Herbicides are chemical substances that are applied to agricultural soils, gardens, lawns, or plants to destroy or to prevent the growth of undesirable vegetation. The herbicides included in this review are generally synthetic organic compounds that are ingredients in commercial herbicide products that were designated active during late 2002 in the U.S. Environmental Protection Agency’s database of registered and canceled pesticide products. The compounds are organized into 21 categories according to their general chemical structures or a common structural group. The herbicides in each category are discussed in terms of their structures, their database electron ionization mass spectra, and their amenability to separation and measurement with gas chromatography, reversed-phase liquid chromatography, and capillary electrophoresis combined with mass spectrometry. Ionization techniques that are considered here are mainly electron ionization, electrospray, and atmospheric pressure chemical ionization. Sixty-six references are provided to herbicide reviews, and to the recent herbicide analytical chemistry and mass spectrometry research literature.

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Keywords: herbicide; chemical structure; mass spectrometry; electron ionization; electrospray; atmospheric pressure chemical ionization; gas chromatography; reversed-phase liquid chromatography; capillary electrophoresis

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This review is dedicated to Professor John B. Fenn*

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*Professor Fenn received the 2002 Nobel prize in chemistry for the discovery and development of electrospray ionization and its applications to peptide and protein studies.

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I. INTRODUCTION

Herbicides are one of several subgroups of the general class of substances known as pesticides. Other pesticide subgroups are bactericides or disinfectants, fungicides, insecticides, miticides, and rodenticides. Herbicides are substances, or mixtures of substances, that are applied to agricultural soils, gardens, lawns, or plants to destroy or to prevent the growth of undesirable vegetation, typically weeds and grasses that compete with crops. Plant growth regulators, defoliants, and desiccants are considered herbicides, but fertilizers, nutrients, and other substances used to promote plant survival and health are not. Herbicides are usually synthetic organic compounds, but some naturally occurring and inorganic substances have been or are used as herbicides. In recent years, herbicides and some other pesticides have become known as agrochemicals, crop-protection chemicals, or seed-protection chemicals.

Synthetic organic compounds were introduced as herbicides during the 1930s, and during the 1940s–1970s hundreds of compounds with herbicidal activities were discovered and became ingredients in commercial products (Howe-Grant, 1995). In general, the structures of those early herbicides are fairly simple, and some of them are still important commercial products. The early herbicides usually have just one chemically functional group, they often contain two or more Cl atoms or several Br atoms, and generally their chemical names are readily interpreted in terms of structures, although common and trade names are often used for those substances. Commercial herbicides developed since the mid-1980s usually have much more complex structures. Those substances often contain acidic and basic groups; multiple F, N, O, and S atoms; few Cl or Br atoms; multiple rings including one or more heterocyclic structures; and, they often have considerable metal ion-chelating capacity. The newer herbicides also have lengthy and complex chemical names, and, therefore, common or trade names and abbreviations are widely used in the scientific and commercial literature. Chemical names are used in this article when convenient, but generally accepted common names or abbreviations are more often used. A standard practice in herbicide common names is the designation of an alkyl ester of a carboxylic acid with an –alkyl group name, for example –methyl, after the common name. Many herbicides have multiple chemical, common, and trade names, and that multiplicity can be a source of confusion in the scientific and trade literature.

There are similarities in the development of new herbicides by the agrochemical industry and in the development of new medicinal drugs by the pharmaceutical industry. In addition to the prevalence of more complex structures in both industries, many of the newer herbicides are plant-enzyme inhibitors, just as many medicinal compounds are animal-enzyme inhibitors. There is intense competition to discover new and more effective herbicides that can be used at lower application doses with fewer undesirable environmental and other side effects. As in the pharmaceutical industry, there is a fairly rapid pace of introduction of new products and cancellation of older products.

Structure determination and chemical analysis are major requirements in herbicide research, commercial herbicide development, and government regulation. Analytical capabilities are required to determine the mechanisms of herbicide action in plants, and metabolic pathways in animals and plants. Analytical skills are also required to investigate environmental transport, degradation, and fate; to measure residue concentrations in food crops; and to monitor compliance with government regulations. Although mass spectrometry was generally important in those studies, the development and exquisite refinement of capillary column gas chromatography/mass spectrometry (GC/MS) during the 1980s greatly expanded the use of MS in herbicide research, development, and regulation. Most compounds in several categories of herbicides—for example, the amides, thiocarbamates, and triazines—are amenable to GC/MS, and many compounds in other categories of herbicides—such as the phenoxy carboxylic acids—are made amenable to GC/MS by simple derivatization reactions. However, some metabolites and degradation products of those compounds are not amenable to GC/MS.

Most compounds in some other categories of herbicides—for example the quaternary ammonium salts and ureas—are not amenable to GC/MS. Similarly, many compounds in categories of herbicides developed since the mid-1980s, which often have complex structures and several functional groups, are not amenable to GC/MS. Before the development of liquid chromatography/mass spectrometry (LC/MS) instruments, mass spectrometry was important, but was not a major factor in studies of those herbicides or their metabolites and degradation products. With the development of the thermospray and particle-beam LC/MS interfaces during the 1980s, there was a rush to apply those techniques to herbicides. The atmospheric pressure chemical ionization (APCI) and electrospray LC/MS techniques have largely replaced the earlier LC/MS techniques, and have revolutionized research, development, and regulatory analyses in many categories of herbicides.

The compounds included in this review are generally those that are ingredients in commercial herbicide products that were designated active during late 2002 in the United States Environmental Protection Agency (EPA) database of registered and canceled pesticide products (http://www.epa.gov/pesticides). That and several related databases can be searched interactively through a system maintained by
the California Department of Pesticide Regulation (http://www.cdpr.ca.gov/docs/epa/epamenu.htm). Active herbicide products are those that are registered by the EPA for specific applications in the United States, and are presumed to be available from commercial sources. Only herbicide products registered by the EPA may be distributed or sold in The United States. However, not all ingredients in all active herbicide products are included because some ingredients are not herbicides, and because new products are registered frequently and older products are often canceled. As previously noted, some commercial herbicide products contain several chemical ingredients that are herbicides. Some of the compounds mentioned in this review may not be available in other countries, and other herbicide products that are not registered for use in The United States may be available in other countries.

In addition, some herbicides are included because of their former commercial or environmental importance. Some of those substances are banned in some countries or they may no longer be used, but they have been studied for many years and they, or their degradation products, may continue to be environmental contaminants. A few compounds were selected because they have reported herbicidal activities, or they are structural analogs or derivatives of herbicides, and their electron ionization (EI) mass spectra are contained in the 2002 release of The National Institute for Standards and Technology (NIST)/EPA/National Institutes of Health (NIH) mass spectral database (NIST, 2002). These criteria result in the inclusion of nearly all herbicides, or their degradation products, that are found and reported frequently in environmental monitoring surveys of air, water, or soil, or that have EPA promulgated maximum contaminant levels in drinking water in the United States (Budde, 2001).

The synthetic organic compound herbicides are organized into 21 categories according to their chemical structures or a common structural group. The definitions of some categories and the placement of some herbicides into categories are somewhat arbitrary because some compounds contain several functional groups of atoms, or contain several or more characteristic structural features. The structures of 119 of those compounds are either shown in the text or are imbedded in 12 tables.

There is a large and diverse scientific and commercial literature devoted to herbicides and, most of that information—for example, herbicide efficacy and toxicity—is beyond the scope of this review. Useful sources of additional information about herbicides include the annual editions of the Merck Index and the Farm Chemicals Handbook (Farm Chemicals). Two volumes published in 1988 and 1991, respectively contain information on the transport and fate of many herbicides in air, plants, soil, and water, but that information is limited to herbicides in use during the 1980s and before (Grover, 1988; Grover & Cessna, 1991). A summary version of this review is scheduled for inclusion in Volume 4 of The Encyclopedia of Mass Spectrometry (Nibbering, 2004).

II. SCOPE OF INFORMATION WITHIN EACH HERBICIDE CATEGORY

Reference EI spectra of many herbicides are available in computer-accessible databases, and the presence or absence of reference spectra is noted for the compounds in each category of herbicides. The reference database for this information is the 2002 release of the NIST/EPA/NIH mass spectral database for personal and instrument computers (NIST, 2002). That database contains most chemical, common, and trade names, Chemical Abstracts Service (CAS) registry numbers, and structures of herbicides whose EI spectra are in the collection. Some herbicides whose spectra are in that database are not sufficiently volatile or thermally stable for their introduction into a mass spectrometer with a conventional vapor inlet system such as a GC column or a heated reservoir. The database spectra of those compounds were probably measured after introduction with a direct insertion probe (DIP); however, neither the inlet systems used nor their temperatures are recorded in the database. The relative abundances in DIP spectra are sometimes significantly different than those in spectra of the same compounds introduced with a GC or a heated reservoir inlet. Nevertheless, the DIP EI spectra are valuable sources of information about molecular ion (M+) stabilities and fragmentation reactions that may be similar to those observed with other sample introduction and ionization techniques. Some comments about the reference EI spectra are generally made including the relative abundance ranges of the M+ ions from the compounds in each category, and the compositions of base peaks or major ions that correspond to losses of small molecules or radicals. A more complete interpretation of those spectra is available in some literature references; however, detailed fragmentation mechanisms have not been determined for some compounds.

