

Positive Material Identification: Qualification, Composition Verification and Counterfeit Detection of Polymeric Material using Mobile FTIR Spectrometers

Application note

Materials

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Introduction

The progress in the development of advanced materials has resulted in an enormous array of polymer, plastic, composite, and elastomer products, components, and objects. Classes of these materials have similar structure, but small deliberate changes in the formulation cause these compounds to have different use and wear properties. Thus, the development and manufacture of these advanced materials and the commercial objects that are created from them drive the need for analytical methods and technology that can rapidly qualify and verify composition of these materials. Furthermore, with the increased globalization of component sources, ensuring authenticity and detecting counterfeit, mislabeled or out-of-specification polymeric material and components is critical.



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For this reason, positive material identification (PMI) is necessary, and a particularly useful technology for analyzing these advanced materials is Fourier transform infrared spectroscopy (FTIR). With the recent availability of Agilent handheld and portable FTIR analyzers, a new dimension has been added to the analysis of polymers, plastics, elastomers and composites.

Now, the analyzer can be brought to the material or object for chemical identification. In this manner, FTIR becomes a truly non-destructive method, and objects that are too large, too valuable or for which a sample cannot be excised without affecting performance, can now be measured without compromise.

Agilent's compact, portable FTIR analyzers are equipped with novel software and sample interfaces that make method execution easy, and optimize analysis results.

PMI can be accomplished with several different types of data analysis techniques; these techniques vary in both complexity and confidence. This application note will cover three distinct types of analysis:

- A. Measurement of a polymeric material to verify its identity via its overall chemical structure.
- B. Determination of the chemical composition of a particular polymer or polymer component to confirm that it meets its required use-specification.
- C. Measurement of the concentration of specific compounds contained in the polymer to ensure that it is within specification for physical performance or consumer safety purposes.

Each of these examples requires a different approach to analysis. In this application note, we will demonstrate how the Agilent portable and handheld FTIR systems non-destructively handle these different analysis scenarios.

Advantages of the Agilent 4300 Handheld FTIR for the positive material identification of polymers

The 4300 Handheld FTIR is the result of Agilent's extensive R&D efforts in material analysis by mid infrared spectroscopy. It is optimized for non-destructive analysis of polymers

- **Light weight.** Make measurements for longer periods with less physical strain. At 2.2 kg (4.8 lb), the 4300 Handheld FTIR is the lightest handheld FTIR in existence.
- **Balanced.** Take more accurate and precise measurements. With a center of gravity located at the handle, the system is comfortable to use.
- **Rapid Scanning.** Scan large surface areas in less time. With the optional MCT detector, the 4300 Handheld FTIR enables measurements to be made more rapidly.
- **Non-destructive.** No need to excise a sample to be analyzed in a lab. The handheld spectrometer is brought to the object or surface to be measured.
- **Immediate results.** Focus on the measurement locations of greatest importance. At-site analysis lets you make decisions in real-time.
- **Versatile.** Analyze a wide range of materials and surface types. A selection of interchangeable, no-alignment sampling interfaces are available.
- **Intuitive.** Easy-to-use software guides less experienced personnel to actionable results, faster. Pre-programmed methods, powered by advanced mathematical models, and reporting features all function automatically behind the scenes.

Instrumentation

Examples of FTIR spectrometers used for PMI are the Agilent Technologies 4300 Handheld FTIR and 4500 series portable FTIR systems. Each spectrometer has its own unique advantages for the analysis of materials.

The 4300 Handheld FTIR (Figure 1) is a battery powered, ergonomically optimized handheld system that weighs 2.2 kg (4.8 lbs). The system's optomechanical and electronic components are engineered for demanding out-of-lab applications. With the choice of interchangeable, permanently aligned sample interfaces, the system quickly analyzes a broad range of materials. These interfaces include: specular reflectance, for reflective surfaces; diffuse reflectance, for scattering and absorbing materials; grazing angle for thin layers on metal surfaces; diamond internal reflectance for analysis of bulk materials; and germanium internal reflectance for polymeric materials with imbedded carbon particles. The 4300 Handheld FTIR system is controlled by an embedded computer and uses Agilent Technologies intuitive, methods-driven MicroLab software for mobile analyzers.



