IONIZATION QUENCHING OF A HYDROGEN ATMOSPHERE FLAME AS A DETECTION METHOD FOR GAS CHROMATOGRAPHY

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SUMMARY

A strong ionization-quenching response has been discovered when organo-metallic compounds combust in a hydrogen atmosphere air diffusion flame. This response can be used to sensitively and selectively detect organometallics after gas chromatography. The detector parameters found to be most important in producing this quenching phenomenon were the concentration of silane in the hydrogen atmosphere, the position at which the hydrogen–silane gas mixture entered the detector and the height of the collecting electrode. Detection limits for tin, lead, and iron were around $1 \cdot 10^{-15}$ g at.wt./sec with selectivities over alkanes ranging from 10^4 to 10^5.

INTRODUCTION

Determination of organometallic compounds by gas chromatography (GC) can be made selectively and sensitively using the ionization response of a unique flame detector called a hydrogen-atmosphere flame ionization detector[1]. This detector can be constructed by reversing the detector gases of a normal flame ionization detector so that air is mixed with the column effluent while hydrogen is brought directly into the detector, producing a flame which burns in a hydrogen atmosphere. When the hydrogen atmosphere is doped with small amounts of silane, positive ions that are produced from the combustion of organometallic compounds can be efficiently collected some 5–10 cm above the flame. The hydrogen-atmosphere flame ionization detector has been used for the successful determination of such compounds as bis-tributyltin oxide in marine paint[2], triphenyltin hydroxide and tricyclohexyltin hydroxide on apple orchard leaves[2], tetraethyllead in "regular" gasoline[3] and methylcyclopentadienylmanganese in unleaded gasoline[3]. Other compounds such as aluminum hexafluoroacetylacetonate and ferrocene have also been detected at the picogram and sub-picogram level[1].

In early developmental work on the hydrogen-atmosphere flame ionization detector occasional negative responses were observed[1]. Negative responses in ionization detectors occur when background ionization is quenched, producing a decrease in measured current. Conditions under which such responses were observed were always unoptimized. These negative responses were considered a nuisance to be

avoided. Recently, however, the analytical utility of flame ionization quenching has been demonstrated using a silicon selective detector[4]. This detector uses a hydrogen atmosphere flame similar to the one described here with the exception that hydrogen is doped with small quantities of volatile metal compounds rather than silane. When concentrations of the volatile metal doping agents were increased to a level substantially higher than normal operating concentrations, peaks for compounds containing silicon were found to give negative responses that were about three times more sensitive than the optimized positive response.

The purpose of this study was to determine if conditions exist in the metal-sensitive hydrogen-atmosphere flame ionization detector at which analytically useful ionization-quenching phenomena could be observed and, if so, to determine which detector parameters are most important in influencing this response.

EXPERIMENTAL

Instrumentation

Studies were performed on a Hewlett-Packard 5830A gas chromatograph equipped for on-column injection with a 6 ft. × 1/4 in. O.D. (2 mm I.D.) borosilicate column packed with 3% SE-30 on 80/100 Chromosorb W HP. The chromatograph was operated as suggested by the manufacturer with the exception that one of the instrument's dual flame ionization detectors was converted to a hydrogen-atmosphere flame ionization detector as described previously[3].

Test compounds

Organometallic and hydrocarbon standards used in this study were tetraethyltin (Alfa Division, Dentron, Danvers, MA, U.S.A.), tetraethyllead (ICN Pharmaceuticals, Life Sciences Group, Plainview, NY, U.S.A.), tetra-*n*-butyllead and ferrocene (Aldrich, Milwaukee, WI, U.S.A.), *n*-decane and *n*-dodecane (Sigma, St. Louis, MO, U.S.A.). Reagent-grade hexane was used as the solvent in the preparation of these test compounds throughout a range of concentrations. Primary standards were prepared at 1 μg/μl with a series of working standards down to 1 pg/μl being produced by successive decade dilutions of the primary standards.