The amenability of compounds in each category of herbicides to separation by GC, reversed-phase liquid chromatography (RPLC), or capillary electrophoresis (CE), is emphasized when that information is available or can be reasonably anticipated. Similar information about derivatives is given if those derivatives are used for chemical analyses. Those separation techniques are probably the most widely used for herbicides and their derivatives, metabolites, and degradation products in agricultural, environmental, and food laboratories. Some experimental variables of the separation techniques, for example, the pH of a RPLC mobile phase, can affect the measured mass spectra, and those variables are mentioned...
as appropriate or when information is available. However, analytical methods issues, such as efficiencies of extraction of herbicides from water, are generally not discussed but are mentioned in a few cases where the solubilities of analytes in water may dictate a particular separation or MS ionization technique. The details of sample preparation, derivatization reactions, and separation techniques are beyond the scope of this article, but references to analytical methods descriptions are provided for many herbicides.

Some comments are generally provided about the EI GC/MS, RPLC/electrospray, CE/electrospray, RPLC/APCI, or the CE/APCI spectra of compounds in each category. In contemporary use, electrospray nearly always includes pneumatic assistance, which is sometimes referred to in the scientific literature as pneumatically assisted electrospray or ion spray. Those techniques are not distinguished in this review, and electrospray is the only term used. Collision-induced dissociation (CID), also called collision-activated decomposition, is frequently used with electrospray and APCI, and the fragmentation of ions by CID is mentioned as appropriate.

Some sample introduction and ionization techniques that were widely used for herbicides for a time, but that are no longer as important or frequently used, are not considered in this review. Those techniques include pyrolysis followed by GC/MS, LC with direct liquid introduction chemical ionization, moving-belt LC/MS, particle-beam LC/MS, thermospray LC/MS, and continuous-flow fast atom bombardment or secondary ion mass spectrometry. Those techniques and their applications to herbicides and other environmental contaminants have been reviewed (Budde, 2001).

When ions in mass spectra are referenced by m/z, the m/z value is of the ion, in a cluster of ions caused by the natural distribution of isotopes, which contains the isotopes with the largest natural abundances. That ion will also be the ion in the cluster of ions with the smallest m/z value.

III. HERBICIDES BY CATEGORY

A. Aliphatic Carboxylic Acids, Esters, and Salts

Some simple aliphatic carboxylic acids have been or are used in herbicide products. Those acids include acetic acid, propanoic acid, dichloroacetic acid, trichloroacetic acid, and 2,2-dichloropropanoic acid, which has the common name dalapon. Acetic acid is used in many herbicide products, but appears mainly as the acetate counter ion of a cationic ingredient, or in an ester of a herbicide alcohol or phenol. Propanoic acid is registered as a fungicide or mold inhibitor on grains, but the herbicide applications of the three halogenated acids are either not active or canceled. Acetic and propanoic acids are sufficiently volatile for GC/MS, and their EI spectra are in the database. The three chlorinated acids have pK_a values below 3 and they are too acidic for GC/MS; however, their methyl and other esters have been widely used for GC/MS analyses (Budde, 2001). The negative-ion electrospray spectra of dichloroacetic acid, trichloroacetic acid, and some other halogenated acetic acids have been studied by direct infusion of solutions of the acids (Debre´ et al., 2000). Those spectra consist of [M-H]^- ions and the corresponding decarboxylated anions.

B. Amides, Including Chloroacetanilides

Amides, especially of chloroacetic acid and substituted anilines, have been and are popular herbicides. Table 1 contains the common names, monoisotopic masses, and structural components of some amide herbicides, including the chloroacetanilides.

Acetochlor, alachlor, butachlor, dimethenamide, metolachlor, and propachlor are amides of chloroacetic acid, and, except for dimethenamide, of aniline or substituted anilines. Other acids used to form the amides in Table 1 include propanoic acid and several substituted benzoic acids. An alkyl or alkylxyalkyl group is usually substituted for the other hydrogen of the amide nitrogen.

The NIST/EPA/NIH database contains the EI spectra of the compounds in Table 1 except dimethenamide and flufenacet. These EI spectra have M^+ ion abundances in the 7–30% range except for isoxaben and metolachlor, which do not have M^+ ions. The compounds with database EI spectra were likely introduced with a DIP; however, most spectra have many ions and base peaks at m/z that are much lower than the M^+ ion. Alachlor, butachlor, metolachlor, napropamide, pronamide, and propachlor are amenable to GC, and are evaluated target analytes in EPA GC/MS method 525.2 for multiple analytes in drinking water (Budde, 2001). Acetochlor, dimethenamide, flufenacet, and propanil are also determined by GC/MS (Natangelo et al., 1999; Zimmerman et al., 2002). Any M^+ ion abundances measured by GC/MS, however, are likely to be lower than those measured with a generally cooler DIP system. The heterocyclic ring with an N-O bond in isoxaben likely renders it susceptible to thermal decomposition during GC, and its database spectrum is unusual for this group of amides in that it has a base peak at m/z 165 and few other ions. The m/z 165 ion is probably the 2,6-dimethoxybenzoyl ion produced by cleavage of the amide bond of the M^+.

Acetochlor, alachlor, dimethenamide, and metolachlor are also determined by positive-ion electrospray LC/MS/MS (Yokley et al., 2002). The initially formed [M+H]^+ ions are converted into characteristic fragment ions in a collision cell, but the compositions of the fragment ions were not reported. The LC/MS/MS technique is especially
valuable when acetochlor and alachlor are in the same sample because they can coelute, and they have the same molecular masses, but they produce some different fragment ions. Other amide herbicides likely are amenable to LC/MS and LC/MS/MS. Amide herbicides of chloroacetic acid degrade in the environment by replacement of the Cl with an SO$_3^-$, CO$_2^-$, or a related acidic group (Ferrer, Therman, & Barceló, 1997). Those reaction products are not amenable to GC/MS without derivatization, but negative-ion electrospray LC/MS and LC/MS/MS have been applied to the determination of those degradation products (Ferrer, Therman, & Barceló, 1997; Vargo, 1998; Yokley et al., 2002).

C. Aminoacids and Derivatives

The very widely used broad spectrum herbicide glyphosate (1) is a tribasic acid that contains carboxylic acid and phosphonic acid groups. A related herbicide is the natural product phosphinothricin, which is used as a herbicide with the common name glufosinate (2). The 2002 release of the NIST/EPA/NIH mass spectral database does not include an EI spectrum of glyphosate, but a spectrum was included in the 1992 release of that database. That spectrum was removed because it contained clear signs of thermal decomposition even with the probable use of a DIP for sample introduction. The spectrum had a 10% M$^+$ ion at m/z 169 and a base peak at m/z 102; however, most of the ion abundance was distributed among various fragment ions with m/z < 83. The EI spectrum of glufosinate is not in the NIST/EPA/NIH database.

Because of the polar structures and acidic protons of 1 and 2 (Schemes 1 and 2), derivatives such as the trimethyl ester, tris(polyfluoroalkyl) esters, or others are required for EI GC/MS or GC/MS/MS determinations of those compounds. Glyphosate is determined with a combined tris(heptafluorobutyl) ester-trifluoroacetyl derivative and EI GC/MS/MS; however, other derivatives are also used (Royer et al., 2000). The major degradation product of 1 in water is aminomethylphosphonic acid, which can be similarly determined (Royer et al., 2000). The ion trap EI spectrum of the fluorinated derivative of 1 does not contain
a $M^+$ ion at m/z 811, possibly because of a mass range limitation of the ion trap; however, a $\sim 83\%$ relative abundance $[M-OC\text{H}_2\text{F}_7]^+$ ion was observed at m/z 612. The only EI spectrum of a glyphosate derivative in the NIST/EPA/NIH database is that of the tris(tert-butylmethylsilyl) triester. That spectrum contains a $\sim 10\% [M+1]^+$ ion at m/z 512, which could be a measurement or transcription error, and a base peak at m/z 454 attributable to the $[M-C\text{H}_5]^+$ ion. Nonpolar solvent and other extractions of 1 and 2 from water give poor or no recoveries because those ionic substances are very soluble, but a dual ion-exchange procedure gave very good recoveries from natural waters (Royer et al., 2000). Because of the poor extraction recoveries of 1, 2, and aminomethylphosphonic acid from water, and the complexities and limitations of derivative formation, GC/MS or GC/MS/MS have not been the preferred analytical procedures for those herbicides.

Compounds 1 and 2 are not amenable to separation with RPLC, and, therefore, derivatives, usually designed for fluorescence detection, are used for those separations. One derivative prepared from 9-fluorenylmethyl chloroformate is used with negative-ion electrospray LC/MS/MS to determine 1, 2, and aminomethylphosphonic acid from water (Vreeken et al., 1998). That procedure has been improved with an isotopically labeled glyphosate internal standard and several other modifications (Lee et al., 2002). The separation of 1 and aminomethylphosphonic acid without derivatization has been accomplished on an anion-exchange column (Bauer et al., 1999). A suppressor is used after the column and before the electrospray interface to exchange sample background and mobile phase cations—for example, Na$^+$ and Ca$^{2+}$—for hydrogen ions. Although the detection limits of the [M-H]$^-$ ions from both analytes are low, retention times are long and the chromatographic peaks are broad.