Figure 1. The Agilent 4300 Handheld FTIR

The resulting portability and versatility of the system make the 4300 Handheld FTIR an effective analyzer for a wide array of polymeric materials. It is a true non-destructive material analyzer since measurement requires no sample preparation and the polymeric material or object is analyzed where it is situated, regardless of size and physical shape.

The 4500 Series FTIR (Figure 2) is a 6.8 kg (15 lb) system that is battery powered and fully portable for use wherever it is needed. It is well suited to the analysis of small polymeric objects such as o-rings, gaskets and other seals. The configuration used here uses a three reflection diamond ATR sample interface. This interface allows easy measurement of polymer samples while providing increased sensitivity. It excels at quantitative measurement using pre-calibrated methods as well as identification/verification of materials via spectral matching via an on-board database of reference materials.



Figure 2. The 4500 series FTIR

Discussion

There is significant need to insure that polymeric materials or products made from polymers are correctly labeled, meet specification and will perform as intended. This latter point is of great importance for both safety and productivity. The ability to determine material suitability is complicated by the large variety of formulations available, as well as the ever-increasing global sources that manufacture and distribute polymer based objects and material. As a sensitive and specific molecular analysis method, FTIR spectroscopy is well suited to the positive identification of polymers, plastics, elastomers, composites, and coatings. This includes verifying the identity of a material, detecting counterfeits, assuring overall quality, ensuring formulation specification are met, and measuring the absence or presence of specific analytes in the polymer material. Three different methods are used to accomplish PMI, depending on the required result of the measurement.

A. PMI - confirming material identity by searching a spectral library

To verify the identity of a material, a library search is executed. The library comprises individual reference spectra of a wide assortment of polymers. A sample is analyzed and then matched to the reference spectra contained in the database. The correlation between sample and each library entry is calculated using a proprietary algorithm. The spectrum of the analyzed material and the spectrum of the best match from the reference library are displayed, with a numerical value indicating the quality of the match. This approach is well established and effective when the material to be analyzed is one of a broad range of materials that possess different structures and compositions. The library search method can detect differences in the 5–10% range between samples and analogous reference spectra.

In the following recycling example, the 4300 Handheld FTIR system, identifies scrap polymer material sourced from electronics equipment.

The diamond ATR interface used features a novel spherical diamond sensor which provides high quality reproducible spectra due to the flexibility of the contact angle between the spherical sensor and the material. This provides analytically superior results when compared to a conventional flat diamond ATR. Using MicroLab software and polymer libraries, the analyzer rapidly clarifies the identity of a polymer. The spectrum and identity of the unknown polymer sample is provided, as well as the spectrum of its best library match and a numerical value that reflects the quality of that match (Figures 4a, 4b).

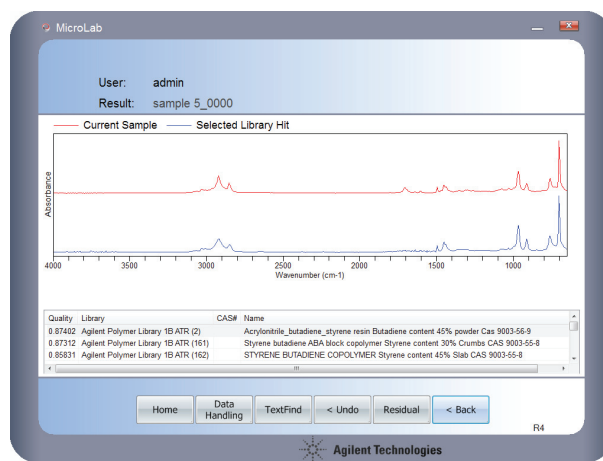


Figure 4a (top), 4b (bottom). After analyzing an unknown sample, Agilent MicroLab software searches the on-board spectral database for best match. The spectrum and identity of the unknown sample is displayed as is the spectrum of its best library match and a numerical value reflecting the quality of the match.

