

CHROM. 5674

## DETERMINATION OF HETERO-ELEMENT CONTENT IN ORGANICS BY ALKALI FLAME-GAS-LIQUID CHROMATOGRAPHY\*

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## SUMMARY

It has been held by *inter alia* CREMER, GUIFFRIDA, and KARMEN that the response of the alkali flame (thermionic) detector is proportional to the amount of hetero-element introduced; other authors disagreed. This paper presents evidence to confirm this proportionality for both positive and negative modes of detector response, and describes its application to determine the percentage of various hetero-elements present in organic compounds. This determination is done by adding a suitable "standard" to an "unknown" compound and comparing their responses on both alkali flame and flame ionization detectors. For such calculations, pairs of model compounds were used which contained either P, N, or I for positive alkali flame response; or Cl, Br, or S for negative response. The accuracy of the results depends on the choice of a suitable standard and proper chromatographic conditions. The percent chlorine content of fifteen organochlorine compounds, for instance, was determined with a standard deviation of 3.6 %.

## INTRODUCTION

Selective detectors in gas chromatography (GC) can perform a dual role; a quantitative one in the determination of known compounds, and a qualitative one in the attribution of particular characteristics (to which the detector responds) to unknown compounds. The current emphasis on surveillance of the environment for possibly harmful trace organics has put increased emphasis on this latter aspect. Several highly selective GC detectors are available and considerable information can be obtained by chromatographing a complex mixture with the help of two or three well-chosen ones. When their response tracings are to be compared, the structural information extractable will be, *nolens volens*, only as valid as our knowledge about detector performance. This study describes, therefore, characteristics of one popular chromatographic device, the so-called thermionic or alkali flame detector (AFD) from this point of view.

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The AFD has been amply reviewed<sup>1-3</sup>. It exists in several modifications and can respond in a positive or negative fashion to various hetero-elements. Its most outstanding characteristic, of course, is its (positive) response to organophosphorus compounds, frequently used in pesticide residue analysis. Most authors agree that the AFD's response is proportional to the amount of hetero-element introduced into the flame, irregardless of the rest of the organic molecule. Other authors disagree, obviously because different detector modifications can lead to divergent conclusions. In most papers, the experimental evidence presented pro or contra linear elemental response is scant, as shown by the following literature survey.

CREMER *et al.*<sup>4</sup> reported proportionality for a "leak detector"<sup>5</sup> in contact with halogens (no compounds given). Using the same detector, BECHTOLD<sup>6</sup> found a ratio of 1:2:3:4 for the peak areas of mono-, di-, tri- and tetrachloromethane. A modification of this detector failed to do likewise for mono- and trichlorobenzene, unless precombustion was used<sup>7</sup>. KARMEN found proportionality with his dual flame detector<sup>8</sup> for di-, tri- and tetrachloromethane, and later he reported that nitrogen in nitrobenzene and in amines and amides were all detected essentially equally<sup>9</sup>. A similar detector showed equal peak-areas for equimolar amounts of chloropropane and chlorobenzene<sup>10</sup>. An all-glass version of the flame ionization-alkali dual flame detector, however, failed to show this type of elemental response for mono-, di-, tri- and tetrachlorobenzene, gave divergent molar ionization efficiencies for five mono-bromoaromatics, and responded to tetraethyl pyrophosphate only slightly more efficiently than to several compounds containing only one phosphorus atom<sup>11</sup>. Yet, the same halides displayed strict elemental response in a single-flame AFD, provided the contribution of the aromatic ring was subtracted<sup>12</sup>. The authors of this study, DRESSLER AND JANÁK, also provided the only report of proportionality in a negative mode (inverted peaks) for seven sulfur compounds<sup>13</sup>. IVES AND GIUFFRIDA<sup>14</sup> described the response of caffeine, isolan, propazine and *m*-dinitrobenzene as proportional to the number of nitrogen atoms reaching the detector, and observed triphenylphosphine and parathion to perform likewise for phosphorus. The detector was GIUFFRIDA's single-flame design, the platinum-iridium helix coated with various alkali salts. Using a pellet-type detector with a rubidium sulfate source, our group found proportionality for a variety of nitrogen compounds<sup>15</sup>. HARTMANN, using essentially the same detector design stated that, as yet, this relationship has not been deduced<sup>16</sup>. He found, however, that the AFD responds to the phosphorus atom in various thiophosphate pesticides<sup>17</sup>. EBING measured relative responses of three *sym.*-triazine herbicides, three chlorinated hydrocarbon insecticides and three thiophosphate pesticides under a variety of detector conditions<sup>18</sup>, and KAWAHARA *et al.* determined the responses of forty phosphorus-containing pesticides at three operating conditions<sup>19</sup>. Both groups, however, conducted these measurements in a context other than the question of elemental response. Hewlett-Packard stated recently that their "nitrogen detector" response is proportional to the number of nitrogen atoms in organic molecules<sup>20</sup>.