**D. Benzoic and Phthalic Acids, Esters, and Salts**

Substituted benzoic and phthalic acids have been used as herbicides for many years, but only a few compounds in this category are used in active products. Dicamba (3) (Scheme 3) or 2-methoxy-3,6-dichlorobenzoic acid is used in many products in the form of the free acid, an ester, or one of several salts. Dacthal (4) (Scheme 4) or dimethyl tetrachloroterphthalate is used in some active products. Endothal (5) (Scheme 5) is used in a few active products, and is derived from phthalic acid by hydrogenation of the benzene ring and oxygenation to form the oxygen-bridged bicyclic structure. Esters of 3 and 5 may be used in some herbicide formulations, but those esters, including 4, may be readily hydrolyzed in soils to the free acids or anions depending on the soil pH.

The EI spectra of 3–5 are in the NIST/EPA/NIH database as are the spectra of the methyl esters of 3 and 5. Although the spectrum of 3 has a $80\% M^+$ ion, the spectrum of 5 does not have a $M^+$ ion because of a probable decarboxylation in the DIP inlet system. The EI mass spectra of 4 and the methyl esters of 3 and 5 are also in the database, and the spectra of 4 and the methyl ester of 3 have $M^+$ ions in the 20–30% range. However, the EI spectrum of the dimethyl ester of 5 does not have a $M^+$ ion, and the base peak at m/z 155 corresponds to loss of OCH$_3$ plus CO from the $M^+$ ion. The free acids 3 and 5 are unsuitable for separation by GC because of thermal decomposition at typical GC operating temperatures, and because of strong interactions between the acids and surfaces or basic sites in injection-port liners and standard GC columns. Dacthal and the methyl esters of 3 and 5 are amenable to separation by GC, and those derivatives are often used in GC-based analytical methods for the herbicides after solvent extraction and conversion of the free acids into the esters.

Carboxylic acids are amenable to separation by RPLC, but an acidic mobile phase is used to suppress ionization in the aqueous solution and to facilitate the separation on a non-polar column (Crescenzi et al., 1995). However, 3 and some other carboxylic acids do not produce abundant positive ions with electrospray or APCI (Crescenzi et al., 1995; Thurman et al., 2001). On the other hand, abundant [M-H]$^-$ ions are formed from some acids during electrospray of slightly acidic mobile phases (Crescenzi et al., 1995; Thurman et al., 2001). Alternatively, the CE separation of negative ions at a pH of ca. 10 followed by negative-ion electrospray can be used for the determination of
carboxylic acids and acidic phenols (Song & Budde, 1998). In general, the \([\text{M-}H]^-\) ions are stable, but decarboxylation to \([\text{M-H-CO}_2]^-\) ions is observed depending on the analyte and on whether conditions that favor CID are present in the electrospray interface. Eight other categories of herbicides include compounds with either carboxylic acid or readily hydrolyzed ester groups, and the general characteristics of those herbicides are often similar to those of the compounds in this category.

E. Benzonitriles

Substituted benzonitriles have been used as herbicides for many years and Dichlobenil (6), or 2,6-dichlorobenzonitrile, and bromoxynil (7), or 3,5-dibromo-4-hydroxybenzonitrile, are ingredients in some active herbicide products. The EI spectra of 6 and 7 (Schemes 6 and 7) are in the NIST/EPA/NIH database, and both spectra have base peak \(\text{M}^+\) ions and no other abundant ions with \(m/z > 88\). Compounds 6 and 7 are amenable to separation by GC, but broad and possibly tailing peaks are likely for the acidic phenol 7. Esters of 7 with n-heptanoic and n-octanoic acids are ingredients in many active herbicide products, but the ester with n-butanoic acid is banned by the EPA in the United States (http://www.epa.gov/oppfead1/international/piclist.htm). Those esters are probably amenable to GC separation, and the EI spectra of the esters of 7 with n-octanoic and n-butanoic acids are in the NIST/EPA/NIH database. The ester of 7 with n-octanoic acid has a molecular mass of 401, but its EI spectrum has no \(\text{M}^+\) ion at \(m/z > 127\), and no significant \(\text{Br}_2^-\) containing ions with a relative abundance >5%. The spectrum of the ester with n-butanoic acid has a 5% \(\text{M}^+\) ion and several fragment ions with \(m/z > 245\) that are \(\text{Br}_2\) ions.

F. Cyclohexanediones

The cyclohexane-1,3-dione herbicides were introduced during the late 1990s, and their structures are often shown as the tautomeric hydroxycyclohexeneones. The common names, monoisotopic masses, and structural components of four representative cyclohexanedione herbicides are shown in Table 2. Among those relatively new compounds, only tralkoxydim has an EI spectrum in the NIST/EPA/NIH database. That spectrum does not have a \(\text{M}^+\) ion at \(m/z 329\), and the only abundant ion with an \(m/z\) greater than the base peak at \(m/z 137\) is a 24% relative abundance ion at \(m/z 283\). The instability of the tralkoxydim \(\text{M}^+\) ion, even with the probable introduction of the substance with a DIP, suggests that compounds in this category are not likely amenable to GC. The structures do suggest that those herbicides can be separated on a RPLC column, and clethodim and sethoxydim have been partially separated on a C-8 RPLC column with electrospray detection of their \([\text{M+H}]^+\) ions (Marek et al., 2000). In addition to the base peak \([\text{M+H}]^+\) ions, several abundant fragments were observed when the interface conditions were optimized for CID. Sethoxydim also gives abundant \([\text{M-H}]^-\) ions and several fragment ions with APCI (Hu et al., 1999).

G. Dinitrophenylamines (Dinitroanilines)

Table 3 contains the common names, monoisotopic masses, and structural components of some dinitrophenylamines, or dinitroanilines that are ingredients in hundreds of active

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Monoisotopic Mass</th>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clethodim</td>
<td>359</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesotrine</td>
<td>339</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sethoxydim</td>
<td>327</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tralkoxydim</td>
<td>329</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TABLE 2. Common Names, Monoisotopic Masses, and Structural Components of Some Cyclohexanedione Herbicides
herbicide products. The EI spectra of the compounds in Table 3 and the spectra of many other compounds with similar structures are in the NIST/EPA/NIH database. The many analogous compounds are usually tertiary or secondary amines, and some of them may have been used in commercial herbicide products that are no longer active in The United States. The relative abundances of the $M^+$ ions in the EI spectra of the compounds in Table 3 are in the range of 5–10%, even with the probable use of a DIP for sample introduction. Those spectra nearly always have base peaks that correspond to the loss of a small alkyl radical from the $M^+$ ion by alpha-cleavage as shown for the widely used herbicide trifluralin (Structure 1).

Compounds in this category are amenable to GC/MS (Stemmler & Hites, 1987); however, with the typical temperature conditions that are required for GC, $M^+$ ions probably will not be observed in the EI spectra of most compounds. With electron-capture ionization GC/MS, however, $M^+$ ions are the base peaks, and only a few low-abundance fragment ions are observed (Stemmler & Hites, 1987).

**H. Diphenyl Ethers**

The herbicides in this category have a 2-chlorodiphenyl ether nucleus in common, and most also have nitro and trifluoromethyl substituents. The common names, monoisotopic masses, and structural components of some diphenyl ether herbicides are shown in Table 4. Those compounds are ingredients in some active herbicide products with the exception of nitrofen, which is banned by the EPA in the United States (http://www.epa.gov/oppfead1/international/piclist.htm). Acifluorfen is often discussed with other aromatic carboxylic acids, but it is

**TABLE 3. Common Names, Monoisotopic Masses, and Structural Components of Some Dinitrophenylamine (Dinitroaniline) Herbicides**

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Monoisotopic Mass</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benfentan</td>
<td>335</td>
<td>-CF₂</td>
<td>-CH₃</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>Butralin</td>
<td>295</td>
<td>-CH₃</td>
<td>H</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>Ethalfluralin</td>
<td>333</td>
<td>-CF₂</td>
<td>-CH₃</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>Oryzalin</td>
<td>346</td>
<td>-O⁻</td>
<td>H</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>Pendimethalin</td>
<td>281</td>
<td>-CH₃</td>
<td>H</td>
<td>H</td>
<td>-CH₃</td>
</tr>
<tr>
<td>Trifluralin</td>
<td>335</td>
<td>-CF₂</td>
<td>H</td>
<td>H</td>
<td>-H</td>
</tr>
</tbody>
</table>

**TABLE 4. Common Names, Monoisotopic Masses, and Structural Components of Some Diphenyl Ether Herbicides**

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Monoisotopic Mass</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Acifluorfen</td>
<td>361</td>
<td>-CF₂</td>
<td>-COOH</td>
<td>-NO₂</td>
<td></td>
</tr>
<tr>
<td>Diclofenac</td>
<td>340</td>
<td>-Cl</td>
<td>H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fomesafen</td>
<td>348</td>
<td>-CF₂</td>
<td>H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lactiflorin</td>
<td>461</td>
<td>-CF₂</td>
<td>H</td>
<td>-CH₃</td>
<td>-NO₂</td>
</tr>
<tr>
<td>Nitrofen</td>
<td>283</td>
<td>-Cl</td>
<td>H</td>
<td>-NO₂</td>
<td></td>
</tr>
<tr>
<td>Oxyfluorfen</td>
<td>361</td>
<td>-CF₂</td>
<td>-OC₂H₅</td>
<td>-NO₂</td>
<td></td>
</tr>
</tbody>
</table>
included in this category because it has the 2-chlorodiphenyl ether structure. General comments about carboxylic acids in sections D and L also apply to acifluorfen.

