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THE NEGATIVE ALKALI FLAME DETECTOR RESPONSE*

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SUMMARY

Under certain conditions, the alkali flame detector will give negative response (inverted peaks) for organic compounds containing halogen, nitrogen, or other elements. With a modification of the alkali flame detector particularly suited for such a study, the range and magnitude of negative response was defined in terms of alkali bead bore, hydrogen flow, carrier gas flow, electrode height, and other parameters. Organic compounds containing chlorine, bromine, iodine, and nitrogen, were used as test substances; an organophosphate was studied under the same conditions for purposes of comparison. Cl, Br, I, N, and C can show either positive or negative response and each can be distinguished from the others by proper choice of parameters. Both halides and carbon compounds show stronger response in the negative mode than in the positive mode. The use of two different carrier gases, nitrogen and helium, did not cause significant differences, except in its effect on the response of nitrogen compounds. In general, a large bead bore, a high hydrogen supply and/or a low carrier gas flow favor negative response. These are also the conditions which establish a large area of contact between flame and alkali surface and, consequently, a large background current. In order to obtain reproducible response of adequate magnitude, the Rb_2SO_4 salt surface must be smooth and homogenous. The described detector functions can be used for qualitative microanalysis of hetero-organic compounds by gas-liquid chromatography.

INTRODUCTION

In the short, but turbulent history¹ of the alkali flame detector (AFD), negative responses (inverted peaks) have been observed by many authors^{2-4,15}. Such behavior was usually considered an interesting nuisance. Few authors tried to use this effect for analytical purposes. DRESSLER AND JANÁK analyzed sulfur compounds as negative peaks⁵. We reported recently on the use of the negative AFD response for the de-

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termination of chlorinated hydrocarbon insecticides⁶. In this field of residue analysis, the electron capture detector is used almost exclusively, and the AFD does not measure up either in sensitivity or reliability.

Nonetheless, a negative peak is an interesting phenomenon in its own right. Most important, in this respect, is the AFD's capability to distinguish between certain atoms. In the above mentioned study⁶, for example, chlorine effected negative, phosphorus positive peaks.

The interest in the negative response appears especially well justified in the area of trace analysis. Chromatographing minute amounts of interesting compounds present in a complex mixture, the best one can hope for is a series of well-separated chromatographic peaks. If these peaks can indicate the presence or absence of a particular heteroelement (by their normal or inverted form) valuable information can be gained. In this study, we have therefore investigated the general behavior of selected halogen, nitrogen, phosphorus, and carbon compounds and tried to define the areas and magnitudes of negative response.

There is a host of parameters influencing the AFD's performance characteristics, which need to be considered in a systematic study. The nature of the salt has been investigated intensively by several authors (ref. 1, pp. 13). Less studied was the surface of these salts, which are in contact with the hydrogen flame. The shape and the position of the electrode in relation to the flame is another critical parameter. Different elements will exhibit response maxima at different electrode heights⁷. Then, the hydrogen, carrier, and air flow are decisive for the performance of the detector, perhaps in this order of relative importance. The magnitude and direction of polarizing voltage is another parameter which has been frequently studied. Most important both in a practical and a theoretical context is the way in which alkali is introduced to the flame (ref. 1, p. 4). Finally, there are several other characteristics of the detector to be considered such as its operating temperature, its geometric and electric design, its pattern of air flow, etc.

Some of the literature on the alkali flame detector is controversial, mainly because different investigators worked with differently designed instruments and the AFD seems to reward every innovation or modification with a wealth of new and unexpected responses. Consequently, the definition of working parameters becomes very important. In this as in other studies, the obtained results depend to a great degree on the particular modification of the detector, the type of alkali source and electrode used, etc., and may not be immediately reproducible by other breeds of alkali flames.

In order to cut down on variables, several AFD features were taken from earlier work and held constant throughout this investigation. For instance, the collector electrode was a platinum loop of 7 mm I.D., which had worked well in a recent study of negative response. Rubidium sulfate was the only salt used, since it had been shown to work well with both halogens and nitrogen. The version of the AFD employed was similar to one reported earlier⁶, with a slightly altered detector configuration to permit frequent alkali bead changes. Other constant parameters included the air flow and the potential on the collector electrode.

The distance of the electrode from the alkali salt surface ("electrode height") has been shown to be of considerable importance. Both in positive⁷ and negative response mode⁸, it can be used to maximize response and discriminate against other

alkali flame-active elements. However, other variables can affect the performance of the AFD to an even greater degree.

The abundant literature on the subject—and our own experience—made it perfectly clear that the shape and temperature of the flame, and the area of its contact with the alkali surface, are of critical importance. This indicates the bore of the alkali bead and the flows of carrier gas and hydrogen as the prime variables. A small bead bore will tend to yield a tall and narrow flame with little contact with the alkali salt, a big bore will produce a low and broad flame which, so to speak, sits on the bead surface. The carrier gas, besides lowering the temperature of the hydrogen flame, will also alter the flame shape. Thus, the carrier flow can become very critical and has to be closely controlled. The dependence of response on the hydrogen flow is perhaps the best documented of the variables in the literature on the AFD (ref. 1, p. 9).

In this work, we have tried to define carrier gas and hydrogen gas flow between the extreme limits, *e.g.*, with hydrogen from the smallest flow which still supports the flame, to the highest flow where the background exceeds the buck-up capability of the electrometer or the noise becomes excessive. In view of several notices on the subject⁸⁻¹⁰, two different carrier gases, nitrogen and helium, were used and also varied within a range as wide as possible.

EXPERIMENTAL

The chromatographic system described earlier⁶ was used throughout this study. In order to facilitate frequent alkali bead changes, the bead was left in the steel ring used for pressing and held on the detector jet tip with a collar as shown in Fig. 1. It was produced in a screw-type pellet press (similar to the Carle model for IR work) with highly polished metal surfaces. Rubidium sulfate (99.9% pure, K & K) was finely ground in an agate mortar, mixed with a small amount of distilled water,

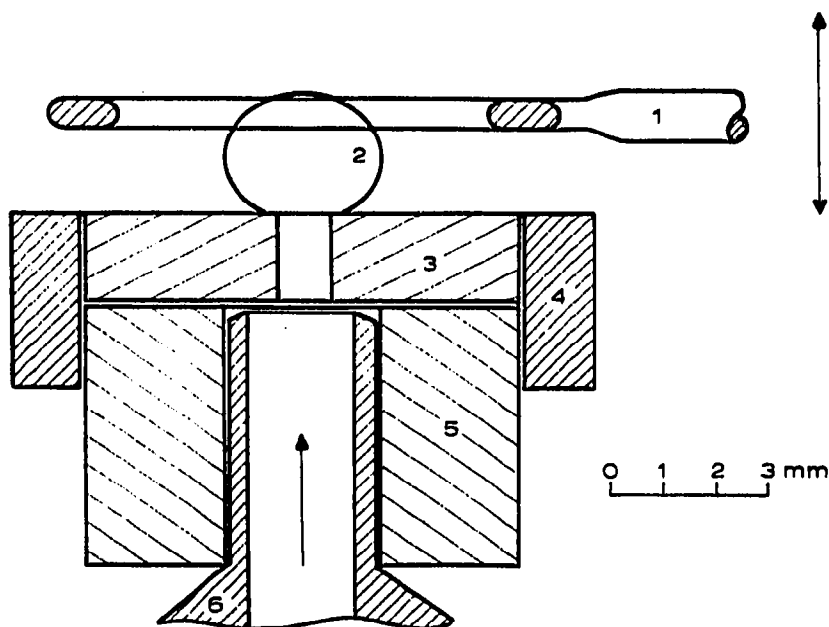


Fig. 1. Modified alkali flame detector. 1 = Adjustable electrode; 2 = hydrogen flame; 3 = rubidium sulfate; 4 = stainless steel; 5 = brass collar; 6 = detector jet tip.

