

# Rapid and reliable phthalate screening in plastics by portable FTIR spectroscopy

## Application note

Consumer products

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### Abstract

A quantitative method for determining the level of plasticizer in plastics is now available for Agilent portable and handheld FTIR analyzers. The calibrated method affords a limit of quantitation as low as 0.1% as well as provides a very rapid means of screening plastic products and components. This ensures that greater volume of plastic materials can be screened more efficiently for compliance with regulatory guidelines.



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## Introduction

Many common plastic consumer products contain high levels of toxic chemical additives known as phthalates. Phthalates are referred to as plasticizers, which are used to make plastics more flexible, durable, and softer. Typically, 15–30% phthalates are added to a base polymer such as polyvinyl chloride (PVC, vinyl) and other widely used polymers. Since there are no chemical bonds between the plasticizer and the polymer, the plasticizers can easily leach out, contaminating the surrounding environment or be ingested by humans. Phthalates are hormone disruptors and phthalate exposure is also linked to other physiological effects including obesity, insulin resistance, kidney and liver damage, ADHD, and possibly other neurological effects in children.

Section 108 of the Consumer Product Safety Improvement Act (CPSIA) permanently prohibits the sale of any “children’s toy or child care article” containing concentrations of more than 0.1 percent of three specified phthalates and three other phthalates are temporarily prohibited in the same products. The Consumer Product Safety Commission (CPSC) has developed a standard operating procedure for the measurement of phthalates and specifies FTIR as a pre-screening procedure (optional) to determine gross phthalate contamination. The CPSC concentration limit, 0.1% each for the six banned phthalates, is based on the individual plasticized parts of a children’s toy or child care product<sup>1</sup>.

In this application note, we show that Agilent FTIR analyzers and associated calibrated methods can be used to accurately measure levels of phthalates in plastics to levels as low as 0.1%. This combination of technology and methodology provides the ability to rapidly screen large numbers of parts and objects for phthalate content with little or no sample preparation. The portability of the Agilent FTIR analyzers enable

these measurements to be made in the field and help to ensure that plastic parts and objects do not enter the commercial marketplace.

### Value of FTIR pre-screening for phthalates

There are substantial benefits gained by pre-screening plastic materials for phthalates with Agilent portable and handheld FTIR spectrometers. Examples include:

- Rapid measurement of total phthalate concentration to a 0.1% limit of quantitation (LOQ) with little or no sample preparation.
- Non-destructive identification of higher level phthalate-containing parts in products that are mostly phthalate free.
- Quick identification of plastic parts that are unlikely to contain plasticizers, such as polyethylene, polypropylene, polystyrene, nylon, polyester, cardboard/paper, or silicone rubber.
- Quick screening and detection of cross contamination between a non-phthalate and a phthalate factory part.

Furthermore, the final concentration of the individual banned phthalates must be determined using the CPSC approved solvent extraction techniques followed by gas chromatography - mass spectroscopy (GC-MS). The efficiency of the GC-MS technique is improved with FTIR pre-screening, as follows:

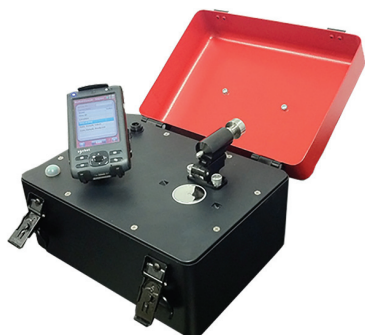
- FTIR pre-screening per sample is far less costly and more rapid than the GC-MS method. This affords the establishment of more productive and better analysis cost-control procedures.
- The FTIR method establishes the dilution factor necessary for the GC sample preparation and helps prevent fouling of the GC-MS.
- Agilent FTIR systems can also flag problem polymers for the GC-MS with an easy to use library search method. Siloxane residues from silicones or polyethylene oxide from polyurethanes are two examples that cause problems for GC-MS analysis, often requiring time consuming cleaning or a new GC column.

<sup>1</sup> Visit <https://www.cpsc.gov/phthalates> for further details regarding phthalate regulations and measurement.

