

levels, and relatively long analyses (approximately 1 h) for MMC samples. The significant advantages over previous methods are the simplification of sample elution directly onto the GC column which minimizes the possibilities of contamination and the ability to positively identify two of the most important organic forms of mercury present in the atmosphere. The identification of individual organic mercury species will enable investigators to determine the relative importance of a given species in the natural cycling of mercury.

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**Registry No.** MMC, 115-09-3; DMM, 593-74-8; Chromosorb 101, 9003-70-7.

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## Multiple-Parameter Optimization of a Hydrogen-Atmosphere Flame Ionization Detector

Dennis G. McMinn

Department of Chemistry, Gonzaga University, Spokane, Washington 99258

Randy L. Eatherton and Herbert H. Hill, Jr.\*

Department of Chemistry, Washington State University, Pullman, Washington 99164-4630

**The response of the hydrogen-atmosphere flame ionization detector (HAFID) depends upon several operating parameters. The present work investigated the significance of these parameters and of interactions between them by using two level factorial analyses of both the positive (using low silane dopant concentration) and negative (using high silane concentration) operating modes. The factorial results were used in sequential simplex searches for optimum parameter values for the detection of ferrocene in both modes. In the positive mode these were 2300 mL/min H<sub>2</sub> flow, 10 ppm SiH<sub>4</sub>, 260 mL/min N<sub>2</sub> + O<sub>2</sub> flow, with a O<sub>2</sub>/N<sub>2</sub> ratio of 1.71, and a collector potential of -285 V. In the negative mode, ferrocene could be detected at the  $2.7 \times 10^{-15}$  mol/s level under optimized conditions of 1500 mL/min H<sub>2</sub>, 50 ppm SiH<sub>4</sub>, 200 mL/min total N<sub>2</sub> + O<sub>2</sub> flow, and O<sub>2</sub>/N<sub>2</sub> ratio of 1.36, and an electrode potential of -90 V.**

The hydrogen-atmosphere flame ionization detector (HAFID) has been shown to be useful for the detection of metal-containing compounds following separation by gas chromatography. Applications to the analysis of volatile metal chelates, metal carbonyls and organometallics have been particularly successful (1-4). Under different operating conditions, silicon-containing compounds can be detected in a sensitive and selective manner (5, 6).

HAFID variables can be adjusted to provide either a positive or an "inverted" response to the organometallic being measured (4). The controlling factor seems to be the concentration of the doping reagent although response is affected by several parameters. To date, a mechanism responsible for the formation of ions in the flame has not been delineated nor has any systematic study to optimize the response of the detector been attempted.

From initial development work, indications are that electrode height, voltage applied at the collector electrode, flow rates of oxygen, air, and hydrogen, and the concentration of the doping reagent have significant effects on the response of a HAFID (7). In these studies, attempts at optimization focused on the variation of one factor while holding all others constant. This single-parameter optimization is inherently inadequate when factors interact. Attempts at optimization by this method are normally time consuming, since a large number of combinations must be investigated. The present project was undertaken to study interactions among the factors listed above and to determine the extent to which true optimal conditions had been reflected in the parameter values chosen in previous work. A combination of a factorial study (8) and a sequential simplex design (9-11) was utilized.

#### EXPERIMENTAL SECTION

A HAFID with silane as the doping gas was constructed with an HP 5830A gas chromatograph equipped for on-column injection with a 6 ft  $\times$  1/4 in. o.d. (2 mm i.d.) borosilicate column packed

Table I. Values of Parameters Chosen for Factorial Study

	H <sub>2</sub> flow, mL/min	SiH <sub>4</sub> concn, ppm in H <sub>2</sub>	[O <sub>2</sub> + N <sub>2</sub> ] flow, mL/min	O <sub>2</sub> /N <sub>2</sub> vol/vol	electrode height, mm
factor number	1	2	3	4	5
positive mode low value	1382	12.2	210	1.19	55
high value	1460	20.0	255	1.36	75
negative mode low value	1382	54.0	210	1.19	<i>a</i>
high value	1460	71.8	255	1.36	<i>a</i>

<sup>a</sup> Electrode height kept constant at 75 mm.

with 3% SE 30. Voltages used for the collector electrode are listed in Table V and represent the sum of potentials from several batteries connected in series.

