Phthalate esters are used extensively as plasticizers in a variety of materials, especially polyvinyl chloride, polyvinyl acetate, polystyrene, cellulose nitrate, polyamides, and polyesters. In these plastics, they serve as intermolecular lubricants to impart flexibility. The general structure of common phthalate plasticizers is shown in Figure 1.

Since plasticizers are not chemically bound to the polymer, significant migration of them into the environment is possible. The most common environmental contaminants are di-2-ethylhexyl phthalate, di-i-octyl phthalate, and di-i-decyl phthalate; less frequently encountered are diethyl phthalate, di-n-butyl phthalate, di-i-butyl phthalate, and mixed n-octyl, n-decyl phthalate.

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GC-MS is often used to characterize plasticizer contaminants at trace levels. GC-MS is a hyphenated technique—the combination of a chromatographic and spectral method. GC separates the mixture while MS (both in the electron impact [EI] and chemical ionization [CI] mode) identifies the separated volatile materials. The combination of the two methods can provide both quantitative and qualitative information about plasticizers in very complex mixtures.

Generally, EI mass spectra of phthalates lack a molecular ion. They are usually characterized by an abundant base peak at m/z 149. In addition, there are other ion(s) that distinguish phthalate structures among themselves and from other families of chemical compounds. For example, the ions indicative of mixed n-nonyl, n-heptyl phthalate are m/z 149, 247, 265, 275, and 293.

There are published reports in which structural identification of phthalates has been solely based on a single mass ion. For example, in Method 625, published by the U.S. EPA, the characteristic mass spectral fragmentation patterns of this class of compounds are rather similar to those of dialkyl phthalates. The spectra of adipates are characterized by a base peak at m/z 129.

GC-MS is used to detect phthalates in simple to very complex matrixes, including plastics. The author's group collected mass spectral data from its MS laboratory, reviewed literature, and consulted the traditional mass spectral libraries. A model 5971A GC-MSD (mass selective detector) (Hewlett-Packard, Palo Alto, CA) was used to obtain the spectra of several industrially important phthalates. Computerized data systems that included libraries of mass spectra were used to aid identification. A compilation of the most important ions that are diagnostic of the usual range of dialkyl phthalates is presented in Table 1. Some of the compounds were not available and the

![Figure 1](https://example.com/figure1.png) General structure of phthalate esters. R, R' = CₙH₂n+1; n = 4-15.
mass spectra were calculated based on the structures presented in Figure 4. Like others, the group relied upon the careful use of \( m/z \) 149 for the characterization of several phthalates. However, ions in the higher mass range were considered for the assignment of structures. Generally, the higher mass ions are of very low abundance and therefore are often overlooked. The data presented in Table 1 are intended to explain the mass fragmentation pattern of dialkyl ortho phthalates and do not explain the fragmentation pattern observed in iso- and terephthalate structures.

How to distinguish between linear and branched dialkyl phthalate

Generally, mass spectra of branched phthalates are grossly similar to those of straight-chain phthalates. Under these situations, it is recommended that reference standards of both samples be chromatographed so that characterization of branched phthalates can be based on both retention time and mass spectra. For example, mass spectra were calculated based on the structures presented in Figure 4. Like others, the group relied upon the careful use of \( m/z \) 149 for the characterization of several phthalates. However, ions in the higher mass range were considered for the assignment of structures. Generally, the higher mass ions are of very low abundance and therefore are often overlooked. The data presented in Table 1 are intended to explain the mass fragmentation pattern of dialkyl ortho phthalates and do not explain the fragmentation pattern observed in iso- and terephthalate structures.

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spectra of both di-2-ethylhexyl phthalate and di-n-octyl phthalate have common ions \( m/z = 149, 261, \) and 279; however, they elute at different retention times.

Conclusions

Many governmental, industrial, and academic institutions routinely perform GC-MS analysis of phthalates in simple to complex matrixes. This report has presented a mass spectral guide for the quick identification of dialkyl phthalates. In addition to ions of \( m/z = 149 \) for the characterization of several phthalates, low abundance ions in the higher mass range have been considered for the assignment of structures. Proper care should be exercised in the use of the guide to prevent any misidentification. For example, the molecular weight (molecular ion, \( m/z = 390 \)) of di-2-ethylhexyl and mixed n-nonyl, n-heptyl phthalate is 390; however, the ions characteristic of di-2-ethylhexyl phthalate are \( m/z = 149, 261, \) and 279, and diagnostic ions of the mixed n-nonyl, n-heptyl phthalate are \( m/z = 149, 247, 265, 275, \) and 293.

References


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