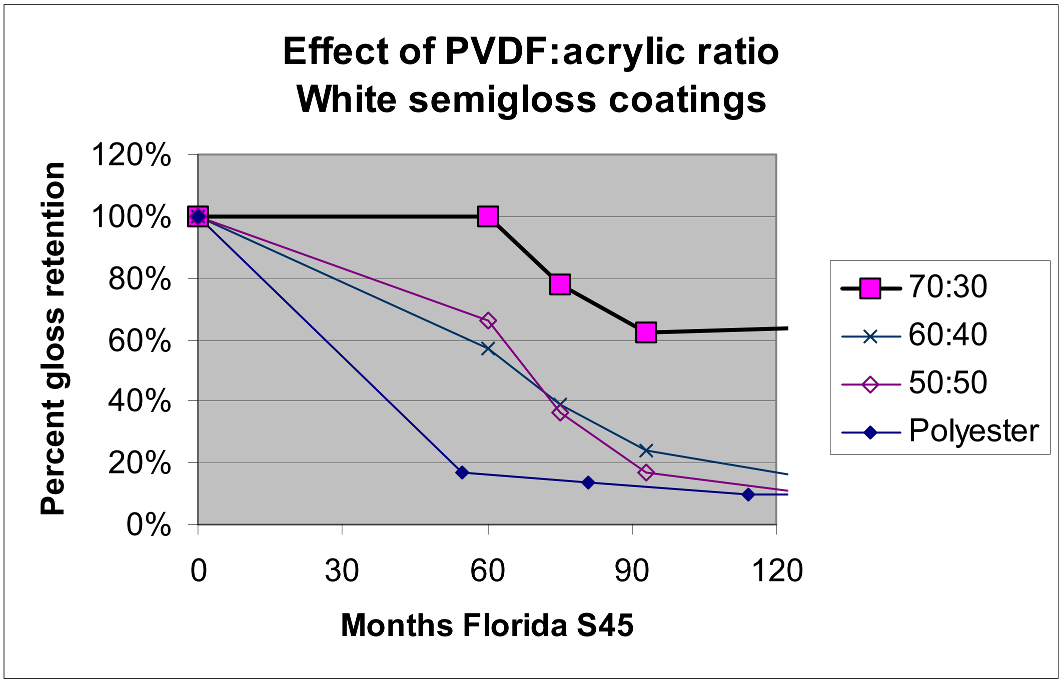


Figure 4. South Florida gloss retention of white PVDF coatings with different PVDF:acrylic ratio. A commercial weatherable polyester control of similar color and gloss level is included for comparison purposes.

When used with weatherable metal oxide pigments, the color and gloss retention of coatings with high levels of PVDF can be extremely impressive. As an example, the following table gives data for blue masstone coatings after 20 years Florida exposure:

PVDF:acrylic ratio	Original 60º gloss	60º Gloss after 20 years exposure	Percent gloss retention	Color change (delta E*)
90:10	42	23	55	5.5
70:30	50	26	53	4.0
50:50	65	23	35	5.2
0:100	81	<10	<10	8.0

The most demanding architectural specifications, such as the AAMA 2605 specification in the United States, require that an entire range of performance properties be met. Topcoats which use a proportion of 70-80% PVDF in the polymer binder are the time-proven way to meet these requirements. For this reason, to ensure quality, certain PVDF grades like KYNAR 500® resin are sold under a license arrangement, which stipulates that coatings advertised as KYNAR 500 coatings must meet minimum compositional requirements for PVDF resin content. This includes a requirement that the topcoat should contain at least 70 wt% PVDF in the polymer binder. Architects and other building component specifiers can specify KYNAR 500 coatings by name. By specifying KYNAR 500 license paints with proven performance over time, they can reduce the chances of receiving less than optimal paint formulations—since the potential cost from a paint failure can be enormous, both in terms of money and in terms of the reputation of the contractor and building owner.