The above list of references is certainly not complete, but it reflects well the divergence of opinions resulting from different detector designs and personal approaches. A majority opinion would perhaps note that the positive responses of the AFD to phosphorus, nitrogen, and chlorine, and its negative response to sulfur, depend primarily on the amount of hetero-element introduced into the flame. Because

of the importance of elemental response for structural information to be derived from the AFD, this study attempts to define in a more comprehensive manner its characteristics both in the positive (phosphorus, nitrogen, iodine) and the negative mode (chlorine, bromine, sulfur).

Strictly speaking, such an attempt can be valid only for the particular detector modification used, although some general conclusions appear feasible. Furthermore, we may well have chosen to examine nitrogen or iodine in the *negative* mode, and chlorine, bromine and sulfur in the *positive* mode (negative response for phosphorus can be obtained but is very poor). However, the modes as stated in the paragraph above reflect the best operating ranges and were therefore a natural choice. The optimization of our particular AFD version for *sulfur* is the only such procedure included in this paper; the optimization for other hetero-elements was reported earlier<sup>21,22</sup>.

If, in fact, the response of the AFD is proportional to the amount of hetero-element introduced, structural data could be obtained from both unknown and unweighed compounds, provided they were compared to a proper standard and detected by both the AFD and another detector, in this case the flame ionization detector (FID).

If we use the response of the FID as a gross estimate of a molecule's carbon content (an assumption which becomes more misleading as the oxygen content of the molecule increases) the following equation should apply for a pair of compounds designated as "unknown" and "standard", respectively:

$$\left[ \frac{\%X}{\%C} \right]_U = \left[ \frac{R_U}{R_{St}} \right]_{AFD} \times \left[ \frac{R_{St}}{R_U} \right]_{FID} \times \left[ \frac{\%X}{\%C} \right]_{St}$$

- R = response
- X = hetero-atom
- C = carbon
- U = Unknown
- St = Standard

A further gross simplification would be to equate the organic rest of the molecule with its carbon content and write, for instance for a chlorine-containing compound:

$$\left[ \frac{\%Cl}{100 - \%Cl} \right]_U = \left[ \frac{R_U}{R_{St}} \right]_{AFD} \times \left[ \frac{R_{St}}{R_U} \right]_{FID} \times \left[ \frac{\%Cl}{100 - \%Cl} \right]_{St}$$

This relationship can be tested easily, of course, with a variety of pairs of suitable hetero-organic compounds; and this paper reports such tests on organics containing Cl, Br, I, P, N, and S.

#### EXPERIMENTAL

The AFD design and the modified Barber-Colman chromatograph were the same as described in an earlier report<sup>22</sup>. The FID analyses were done on a MicroTek 220 at flow conditions roughly optimized for maximum carbon response. Well-conditioned 10% Carbowax 20M on Chromosorb-W, HP, 80-100 mesh and 10% OV-17 on

Chromosorb-W, HP, 80-100 mesh, were used in both chromatographs, although no effort was made to match columns or carrier gas flow rates.

It should be mentioned in this context, that the FID response of phosphorus-containing compounds presented some problems. Even though the MT-220 dual FID had never contacted alkali salts (with the possible exception of prenatal silver solder flux), an increase in hydrogen flow increased the response to organophosphate. We found essentially the same behavior in FID's manufactured by F&M, Perkin-Elmer and Varian-Aerograph. Fig. 1 shows a comparison of *n*-octadecane and tri-*n*-butylphosphate obtained from the last detector. Keeping the detector well heated and the flame high for four weeks prior to a repetition of the experiment failed to induce any drastic changes, although phosphorus response dropped slightly. The question, whether the effect results from the large flame *per se*, or from small amounts of alkali effusing from the detector environment, was not further investigated. Some care had to be exercised, however, to prevent this effect from influencing the experimental results.

Equal-weight amounts of various hetero-organics were dissolved in hexane or acetone and injected into the AFD-GC for elemental response measurements, at column bath temperatures suitable for precise peak integration. Compounds used were those available in the laboratory at the time of the experiment. The settings of gas flows and electrode height were chosen to give the best compromise between the conditions for maximal hetero-atom response, optimal response-noise ratio and maximal discrimination against carbon response. Calibration curves for selected hetero-organics were initially established to ensure analysis within the linear range of the AFD; Fig. 2 shows the one for nitrogen as an example.

