A new gas chromatography method was used to analyze phthalate plasticizer concentration after poly(vinyl chloride) sample dissolution with consequent phthalate extraction and polymer precipitation.

Poly(vinyl chloride) (PVC) became one of the most useful materials known today after Waldo Lonsbury Semon’s discovery of plasticization in 1926. The use of plasticizers as such, however, began in the mid-1860s when castor oil was added to soften cellulose nitrate. Plasticized PVC is used in food packaging, shoes, furniture, cars, toys, medical devices, clothing, plumbing, tool handles, and many other applications. The most popular plasticizer for PVC is di(2-ethylhexyl) phthalate (DEHP). Like many other materials in consumer use, DEHP was suspected as possibly causing adverse physiological effects. Although the debate over the existence of adverse DEHP effects continues, the analysis of DEHP and other phthalates present in PVC parts is required by regulatory agencies. The concentration of tri(2-ethylhexyl) trimellitate, di(2-ethylhexyl) terephthalate, and other plasticizers currently replacing DEHP in commercial products is also often examined.

To quantify the amount of phthalate plasticizers in PVC, analytical methods based on solvent extraction of phthalates from the polymer parts and consequent chromatographic analysis are employed. In many cases the solvent of choice does not dissolve PVC, and the extraction only partitions the phthalate between the polymer part and the solvent, leaving some amount of plasticizer remaining in the PVC. Phthalate extraction from the PVC solid is time-consuming, since molecular diffusion occurring during extraction from polymers is very slow. To reduce measurement uncertainty, and to accelerate and simplify the extraction of phthalate plasticizers from PVC, the US Consumer Product Safety Commission developed an analytical approach in which an entire sample of plasticized PVC was used after dissolving it in tetrahydrofuran (THF). The dissolved PVC was then precipitated from THF by a nonpolar solvent (hexane), while phthalate plasticizers remained in the hexane/THF solution. Since PVC precipitation produced a stable PVC suspension, it was recommended that the solution should be filtered.

We extended the method based on complete PVC dissolution by eliminating the need for solution filtration. In our approach we also dissolved plasticized PVC in a polar solvent, methyl ethyl ketone (MEK), then precipitated PVC by adding a nonpolar solvent (hexane), forming a PVC suspension. However, instead of filtration we broke the PVC suspension and precipitated the PVC by adding an aqueous solution of a strong electrolyte such as sodium chloride. The electrolyte cleanly precipitated and aggregated the PVC into a water-organic layer interface (see Figure 1). The ‘salting out’ effect described quantitatively by Setschenow and Debye ensured that MEK and hexane formed an organic layer with a clean boundary where relatively nonpolar phthalate plasticizers were concentrated. The sample of organic layer was then analyzed using our new gas chromatography (GC) procedure.

Several gas chromatographic techniques were used for the analysis of phthalates in the past. We developed another straightforward GC method of phthalate analysis using a Supelcowax 10 capillary column, designed for solute separation primarily based on molecule polarity. After injection of the analyte solution, the column was held at 100°C until the analytes eluted.
for 5 min, then the temperature was raised to 300°C at 5°C/min, and held at 300°C for 5 min. Anisole was used as an internal standard. Our GC method allowed simultaneous determination of high- and low-boiling PVC formulation components (see Figure 2).

Poly(vinyl chloride) and other polymers may contain a variety of additives, such as acid and radical scavengers, and antioxidants: for example, 4-methoxy phenol (monomethyl hydroxyl quinone ester, or MEHQ) and 3,5-di-tert-butyl-4-hydroxytoluene (butylhydroxytoluene, or BHT). We used the Supelcowax 10 capillary column and the GC conditions described above to demonstrate that our developed approach would allow separation of stabilizers from each other and from the phthalate plasticizers (see Figure 3). The BHT and MEHQ separation discussed as an example of the capabilities of the GC analysis may require less preparative work than the corresponding liquid chromatographic methods.

We successfully used our approach to find the phthalate plasticizer concentration in a variety of plasticized PVC samples, such as pellets, films, and finished parts, both developmental and commercial. We were also able to quantify the organic stabilizers and radical scavenger additives present in some PVC samples. The extraction of plasticizers from PVC by a solvent that does not dissolve PVC may be incomplete and is definitely slow. Therefore, an approach based on complete dissolution of the samples reduces the possibility of errors in quantitative analysis. The precipitation of the PVC colloid using an aqueous electrolyte solution further improved the accuracy and precision of the method. Due to its robustness, the method could be further modified and optimized for different tasks, just as we modified the method first presented by the scientists from the US Consumer Product Safety Commission. For instance, the type and amount of solvent used to dissolve PVC samples can be changed, or the thermal regime of the GC oven can be altered.

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