

Flame infrared emission detection of hydrogen

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ABSTRACT

The feasibility of using flame infrared emission (FIRE) for the detection of organic hydrogen was demonstrated. A FIRE radiometer was modified to monitor the 2.7- μm water vapor band emission and was used as a gas chromatographic detector. The system provided good quantification of hydrogen at moderate sensitivity. Detection limits for pentane were found to be 0.05 μl or 31 μg using the hydrogen/air flame. Maximum signal was monitored using a 1:1 stoichiometric flame at a height-in-flame of 3.7 mm, very similar to carbon mode FIRE studies. While no direct interferences were found, the presence of chlorine in the analyte compound did show a quenching effect. The hydrogen mode can be combined with carbon mode FIRE and with other detection methods, such as flame ionization detection, to give a detection system of great versatility, both in gas chromatography and various process monitoring applications.

INTRODUCTION

The fact that organic compounds, made up of carbon and hydrogen, combust to form carbon dioxide and water vapor has been known for many years. That this combustion reaction is efficient for the conversion of organic reactants to these products is attested to by the fact that combustion and incineration are major methods of destruction for hazardous organic materials. Analytically, carbon dioxide and water vapor have been used as analytes in determinations of carbon and hydrogen by gravimetric procedures and in IR absorption analysis in process monitoring [1].

The infrared emissions from flames were originally studied in detail by Plyler [2] who noted bands at 2.7 and 4.3 μm for a bunsen flame. The 4.3- μm band was assigned to carbon dioxide while the 2.7- μm band was assigned to both water vapor, from a fundamental vibration, and to the overtone of the carbon dioxide emission band. This and other early studies were carried out to model the emissions from jet aircraft engines, mainly to enable the construction of IR missile guidance systems. While it was noted that these emissions were at least semi-

quantitative, no interest was shown in IR emission for analytical work for some time.

Recently, the feasibility of using IR emission from a flame for analysis was shown, using the 4.4- μm carbon dioxide emission band [3]. A special IR radiometer was constructed and used to determine organic compounds as a function of carbon dioxide emission as the compounds were burned in a hydrogen/air flame. This method was applied to monitoring the chromatographic effluent from both liquid and gas chromatography [3,4], with good results. While other recent work has dealt with the determination of carbonate and chlorine from aqueous solutions by flame infrared emission (FIRE) [5,6], no work has been attempted using the 2.7- μm band. This paper investigated the utility of using this band for the quantitation of hydrogen from organic compounds.

EXPERIMENTAL

Instrumentation

A Varian Aerograph Model 705 gas chromatograph (Varian, Palo Alto, CA, USA) was used in this study. A small opening was made in the side of

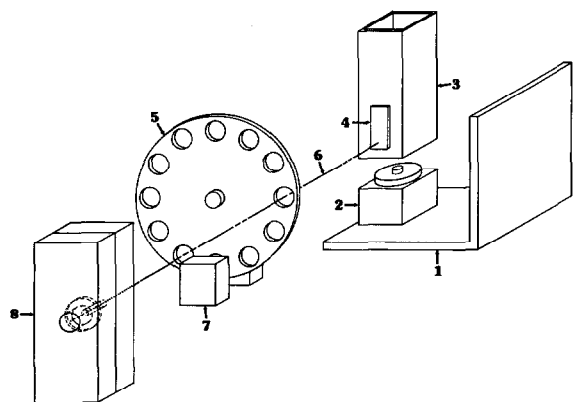


Fig. 1. Isometric close-up of FIRE system. 1 = Mount; 2 = burner; 3 = chimney; 4 = salt window; 5 = chopper; 6 = optical path; 7 = reference sensors; 8 = PbSe detector/filter/aperture assembly.

the oven to allow a stainless steel capillary tube of 1.5 mm I.D. to pass from the column end into a special hydrogen-air burner [4]. The FIRE detector used in this study was a modified version of that employed by Hudson *et al.* [7] as used in combination with a flame ionization detector (FID). The FIRE radiometer used a 630-Hz optical chopper, 2.4 mm I.D. aperture for field of view limiting, and a PbSe IR sensor as described previously. Modifications for hydrogen detection included: the use of a bandpass filter centered at $2.7 \mu\text{m}$ (Oriel Corp, Stratford, CT, USA), with a bandwidth of $0.1 \mu\text{m}$ full-width at half-height, mounted directly in front of the PbSe IR sensor; the addition of a height controller with adjustments in 1-mm increments for precise height in flame studies; substitution of a chimney painted flat black and mounted over the burner to reduce air drafts caused by the chopper blade and minimize background noise; and the use of a salt window mounted on the chimney to pass IR emissions, but further block air drafts. Fig. 1 shows a diagram of the radiometer.