Compounds used in the study of elemental response were then combined in pairs which could be chromatographed as mixtures on both instruments (AFD-GC

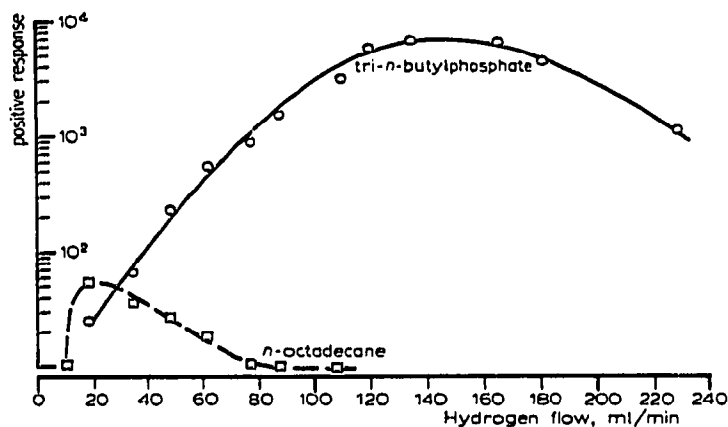


Fig. 1. Effect of hydrogen flow on carbon and phosphorus response on Varian-Aerograph 1520 FID. Compounds: *n*-octadecane and tri-*n*-butylphosphate. Flow rates (ml/min):  $N_2 = 25$ ; air = 560.

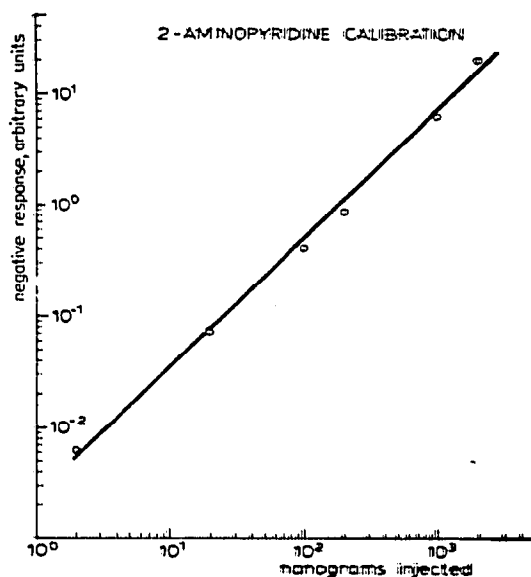


Fig. 2. Linear range of nitrogen response measured with 2-aminopyridine in AFD-GC. Pellet:  $Rb_2SO_4$ , 1-mm bore. Electrode height: 6 mm. Flow rates (ml/min):  $H_2 = 30$ ; He = 53; air = 215.

and FID-GC), using the conditions indicated in Figs. 3-10. Consecutive injections of single compound solutions were employed only when the pair did not separate or gave otherwise unwieldy peaks. For calculation, according to the "% CI" formula, one substance was assigned arbitrarily the role of the Standard, the other one the role of the Unknown.

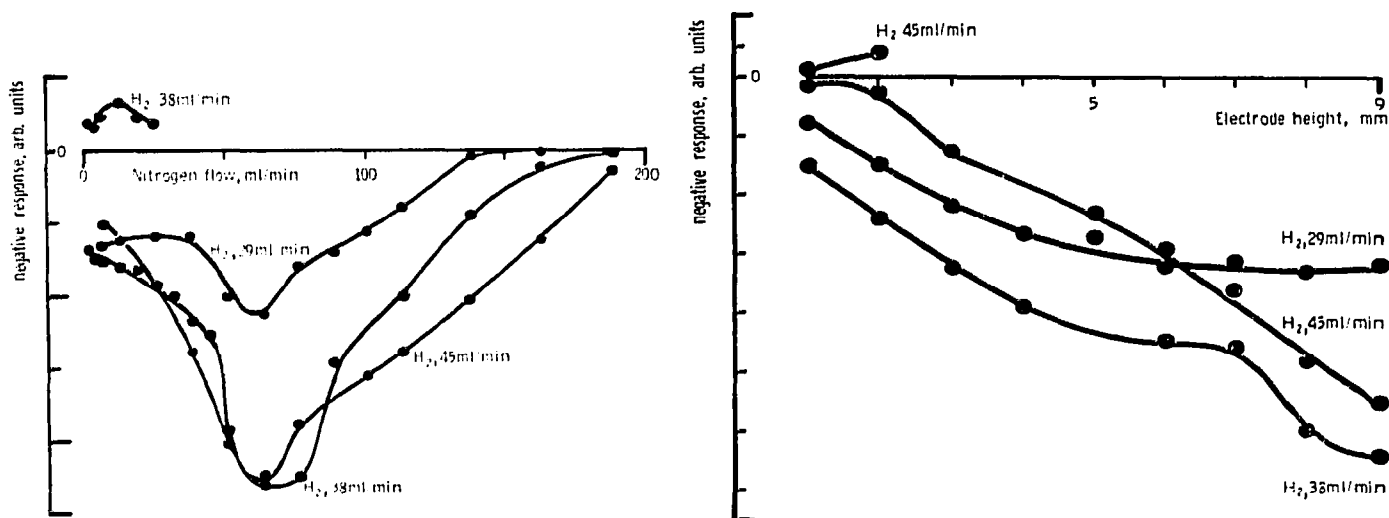


Fig. 3. Effect of carrier gas flow on sulfur response. Compound: thiophene. Pellet:  $\text{Rb}_2\text{SO}_4$ , 1-mm bore. Electrode height: 2 mm. Flow rates (ml/min):  $\text{H}_2 = 45; 38; 29$ ; air = 215.

