Enhanced Sensitivity to Detect Phthalates by FT-IR

Key Words
ATR, Child Safety Law, FT-IR, Hot Pressed Film, Infrared, Phthalates, Plasticizers, Poly(vinyl chloride), PVC, Transmission

Plasticized polyvinyl chloride plastics are used extensively in products around the world. PVC phthalate plasticizers have traditionally been found in a multitude of products including toys and blood bags, tubes, cables etc. Recent evidence that the phthalate plasticizers may cause health problems, particularly in children, has resulted in many countries prohibiting the use of phthalates in toys. In this presentation we will describe how FT-IR can be used to rapidly identify the presence of phthalates in plastics at the levels commonly found in commercial products including toys.

Certain phthalates were banned in Europe several years ago and more recently in the US and other countries. In the United States, the Consumer Product Safety Commission (CPSC) is responsible for insuring that government regulations are followed. The Child Safety Law actually prohibits the presence of several phthalate compounds at levels exceeding 0.1 wt % even though the commercial levels are often greater than 10%.

Previous work from Thermo Fisher Scientific demonstrated that FT-IR spectroscopy could rapidly screen for the presence of phthalates at commercial levels by a simple ATR method. However, a "push button" method that provided a good looking report had not been implemented. In this application note we will describe some "application templates" that we have created to provide a routine way to check for phthalates in samples. The first application is based on our previous ATR techniques. We have also created a second approach where we produce a 500 micron thick film by hot pressing a sample and then acquire a transmission spectrum by measuring the infrared energy getting through the sample. This technique increases the sensitivity by almost a factor of fifty, enabling the detection of phthalates below the 0.1 wt % level, if other additives in the plastic formulation do not cause spectral interference. However, we have observed that the success of the analysis at low levels is very dependent on the specific components present in the plastic. We consider this application package to be a set of recipes to be used as a basis for creating more robust methods focused on the specific samples of interest.

Figure 1:
Smart iTR accessory in a Nicolet iS10, showing a sample being analyzed nondestructively

For many products, an excellent spectrum can be obtained simply by placing the toy on the ATR crystal and pressing down with the pressure tower. This is shown for a toy "Yellow Rubber Duck" in Figure 1, where the toy is mounted on the Thermo Scientific™ Smart iTR™ accessory with a diamond crystal used in a Thermo Scientific™ Nicolet™ iS™10 FT-IR spectrometer*.

Many people are concerned about phthalates in the plastisol inks and screen transfers used on t-shirts for children. In this application, a spectrum is acquired from the printed area on a T-shirt in less than a 10 seconds. We then verify that the sample is a PVC plastisol by comparing the peaks in a specific region of the spectrum to those in a reference spectrum of PVC before we look for phthalates. A sophisticated match algorithm is applied to the peaks in a region specific to phthalates. When the presence of phthalates is confirmed, we produce the report shown in Figure 2, which clearly states that this area of the shirt contains phthalates.

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When the match value for phthalate is low, the report states that the result is “Inconclusive”. The ATR measurement does not have the sensitivity to confirm that phthalates are not present above the 0.1 wt % limit and recommends that the operator try the Hot Pressed Film technique or the GC/MS method suggested by CPSC.

For thermo-plastics such as polyethylene or PVC, heating a sample to the melting point and pressing a film is quite easy. A number of companies provide temperature controlled heated platens for traditional sample presses and these make this a quick process taking less than five minutes. Figure 3 shows the Universal Film Maker kit that is available from Thermo Fisher Scientific overlaid on a spectrum acquired from a 500 micron thick film. The scale expanded region is used to check for the presence of phthalates and reveals that the instrument sensitivity of the transmission spectrum is almost 50 times better than that obtained with the ATR technique. This provides the sensitivity to detect phthalates at the 0.1 wt % level. However, the technique also increases the intensity of any peaks resulting from the presence of other additives in the plastic and in some cases these will interfere with the peaks used to confirm the presence of phthalates which increases the standard error and the uncertainty of the results.