## Experimental

### Instrumentation

Agilent's portable and handheld FTIR instruments offer rapid, reliable, easy to use, and non-destructive analysis of phthalates in plastics. The self-contained and portable Agilent 4500a (Figure 1) is the primary choice for phthalate screening and plastic identification. It features a three reflection diamond ATR sensor that is approximately 3 mm in diameter. Plastic samples are held against this sensor for ~60 s while the FTIR scans the sample. The software interface is very simple to operate and designed for use by non-technical factory personnel. The handheld Agilent 4100 Exoscan or 4200 Flexscan systems (Figure 2) are also available to measure phthalates. The Agilent 4500a measures total phthalates ~0.1% whereas the 4100 Exoscan/Flexscan systems measure to ~1% total phthalates. In addition to quantitative measurements of phthalates, all Agilent handheld and portable FTIR analyzers offer spectral library searching to verify the composition of the polymer and the primary type of phthalate present.



**Figure 1.** The Agilent 4500a is equipped with a three reflection diamond ATR and polymer press for optimum sample contact. This system can detect total phthalates to 0.1%.

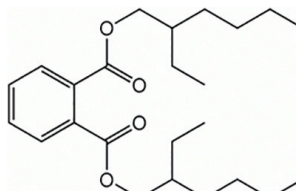


**Figure 2.** The Agilent 4100 Exoscan (left) or Flexscan (right), equipped with a one reflection spherical diamond ATR sensor, can detect total phthalates to 1%.

## Method and measurements

### Phthalate structure and infrared spectra

Phthalates are the di-esters of phthalic acid, and have an ortho substituted aromatic ring (Figure 3). This ortho aromatic group has a strong absorbance band at  $741\text{ cm}^{-1}$  in the infrared spectrum (Figure 4). This band has little interference from either PVC or other phthalate replacements which are not ortho aromatics compounds. Some other useful bands for infrared analysis of phthalates are the doublet bands at  $1601\text{ cm}^{-1}$  and  $1581\text{ cm}^{-1}$ . These bands are due to the aromatic ring quadrant stretching vibration, and change in frequency and intensity depending on the aromatic ring substitutions. All of these bands are specific to all phthalates and are used in Agilent's portable handheld and mobile FTIR phthalate quantitative methods. The Agilent phthalates method uses peak height or peak area absorbance measurements to create Beer-Lambert Law univariate or multivariate PLS calibrations. This capability is more sensitive, accurate, and quantitative than library search methods. Differences in the aliphatic stretch region of the FTIR spectrum can be used to identify the specific phthalate present, assuming it is the primary phthalate in higher concentrations.



**Figure 3.** The chemical structure of di-2ethylhexyl phthalate (DEHP, also known as DOP). Other phthalates are structurally similar, possessing different aliphatic side chains.

### Preparation of calibration standards

Vinyl toys, sports equipment, and other products are often made from non-phthalate plasticizers that are generally considered safer for children. Many of these replacement plasticizers cause interference for the FTIR analysis of phthalates. One example is the common phthalate replacement called DOTP, which is a terephthalate instead of an orthophthalate such as DEHP. The slightly different chemical structure of DOTP causes it to be less biologically hazardous; however, it has IR absorbance bands in the same 1600–1500  $\text{cm}^{-1}$  and 800–700  $\text{cm}^{-1}$  regions of the IR spectrum used to detect the banned phthalates. Despite such interferences, specific calibration models have been developed which accurately predict total phthalates.

Our research indicates that individual calibrations for the most common replacement plasticizers improve the detection limit and capability of FTIR to measure phthalates. The five most common non-phthalate plasticizers used in this experiment are 1,2-cyclohexane dicarboxylic acid di-isononyl ester (DINCH, obtained from BASF), dioctyl adipate (DOA), dioctyl terephthalate (DOTP, aka. DEHTP), trioctyl trimellitate (TOTM), acetyl tributylcitrate (ATBC). Five sets of plasticized vinyl samples are created to calibrate the FTIR, each having mixtures of phthalate (DEHP) and the non-phthalate plasticizers. Each set of calibration standards are

prepared by dissolving pure polyvinyl chloride (PVC) in tetrahydrofuran (THF) with known weights of DEHP and non-phthalate plasticizers. The resulting mixtures are gently heated until the PVC is completely dissolved and the samples are then cast into a disc shape. The resulting polymer disc is allowed to dry at room temperature overnight, and a final drying step occurs in a vacuum oven for 4 hours at 60 °C which removes any residual THF in the vinyl sample. Two sets of phthalates in DINCH and DOA provided by the CPSC were also used in the calibration sets. The CPSC total phthalates standards are prepared using equal quantities of the six currently banned phthalates (DEHP, DBP, BBP, DINP, DIDP, and DNOP).