filled into the steel ring, the pellet press closed, and pressure applied in stages with the help of a torque wrench. In intervals of about 5 min, from 5 to 35 ft. lbs. were applied in 5 ft. lb. steps. The final pressure on the bead was estimated in the order of 10^4 to 10^5 p.s.i. The amount of rubidium sulfate filled approximately half of the steel ring. The alkali salt pellet was left in the steel ring and drilled with a high-speed drill press. The salt surface must come out clean and smooth in order to obtain adequate and reproducible negative response.

Chlorobenzene, bromobenzene, iodobenzene; benzylamine, aniline; triethylphosphate, trimethylphosphate; *p*-xylene, *n*-decane, *p*-cymene, 1-octanol, and anisole served as test compounds. The halides were used in concentrations of 1% (w/v) and 0.01% (w/v), the nitrogen and carbon compounds at 1% (v/v), the phosphorus compounds at 0.0001% (w/v) and 0.001% (v/v) in *n*-hexane or acetone.

Unless otherwise indicated, all response profiles were measured with the collector electrode of 7 mm I.D. at +240 V, and an air flow of 250 ml/min. Several Rb_2SO_4 pellets were produced with bores of 0.50, 0.75, 1.0, 1.5, 2.0, and 3.0 mm. In a systematic way, the electrode height, the hydrogen flow, and the carrier gas flow of both nitrogen and helium were varied.

Table I shows the symbols and abbreviations used throughout this paper. The precise conditions of the measurement series are either given in the legends or are evident from the figures.

TABLE I

Cl	—△—	chlorobenzene	C	△	△	<i>p</i> -xylene
Br	—□—	bromobenzene	C	—□—	—□—	<i>n</i> -decane
I	—○—	iodobenzene	C	○	○	<i>p</i> -cymene
N	—▽—	aniline	C	▽	▽	1-octanol
P	—◇—	triethylphosphate	C	◇	◇	anisole
			N	—▼—	—▼—	aniline

RESULTS AND DISCUSSION

Any study on the characteristics of the AFD will encounter the problem of reproducibility. As BRAZHNIKOV *et al.* have stated in their recent comprehensive review¹, there are many conflicting data on the AFD to be found in the literature and what holds true for one particular modification of the detector may not necessarily hold true for another.

It seemed in this study that negative response characteristics are somewhat harder to reproduce than positive ones. With several beads, no (or a very small) negative response was obtained. Negative response appears related to the smoothness and evenness of the bead surface. A jagged or cracked surface causes a great decrease if not virtual elimination of negative response.

Once the technique of bead production was perfected, and smooth, hard surfaces

were obtained in every case, the results became reproducible. Results from beads with different diameters fitted very well into series, thereby indicating the validity of the obtained data.

Rubidium sulfate is not the easiest of salts to press and drill, but was chosen for its good performance with different kinds of elements in the AFD. The use of a sulfate demands some skill in the production of the bead. Alkali halides, on the other hand, which are quite easy to press, were not used because the reported depression of halogen response⁸.

The picture of the AFD modification (Fig. 1) shows a typical rubidium sulfate bead (in this case with a 1-mm inner bore) which has approximately the same characteristics as the bead which has been reported⁶. The only change from the earlier version was to keep the alkali salt bead in the steel ring used for pressing, and to mount it on the detector jet tip with a brass collar. This allowed frequent exchange of beads which did not get chipped, or scratched on their surface, or lose their firm seat on the detector jet tip.

Size and direction of the collector potential

In our instrument, the collector electrode of the AFD is connected to a battery box which in turn feeds the signal to the electrometer. The detector jet tip and the detector housing are on ground potential. It was interesting to check the dependence of the background current on the magnitude and the direction of the potential on the collector electrode, since this profile is undoubtedly a function of detector design¹¹. The results are shown in Fig. 2. While positive response (especially with phosphorus compounds) can be very much greater than the background current, negative response can obviously not exceed this amount. Therefore, the available background current is of considerable interest for a negative response study—a characteristic akin to the electron capture detector.

The background current measured with the positive collector electrode varies with the applied potential and has not yet reached saturation at 290 V. On the other

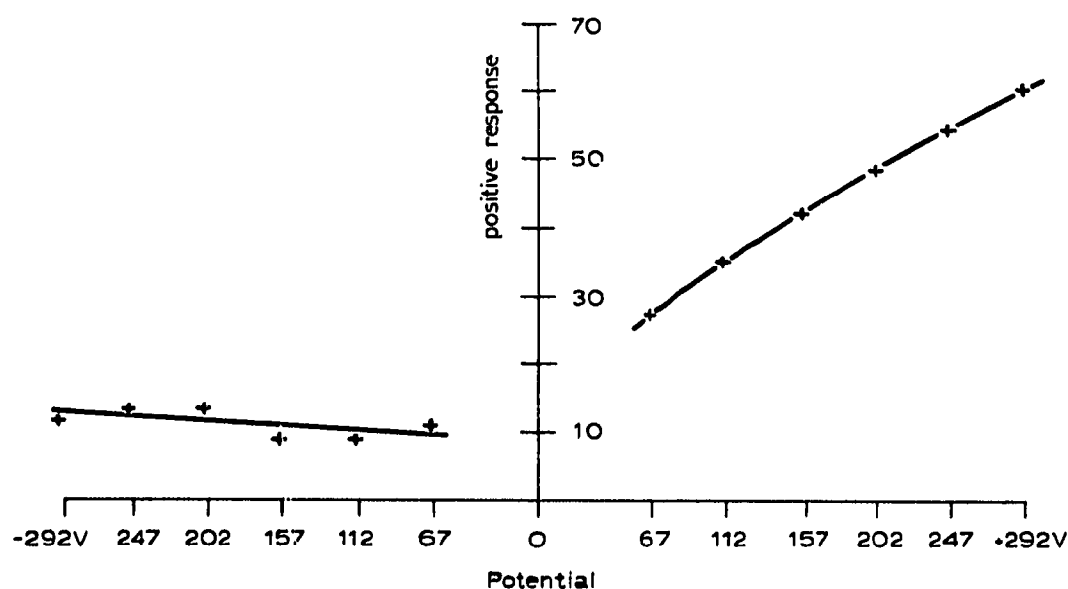


Fig. 2. Background current at various potentials. Electrode height, 2 mm.