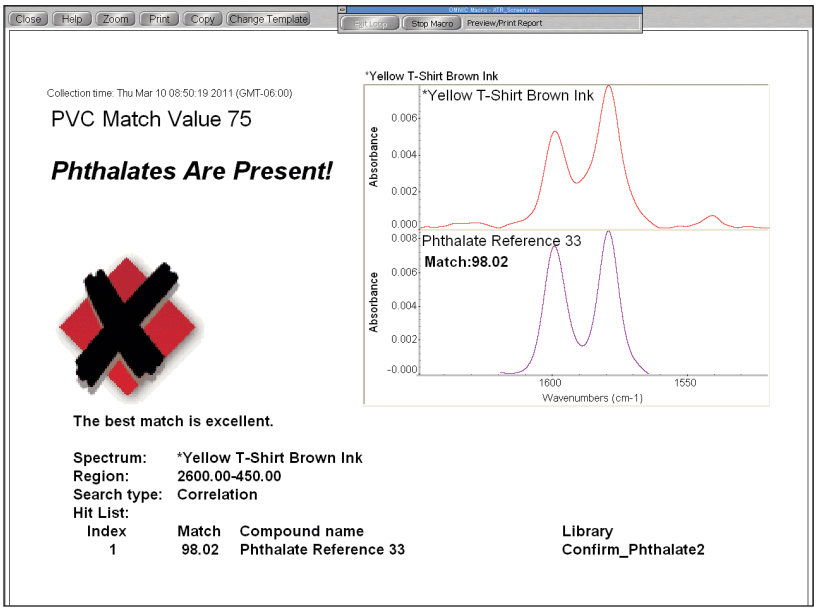

Figure 2: A warning report is created (red X) if the match value for phthalate is high

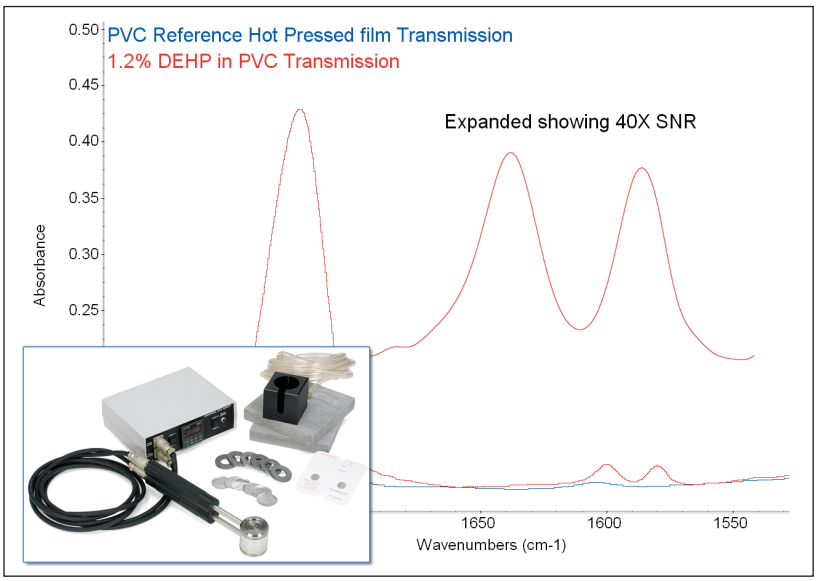

Figure 3: A picture of the Universal Film Maker and the spectrum from a sample pressed in to a 500 micron thick film

The expanded spectral region shows the two small peaks generally used to confirm the presence of phthalates. The extra throughput and longer pathlength obtained with transmission spectroscopy and a 500 micron thick sample provides almost a factor of fifty better signal-to-noise ratio (SNR) over ATR spectroscopy.