The vinyl disc coupons are all plasticized with increasing DEHP in non-phthalate plasticizers. Each set consists of samples with 0%, 0.5%, 1.5%, 3%, 6%, 9%, 13.6%, 20%, and 30% total phthalates and the balance of the non-phthalate plasticizers is varied to produce samples with 28–34% total plasticizer. The calibration coupons are measured in five areas on the 4500 three reflection ATR using the press. The FTIR spectral data is used to create high and low phthalates partial least squares (PLS) chemometric models for each set of samples. The low calibration uses the 0–3% total phthalates data and the high calibration uses the 3–34% range.

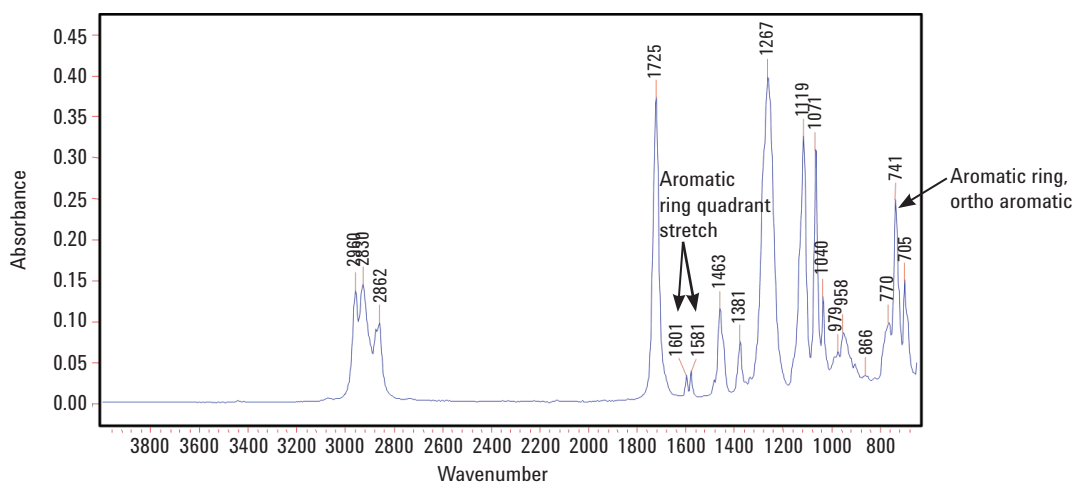
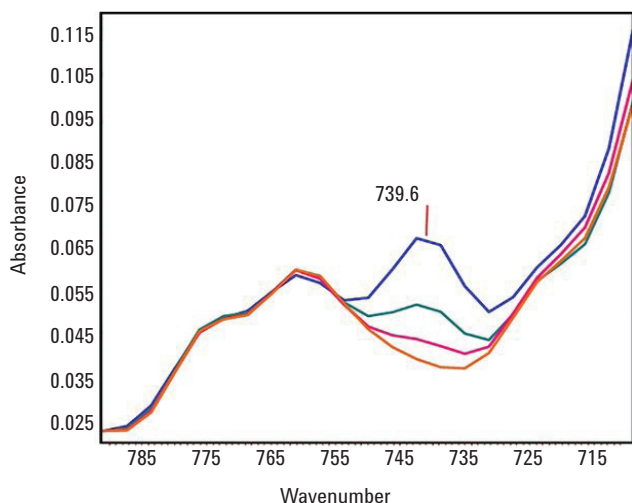
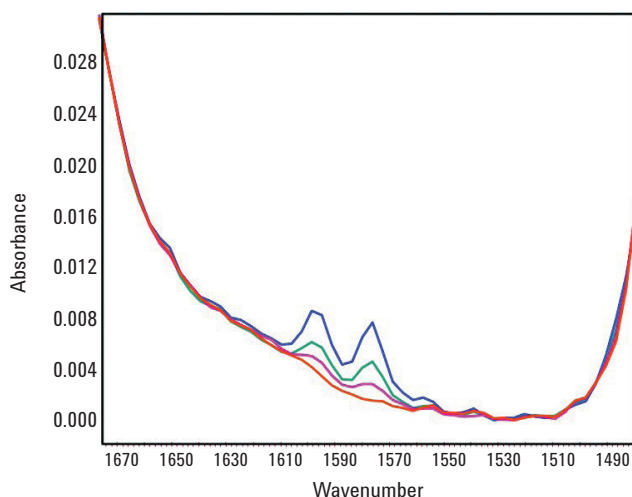