As another example, seals, gaskets and o-rings used in production equipment in the chemical, pharmaceutical, and petroleum industries must be of the correct composition. These materials are often filled with carbon particles to enhance their strength and these particles tend to scatter infrared radiation. For this reason, a germanium ATR sample interface is used with the 4300 Handheld FTIR system. Due to the higher index of refraction of germanium, internally reflected infrared radiation does not penetrate the sample as deeply as with the diamond ATR, resulting in less scatter, fewer background effects and better quality spectra. An onboard ATR library of carbon-black filled polymers rapidly verifies the identity and composition of seals and also provides information about the match quality (Figure 5).

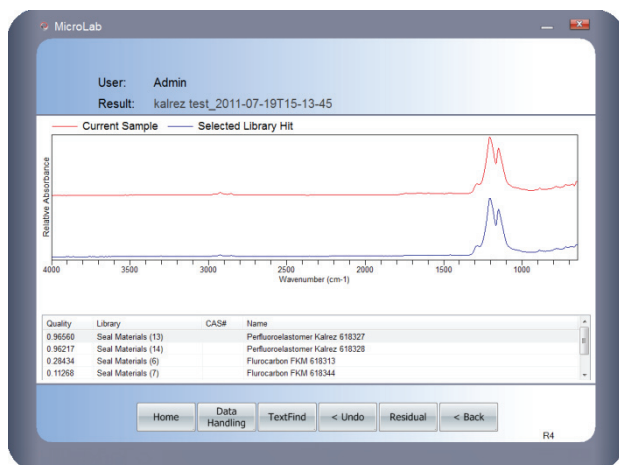


Figure 5. Analysis of a carbon black filled seal material is carried out using the spherical germanium ATR sample interface. After searching the on-board data base of polymer seals, the identity of the unknown seal is displayed.

B. PMI - confirming how well a material sample matches required specifications via discriminant analysis

The library search, discussed previously, provides a simple methodology for many routine identification needs. In some cases, though, a more thorough analysis is required in order to differentiate between similar types of materials. In the case of seals and gaskets, variations in polymer formulation and additives can make a significant difference in performance. Also, counterfeit or off-spec samples must be detected before they are used in critical applications. As a result, a more detailed analysis is required to differentiate, identify, and authenticate sealing materials, which may have similar spectra but with performance variations that result from slight disparity in formulation, whether intentional or otherwise. When investigating a sample set of materials to determine how well an individual example meets pre-established specifications, the Agilent FTIR systems use a method based on discriminant analysis.

In this case, multiple spectra are stored that represent a specification set for an individual class of material. Partial least squares or principal component analysis is used to determine commonality of a sample with the overall sample set in the class. A statistical measurement is made to determine if the exact specification of the specific sample is accommodated in the general specification set of the material class. In this manner, materials can be identified as acceptable or non-acceptable. This form of measurement allows differences of 1-5% to be distinguished between a sample of a material and the desired specifications of the reference class. Simply, it is a powerful means for quickly determining whether a sample is “good or bad”, counterfeit or authentic. With Agilent’s MicroLab software, the identity of the material is displayed and conditional reporting enables pass/fail determination.

As an example, discriminant models were created to identify two different types of seals which are used in the petroleum industry. The first calibration predicts VMQ 01 (silicone) type o-rings and the second group predicts FKM type 1 o-rings. Both models were made using a partial least squares discriminant analysis (PLS-DA) technique. A single calibration set was collected for both methods. The calibration set is comprised of 10 or more samples each of 18 different elastomers, resulting in a total of 275 spectra. A list of the types of o-rings included in the calibration is shown in Table 1.

For each calibration, values were assigned to the spectra; a value of “0” was given to the target group, while the non-target samples were given higher values.

Table 1. O-ring categories

O-ring type	Description
FEPM type 1	FEPM A90h
FEPM type 2	PP TFE PMVE
FFKM type 1	G 80A
FKM type 1	GFLT5 tetrapolymer
FKM type 2	ETPS tetrapolymer
FKM type 3	GFS tetrapolymer
FKM type 4	Tetrapolymer type B
FKM type 6	GLTS tetrapolymer
FKM type 7	FKM tetrapolymer, ultra low temp
FKM type 8	Copolymer type A
FKM type 9	Copolymer type A V95x
FVMQ type 1	Fluorinated PDMS
NBR type 1	Nitrile rubber, low CAN
NBR type 2	Nitrile rubber, medium CAN
HNBR type 1	Hydrogenated butadiene rubber
HNBR type 3	HNBR, low CAN
VMQ type 1	Polydimethyl siloxane
CR type 1	Chloroprene
EPDM type 3	PP TFE

