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Photoionization Detector Sensitivity of Organic Compounds*

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Abstract

Using a gas chromatograph equipped with a high temperature photoionization detector, a wide variety of organic compounds was analyzed. Relative detector sensitivities were determined on a molar basis and on a weight basis and were normalized against the detector response for benzene. By analyzing sets of organic compounds of like functionality but different numbers of carbons, several conclusions were derived relating PID sensitivity to molecular structure. In general, relative PID sensitivities should be compared on a molar basis rather than on a weight basis. PID sensitivity depends primarily upon carbon number, functional groups, and bonding type.

Introduction

The photoionization detector (PID) is designed to detect species in the effluent from a gas chromatograph by utilizing the principle of photoionization. Photoionization occurs when the absorption of a photon by a molecule leads to ionization via the reaction:

$$RH + h\nu \rightarrow RH^+ + e^-$$

where RH is an ionizable molecule and hv is a photon with an energy $\geq$ the ionization potential (IP) of the molecule.

With the development of a stable PID with a sealed UV source (HNU Systems, Inc., Newton Upper Falls, Massachusetts), interest in the detector has increased. The development and performance of the detector have been documented (1-5), as well as a number of diverse applications (6-12). By utilizing UV lamps with different photon energies, the detector can be easily modified for almost universal or quite select detection of compounds.

If the ionization potential of the compound is less than the lamp energy, then the photoionization detector will respond to that molecule. As a result, tables of IPs can be used to determine whether or not the detector may be useful (6). However, these parameters of lamp energy and IP do not indicate the relative detector sensitivity for various compounds. This lack of information for concisely defining the factors affecting PID sensitivity has limited its acceptance.

Some instrumental parameters effecting PID sensitivity include: (A) lamp intensity, (B) lamp seal, and (C) flow rate through the detector. The lamp intensity is adjustable with a dial on the HNU Systems electrometer/power supply unit. The intensity can be diminished if the detector window becomes dirty or coated with material from column bleed or samples. The lamp seal is optimized at the time the UV lamp is installed in the detector. The sensitivity increases (almost exponentially) as flow rate decreases (5). With high efficiency, packed gas chromatography columns' flow rates between 8-12 cc/min can be normally used for high sensitivity.

Logically, the detector sensitivity also depends upon ionization efficiency, a parameter related to the tightness with which electrons are held to a molecule. By investigating detector response for a wide variety of organic compounds, general rules have been derived for predicting PID sensitivity based upon organic compound structure.

Experimental

The HNU Systems, Inc. high-temperature photoionization detector, Model PI-51-02, was installed on a Hewlett-Packard (Palo Alto, California) 5700 gas chromatograph (GC). Using a 10.2 eV lamp, a wide variety of organic compounds was analyzed on several different GC columns. Peak areas were integrated with a Spectra-Physics (Arlington Heights, Illinois) Systems I computing integrator. Relative detector sensitivities were determined on a molar basis and on a weight basis and were normalized against the detector response for benzene. Using the data obtained from analyzing sets of compounds of like functionality but different numbers of carbons, conclusions were derived that related PID sensitivity to molecular structure.

The chemical standards were obtained from Supelco, Inc., (Bellefonte, Pennsylvania) (PolyScience Corp. analytical standards kits, Niles, Illinois). The chemical purities were all > 95%.