With the exceptions of fomesafen and lactofen, the 2-chlorodiphenyl ethers in Table 4 have EI spectra in the NIST/EPA/NIH database. Even though those spectra were likely obtained with DIP sample introduction, the spectrum of acifluorfen does not have a $M^+$ ion, but a base peak at $m/z$ 317 that is caused by either thermal decarboxylation or the loss of CO$_2$ from the unstable $M^+$ ion. Diclofop-methyl, nitrofen, and oxyfluorfen have $M^+$ ions in the 35–100% range, and it is reasonable to expect that fomesafen and lactofen would behave similarly with DIP introduction.

Oxyfluorfen is amenable to GC separation (Wong et al., 2003), and nitrofen, with a similar structure, should have favorable properties for GC. The esters diclofop-methyl and lactofen may be amenable to GC separation, but the acid acifluorfen and the sulfonamide fomesafen require derivatization for GC. The EI spectra of the methyl ester of acifluorfen and the N-methyl derivative of fomesafen are not in the NIST/EPA/NIH database.

The compounds in Table 4 are amenable to RPLC separation (Laganà et al., 2000). Acifluorfen and fomesafen were separated on a C-18 column, with a slightly acidic mobile phase, followed by electrospray to give [M-H]$^-$ ions. Lactofen and oxyfluorfen were also separated on a C-18 column, but without acid in the mobile phase. For the latter compounds, APCI provided abundant [M-H]$^-$ ions. The [M-H]$^-$ ions from both ionization techniques were subjected to CID, and the more-abundant and higher-$m/z$ fragment ions observed are caused by losses of substituent groups from the diphenyl ether nucleus. Acifluorfen can also be separated by CE, and the base peak with electrospray is either the [M-H]$^-$ or the [M-CO$_2$H]$^-$ ion depending on whether interface conditions minimize or favor CID (Song & Budde, 1998; Rodriguez, Mañes, & Picó, 2003). The ester diclofop-methyl is considered in section L because it is readily hydrolyzed in the environment to a phenoxy carboxylic acid.

### I. Imidazolinones

Imidazole ($C_3H_4N_2$) is a five-member aromatic ring that contains two nonadjacent N atoms. Imidazolinones have an imidazole ring in which one of the adjacent CH groups is replaced by a C=O with the loss of one ring double bond. Table 5 contains the common names, monoisotopic masses, and structural components of some substituted imidazolinones that are ingredients in many active herbicide products. The four carboxylic acids in Table 5, which are used as either the free acids or salts, do not have EI spectra in the NIST/EPA/NIH database. However, the EI spectrum of the ester imazamethabenz-methyl, which is a mixture of two isomers as shown in Table 5, is in the database, and it has a 7% $M^+$ ion. The low abundance of the $M^+$ ion, even with the likely use of a DIP for sample introduction, suggests either thermal decomposition or an unstable $M^+$ ion.

There is evidence for thermal decomposition of imazamethabenz-methyl during GC/MS (Atienza et al., 1996), but when its ring N-H is converted to a N-CH$_3$, a derivative that is apparently amenable to GC/MS is produced (Anisuzzaman et al., 2000). However, the EI GC/MS spectra of the separated isomers of imazamethabenz-methyl have <10% abundant $M^+$ ions. Dimethyl derivatives of the four acids in Table 5 are also amenable to GC/ MS (Anisuzzaman et al., 2000); the spectrum of the dimethyl derivative of imazapyr is in the NIST/EPA/NIH database, and it has a 10% $M^+$ ion. With electron-capture ionization GC/MS, the dimethyl derivative of imazethapyr gives an abundant and singular $M^-$ ion (Stout, daCunha, & Allardice, 1996), and the dimethyl derivatives of the other acids should behave similarly.

### Table 5. Common Names, Monoisotopic Masses, and Structural Components of Some Imidazolinone Herbicides

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Monoisotopic Mass</th>
<th>Structural Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imazamethabenz-methyl</td>
<td>289</td>
<td><img src="image" alt="Imazamethabenz-methyl" /></td>
</tr>
<tr>
<td>Imazamox</td>
<td>305</td>
<td><img src="image" alt="Imazamox" /></td>
</tr>
<tr>
<td>Imazapyr</td>
<td>261</td>
<td><img src="image" alt="Imazapyr" /></td>
</tr>
<tr>
<td>Imazaquin</td>
<td>311</td>
<td><img src="image" alt="Imazaquin" /></td>
</tr>
<tr>
<td>Imazethapyr</td>
<td>289</td>
<td><img src="image" alt="Imazethapyr" /></td>
</tr>
</tbody>
</table>
The imidazolinone herbicides are amenable to separation by RPLC on C-8 and C-18 columns with slightly acidic mobile phases (Stout et al., 1996a,b; Stout, daCunha, & Safarpour, 1997; Rodriguez & Orescan, 1998; Krynitsky et al., 1999). In contrast to other carboxylic acids that are generally best detected as [M-H]− ions (sections D and L), the slightly basic N atoms in the imidazolinone herbicides favor the formation of abundant [M+H]+ ions with electrospray. Generally, few or no other ions are observed unless the ion source is optimized for CID, or a collision cell and a tandem instrument is used. With CID, fragment ions in the 10–50% relative abundance range are observed (Stout et al., 1996a; Rodriguez & Orescan, 1998; Krynitsky et al., 1999). The electrospray RPLC/MS technique probably is the favored choice for analyses of water, soil, and plant tissue extracts (Stout et al., 1996a,b; Stout, daCunha, & Safarpour, 1997; Rodriguez & Orescan, 1998; Krynitsky et al., 1999).

J. Miscellaneous Heterocyclics

Isoxazole (C₃H₃NO) is a five-member unsaturated ring that contains an N-O bond. That ring structure is present in several compounds that are ingredients in active herbicide products—for example, the amide isoxaben in Table 1. Isoxaflutole (8) (Scheme 8) has an isoxazole ring, but in the environment the N-O bond opens to give the diketonic nitrile (9) (Scheme 9) that is the active plant enzyme inhibitor and the substance likely to be found in water, soil, or plant tissue samples (Taylor-Lovell, Sims, & Wax, 2002). The NIST/EPA/NIH database does not have an EI spectrum of 8 or 9; however, those compounds were separated on a C-18 RPLC column with a slightly acidic mobile phase, and they were detected as their [M-H]− ions with electrospray (Lin et al., 2002). No other ions were reported in that study.

An herbicide with a five-member heterocyclic structure similar to isoxazole is dimethazone (10) (Scheme 10), which has an EI spectrum in the NIST/EPA/NIH database. The spectrum does not have a M+ ion, but it has a 67% [M-Cl]⁺ ion at m/z 204, and the base peak at m/z 125 is the chlorotropylium ion. The instability of the M+ ion suggests that 10 may be subject to thermal decomposition in a GC injection port or column oven; however, like many compounds with one or more mildly basic nitrogens, it should be separable on a RPLC column and should give [M+H]+ ions with electrospray and APCI.

Another heterocyclic nitrogen compound is flumioxazin (11) (Scheme 11). This substance is an ingredient in several active herbicide products, but its EI spectrum is not in the NIST/EPA/NIH database. The complexity of the structure and the molecular mass of 354 suggests that 11 may be subject to thermal decomposition in a GC injection port or column oven, but that it should be separable on a RPLC column and should give [M+H]+ ions with electrospray and APCI.

The compound oxadiazon (12) (Scheme 12) is an ingredient in some active herbicide products. The EI spectrum of oxadiazon in Figure 1 has a 17% M+ ion at m/z 344, and abundant Cl₂-containing fragment ions at m/z 302, 258, and 175. Despite a structure with a heterocyclic ring that contains a N-N bond that suggests thermal instability, 12 is amenable to separation by GC; the major fragment ions at m/z 302, 258, and 175 are also present in the GC/MS EI spectra (Tanabe et al., 1996; Wong et al., 2003). The m/z 302 ion is likely the odd-electron [M-C₃H₆]⁺ ion, the m/z
258 ion is probably the odd-electron [M-C₃H₆-CO₂]⁺, and the m/z 175 ion may be the residual aromatic ring with Cl₂, OH, and N substituents. Oxadiazon should also be separable on a RPLC column, and it is reasonable to expect that it will give abundant [M+H]⁺ ions with electrospray and APCI.

K. Phenols

Only phenols derived from hydroxybenzene by substitution of one or more hydrogens with another atom or group of atoms are considered in this section. Hydroxybenzene derivatives were used as herbicides for many years, but most, if not all, are no longer commercial products, and some have been banned by the EPA in the United States (http://www.epa.gov/oppead1/international/piclist.htm). The herbicide dinoseb, which is banned, is 2,4-dinitrophenol with a sec-butyl group substituted for an H adjacent to the hydroxyl group. Dinoseb salts and dinitrocresols, which were introduced as herbicides during the early 1930s (Howe-Grant, 1995), are also banned in the United States. The phenol bromoxynil is discussed in section E, but the comments in this section also apply to that acidic compound. Phenols, especially the di- and trichlorophenols, are degradation products of some herbicides in other categories—for example, the phenoxy carboxylic acids in section L.

Substituted hydroxybenzenes are amenable to GC/MS (Budde, 2001), and their EI mass spectra are in the NIST/EPA/NIH database. The phenols that are or were used as herbicides have multiple, strongly electron-withdrawing groups, and they are among the most acidic of phenols, with pKₐ values in the 4–5 range. Those compounds often give broad and tailing GC peaks because of interactions of the analytes with basic sites in injection port liners and GC columns, and, therefore, they have higher GC/MS detection limits than most phenols. The most acidic phenols are also determined with LC/MS or CE/MS, and with GC/MS after conversion to their GC-amenable methyl ethers or other volatile ethers or esters.