Figure 4. The FTIR spectrum of pure DEHP, with useful quantitative bands identified

The FTIR spectra are collected using 240 co-added scans at 8 cm<sup>-1</sup> resolution, which results in a 60 s scan time. The total phthalates FTIR PLS calibrations are created using the 740 cm<sup>-1</sup> (Figure 5) and 1620–1560 cm<sup>-1</sup> (Figure 6) phthalate regions of the IR spectra. The PLS chemometric modeling improves spectral calibrations using features like mean centering and derivatives to minimize spectral interferences such as environmental noise or baseline variations.



**Figure 5.** PVC samples plasticized with DINCH and phthalates, 0.00% (orange), 0.60% (pink), 1.76% (green), and 3.29% total phthalates (blue).



**Figure 6.** PVC samples plasticized with DINCH and phthalates, 0.00% (orange), 0.60% (pink), 1.76% (green), and 3.29% total phthalates (blue).

## Results and discussion

### Calibration

We find that all of the PLS models for low concentration phthalates perform similarly to the example plot of low phthalates in DINCH (Figure 7). A correlation coefficient of  $R^2=0.9984$  indicates very good agreement between the spectral absorbance and concentration of phthalates. The spectra of the higher range of phthalates in DINCH for PVC coupons (Figure 8), indicate a very strong correlation to the same phthalate absorbance regions as seen in the low concentration samples. The actual vs. predicted calibration plot for the high phthalates in DINCH (Figure 9) has a correlation coefficient of  $R^2=0.9992$ . The PLS chemometric models for the other four plasticizers demonstrate similar performance (Table 1). Additional PLS calibration models are also created for samples with high amounts of fillers, such as calcium carbonate or silicates, and another model to handle samples with a mixture of DOTP and DOA or DINCH. The limit of quantitation for complete phthalates method is determined by making known 0.1% phthalate (DEHP) standards in DINCH, DOTP, and ATBC. The standard deviations of five replicate measurements of the 0.1% validation standards can be stated as the limit of detection (LOD, Table 1). Three times the standard deviation yields the limit of quantitation (LOQ). Therefore, the LOD for phthalates in DINCH plasticized PVC is 0.02% total phthalates and a LOQ of 0.06%. The limits for each calibration are shown in Table 1.

**Table 1.** The correlation coefficient's ( $R^2$ ), limit of detection (LOD) and limit of quantitation (LOQ) are shown for each full range calibration of phthalates (DEHP) in plasticized PVC.

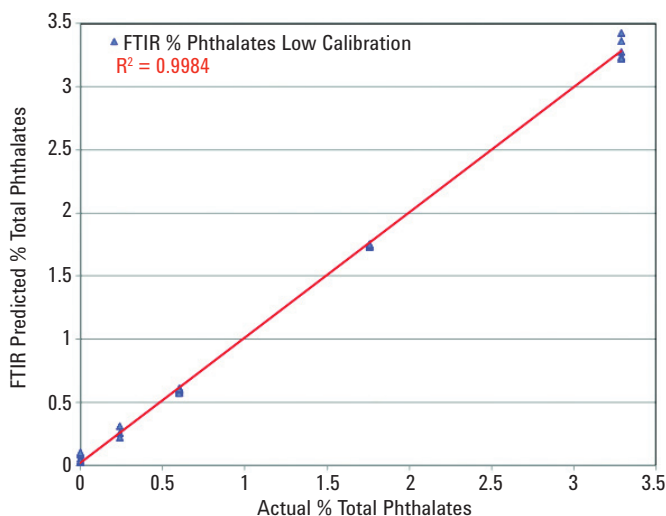
Calibration	$R^2$	LOD	LOQ
DEHP in DINCH	0.9992	0.020	0.06
DEHP in DOTP	0.9972	0.050	0.15
DEHP in ATBC	0.9998	0.024	0.07
DEHP in DOA	0.9992	0.02*	0.06*
DEHP in TOTM	0.9995	0.05*	0.015*

\* Estimated based on performance of similar calibrations.

