

## Flame infrared emission–flame ionization detector for gas chromatography

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### ABSTRACT

The utility of combining flame infrared emission detection (FIRE) and flame ionization detection (FID) into one system is discussed. An improved flame infrared detector using the 4.3  $\mu\text{m}$   $\text{CO}_2$  emission band was constructed and fitted with electrodes to monitor the ionization in the hydrogen–air flame. The resulting system was found to provide the superior quantitation of moles carbon of FIRE and the greater sensitivity of FID. The system was successfully applied to the determination of carbon dioxide, carbon monoxide and hydrocarbons in gas mixtures.

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### INTRODUCTION

For the past several decades, flame ionization detection (FID) has held the distinction of being the most popular universal detection system available for use in gas chromatography (GC)<sup>1</sup>. There are, however, a number of limitations to this method of detection. For example, FID exhibits greater response to compounds containing acetylenic groups, while showing less response for alcohols and chlorinated compounds. Also, FID does not respond at all to carbon monoxide and carbon dioxide. Furthermore, other compounds, such as carbon disulfide, exhibit very little response.

Thermal conductivity detection (TCD) also has been used extensively in GC and gas analysis<sup>1</sup>. TCD has the advantage of responding not only to compounds containing carbon, but also the fixed gases. The major disadvantage of TCD is the lack of sensitivity. Additionally, the TCD response varies directly with the heat capacity and not number of moles carbon. As with FID, there is a structure factor present, requiring that standards be run before comparison of chromatographic peaks.

To enable the sensitive analysis of mixtures of gases, several methods have been used. These include the sequential connection of TCD and FID<sup>2</sup>, the use of several columns with back-flushing of certain gases<sup>3</sup>, and the addition of a methanation

chamber to an FID-equipped gas chromatograph<sup>4</sup>. All of these methods complicate the analysis, adding more complexity and, therefore, more possible variables.

Recently, Hudson and Busch<sup>5</sup> introduced infrared emission from a flame as the basis for detecting organic compounds, initially in liquid chromatography and later in GC<sup>6</sup>. This detection method used a hydrogen-air flame to first combust compounds and then to vibrationally excite the carbon dioxide product while monitoring the resulting band at 4.3  $\mu\text{m}$  with a filter photometer system. The flame infrared emission detection (FIRE) system for GC was developed, exhibiting good sensitivity and wide linear range. Additionally, FIRE gave sensitive response to carbon dioxide, carbon monoxide and carbon disulfide.

This paper reports on work done to combine the concepts of flame ionization and flame infrared emission into one gas chromatographic detector. Also, modifications were made in the infrared flame photometer system design of the combined FIRE-FID system resulting in improved response and sensitivity in the FIRE mode. These modifications are discussed also.

## EXPERIMENTAL

### *Instrumentation*

A Shimadzu (Kyoto, Japan) Model GC-8A gas chromatograph equipped with temperature programming and dual flame ionization detectors was used for the study. A small covered port in the side of the oven wall was used to bring column effluent out to the hydrogen-air burner via a stainless-steel tube of 1.5 mm I.D. A specially designed burner, as reported previously<sup>6</sup>, was used to combust the eluted components. The previously described IR radiometer was modified with a field of view limiter made by drilling a hole of 2.4 mm I.D. through a 12.7 mm aluminum plate. This plate was mounted directly in front of and centered on the PbSe (P-2038-SPECIAL, Hamamatsu, San Jose, CA, U.S.A.) IR sensor. The PbSe sensor included an integral narrow bandpass filter centered on 4.45  $\mu\text{m}$ . A special 600-Hz chopper was designed which allowed closer positioning of the PbSe sensor to the burner and flame. Shields of sheet aluminum painted flat black limited the viewed detector background and minimized air drafts. The PbSe sensor and its associated preamplifier were powered from a 24-V battery. The amplified signal was processed with an Ithaco Model 3921 lock-in-amplifier and recorded on a Shimadzu Model C-R6A Chromatopac chromatographic integrator.

