Measuring and Verifying Performance of FTIR for Rapid Phthalate Screening

Application Note

Materials Testing and Research

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Introduction

Phthalates are widely used as plasticizers to make polymers more flexible in industrial and household products. However, lower molecular weight *ortho*-phthalate plasticizers have serious health effects and are restricted or banned in many countries for use in children's products. In addition, several government agencies restrict or are investigating restricting *ortho*-phthalates (*ortho*-dialkyl phthalates, *o*-DAPs) in other consumer products [1,2]. One of the most common plastics that can contain higher levels of plasticizers is polyvinyl chloride (PVC), which is widely used in juvenile and industrial products. PVC is used in many industries, and the respective supply chains provide numerous finished products, components, and subassemblies that can contain phthalates.

For this reason, a screening method for phthalates is needed that is more rapid, simple, and supportive of the regulated gas chromatograph/mass spectroscopy (GC/MS) method [3], because GC/MS screening is time-consuming and expensive. By screening samples, only those identified as PVC polymers, or polymers that show traces of *ortho*-phthalates, are sent for analysis.

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FTIR screening complements GC/MS for phthalate measurement in polymers

- The Agilent 4500 Portable FTIR provides accurate and sensitive detection of phthalates in PVC and other polymers.
- Since the FTIR method is very rapid, easy to implement, requires no consumables, and requires no sample preparation, large numbers of polymer objects can be quickly screened.
- Samples that are positive for phthalates by FTIR screening can then be sent for GC/MS analysis. This helps reduce the number of samples that must be processed by the slower and more complicated GC/MS method.
- Since the 4500 FTIR is fully portable, the screening method can be implemented at all stages of the supply chain. This portability enables far more thorough examination of materials before they reach consumers.
- Screening samples with FTIR enables the GC/MS analyst to better understand the sample matrix. Since the GC/MS method for phthalates involves solvent extraction, this understanding helps minimize the possibility of contaminating the GC/MS injector and columns.
- The economic value of FTIR screening for phthalates is substantial, mitigating costly errors that can lead to product liability.
- The FTIR method is surface sensitive, providing direct information about the location of phthalate contamination.

In a previous application note, we used the 4500 Portable FTIR analyzer to provide a rapid method for measuring phthalates in PVC without the need for sample preparation. In this application note, we demonstrate and prove the analytical effectiveness of that method, and the ability to detect phthalates in polymers other than PVC. Measurements made using the 4500 FTIR method on prepared samples of PVC impregnated with phthalates demonstrate excellent agreement with the known amounts of phthalate present. In addition, we show that the 4500 FTIR system is an effective screening device, by detecting the presence of phthalates in a series of commercial products previously analyzed by GC/MS.

Materials and Methods

A series of phthalates in PVC were prepared gravimetrically by a commercial laboratory using certified reagents (Table 1). The phthalates used in these standards were a mixture of the permanently banned phthalates: dioctyl phthalate (DOP or DEHP), dibutyl phthalate (DBP), and benzyl butyl phthalate (BBP) [1], mixed with an approved replacement plasticizer, diisononyl cyclohexane-1,2-dicarboxylate (DINCH). The FTIR method was calibrated with DEHP in PVC with various replacement plasticizers; testing the method with other types of banned phthalates, such as DBP and BBP, proves its effectiveness to detect any type of *ortho*-phthalate. PVC products are produced with sufficient plasticizer to make them soft and pliable, typically 20-35 wt% total plasticizer. To reproduce a typical vinyl toy composition in the evaluation standards, the total plasticizer concentration of 33-35 wt% was used.

Table 1. Phthalates Used as Standards for Evaluation

Standard deviation (2 sigma) –4.0 % (*Relative)

	Restricted phthalate mix concentration (wt %)				
Standard no.	**Dioctyl phthalate (DOP)**	**Di-*n*-butyl phthalate (DBP)**	**Benzyl butyl phthalate (BBP)**	**DINCH**	**Total restricted phthalates**
1	0	0	0	34.015	0
2	0.121	0	0	33.966	0.121
3	0.507	0	0	33.444	0.507
4	0	0.108	0	33.21	0.108
5	0	0.703	0	34.286	0.703
6	0	0	0.093	33.031	0.093
7	0	0	0.74	33.355	0.74

* The 4.0 % relative uncertainty is based on errors from the weighing of the raw materials at 95 % confidence level, or k = 2.

In addition to the evaluation standards (Tables 1 and 2), a series of retail home and juvenile products, previously measured by GC/MS, were examined using the same FTIR analyzer and the same acquisition parameters. The FTIR results were obtained using the unique Agilent phthalate screening method (Table 3).

The samples were measured using the 4500 FTIR analyzer. Spectra consisted of 240, co-added scans recorded at 8 cm^{-1} resolution, one minute scan time. An exclusive three-reflection diamond attenuated total reflectance (ATR) sample interface was used for the measurements. No sample preparation was required, and the spectra were analyzed using the Agilent proprietary automated phthalate screening method, which measures phthalate levels to 0.1 %.

