



An improved multiple flame photometric detector for gas chromatography

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ABSTRACT

An improved multiple flame photometric detector (mFPD) is introduced, based upon interconnecting fluidic channels within a planar stainless steel (SS) plate. Relative to the previous quartz tube mFPD prototype, the SS mFPD provides a 50% reduction in background emission levels, an orthogonal analytical flame, and easier more sensitive operation. As a result, sulfur response in the SS mFPD spans 4 orders of magnitude, yields a minimum detectable limit near 9×10^{-12} gS/s, and has a selectivity approaching 10^4 over carbon. The device also exhibits exceptionally large resistance to hydrocarbon response quenching. Additionally, the SS mFPD uniquely allows analyte emission monitoring in the multiple worker flames for the first time. The findings suggest that this mode can potentially further improve upon the analytical flame response of sulfur (both linear $-HSO$, and quadratic $-S_2$) and also phosphorus. Of note, the latter is nearly 20-fold stronger in S/N in the collective worker flames response and provides 6 orders of linearity with a detection limit of about 2.0×10^{-13} gP/s. Overall, the results indicate that this new SS design notably improves the analytical performance of the mFPD and can provide a versatile and beneficial monitoring tool for gas chromatography.

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1. Introduction

The analysis of volatile sulfur-containing compounds is an important area that is often addressed using gas chromatography (GC) with sulfur-selective detectors including, for example, the sulfur chemiluminescence detector (SCD) [1,2] and the atomic emission detector (AED) [3,4]. One of the most commonly used devices in this regard is the flame photometric detector (FPD), which is well-known for its sensitive and selective detection of organic compounds containing sulfur, phosphorus, and several other elements [5–11]. Accordingly, GC-FPD remains widely employed in a large number of sulfur and phosphorus monitoring applications aimed at various concerns including chemical warfare [12–14], environmental emissions [15–17], pesticide residues [18,19], petroleum quality [20–23], and food production [24–27].

In addition to its favorable response attributes and analytical performance, other advantages of the FPD include its relatively robust design, low cost, and simple operation [28–30]. However, some significant disadvantages also exist. For instance, sulfur response is non-linear and often quadratic due to the predominant chemiluminescence of S_2^* [10]. As well, S_2^* emission intensity

can greatly vary among compounds, leading to a relatively non-uniform response factor over a broad range of analytes [31–33]. Finally, and perhaps most serious, severe analyte response quenching occurs in the presence of co-eluting hydrocarbons, which can significantly impede compound identification and quantification in complex matrices [34–37].

Recently, we have reported a novel multiple flame photometric detector (mFPD) which can help overcome these issues [38–40]. The mFPD employs a quartz tube that houses several small flames burning in-series along its length. There, the analytes travel through initial “worker” flames, where they are processed and degraded into emitting species, prior to entering a final counter-current “analytical” flame where the emission signal is monitored [38]. This arrangement presents some interesting properties in the mFPD. For instance, it offers analytical sensitivity that is reasonable relative to a conventional single flame FPD, and improved over a dual-flame FPD mode [38,41]. Further, a useful linear sulfur response mode can also be readily established in this device [39]. Most notably, however, the mFPD additionally provides greatly enhanced analyte response uniformity and a large resistance to hydrocarbon signal quenching, even relative to a dual flame FPD mode, which was also found to offer these attributes but to a lesser extent [38–40].

Despite its promising attributes, in working with the mFPD we have encountered a number of difficulties in its basic design that

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hinder its current performance. For example, the simple quartz tube burner used in the initial mFPD prototype allows for easy monitoring of the flames, but is inherently very fragile and requires a bulky cumbersome detector housing [38]. Further, considerable analyte emission can be lost through the quartz walls on the backside of the flame. Even more important, though, the current mFPD design suffers from high background emission from the worker flames. This arises because the cement used to fix the stainless steel capillary burners into the quartz tube wall produces an intense glow when contacting the flames [38]. In all, these features can very negatively impact the sensitivity of the mFPD and make it difficult to operate. Therefore, an improved mFPD design that can bypass these issues is needed in order to promote wider implementation and development of the device.

This paper presents the properties and operating characteristics of an improved mFPD device. The design is based upon a novel use of fluidic channels machined into a planar stainless steel (SS) surface to primarily direct flame gas flows and analyte emission. The analytical performance attributes of this new mFPD are presented and discussed. As well, where possible, these findings are evaluated relative to that of the original quartz tube prototype in order to help illustrate its advantages. Finally, a promising new multiple flame monitoring mode of this mFPD is introduced, which was previously impossible to access in the initial quartz device.

2. Experimental

2.1. Detector design

A schematic diagram of the SS mFPD is presented in Fig. 1. The device is primarily composed of a planar channeled face piece (Fig. 1A) and a matching cover plate (Fig. 1B). Both pieces are machined from 316 grade SS using a computer numerical controlled mill. As seen in Fig. 1A, the face piece comprises a flat rectangular SS block (6.5 cm × 3.0 cm × 0.635 cm) attached to a SS tube (0.20 cm i.d. × 0.635 cm o.d.; 5.0 cm length). A 2 mm hole drilled into the block connects the inner bore of this tube to the channeled surface (Fig. 1C) as depicted by the dotted line in the figure.