At relatively low silane concentrations, response is normal: i.e., the solvent and the sample both cause an increase in current. This we refer to as the positive response mode. At high silane concentrations, the current is decreased from that of background when ferrocene is eluted. This results in an "inverted" peak, referred to as the negative response mode of the detector. Throughout this study response was measured for ferrocene (Aldrich Chemical Co., Milwaukee, WI) dissolved in reagent-grade hexane. It required 1.5 min to elute from the column at 150 °C.

**Factorial Study.** In the initial phase of this investigation, a two-level factorial study was designed to evaluate interactions among the parameters involved (8, 12). For the positive response mode, five factors were chosen: electrode height, silane concentration, hydrogen flow rate, total flow of oxygen plus nitrogen, and the ratio of oxygen to nitrogen. In the negative response mode the electrode height was held constant at 75 mm since earlier experience had shown that variations on either side of this height greatly diminished the response (4). The other four factors were included in the study.

Careful control over flow rates was necessary in order to accommodate this factorial study. Changes in hydrogen flow required an adjustment in silane flow in order to keep silane concentration constant. Similarly, nitrogen was provided by using compressed air so that changes in air flow affected both the oxygen and nitrogen flow. The values of the various parameters are summarized in Table I.

**Simplex Study.** The simplex method, as described by Deming and Morgan (10), is a rapid and simple procedure for optimizing an analytical system which does not rely on traditional testing of significance. Long (11) has given a straightforward exposition of its use and has noted that factorial experiments are a good way to judge the significance of possible factors. For simplicity, we defined the "optimum" for this system to be the maximum peak height for a 1.0 ng sample of ferrocene. In the tables, response has been converted into current (in amperes).

On the basis of the factorial study performed here (see Results), a simplified approach was used to optimize response of the HAFID. In essence, two parameters which interacted strongly were paired and the response was maximized by utilizing a two-dimensional simplex in which these were varied while the other parameters were held constant. Then another pair of interacting factors was selected and the same procedure followed. The technique chosen for this work used simplexes with fixed step sizes, simplifying the calculations. Simplex optimization using variable step sizes has also been reported (10). Two-factor simplexes are simple to perform and the progress can be followed graphically. In addition, this approach reduces the number of valves which must be adjusted at each experimental point. Results obtained from this "quasi-optimization" were used to assign starting values for a complete 5-factor simplex.

Electrode height has a significant effect on the response (see Results). Although in theory it would be possible to vary electrode height throughout a simplex scheme, in practice this is a difficult procedure given the present detector design. An electrode height of 75 mm was chosen as a convenient value (4) and optimization performed at this height. Variation in voltage at the collector electrode is more easily controlled and hence voltage was included in the simplex studies. A series of batteries rather than a continuously variable voltage source was used since the former resulted in a more stable voltage with less background interference. Some compromise however was required in the simplex schemes

because voltages could only be adjusted in increments. beginning values and step sizes for the various simplex studies are given in Table IV.

## RESULTS AND DISCUSSION

Table II summarizes the experimental values obtained for response at each of the combinations of parameters for the positive and the negative response modes. The arrangement of data is in the standard order (8) where a plus (+) sign indicates the factor was set at the high level and a minus (−) sign shows the factor to be at the low level as defined in Table I. For the positive response mode, 2<sup>5</sup> combinations are possible while for the negative response mode 2<sup>4</sup> are possible.

Analysis of the data was performed by using the general linear models procedure of release 82.3 of SAS (Statistical Analysis System) (13) at the Washington State University Computing Service Center. The factorial technique assumes that each response can be decomposed into single and multiple factor contributions. A linear model is used: i.e., for *k* factors

$$Y = b_0 + b_1X_1 + b_2X_2 + \dots b_kX_k + b_{12}X_1X_2 + \dots \quad (1)$$

*Y* is a HAFID response, the regression coefficients, *b*, give the mean effects of changing each parameter alone, from its low value to its high value (single subscript), and the interactions among parameters (multiple subscripts). The term *b*<sub>0</sub> designates the grand mean of all the responses. The regression coefficients obtained are summarized in Table III. Values for terms not shown in Table III were not found significant at the 95% confidence level. For the positive mode model, the multiple correlation coefficient (*R*<sup>2</sup>) was 0.961. The error mean square was 0.0034 with 64 degrees of freedom. For the negative mode model, *R*<sup>2</sup> was 0.941. The error mean square was 0.0016 with 32 degrees of freedom.