A modified preamplifier circuit with a LF411 low offset low-drift field effect transistor (FET) input operational amplifier with adjustable gain control, and a reference circuit using a LM311 high-performance voltage comparator were designed and used. This circuit is shown in Fig. 2. The amplified PbSe signal was processed by an Ithaca Model 3981 (Ithaca, NY, USA) PC lock-in-amplifier (LIA) sys-

tem, which was installed in a Zenith 12 MHz IBM-AT compatible computer (Zenith Data Systems, St. Joseph, Michigan, USA). Software was written to control the LIA, display data, and allow digital storage and retrieval of data [8,9]. A hand-held solid-state laser (Emerging Technologies, Little Rock, AR, USA) was used to optically align the burner and PbSe IR sensor, allowing a precise determination of optical path for positioning and height-in-flame measurements.

Hydrogen, used as flame fuel, was obtained locally, as were the helium and nitrogen carrier gases. Air used as flame oxidant was compressed, filtered, and dried in house. Oxygen was used as the oxidant in some studies, and was obtained locally. Gas flows were monitored and controlled using flow meters with built-in metering valves (Cole-Parmer, Chica-

TABLE I
SIGNAL/MOL HYDROGEN

Compound	Signal/mol H	
	Air oxidant	Oxygen oxidant
Pentane	11.87	—
Hexane	11.58	5.127
Heptane	11.03	4.659
Octane	11.12	4.272
Nonane	11.19	—
Cyclohexane	11.77	5.810
Methylcyclohexane	10.93	4.327
3-Methylpentane	11.62	—
<i>tert.</i> -Butanol	10.24	3.967
Methanol	7.84	4.098
Ethanol	9.02	4.844
1-Propanol	10.71	4.935
2-Propanol	10.69	4.821
Carbon tetrachloride	0.00 ^a	0.000 ^a
Chloroform	0.00 ^a	0.000 ^a
Dichloromethane	N/A ^a	N/A ^a
Tetrachloroethane	N/A ^a	N/A ^a
Benzene	25.16 ^a	5.149
Toluene	23.18 ^a	2.143
2-Butanone	11.85	5.573
Butylacetate	11.42	1.172
Mean	11.60	4.30
S.D. ($n-1$)	1.12	1.24

^a These compounds not included in mean and standard deviation calculation (see text). N/A: Some signal for large injections, negligible relative to other listed compounds (see text).

