Mechanism of sulfur emission quenching in flame photometric detectors

Lev Kalontarov, Hongwu Jing, Aviv Amirav, Sergey Cheskis*

School of Chemistry, Sackler Faculty of Exact Sciences, Tel Aviv University, Ramat Aviv, Tel Aviv 69978, Israel

Abstract

The effect of sulfur emission quenching by CH_4, CO, CO_2 and octane was studied using pulsed flame photometric detection (PFPD). It was established that quenching is more efficient at the long time delayed emission. The dependence of quenching efficiency on quencher concentration was found to be similar for all of the above compounds when it was normalized to the concentration of carbon atoms. It is proposed that the dominant reaction leading to sulfur emission quenching is $CO + S = COS$ whereas CO is probably the main product of hydrocarbon combustion in a hydrogen-rich hydrogen–air flame. The experiments and model calculation indicate that CO-induced catalytic hydrogen recombination also promotes quenching and thus quenching is a universal phenomenon in FPD. A quenching-free dynamic range is defined; it is 10^5 for pulsed FPD. It is shown how quenching is identified and largely reduced with pulsed FPD.

1. Introduction

One of the most important aspects which limits the application of flame photometric detection (FPD) in the determination of sulfur-containing compounds is the sulfur emission quenching by co-eluting organic compounds [1–11]. The decrease in sulfur response with addition of hydrocarbons has been found for all existing types of FPD instruments: continuous FPD monitors [1], gas chromatographic (GC)-based FPD [2–11], supercritical fluid chromatography (SFC) FPD [12] and pulsed FPD (PFPD) [13]. It is difficult to draw a complete picture of the phenomenon based on the results of the work cited. Rupprecht and Phillips [2] demonstrated

that if mixtures of sulfur compounds and hydrocarbons are subsequently injected into a flame photometric detector, the sulfur response is less than for an equivalent amount of sulfur admixed with nitrogen. An increase in hydrocarbon concentration yields smaller responses, leading eventually to complete suppression of the signal. An increase in the carbon number of the diluting gas in the order ethane, propane, butane also diminished the signal. When the diluent gas was carbon dioxide, interference was much less and complete suppression was not observed. Fredriksson and Cedergren [3,4] have also shown that carbon monoxide is an efficient quencher of sulfur emission and carbon dioxide has lower efficiency. They found that quenching depends on the stoichiometry of the flame, i.e., in leaner hydrogen–air mixtures the degree of quenching is reduced. Unlike these workers [2–4], Weber et

---

* Corresponding author.

al. [1] established that carbon dioxide is very effective in inducing quenching, leading to complete suppression of the sulfur signal at about 3000 ppm of CO_2. Moreover, they have shown that the interference with the emission is independent of the concentration of the sulfur-containing compound. The same result had been obtained earlier by Sugiyama et al. [8] for hydrocarbon quenching agents. Sugiyama et al. [8] also found that the quenching efficiency increases exponentially with increase in the quencher concentration. It has been shown by Maruyama and Kakemoto [11] that the extent of quenching varies inversely with the concentration of the sulfur compound. However, the reverse dependence has been found by Olesik et al. [12] for hydrogen–oxygen flames.

The above brief review shows that there are contradictions in the literature on the phenomenology of sulfur emission quenching. The quenching efficiency depends on the type of FPD instrument, the method of mixing reacting gases and the composition of the flame. Nevertheless, it is commonly agreed that even minute amounts of hydrocarbons, if present in the flame, cause the quenching effect which hampers the accurate determination of sulfur compounds. This problem is further exacerbated by uncertainty about the existence of quenching and hydrocarbon-related emission signal due to the limited FPD selectivity. This aspect of the problem has been solved to some extent in PFPD [13]. The concept of PFPD is based [13–15] on a flame propagating in the detector from the igniter to the fuel gas source. The rate of fuel–oxidant gas flow is made insufficient for continuous flame operation, and therefore the propagating flame is observed in a pulsed periodic manner. The most important feature of the pulsed flame is the ability to obtain kinetic information about the processes involved. In particular, it has been shown [13,15] that there is a time delay between sulfur emission and the emission from the propagating flame front. The temporal profile of the sulfur response depends on the presence of quenchers, i.e., both the intensity and the kinetics of the emission are sensitive to quenching, which facilitates its discovery, while hydrocarbon residual emission is filtered also in time.