Fig. 4. Effect of electrode height on sulfur response. Compound: di-*n*-propyldisulfide. Pellet:  $\text{Rb}_2\text{SO}_4$ , 1-mm bore. Flow rates (ml/min):  $\text{H}_2 = 45; 38; 29$ ; He = 53; air = 215.

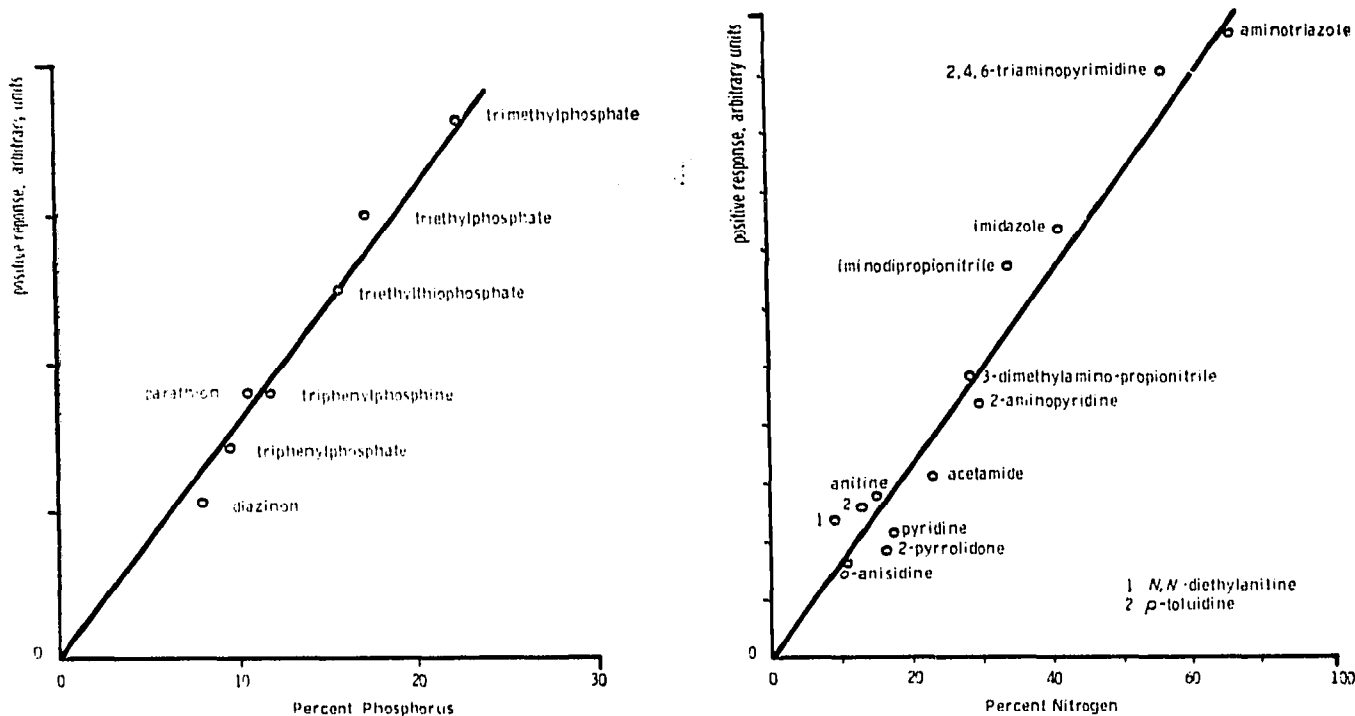


Fig. 5. Elemental phosphorus response. Pellet:  $\text{Rb}_2\text{SO}_4$ , 1-mm bore. Electrode height: 10 mm. Flow rates (ml/min):  $\text{H}_2 = 33$ ;  $\text{N}_2 = 50$ ; air = 215.

Fig. 6. Elemental nitrogen response. Pellet:  $\text{Rb}_2\text{SO}_4$ , 1-mm bore. Electrode height: 6 mm. Flow rates (ml/min):  $\text{H}_2 = 28$ ;  $\text{N}_2 = 45$ ; air = 215.