One of the goals implicit in the choice of the factor levels used in this study was an attempt to find an optimum situation which used a moderate hydrogen flow. Hydrogen flows as high as 2200 mL/min have been used in the past (4). We investigated the HAFID response in a region of more moderate flow. Associated with this choice was the use of lower silane doping. All other parameters were similar to those chosen previously (3, 4).

At these levels, the factorial analysis of the positive mode response indicates that all five factors are statistically significant at the 95% confidence level. Thus inclusion of all five factors in a simplex study is indicated. It is of interest to note that at these levels the negative response mode is insensitive to changes in hydrogen flow (factor 1) and the oxygen-to-nitrogen ratio (factor 4). Normally, one would drop these two factors and include only the remaining two in a simplex study. However, since there was a significant interaction between hydrogen flow and the O<sub>2</sub>/N<sub>2</sub> ratio detected (Table IIIB), these two factors were also included in the negative mode simplex study.

Results of the factorial analysis showed that interactions between silane concentration and flow of oxygen plus nitrogen (factors 2 and 3) were important in both the positive and negative response modes. These two effects were thus combined in a simplex optimization scheme for the positive mode

Table II. Results of Factorial Study

combination no.	designation of factor no. <sup>a</sup>					exptl response, A × 10 <sup>10</sup>			
	X1	X2	X3	X4	X5	trial 1	trial 2	trial 3	mean
A. Positive Response Mode									
1	-	-	-	-	-	0.35	0.45	0.29	0.36
2	+	-	-	-	-	0.54	0.52	0.49	0.51
3	-	+	-	-	-	0.19	0.15	0.09	0.15
4	+	+	-	-	-	0.42	0.34	0.42	0.39
5	-	-	+	-	-	0.70	0.90	0.77	0.79
6	+	-	+	-	-	0.79	0.84	0.87	0.83
7	-	+	+	-	-	0.84	0.77	0.61	0.74
8	+	+	+	-	-	0.76	0.67	0.64	0.69
9	-	-	-	+	-	0.68	0.62	0.51	0.60
10	+	-	-	+	-	0.79	0.83	0.83	0.82
11	-	+	-	+	-	0.47	0.44	0.37	0.42
12	+	+	-	+	-	0.58	0.71	0.47	0.59
13	-	-	+	+	-	1.00	0.91	0.97	0.96
14	+	-	+	+	-	0.81	0.89	0.91	0.87
15	-	+	+	+	-	0.67	0.83	0.78	0.76
16	+	+	+	+	-	0.71	0.71	0.82	0.74
17	-	-	-	-	+	0.43	0.35	0.40	0.39
18	+	-	-	-	+	0.45	0.50	0.41	0.45
19	-	+	-	-	+	0.27	0.36	0.32	0.32
20	+	+	-	-	+	0.20	0.32	0.24	0.25
21	-	-	+	-	+	0.19	0.15	0.19	0.18
22	+	-	+	-	+	0.36	0.29	0.20	0.29
23	-	+	+	-	+	0.05	0.08	0.07	0.07
24	+	+	+	-	+	0.25	0.17	0.15	0.19
25	-	-	-	+	+	0.48	0.54	0.58	0.53
26	+	-	-	+	+	0.62	0.62	0.56	0.60
27	-	+	-	+	+	0.33	0.40	0.35	0.36
28	+	+	-	+	+	0.43	0.44	0.43	0.43
29	-	-	+	+	+	0.26	0.22	0.21	0.23
30	+	-	+	+	+	0.56	0.46	0.52	0.51
31	-	+	+	+	+	0.15	0.13	0.12	0.13
32	+	+	+	+	+	0.43	0.44	0.43	0.43
B. Negative Response Mode									
1	-	-	-	-	-	0.59	0.58	0.56	0.58
2	+	-	-	-	-	0.71	0.66	0.55	0.64
3	-	+	-	-	-	0.59	0.60	0.55	0.58
4	+	+	-	-	-	0.51	0.61	0.51	0.54
5	-	-	+	-	-	0.26	0.34	0.35	0.32
6	+	-	+	-	-	0.25	0.29	0.32	0.29
7	-	+	+	-	-	0.37	0.46	0.40	0.41
8	+	+	+	-	-	0.55	0.50	0.55	0.53
9	-	-	-	+	-	0.55	0.59	0.59	0.58
10	+	-	-	+	-	0.68	0.62	0.59	0.63
11	-	+	-	+	-	0.57	0.61	0.62	0.60
12	+	+	-	+	-	0.58	0.61	0.55	0.58
13	-	-	+	+	-	0.40	0.41	0.36	0.39
14	+	-	+	+	-	0.19	0.15	0.24	0.19
15	-	+	+	+	-	0.50	0.50	0.51	0.50
16	+	+	+	+	-	0.49	0.46	0.50	0.48