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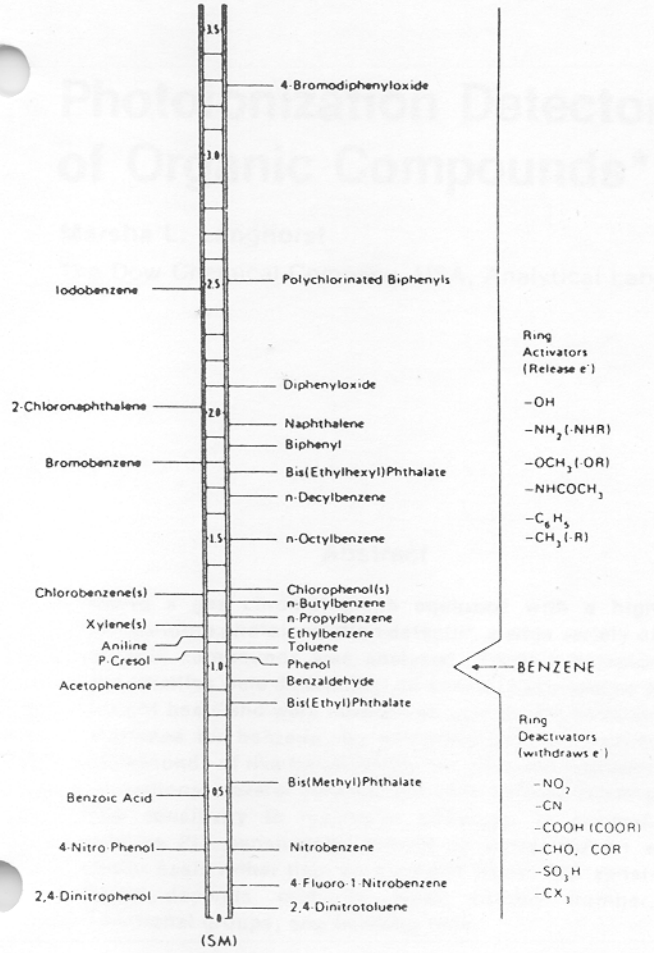

Figure 7. Molar sensitivity relative to benzene for substituted benzenes.

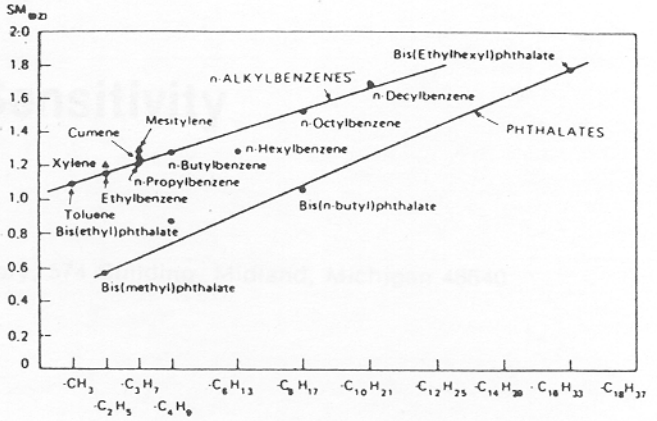

Figure 8. SM vs. carbon number of alkyl group for alkylbenzenes and phthalates.

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Calculations

The molar sensitivity relative to benzene is calculated using the following equation:

$$SM = \frac{A}{A_{(BZ)}} \times \frac{B_{(BZ)}}{B} \qquad \text{Eq. 1}$$

where A is the peak area of compound of interest, $A_{(BZ)}$ is the peak area of the benzene peak, B is the molar concentration of the compound of interest (nmoles/ml), and $B_{(BZ)}$ is the molar concentration of the benzene standard solution (nmoles/ml).

The relative sensitivity normalized to benzene on a weight basis is calculated using the following equation:

$$S = \frac{A}{A_{(BZ)}} \times \frac{C_{(BZ)}}{C} \qquad \text{Eq. 2}$$

where C is the concentration of compound of interest (μg/ml) and $C_{(BZ)}$ is the concentration of benzene in standard solution (μg/ml).

Results and Discussion

The detector response relative to benzene on a molar basis for a large number of organic compounds is detailed in Table I. From these data, it can be concluded that PID sensitivity depends upon the following chemical structure parameters: (A) carbon number, (B) functional groups (e.g., -OH, -COOR, etc.), and (C) bonding type (e.g., double bonds, aromatic, etc.). More specific conclusions are listed in Table II.