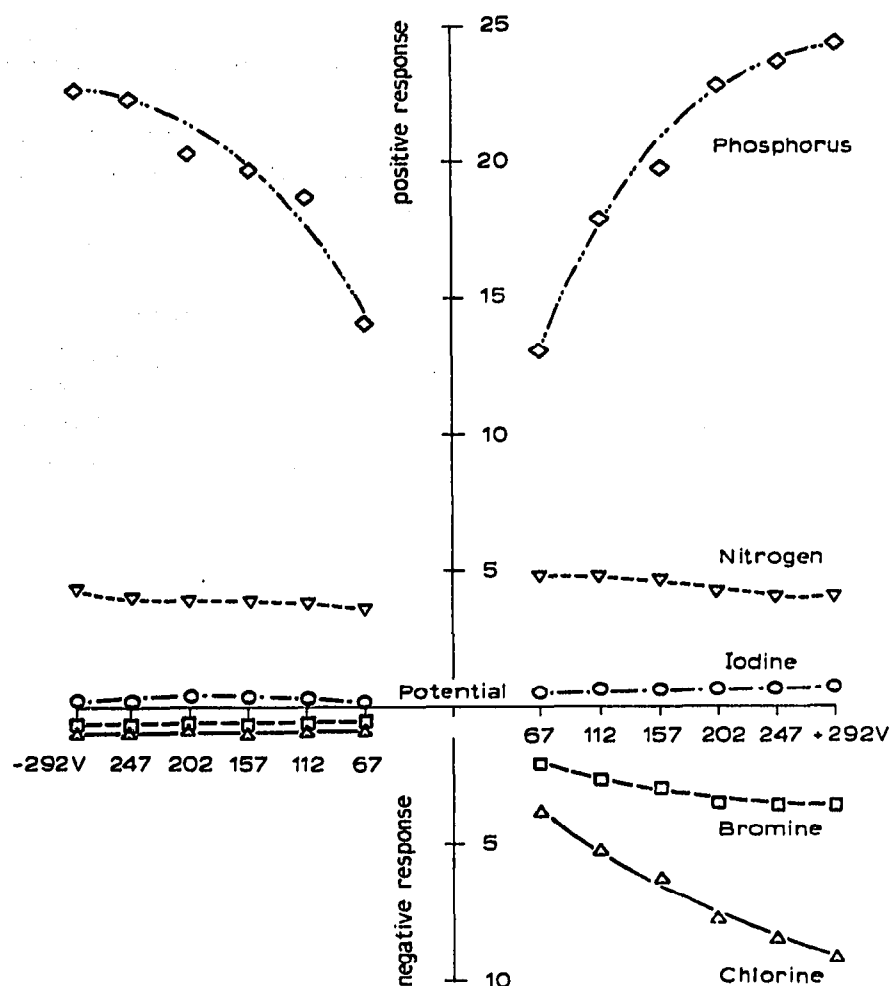


Fig. 3. Response profiles at various potentials. Electrode height, 2 mm. 1- μ l triplicate injections of 0.01% solutions of chlorobenzene, bromobenzene, iodobenzene, and benzylamine; and 0.001% solution of triethylphosphate. Column temperatures: 90° (Cl, Br, I), 170° (N, P). Flow rates, in ml/min: H₂, 33; N₂, 50; and air, 250.

hand, the background measured with a negative collector electrode potential is significantly smaller and essentially independent of the applied voltage. This indicates that ions other than Rb⁺ and e⁻ play a major part. Since electrons are easier collected than alkali cations, one would expect their complete collection well within the applied range of potential. On the other hand, the current due to Rb⁺ should vary considerably with the potential.

Fig. 3 shows the response of several volatile compounds as affected by the magnitude and the direction of the applied potential. Phosphorus response rises with the applied potential and shows the same type of curve as the background current (at positive potential); this is in accord with other versions of the AFD. The responses at negative and positive potentials are almost exact mirror images of each other. Consequently, phosphorus response at negative potential does not parallel anymore the background current.

Nitrogen shows approximately the same response regardless of the size or direction of the potential.

The halogens, on the other hand, show a clearly different behavior. The negative response of bromine and chlorine appears to parallel the background current (the potential) on both sides. Halide response is thus greatly diminished at negative potentials and does not exhibit the symmetrical curves like phosphorus. This makes some sense since negative response represents a reduction in available background current.

The regular battery box used with the Barber-Colman gas chromatograph contains a 240-V battery. This seemed good enough for all further measurements and those were consequently conducted at a positive potential of 240 V on the collector electrode. A thorough study of the interesting relationship between potential and response was outside the scope of this study, which is mainly concerned with relative response profiles.

The effect of electrode height

The response of the AFD is a function of the shape of the collector electrode^{12,13,15} and its height above the alkali salt bead, or in other words, its position in regard to