The first example shows classification of a VMQ type o-ring. The silicone base polymer of VMQ type o-rings is chemically quite different than other types of o-rings. Consequently, the infrared spectra measured by the 4300 Handheld FTIR ATR with the germanium ATR sample interface are likewise different from the rest of the data set. Since the differences between the target group and the other o-rings were so great, the calibration was easily accomplished using only two groups. The target VMQ o-rings were given a value of “0” while the samples in the rest of the calibration set (the non-target o-rings) were given a value of “10”. The classification results using cross validation are shown in Figure 6.

The model uses mean centering, area normalization, and a 9-point Savitsky-Golay first derivative as preprocessing and 6 factors. As shown in the figure, the data set is clearly divided into two groups. A threshold can be set on the PLS value which clearly distinguishes VMQ o-rings from others.

In a second example, the target group was a FKM Type 1 elastomer. The calibration set contained 8 different categories of FKM materials. These materials all have very similar formulations, however each category has unique properties so it is important to distinguish between the different FKM types. In order to obtain a good separation between the different FKM groups, several values were assigned in the calibration set. The target group of FKM Type 1 was assigned a value of 1. Spectra of samples from the 7 other FKM groups were assigned a value of 10. Samples which had greater chemical differences, such as nitrile rubber, hydrogenated butadiene rubber, EPDM and chloroprene were given a value of 15.

Finally, samples which were very different, such as dimethyl siloxanes (PDMS) and fluorinated PDMS, were given a value of 20. This range of values allowed the model to accurately distinguish FKM Type 1 from other FKM types from other kinds of elastomers.

The classification results using cross validation are shown in Figure 7. Similar to the previous method, the data was preprocessed by mean centering, area normalization and a 9 point Savitsky-Golay first derivative. Seven factors were used in this method.

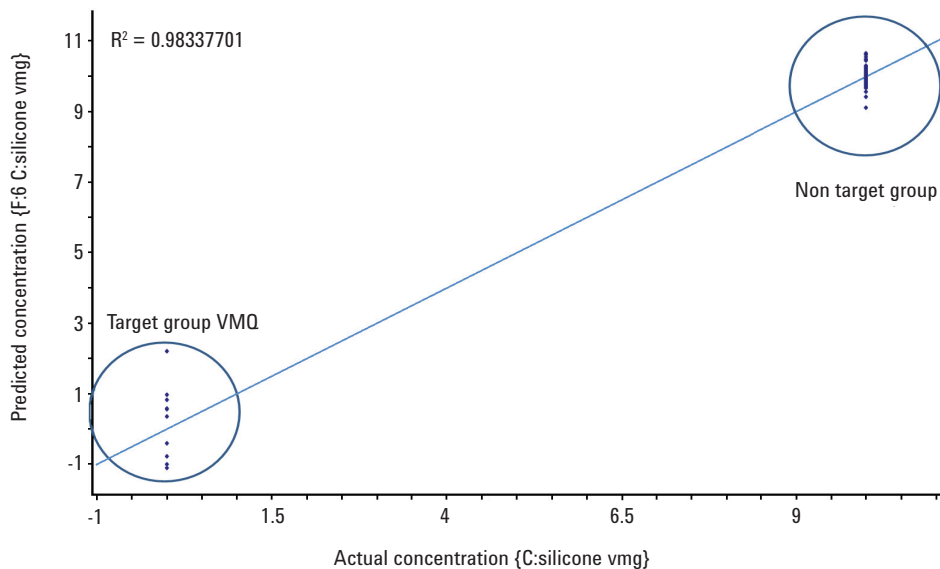


Figure 6. Classification of VMQ elastomers.