Table I. Sensitivity of Compound Relative to Benzene on a Molar Basis (Benzene = 1.0)

Compound	SM (Bz)
n-ALKANES	
n-Heptane	0.032
n-Octane	0.080
n-Nonane	0.14
n-Decane	0.23
n-Undecane	0.30
n-Dodecane	0.37
n-Tridecane	0.46
n-Tetradecane	0.53
n-Pentadecane	0.59
n-Hexadecane	0.71
n-Heptadecane	0.72
n-Octadecane	0.79
n-Nonadecane	0.86
n-Eicosane	0.93
n-Heneicosane	1.03
n-Docosane	1.13
ALKANES: BRANCHED & CYCLIC	
2,2-Dimethylbutane	0.037
2,3-Dimethylbutane	0.032
2-Methylpentane	0.011
3-Methylpentane	0.027
2,4-Dimethylpentane	0.080
3-Methylhexane	0.075
2,3-Dimethylpentane	0.10
2,2,4-Trimethylpentane	0.21
2,4- & 2,5-Dimethylhexane	0.15
2,3,4-Trimethylpentane	0.22
3-Methylheptane	0.13
2,2,5-Trimethylhexane	0.26
Cyclohexane	0.18
Methylcyclohexane	0.28
Decahydronaphthalene	1.04
1-ALKENES	
1-Heptene	0.54
1-Octene	0.55
1-Nonene	0.58
1-Decene	0.67
1-Undecene	0.70
1-Dodecene	0.73
1-Tridecene	0.81
1-Tetradecene	0.87
1-Pentadecene	0.92
1-Hexadecene	0.99
1-Heptadecene	1.06
1-Octadecene	1.10
1-Nonadecene	1.17
ALKENES, DIENES, ALKYNES	
2-Heptene	0.51
3-Heptene	0.58
3-Methyl-1-butene	0.52
1,9-Decadiene	1.07
2-Octyne	2.75
KETONES	
Acetone	0.35
2-Butanone	0.40
2-Pentanone	0.45
2-Hexanone	0.52
2-Heptanone	0.59
2-Octanone	0.71
2-Nonanone	0.78
3-Pentanone	0.54
3-Heptanone	0.68
3-Octanone	0.73
4-Heptanone	0.70
5-Nonanone	0.82
KETONES: BRANCHED & CYCLIC	
3-Methyl-2-butanone	0.58
3-Methyl-2-pentanone	0.60
4-Methyl-2-Hexanone	0.62
3-Methyl-2-heptanone	0.72
2-Methyl-3-pentanone	0.62
5-Methyl-2-hexanone	0.65
5-Methyl-3-heptanone	0.75
3,3-Dimethyl-2-butanone	0.65
2,4-Dimethyl-3-pentanone	0.70
2,6-Dimethyl-4-heptanone	0.81
Cyclopentanone	0.57
Cyclohexanone	0.62
2-Methylcyclohexanone	0.66
3-Methylcyclohexanone	0.66
4-Methylcyclohexanone	0.63
2,3-Butanedione	0.45
ALDEHYDES	
Butanal	0.30
Pentanal	0.36
Hexanal	0.41
Heptanal	0.45
Octanal	0.49
Nonanal	0.53
ALCOHOLS	
1-Butanol	0.023
1-Pentanol	0.053
1-Hexanol	0.086
1-Heptanol	0.12
1-Octanol	0.16
1-Nonanol	0.20
1-Decanol	0.25
1-Undecanol	0.29
1-Dodecanol	0.36
Isobutanol	0.029
ESTERS	
Methyl propionate	0.010
Methyl butanoate	0.039
Methyl pentanoate	0.082
Methyl hexanoate	0.096
Methyl heptanoate	0.14
Methyl octanoate	0.15
Methyl nonanoate	0.26
Methyl decanoate	0.33
Methyl dodecanoate	0.48
Methyl tetradecanoate	0.66
Methyl hexadecanoate	0.82
Ethyl acetate	0.020
Ethyl butanoate	0.15
Ethyl hexanoate	0.24
Ethyl octanoate	0.32
Ethyl decanoate	0.51
Ethyl dodecanoate	0.70
Propyl acetate	0.025
Propyl butanoate	0.21
Butyl acetate	0.044
AROMATIC HYDROCARBONS	
Toluene	1.09

(continued on next page)

factor affecting sensitivity. At high carbon number, the plot of *SM* vs. carbon number tends to parallel or meet the line for *n*-alkanes. That is, carbon number is then the predominant factor affecting response. In general, the sensitivity of *n*-alkanes < 1-alcohols < esters < aldehydes < ketones of the same carbon number.

