Journal of the Arkansas Academy of Science

Volume 46 Article 27

1992

# Development of a Variable Wavelength Flame Infrared Emission Gas Chromatography Detector

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## Recommended Citation

Zhang, Weiqun; Hudson, M. Keith; and Mofidi, Mokhtar (1992) "Development of a Variable Wavelength Flame Infrared Emission Gas Chromatography Detector," *Journal of the Arkansas Academy of Science*: Vol. 46 , Article 27.
Available at: http://scholarworks.uark.edu/jaas/vol46/iss1/27

Table 3. Percent of food items consumed by raccoons of both sexes for the four geographic regions of Arkansas.

| Region | Sex | Acorns | Non Acorns | Total Plants | Tres. Verts. | Aqu. Verts. | Total Verts. | Insects | Other Invert. | Total Invert. |
|---|---|---|---|---|---|---|---|---|---|---|
| Delta | ♂ | 31 | 49 | 80 | 20 | 29 | 49 | 7 | 6 | 13 |
| | ♀ | 71 | 13 | 84 | 10 | 29 | 39 | 10 | 11 | 21 |
| Ozark | ♂ | 43 | 34 | 77 | 15 | 12 | 27 | 16 | 12 | 28 |
| | ♀ | 55 | 29 | 84 | 13 | 7 | 20 | 23 | 6 | 29 |
| Ouachita | ♂ | 67 | 17 | 84 | 7 | 10 | 17 | 11 | 13 | 24 |
| | ♀ | 69 | 9 | 78 | 14 | 3 | 17 | 14 | 10 | 24 |
| G.C.P. | ♂ | 66 | 25 | 91 | 13 | 5 | 18 | 20 | 19 | 39 |
| | ♀ | 67 | 25 | 92 | 4 | 3 | 7 | 28 | 16 | 44 |

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## DEVELOPMENT OF A VARIABLE WAVELENGTH FLAME INFRARED EMISSION GAS CHROMATOGRAPHY DETECTOR

All matter above absolute zero, whether solid, liquid, or gas, continually absorbs and re-emits radiation due to the thermal agitation of its molecules, and is classified as a non-selective (blackbody or graybody) or selective radiator. Non-selective radiators emit a continuous spectral curve which has a maximum emittance at a specific wavelength which varies with temperature. Most heated solids behave as this kind of radiator. Selective radiators, such as hot gases and flames, emit radiation only over specific wavelength intervals depending on the molecular or atomic composition of the source (Fig. 1). Because the spectral lines or bands at certain wavelengths reveal the spectral characteristics of a selective radiator, they may be used for detection and analytical identification and are widely used in the determination of the functional components of organic compounds.

Different methods have been employed to determine the composition of compounds quantitatively or qualitatively. For example, the gravimetric procedure can be used for the determination of carbon and hydrogen (Ma and Ritter, 1975). Mass spectrometry procedures, in which charged particles are sorted according to their mass/charge ratio, give excellent information about molecular weight and structure. Nuclear Magnetic Resonance and the Infrared Absorption methods, such as FT, and dispersive, IR give significant organic functionality information (Willard, *et al.* 1988).

Combustion flames have been widely employed in detection systems for chromatography, either as spectroscopic sources as in the case of flame photometric detectors or as ionization cells as in the case of flame ionization detection. However, a recently developed method using combustion flames is flame infrared emission (FIRE) detection. Carbon dioxide ($CO_2$) and water vapor ($H_2O$) IR emissions can be monitored in order to make carbon and hydrogen determinations. In the range of 2 to 5 µm, $CO_2$ emits the strongest band centered at 4.4 µm, while $H_2O$ emits a band at 2.7 µm (Fig. 2) (Plyler, 1948). This use of IR emission has great potential usefulness since about 20% of the energy from a flame is emitted in this region compared to about 0.4% for the visible spectrum. For transparent flames such as the hydrogen/air flame, the visible emission is negligible and most of the radiated energy falls in the infrared region of the spectrum.

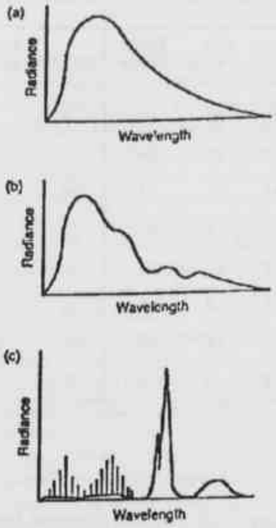

Figure 1. Emission Spectra of a (a) Blackbody, (b) Graybody, and (c) Selective Radiator.

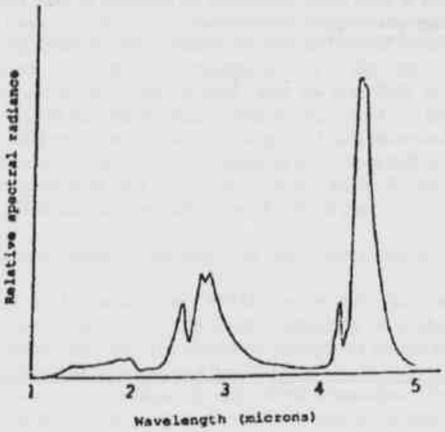

Figure 2. IR Emission Spectrum of a Methane / Air Flame.