Methods to Determine the PVDF Content of a Paint

A number of analytical methods exist to determine the PVDF content of a paint. For wet paint samples, simple extraction methods can be used. These methods take advantage of different solubility characteristics of PVDF, acrylic resins, and pigments. Figure 5 is an outline of one such method. In this method, toluene is used to extract the acrylic phase from the paint. Both the PVDF resin and most pigments are highly insoluble in toluene. However, PVDF resin is soluble in dimethyl formamide (DMF). By using first toluene and then DMF in sequence, the three fractions—acrylic, PVDF and pigments—can be separated cleanly from each other.

Laboratory tests of an optimized solvent extraction method of this type show an accuracy of about ± 3 wt%, for determinations of the percent PVDF on coating binder.

In our laboratory, analytical methods based on vibrational spectroscopy (infrared and Raman) have been developed[8], to determine the PVDF content of paints. This method can be used on small amounts of dried paint. It is based on the fact that PVDF and acrylic resins, like other kinds of resins, all have infrared absorption and Raman scattering bands at highly characteristic frequencies. As a result, vibrational spectroscopy can be easily used to examine a painted product, and determine the chemical nature of the topcoat—whether it is polyester, acrylic, PVDF/acrylic, etc.

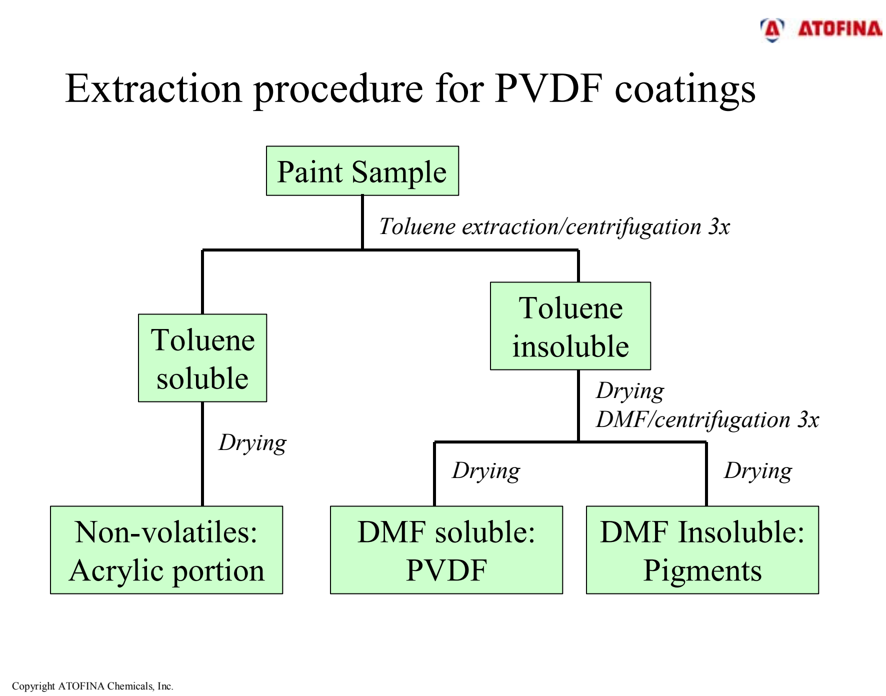


Figure 5. Schematic diagram of solvent extraction method to determine PVDF content of a paint.

The intensity of each vibrational band is proportional to the concentration of the material producing it, so this property can be used to quantify the amounts of PVDF resin and acrylic in a coating. First, a series of paint standards must be constructed. In our studies we used a series of coatings containing various ratios of PVDF resin and PMMA, from 100% PVDF to 100% PMMA in 10% intervals. For each instrument that will be used, a calibration curve must then be established. Figure 6 shows a typical curve, and spectra, for a micro-Fourier Transform infrared instrument[9]. The calibration curve was constructed using TQ Analyst® (Thermo-Nicolet) commercial software.