Silane doping

Mixtures of silane in hydrogen at the ppm level were prepared using a 1% silane in hydrogen gas cylinder (Airco Specialty Gases, Santa Cruz, CA, U.S.A.) and varying the mixing rate of the doped hydrogen with pure hydrogen. Gases were mixed such that the silane volume–volume mixing ratio varied from 1 to 550 ppm in hydrogen.

Electrode height

The distance between the collecting electrode and the flame jet tip was varied by the insertion of detector housing spacers of different lengths between the detector base and cap. The electrode constructed of an 1/8 in. I.D. stainless-steel tube, was friction fitted onto the male portion of a BNC connector (Amphenol UG-1094/u) that was mounted in the detector's cap. To provide a surface for the collecting electrode, the end of the stainless-steel tube was flattened and bent 90°. This extended

electrode plus a selected combination of detector housing spacers allowed the electrode height to be varied from 1 to 14 cm above the flame jet tip.

Position of hydrogen–silane entrance

Since the entrance orifice for the hydrogen and silane gases was fixed into the detector wall by the basic design of the Hewlett-Packard (HP) flame ionization detector, the flame jet length was varied to achieve different relative positions of the gas entrance and the flame. Using flame jets of different lengths, hydrogen and silane were introduced from 2 cm above to 6 cm below the jet. Jept tips were constructed of 1 mm I.D. quartz tubes inserted into the HP jet. The jet was drilled out to a depth of several millimeters so that a tight friction-fit could be established between the quartz tube and the original jet. Various detector housing spacers were used in combination with each flame jet length in order to maintain a constant electrode height throughout this series of experiments.

RESULTS AND DISCUSSION

For the purpose of this discussion the term "positive mode" will be used to refer to conditions under which the detector exhibited an increase in conductivity when test organometallic compounds were introduced into the flame. Positive mode operation of the hydrogen-atmosphere flame ionization detector has been the normal mode of operation in the past. The term "negative mode" will refer to detector conditions under which the conductivity of the detector cell decreased as organometallic compounds combusted in the flame.

Analytically useful ionization-quenching responses were first discovered during a series of experiments designed to investigate both electrode height and silane concentration. Electrode height and silane concentration studies have previously been reported[1,5]. However, once the silane concentration was substantially past optimum for a postive response, no higher concentrations were investigated. In this study concentrations up to 550 ppm of silane in hydrogen were investigated.

Optimal silane concentrations for the positive mode typically occur below 50 ppm. For convenience, doping levels below 50 ppm will be referred to as the low-doping level and concentrations above 50 ppm will be referred to as the high-doping level. Ionization quenching was only observed under high-level doping conditions and then only at certain electrode heights.

Figs. 1–5 provide examples of the responses obtained for test compounds as the electrode height was varied, with a silane doping concentration of about 200 ppm. In each figure, responses occurring when both the positive and negative ions are collected at the electrode are plotted. Positive and negative ion collection are not to be confused with positive and negative (quenching) responses. The former refers to the charge on the ion that is being collected at the electrode while the latter refers to the overall conductivity of the detector cell.