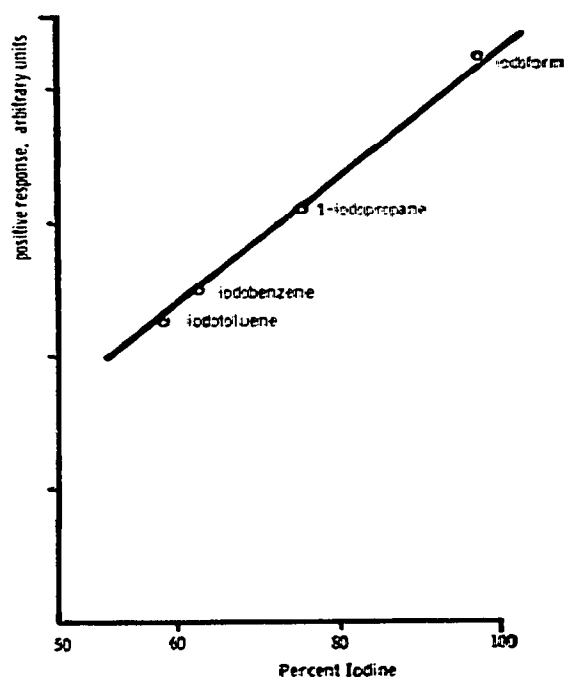


Fig. 7. Elemental iodine response. Pellet:  $\text{Rb}_2\text{SO}_4$ , 1-mm bore. Electrode height: 10 mm. Flow rates (ml/min):  $\text{H}_2 = 33$ ;  $\text{N}_2 = 50$ ; air = 215.

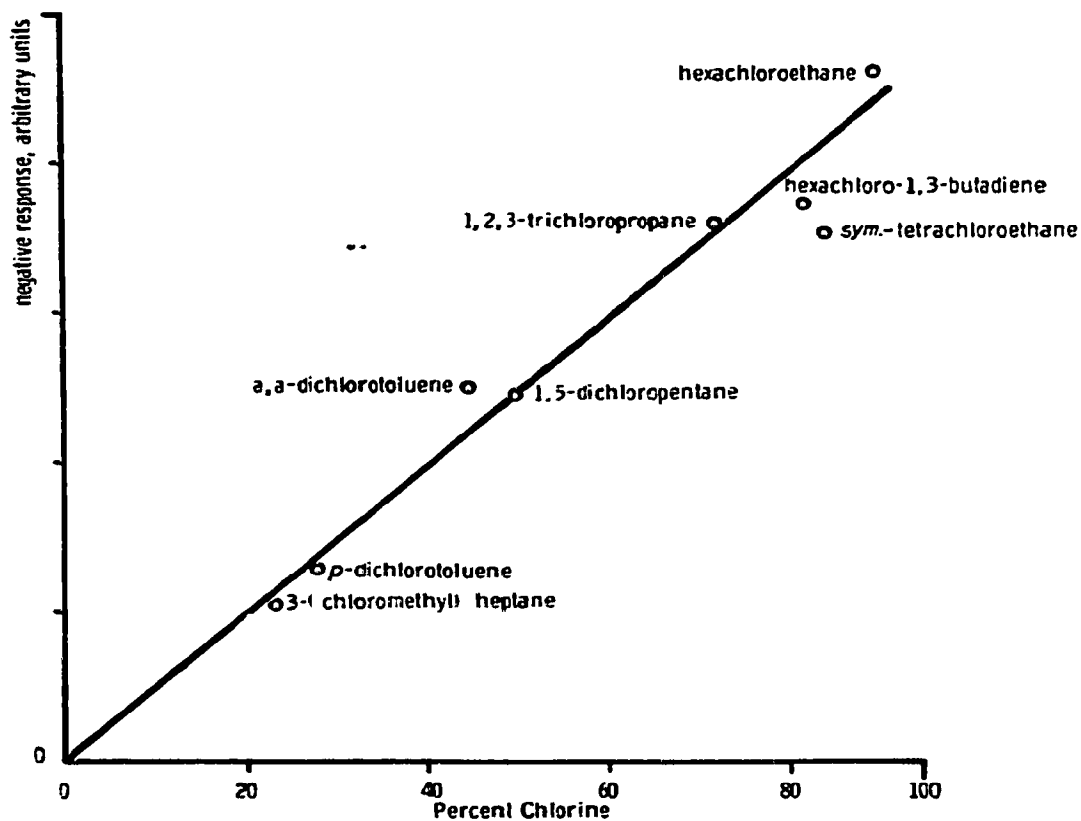


Fig. 8. Elemental chlorine response. Pellet:  $\text{Rb}_2\text{SO}_4$ , 1-mm bore. Electrode height: 2 mm. Flow rates (ml/min):  $\text{H}_2 = 38$ ;  $\text{N}_2 = 17$ ; air = 215.

