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IMPROVED FLAME PHOTOMETRIC DETECTOR FOR THE ANALYSIS OF SULFUR COMPOUNDS BY GAS CHROMATOGRAPHY

J. N. DRISCOLL* and A. W. BERGER

HNU Systems, Inc., 160 Charlemont St., Newton, MA 02161 (U.S.A.)

SUMMARY

The design of the flame photometric detector has not been changed significantly in more than two decades. Major problems in the use of this detector for quantitative analysis are variation in the response with molecular structure of a sulfur-containing species, and hydrocarbon quenching. The variable response noted with the FPD may, in part, be associated with the wavelength shift of the interference filter bandpass for off-axis radiation.

We have developed a flame photometric detector which employs rare-earth glass filters that transmit a wavelength-stable band for characteristic sulfur emission. With optimized flame conditions, we find a three-fold increase in sensitivity and control of quenching reactions, and this leads to straightforward analysis of different sulfur-containing fuels.

INTRODUCTION

The flame photometric detector (FPD) was first described by Drager and Drager¹ and Brody and Chaney^{2,3} more than 20 years ago. There have been relatively few improvements in the detector design over that time period with the exception of the dual-flame detector, described by Patterson^{4,5}.

The FPD has a complex mechanism which is still not well understood, as evidenced by the recent review of Farwell and Barinaga⁶. They conclude that it is remarkable that the FPD may be used for quantitative work, in view of the complexity of formation, excitation, and quenching of the chemiluminescent species (S_2^*) in the flame.

The FPD has been shown to have a number of inherent problems, such as non-linear (exponential) response, variation in the response factor with molecular structure, and quenching by hydrocarbons and other species which are eluted together with the sulfur compounds. Zehner and Simonaitas⁷, Aue and Flinn⁸, and Cardwell and Marriott⁹ have used dopants such as SO_2 or CS_2 , to linearize the output of the detector. The difficulty with this procedure is that the dynamic range is reduced and the linear output is dependent on the dopant and the solute. Bradley and Schiller¹⁰ have converted all sulfur compounds to SO_2 in a pyrolysis furnace prior to analysis by the detector in order to eliminate the variability of the exponential re-

sponse. Sevcik and Phuong Thao¹¹ have evaluated the selectivity of the FPD and suggested that the unsuitable geometry of the interference filters resulted in interference from hydrocarbons and heteroatoms. Interference filters are effective only when transmitting "well-collimated" light. Most commercial FPDs do not collimate the radiation from the flame. Sevcik and Phuong Thao¹¹ found that the selectivity of the detector improved with respect to hydrocarbon and heteroatom interference when the flame output was collimated.

In spite of the many problems, the FPD has endured, and the sulfur selectivity is still unmatched by any other detector. We describe a new detector which employs a rare-earth glass filter¹² in place of the interference filter to eliminate some of the problems discussed above.

EXPERIMENTAL

The initial work was conducted with a FPD which was modified by the substitution of a rare-earth glass filter (described in the following section) for the standard interference filter. In addition, the detector inlet was redesigned to minimize the dead-volume. The photomultiplier current was monitored with a HNU PI 52 electrometer (HNU Systems, Newton, MA, U.S.A.). The principal gas feeds to the FPD were individually regulated and fitted with flow controllers. Flow meters were calibrated versus orifice plate meters and/or bubble meters.

A HNU Systems gas chromatograph (Model 421) with an integral photoionization detector (PID) was employed in the isothermal mode with either an 8 ft. \times 1/8 in. PTFE column packed with acid-washed Haye Sep D or a 10 m \times 0.32 mm fused-silica Poraplot Q column (Chrompack, Tahway, NJ, U.S.A.). Samples were injected with a HNU six-port gas sampling valve operated at ambient temperature. The carrier gas was high-purity nitrogen or argon (Liquid Carbonic, Cambridge, MA, U.S.A.). The low-level standard contained four sulfur compounds in nitrogen (Scott, Plumsteadville, PA, U.S.A.). At the temperatures used for the separations, dimethyl disulfide was not eluted during the analysis. All other chemicals used were of ACS grade or equivalent. The chromatographic signals were recorded on a Spectra-Physics integrator (San Jose, CA, U.S.A.) or a Linseis recorder (Princeton, NJ, U.S.A.). The experimental variables, flow-rates, temperatures, etc., are described with the results discussed.