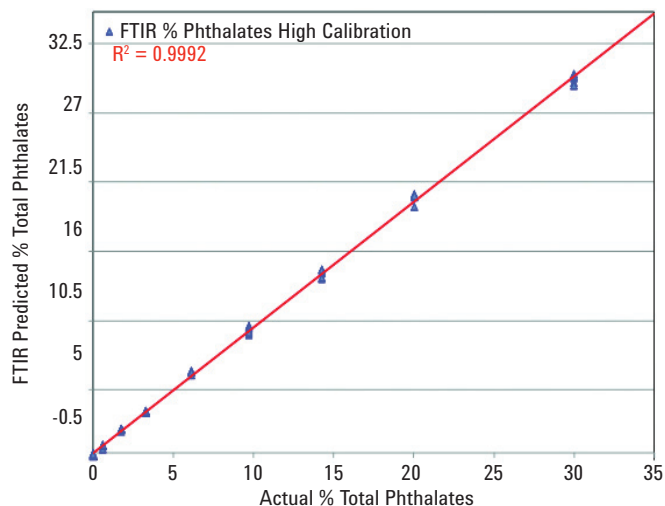
Samples with surface contamination or high amounts of carbonate, silicate, or silica fillers will cause the LOQ to increase. ATR is a surface technique, and therefore the polymer surface to be measured should be as clean as possible. Vinyl parts or toys should be measured in an unpainted area. Some samples with high surface contamination may need to be cut to measure a fresh polymer surface.

### Conditional reporting and display of results

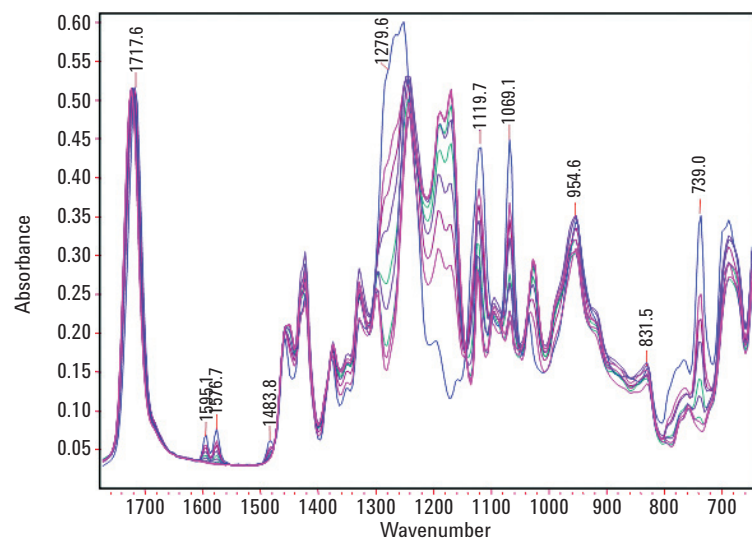
The unique conditional reporting feature in the MicroLab PC software allows calibrations to be displayed only if specified conditions are met. The conditional reporting parameters for the phthalates methods use the most appropriate calibration depending on unique modeling statistical conditions, or the concentration results of other models (Figure 10).



**Figure 7.** PLS actual vs. predicted calibration plot of PVC samples plasticized with DINCH and 0–3% total phthalates.



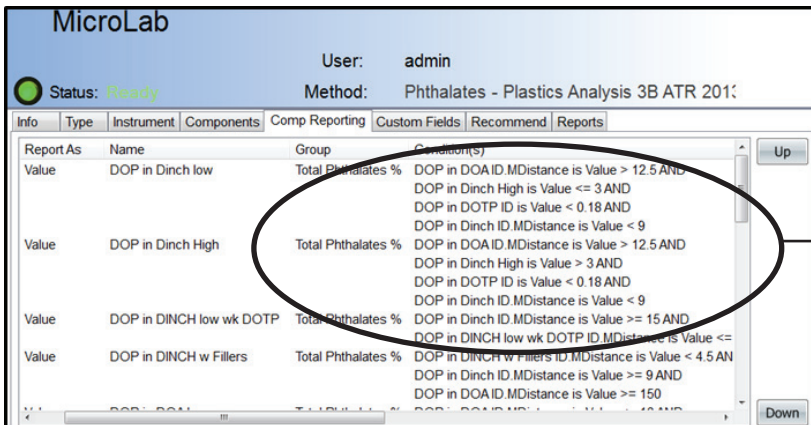
**Figure 9.** High phthalates PLS actual vs. predicted plot of PVC samples plasticized with DINCH, 0–30% total phthalates.