On the surface of the block, precision milled U-shaped channels (1 mm wide × 1 mm deep) were used to direct gas flows to the individual flames. These were comprised of a central channel to flow hydrogen and carrier gas laterally through the device, and five branching orthogonal channels to flow pure oxygen to micro-flames supported at their intersection. Four of these channels (spaced 0.5 cm apart) were added 4.0 cm below the central channel outlet and used to support worker flames. The remaining channel was added 2.0 cm below the outlet and used to support an 'orthogonal' analytical flame (described later in the text). From this position to the outlet, the central channel was also extended to 2 mm wide × 1 mm deep. This is because early design optimization revealed that a 1 mm channel provided the best worker flame performance, while a 2 mm channel produced enhanced analyte emission at the analytical flame. This arrangement was deemed optimal for operations in further studies.

A SS cover plate (6.5 cm × 3.0 cm × 0.75 cm) with two holes in it was constructed (Fig. 1B). One hole (1.0 cm diameter) was centered 2.0 cm from the central channel outlet and used to monitor the analytical flame. The other (2.0 cm diameter) was centered 4.75 cm from the outlet and used to monitor the worker flames. A 1.5 mm thick quartz window was snugly fit into each and sealed into place using a high temperature silicon gasket, such that they were mounted flush with the inner wall of the cover plate. When assembled, the windows rested flat against the channels of the face piece. On the outer wall of the cover plate each hole was threaded to

accommodate a cap for the worker flame window and a light guide adapter for the analytical flame window. In this way, all flames could be easily viewed during operation or covered/monitored as appropriate. The inner side of each piece was polished to a mirrored finish and they were bolted to one another in the corners. The assembled device was leak tested and found to direct gas flows consistently only through the channels.

The mFPD was affixed by a SS nut to the detector base of a Shimadzu GC instrument (Model GC-8A; Shimadzu Corp., Tokyo, Japan) which delivered analytes and hydrogen to the flames. The capillary separation column used was led through the connection and into the SS tube of the mFPD such that it deposited column effluent at the base of the central channel. Oxygen was supplied to the orthogonal flames through SS capillaries (0.584 mm i.d. × 0.902 mm o.d.; McMaster-Carr Supply Company, Atlanta, USA) inserted just inside each channel and sealed into place with high temperature silicone adhesive (Permatex, Hartford, USA).

2.2. General operating parameters

Flames were readily ignited at the end of each orthogonal channel by a spark presented at the central channel outlet of the SS mFPD while flowing high purity oxygen (Praxair, Calgary, AB, Canada) and high purity hydrogen (Praxair) through the system. Gas flow rates were optimized for each mode of operation. The typical flows used for monitoring sulfur in the SS mFPD were 30 mL/min of total oxygen distributed evenly across the worker flames (i.e. 7.5 mL/min in each channel), 12 mL/min of oxygen supplied to the analytical flame, and 100 mL/min of hydrogen. Variations of gas flows pertaining to other modes of operation will be outlined in the text.

Separations were performed on a DB-5 (5%-phenyl-95%-methylpolysiloxane) megabore column (30 m × 0.53 mm i.d.; 1.0 μm thickness; Agilent Technologies, Mississauga, ON, Canada) with high purity helium (Praxair) as the carrier gas at a flow rate of 11 mL/min. The injector/detector temperature was held at 300 °C. An isothermal oven temperature of 90 °C was used for all sulfur and phosphorus analytes except for the diesel fuel analysis, which employed a temperature program of 70 °C for 5 min, then increasing to 280 °C at 5 °C/min. Analyte emission was monitored at the analytical viewport through a quartz light guide (150 mm × 9.21 mm o.d.) leading to a photomultiplier tube (PMT; R-1104; Hamamatsu, Bridgewater, USA). An optical filter was situated between them to selectively monitor each mode. In the quadratic S₂* sulfur mode, emission was routinely monitored using a 393 nm (12 nm bandpass) interference filter (Oriental Instruments, Stratford, USA). Conversely, the linear HSO* sulfur mode used a 750 nm (40 nm bandpass) interference filter (Thorlabs, Newton, USA), while the HPO* phosphorus mode employed a 527 nm (10 nm bandpass) interference filter (Melles Griot, Rochester, USA).

2.3. Reagents and supplies

Test analytes used for calibrations included tetrahydrothiophene (97%; Fluka Chemika, Oakville, Canada), trimethyl phosphite (99% Sigma-Aldrich, Oakville, Canada), dodecane (99%; Sigma-Aldrich), and benzene (99%; EMD Chemicals, Gibbstown, USA). Standard solutions of these analytes were made in *n*-hexanes (95%; Anachemia, Montréal, Canada) at varying concentrations. Quenching experiments employed a thianaphthene (99%; Sigma-Aldrich) standard spiked into commercial diesel fuel (purchased at a local vendor) at different concentrations. All other details and conditions used are described in the text.

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