The rare-earth glass filter used was assembled by HNU. The rare-earth glass was designed by E. Snitzer and supplied by BED Corp. (Waltham, MA, U.S.A.). HNU has arranged to fabricate the filter for FPDs of its manufacture.

RESULTS AND DISCUSSION

A new type of optical filter was described by Snitzer¹² which employs rare earth glasses to form a class of absorption type band pass filters. One of the problems with interference filters was discussed by Sevcik and Phuong¹¹. They suggested that radiation from the flame, incident on the surface of the interference filter at angles other than 90° can result in a bandpass which is broader than the nominal value. This results in interference from hydrocarbon and heteroatoms. They were able to improve the design through the use of a lens system and a light pipe. Their results for pesticides

(S/P ratios) were in excellent agreement with the theoretical values only when interference filters were properly utilized.

Rare-earth glass filters which function by ionic absorption throughout the bulk of the filter material are not wavelength-dependent on the angle of incidence. Snitzer^{1,2} has shown that the rare-earth groups which have partially filled 4f electron shells can be used to form a large class of bandpass optical filters. A summary of the rare-earth glass absorption regions is shown in Fig. 1. A filter for sulfur was tailored by us to match certain emission lines of S₂*. The filter was composed of several rare earths to define the bandpass. The transmission spectrum is shown in Fig. 2A and can be compared with the transmission spectrum of the conventional interference filter in Fig. 2B. Note that the two primary peaks (Fig. 2A) match sulfur emission lines which are indicated at the top of Fig. 2A. Some of the weaker transmission bands at shorter wavelengths also match the sulfur emission lines. Since both bands in the filter are near the emission maximum for S₂*, one might expect that the sensitivity of the rare-earth filter on the FPD would increase by a factor of *ca.* 2 two under ideal conditions since this filter will allow more S₂ energy to pass through. The results were obtained by substituting filters and keeping the detector operating conditions the same to minimize any operational differences.

The actual signal-to-noise data (RE/IF) found for the two detectors was 1.95 ± 0.1 for the Scott Standard and 2.7 ± 0.1 for the sulfur in propane fuel. The Scott standard concentrations were nominally 4 ppm. The sulfur compound in propane fuel was not otherwise analyzed but is expected to be at about the 5 ppm level (normal for industry practice). There was no apparent difference in the noise level for the two