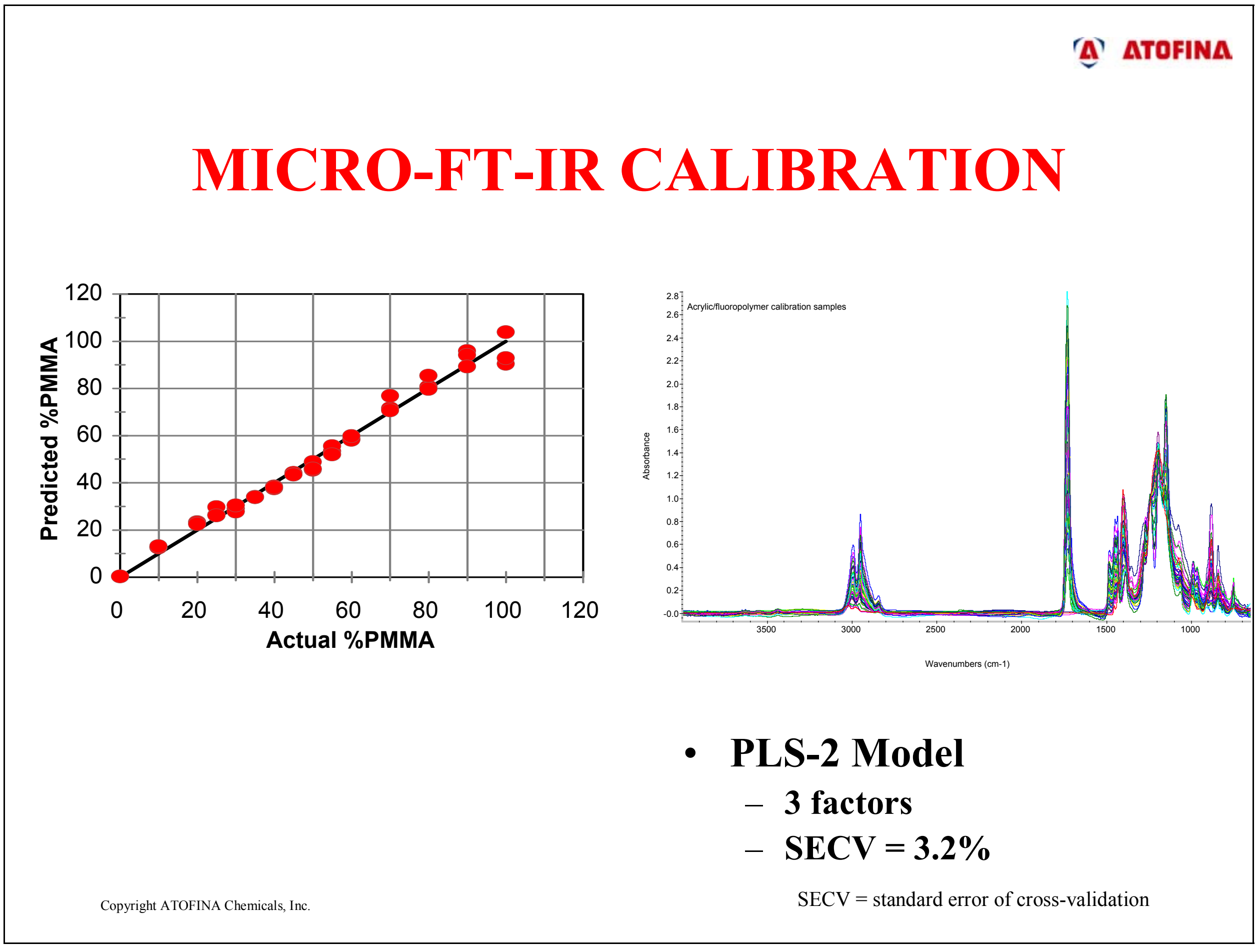


Figure 6. Calibration curve for Micro-FT-IR unit.

After construction of the calibration curve, the robustness of the method was checked by submitting a series of unknowns, with varying % PVDF levels and using a variety of different acrylics. In the range of commercial interest (i.e. at around 70% PVDF, 30% PMMA), the method was found to have an accuracy of 2-3% (Figure 7).