From the data in Table I a number of other conclusions can be drawn. Sensitivity of alkanes < alkenes < aromatics. Figure 5 shows that branched compounds are generally more sensitive than nonbranched compounds. This figure compares alkanes with one, two, or three branching methyl groups attached.

Table III shows data to support the conclusion that cyclic compounds are more sensitive than their noncyclic analogs. For halogenated compounds, sensitivity increases in the order fluorine-substituted compounds < chlorine-substituted compounds < bromine-substituted compounds < iodine-substituted compounds. This is illustrated in Figure 6 with halogenated benzenes.

For substituted benzenes, electron-releasing groups (ring activators) increase sensitivity, and electron-withdrawing groups (ring deactivators) decrease sensitivity relative to benzene itself. Figure 7 lists activating and deactivating groups and shows how these substituents affect molar sensitivity relative to benzene. For alkyl benzenes and phthalates sensitivity increases as the carbon number of the alkyl chain increases (see Figure 8).

These general conclusions should increase the utility of the PID by giving the analyst a better understanding of its applicability and performance.

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Table III. Comparison of Molar Sensitivity of Cyclic and Noncyclic Compounds

Noncyclic Compound	SM (Bz)	Cyclic Compound	SM (Bz)
Hexane	<0.032	Cyclohexane	0.18
3-Methylhexane	0.075	Methylcyclohexane	0.18
2-Pentanone	0.45	Cyclopentanone	0.57
3-Pentanone	0.54		
2-Hexanone	0.52	Cyclohexanone	0.62
4-Methylhexanone	0.62	2-Methylcyclohexanone	0.66
		3-Methylcyclohexanone	0.66
		4-Methylcyclohexanone	0.63
Decane	0.23	Decahydronaphthalene	1.04
Diethyl ether	0.36	Tetrahydrofuran	0.39

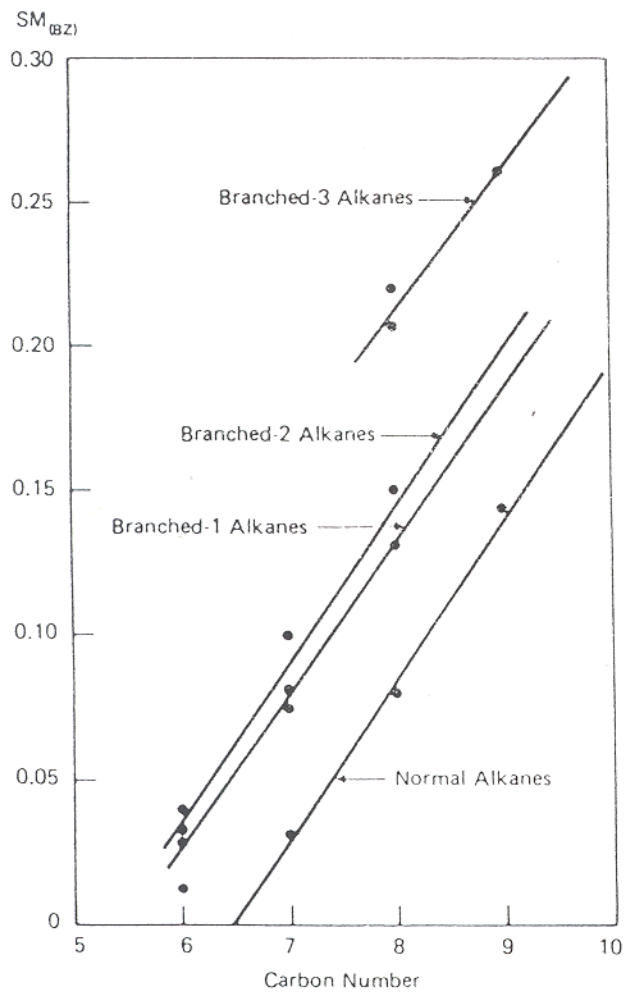

Figure 5. SM vs. carbon number for straight chain vs. branched hydrocarbons.