Experiments demonstrating the analytical potential of using the 4.4 μm carbon dioxide emission band as a means of detecting organic compounds for both liquid and gas chromatography detection composed the initial work in this area (Hudson and Busch, 1987, 1988). These and other studies showed that the $CO_2$ emission was useful quantitatively and could be used for analysis of some compounds that cannot be detected by FID (Hudson, *et al.*, 1990). Non-chromatographic applications of FIRE include the determination of total inorganic carbon and volatile organics (Busch, *et al.*, 1989) in water samples. The determination of chloride ion and available chlorine in aqueous samples has also been demonstrated (Kubala, *et al.*, 1989) by using the intensity of the infrared emission due to the stretching vibration of HCl at 3.8 ,um. Other studies have indicated an HF band at 2.9 μm, partially obscured by the water band emission.

A prototypical variable wavelength flame infrared emission gas chromatograph detector, consisting of a gas chromatograph (GC), burner, lead selenide (PbSe) detector, infrared filter, preamplifier electronics, chopper, reference electronics, lock-in amplifier and computer, is shown in Fig. 3. This FIRE unit is similar to others previously described, differing mainly in the use of a circularly variable filter and in the mechanical layout of the radiometer to allow adjustment of the wavelength. To summarize the methodology, a small amount of sample, typically 0.1 to 5 μl, is injected into the GC where it is volatilized and then introduced into the center of the burner. As the sample flows into the flame zone or cell, it is combusted and the infrared emission energy is monitored through the 2.1 to 4.8 μm narrow bandpass circular variable infrared filter. Detection is accomplished via a PbSe photoconductive cell IR detector. This detector is mechanically chopped at 630 Hz, chosen since it is above the PbSe flicker noise threshold, and is amplified by a preamplifier circuit (Mofidi and Hudson, 1992). An Ithaco Model 3981 PC Board lock-in-amplifier demodulates the signal and a Zenith 80286 AT compatible computer provides instrument control, data storage, and processing, utilizing software written in house (Hudson and Hood, 1991.)

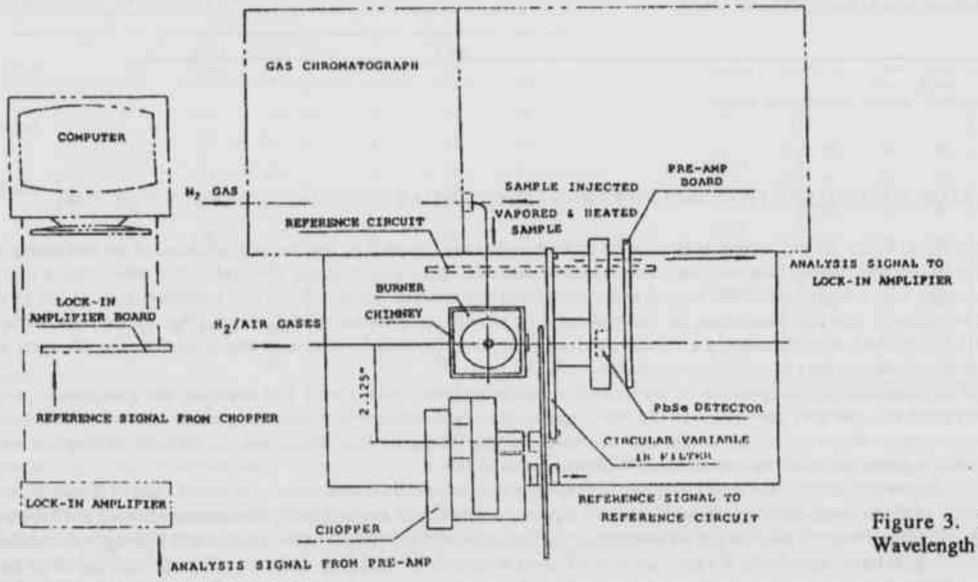

Figure 3. Experimental Layout of the Variable Wavelength FIRE Dectector.

The variable wavelength FIRE detector has only been utilized with manual wavelength control at this time. However, the limited data collected indicate that the system can be used to monitor the carbon dioxide and water peaks at 4.4 and 2.7 µm with results similar to those seen using the single wavelength, fixed filter radiometers previously employed (Hudson, *et al.*, 1990; Mofidi, *et al.*, 1992). Fig. 4 shows the results obtained for the repetitive injection of one µl of hexane at the 4.4 µm $CO_2$ and 2.7 µm $H_2O$ bands. Each injection was made with the filter adjusted in half degree increments to locate the maximum signal setting. Fig. 5 shows the signal obtained when the process was repeated for carbon tetrachloride. While these signals are noisier than those seen previously, note that the system has not been optimized. Fig. 6 shows the results obtained for the injection of 3 µl of carbon tetrachloride at the 3.8 µm HCl band. This band appears significantly noisier when compared to the $CO_2$ and $H_2O$ bands. However, this data was taken using the same parameters as those used for carbon and hydrogen data collection, ie, an oxidizing flame was used. Some previous studies indicate that a reducing flame, using only entrained air for flame support, is optimum for HCL emission (Kubala, 1989).