By producing samples with a known thickness (500 µ), creating a Classical Least Squares (CLS) quantitative method to determine phthalate concentration is straightforward. One advantage of using a multivariate statistical analysis technique such as CLS is the availability of a standard error term. This term is based on the goodness of the curve fit between the sample spectrum and the spectra included in the CLS model. We recommend that the reported concentration be at least three times the standard error for a reliable result with high confidence. One of the major concerns related to the presence of phthalates is when small amounts of contamination are present in a plastic where the main plasticizer is an allowed substance such as DINCH. DINCH (Diisononyl cyclohexane-1,2 dicarboxylate) is an approved plasticizer for use with polyvinyl chloride polymers that is produced by the company BASF. Figure 4 shows the results of applying a Thermo Scientific™ TQ Analyst™ software method to a spectrum that is the result of subtracting the spectrum from a hot pressed film of PVC containing DINCH as the plasticizer from a spectrum of the same material spiked with 0.24 wt % total phthalates.

The SNR is excellent in the difference spectrum and the CLS method calculates a concentration of 0.17 wt % with a standard error of 0.011. The sample would fail the screen because the phthalate concentration is above the 0.1 wt % allowed by law.

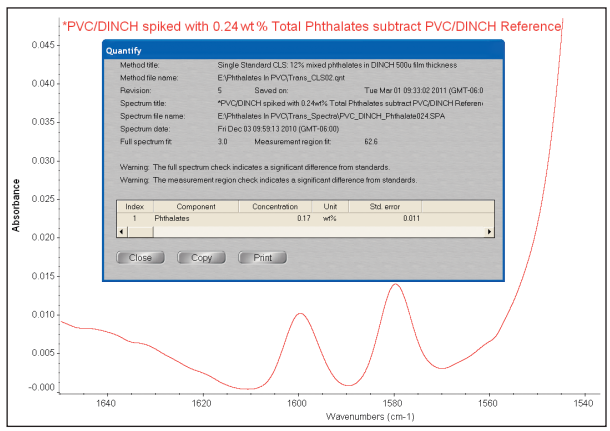

Figure 4: The results of applying a Classical Least Squares quantitative analysis method to the spectrum of a sample containing 0.24 wt % total phthalates after subtracting a reference spectrum

If we do not subtract out the spectral features from the plastic reference, we still get a concentration of 0.18 wt % but the standard error term has increased to 0.16 wt %. Based on the higher standard error we would report that this result to be "Inconclusive" even though the calculated concentration is the same. This report is shown in Figure 5.

The only case where a sample will pass the screen is when the calculated concentration is below 0.1 wt % and the standard error is below 0.033 wt %. When this occurs, the report shown in Figure 6 is produced. Based on our present research we have chosen to report that we are confident no phthalate is present above 0.1 wt % and to not report either the calculated concentration or the standard error.

In this application note we have described a two step process to determine if phthalates are present in a sample. We believe that the ATR technique has the flexibility to provide a fast reliable answer to quickly check samples for the presence of phthalate plasticizers at the levels commonly found in commercial products. If this measurement is inconclusive, we believe that pressing a sample into a 500 µ thick film provides the signal-to-noise ratio necessary to detect phthalates below the 0.1 wt % level required by law. However, the presence of additives in many plastic formulations may introduce peaks in the analysis region that can interfere with the reliability of the analysis. We have shown that excellent results can be obtained for many samples contaminated with small amounts of phthalates if a reference sample of uncontaminated material is available for a spectral subtraction.