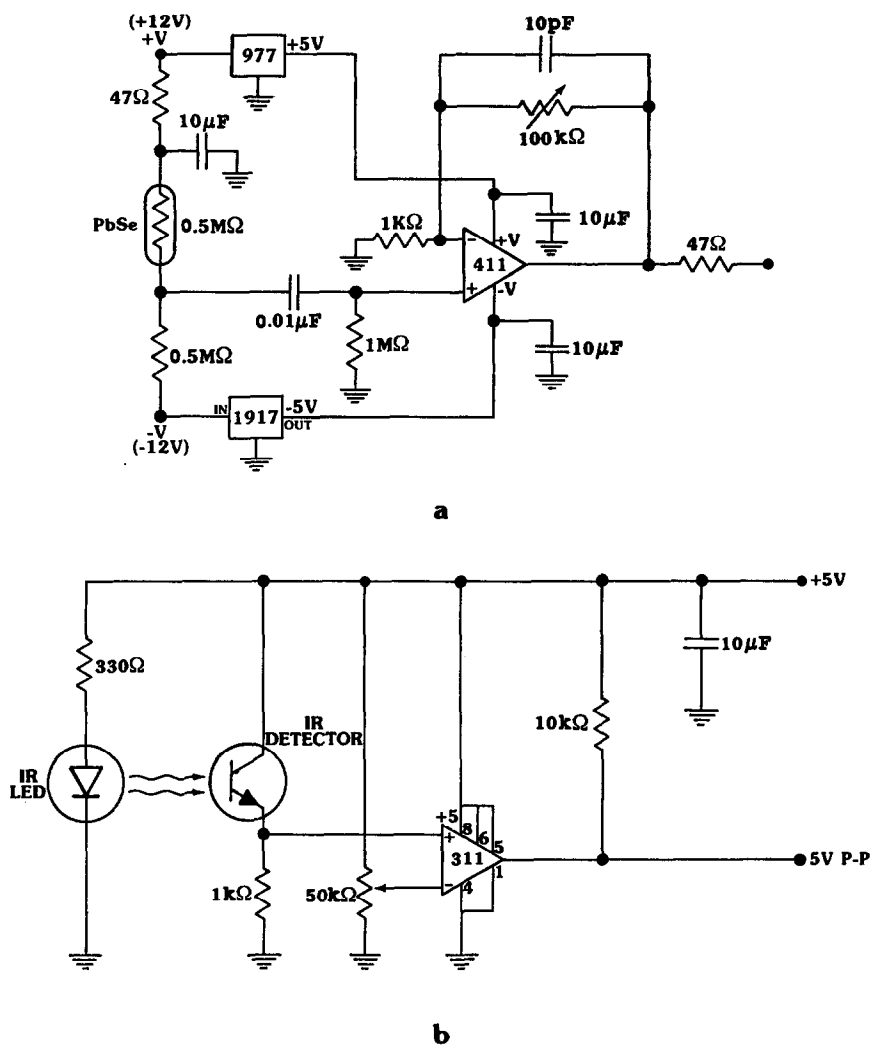


Fig. 2. (a) Preamplifier circuit; (b) reference circuit.

go, IL, USA). The column used was a 2-m 10% OV-101 on Chromosorb W HP packed in stainless steel (1/4 in.) (Supelco, Bellefonte, PA, USA).

Reagents

A variety of liquid organic compounds, totaling 21, were tested. These are shown in Table I. All compounds were reagent grade or the best possible grade.

Procedure

Injections of each individual liquid compound were made to measure the detector's response per

mol of hydrogen using a Hamilton syringe Model 801 (Hamilton, Reno, NV, USA). For each compound injected during response studies, the injection inlet and column temperature were held higher than the boiling point of the specific compound being tested to ensure complete vaporization of the sample and passage through the column with little interaction. Detection limits were determined by using pentane and hexane in a 1:50 ratio. The column temperature was held above the boiling point of pentane and below that of hexane to allow effective separation while minimizing column effects on the pentane.

Burner flow-rates were typically 116 ml/min hydrogen and 330 ml/min air. Carrier flow was 43 ml/min for both helium and nitrogen. Sample injections were typically 1 μ l. Other flow-rates and injection volumes were used, as indicated in the discussion.

RESULTS AND DISCUSSION

To study the fire for hydrogen, several parameters were considered which necessitated changes in the FIRE radiometer as previously used for carbon quantification [4,7]. The water vapor band, centered at 2.7 μ m, required an obvious change in the band-pass of the IR filter used. The 2.72 ± 0.05 μ m filter was the most suitable for this purpose which was readily available from optical suppliers. The narrow bandwidth limited the amount of blackbody radiation incident on the PbSe detector while allowing passage of most of the water band. Also, its transmittance (T) of 70% gave a good optical throughput at the detector. Flame drafts interfere with the stability of the hydrogen/air flame and cause a dramatic increase in observed noise. The burner chimney was designed to completely eliminate the effect of outside influences on the flame. The chimney's salt plate window effectively allowed the IR radiation to pass through the system while blocking the chopper induced air drafts. The chimney also served to form the essentially isothermal background on which the flame was viewed, further enhancing stability. The addition of the height controller to the burner base, along with the laser alignment unit, allowed much greater precision for the height in flame measurements. The modified preamplifier and reference circuits were used to decrease noise in those circuits and to allow variable gain in the preamplifier.

The use of a PC based lock-in-amplifier gave the operator greater control over the FIRE detection system. The software allowed the operator to set all lock-in parameters and to acquire, process, and store data to disk. Data could be retrieved for further processing and analysis.

Initial studies of the water and carbon dioxide bands indicated several important differences. First, the use of a hydrogen/air flame causes a 2.7- μ m water vapor band background. Interestingly, hydrogen was chosen as the fuel in early FIRE work be-

cause there was no significant background at the 4.3- μ m carbon dioxide band. Unfortunately, there is no analogous fuel for hydrogen studies at 2.7 μ m. In order to quantify hydrogen, the background would have to be constant enough to differentiate the small differences in signal between the flame and flame plus sample. Secondly, most references indicate that the 2.7- μ m band is due to both water and an overtone of carbon dioxide [2,3]. If this were true, a suitable calibration factor would have to be determined to achieve useful results from this band. A third difference is the emission intensity difference of water vapor compared to that of carbon dioxide. Obviously, two hydrogen atoms are required to form one water molecule, whereas carbon dioxide requires only one carbon atom, but how this difference effects sensitivity was not apparent.