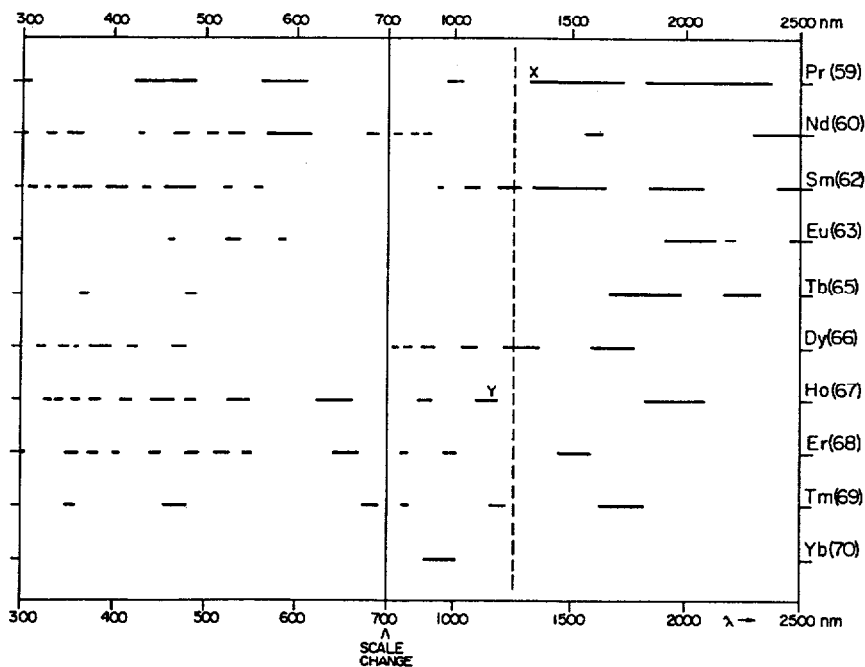


Fig. 1. Summary of rare-earth glass absorption regions (by permission of BED Corp.).

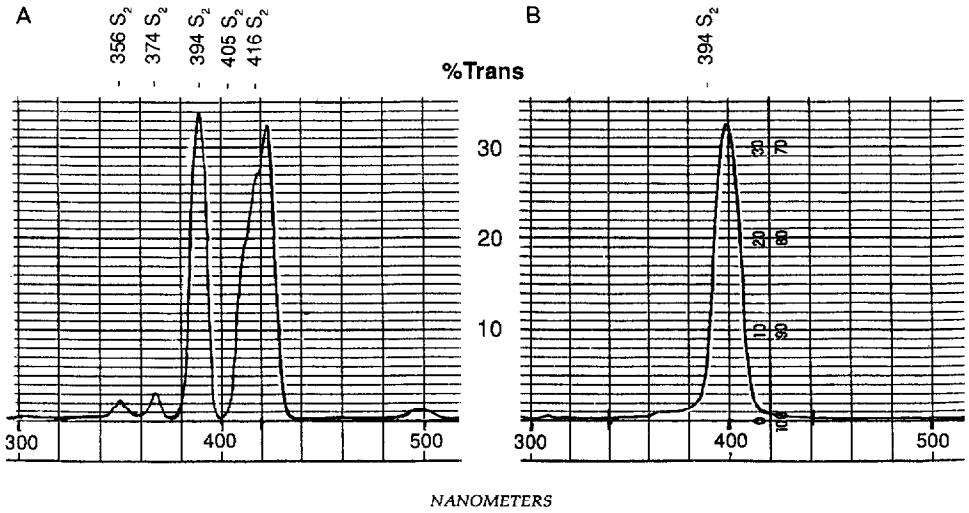


Fig. 2. Comparison of transmission spectra. (A) Rare-earth glass filter; (B) interference filter.

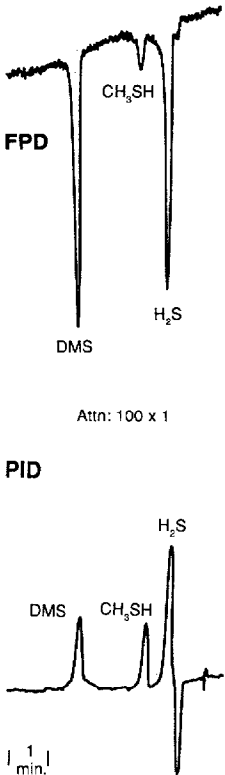


Fig. 3. Chromatogram of sulfur compounds on a Poraplot column. Conditions: 10 m \times 0.32 mm I.D. Poraplot Q; detectors in-series; carrier: He, 3 ml/min; oven: 125°C; detectors: 200°C sample loop: 405 μ l. Rare-earth glass filter.

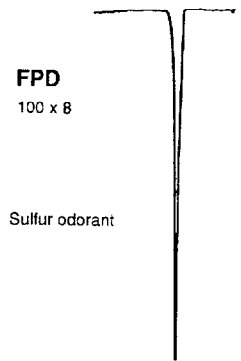


Fig. 4. Chromatogram of sulfur in propane fuel with FPD (rare-earth filter) and Poraplot column. Conditions: same as Fig. 3.

detectors operated under the same conditions, so that we were able to achieve the desired improvement in signal-to-noise level that was expected.