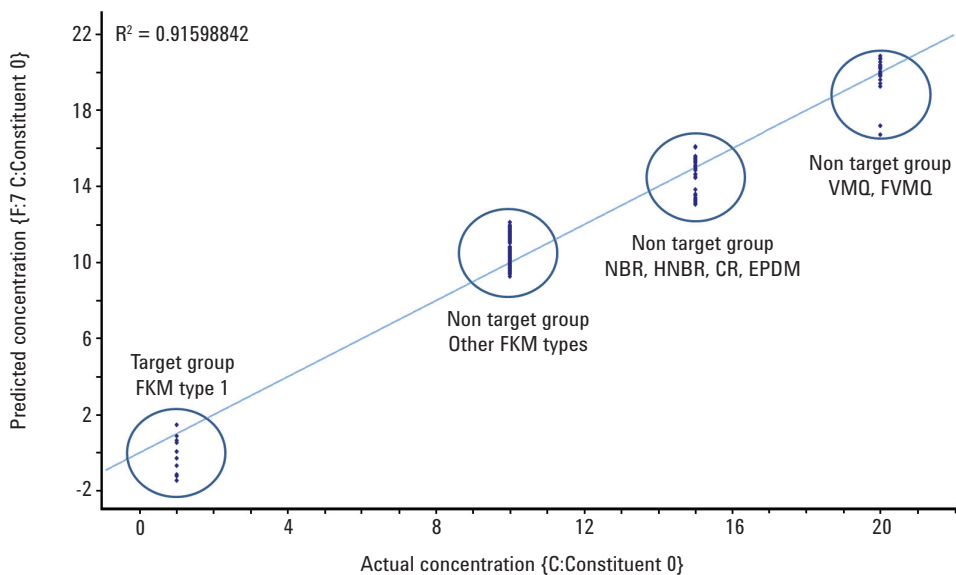


Figure 7. Classification of FKM Type 1 elastomers.

The calibration shown above was incorporated into a Microlab PC method. The method was configured using both the “threshold” and “conditional reporting” features in Microlab. Based on the results of the cross validation, predictions with a value of 3 or less confirm the sample to be within the target group of FKM Type 1. In the Microlab method, a threshold of 3 was set such that samples within the target group are shown in green while those outside the target group are shown in red. Furthermore, the conditional reporting feature was used to display a message of “Confirmed FKM Type 1” for samples within the target group and the message “NOT FKM TYPE 1” for samples outside the target group. An example of the results are shown in Figures 8 and 9 for target and non-target groups respectively.

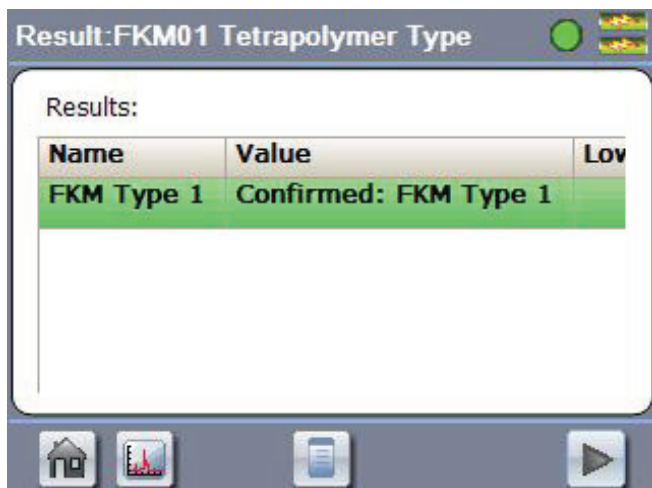


Figure 8. Results screen showing a positive confirmation of FKM Type 1 elastomer based on the calibration shown in figure 7.

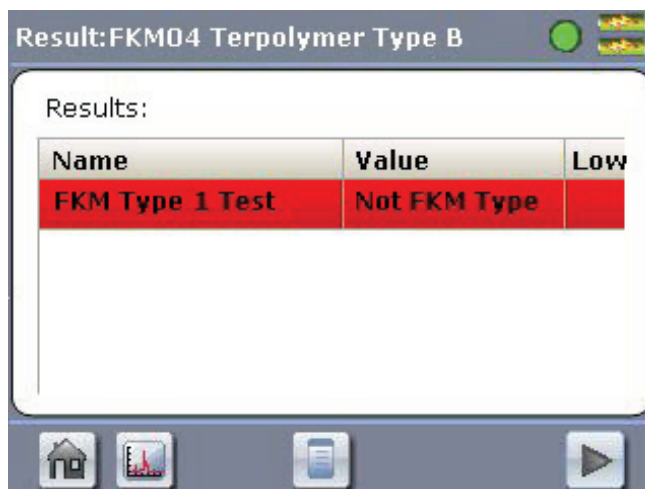


Figure 9. Results screen showing a negative result for a sample of FKM Type 4 tested against the calibration shown in figure 7 for the confirmation of FKM Type 1 elastomer.