Origins and characteristics of the 2.7- μ m emission band

If the 2.7- μ m emission band actually was a combination band of water vapor and carbon dioxide, data interpretation would be a great deal more complicated and minimally require a subtraction procedure based on the intensity of the carbon dioxide band at 4.3 μ m. Since this was deemed of primary importance to the overall feasibility of any method we would base on 2.7- μ m emission, this effect was investigated first. Carbon compounds that do not contain hydrogen were injected to quantify the effect of the carbon dioxide overtone at 2.7- μ m without the presence of compound-produced water vapor. Injections of carbon monoxide, carbon dioxide, and carbon tetrachloride were made, up to 0.5 ml for the gas and 10 μ l for the liquid samples. We had expected some small to moderate contribution from the carbon dioxide overtone at the 2.7- μ m band region since this was indicated in the literature [2,3]. No signal was monitored at 2.7 μ m for any size injections of these compounds. If there is a contribution from a carbon dioxide overtone at this wavelength, it is negligible under the conditions employed in this study. This observation allowed all resulting 2.7- μ m data to be treated using calibration curves at least squares fits, greatly simplifying data analysis.

The emission intensity of the water molecule at 2.7 μ m compared to that for the carbon dioxide molecule at 4.3 μ m is experimentally considerably

lower. This intensity difference is the product of several factors: the response of the PbSe detector at the two wavelengths, the number of moles of hydrogen *versus* the number of moles of carbon contained in the sample compound, the bandpass and %*T* of the filters employed, and the actual IR emissivity difference between the two combustion products. The detectivity or response factor, D^* , at 25°C of the PbSe detector at 2.7 μm is $6 \cdot 10^8 \text{ cm} \cdot \text{Hz}^{1/2}/\text{W}$. At 4.4 μm , the detectivity is $3.2 \cdot 10^8 \text{ cm} \cdot \text{Hz}^{1/2}/\text{W}$. A 70%*T* filter having a 0.1- μm bandpass centered at 2.72 μm was used for hydrogen. This filter exhibits less throughput when compared to the 87 %*T*, 0.6- μm bandpass filter as used previously with carbon. However, the hydrogen mode was operated in a source noise limited condition, as was the previous carbon mode unit. Comparisons of the relative change in signal monitored indicate that there is less IR emission for each water molecule than for carbon dioxide molecules. However, this could not be accurately quantified with this experimental setup.

The large signal seen for the hydrogen flame at 2.7 μm is certainly the limiting factor in the FIRE detection of hydrogen. While significant work was expended to achieve a smaller flame size to reduce background, the original burner configuration [4] was found to be optimum in regard to flame geometry and signal output. The actual limiting noise from the flame is not the larger DC component of the background signal, but the relatively small AC component superimposed on top of it.

Detection limits for the hydrogen detector were studied by using repetitive injections of a pentane in hexane mixture, as used in the previous carbon mode study [7]. In this case, noise was measured from digitally stored chromatograms by taking the standard deviation over an area of 30 or more seconds run time where no injections were made. Peak heights for a series of repetitive injections near the noise level were compared to arrive at an average injection size which resulted in a signal equal to two times the average peak to peak noise figure. The signal-to-noise ratio = 2 was chosen on the basis of its use in the literature and to allow ease of comparison to other methods. A detection limit for pentane of 0.05 μl , corresponding to 31 μg , was found. This level is over an order of magnitude larger than that seen for carbon mode signals, which were 0.002 μl and 1.5 μg pentane. This difference seems due to the

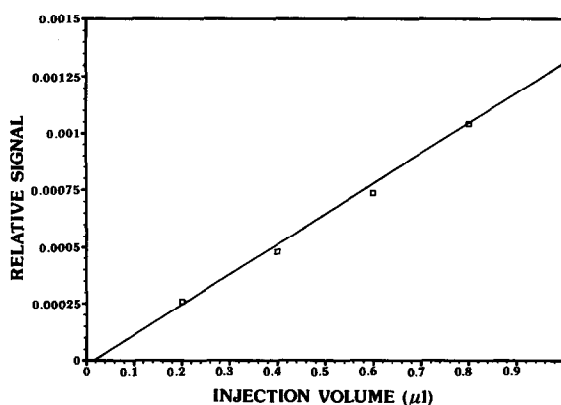


Fig. 3. Relative signal for hexane vs. injection volume.

higher source noise limit imposed by the hydrogen flame background at 2.7 μm .