## RESULTS

Figs. 3 and 4 show the profiles used for optimization of sulfur response, Figs. 5-10 give the elemental response data for phosphorus, nitrogen and iodine in a positive mode; and chlorine, bromine and sulfur in a negative mode. Table I presents the results from the "Unknown-Standard" calculations, summarized in the last column

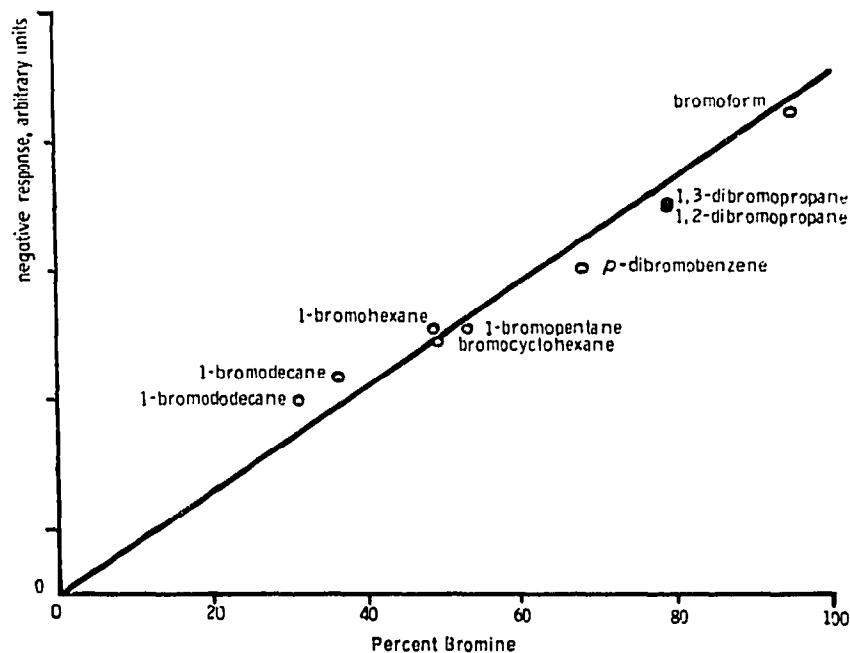


Fig. 9. Elemental bromine response. Pellet:  $\text{Rb}_2\text{SO}_4$ , 1-mm bore. Electrode height: 7 mm. Flow rates (ml/min):  $\text{H}_2 = 38$ ;  $\text{N}_2 = 17$ ; air = 215.

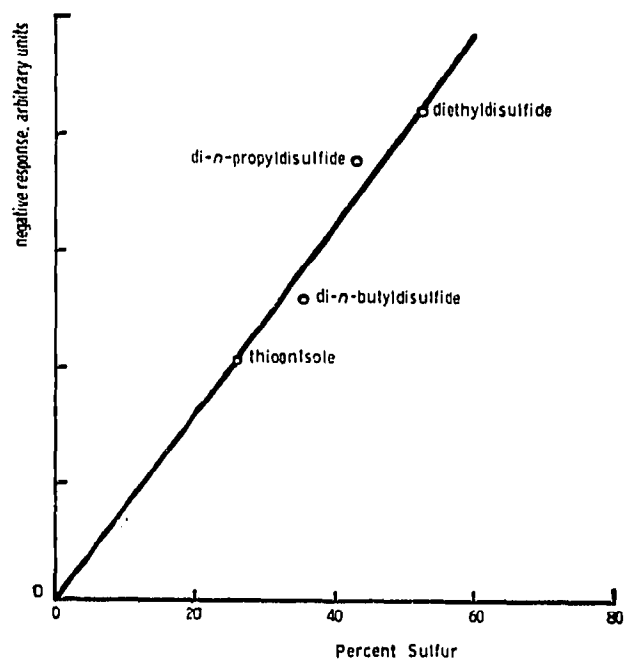


Fig. 10. Elemental sulfur response. Pellet:  $\text{Rb}_2\text{SO}_4$ , 1-mm bore. Electrode height: 2 mm. Flow rates (ml/min):  $\text{H}_2 = 28$ ; He = 55; air = 215.