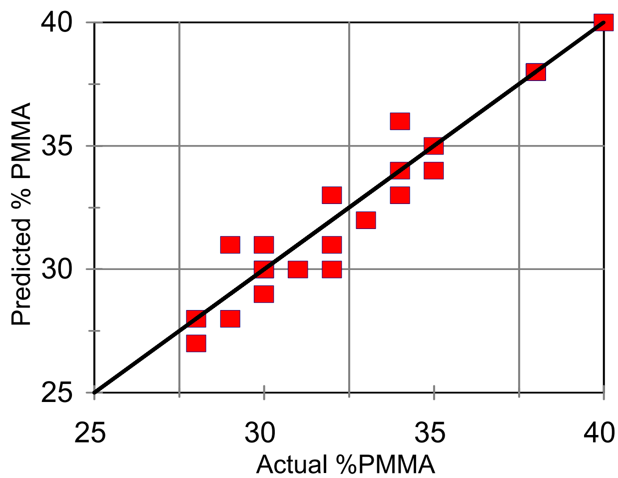


Figure 7. Predicted vs. actual acrylic value for unknowns, in validation test for micro-FT-IR method. Actual standard error of verification over this range: 2.3%

Subsequent experiments have shown that the infrared method is relatively insensitive to the choice of acrylic or pigment type. However, a separate calibration curve needs to be established if the fluoropolymer composition varies significantly from that of PVDF homopolymer.

Using either "wet" laboratory methods, or more modern spectroscopic methods like these, it is not difficult to determine the PVDF content of a paint, to ensure that it meets the standard of 70% PVDF.

Conclusion

PVDF coatings, containing at least 70 wt% PVDF on coating binder, have an outstanding balance of properties including very favorable outdoor weathering properties. To ensure that the building industry receives the highest possible quality materials, KYNAR 500® PVDF resin is only sold under a license program. By specifying KYNAR 500 license coatings, architects and materials specifiers can have confidence that the coatings they will receive have a proven performance over time. One component of the KYNAR 500 license agreement is that the coatings must contain at least 70% PVDF. The PVDF content of both wet and dry paint samples can be determined by a variety of analytical techniques.

---

[1] K. Johns, *Fluorine in Coatings: PRA Conference Proceedings* **1994**, Paper 2.

[2] R.A. Iezzi, "Fluoropolymer Coatings for Architectural Applications, Modern Fluoropolymers (Wiley, 1997), p. 14.

[3] S.R. Gaboury and K.A. Wood*, Surface Coatings International Part B: Coatings Transactions* 85, B4, 243-332, **November 2002**.

[4] Y. Ando et. al., *J. Polymer Sci. Part B*,. 32,179-185 **1994**; see also later articles such as J. Mijovic, J.-W. Sy, and T.K.Kwei*, Macromolecules* 30, 3042-3050, **1997.**

[5] A. Tanaka, *et al*., *Polym. J*. 22(6), 463, **1990**.

[6] See, for instance, J.-L. Gardette, B. Hailhot, F. Posada, A. Rivaton, and C. Wilhelm, Macromol. Symp. 143, 95-109, **1999**; M.R. VanLandringham, N. Tinh, W.E. Byrd, and J.W. Martin, Journal of Coatings Technology 73(923), 43-50, **2001**.

[7] K. Wood, *Macromol. Symp*. 187, 469-479, **2002**.

[8] D. Garcia, F. Borden , D. Huart, L. Hedhli, R. Perrinaud, C. Olmstead and K. Wood, "Infrared and Raman Analysis of Acrylic-Fluoropolymer Coatings", paper delivered at Pittcon 2003 conference, **March 2003**.

[9] Nicolet Magna-550 & Nic-Plan microscope; 128 scans, 4 cm^{-1} resolution, MCT detector. Similar calibration curves have been constructed for a Biorad 60 infrared spectrometer with grazing angle accessory, and for a Nicolet FT-Raman 960. The Raman method can also be used to analyze liquid paints.