Two dinitrocresol herbicides were separated from a variety of nitro- and chlorophenols on a C-18 RPLC column with a slightly acidic mobile phase (Puig et al., 1997). Mainly, [M-H]⁻ ions were formed with APCI, but [M-H-NO]⁻, [M-H-NO₂]⁻, and other fragment ions were formed when the ion-source conditions were optimized for CID. Dinoseb was included in a similar study with RPLC/APCI/MS, and abundant [M-H]⁻ ions were observed (Hu et al., 1999). The dinoseb [M-H-NO]⁻ and [M-H-NO₂]⁻ fragment ions were also produced with ion-source...
conditions that favored CID. Dinoseb was among a few acidic phenols and some carboxylic acids studied by CE/electrospray/MS; however, under the conditions used, only the \([\text{M-H}]^-\) ion of dinoseb was observed (Song & Budde, 1998).

**L. Phenoxyacarboxylic Acids, Esters, and Salts**

Phenoxyacarboxylic acids were introduced as herbicides during the 1940s (Howe-Grant, 1995), and 2,4-dichlorophenoxyacetic acid (2,4-D) is still among the most widely used. Table 6 contains the common names or abbreviations, monoisotopic masses, and structural components of some of those acids. That group of compounds is designated the traditional phenoxyacarboxylic acids, and they are used as free acids, esters, and salts; however, the esters may be fairly rapidly hydrolyzed depending on soil pH and other conditions. The compounds 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and 2-(2,4,5-trichlorophenoxy)propanoic acid (sylvex) in Table 6 are banned by the EPA in the United States (http://www.epa.gov/oppfed1/international/piclist.htm). The other compounds in Table 6 are ingredients in many active herbicide products, and they are characterized by just one or two Cl atoms, and sometimes a CH₃ group, substituted for a H on the phenyl rings.

The EI spectra of the free acids in Table 6 are in the NIST/EPA/NIH database, and those compounds were very likely introduced with a DIP because they are too nonvolatile and thermally unstable for a GC or a heated-reservoir inlet. The database spectra usually have M⁺ ions in the 35–80% relative abundance range, although three are in the 5–15% range. The base peaks contain all the Cl atoms of the molecules; generally, they are even-mass ions formed by cleavage of the bond between the ether oxygen and the first carbon of the acid group, with a transfer of a H atom to the aromatic ring that has the positive charge. The methyl esters of those acids, and sometimes other esters, are used for GC/MS determinations of this group of herbicides (Budde, 2001). The EI spectra of the methyl esters of the compounds in Table 6 are in the NIST/EPA/NIH database, and, except for the two butanoic acid esters, have M⁺ ions in the 30–80% relative abundance range. When the esters are used as herbicides, they may, depending on soil conditions, persist in a sample, and can be directly determined by GC/MS. However, analytical methods generally specify a strong base hydrolysis of any residual esters before conversion of the acids to methyl esters for GC/MS (Budde, 2001).

The traditional phenoxyacarboxylic acids are amenable to separation with RPLC and CE, and the results are very similar to those described for the acids in section D. In an acidic mobile phase, abundant positive ions are not produced with electrospray or APCI (Crescenzi et al., 1995; Hu et al., 1999; Thurman et al., 2001). However, those acids give relatively abundant [M-H]⁻ ions with electrospray and APCI, and relatively abundant fragment ions are also observed with APCI (Hu et al., 1999). The fragment ions result from cleavage of the bond between the ether oxygen and the first carbon of the acid group with retention of the negative charge on the fragment that contains the aromatic ring. The acid anions can also be separated by CE at a pH of ca. 10 followed by negative-ion electrospray (Song & Budde, 1998). The [M-H]⁻ ions are the base peaks with CE, but the same fragment ions obtained with APCI are observed with CE/electrospray when conditions that favor CID are present in the interface.

Table 7 contains the common names, monoisotopic masses, and structural components of some herbicides that are phenoxypropanoic acid esters. Those compounds are more recently developed herbicides whose structures are more complex than the structures of the compounds in Table 6. Although the compounds in Table 7 are either devoid of Cl or contain only a single Cl atom, they each have two ether linkages, and a heterocyclic ring system similar to those found in several other categories of herbicides, and they are all esters that are generally rapidly hydrolyzed depending on soil pH and other conditions. The structural differences in the two groups of related herbicides in Tables 6 and 7 affect their chromatographic separation and their mass spectra.

With the exception of clodinafop-propargyl, the EI spectra of the esters in Table 7 are in the NIST/EPA/NIH

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**TABLE 6.** Common Names, Monoisotopic Masses, and Structural Components of Some Phenoxyacarboxylic Acid Herbicides

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Monoisotopic Mass</th>
<th>R</th>
<th>n</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-D</td>
<td>220</td>
<td>-H</td>
<td>0</td>
<td>-Cl</td>
<td>-Cl</td>
<td>-H</td>
</tr>
<tr>
<td>MCPA</td>
<td>200</td>
<td>-H</td>
<td>0</td>
<td>-CH₃</td>
<td>-Cl</td>
<td>-H</td>
</tr>
<tr>
<td>2,4,5-T</td>
<td>254</td>
<td>-H</td>
<td>0</td>
<td>-Cl</td>
<td>-Cl</td>
<td>-Cl</td>
</tr>
<tr>
<td>Dichlorprop</td>
<td>234</td>
<td>-CH₃</td>
<td>0</td>
<td>-Cl</td>
<td>-Cl</td>
<td>-H</td>
</tr>
<tr>
<td>Mecoprop</td>
<td>214</td>
<td>-CH₃</td>
<td>0</td>
<td>-CH₃</td>
<td>-Cl</td>
<td>-H</td>
</tr>
<tr>
<td>Silvex</td>
<td>268</td>
<td>-CH₃</td>
<td>0</td>
<td>-Cl</td>
<td>-Cl</td>
<td>-Cl</td>
</tr>
<tr>
<td>2,4-DB</td>
<td>248</td>
<td>-H</td>
<td>2</td>
<td>-Cl</td>
<td>-Cl</td>
<td>-H</td>
</tr>
<tr>
<td>MCPB</td>
<td>228</td>
<td>-H</td>
<td>2</td>
<td>-CH₃</td>
<td>-Cl</td>
<td>-H</td>
</tr>
</tbody>
</table>
TABLE 7. Common Names, Monoisotopic Masses, and Structural Components of Some Herbicides That Are Esters of 4-Aryloxyphenoxypropanoic Acid

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Monoisotopic Mass</th>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clodinafop-propargyl</td>
<td>350</td>
<td>C3H4N2O</td>
<td></td>
</tr>
<tr>
<td>Fenoxaprop-ethyl</td>
<td>361</td>
<td>C3H4O</td>
<td></td>
</tr>
<tr>
<td>Fluazifop-butyl</td>
<td>363</td>
<td>F3C3H4O</td>
<td></td>
</tr>
<tr>
<td>Quizalofop-ethyl</td>
<td>372</td>
<td>C3H4O</td>
<td></td>
</tr>
</tbody>
</table>

M. Pyridines

Herbicides in this category are pyridines with at least three and often four or five hydrogens replaced by another atom or a group of atoms. Some other categories of herbicides that are defined by a different common structural feature also have compounds with pyridyl groups. Table 8 contains the common names, monoisotopic masses, and structural components of six pyridine herbicides that are ingredients in active herbicide products. All of the compounds in Table 8 are carboxylic acids, esters, or a thioester and, like the carboxylic acids described in other categories, some are used as salts. The esters may be rapidly hydrolyzed in the environment, depending on soil pH and other conditions.

The EI spectra of the similar carboxylic acids clopyralid, picloram, and triclopyr are in the NIST/EPA/NIH database. The spectrum of clopyralid does not have a $M^+$ ion, but the spectra of the other two acids have $M^+$ ions in the 30–45% relative abundance range. Those spectra were likely measured with DIP sample introduction, and the base peaks of the acids correspond to either decarboxylation, or the loss of the oxacyclic acid group in triclopyr, which could occur before or after ionization. Spectra of the...
other compounds in Table 8 are not in the NIST/EPA/NIH database.

Although the three carboxylic acids are not amenable to separation by GC, their methyl esters are, and derivatization has been the standard technique for the determination of those herbicides (Budde, 2001). The EI spectra of the three methyl esters are in the NIST/EPA/NIH database, and all have M⁺ ions in the 20–30% range and several fragment ions that facilitate the identification of the analytes. The herbicide esters and thioester in Table 8 do not have EI spectra in the NIST/EPA/NIH database, but two of them, dithiopyr and thiazopyr, are amenable to GC/MS (Tanabe et al., 1996; Pérez, Sánchez-Brunete, & Tadeo, 1997). Both compounds have M⁺ ions and several abundant fragment ions in their EI spectra. Fluroxypyr is the ester of a C₈ alcohol, and it may be amenable to GC; however, it may also be readily hydrolyzed in the environment, and may be amenable to determination as the methyl ester. However, the spectrum of the methyl ester is not in the NIST/EPA/NIH database.