The flame ionization detector used Plexiglass-supported high-voltage electrodes from a Beckman (Fullerton, CA, U.S.A.) GC4 chromatograph modified to fit the FIRE hydrogen-air burner. The 1  $\times$  3 cm electrodes were positioned vertically and placed 7 mm apart, centered over the flame. Various heights were tried. The bottom limit (3.5 mm above the burner head) was found to be the minimum safe electrical working distance from the burner. Fig. 1 shows a close-up view of the electrodes and burner assembly and their mounting relative to the chopper-IR sensor used with the FIRE. A sodium chloride window was cemented to the Plexiglass electrode supports for some of the experiments. A Hewlett-Packard (Avondale, PA, U.S.A.) Model 6209B d.c. power supply supplied 300 V d.c. Current was monitored on a Keithley (Cleveland, OH, U.S.A.) Model 610BR electrometer. A Varian (Palo Alto, CA, U.S.A.) Aerograph recorder was used to record the signal monitored as a chromatogram.

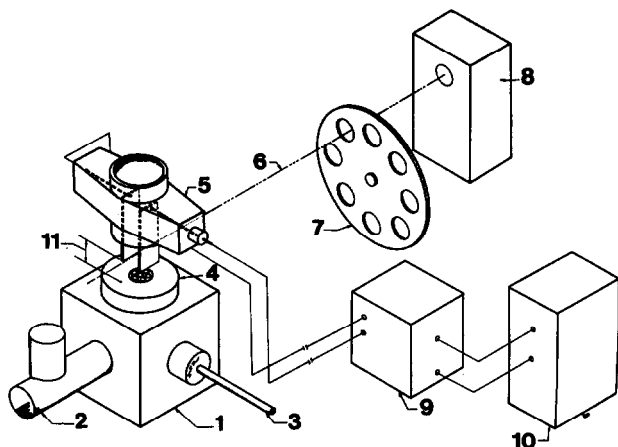


Fig. 1. Isometric close-up of FIRE-FID system. 1 = Burner body; 2 = fuel gas inlets; 3 = effluent capillary; 4 = burner head; 5 = electrode assembly; 6 = optical path; 7 = chopper; 8 = PbSe detector; 9 = electrometer; 10 = recorder; 11 = electrode height.

All flame or carrier gas flows were monitored using flow meters with integral metering valves (Cole-Parmer, Chicago, IL, U.S.A.). Hydrogen and helium were obtained locally. The air used was compressed, dried and filtered on site. Copper tubing (1/8 in.) was used in construction of all columns. Helium was used as the carrier gas in all experiments.

### Reagents

A total of 21 different liquid organic compounds were analyzed, as specified in Table I. All compounds were reagent grade or the best possible grade.

Gas samples were obtained from Aldrich (Milwaukee, WI, U.S.A.), Matheson (Secaucus, NJ, U.S.A.) and Airco.

### Procedure

An injection of  $1 \mu\text{l}$  of the pure liquid was made to measure detector response per mole carbon in the compound. In the response studies, the oven temperature was elevated above the boiling point of sample compounds to minimize sample interactions with the column stationary phase. Detector response studies with respect to moles carbon were performed only for the modified FIRE system. Ratioed pentane-hexane solutions were injected to study detection limits. The column oven temperature was held above the boiling point of pentane but below that of hexane to effectively separate pentane from the hexane solvent and allow the pentane to travel through the column with minimal stationary phase effects. A 10% OV-101 on Chromosorb W AW 80-100 mesh column was used for all liquid samples, with a carrier flow-rate of 35 ml/min. Detection limits for both the FIRE and FID systems were evaluated in this manner.

All gaseous compounds were collected over water at  $23^\circ\text{C}$ . Mixtures of gases were collected initially into a 500-ml graduated cylinder to allow measurement of gas volumes, and then transferred into 250-ml flasks, equipped with Subaseal (Aldrich)

rubber septa to allow gas-tight syringe (0.5 ml Hamilton) sample removal. Pure gaseous samples were directly collected in 250-ml flasks.