Figs. 1 and 2 provide response profiles of two hydrocarbons, decane and dodecane, respectively. Both produced similar and expected patterns, with the largest responses occurring at low electrode heights when negative ions or electrons were collected. As shown here, positive ions were generally less efficiently collected than negative ions or electrons. More efficient collection of positive ions can occur if the
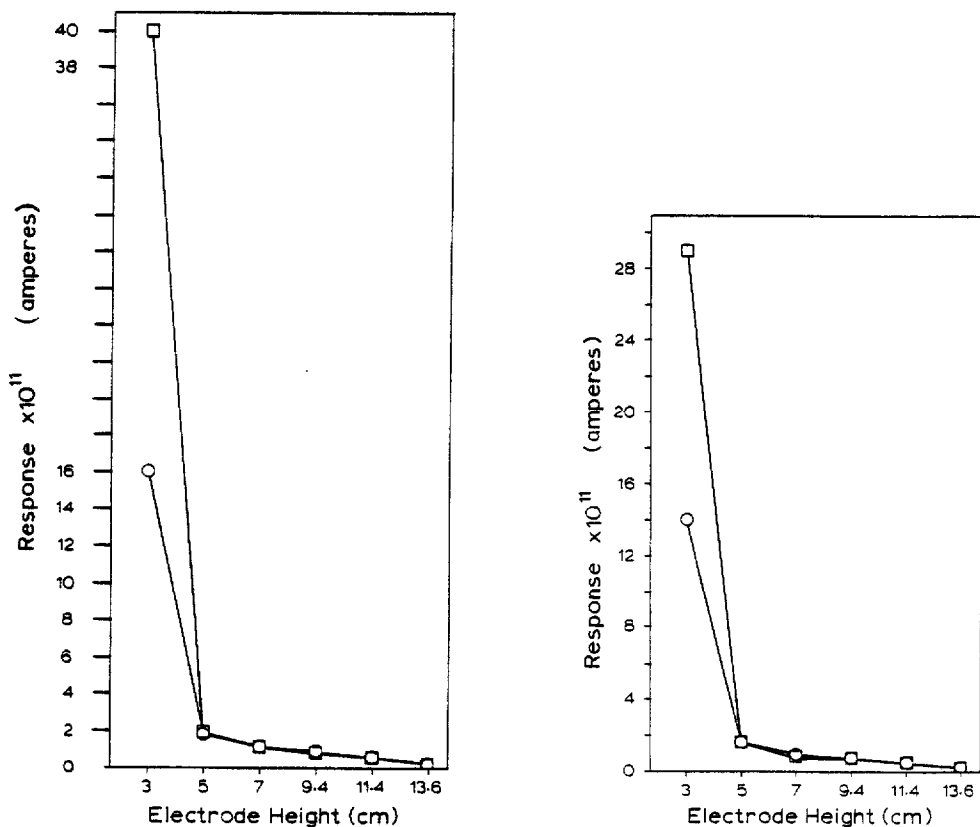
Fig. 1. Decane response *vs*. electrode height. Amount per injection, 1 μg. Detector conditions: temperature, 225°C; hydrogen flow-rate, 1600 ml/min; oxygen flow-rate, 150 ml/min; air flow-rate, 120 ml/min; silane concentration, 208 ppm; electrode potential, −90 V and +90 V; hydrogen–silane entrance, 1.3 cm above flame. Chromatographic conditions: column, 3% SE-30; carrier gas (helium) flow-rate, 30 ml/min; temperature 1, 100°C; time 1, 2 min, rate, 10°C/min, temperature 2, 150°C. (○) Positive ions; (□) negative ions.

Fig. 2. Dodecane response *vs*. electrode height. Conditions are the same as in Fig. 1.

electric field is increased either by decreasing the electrode height or by increasing the voltage on the electrode. The fact that hydrocarbon response decreases significantly at higher electrode heights leads to one advantage of the hydrogen-atmosphere flame ionization detector, the discrimination against hydrocarbons and other compounds that do not contain metal atoms. This response pattern is typical for hydrocarbons in flame ionization detectors.