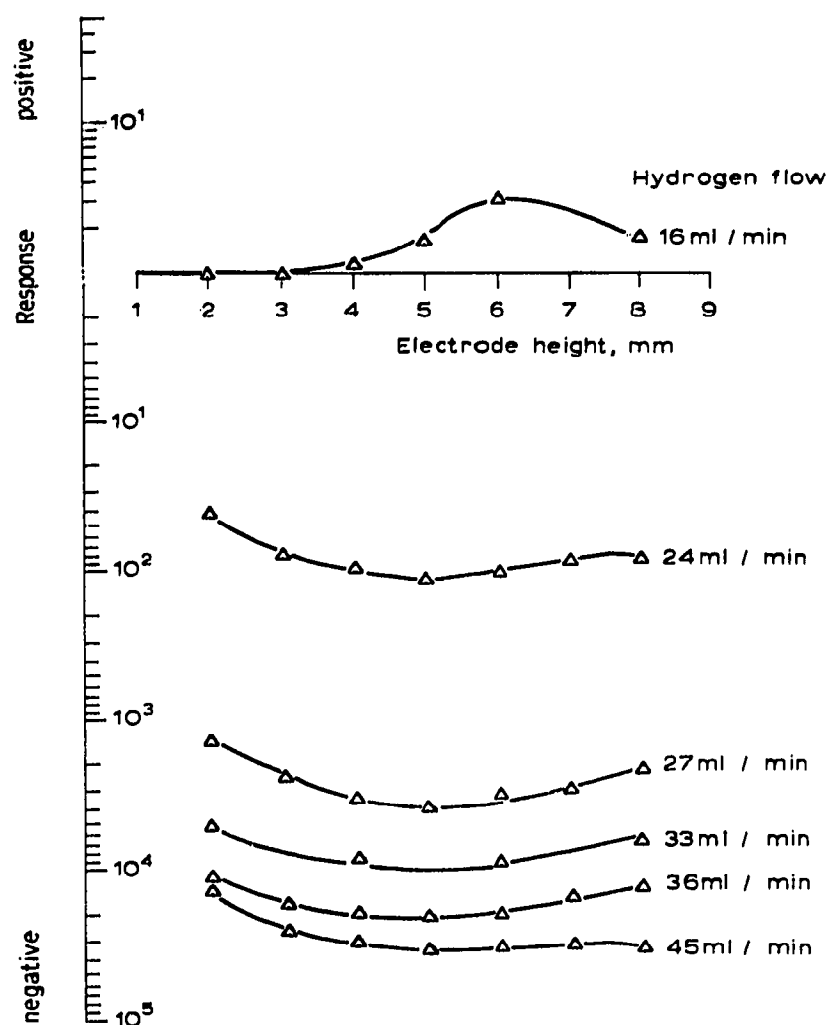


Fig. 4. Chlorine response profiles at various electrode heights and hydrogen flows. 1- μ l triplicate injections of 1% chlorobenzene. N_2 flow rate, 50 ml/min.

the flame⁷. Different elements have response maxima at different electrode heights and this phenomenon can be used to determine one particular element at optimum sensitivity and discriminate against other alkali flame-active elements^{6,7}.

Consequently, the variations of response with different electrode heights were monitored for each particular setting of bead diameter and flow parameters, from 1 to 9 mm above the bead. Typical of such a measurement is the one shown in Fig. 4. The curves were measured with chlorine; bromine behaves similarly but iodine is much more erratic.

As this study progressed, flow parameters were measured over a large range and the effects shown in these studies were of much larger magnitude than the ones brought about by the change in the electrode height at one particular setting. The relatively large diameter of the collector electrode might also tend to diminish the effect of electrode height. While it is very important to find the optimum height for some particular type of analysis, averages, and later the response at a fixed height (2 mm above the bead), were used in the context of this study. These may be considered representative of the general trends observed.

Effect of bead bore

The effect caused by varying inner diameters of the salt bead has never been extensively investigated except in one study¹⁴. The fact that a narrow bore produces a tall, narrow flame, and a wide bore a low and broad one, underscores its importance for the AFD. A tall and narrow flame will be farther away from the electrode and will contact less alkali surface. Consequently, the AFD will show a lower background current. A broad flame will get closer to the electrode (at a low electrode height), it will touch a greater alkali surface area and produce a higher amount of background

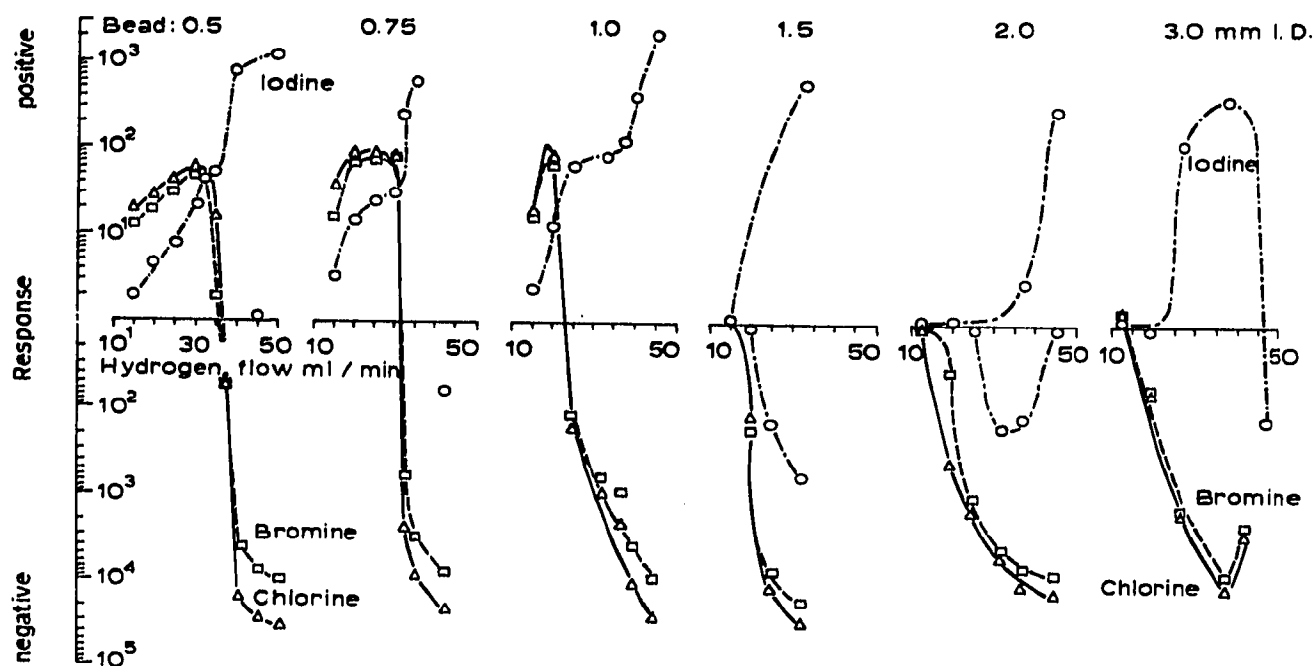


Fig. 5. Halogen response profiles at various hydrogen flows and bead bores. Electrode height, 2 mm. 1- μ l triplicate injections of a 1% solution of chlorobenzene, bromobenzene and iodobenzene. N_2 flow rate, 50 ml/min.

current. Regardless of whether a surface mechanism or a mechanism operative in the flame is assumed, the area in contact with the flame and the temperature in the contact region will be decisive factors in determining the response.

Fig. 5 shows the dependence of halogen response on the bead bore (inner diameter), measured for each bead with different hydrogen flows. In this as in the other figures of this paper, the symbols and abbreviations shown in Table I are used. The study shows a consistent behavior of the response profiles as the bead diameter is increased. Bromine and chlorine show both positive and negative response at small bead diameters. The area of positive response, however, decreases until it is virtually nonexistent for bead bores higher than 1.5 mm. This is clearly seen by following the hydrogen flows at which the response profile crosses the abscissa and the response turns from positive to negative. With bead diameters of 0.5, 0.75, 1.0, and 1.5 mm, the crossover points lie at 36, 32, 23, and 15 ml/min of hydrogen, respectively. As the bead diameter increases, the iodine, whose response has been positive up to 1.0 mm, begins to exhibit split peaks, *i.e.*, a negative and a positive peak as indicated by a double set of data in the figures. This peak shape is similar to that shown for bromine in chromatogram No. 4, Fig. 12; it should not be confused with the familiar rabbit ear