Up to 0.5 ml of gaseous sample was injected onto the column (3 m Porapak R, 80–100 mesh, 23°C) to establish calibration curves. Carrier flow for all calibration curves was 25 ml/min. For gas mixtures where separation of carbon monoxide and methane was desired, the Porapak R column was run at sub-ambient temperature for 1.5 min to allow carbon monoxide and methane to elute. Subambient temperatures were achieved by placing a container of dry ice on the floor of the oven chamber with the oven circulator fan running. This allowed the circulated chamber air to reach a lower temperature of approximately  $-30^{\circ}\text{C}$ . The column also reached this temperature after approximately 30 min. The oven was then raised to  $200^{\circ}\text{C}$  at a rate of  $32^{\circ}\text{C}/\text{min}$ . The column was maintained at this final temperature for approximately 4 min, allowing butane to completely elute. If separation of carbon monoxide and methane was not necessary, a temperature of  $25^{\circ}\text{C}$  was used at the start of the temperature program. An initial carrier flow-rate of 25 ml/min was used in all the gas mixture studies. As the eluted compounds combusted in the hydrogen–air flame, two chromatograms were recorded simultaneously, one from FIRE and one from FID.

## RESULTS AND DISCUSSION

### *FIRE modification*

The flame infrared emission detector used in this study was similar to units previously reported by Hudson and Busch<sup>5,6</sup>. Modifications were made in four areas: chopping rate, detector field of view, infrared filter type and the addition of an infrared window.

The chopper design used a 3000 rpm electric motor with a 12-hole chopper blade which resulted in a 600-Hz chopping rate. Comparing this rate with the previously reported rate of 90 Hz, an improvement in flicker, or  $1/f$ , noise is expected. In fact, at the rate of 600 Hz, flicker noise should be insignificant.

The detector utilized an aperture for field of view limiting, therefore, the PbSe device "saw" only the analytical flame and the area directly behind the flame. The field of view limiter restricted the amount of background radiation incident on the detector. This resulted in an overall decrease in baseline level and greatly decreased the effect of activity present in the laboratory, practically eliminating that source of noise.

Previously reported detectors used a high pass filter with a cut-off of  $3.5\ \mu\text{m}$  and a PbSe device with a cut-off above  $5.0\ \mu\text{m}$ . This resulted in a bandwidth of at least  $1.5\ \mu\text{m}$  which is much wider than the  $4.3\text{-}\mu\text{m}$  carbon dioxide emission band. A different PbSe device was selected in this study which included an integral infrared filter with a center wavelength of  $4.45\ \mu\text{m}$  ( $\pm 0.1\ \mu\text{m}$ ) and a bandwidth of  $0.65\ \mu\text{m}$  at 50% transmittance. This detector–filter combination gave a decrease in overall signal but since the noise level decrease was greater, the signal-to-noise ratio was increased. A further decrease in bandpass should result in even better signal-to-noise ratios.

An infrared window was placed between the burner flame and the chopper–detector assembly to eliminate the effect of air drafts caused by the chopper blade. As with the other modifications, the window resulted in a decrease in signal which was compensated for by a corresponding decrease in noise level.

Overall, the combination of these improvements gave a substantial increase in

signal-to-noise ratio, compared to FIRE units previously reported<sup>6,7</sup>. Injections of a pentane in hexane solution were used to ascertain the exact signal-to-noise ratio of the modifications. Using the criteria of detection limit equal to twice the noise, a detection limit for pentane of 0.002  $\mu\text{l}$  was found which corresponds to about 1.5  $\mu\text{g}$  of pentane.

Initially, it was thought that the use of a smaller hydrogen-air flame would result in better sensitivity and greater signal-to-noise ratio. Burners were constructed using smaller capillary tubes for flame support. These burners would not maintain the hydrogen-air flame. Therefore, the 1.5 mm capillary tubes were used and flame gas flow-rates were decreased. Flow-rates of 130 ml/min hydrogen and 340 ml/min air were found to be optimum for signal-to-noise ratio and stabilization of the FIRE chromatographic baseline. It can be noted that these flow-rates, while lower, give the same flame stoichiometry as previously reported<sup>6</sup>.