<sup>a</sup> Factor numbers are given in Table I.

(simplex I) and "optimized" while keeping factors 1 and 4 (hydrogen flow and O<sub>2</sub>/N<sub>2</sub> ratio) constant. The settings which resulted in the maximal response from this combination (Table IV) were then maintained while factors 1 and 4 were varied in a second simplex (simplex II). A boundary condition was imposed in simplex II because of a flow restrictor on the oxygen line. Thus, in simplex II, the O<sub>2</sub>/N<sub>2</sub> ratio could not be increased beyond a value of 1.71 when the total flow of O<sub>2</sub> + N<sub>2</sub> was high. At lower total flows, a slightly higher ratio could be accommodated (see for example Table V, vertex 9). After an O<sub>2</sub>/N<sub>2</sub> ratio of 1.71 was reached, only the hydrogen flow was increased as the optimum was sought. The results of this quasi-optimization gave values for the flow rates (Table IV) that turned out to be quite close to those found at the eventual optimum and allowed simplex III (where all five factors were varied) to proceed quickly.

The progress of simplex III is shown in Table V. Six vertices are required to set the initial simplex. The optimum occurred at vertex 19. The simplex was terminated at vertex 25 since the measured response was not improving. The optimum occurred at flow rates which were only slightly different than those used to begin the simplex, but the applied voltage was significantly different. Final values gave a response nearly 20 times as great as was obtained from the combination used to initiate simplex I.

Simplexes IV and V are analogous in design to I and II and were used to "optimize" negative response by combining a pair of two-dimensional simplexes. The progress of simplex IV is shown in Figure 1. It shows an example of the use of the  $k + 1$  rule (10), in which a vertex response is checked if it remains in  $k + 1$  simplexes, where  $k$  is the dimension of the simplex. The simplex was allowed to circle vertex 3 to map

Table III. Regression Coefficients from Factorial Analysis

	A. positive response mode	B. negative response mode
est std error	0.0060	0.0060
95% conf int	±0.067	±0.046
$b_0$	0.49	0.49
$b_1$ H <sub>2</sub> flow	0.050	(-0.0040)
$b_2$ SiH <sub>4</sub> concn	-0.071	0.039
$b_3$ O <sub>2</sub> + N <sub>2</sub> flow	0.038	-0.10
$b_4$ O <sub>2</sub> /N <sub>2</sub> ratio	0.075	(0.0044)
$b_5$ elec height	-0.15	
$b_{14}$	<i>a</i>	-0.019
$b_{23}$	0.015	0.054
$b_{34}$	-0.020	<i>a</i>
$b_{35}$	-0.12	
$b_{123}$	<i>a</i>	0.031
$b_{134}$	<i>a</i>	-0.020
$b_{135}$	0.049	
$b_{145}$	0.019	
$b_{345}$	0.026	
$b_{12345}$	-0.014	

<sup>a</sup> Values not significant at the 95% confidence level.

the area before retesting. Upon retesting, the response at vertex 3 was found to be lower than the previous value. This resulted in the decision to drop vertices 5, 6, and 7. Strict application of the  $k + 1$  rule as the simplex begins to circle a maximum value is necessary since traditional significance testing of the experimental responses is not used in this technique. Simplex VI was a 5-factor simplex which included voltage changes but in this case resulted in no improvement in response.