Linear range was studied for injections of several different compounds. Fig. 3 shows the results of successively decreasing injections of hexane, indicating a linear relationship. The same solutions used for detection limit studies demonstrated a similar linear relationship at lower injection volumes for pentane. The linear range for hydrogen detection is similar to that for carbon mode operation, limited on the low end by the water vapor flame background noise. High end limits were found to be the same as for the carbon mode, limited by GC column overload. This indicates a linear range of slightly over three orders of magnitude.

Quantification of moles hydrogen

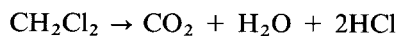
Carbon-mode FIRE detection has been shown to give a similar signal with regard to moles of carbon introduced into the flame, regardless of the functionality of the compound [7]. A study was conducted of the hydrogen mode unit to ascertain the functionality effects seen at 2.7 μm . Repetitive injections, normally 1 μl , of several sample compounds were made and the results were tabulated. The raw data were converted to give relative signal per mole hydrogen by using the injected volume, the density of the compound, compound formula weight, and the number of moles of hydrogen contained in the compound. Table I lists the compound, the relative signal integrated area, and the relative signal per mole of hydrogen calculated for each. An overall average signal of 12.43, with a standard deviation of

4.55, was obtained. This level of quantification does not compare favorably with the previously studied carbon mode average of 2.35 with a standard deviation of 0.19 [7].

Closer inspection of the data in Table I does reveal some trends. The chlorinated compounds show either no signal or such a small signal that areas could not be accurately determined. While no signal was expected for hydrogenless carbon tetrachloride, all other halocarbons tested contained hydrogen. Note also that the aromatics indicated a much larger signal than expected. The only other group showing a difference in signals was the lighter alcohols, with a slightly suppressed signal. If the aromatic and chlorinated functionalities are removed from the response calculations, an average of 11.60 value with a standard deviation of 1.12 results. This figure is significantly better and similar to that obtained for carbon-mode operation.

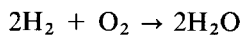
Several factors may enter into this difference seen in response for various functional groups. Looking first at the aromatics, it can be noted that initial carbon mode studies revealed similar data [3,8]. This was attributed to the tendency of aromatics to combust to carbon particles, which result in a significant blackbody emission. While this effect was apparently minimized in later carbon work, which used a similar radiometer and burner as this study, some blackbody emission may still be involved. The blackbody curve has greater intensity at 2.7 than at 4.4 μm , and still may be the mechanism giving rise to the greater observed signal levels. This hypothesis is supported by data collected using a hydrogen/oxygen flame on the burner. Data for the aromatics show a sharp decrease in emission, roughly in line with other compounds. The higher flame temperatures associated with oxygen operation should have resulted in less carbon particle formation.

The effect giving less signal for the halocarbons and alcohols may be found by considering the reactions for the combustion of all elements present in the tested compounds. Choosing dichloromethane and methanol as examples:



Carbon combusts to carbon dioxide, hydrogen to water vapor, and chlorine to hydrogen chloride,

when present. Note that the flame supplies hydrogen and oxygen to these reactions and combusts by the balanced equation:



For carbon, the predominant path is to combine with oxygen and form, eventually, carbon dioxide. This has been shown to occur at near 100% efficiency [7]. Recent work has also been performed on combustion of chlorine, using a reducing flame, showing quantitative formation of hydrogen chloride which was then monitored by FIRE at 3.8 μm [6]. However, for hydrogen two pathways exist. The organic hydrogen may combine with oxygen to form a water vapor molecule, as usually expected for combustion, or may combine with a chlorine atom to form a hydrogen chloride molecule. The latter pathway, while obvious from the reactions, was not expected to be significant prior to the response experimental studies. However, if one examines the occurrences in the flame regions, it may be that the combination of organic hydrogen and chlorine is the preferred mechanism.