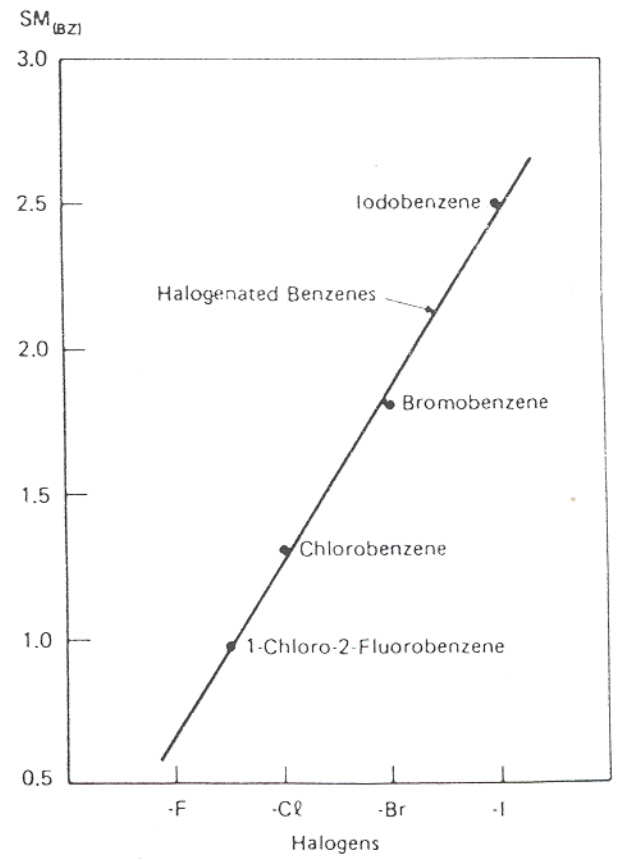

Figure 6. SM vs. halogen for halogenated benzenes.

Table I. (continued)