Following the scheme outlined in the Experimental Section, one can see that optimization was accomplished by the first simplex search (simplex IV). The second two-parameter search (simplex V) was performed to verify the conclusion from the factorial study that hydrogen flow and O<sub>2</sub>/N<sub>2</sub> ratio were unimportant in this region. When allowed to vary, the

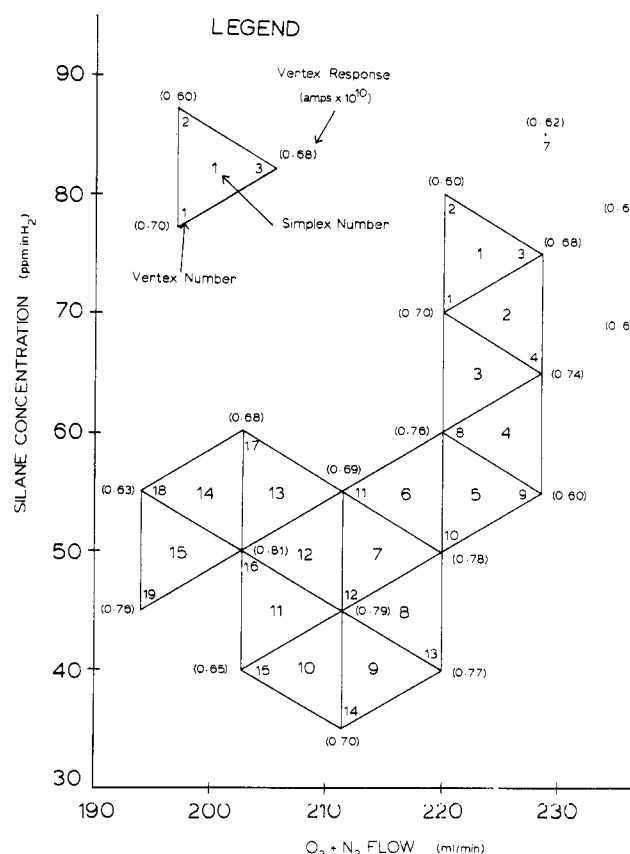


Figure 1. Progress of simplex IV. Vertices 5, 6, and 7 were rejected by application of the  $k + 1$  rule. Optimum conditions are at vertex 16.

optimal values of these parameters remained unchanged.

In previous work there has been much speculation about the interaction of the various parameters and the possible mechanism responsible for the response of the HAFID. The present study identifies the primary parameter interactions

Table IV. Values of Parameters for Simplex Studies

simplex	factor no. <sup>a</sup>					response, A × 10 <sup>10</sup>
	1	2	3	4	5	
A. Positive Response Mode						
I. starting value	1512	8.0	210	1.36	90	0.14
step size	0	3.0	10	0	0	
final value <sup>b</sup>	1512	7.21	258.5	1.36	90	0.77
II. starting value	1512	7.21	258.5	1.36	90	0.77
step size	72	0	0	0.10	0	
final value	2304	7.21	258.5	1.71 <sup>d</sup>	90	2.24
III. starting value	2304	7.21	258.5	1.71	180	2.51
step size	72	3.0	-20	-0.20	90	
final value	2278	9.90	260.6	1.71 <sup>d</sup>	285	2.82
B. Negative Response Mode						
IV. starting value	1512	70.0	220	1.36	90	0.70 <sup>c</sup>
step size	0	10.0	10	0	0	
final value	1512	50.0	202.8	1.36	90	0.81
V. starting value	1512	50.0	202.8	1.36	90	0.81
step size	72	0	0	0.10	0	
final value	1512	50.0	202.8	1.36	90	0.81
VI. starting value	1512	50.0	202.8	1.36	90	0.81
step size	72	10.0	10.0	0.10	90	
final value	1512	50.0	202.8	1.36	90	0.81

<sup>a</sup> Factors 1-4 are given in Table I, factor 5 is potential (negative) applied at collector electrode (in volts). <sup>b</sup> Final values for simplex I reflect using smaller step sizes as the optimum was neared. <sup>c</sup> Negative mode response is a decrease from background current. <sup>d</sup> This is a boundary condition since flow of oxygen is restricted.