C. PMI - measuring the level of specific analytes in materials via quantitative analysis

In many cases the exact amount of a specific analyte component in a material sample is critical to performance or acceptability. Some product specifications require that a material have a minimum level of specific compounds to ensure performance; in others, there is a maximum allowable quantity for health and safety reasons. Accurate quantitative analysis of these specific analytes ensures that a material meets specifications. In these cases, univariate or multivariate analysis methods are used to measure the specific analyte of interest. The absence or presence of the analyte is used to qualify the acceptance of the material sample. This approach gives the highest level of confidence and can measure to 0.1% detectable difference.

An example of the use of the Agilent 4500 FTIR system for quantitative analysis is in the determination of the levels of phthalate plasticizers in children’s toys. Phthalates are known to be endocrine disruptors and the maximum allowable concentration in toys is 0.1%.

Vinyl samples containing the phthalate substitute DINCH (1,2-cyclohexane dicarboxylic acid diisononyl ester), along with varying levels of phthalate plasticizer were measured using the Agilent 4500 FTIR equipped with the reflection diamond ATR sample interface (Figure 10). The total phthalate concentration was

determined by developing a calibration consisting of the peak area of the 744 cm^{-1} phthalate band ratioed against the total absorbance area from 1500–800 cm^{-1} , as a function of concentration (Figure 11). The limits of quantitation for the phthalate compound using this calibration is approximately 0.1%.

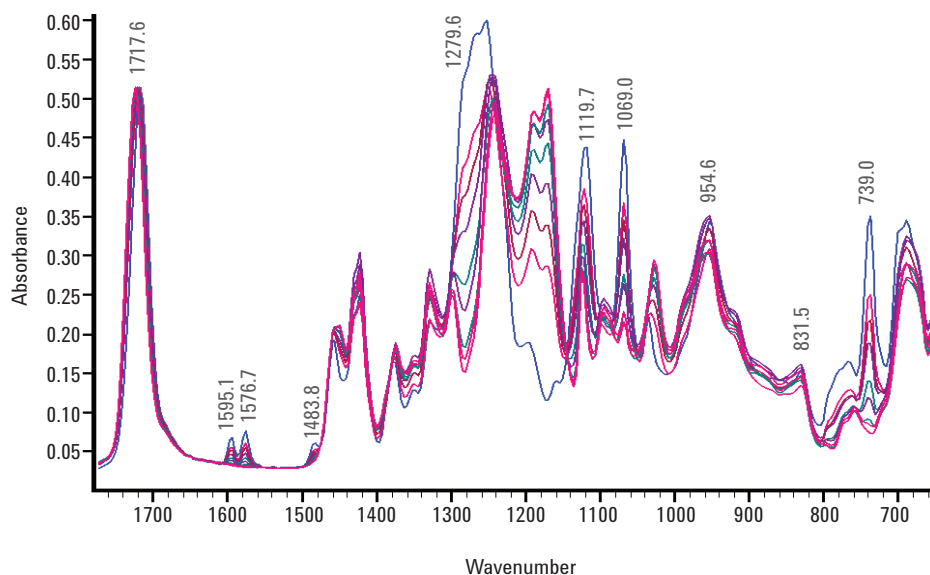


Figure 10. The FTIR spectral overlay of the full concentration range (0-30%) of phthalates in DINCH replacement plasticizer used in the high phthalates calibration.