Compound	SM (Bz)
(Aromatic Hydrocarbons)	
Ethylbenzene	1.16
n-Propylbenzene	1.21
n-Butylbenzene	1.27
n-Hexylbenzene	1.29
n-Octylbenzene	1.52
n-Decylbenzene	1.69
o-Xylene	1.14
m-Xylene	1.15
p-Xylene	1.20
Cumene	1.22
p-Cymene	1.27
Mesitylene	1.27
PAHs/PNAs	
Naphthalene	1.97
Anthracene	2.44
Phenanthrene	2.50
1,2-Benzanthracene	2.46
Chrysene	2.96
Pyrene	3.02
Triphenylene	3.08
Fluorene	2.08
Fluoranthene	2.85
Acenaphthene	3.06
Biphenyl	1.88
p-Terphenyl	2.20
SUBSTITUTED BENZENES	
Ring Activators	
Phenol	1.05
Aniline	1.13
1,2-Dimethoxybenzene	1.19
Ring Deactivators	
Nitrobenzene	0.29
Benzoic acid	0.50
Benzaldehyde	0.96
Acetophenone	0.94
Chlorobenzenes	
1,3-Dichlorobenzene	1.42
1,4-Dichlorobenzene	1.39
1,2-Dichlorobenzene	1.30
1,3,5-Trichlorobenzene	1.26
1,2,4-Trichlorobenzene	1.20
1,2,3-Trichlorobenzene	1.44
1,2,4,5-Tetrachlorobenzene	1.28
1,2,3,4-Tetrachlorobenzene	1.40
Pentachlorobenzene	1.32
Hexachlorobenzene	1.25
Chlorobenzenes average =	1.30
Chlorophenols	
2-Chlorophenol	1.19
3-Chlorophenol	1.32
4-Chlorophenol	1.30
2,3-Dichlorophenol	1.34
2,4-Dichlorophenol	1.34
2,5-Dichlorophenol	1.34
2,6-Dichlorophenol	1.33
3,4-Dichlorophenol	1.37
3,5-Dichlorophenol	1.35
2,3,4-Trichlorophenol	1.28
2,3,5-Trichlorophenol	1.28
2,3,6-Trichlorophenol	1.47
2,4,5-Trichlorophenol	1.32
2,4,6-Trichlorophenol	1.30
3,4,5-Trichlorophenol	1.20
2,3,4,5-Tetrachlorophenol	1.14
2,3,4,6-Tetrachlorophenol	1.43
2,3,5,6-Tetrachlorophenol	1.38
Pentachlorophenol	1.18
Chlorophenols average =	1.32
Polychlorinated Biphenyls	
2,3-Dichlorobiphenyl	2.18
4,4'-Dichlorobiphenyl	2.47
2',3,4-Trichlorobiphenyl	2.40
2,2',5,5'-Tetrachlorobiphenyl	2.43
2,3',4',5-Tetrachlorobiphenyl	2.39
3,3',4,4'-Tetrachlorobiphenyl	2.96
2,2',4,5,5'-Pentachlorobiphenyl	2.45
2,2',3,4,5'-Pentachlorobiphenyl	2.80
2,2',3,4,5,6'-Hexachlorobiphenyl	2.55
2,2',4,4',5,5'-Hexachlorbiphenyl	2.60
PCBs average =	2.53
Phthalates	
bis(Methyl)phthalate	0.56
bis(Ethyl)phthalate	0.87
bis(n-Butyl)phthalate	1.06
bis(2-Ethylhexyl)phthalate	1.78
Butylbenzylphthalate	1.78
Halogenated	
Monochlorobenzene	1.30
Bromobenzene	1.82
Iodobenzene	2.50
1-Chloro-2-fluorobenzene	0.98
1-Fluoro-4-nitrobenzene	0.15
Mixed Functionality	
p-Cresol	1.07
2,4-Dimethylphenol	1.10
2-Chloro-5-hydroxy toluene	1.20
2,4-Dinitrotoluene	0.062
4-Nitrophenol	0.29
2,4-Dinitrophenol	0.094
Diphenyloxide	2.10
Dibenzofuran	0.86
Dibenzo-p-dioxin	0.93
Dibenzothiophene	1.31
4-Bromodiphenyloxide	3.30
2-Chloronaphthalene	2.04
MISCELLANEOUS	
3-Hexene-1-ol	0.46
Hexachlorocyclohexane	0.027
Hexachlorocyclopentadiene	0.88
Hexachloro-1,3-butadiene	1.34
Mesityloxide	0.611
1-Bromobutane	0.066
1-Iodobutane	1.93
1,2-Dibromobutane	0.081
Diethyl ether	0.36
Tetrahydrofuran	0.39
Pyridine	0.50
Isopentanol	0.057
tert-Pentanol	0.054
1,4-Butanediol	0.10

Table II. Conclusions on a Molar Basis

- Sensitivity increases as carbon number increases.
- For n-alkanes, SM = 0.0715n - 0.457 where SM = molar sensitivity relative to benzene (Benzene = 1.0) and n = carbon number.
- Sensitivity for alkanes < alkenes < aromatics.
- Sensitivity of alkanes < alcohols ≤ esters < aldehydes < ketones.
- Sensitivity of cyclic compounds > noncyclic compounds.
- Sensitivity of branched compounds > nonbranched compounds.
- Sensitivity of fluorine-substituted < chlorine-substituted < bromine-substituted < iodine-substituted compounds.
- For substituted benzenes, ring activators (electron-releasing groups), increase sensitivity and ring deactivators (electron-withdrawing groups) decrease sensitivity (exception: halogenated benzenes).