All the compounds in Table 8, either as the free acids or esters, should be amenable to separation by RPLC and detection with electrospray and APCI. Clopyralid and picloram were separated on a C-18 column, and with electrospray clopyralid gave a [M-H]⁻ ion base peak (Crescenzi et al., 1999). With the electrospray conditions used, picloram gave a 70% relative abundance [M-H]⁻ ion and a [M-CO₂-H]⁻ ion base peak. Picloram was among the acids separated as anions by CE and detected with negative-ion electrospray (Song & Budde, 1998; Rodriguez, Mañes, & Picó, 2003). Depending on the conditions in the ion source, either the [M-H]⁻ ion or the [M-CO₂-H]⁻ ion was the base peak.

Fluridone (13) (Scheme 13) is an ingredient in some active herbicide products, and it has a pyridinone ring that is derived from pyridine. The EI spectrum of fluridone is in the NIST/EPA/NIH database, and has a 45% relative abundance M⁺ ion, a base peak [M-H]⁻ ion, and few other ions. Fluridone is amenable to separation by GC/MS, and it is an evaluated target analyte in EPA GC/MS method 525.2 for multiple analytes in drinking water (Budde, 2001).

### N. Pyridazines

Pyridazine is a six-member aromatic ring that contains two adjacent N atoms, and some herbicides with this structure, or a closely related structural group, are categorized as pyridazines. A few compounds with pyridazyl groups are also present in some other categories of herbicides that are defined by a different common structural feature. The compounds fluthiacet-methyl (14), norflurazon (15), pyrazon (16), and pyridate (17) (Schemes 14–17) either have a pyridazine ring or a closely related structure, and they are ingredients in some active herbicide products.

The EI spectrum of 14, which is a relatively new herbicide, is not in the NIST/EPA/NIH database; however, this compound may be sufficiently thermally stable for DIP introduction and possibly be amenable to GC/MS. The EI spectrum of 15 is in the NIST/EPA/NIH database, and it has a base peak M⁺ ion and abundant fragment ions that correspond to the [F₃C-C₆H₄N₂]⁺ and the [F₃C-C₆H₄]⁺ ions. It is amenable to separation by GC/MS, and it is an evaluated target analyte in EPA GC/MS method 525.2 for multiple analytes in drinking water (Budde, 2001). The EI spectrum of 16 from the NIST/EPA/NIH database is shown in Figure 2. Three ions from the EI GC/MS spectrum of 16 have been reported, and the relative abundances of the three ions suggest that the complete EI GC/MS spectrum may be very similar to the database spectrum (Lacorte et al., 2000). The three GC/MS ions are a 71% M⁺ ion at m/z 221, a 25% ion at m/z 105 that is not likely the reported [M-C₈H₆N]⁺, and a base peak [C₆H₅]⁺ ion. The EI spectrum

---

**SCHEME 13.**

**SCHEMES 14, 15, 16 and 17.**
of 17 is in the NIST/EPA/NIH database; it does not have a M\(^+\) ion at \(m/z\) 378, and the only abundant higher \(m/z\) ions are a cluster at \(m/z\) 205–209. Those ions appear to be caused by cleavage of the side chain at the bond that connects the carbonyl group and the phenolic oxygen to give the [M-C\(_9\)H\(_7\)OS]\(^+\) ion, and related ions caused by the \(^{37}\)Cl isotope and ions that are formed with hydrogen rearrangement to the aromatic system. This compound was likely introduced with a DIP, and the instability of the M\(^+\) suggests that it may not be amenable to GC/MS. Compounds 14–17, like most compounds with one or more mildly basic nitrogens, should be separable by RPLC and should give abundant [M+H]\(^+\) ions with electrospray and APCI.

O. Quaternary Ammonium Salts

Quaternary ammonium salts have one or more N atoms that have all five valence electrons engaged in single or multiple bonds with other atoms. Therefore, each quaternary N carries a formal positive charge. Diquat (18), difenzoquat (19), and paraquat (20) (Schemes 18–20) are quaternary ammonium salts that are ingredients in some active herbicide products. Diquat and paraquat are often called bipyridiniums, and they were introduced as herbicides during the early 1960s (Howe-Grant, 1995). Both compounds are doubly charged cations that are usually associated with bromide and chloride counter ions, respectively. Difenzoquat, which contains a pyrazole heterocyclic structure, usually has a methyl sulfate counter-ion.

The EI spectra of 18 and 19 are not in the NIST/EPA/NIH database, but the spectrum of 20 is in the collection,

![SCHEMES 18, 19 and 20.](image-url)
and it was very likely measured with a DIP for sample introduction. The spectrum of 20 does not have a M$^+$ ion at m/z 93, but it has a singly charged base peak at m/z 156, and low-abundance singly charged ions at m/z 171 and at the molecular mass 186. The base peak is probably caused by double thermal demethylation of 20, the m/z 171 ion by a single demethylation of 20, and the m/z 186 ion by reduction of 20 by an electron, an anion, or some other reducing agent in the sample.

Those quaternary ammonium cations, which are not volatile without decomposition, are not amenable to separation by GC; however, they can be separated by CE or ion-pair RPLC, and determined with electrospray and mass spectrometry. The dications 18 and 20 were separated in 10 min with CE (Song & Budde, 1996; Núñez, Moyano, & Galceran, 2002). Depending on the conditions in the electrospray interface and in the acidic electrolyte solution, the base peaks are the M$^{2+}$ ions at m/z 92 and 93, respectively (Song & Budde, 1996), the [M$^{2+}$+H$^+$]$^+$ ions at m/z 183 and 185 (Song & Budde, 1996), or the singly charged ions at the molecular masses 184 and 186 (Núñez, Moyano, & Galceran, 2002). Collision-induced dissociation was used to investigate the fragmentation of the m/z 184, 249, and 186 ions of 18–20, respectively (Núñez, Moyano, & Galceran, 2002).

The RPLC separation of those cations is accomplished with C-1, C-3, or C-8 silica columns, and a mobile phase that contains trifluoroacetic or heptafluorobutanoic acid (Taguchi et al., 1998; Castro, Moyano, & Galceran, 2001; Grey, Nguyen, & Yang, 2002). The trifluoroacetate (TFA) and heptafluorobutanoate anions and analyte cations form ion pairs that facilitate separation on the RPLC columns. Some ion-pairs—for example, [M$^{2+}$+TFA$^-$]$^+$—may persist after electrospray, but their concentrations can be reduced by the post-column addition of weaker and less volatile organic acids—for example, propanoic acid, and aliphatic alcohols (Taguchi et al., 1998; Castro, Moyano, & Galceran, 2001). In addition to the ion pairs, the ions observed with CE/electrospray are also observed with RPLC, and the fragmentation of some ions has been studied by CID (Castro, Moyano, & Galceran, 2001).

P. Sulfonylureas

The sulfonylureas are a category of herbicides developed since the mid-1980s. Table 9 contains the common names, monoisotopic masses, and structural components of 14 sulfonylurea herbicides that are ingredients in active herbicide products. The herbicide tribenuron-methyl, which is not in Table 9, is a N-methyl derivative of metsulfuron-methyl. The NIST/EPA/NIH database contains the EI spectra of only two of the 14 sulfonylureas in Table 9 and both compounds were likely introduced with a DIP. The EI spectra of chlorsulfuron and sulfometuron-methyl do not have M$^+$ ions, and their most abundant ions are generally at m/z values that indicate substantial fragmentation. The sulfonylureas are polar and generally thermally unstable at typical GC injection port and column temperatures.

When the two mildly acidic urea H atoms are replaced by CH$_3$, more volatile and stable derivatives are produced; some of those derivatives are amenable to separation of GC (Klaffenbach & Holland, 1993). That derivatization reaction is complicated by the tautomeric equilibrium that allows the formation of bis(N-methyl) and N-methyl-O-methyl derivatives that are separable by GC and that have slightly different mass spectra. Among the compounds in Table 9 (Structure 2) the N,N-dimethyl derivatives of chlorimuron-ethyl, chlorosulfuron, primisulfuron-methyl, and triasulfuron were separated by GC, and their EI and positive-ion chemical ionization (isobutane) spectra were measured (Klaffenbach & Holland, 1993). The EI spectra do not have M$^+$ ions, and show considerable fragmentation similar to that of the N,N-dimethyl derivative of metoluron-methyl. The EI spectrum of the latter is in the NIST/EPA/NIH database and is shown in Figure 3 with no M$^+$ ion at m/z 409 and most ion abundance at m/z 210 or less. The CI spectra generally have abundant, but not base-peak, [M+H]$^+$ ions, and significant fragmentation occurs even with the low-energy proton transfer from the trimethylcarbonium reagent ion.

The sulfonylurea herbicides are readily separated with RPLC and a slightly acidic mobile phase. Electrospray gives abundant [M+H]$^+$ ions that are the base peaks with conditions that do not favor CID in the interface (Di Corcia et al., 1997a; Rodriguez & Orescan, 1998). Fragmentation of those ions occurs with CID conditions to give two or more fragment ions.

Q. Sulfonamides and Other Sulfur Compounds

This category includes sulfonamides and other sulfur compounds that are not logically in other categories, and that are ingredients in active herbicide products. The compounds asulam (21), cloransulam-methyl (22), and flumetsulam (23) are sulfonamides; bentazon (24) is a cyclic diamide of sulfuric acid; and ethofumesate (25) (Schemes 21–25) is a methylsulfonic acid ester.