Results and Discussion

The results from the total phthalate method are shown in Table 2.

Table 2. Comparison of Total Phthalates Measured Gravimetrically and by FTIR

Standard sample number	Total phthalates wt % gravimetric	Total phthalates wt % FTIR
1	0.000	0.00
2	0.121	0.17
3	0.507	0.54
4	0.108	0.12
5	0.703	0.79
6	0.093	0.17
7	0.740	0.96

These results show that for homogenous, uniform samples containing *ortho*-phthalates, the Agilent FTIR method, which is largely a surface technique, provides accurate measurement of total phthalate to the 0.1 % level. Children's toys and other juvenile products are restricted in many parts of the world from having phthalate concentrations greater than 0.1 %.

Since phthalates are not chemically bound to the PVC polymer matrix, they can be extracted by children placing the item in their mouths or by contact with other polymers that were manufactured without phthalates. This migration phenomenon can cause some surfaces of a vinyl material to have toxic levels of phthalates even-though the part as a whole may meet the regulatory 0.1% phthalates limit. The surface sensitivity of the FTIR technique allows quick analysis of all the surfaces of a vinyl or polymer part.

The Agilent system analyzes total phthalate in standards prepared in PVC accurately and precisely. How does it cope with real-world samples? To examine such samples in more detail, a series of commercially available products previously assessed for phthalates by GC/MS were analyzed using the 4500 FTIR. The results are shown in Table 3.

For these objects, analysis becomes more complex and more complicated. Some of the products are uniform and consist only of PVC. Others are multilayered or even partially constructed of materials other than plastic. It is necessary to understand how the sample preparation method used in GC/MS measures the sample compared to the no-sample-prep FTIR method to understand why the absolute numerical results between the techniques can differ.

Table 3. Analysis of Phthalates in Commercial Products Using the Agilent 4500 Portable FTIR

Sample name	Side, color, description	GC/MS wt % total phthalates	FTIR wt % total phthalates	Polymer type
Wrench handle cover	Side 1, Grey rough grip	18.93	28.13	PVC, high carbonate filler
	Side 2, Green	18.93	33.63	PVC, high carbonate filler
Glove	Side 1, outside	37.50	34.58	PVC w/ DINP
	Side 2, inside	37.50	30.69	PVC w/ DINP, high talc
Shower curtain liner	Side 1	18.20	23.78	PVC w/ DEHP, low fillers, rough texture
	Side 2	18.20	23.82	PVC w/ DEHP, low fillers, rough texture
Wall art stiker	Side 1, front surface no ink area	15.81	6.86	PVC mainly DEHP, rough matte finish
	Side 2, adhesive	15.81	9.60	Polyacrylate adhesive
	paper backing, glossy non-stick	15.81	1.24	Silicone coating
	paper backing, matte	15.81	0.12	Paper, high carbonate and talc
Pink flip flop strap	Side 1	33.13	47.38	PVC w/DBP
	Side 2	33.13	47.20	PVC w/DBP
	Attached ribbon	33.13	0.00	Nylon polyester blend
	Attached ribbon fibers	33.13	0.00	PET fibers
Pencil case	Side 1, smooth polymer	0.00	0.00	Polyurethane
	Side 2, Fabric backing	0.00	0.00	PET fabric
Blue carry all	Side 1, clear polymer	0.05	0.00	PVC w/ DOTP
	Side 2, clear polymer	0.05	0.00	PVC w/ DOTP
3-Ring binder	Side 1, Red poly film rough	16.57	12.83	PVC w/ DINP and DIDP, high carbonate filler
	Side 2, Red poly film smooth	16.57	11.95	PVC w/ DINP and DIDP, high carbonate filler
Blue bill fold	Side 1, poly film	4.46	8.99	PVC w/ DEHP, high carbonate filler
	Side 2, Fabric backing	4.46	0.34	PET fabric
	Weight adjusted for GC/MS calc.	6.13	6.13	PET fibric partially removed
Animal print backpack	Side 1, textile poly film side	5.44	11.48	PVC w/ DEHP, very high carbonate filler
	Side 1, textile fabric side	5.44	0.48	PET fabric

The GC/MS sample preparation method often consists of the cryogenic grinding of a weighed, bulk polymer followed by solvent extraction of the phthalates. Cryogenic grinding is expensive and time-consuming, and the bulk sample can contain several different polymers and even nonpolymeric materials. Cryogenic grinding is the best way to prepare plastic samples for solvent extraction, but many labs only cut the sample by hand into small 1-mm pieces before extraction. The whole prepared sample is extracted to yield the solution injected into the GC/MS. Some components in the bulk sample contain phthalates, some do not, but it is the weight percentage of phthalate that is reported. In fact, the mass of the nonphthalate components acts as a diluent and reduces the overall phthalate weight percent. Another important factor is that the amount of phthalate measured depends the efficiency of the extraction, which is often not 100 %. Efficiency can be affected by the composition of the bulk sample that is being extracted, as well as the effectiveness of the grinding process.