Figs. 3–5 are similar plots for the test organometallics and demonstrate that response patterns are quite different from those of hydrocarbons. At the low electrode heights and at very high electrode heights organometallic response was always weak and positive. Only at intermediate electrode heights (in this case when the electrode was 7 cm above the jet tip) was response produced by a sharp decrease in the conductivity of the detector cell. It should be noted here that each point on these graphs
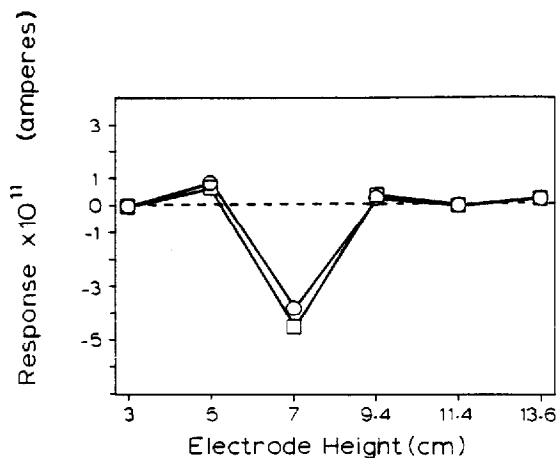
Fig. 3. Ferrocene response *vs.* electrode height. Amount per injection, 1 ng. Other conditions are the same as in Fig. 1.

is an average of three separate injections with a relative standard deviation of less than 5%. Furthermore, investigations at other silane concentrations produced similar patterns. The negative response has been found to occur only in a very narrow electrode height range from about 6 to 8 cm above the jet tip. Thus 7 cm is not necessarily the optimum height for this response but rather has been chosen here simply to dramatize the effect.

Another observation which can be made from Figs. 3–5 is that the polarity of the potential on the collecting electrode has little effect on the negative mode response. This is not the case in the postive mode where positive ions have been found to be collected more efficiently than negative ions[1]. In the positive mode, differences in collection efficiencies for the two polarities suggest that response is in some way related to the mobility of the ions formed from the organometallic compounds. The independence of the negative mode response with respect to electrode polarity is not
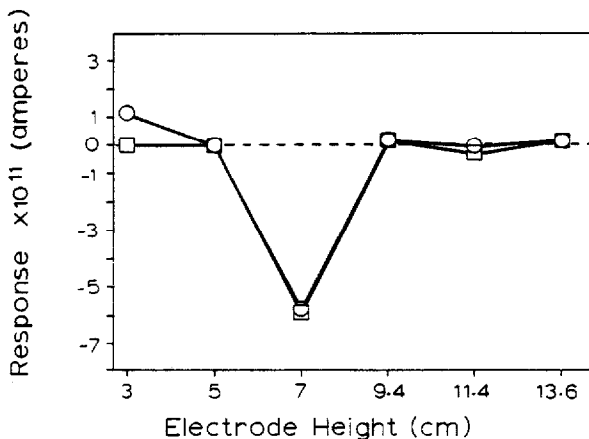

Fig. 4. Tetraethyllead response *vs.* electrode height. Conditions are the same as in Fig. 3.
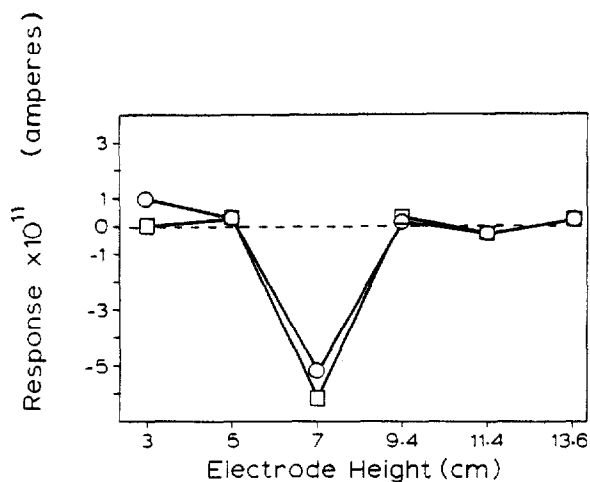
Fig. 5. Tetraethyltin response *vs.* electrode height. Conditions are the same as in Fig. 3.

surprising since, in the quenching process, ions are being neutralized rather than created. Unfortunately, it is not clear why the negative response occurs only when the electrode is positioned within a certain height range.