The amide H atoms of 21–24 are mildly acidic, and those herbicides may be used as salts, or become partially ionized in solution or in the soil, depending on the pH.
Asulam (21) also contains a carbamate substructure, and it is sometimes categorized into that group of herbicides. The EI spectra of 21, 24, and 25 are in the NIST/EPA/NIH database, and samples were likely introduced with a DIP. The EI spectra have M⁺ ions in the 18–28% relative abundance range, and five or more major fragment ions that are indicative of the structures. However, the amides 21–24 are subject to thermal decomposition, and very likely are not amenable to GC/MS. The sulfonic acid ester 25 is sufficiently thermally stable for GC, and gives an EI GC/MS spectrum remarkably similar to that in the database except for a somewhat lower M⁺ ion relative abundance (Terreni et al., 1994).

The amides 21–24 are amenable to separation by RPLC and CE. Asulam (21) and bentazone (24) were separated with a slightly acidic mobile phase on a C-18 column, and their spectra were measured with APCI (Hu et al., 1999). However, 21 gave more-abundant positive ions than negative ions because of the basic amino group, and 24 gave more-abundant negative ions. The asulam spectrum base peak is the [M+H]⁺ ion, and the spectrum also contains three abundant fragment ions. With similar conditions, the bentazone [M-H]⁻ is the only ion observed; but, with ion-source potentials that favor CID, several abundant fragment ions are produced. Several investigators separated 24 on a RPLC column, and used electrospray to produce the [M-H]⁻ ion base peak and, with CID, several abundant fragment ions (Crescenzi et al., 1999; Lagana et al., 2002). Bentazone was also separated with a group of acidic phenols and acids by CE and, with electrospray, the only ion observed is the [M-H]⁻ ion (Song & Budde, 1998).

### TABLE 9. Common Names, Monoisotopic Masses, and Structural Components of Some Sulfonyleurea Herbicides

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Monoisotopic Mass</th>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bensulfuron-methyl</td>
<td>410</td>
<td><img src="image1" alt="Structure" /></td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>Chlorimuron-ethyl</td>
<td>414</td>
<td><img src="image3" alt="Structure" /></td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>Chlorsulfuron</td>
<td>357</td>
<td><img src="image5" alt="Structure" /></td>
<td><img src="image6" alt="Structure" /></td>
</tr>
<tr>
<td>Ethamsulfuron</td>
<td>410</td>
<td><img src="image7" alt="Structure" /></td>
<td><img src="image8" alt="Structure" /></td>
</tr>
<tr>
<td>Halosulfuron-methyl</td>
<td>434</td>
<td><img src="image9" alt="Structure" /></td>
<td><img src="image10" alt="Structure" /></td>
</tr>
<tr>
<td>Metsulfuron-methyl</td>
<td>381</td>
<td><img src="image11" alt="Structure" /></td>
<td><img src="image12" alt="Structure" /></td>
</tr>
<tr>
<td>Nicosulfuron</td>
<td>410</td>
<td><img src="image13" alt="Structure" /></td>
<td><img src="image14" alt="Structure" /></td>
</tr>
<tr>
<td>Primisulfuron-methyl</td>
<td>468</td>
<td><img src="image15" alt="Structure" /></td>
<td><img src="image16" alt="Structure" /></td>
</tr>
<tr>
<td>Prosulfuron</td>
<td>419</td>
<td><img src="image17" alt="Structure" /></td>
<td><img src="image18" alt="Structure" /></td>
</tr>
<tr>
<td>Rimsulfuron</td>
<td>431</td>
<td><img src="image19" alt="Structure" /></td>
<td><img src="image20" alt="Structure" /></td>
</tr>
</tbody>
</table>

Asulam (21) also contains a carbamate substructure, and it is sometimes categorized into that group of herbicides. The EI spectra of 21, 24, and 25 are in the NIST/EPA/NIH database, and samples were likely introduced with a DIP. The EI spectra have M⁺ ions in the 18–28% relative abundance range, and five or more major fragment ions that are indicative of the structures. However, the amides 21–24 are subject to thermal decomposition, and very likely are not amenable to GC/MS. The sulfonic acid ester 25 is sufficiently thermally stable for GC, and gives an EI GC/MS spectrum remarkably similar to that in the database except for a somewhat lower M⁺ ion relative abundance (Terreni et al., 1994).

The amides 21–24 are amenable to separation by RPLC and CE. Asulam (21) and bentazone (24) were separated with a slightly acidic mobile phase on a C-18 column, and their spectra were measured with APCI (Hu et al., 1999). However, 21 gave more-abundant positive ions than negative ions because of the basic amino group, and 24 gave more-abundant negative ions. The asulam spectrum base peak is the [M+H]⁺ ion, and the spectrum also contains three abundant fragment ions. With similar conditions, the bentazone [M-H]⁻ is the only ion observed; but, with ion-source potentials that favor CID, several abundant fragment ions are produced. Several investigators separated 24 on a RPLC column, and used electrospray to produce the [M-H]⁻ ion base peak and, with CID, several abundant fragment ions (Crescenzi et al., 1999; Lagana et al., 2002). Bentazone was also separated with a group of acidic phenols and acids by CE and, with electrospray, the only ion observed is the [M-H]⁻ ion (Song & Budde, 1998).
FIGURE 3. The database EI spectrum of the $N,N$-dimethyl derivative of metsulfuron-methyl. (Reproduced with permission from NIST, 2002. Copyright 2002 U.S. Department of Commerce on behalf of the United States of America.)

SCHEMES 21, 22, 23, 24 and 25.
Flumetsulam (23) was separated on a C-8 RPLC column with a slightly acidic mobile phase, and the multiple basic N atoms of this compound favor the formation of base peak [M+H]+ ions with electrospray (Rodriguez & Orescan, 1998). Several abundant fragment ions are observed with ion-source conditions that favor CID.

R. Thiocarbamates and Carbamates

Table 10 contains the common names, monoisotopic masses, and structural components of some thiocarbamate herbicides that are ingredients in active herbicide products. Another thiocarbamate herbicide is molinate (26) (Schemes 26 and 27), and phenmedipham (27) is a carbamate herbicide; however, most carbamate pesticides are either insecticides or fungicides. The EI spectra of 26, 27, and the compounds in Table 10 are in the NIST/EPA/NIH database, and they were probably introduced with a DIP or perhaps a GC. Except for triallate, the EI spectra have M⁺ ions in the 3–25% relative abundance range, and triallate has a base peak [M-Cl]+ ion. Thiocarbamates are generally sufficiently volatile and thermally stable for separation by GC (Tanabe et al., 1996; Budde, 2001; Wong et al., 2003) but the dicarbamate 27 may be thermally unstable at typical GC operating temperatures. The M⁺ ion abundances in GC/MS spectra are probably reduced when compared to the database spectra because of typically hot GC injection ports and column ovens. Butylate, cycloate, eptam, molinate, and pebulate are evaluated target analytes in EPA GC/MS method 525.2 for multiple analytes in drinking water (Budde, 2001). The thiocarbamate and carbamate herbicides should be separable by RPLC, and it is reasonable to expect abundant [M+H]+ ions with electrospray and APCI.

S. Triazines and Related Compounds

Triazines are six-member aromatic rings that contain three carbons and three nitrogens. Although there are three possible arrangements of the carbons and nitrogens in the ring, nearly all triazine herbicides have the symmetrical structure with alternating carbons and nitrogens. Table 11 contains the common names, monoisotopic masses, and structural components of some triazine herbicides that are ingredients in active herbicide products. Many other substituted triazines have been reported, and some of those triazines may have been candidate herbicide ingredients, or were ingredients in herbicide products that are canceled in The United States. Two related active herbicide ingredients are metribuzin (28) (Scheme 28), which is derived from unsymmetrical triazine, and hexazinone (29) (Scheme 29), which is derived from a symmetrical triazine. Some of the compounds in the triazine category were introduced as herbicides during the mid-1950s (Howe-Grant, 1995).

The EI mass spectra of 28, 29, and seven of the eight compounds in Table 11 are in the NIST/EPA/NIH database, and they were probably introduced with a DIP or perhaps a GC. The EI spectrum of Irgarol 1051 is not in the database, but its EI GC/MS spectrum has a 100% relative abundance M⁺ ion and a 77% [M-15]+ ion (Readman et al., 1993). Although the database EI mass spectra of the other compounds in Table 11 have M⁺ ions in the 35–100% relative abundance range, the EI spectra of 28 and 29 have M⁺ ions of only approximately 5% relative abundance. The EI spectra of many other substituted triazines are also in the database. Most of the triazines in Table 11 and other substituted triazines that have ethyl or larger alkylamino groups as ring substituents, have either base peaks or major

**TABLE 10.** Common Names, Monoisotopic Masses, and Structural Components of Some Thiocarbamate Herbicides

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Monoisotopic Mass</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butylate</td>
<td>217</td>
<td>-C₃H₇</td>
<td>H</td>
<td>-CH₃</td>
</tr>
<tr>
<td>Cycloate</td>
<td>215</td>
<td>-C₃H₇</td>
<td>-C₃H₇</td>
<td></td>
</tr>
<tr>
<td>Eptam</td>
<td>189</td>
<td>-C₃H₇</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>Pebulate</td>
<td>203</td>
<td></td>
<td>-C₃H₇</td>
<td></td>
</tr>
<tr>
<td>Thiobencarb</td>
<td>257</td>
<td></td>
<td>-C₃H₇</td>
<td></td>
</tr>
<tr>
<td>Triallate</td>
<td>308</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
ions caused by the loss of a small alkyl radical from the \( M^+ \) ion by the alpha-cleavage reaction described for the dinitrophenylamines (section G). The fragmentation of the \( M^+ \) ions and the major EI fragment ions of 11 substituted triazines, including five in Table 11, have been studied by collision induced dissociation (Vincze & Yinon, 1997).