We have compared the FPD with the PID for a "clean" sample, a calibration gas, which contains a series of sulfur compounds in nitrogen. The PID was coupled in-series with the FPD downstream. A typical chromatogram for these two detectors is shown in Fig. 3. The amplifier sensitivity for the two detectors was similar, and the chromatograms were similar except for the negative peak in the PID. This peak may be due to a contaminant in the cylinder such as Freon, to which the PID responds but which has no response on the FPD. When the propane fuel gas was used as a sample,

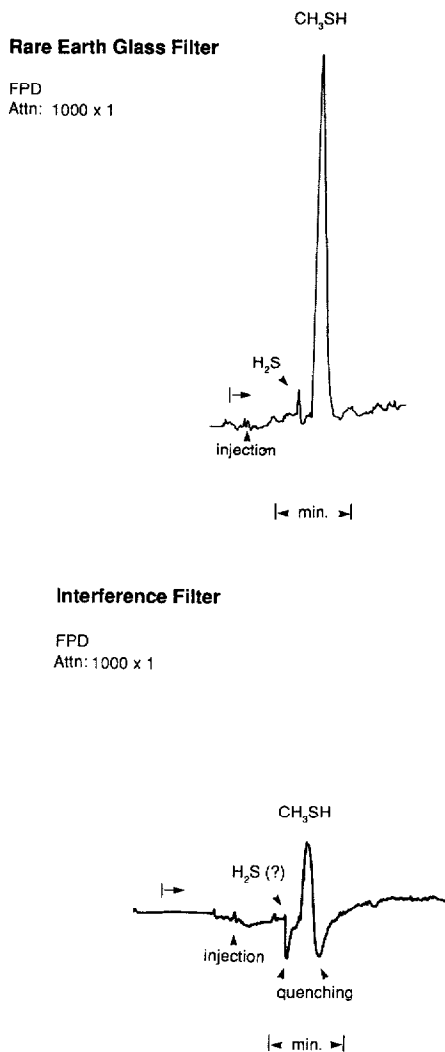


Fig. 5. Comparison of propane fuel with various FPDs (interference filter and rare-earth glass filter). Conditions: 8 ft. \times 1/8 in. PTFE, 2 mm I.D., acid washed Haye Sep D packing; carrier: Ar, 29 ml/min; oven: 150°C; detectors: 180°C; sample loop 405 μ l.

the optimized FPD with a rare-earth glass filter showed only one peak (Fig. 4) at about the same level as the calibration gas; the PID showed a large off scale response presumably for propylene, an impurity plus a second peak for the odorant (sulfur compound). The problem of sulfur selectivity or lack thereof arises for the PID. In Fig. 5, the results for the same sample (packed column) and the rare earth filter and interference filter FPDs are compared. Note the severe quenching of the response by the hydrocarbon for the interference filter, while the rare-earth filter presents no such problem. In fact, a low-level (ppb) H₂S peak was also observed with this sample.

The rare-earth glasses have a number of additional advantages including the lack of temperature and aging effects common to interference filters. Rare-earth glasses are, in fact, used as wavelength calibration standards by virtue of their inherent stability. Other potential uses of the rare-earth band-pass filters include the measurement of phosphorus, tin, and selenium compounds. Similar improvements in results would be expected with these filters.

CONCLUSIONS

Our optimized rare-earth-filter based FPD appears to have the potential to solve a number of problems from which the detector has suffered since its inception. The use of these filters improves the selectivity by eliminating the problem of angular dependence, which occurs with interference filters. At the same time, the sensitivity of the detector is improved by a factor of 2–3 by observing a number of the S₂ emission lines simultaneously.

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