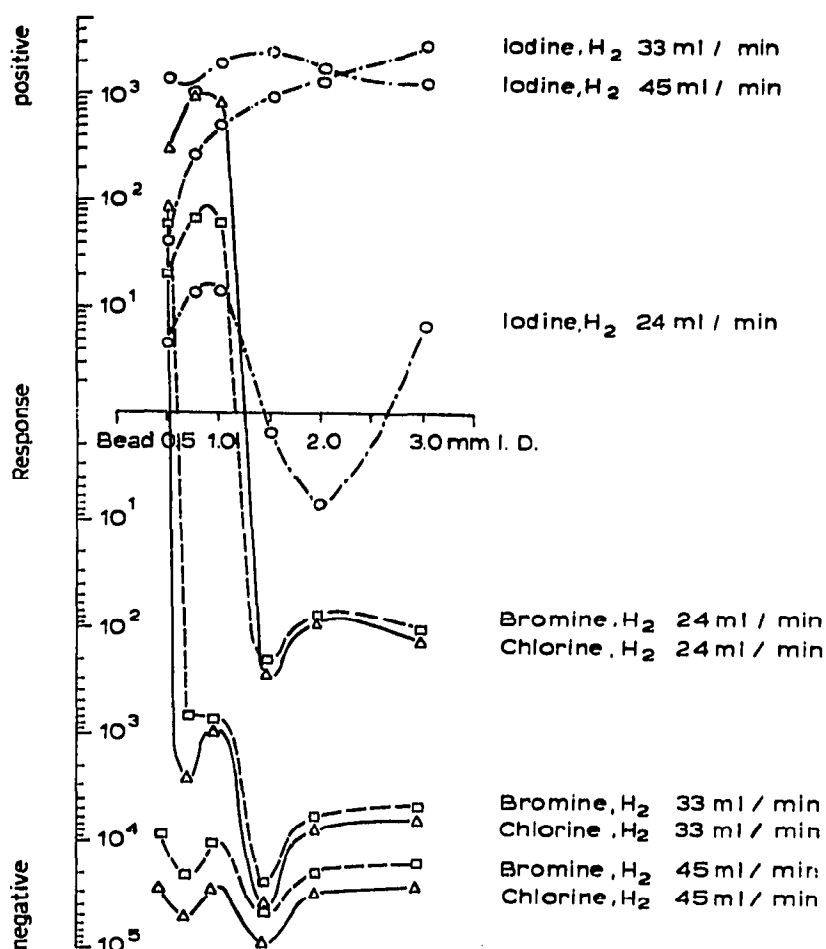


Fig. 6. Halogen response profiles at various bead bores at three selected hydrogen flows. Data are averages from measurements at electrode heights between 1 and 9 mm. 1- μ l triplicate injections of 1% chlorobenzene, bromobenzene and iodobenzene. N₂ flow rate, 50 ml/min.

peak which represents a concentration phenomenon. As the large bead bores are approached, iodine finally begins to turn toward negative response.

It appears from Fig. 5 that a larger bead diameter and a higher hydrogen flow rate favor the negative mode of response. The maxima of negative response measured for chlorine and bromine are much larger than those of the positive response range, and they show little variation with bead bore. The recorded data were measured with the electrode 2 mm above the bead.

Fig. 6 shows some of the same data brought into a different form. Response profiles were measured with electrode heights of 1 to 9 mm and the averages values were plotted for chlorine, bromine, and iodine at three different hydrogen flows. Again, larger bead bores favor the negative response, at least for bromine and chlorine. From 1.5 mm I.D. upward, the negative response for bromine and chlorine as well as the positive response for iodine remain in approximately the same order of magnitude.

For the purpose of comparison, Figs. 7 and 8 show the relationship between the response of a phosphorus compound and the hydrogen flow as well as the bead bore diameter. The response is positive throughout and, of course, much larger than that obtained for halogen or nitrogen on an equal weight basis. Fig. 7 shows several somewhat similar response profiles resulting from different bead bores. The response, as expected, varies in an approximately linear fashion with the hydrogen flow and the different bead diameters do not seem to cause any appreciable or noteworthy effect.

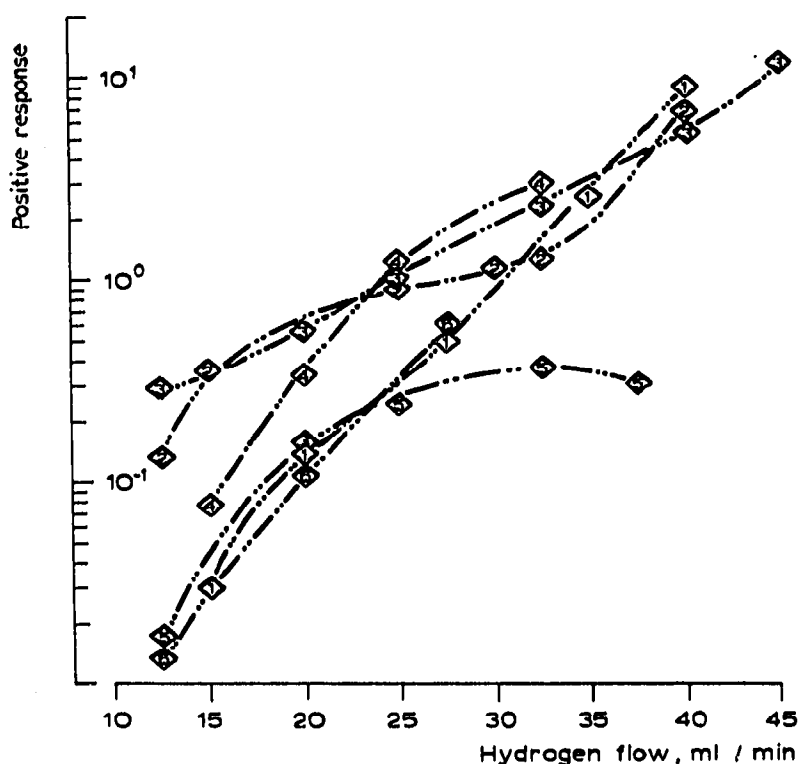


Fig. 7. Phosphorus response profiles for varying hydrogen flow and six bead bores. Electrode height, 2 mm. 1- μ l triplicate injections of 0.0001% triethylphosphate. N_2 flow rate, 50 ml/min. Bead bores, in mm: 0.50 (1), 0.75 (2), 1.0 (3), 1.5 (4), 2.0 (5), 3.0 (6).