Initially, we assumed that the hydrogen and oxygen in the flame, from the fuel and air supplies, would be present in enough excess to assure that organic carbon would combust to carbon dioxide, organic hydrogen to water vapor, and organic chlorine to hydrogen chloride. On closer examination, it becomes clear that this is not necessarily the case. It is required for the breakage of bonds that sufficient thermal energy be imparted to the molecule. This requires that some amount of hydrogen and oxygen from the supply be combusted to generate sufficient heat prior to compound combustion. A significant amount of supply gas must be combusted before organic compound breakup, which would then occur higher in the flame. In this case, as organic carbon, organic hydrogen, and organic chlorine are converted, they begin to seek another atom with which to combine and form a stable combustion product. Organic carbon normally reacts to form carbon dioxide, and is removed from the reactant stream. Organic hydrogen has the two aforementioned pathways, however, the organic chlorine atom is spatially much closer than a hydrogen from the flame gas supply. It would appear that much of the organic hydrogen is taken up by chlorine, giving hydrogen chloride at the expense of water vapor

and the 2.7- μm emission band. A similar argument for alcohols is not as clear. While OH radical formation is known to occur in spectroscopic flames [10], little is known about any IR emission attributed to OH. Additionally, organic hydrogens may not recombine preferentially with OH from the same carbon chain. A lone hydrogen may have to scavenge a flame fuel OH to form a water molecule, which would be in lower concentration, and not emit until in a higher, cooler flame zone, if at all. In any case, a stable OH with no emission or emission at another wavelength would cause a decrease in water vapor band intensity at 2.7 μm . The higher temperature of the hydrogen/oxygen flame was expected to minimize this effect, and this is verified by the data in Table I. Oxygen operation had little or no effect on the signals monitored for halocarbons.

Several fuel to air ratios were used in an attempt to achieve a greater signal-to-noise ratio, lower detection limits, and better relative response. In studies of HCl emissions, Kubala *et al.* [6] used a hydrogen rich flame. However, for hydrogen quantification, the same flame stoichiometry was used as for previous carbon studies, that is, essentially 1:1. Results with hydrogen/oxygen operation were not generally as satisfactory as when air was used as the oxidant. This is thought to be primarily due to the burner design. Height-in-flame measurements were carried out concurrently with the fuel/air studies. For the 1:1 stoichiometric flame a maximum signal height of 3.7 mm above the burner head was found. This height is very similar to that previously reported for carbon mode FIRE work.

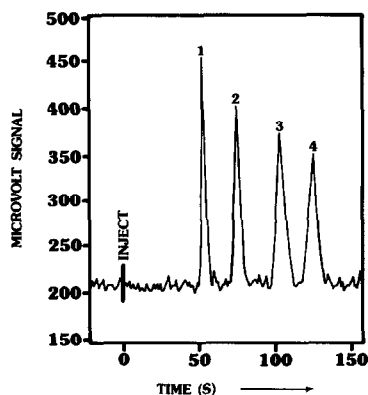


Fig. 4. Chromatogram for equal volume mixture injection (4 μl). Peaks: 1 = pentane; 2 = hexane; 3 = cyclohexane; 4 = heptane.

Fig. 4 shows a chromatogram obtained using the FIRE hydrogen mode detector. An injection of 4 μl of an equal volume mixture of pentane, hexane, heptane, and cyclohexane was made with an injector temperature of 150°C, a column temperature of 75°C, and a carrier flow-rate of 40 ml/min. The relative high noise associated with the 2.7- μm background is readily apparent in this chromatogram. However, the authors feel that this figure demonstrates the utility of selective detection of organic hydrogen and the performance of this FIRE detection mode.

CONCLUSIONS

FIRE detection can be used in a hydrogen mode to detect and quantify organic hydrogen. This mode does not result in as good a quantitation as the carbon mode, nor is it as sensitive. However, this study suggests that hydrogen mode FIRE can be combined into an instrument for multimode detection. Such a carbon/hydrogen detector would reveal significantly more information in a chromatogram than a single mode unit. Also, many of the problems associated with hydrogen and carbon FIRE modes may be overcome through the use of properly designed furnace based system, eliminating the flame background problem. The authors are currently working on such a multimode FIRE detector for carbon/hydrogen determination. Such an instrument, especially utilizing furnace-based combustion and excitation, should result in much greater utility in gas chromatographic and in many industrial process monitoring applications, as well as possibly providing a new device for measuring carbon/hydrogen ratios.

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