When the FIRE hydrogen-air flame is functioning at high efficiency, all organic compounds are expected to completely combust, giving a proportionate number of moles of carbon dioxide. Ideally, the signal monitored from the 4.3- $\mu\text{m}$  carbon dioxide emission should be directly proportional to the number of moles carbon in the sample. Earlier work had roughly indicated this trend, but the data showed anomalous behavior for certain compounds. Table I shows the results of the injection of 1  $\mu\text{l}$  of a variety of organic compounds, listing peak areas and signal per mole carbon. Signals

TABLE I  
SIGNAL PER MOLE CARBON

<i>Compound</i>	<i>Peak area</i>	<i>Signal per mole carbon (<math>\times 10^9</math>)</i>
Pentane	111 787	2.58
Hexane	123 995	2.70
Heptane	117 641	2.46
Octane	114 119	2.32
Cyclohexane	138 027	2.49
Methyl cyclohexane	132 364	2.41
Cyclooctane	124 914	2.10
Benzene	172 746	2.56
Toluene	152 118	2.31
Methanol	58 826	2.52
Ethanol	79 223	2.31
1-Propanol	90 152	2.25
2-Propanol	97 397	2.48
1-Butanol	91 506	2.09
t-Butanol	107 929	2.54
Carbon tetrachloride	22 521	2.17
Dichloromethane	32 982	2.11
Chloroform	28 678	2.31
Tetrachloroethane	36 824	2.01
2-Butanone	110 019	2.46
Butyl acetate	99 851	2.19
Mean value		2.35
Standard deviation ( $n-1$ )		0.19

per mole carbon were calculated from the injected volume, density of the compound, formula weight of the compound and the number of moles carbon contained in the compound. As shown in Table I, an average signal per mole carbon for all compounds injected of  $2.35 \cdot 10^9$  was found, with a standard deviation of 0.19.

The discrepancies found in comparing the data presented in Table I and the reported responses in the literature<sup>6,7</sup> can be explained in view of the instrument modifications. The use of the aperture limiter and the narrow bandpass filter each contribute to this difference. Some compounds may favor multiple emission from each carbon dioxide. By limiting the view of the detector to one area of the flame zone, any secondary emission by excited carbon dioxide may occur outside the view of the detector. Secondly, and most importantly, some compounds combust not only to carbon dioxide, but give other products in small amounts. For example, aromatic compounds are known to burn with a sooty flame characteristic of carbon particle formation. Using the detector-filter combination of Hudson and Busch, the wide bandpass would allow blackbody radiation from carbon particles to be monitored. The described system would limit greatly that effect.

The signal observed suggested that all compounds were combusted with about the same degree of efficiency, if not 100% then a constant percentage. This response suggests that FIRE may be used for standardless analysis, that is, where no standards are available. The advantages of this type response are obvious when compared to either TCD or FID, each of which must have standards for each component for accurate quantitation.

#### *FID design and performance*

Best FID response was found with the Keithley electrometer set on the  $10^{-10}$  A scale. The scale multiplier could then be used to select the overall sensitivity.

The FID section of the combination detector gave response to various compounds as expected<sup>1-3</sup>. The FID sensitivity easily exceeded that of FIRE for compounds which both systems responded to. As a basis for comparison, the detection limit of the FID unit for the same pentane in hexane solutions as used in the FIRE studies was evaluated. Using a carrier flow-rate of 25 ml/min, a detection limit of  $0.000006 \mu\text{l}$  was found by averaging the signal for 5 injections of  $0.1 \mu\text{l}$  of a 1 part pentane in 5000 parts pentane in hexane solution, giving a signal-to-noise ratio of 10. The amount that would give a signal-to-noise ratio of 2 was then calculated. This corresponded to about 4.5 ng pentane, which when compared with modern, commercially available units was not as sensitive. This can be explained by examining several factors. First, the specialized burner was optimized for FIRE. This burner is a premixed hydrogen-air system, as opposed to the non-premixed type found in most, if not all, FID units. Studies have shown that the non-premixed burner supports greater ionization in the flame<sup>1</sup>, hence greater FID signal. Secondly, the electrode assembly was chosen to not interfere with FIRE. This unit used two flat electrodes on opposite sides of the flame. Most modern FID units utilize the actual flame jet as the positive electrode, with the negative electrode typically of cylindrical shape and surrounding the flame which has been found to give better response. Another factor affecting the detection limit was the nature and origin of the limiting noise. As previously noted, this unit was not fully shielded, either from the surroundings or from the FIRE components. The slight vibrations from the chopper assembly seemed to be