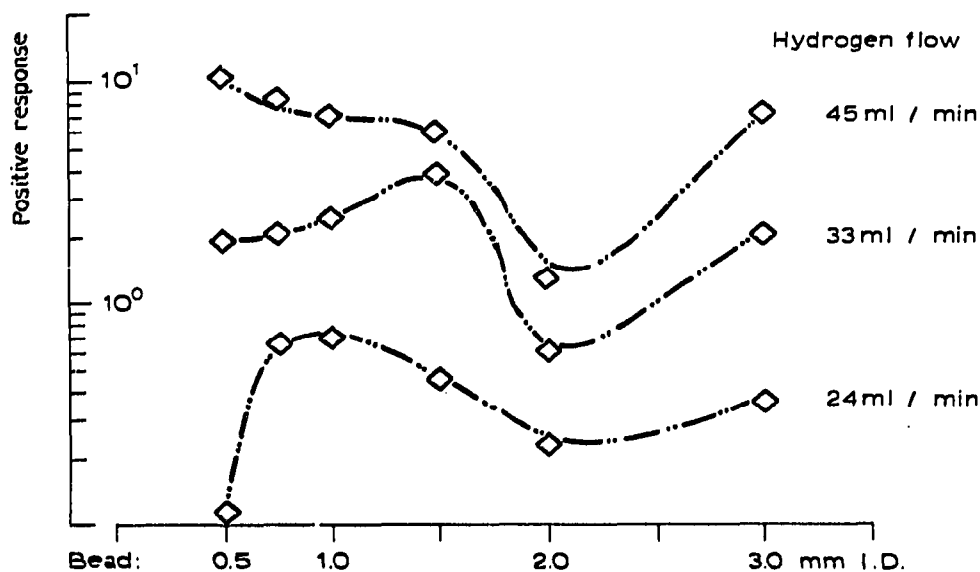


Fig. 8. Phosphorus response profiles at different bead bores and three selected hydrogen flows. Data are averages from measurements at electrode heights between 1 and 9 mm. 1- μ l triplicate injections of 0.0001% triethylphosphate. N_2 flow rate, 50 ml/min.

In Fig. 8, three hydrogen flows selected from the same experimental series are used to plot the response profiles for a variation in bead bore. If phosphorus compounds are determined with this particular AFD version, a bore of approximately 1 mm I.D. would probably be the one of choice. The effect introduced by various hydrogen flows is greatest with the very narrow bore; at 45 ml/min, the response is about a hundred times as large as at 24 ml/min of hydrogen. This response ratio decreases and then again increases with increasing bead bore.

It should be noted that it is possible to obtain negative response even for phosphorus, when other electrode dimensions and flow parameters are used. The negative response for phosphorus, however, is dwarfed by the normal positive one and no particular effort was made to characterize these negative ranges for phosphorus.

Effects of carrier gas

We had initially assumed that the influence of the carrier gas flow on the response would be relatively small in comparison with the effects of the hydrogen flow. This, however, was not the case, and the carrier gas supply proved to be a decisive parameter in determining the amount of response. Both nitrogen and helium are commonly used as carrier gases with the AFD and were also used in this study. Of the two, helium is supposed to yield the better response⁸⁻¹⁰.

Fig. 9 shows the response profiles for the halogens in dependence on the carrier gas flow. Both helium and nitrogen are used at different levels of hydrogen. Halide response generally increases with decreasing carrier gas flow, that is, under conditions characterized by a flame of higher energy in contact with more alkali salt surface. Only chlorine is negative at the lowest hydrogen flow; bromine and iodine remain positive. As the hydrogen supply is increased, bromine begins to shift and joins chlorine on the negative side. At the very highest hydrogen flow, iodine begins to turn negative also. This is an instructive example for the fact that conditions which favor

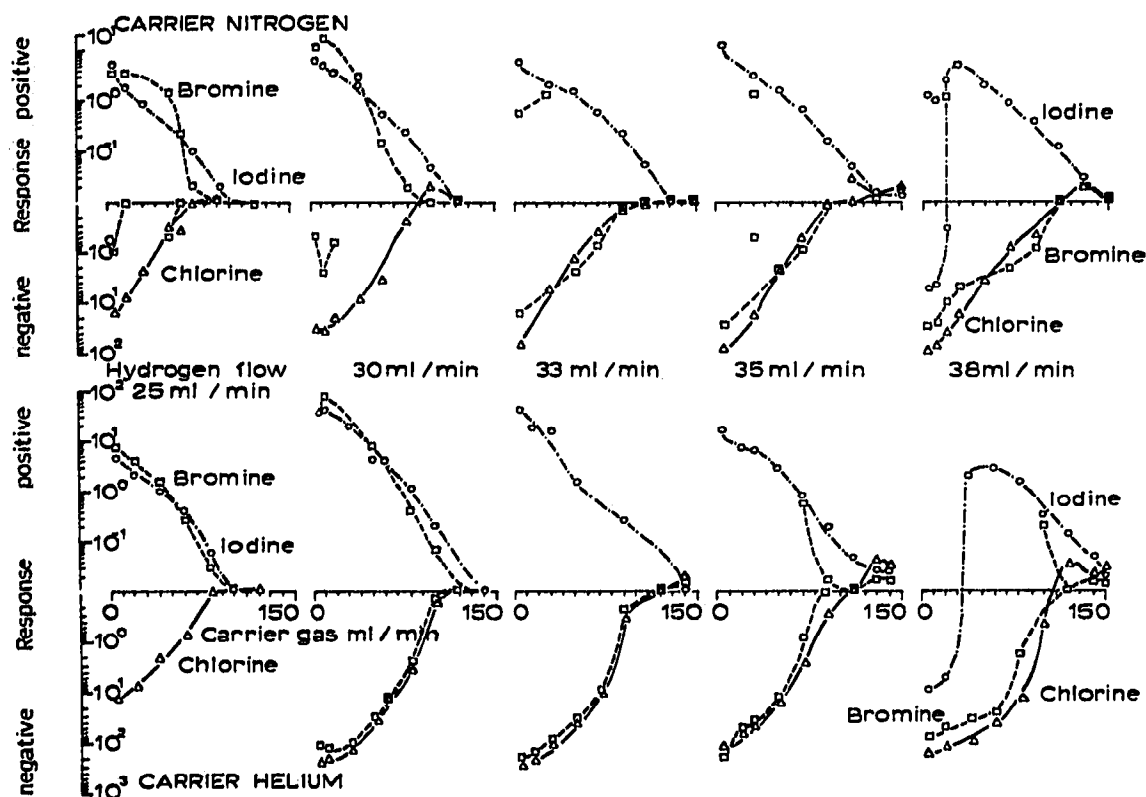


Fig. 9. Halogen response profiles for varying carrier gas flow (nitrogen and helium) and five selected hydrogen flows. Electrode height, 2 mm. Bead bore, 1.0 mm. 1- μ duplicate injections of 0.01% chlorobenzene, bromobenzene and iodobenzene.

a larger and higher energy contact of the flame with the alkali salt surface tend to favor negative response. These conditions are high hydrogen flow, low carrier gas flow, and a large bore diameter.

While an increase in carrier gas diminishes the negative response, it likewise diminishes, in most cases, the positive response. It should be noted that the data in Fig. 9 were obtained with amounts of halides different from those represented in the previous figures and this fact should be accounted for when response values are compared. Fig. 9 shows that little difference exists between nitrogen and helium in the context of halogen response profiles.