The compounds in Table 11, as well as 28 and 29, are amenable to separation by GC and, except for cyromazine and irgarol 1051, they are evaluated target analytes in EPA GC/MS method 525.2 for multiple analytes in drinking water (Budde, 2001). Similarly, the dealkylated degradation products of those herbicides are generally amenable to separation by GC (Thurman et al., 1994).

Some triazine herbicides and their degradation products have been separated by RPLC, and their APCI and electrospray mass spectra were measured (Di Corcia et al., 1997b; Ferrer, Hennion, & Barceló, 1997). The APCI technique gives primarily \([M+H]^+\) ions (Ferrer, Hennion, & Barceló, 1997), but fragment ions are observed with electrospray and conditions that favor CID (Di Corcia et al., 1997b). The LC/MS techniques are appropriate for triazine metabolites and their degradation products that are not amenable to GC/MS, but they may not provide advantages over EI GC/MS for most triazine herbicides and their dealkylated degradation products that are amenable to GC/MS.

T. Triazoles

A triazole is a five-member aromatic ring that contains three N atoms in the 1,2,3 or 1,2,4 positions. Amitrole (30) (Scheme 30) is 5-amino-1H-[1,2,4]triazole, and it is an ingredient in several active herbicide products. The proton of the ring N is liable, and 30 can exist in several tautomeric forms; however, the structure shown is reported to be the commercial product and the dominate form (Dzygiel, Masiukiewicz, & Rzeszotarska, 2002). Several related compounds that are ingredients in active herbicide products are carfentrazone-ethyl (31) (Scheme 31) and sulfentrazone (32) (Scheme 32), which have oxidized and substituted 1,2,4-triazole structures.

The EI mass spectra of 30 and 31 are in the NIST/EPA/NIH database, and they were probably introduced with a DIP or perhaps a GC with 31. The spectrum of 30 has a base peak \( M^+ \) ion at \( m/z \) 84 and an abundant \([M-HCN]^+\) fragment ion. The spectrum of 31 contains a 28% \( M^+ \) ion at \( m/z \) 411, a 35% \([M-Cl]^+\) ion at \( m/z \) 376, and four other abundant ions that may be characteristic of that structure.

The primary amine 30 is not amenable to separation by GC because of likely interactions with acidic sites in the injection-port liner, column, or stationary phase, and also because of probable thermal decomposition (Bobeldijk et al., 2001). However, the acetyl derivative can be separated by GC (Bobeldijk et al., 2001; Dzygiel, Masiukiewicz, & Rzeszotarska, 2002), and its EI spectrum, which is in the NIST/EPA/NIH database, has a 12% \( M^+ \) ion and a \([M-42]^+\) base peak. The herbicide 31 may be amenable to separation by GC, but 32 is less likely because of the acidic proton on the sulfonamide N atom.

The compounds in Table 11, as well as 28 and 29, are amenable to separation by GC and, except for cyromazine and irgarol 1051, they are evaluated target analytes in EPA GC/MS method 525.2 for multiple analytes in drinking water (Budde, 2001). Similarly, the dealkylated degradation products of those herbicides are generally amenable to separation by GC (Thurman et al., 1994).

Some triazine herbicides and their degradation products have been separated by RPLC, and their APCI and electrospray mass spectra were measured (Di Corcia et al., 1997b; Ferrer, Hennion, & Barceló, 1997). The APCI technique gives primarily \([M+H]^+\) ions (Ferrer, Hennion, & Barceló, 1997), but fragment ions are observed with electrospray and conditions that favor CID (Di Corcia et al., 1997b). The LC/MS techniques are appropriate for triazine metabolites and their degradation products that are not amenable to GC/MS, but they may not provide advantages over EI GC/MS for most triazine herbicides and their dealkylated degradation products that are amenable to GC/MS.
Various derivatives of 30 have been used for RPLC separations (Bobeldijk et al., 2001; Dzygiel, Masiukiewicz, & Rzeszotarska, 2002), and 30 itself may also be amenable to RPLC separation (Dzygiel, Masiukiewicz, & Rzeszotarska, 2002). The APCI spectrum of the 9-fluorenylmethoxycarbonyl derivative of 30 gave primarily the $[M+H]^+$ ion, and only two product ions after CID of the $[M+H]^+$ ion (Bobeldijk et al., 2001). The herbicides 31 and 32 do not appear to have been investigated by RPLC/MS, but it is reasonable to expect that they can be separated by RPLC, and that they will give abundant $[M+H]^+$ ions with electrospray and APCI.

**U. Ureas**

Substituted ureas were introduced as herbicides during the early 1950s (Howe-Grant, 1995), and some of those compounds are still among the most widely used. Table 12 contains the common names, monoisotopic masses, and structural components of some urea herbicides. The compounds bromacil (33) (Scheme 33) and terbacil (34) (Scheme 34), which are substituted uracils and are often classified as uracil herbicides, are included in the urea category because they are substituted cyclic ureas.

The EI spectra of 33, 34, and the compounds in Table 12—except diflufenpyr—are in the NIST/EPA/NIH database, and those spectra were likely measured with a DIP for sample introduction. Although the database EI spectra generally have M$^+$ ions in the 5–38% relative abundance range, most are in the lower end of that range. The EI spectra of the popular herbicides diuron, fluometuron, linuron, and siduron are further characterized by few or no fragment ions that correspond to losses of small groups or single atoms from the M$^+$ ion. Furthermore, the $m/z$ of the base peaks in their spectra are generally <100; therefore those spectra are among the least informative of composition and structure.

Generally, urea herbicides are susceptible to decomposition in hot GC injection ports and column ovens,

![SCHEMES 30, 31 and 32.](image1)

**TABLE 12.** Common Names, Monoisotopic Masses, and Structural Components of Some Urea Herbicides

<table>
<thead>
<tr>
<th>Common Name</th>
<th>Monoisotopic Mass</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diflufenuron</td>
<td></td>
<td></td>
<td></td>
<td>-H</td>
</tr>
<tr>
<td>Diflufenpyr</td>
<td></td>
<td></td>
<td></td>
<td>-H</td>
</tr>
<tr>
<td>Diuron</td>
<td></td>
<td>Cl</td>
<td>-CH$_3$</td>
<td>-CH$_3$</td>
</tr>
<tr>
<td>Fluometuron</td>
<td></td>
<td>Cl</td>
<td>-CH$_3$</td>
<td>-CH$_3$</td>
</tr>
<tr>
<td>Linuron</td>
<td></td>
<td>Cl</td>
<td>-CH$_2$</td>
<td>-O-CH$_3$</td>
</tr>
<tr>
<td>Siduron</td>
<td></td>
<td>Cl</td>
<td></td>
<td>-H</td>
</tr>
<tr>
<td>Tebuthiuron</td>
<td></td>
<td>-CH$_3$</td>
<td>-CH$_3$</td>
<td>-CH$_3$</td>
</tr>
<tr>
<td>Thidiazuron</td>
<td></td>
<td></td>
<td></td>
<td>-H</td>
</tr>
</tbody>
</table>

**SCHEMES 33 and 34.**
and they are not amenable to separation by GC. Exceptions, however, are tebuthiuron in Table 12, 33, and 34, which are evaluated target analytes in EPA GC/MS method 525.2 for multiple analytes in drinking water (Budde, 2001). Because of the thermal instability and longevity of some herbicides in this category, separations by RPLC have been reported by several investigators who utilized APCI and electrospray mass spectrometry (Ferrero, Hennion, & Barceló, 1997; Crescenzi et al., 1999; Hu, Aizawa, & Magara, 1999; Maizels & Budde, 2001; Thurman et al., 2001; Wang & Budde, 2001). The compounds most frequently studied are diuron, fluometuron, linuron, and siduron, and they give abundant [M+H]+ ions with both ionization techniques and some fragment ions under conditions that favor CID. Real-time on-line exact m/z measurements with electrospray and time-of-flight mass spectrometry were introduced as an alternative to CID of prevalent [M+H]+ ions for the confirmation of urea herbicides and other analytes (Maizels & Budde, 2001).

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URL available: http://www.epa.gov/pesticides

URL available: http://www.cdpr.ca.gov/docs/epa/epamenu.htm


Mercier Index. Whitehouse Station, NJ: Merck & Co., Inc.


William L. Budde is a research environmental scientist in the Microbiological and Chemical Exposure Assessment Research Division of the National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency (EPA), in Cincinnati, Ohio. He received a B.S. in chemistry from Xavier University in 1957, an M.S. in chemistry from Xavier University in 1959, and a Ph.D. in physical-organic chemistry from the University of Cincinnati in 1963. He has been employed by the EPA since 1971, and he conducts research in analytical chemistry and mass spectrometry to develop analytical methods for the identification and measurement of organic compounds in the aquatic and related environments. Most of his research has been concerned with GC/MS and LC/MS. He has lectured widely and has published more than 60 scientific journal articles and book chapters. He is the author of the book Analytical Mass Spectrometry: Strategies for Environmental and Related Applications that was co-published by The American Chemical Society and Oxford University Press in 2001.