the source of the limiting noise on FID since FID had less noise without the FIRE components active. Since the purpose of this work was to investigate the combination detector, all detection limits are stated for both detection modes active.

One effect not expected with FID was noted. With the configuration used in this study, a decrease in carrier flow-rate resulted in decreased sensitivity. This phenomena may be due to the physical configuration of the FID system constructed for this study. However, the authors have not evaluated this further.

Concomitant operation of FIRE-FID confirmed no significant interference observed in either the FIRE or FID chromatograms. The parallel, flat electrodes could be positioned out of the field of view of the FIRE system. While this was not optimum for FID, it did control any blackbody background problems that a more typical cylindrical FID electrode may have introduced to FIRE. The configuration of the Plexiglass electrode mounts and IR window isolated the flame from the chopper air drafts. A schematic representation of the overall FIRE-FID system is shown in Fig. 2.

#### *Analysis of gas mixtures.*

The FIRE-FID detector was used to analyze gaseous mixtures of carbon monoxide, carbon dioxide and hydrocarbons. Ratioed synthetic samples were made of the gases and injected. Sample 1 contained 57% methane, 20% carbon monoxide, 20% carbon dioxide, 1% ethane, 1% propane and 1% butane (v/v). Sample 2 consisted of 49% carbon monoxide, 49% carbon dioxide, 1% methane and 1% ethane (v/v).

Chromatograms of samples 1 and 2 are shown in Figs. 3 and 4, respectively. Both chromatograms showed that carbon monoxide and carbon dioxide are detected only with the FIRE unit. All the hydrocarbons are detected by both units, when present in sufficient concentration. Fig. 3 graphically illustrates this, as peaks 1 and 3 are due to carbon monoxide and carbon dioxide, respectively, and are present only in the FIRE chromatogram. The FIRE detector responds to these gases with the same response per mole carbon seen for all carbon containing species. Peaks 2, 4, 5 and 6 are for the hydrocarbon gases, and these are seen in both the FIRE and FID modes.

Fig. 4 is the isothermal chromatogram for the separation of four gases, In this case, carbon monoxide and methane are not separated completely on the column. However, this chromatogram illustrates one advantage of the FIRE-FID combina-

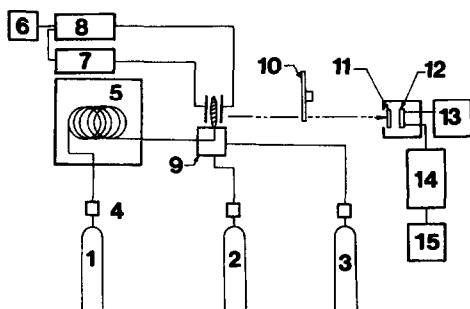


Fig. 2. Schematic diagram of FIRE-FID apparatus. 1 = Carrier gas; 2 = air; 3 = hydrogen; 4 = flow meters; 5 = chromatograph; 6 = FID recorder; 7 = 300 V power supply; 8 = electrometer; 9 = burner assembly; 10 = chopper; 11 = IR filter; 12 = PbSe device; 13 = 24 V power supply; 14 = lock-in-amplifier; 15 = FIRE recorder.