The same conclusion does not hold true for the measurements depicted in Fig. 10. A series of carbon compounds is shown in comparison to a nitrogen compound. Since the response profiles for carbon compounds do not vary much according to their structure, the data points for all of them are recorded, but a curve is drawn only for *n*-decane. The study shows several interesting effects. First, the response curves for nitrogen and carbon compounds are very dissimilar at low hydrogen levels, but become more and more alike at high hydrogen flow rates. Secondly, the response for nitrogen seems decidedly lower with helium as a carrier gas than with nitrogen. This effect becomes especially noticeable with a large hydrogen supply. Thirdly, and in concurrence with other results in this study, the higher hydrogen flow seems to favor the negative response, as can be seen by the crossover points for carbon compounds of 60, 95, and 110; and 80, 100, and 120 for the respective hydrogen flows of 25, 30,

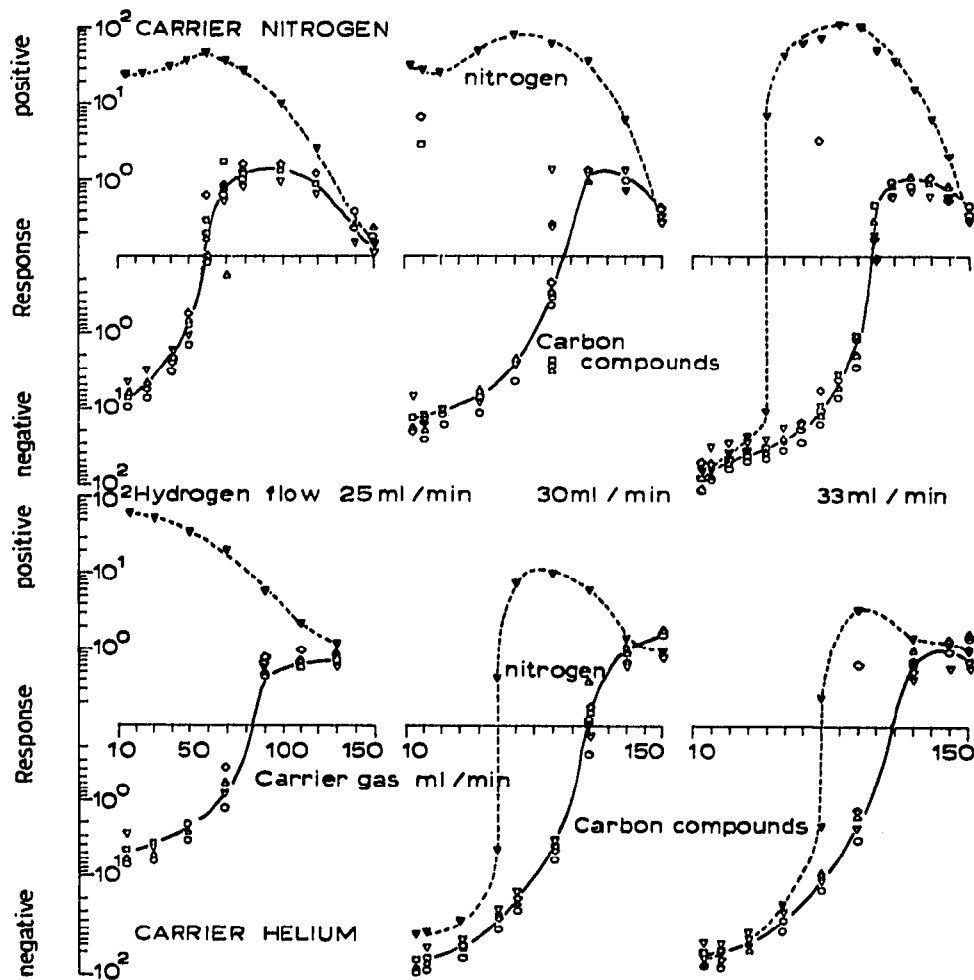


Fig. 10. Nitrogen and carbon response profiles for varying carrier gas flow (nitrogen and helium) and three selected hydrogen flows. Electrode height, 2 mm. Bead bore, 1.0 mm. 1- μ l single injections of 1% aniline and 1% each of *p*-xylene, *n*-decane, *p*-cymene, 1-octanol, and anisole.

and 33 ml/min. Fourthly, the negative response for carbon compounds seems to be about one order of magnitude larger than the positive response and it is apparently not dependent on chemical structure. It should be remembered that the nitrogen compound used in the study, aniline, contains six carbon atoms and only one nitrogen atom. Therefore, the response profile for this compound is made up from contributions both of carbon and nitrogen. In areas, however, where the aniline peak is much larger than the carbon compound signal the recorded curves can be considered fairly representative of the true nitrogen response profile.

The greatest importance of response profiles such as these lies in the possibility to distinguish nitrogen-containing compounds from those containing only carbon, hydrogen, and oxygen. This is achieved from chromatograms only. Split peaks were obtained occasionally in our studies. Where this occurred, the data were recorded both for the area of the negative and that of the positive peaks. Several such data can be noticed in Fig. 10; however, most measurements follow a consistent curve.

It is an interesting but unexplained conclusion from Fig. 10 that better response for nitrogen compounds is obtained with nitrogen as carrier gas than with helium.

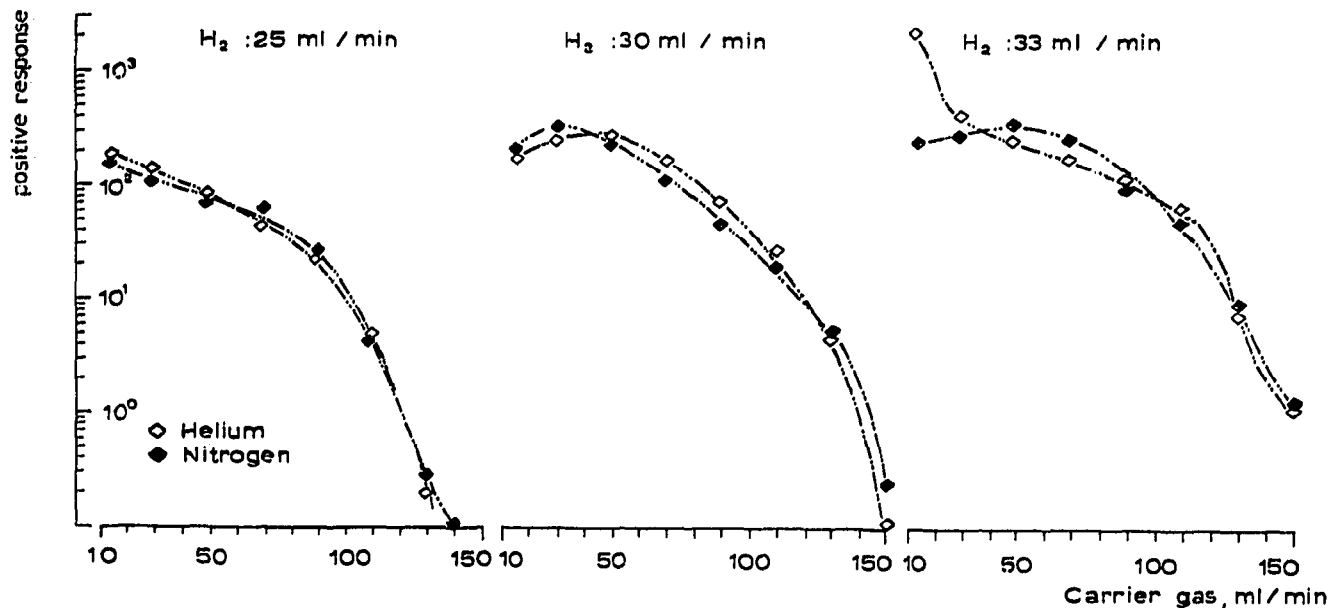


Fig. 11. Phosphorus response profiles for varying carrier gas flow (nitrogen and helium) and three selected hydrogen flows. Electrode height, 2 mm. Bead bore, 1 mm. 1- μ l triplicate injections of 0.001% trimethylphosphate.