In general, sensitivity increases as carbon number increases. For *n*-alkanes, molar sensitivity is linearly related to carbon number by the relationship:

$$SM = 0.715n - 0.475$$

where *SM* is the molar sensitivity relative to benzene and *n* is the carbon number (see Figure 1). This line was drawn for C_7 through C_{22} *n*-alkanes. C_1 through C_6 alkanes were excluded because they have ionization potentials greater than or equal to 10.2 eV and therefore give little or no response when the PID is equipped with a 10.2-eV lamp. Figure 2 shows relative sensitivities normalized to benzene on a *weight* basis for *n*-alkanes and 1-alkenes. For alkanes, the relationship is nearly linear at low carbon numbers. It was concluded that PID sensitivities could be better compared on a molar basis

rather than on a weight basis.

Series of 1-alkenes, alcohols, aldehydes, ketones, and esters were also analyzed. For these compounds, functional groups and bonding structure also affect detector sensitivity as well as carbon number (see Figures 1 and 3-4). At low carbon numbers, the bonding type or functional group is the primary

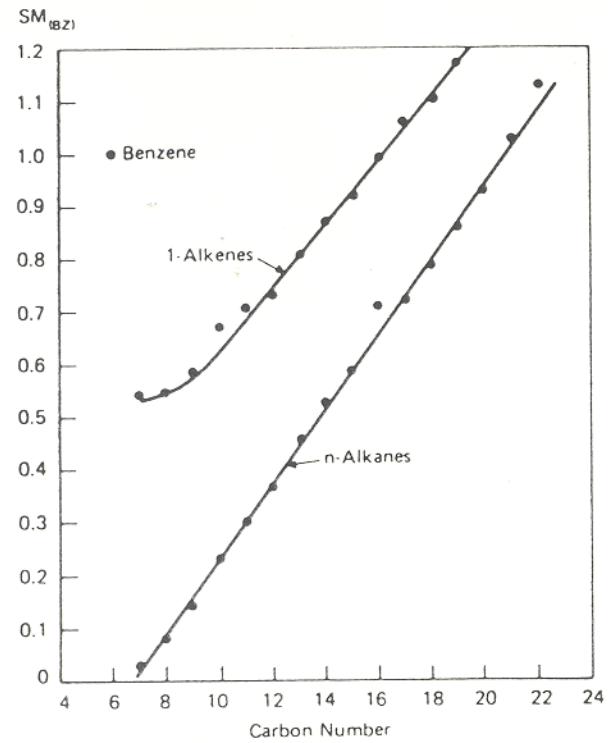

Figure 1. Molar sensitivity relative to benzene vs. carbon number for n-alkanes and 1-alkenes.