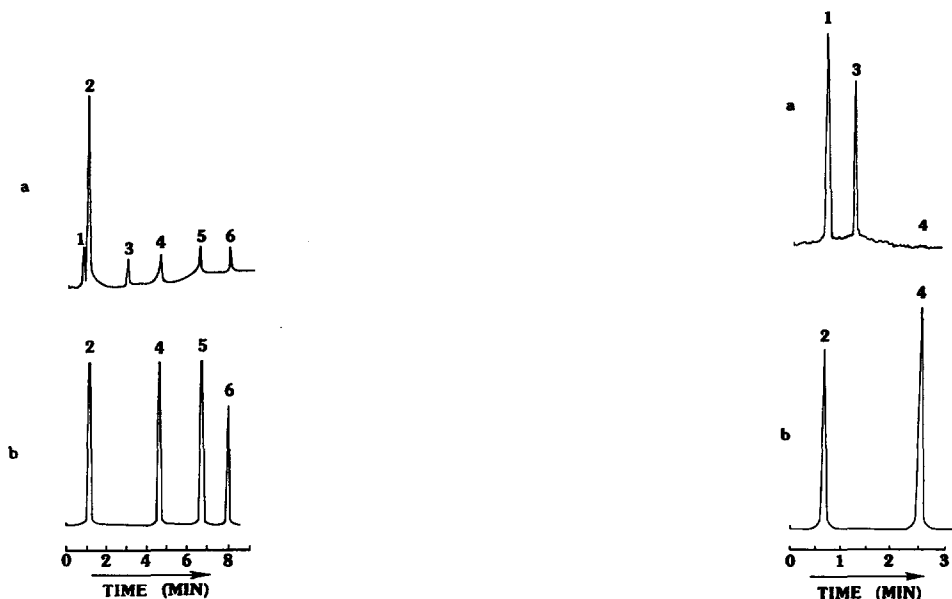


Fig. 3. Dual FIRE-FID chromatogram for gas mixture sample 1 (see text). (a) FIRE mode; (b) FID mode. Peaks: 1 = carbon monoxide; 2 = methane; 3 = carbon dioxide; 4 = ethane; 5 = propane; 6 = butane.

Fig. 4. Dual FIRE-FID chromatogram for gas mixture sample 2 (see text). (a) FIRE mode, (b) FID mode. Peaks: 1 = carbon monoxide; 2 = methane; 3 = carbon dioxide; 4 = ethane.

tion unit in that peak 1, in the FIRE mode, represents predominantly carbon monoxide. Peak 2, in the FID mode, represents methane present in small amounts in the sample. While the two components are not separated on the column, they are separately detected, allowing individual analysis. Peak 3 is due to the carbon dioxide in the sample, and is seen only in the FIRE mode. Peak 4 is due to ethane and is seen only in the FID mode, at this concentration.

In addition, only a fraction of the expected response for the hydrocarbon gases using the FID was observed due to the decrease in carrier flow-rate seen with the Porapak R column upon increasing column temperature. As the carrier flow-rate is decreased, the response drops off with this FID configuration. This effect was noted also in the detection limit studies on pentane.

## CONCLUSIONS

FIRE can be applied generally to all carbon containing species. The superior quantitation of carbon seen with FIRE compared to other methods is a definite advantage. FIRE is more sensitive than TCD and, while not as sensitive as FID, offers an attractive alternative for those samples not requiring the extreme sensitivity found using FID.

However, the combination detector described in this work allows the analyst the advantages of both types of detection in the dual mode. If a particular compound is present in sufficient amounts to be detected by FIRE, the superior quantitation of that



method is seen. For compounds present in small amounts, FID may be used. This synergistic approach has two obvious strengths. Compounds that are not detected by one method may be detected by the other, such as the carbon monoxide and carbon dioxide used in this study. FIRE is more sensitive for both these gases than either TCD alone or in combination with FID. Also, it is not always necessary to separate certain compounds to analyze them, thereby potentially eliminating hours of laborious methods development. At this time, no compounds have been encountered that FID exhibits a response to that FIRE does not. The reverse situation is true for the compounds mentioned above and is indicated for some other classes of compounds, such as the halogenated hydrocarbons.

Additional work is being undertaken to study the process of combustion in the hydrogen-air flame. Basic insights gained in such a study should reveal additional information useful in the design and implementation of the FIRE and FIRE-FID systems.

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