In Fig. 11, a similar comparison of the effects of nitrogen and helium as carrier gases is recorded for a phosphate. In our modification of the AFD, the difference between helium and nitrogen appears negligible.

Application of the negative AFD response

In an earlier study⁶, we have used the negative response of the AFD toward chlorine for the determination of chlorinated hydrocarbon insecticides. No such application is included in the present study. It is obvious, however, that the defined conditions can be used to affirm the suspected presence of a particular hetero-atom in a molecule represented by a peak in the chromatogram. Fig. 12 shows several typical chromatograms obtained in the serial measurements. Halogen, nitrogen, and carbon compounds are represented by both negative and positive peaks, including some chromatograms with "mixed" responses. It is the latter case which allows us to distinguish between the hetero-elements.

These chromatograms were all run after a very short equilibration of the detector. This was necessary for finishing a particular series of measurements in a reasonable time under the same conditions. In an actual analysis, however, the electrode height should be optimized and the detector given adequate time for equilibration. This results in chromatograms which are both more reliable and of greater aesthetic appeal.

Chromatogram No. 4 in Fig. 12 contains a split bromine peak. It is interesting to note that split peaks generally show the same pattern (*e.g.* the negative peak is followed by the positive peak) for one particular element in a series of measurements. In the same series of measurements, however, another hetero-atom might show the opposite peak behavior (*e.g.* the positive peak is followed by the negative one). Such, for instance, was the case with halogen and carbon compounds in one of the described series.

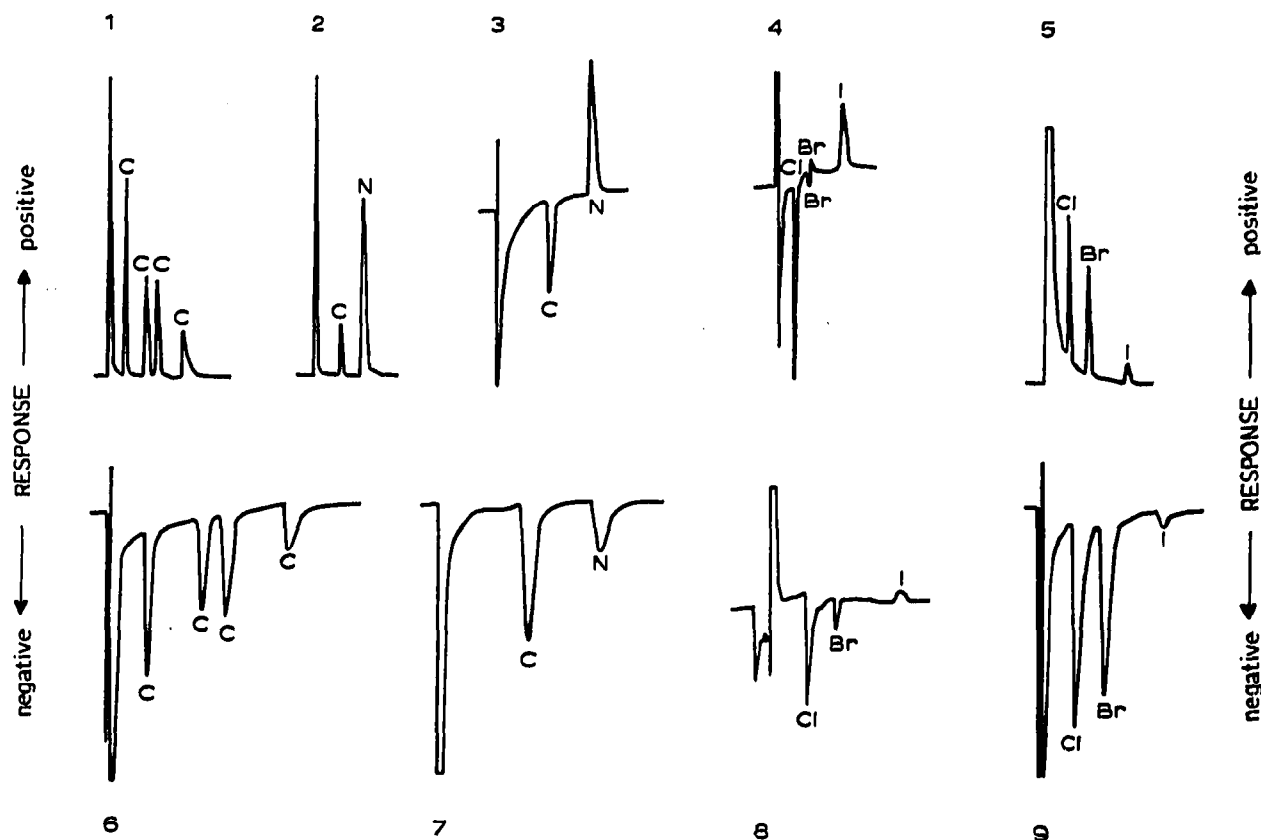


Fig. 12. Typical chromatograms at various flow rates.

	Chromatogram No.									
	1	2	3	4	5	6	7	8	9	
N ₂ (He) flow rate (ml/min)	92	92	46	78	50	37	(27)	42	(43)	
H ₂ flow rate (ml/min)	26	26	33	30	16	33	30	37	37	

Electrode heights, 6 mm (No. 5) and 2 mm (all others). Bead bore, 1.0 mm. Compounds as listed in Table I.

In summary, this study covers some of the more important variables which influence the ranges and magnitudes of negative response for several alkali flame-active elements. It does not—nor could it within the context of one paper—attempt to cover all of the parameters which may affect response. Simple as the AFD appears to the eye, a thorough study of its characteristics can become quite involved; not to mention any attempts directed at elucidating its *modus operandi*.

The negative response of the alkali flame detector still represents somewhat of a curiosity. It can be used to a certain advantage in quantitative measurements of halides or nitrogen compounds. Its main potential, in our opinion, lies in its capability to distinguish between several hetero-elements in organic compounds separated by gas chromatography.

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