** Experiment can be conducted using the Thermo Scientific Nicolet iS5, iS10, or iS50 FT-IR spectrometer systems.*

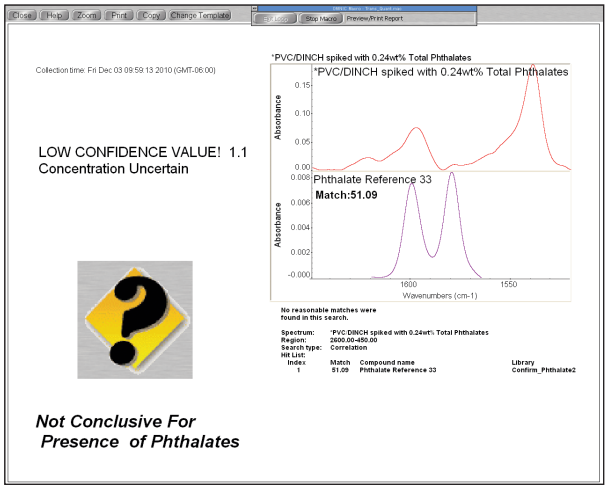

Figure 5: The yellow question mark means that the measured concentration is less than three times the reported standard error

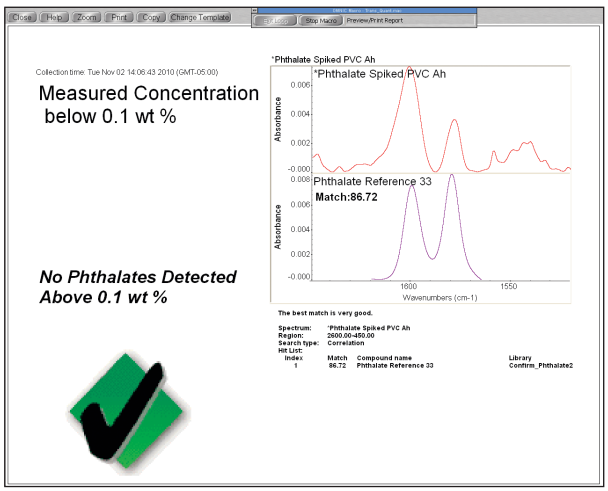

Figure 6: The green check mark indicates that the measured concentration is less than 0.1 wt % and has a standard error below 0.033 wt %

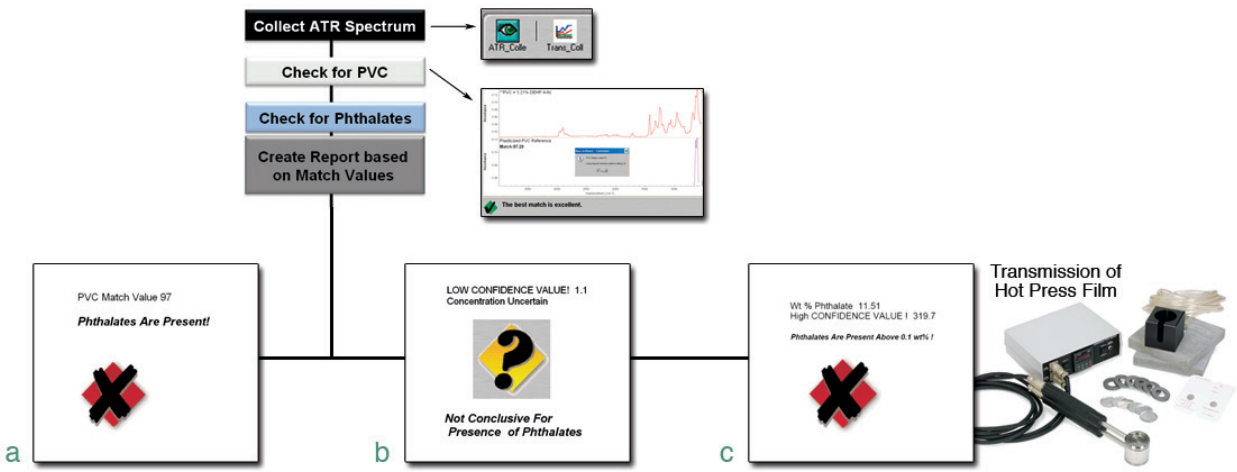

Figure 7: Phthalates analysis FT-IR workflow showing a conclusive identification of phthalates present (a), an inconclusive measurement (b) and a recommendation to perform either a Hot Pressed Film technique or GC/MS method (c)

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