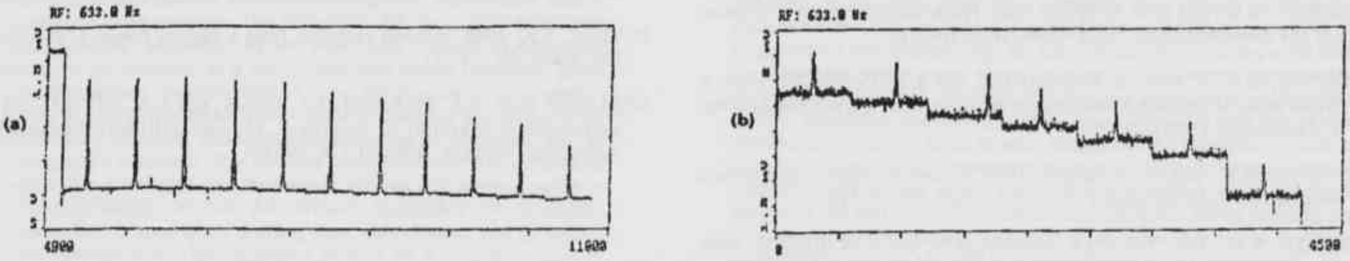

Figure 4. Response as a Function of Filter Angle for Hexane at (a) 4.4 µm and (b) 2.7 µm.

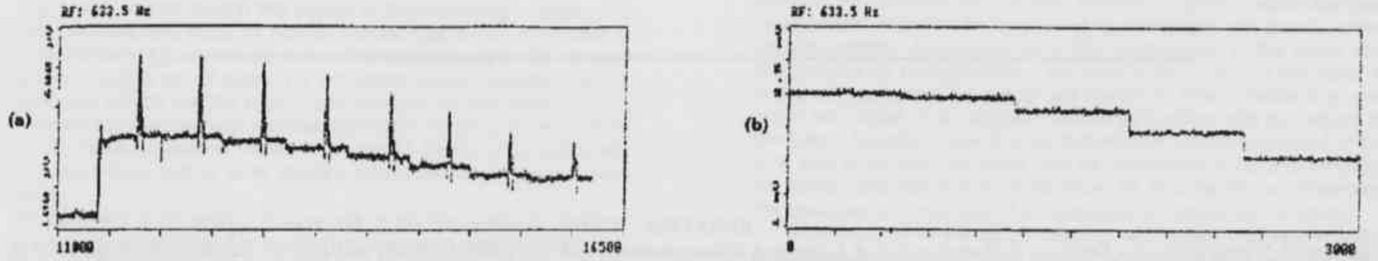

Figure 5. Response as a Function of Filter Angle for Carbon Tetrachloride at (a) 4.4 µm and (b) 2.7 µm.

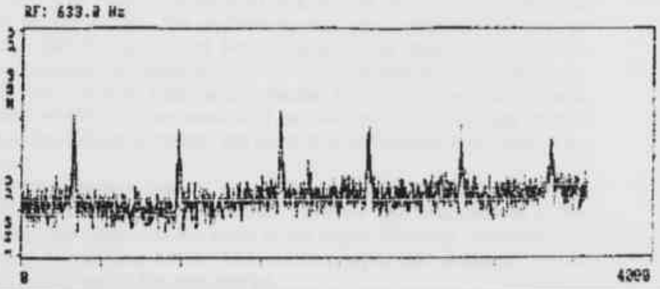

Figure 6. Response as a Function of Filter Angle for Carbon Tetrachloride at 3.8 µm.

These results indicate that the variable wavelength FIRE radiometer concept will perform at a reasonable level as compared with fixed filter FIRE units. The radiometer, while discussed here as a GC detector, can also be applied to process applications, such as flame detection, combustion control monitoring, and rocket plume diagnostics. Computer control can be extended to allow automated wavelength scanning for many of these applications. The authors expect to continue optimizing this unit, applying it to a study of the effect of the presence of organic chlorine on the formation of water vapor in combustion flames by monitoring the 2.7 and 3.8 µm bands.

## ACKNOWLEDGMENTS

This work was partially funded by a grant from the Arkansas Science and Technology Authority and by Hercules Aerospace, McGregor, Texas.

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## ERRATUM

In the article "Preparation of a Series of N-Phenylamides of 5-Bromo-6-Chloronicotinic Acid" by Frank L. Setliff and Jody Z. Caldwell which appeared in Volume 45 (1991) of the Proceedings of the Arkansas Academy of Science, on page 93 the entire table headings (including the table number) of Tables 1 and 2 should be reversed.