Table V. Progress of Simplex III

reject vertex	vertex	factor number <sup>b</sup>					response, A × 10 <sup>10</sup>
		1	2	3	4	5 <sup>d</sup>	
	1	2304	7.21	260	1.71	180	2.51
	2	2304	7.21	260	1.71	270	2.71
	3	2360	7.21	260	1.71	225	1.68
	4	2325	9.66	260	1.71	225	2.36
	5	2325	7.82	244	1.71	225	2.38
	6	2325	7.82	257	1.56	225	2.36
3	7	2273	8.68	252	1.65	225	2.72
4	8	2285	5.84	249	1.63	225	2.05
6 <sup>a</sup>	9	2269	6.88	249	1.80	225	2.51
8	10	2303	9.28	257	1.81	225	2.74
5	11	2254	7.89	267	1.76 <sup>c</sup>	225	- <sup>c</sup>
9 <sup>a</sup>	12	2303	9.23	269	1.65	225	2.57
11	13	2339	8.76	252	1.65	225	1.93
1	14	2302	10.05	256	1.68	285	2.37
13 <sup>a</sup>	15	2253	9.02	266	1.75 <sup>c</sup>	270	- <sup>c</sup>
14 <sup>a</sup>	16	2270	7.31	266	1.75 <sup>c</sup>	195	- <sup>c</sup>
15 <sup>a</sup>	17	2325	7.66	256	1.68	195	1.97
16 <sup>a</sup>	18	2331	9.50	252	1.65	270	2.21
17 <sup>a</sup>	19	2278	9.90	261	1.71	285	2.82
18	20	2251	8.21	268	1.76 <sup>c</sup>	225	- <sup>c</sup>
2 <sup>a</sup>	21	2257	10.91	263	1.72	210	2.64
20	22	2313	10.99	253	1.66	225	1.97
12	23	2263	10.68	245	1.76	270	2.35
22 <sup>a</sup>	24	2235	8.80	258	1.81	270	2.57
23	25	2272	8.35	271	1.71 <sup>c</sup>	225	- <sup>c</sup>

<sup>a</sup> Second lowest value rejected. <sup>b</sup> Factors numbered as in Table IV. <sup>c</sup> Outside available value due to oxygen flow restriction; low value assigned for response. <sup>d</sup> Rounded off to nearest attainable voltage.

Table VI. Single-Factor and Simplex-Optimized Parameter Values

	1 H <sub>2</sub> flow, mL/min	2 SiH <sub>4</sub> concn, ppm	3 (O <sub>2</sub> + N <sub>2</sub> ) flow, mL/min	4 O <sub>2</sub> /N <sub>2</sub> vol/vol	5 collector potential, V
A. Positive Mode					
single-factor	1600	31.25	270.0	1.81	-90
simplex	2278	9.90	260.6	1.71	-285
B. Negative Mode					
single-factor	2200	137.0	270.0	1.81	-90
simplex	1512	50.0	202.8	1.36	-90

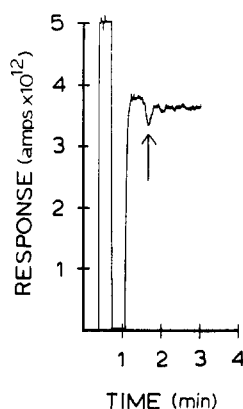
which are important for the response to ferrocene and is the first attempt to systematically vary factors known to be responsible for variations in this response. Physical interpretation of the single-factor mean effect regression coefficients in the presence of significant interaction coefficients can be misleading. However, the single-factor terms can be used to indicate the change required to improve the response. For example, in the positive mode, the hydrogen flow effect ( $b_1$ ) has a positive sign which indicates that changing from low to high hydrogen flows increased response. One might expect, then, that the optimum flow rate would lie closer to the high value or perhaps might exceed it. The results of the positive mode simplex optimization (Table IV) demonstrate that this was the case.

Further examination of the factorial and simplex results produces similar correspondences. One should note that the largest main effect in the positive mode is that of electrode height ( $b_5$ ). The relatively large negative value indicates that the optimum height would lie nearer to 55 mm than the currently accepted value of 75 mm (4). At the constant voltage used in this part of the study, the effect of lowering the electrode height would be an increase in the electric field strength between the flame and collector electrode. In the simplex study, electrode height was fixed due to the physical constraints of the system. The potential applied to the electrode was allowed to vary and it settled upon a higher

voltage as an optimal value. The effect of higher voltage is an increased electric field strength. Thus, from both the factorial study and the simplex study, it appears that electric field strength is of primary importance, compared to electrode position or potential, in optimizing the detector.