Under normal operation of the hydrogen-atmosphere flame ionization detector described in this paper, the hydrogen–silane gas entrance is located 2.0 cm above the
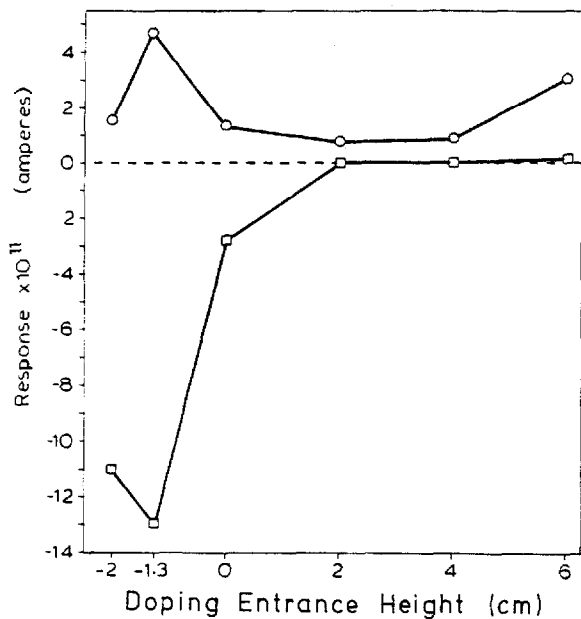

Fig. 6. Tetraethyltin *vs.* hydrogen–silane entrance position. Electrode height, 6.3 cm; electrode potential, −90 V; 3% SE-30 column; oven temperature, 105°C; silane concentration, 15 and 300 ppm. All other conditions are the same as in Fig. 1. (O) 15 ppm silane; (□) 300 ppm silane.

flame jet. In general, however, it is more desirable to introduce detector gases below the flame, producing less turbulance in the flame. In fact, the introduction of hydrogen below the flame jet in the silicon selective hydrogen-atmosphere flame ionization detector has been shown to improve sensitivity[6]. In order to determine what effect, if any, the location of the hydrogen–silane entrance had on response, quartz tubes of different lengths were inserted into the commercial jet, allowing the flame to burn below, at, and above the gas entrance. Entrance heights were measured relative to the jet tip. A negative entrance height means the jet tip was below the gas entrance.

Fig. 6 shows tetraethyltin responses for both low-doping (15 ppm) and high-doping (300 ppm) levels of silane as the relative distance between the flame and the gas entrance is varied. The collector electrode height was held constant at 6.3 cm above the flame jet. This demonstrates quite clearly the difference between low- and high-doping levels of silane. In the positive mode (low doping), response is relatively unaffected by the position of the hydrogen gas entrance. At 1.3 cm below the entrance there was a 3-fold increase in response. In the negative mode (high doping) there was a multifold increase in sensitivity from no response at 2 cm above the entrance to a maximum of $1.3 \cdot 10^{-10}$ A at 1.3 cm below the entrance. Thus, in addition to electrode height and doping concentration, the position at which the dopant enters the detector must be considered in order to achieve an optimal negative signal.

The amounts of silane required to produce a maximum organometallic response at each hydrogen entrance position are shown in Fig. 7. As can be seen, concentration requirements for the positive mode appeared to be relatively independent of the gas entrance position while in the negative mode, the optimal concentration varied from about 50 ppm up to 280 ppm silane. Note that this graph does not provide information on which position produced the most sensitive response. It only reports the concentration of silane that was required at that position to produce a maximal response.
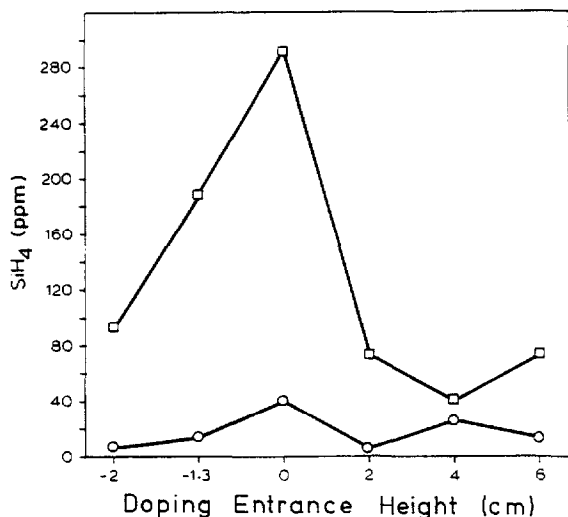