In contrast, the FTIR method is fundamentally a surface measurement (that is, not the bulk sample). Therefore, depending on which component surface is analyzed, the phthalate level can be present in higher or lower concentration than the amount in the extracted GC/MS bulk sample. A key factor is that the 4500 FTIR system has the sensitivity to detect phthalate at regulatory levels and can rapidly measure different areas of the object of interest. This ability enables the Agilent system to screen objects effectively. Objects considered important can be sent for full GC/MS analysis. In contrast, if the object consists only of bulk PVC, the numerical agreement between the FTIR and GC/MS is good.

Analysis of the sandal strap in Table 3 is an example. GC/MS measurement of the bulk sample yielded a value of 33.13 weight % total phthalate. The FTIR method, which measures each of the components separately, determined that phthalates were present at high levels in the PVC strap (Side 1, 47.38 weight %, Side 2, 47.2 weight %). They were not present in the PET or nylon ribbons.

Again, in Table 3, contrast the sandal example with the glove, which is constructed of PVC only. In this case, the bulk (GC/MS, 37.50 weight %) and surface (FTIR, outside surface, 34.58 %, inside surface 30.69 weight %) measurements are in close agreement.

As another example of bulk versus surface and how the dilution effect influences results, we examined the billfold in Table 3 in closer detail. The billfold consisted of a PET fabric layer and a PVC polymer layer (Figure 1). A GC/MS analysis of a 0.2624 g bulk sample yielded a DEHP level of 4.462 weight % or 0.0117 g DEHP. For the FTIR analysis, we mechanically separated the two layers and measured the PVC layer, which yielded a DEHP level of 8.99 weight %, or nearly twice the GC/MS value. Since the PET layer, which had been removed from the 0.2624 g sample, weighed 0.1907 g, the weight % of DEHP, discounting the dilution effect by the PET layer, was 0.0117/0.1907 = 6.13 weight %. The recalculated GC/MS result (6.13 %) agreed more closely with the FTIR measurement (8.99 weight %). Differences between the two results are mostly related to the fact that some of the PET fibers were imbedded in the PVC layer and could not be removed during the mechanical separation. The remaining difference in concentration is explained by known variables such as solvent extraction efficiency, sample preparation, and mass dilution due to inorganic fillers in the sample.

Figure 1. Different layers of a billfold tested for phthalates.

Measurement of phthalates via GC/MS typically costs $250-500 depending on how many phthalates are quantified and sample preparation factors. If an organization needs to test 50 samples a month at the average cost of $350 each, the total phthalates testing costs would be $210,000 per year. If screening for phthalates using this FTIR method reduces the number of samples sent for GC/MS by 70%, the organization would save $147,000 per year, making the return on investment for a FTIR screening program less than 4 months.

Agilent 4500 Portable FTIR for polymer and phthalate analysis

Positive material identification

- An advanced spectral search algorithm and extensive, onboard spectral database enables polymeric materials to be identified in seconds.
- Identify PVC, which can contain phthalates, as well as other polymers.
- Analysis is accomplished without the need for sample preparation, and often nondestructively.

Phthalate screening

- If a polymer is identified as PVC, the Agilent proprietary method will measure the total amount of *ortho*-phthalates, even in the presence of fillers, carbon black, and nonphthalate plasticizers.
- The 4500 FTIR can accurately achieve a limit of quantitation (LOQ) to 0.1 % and a limit of detection (LOD) down to 0.05 % total *ortho*-phthalates in PVC using an exclusive calibrated method with conditional reporting algorithm.
- In polymers identified as other than PVC, the 4500 FTIR automatically selects the appropriate calibration to enable the detection of phthalates. This facility enables the system to function as a powerful screening tool to identify samples for GC/MS measurement.

Conclusions

The GC/MS method is the regulated method for the analysis of phthalates in PVC and other polymers. At present, only GC/MS analysis provides a result that meets the requirements for certification of phthalate content. Conversely, the FTIR method is effective for detecting phthalates and is, therefore, useful as a rapid screening method, and complements the GC/MS method. The Agilent 4500 Portable FTIR method is an order of magnitude faster than GC/MS and does not require sample prep or consumables. It can be successfully executed by persons with varied experience, and, very importantly, uses a fully portable, battery-powered system. Portable FTIR is, therefore, a powerful screening tool that enables large numbers of PVC and other industrially important polymers to be screened for total *ortho*-phthalates. This helps to increase the number of samples that can be processed. At the same time, the sample load on the GC/MS is reduced by enabling the analyst to concentrate efforts on those critical samples identified by the FTIR screen. Screening polymers for phthalates using the 4500 Portable FTIR is cost-effective, with a short return on investment, helping minimize costly errors that can lead to product liability issues.

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