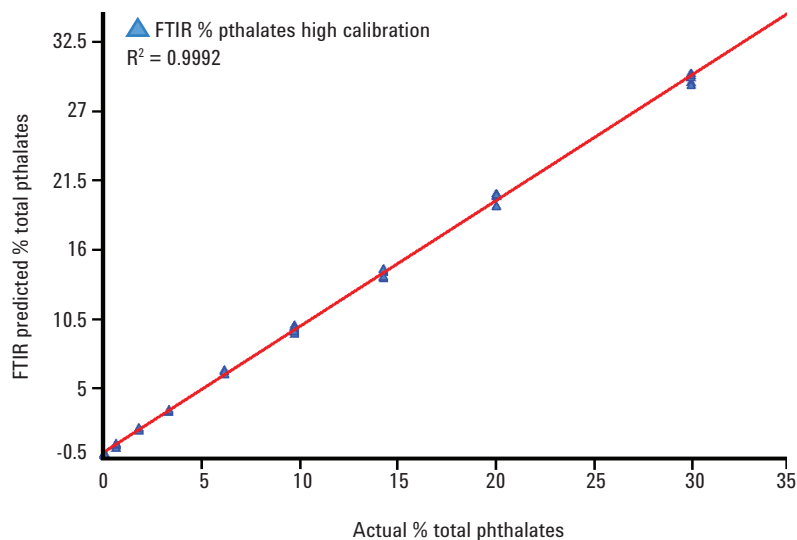


Figure 11. High phthalates PLS actual vs. predicted plot of PVC samples plasticized with DINCH replacement plasticizer, 0-30% total phthalates.

Samples of material used in toys can be measured directly by pressing the polymer against the diamond sensor. The analyzer is equipped with Agilent MicroLab software and the pre-calibrated method can be executed with a single command. A colored warning is displayed if the levels of phthalate exceed pre-determined acceptable levels (Figure 12).

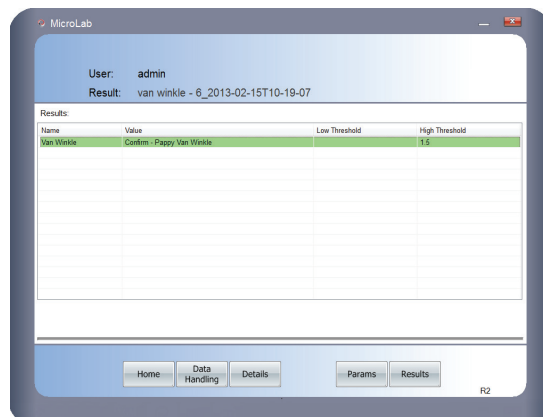
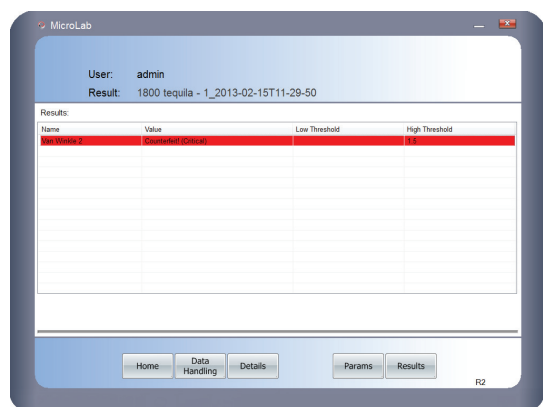


Figure 12. Sample of toy containing phthalate (top) is measured on the three reflection diamond ATR sample interface and the pre-calibrated method displays whether the sample passes or fails the analysis with regard to amount of phthalate present.

Conclusion

The need to identify, verify specifications, ensure authenticity, and detect counterfeits in polymer materials is of significant global importance in manufacturing industries. Manufacturing safety, productivity, and human health considerations are the drivers for this need.

We have shown how Agilent 4300 Handheld FTIR and 4500 series FTIR spectrometers can aid in PMI by three different analytical approaches to solving the requirements of a specific polymer application. Whether spectral search, discriminant analysis, or quantitative analysis is required to verify the identity and specifications of a material, the Agilent spectrometers can meet the required need.

Furthermore, these analyzers are engineered for use in the field, so the measurement can be made where and when needed, without the requirement to excise samples to be brought to a lab for analysis. Thus, the systems are true non-destructive analyzers and objects can be measured in situ, regardless of size, shape and configuration.

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