**Figure 8.** The FTIR spectral overlay of the full concentration range (0–30%) of phthalates in DINCH used in the high phthalates calibration.

One such statistical comparison is called Mahalanobis Distance (M-Distance), which indicates how well a spectrum matches the set used in the calibration model. In addition to M-Distance, the conditional reporting can be used to choose if the high or low model will be reported. For example, if the phthalates in DINCH value is less than or equal to 3% then the low calibration will be shown and if the high calibration is greater than

3% then the high calibration will be displayed. When a sample spectrum agrees with the conditions for any of the models, only the "Total Phthalates %" value will be displayed with the appropriate calibration selected automatically. The 0.00% phthalates result (Figure 11) is from a toy mermaid doll (Figure 13). A toy spider also indicates 0.00% phthalate using the method. The 30.17% phthalate result (Figure 12) is from the measurement



Method set up page:  
Conditions with logic and limits set

Figure 10. The phthalate method editing display shows the multiple conditions placed on each calibration, which improves the accuracy of the measurement.

Status: Ready		Result: Toy mermaid, purple tail_2013-11-12T12-1	
Part Type (i.e. Toy Doll)		Manufacturer	
Sub Part Type (i.e. Doll's Shoe)		Physical Properties (i.e. Red Soft Pla...	
Part #		Date Sample Taken	
Serial #		Date Sample Analyzed	
Lot #		Location	
Results:			
Name	Value	Low Threshold	High Threshold
Total Phthalates %	0.00		0.5
Plasticizer ID 1	Active		
Plasticizer ID 2	Active		
Plasticizer ID 3	Active		
Plasticizer ID 4	Active		
Plasticizer ID 5	Active		
Plasticizer ID 6	Active		
Plasticizer ID 7	Active		

Figure 11. The analysis results from a toy mermaid doll, made from plasticized PVC, indicate no phthalates are detected by the FTIR method.

Status: Ready		Result: orange toy horse, high phthalates r1_2013	
Part Type (i.e. Toy Doll)		Manufacturer	
Sub Part Type (i.e. Doll's Shoe)		Physical Properties (i.e. Red Soft Pla...	
Part #		Date Sample Taken	
Serial #		Date Sample Analyzed	
Lot #		Location	
Results:			
Name	Value	Low Threshold	High Threshold
Total Phthalates %	30.17 (Critical)		0.5
Plasticizer ID 1	Active		
Plasticizer ID 2	Active		
Plasticizer ID 3	Active		
Plasticizer ID 4	Active		
Plasticizer ID 5	Active		
Plasticizer ID 6	Active		
Plasticizer ID 7	Active		

Figure 12. The analysis results from an orange toy horse, made from plasticized PVC, indicate very high phthalates are detected by the FTIR method.

of an orange toy horse (Figure 13). A toy doll shoe also indicates very high phthalates.

Additional polymer library search methods can be used to identify unknown plastic materials and can identify high phthalates or non-phthalate plasticized polymers. The library search method provides a hit quality index (0–1.0000) to indicate the similarity of the match with the unknown.

## Conclusions

CPSIA has specified a ban on the most widely used phthalate plasticizers in children's toys or parts that could easily be put in a child's mouth. We have shown that the Agilent 4500a portable FTIR equipped with three reflection diamond FTIR spectrometers accurately measures total phthalates in plastics and functions as a rapid screening tool for these hazardous substances. This capability allows for quantitation of phthalates to the regulated level of 0.1% for a single banned phthalate. Multiple calibrations and advanced conditional reporting features in Agilent's MicroLab PC software makes the FTIR phthalates method more flexible at measuring phthalates in PVC with other legal types of plasticizers. Additionally, plastics parts can be identified to improve the efficiency and productivity of the GC-MS gold standard method.

The compact size, ruggedness and portability of the Agilent 4500a FTIR system allows plastic parts and objects to be rapidly screened in the field as needed. This benefit helps to ensure that hazardous plastic material does not reach the consumer market.



**Figure 13.** The Agilent FTIR pre-screening method for phthalates determined that toys in the top image have no phthalates, whereas toys in the lower image have high levels of phthalates.

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Published December 4, 2013

Publication number: 5991-3649EN