Fig. 7. Silane optimum *vs.* hydrogen–silane entrance position. Conditions are the same as in Fig. 6.

Fig. 8 provides the best negative response achievable at each entrance position for all of the test compounds. Again, responses for the hydrocarbons were the least influenced by different entrance positions. Under no conditions during these experiments were negative peaks achieved for the alkanes. When negative responses could not be obtained for organometallics, the minimal positive response was taken to be the maximal negative response. The largest negative responses for organometallics were found when the hydrogen and silane were introduced above the flame. When the entrance was near the flame such that the gas flow could perturb the burning pattern, all responses became more positive in character. That is, the magnitude of negative responses decreased and the magnitude of positive responses increased. In fact, at one position (2 cm below the jet tip), ferrocene did not produce a negative response at any silane doping concentration. At lower gas entrance positions the
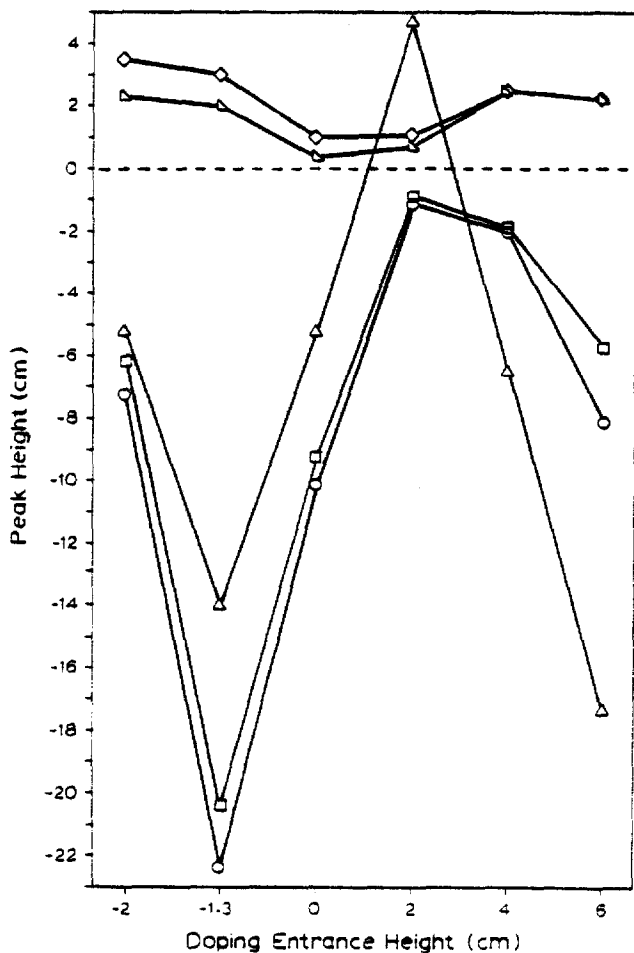

Fig. 8. Optimal response for each hydrogen–silane entrance position. Oven temperatures: (□) tetraethyltin, 105°C; (○) tetraethyllead, 125°C; (◇) n-decane, 125°C; (◟) n-dodecane, 110°C; (△) ferrocene, 150°C. With the exception of silane concentrations, conditions are the same as in Fig. 6. Silane concentrations can be determined from Fig. 7.

negative responses again tended to increase its magnitude for the organometallic compounds. As pointed out earlier, this study was accomplished by increasing the length of the flame jet from its normal position relative to the hydrogen–silane entrance orifice. Thus the highest position which could be tested above the jet tip corresponded to the normal configuration of the detector. Since the normal configuration provided excellent (although not optimal) responses, minimal detectable quantities and selectivities for this detector were determined when the detector was in its normal configuration. It may be possible to significantly improve upon these values by optimizing detector geometry.