In the positive response mode the electric field above the flame has a large effect and interacts strongly with the air flow (see  $b_{35}$  in Table IIIa). There are also tertiary interactions with several combinations of parameters. The effect of electric field is dramatized in simplex III, where response is increased as voltage is increased. The effect of potential changes is negligible when looking at negative responses (simplex VI); yet the position of the electrode has been found critical (4). More work is needed to understand the relationship between electric field strength and the electrode position on the response of the detector. Other interactions are also different when the two modes are compared, which makes it likely that the mechanisms responsible for the positive and negative response are not the same.

Table VI summarizes the results of this study. Previously reported single-factor optimized conditions for the positive mode (3) and the negative mode (4) are given along with the optimum conditions found during this work. Comparing the two methods of optimization reveals dramatic differences. The simplex search allowed the significant interactions listed in Table IIIa to be operative in optimization. These interactions



**Figure 2.** Negative response mode chromatogram at simplex optimum. The sample is 0.1 pg of ferrocene.

and the strongly significant electrode height main effect lead the simplex to a higher optimum collector voltage than was previously reported. The single-factor optimum hydrogen flow was in the moderate flow region but, as noted before, the simplex algorithm required a higher hydrogen flow for optimum ferrocene response. The algorithm also found a lower optimum silane concentration and a lower oxygen plus nitrogen flow.

A similar single-factor optimization scheme was used to obtain the negative mode optimum conditions. The current results indicate that silane concentration and oxygen plus nitrogen flow were the only significant factors at these levels. The hydrogen flow remained at the moderate level chosen for

convenience, the oxygen to nitrogen ratio was determined by the oxygen plus nitrogen total flow required by the algorithm, and the collecting potential remained at the previously selected value of -90 V.

Under these conditions the negative mode was found to be more sensitive for ferrocene than the positive mode. Figure 2 shows a peak for 0.1 pg of ferrocene under negative mode optimized conditions. When calculated in terms of molar detection limits, this response corresponds to  $2.7 \times 10^{-16}$  mol/s.

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## Temperature Dependence of Plasma Chromatography of Aromatic Hydrocarbons

David M. Lubman

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

The temperature dependence of the reduced mobility parameter ( $K_0$ ) of various aromatic hydrocarbons is investigated in plasma chromatography. The ions are produced by two methods in this study, i.e., laser resonant two-photon ionization (R2PI) and the Ni  $\beta$  source ion/molecule reactor technique. The reduced mobilities have been determined as a function of temperature and in most cases are found to compare favorably for the two different ionization sources, thus providing a standard for accurately determining  $K_0$  values ( $\pm 2.5\%$ ). The observed value of  $K_0$  has been found generally not to vary significantly as a function of temperature over the range 220-85 °C. In addition, we have carefully tabulated values of  $K_0$  as a function of temperature for a variety of aromatic hydrocarbons of interest which may serve as a valuable reference for future analytical studies.

Plasma chromatography (PC) provides a sensitive technique for detection of organic compounds under atmospheric pressure conditions (1-33). Atmospheric pressure ionization in conventional PC is based upon the use of a  $^{63}\text{Ni}$   $\beta$  source to generate low-energy electrons which initiate a series of ion/molecule reactions. This ion/molecule chain then

transfers the charge to the trace organic compounds of interest. Previously, we introduced a new method of ionization for PC involving the use of laser resonant two-photon ionization (R2PI) (1-5). This technique provides direct ionization of molecules at atmospheric pressure obviating the often non-specific nature of the ion/molecule technique. One might therefore expect the laser technique to be less sensitive to the effect of competing ion/molecule reactions. In addition, this technique is capable of spectral selectivity in analysis based upon the one photon absorption spectrum (2, 4) or the effective two-photon ionization limit (IP) of molecules (3).

Once ionization has been performed, the plasma chromatography technique depends upon the separation of ions in a clean drift gas according to their mobilities under the influence of an applied electric field. The ion mobility,  $K$ , depends on  $N$ , the neutral gas number density,  $T$ , the temperature, and  $E/N$ , the ratio of the electric field to gas density for a given system. Since the transit time of an ion through the drift region is controlled by the number of collisions the ion makes with the molecules of the drift gas, it would be expected that the mobility would be inversely proportional to the number density. The dependence on  $N$  is generally removed by reporting  $K$  at a standard density corresponding to 0 °C and 1 atm (6). Thus, experimental results are reported