TABLE I

CALCULATION OF PERCENTAGE HETERO-ATOM CONTENT FROM AFD AND FID RESPONSES

<i>Chlorine compounds</i>	<i>Cl theor. (%)</i>	<i>Cl calc. (%)</i>
Hexachloroethane	90.0	
<i>p</i> -Dichlorotoluene	41.1	43.7
3-(Chloromethyl)heptane	23.9	
Hexachloroethane	90.0	86.5
1,2,4,5-Tetrachlorobenzene	65.8	
1-Chloronaphthalene	21.8	28.0
$\alpha,\alpha$ -Dichlorotoluene	44.1	
Benzylchloride	28.0	26.4
1,5-Dichloropentane	50.3	
1,4-Dichlorobutane	55.8	60.0
$\alpha,\alpha,\alpha$ -Trichlorotoluene	54.5	
1-Chloronaphthalene	21.8	27.4
<i>sym.</i> -Tetrachloroethane	84.6	
Benzylchloride	28.0	24.7
1,5-Dichloropentane	50.3	
$\alpha,\alpha$ -Dichlorotoluene	44.1	44.0
<i>p</i> -Dichlorobenzene	48.3	
1,2,3-Trichloropropane	72.2	73.5
1,5-Dichloropentane	50.3	
<i>sym.</i> -Tetrachloroethane	84.6	84.2
1,2,3-Trichloropropane	72.2	
1,2,4-Trichlorobenzene	58.7	58.7
Benzylchloride	28.0	
Hexachloro-1,3-butadiene	81.7	82.7
1,2,3-Trichloropropane	72.2	
1,5-Dichloropentane	50.3	55.4
<i>Bromine compounds</i>	<i>Br theor. (%)</i>	<i>Br calc. (%)</i>
Ethylenedibromide	85.3	
1-Bromohexane	48.4	44.8
Bromobenzene	51.0	
Bromocyclohexane	49.0	48.8
1,2-Dibromopropane	79.5	
1-Bromopentane	53.0	51.4
Dibromomethane	91.9	
1-Bromopentane	53.0	51.9
Ethylenedibromide	85.3	
2-Bromopentane	53.0	50.8
Bromoform	94.8	
Bromocyclohexane	49.0	46.3
Bromobenzene	51.0	
1,3-Dibromopropane	79.5	81.6
Ethylenedibromide	85.3	
1-Bromo-5-methylbutane	53.0	49.0
1-Bromo-2-methylpropane	48.7	
1-Bromo-3-methylbutane	53.0	49.1
<i>Iodine compounds</i>	<i>I theor. (%)</i>	<i>I calc. (%)</i>
2-Iodopropane	74.7	
1-Iodopropane	74.7	72.5
<i>p</i> -Iodotoluene	58.2	
Iodobenzene	62.2	61.3



TABLE I (continued)

<i>Nitrogen compounds</i>		<i>N theor. (%)</i>	<i>N calc. (%)</i>
Aniline		15.0	
2-Aminopyridine		29.8	27.2
Aniline		15.0	
<i>p</i> -Toluidine		13.1	13.7
Acetamide		23.7	
Pyridine		17.7	13.4
Aniline		15.0	
<i>o</i> -Anisidine		11.4	13.1
Pyridine		17.7	
Aniline		15.0	17.9
<i>N,N</i> -Dimethylaniline		11.5	
Pyridine		17.7	17.6
<i>N,N</i> -Dimethylaniline		11.5	
<i>N,N</i> -Diethylaniline		9.3	8.7
<i>N,N</i> -Dimethylaniline		11.5	
2,4-Dimethylaniline		11.5	9.2
<i>p</i> -Toluidine		13.1	
2-Pyrrolidone		16.5	19.8
Iminodipropionitrile		34.1	
Imidazole		41.1	36.3
3-Dimethylamino-propionitrile		28.5	
<i>N,N</i> -Diethylaniline		9.3	6.8
<i>Phosphorus compounds</i>		<i>P theor. (%)</i>	<i>P calc. (%)</i>
Triphenylphosphine		11.8	
Triphenylphosphite		10.8	8.7
Parathion		10.6	
Triphenylphosphine		11.8	7.6
Triethylphosphate		17.0	
Tri- <i>n</i> -butylphosphate		11.6	9.2
Trimethylphosphate		22.1	
Triethylphosphate		17.0	7.5
Diazinon		8.1	
Trimethylphosphate		22.1	24.4
<i>Sulfur compounds</i>		<i>S theor. (%)</i>	<i>S calc. (%)</i>
Di- <i>n</i> -butyldisulfide		35.9	
Thioanisole		25.8	20.4
Di- <i>n</i> -propyldisulfide		42.7	
Thioanisole		25.8	25.3
Di- <i>tert.</i> -butylsulfide		21.9	
Di- <i>n</i> -propylsulfide		27.1	23.3
Di- <i>tert.</i> -butylsulfide		21.9	
Di- <i>n</i> -propyldisulfide		42.7	35.5
Di- <i>n</i> -propylsulfide		27.1	
Di- <i>n</i> -propyldisulfide		42.7	40.3
<i>Hetero-atom</i>	<i>No. examples</i>	<i>Standard deviation (%)</i>	<i>Response</i>
Chlorine	13	± 3.5	negative
Bromine	9	± 2.8	negative
Iodine	2	(± 2.4)	positive
Nitrogen	11	± 2.9	positive
Phosphorous	5	± 5.6	positive
Sulfur	5	± 5.0	negative

TABLE II

VARIATION OF "STANDARD"—"UNKNOWN" RATIOS

Ratio $\alpha$ - $\alpha$ -Dichlorotoluene-benzylchloride		Benzylchloride Cl calc. (%)
(44.1% Cl theor.) Ratio	(28.0% Cl theor.)	
I	: I	26.7
I	: 2	26.3
I	: 3	26.0
I	: 5	30.1
I	: 7	33.6
I	: 10	31.6

with standard deviation values included. Additionally, Table II shows calculations done on one pair with varying ratios of Unknown to Standard.