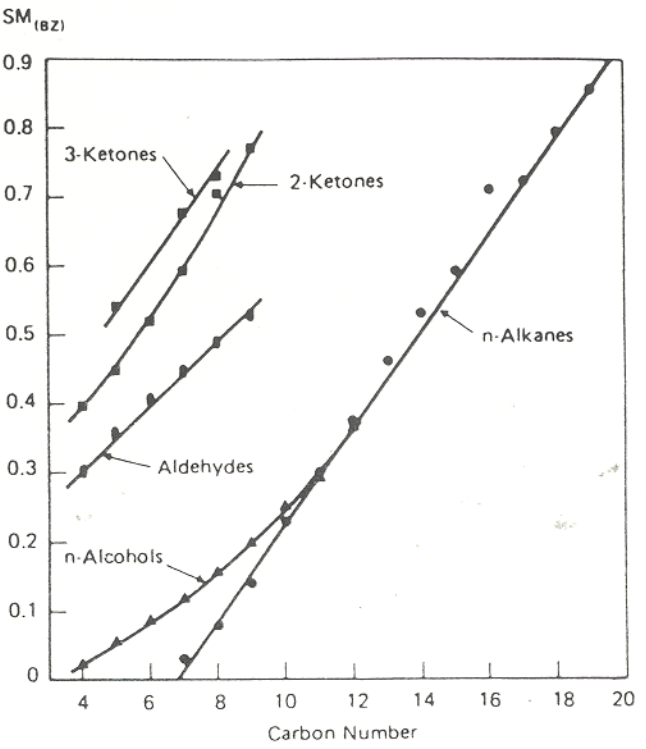

Figure 3. Molar sensitivity relative to benzene vs. carbon number for 1-alcohols, aldehydes, and ketones.

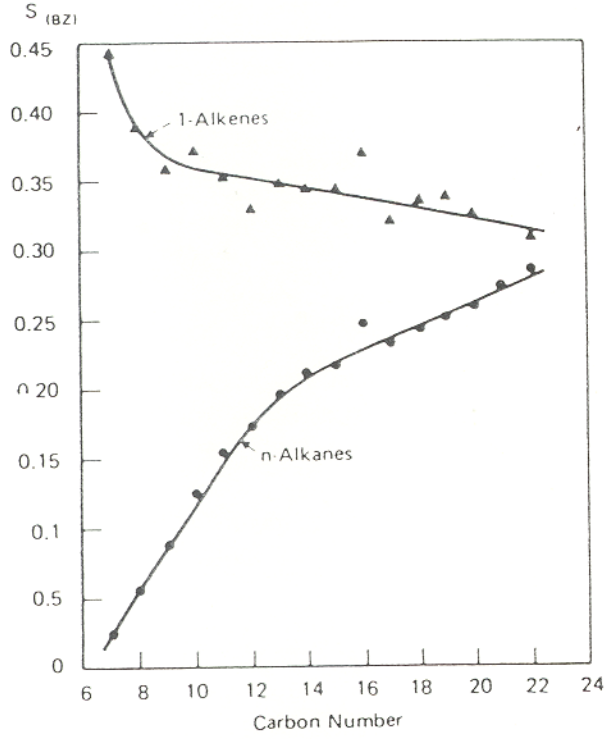

Figure 2. Sensitivity relative to benzene on a weight basis vs. carbon number for n-alkanes and 1-alkenes.

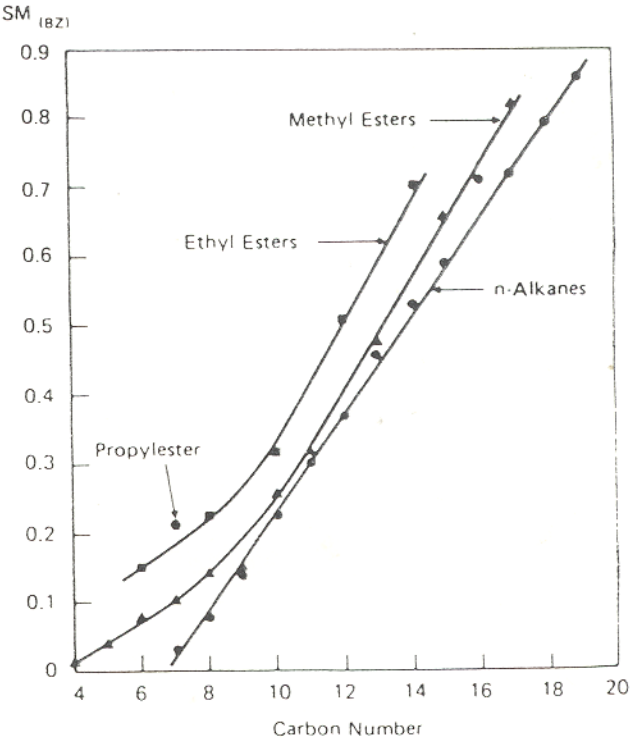

Figure 4. Molar sensitivity relative to benzene vs. carbon number for methyl, ethyl, and propyl esters.