TABLE I

MINIMAL DETECTABLE LIMITS

Detector conditions: hydrogen flow-rate = 2 l/min; silane concentration = 200 ppm; helium flow-rate (GC carrier gas) = 30 ml/min; air flow-rate = 120 ml/min; oxygen flow-rate = 150 ml/min; electrode height = 7 cm; hydrogen–silane entrance = 1.3 cm above flame; electrode potential = −90 V.

Compound	g/sec	g at.wt./sec
Decane	$2.0 \cdot 10^{-8}$	$1.4 \cdot 10^{-9}$ for carbon
Tetraethyltin	$2.4 \cdot 10^{-13}$	$1.0 \cdot 10^{-15}$ for tin
Tetraethyllead	$1.8 \cdot 10^{-13}$	$5.6 \cdot 10^{-16}$ for lead
Dodecane	$1.4 \cdot 10^{-8}$	$8.2 \cdot 10^{-10}$ for carbon
Ferrocene	$2.9 \cdot 10^{-13}$	$1.6 \cdot 10^{-15}$ for iron

Table I shows minimal detectable limits (MDLs) for each compound in the test mixture. It is important to note that even though the conditions under which these MDLs were obtained were not optimal, detection limits for the organotin and organolead compounds were lowered about an order of magnitude compared with their values in the positive mode. Ferrocene had about the same detection limit in both modes. For comparison to other analytical detection methods it is of interest to report these detection limits in terms of g at.wt./sec for the metal of interest. When reported in this manner, detection limits were found to be $1.0 \cdot 10^{-15}$ g at.wt./sec for tin, $5.6 \cdot 10^{-16}$ g at.wt./second for lead and $1.6 \cdot 10^{-15}$ g at.wt./sec for iron. Response selectivities for organometallics over hydrocarbons can be estimated from Table I to be in the range from 10^4 to 10^5.

CONCLUSIONS

How does the negative mode operation of the hydrogen-atmosphere flame ionization detector compare with the positive mode for the detection of organometallics? Although it is a bit too early in the investigation of this ionization-quenching phenomenon to unconditionally recommend one method over the other, a number of general conclusions can be made with respect to the two modes of operation.

The negative mode has definite advantages in that it produces a more sensitive response than the positive mode and that negative peaks, coupled with retention data, provide more conclusive identifications of organometallic compounds. In this study, however, parameter settings necessary to produce the negative response had

to be carefully controlled and further research is needed before their relationship to the mechanism of this response is understood. Furthermore, the relatively high silane concentration required for the negative mode may prove to cause long term degradation of response as SiO_2 forms in the detector and deposits on the collector electrode. Thus for dependability and reliability with respect to routine analyses the positive mode remains the method of choice because its response characteristics have been more completely investigated. Nevertheless, ionization quenching can be an effective method for obtaining analytical measurements. The electron capture detector is a prime example of an ionization-quenching detector which is currently being used for GC. Recently, we have used the negative mode of the hydrogen-atmosphere flame ionization detector with excellent results for the determination of organotins in apple orchard leaves[7].

Needles to say, more research needs to be conducted on this intriguing flame phenomenon. Many questions remain unanswered: will the negative mode be more analytically useful in detecting trace quantities of volatile organometallics than the positive mode of this flame detector? How does its mechanism compare with that of the positive mode? For now, however, it must suffice to say that the response exists, exhibits some interesting ionization phenomena, and appears to have real potential as a trace analytical method.

ACKNOWLEDGEMENTS

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