It should be mentioned that we experienced some difficulties in initial experiments to obtain elemental response lines going through the origin in the case of bromine, iodine and nitrogen. A different setting of the electrode (higher above the salt surface) removed the problem. A series of nitro compounds, however, had to be eliminated from the nitrogen experiment because their AFD response did not conform to our ideas of proportionality.

#### DISCUSSION

With the exception of the nitro compounds cited above, all hetero-organics gave responses proportional to their elemental composition on the AFD operating in either positive or negative mode. The data shown in Figs. 5-10 are certainly not ideal, but probably as good as one can expect them to be under the circumstances. Impurity of standards, partial decomposition on the column, disparate column bath temperatures, sensitivity changes of the AFD, and several other effects could have influenced the outcome. It may be significant that we could not discern any particular patterns related to compound type; rather, the deviations from the straight line seemed to be distributed at random.

This result is borne out by the subsequent calculations of percent hetero-atom content in "Unknowns". The data are rather crude, but show very clearly the feasibility of such an approach. Again, deviations from theoretical values seem to be distributed at random.

Several obvious improvements could be made to eliminate some sources of error. We worked with two different chromatographs (Barber-Colman and MicroTek 220) mainly because all available gas chromatographs in our laboratory, except the MT 220, at one time or another had been used for AFD studies and could not be relied on for unperturbed FID response. However, injecting on a single column and splitting the effluents after GC separation to flow to carefully-separated AFD's and FID's, would seem to constitute the far preferable approach. Errors introduced by imprecise injection, decomposition in the injection port or on the column, unreliable comparisons of dissimilar-shaped peaks, etc., would all be avoided. The absolute

split-ratio should not matter, as long as it remains the same for each compound and as long as it allows both detectors to operate within their linear range.

Another approach to better data may come from the proper choice of a standard. We had, quite deliberately, chosen compounds at random for our comparisons. It is obvious, however, that a standard close in chemical characteristics to the Unknown would tend to cancel out some of the error arising from our assumption of an FID response proportional to carbon content, or even proportional to the total C-H-O fraction, of the compounds involved. In practice, some knowledge of the chemical constitution of the "Unknown" is usually available to the analyst.

The suggested avenues for improvement, may in fact, be crucial if this dual-detector approach were to be extended from pure standards to the complex mixtures found in biochemical or environmental samples.

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CHROM. 5686

## AN INVESTIGATION INTO HYDROGEN BONDING IN GAS-LIQUID CHROMATOGRAPHY

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## SUMMARY

Aromatic ketones and a nitroso compound, providing the oxygen donor atom for hydrogen bonding, have been studied. The energies of the spectroscopic solvent shifts of the donor molecules have been correlated with gas-liquid chromatographic retention index data when the donor molecules are used as the stationary phases. Linear relationships for both hydrogen bonding and non hydrogen bonding solvents have been established and hydrogen bonding energies for several systems are tabulated. The significance of the solute-solvent interactions between the ketones studied and chloroparaffins, alcohols and amines is discussed.

## INTRODUCTION

That hydrogen bonding, when it occurs, is an important factor in retention in gas-liquid chromatography, is an accepted fact. The hydrogen bonding effect has been discussed by AMBROSE AND AMBROSE<sup>1</sup>, PURNELL<sup>2</sup> and DAL NOGARE AND JUVET<sup>3</sup> in general terms and compared with EWELL *et al.*'s<sup>4</sup> classification scheme for hydrogen bonding in fractional distillation. Any study in solvent selectivity is made complex by the various forces which have to be considered, *i.e.* (a) dispersion forces which operate in all systems at all times, (b) orientation forces arising from the interaction of permanent dipoles, of which hydrogen bonding is an extreme case and (c) induction forces caused by the polarization of normally non-polar molecules when they are subjected to the field of a molecule having a permanent dipole. Solute-solvent systems showing a high degree of attraction, for instance ketone-alcohol systems, will demonstrate negative deviations from Raoult's Law — the solute being well retained by the solvent which can then be said to show high selectivity for the solute.

The Kováts<sup>5</sup> retention index ( $I$ ) is a parameter which can be used to study the extent of solute-solvent interactions in gas-liquid chromatography, ROHR-SCHNEIDER<sup>6</sup> having used the index increment ( $\Delta I$ ) to describe the polarity of various stationary phases with respect to squalane. For a given solute, the index increment,  $I_{\text{stationary phase}} - I_{\text{squalane}}$ , is a measure of the solute-solvent interaction in terms of the orientation and induction forces described above. The quantitative interpretation of experimental results however, is virtually impossible at the present. Useful work