Considerable efforts have been devoted to overcoming quenching [3,4,9] and it has been claimed that this problem can be minimized in a dual-flame photometric detector [2,16,17]. In this FPD design, the first flame serves for oxidizing the hydrocarbon samples and sulfur emission is then generated and detected in the second hydrogen-rich flame. Some positive results with respect to quenching have also been reported using furnace/single-flame detectors [3,4] and in supercritical fluid chromatography–FPD [12].

The greatest confusion and contradictions are associated with the mechanism of sulfur emission quenching. Several possible reasons for quenching have been proposed [8–10,12,18,19]: (a) collisional deactivation of the S_2^* excited state by hydrocarbons or their oxidation products [8,18], (b) absorption of sulfur emission by a quencher [18], (c) the chemical reaction of hydrocarbons or their products with sulfur atoms and/or hydrogen atoms [8,13], (d) the hydrocarbon-induced temperature variations of the flame [19], (e) collisional deactivation governed by the diffusional quenching constant [10] and (f) quencher induced deactivation of some other excited flame species [10].

A new approach to the study of quenching has appeared with the development of PFPD. A model for sulfur emission in PFPD has been developed [20] and it has been proposed that the quenching is concerned with the reaction of sulfur atoms with carbon monoxide. Based on computer simulation [20], it was shown that CO is the main product of hydrocarbon combustion in hydrogen rich flames. In this paper, we present new experimental and computational results on sulfur emission quenching in PFPD induced by octane, methane, CO and CO_2, and a quenching mechanism is discussed.

2. Experimental

We used two types of PFPD instruments for the study of quenching. Octane-induced quenching has been investigated by means of a PFPD instrument mounted on a gas chromatograph. Its construction has been described in detail previously [13]. In brief, the combustible gases H_2

and air are mixed together in a small quartz combustor flame chamber (quartz tube, 12 mm × 3 mm I.D.) and flow to a continuously heated igniter (Kanthal AF 0.25 mm wire). The ignited flame then propagates back to the gas source, where it is extinguished until the next portion of gases fills the chamber and a new act of ignition occurs. This detector was mounted on a Varian Model 3600 gas chromatograph with a laboratory-made mount. The mount included a separate entrance for controlling the vaporization rate of liquids [tetrahydrothiophene (THT) in a small glass tube]. Typical gas flow-rates were 10 ml/min of hydrogen and 18 ml/min of air with pulse repetition rate of 3 Hz. In these experiments a constant sulfur background injected in the form of THT was quenched by a variable and known amount of octane eluting from the GC column.

Quenching by CH_4, CO and CO_2 was studied in a similar PFPD instrument that is able to measure the flame emission in two positions. Fig. 1 shows a schematic diagram of this detector. The hydrogen, air and nitrogen containing 100 ppm of SO_2 (Matheson) were mixed together using an Omega FL-6GP gas mixer. Their flow-rates could be regulated from 1.0 to 100 ml/min. The flow of the gas quencher was separately supplied to a gas line connected to the PFPD where it was mixed with the fuel–oxidant gas mixture and N_2-SO_2. Then the mixture entered the combustor (Pyrex tube, 80 mm × 4 mm I.D.) and the cycles of pulsed flame propagation took place as described above. The total gas flow-rate

was about 120–130 ml/min. The flow of the gas quencher was regulated from 0.07 to 10 ml/min by an Omega FL-310 flow meter and its concentration was calculated in parts per million (ppm) of the total gas flow (H_2 + air + SO_2 – N_2 + quencher). The flow of SO_2-N_2 was about 1% of the total flow (1 ppm SO_2). The typical flow-rates of fuel–oxidant gases were 65 ml/min H_2 and 55 ml/min air.

The design of this PFPD system allows the measurement of flame emission at two points (A and B in Fig. 1). Such an arrangement permits the direct measurement of the flame front velocity. The light emission at point A was collected by a quartz lens ($F = 30$ mm) and detected by a photomultiplier. A Spex 270 M monochromator was used for the analysis of the light emitted from point B and for the selection of the sulfur emission at 395 nm. Two Hamamatsu R 269 photomultipliers were employed for the emission detection. The signals from the photomultipliers were analysed by a LeCroy 9310 digital oscilloscope–averager and then transferred to a computer for additional processing.

3. Analysis of existing mechanisms for sulfur emission quenching

The mechanisms cited in the Introduction for sulfur emission quenching can be divided into two large groups according to the possible physical or chemical character of the quenching process. Of all the physical concepts, only the mechanisms concerned with collisional deactivation of excited sulfur species by hydrocarbons or their products are of some interest. As has already been noted by Olesik et al. [12], the concentration of hydrocarbon intermediates and the optical path length in FPD are too small to screen the emitted light from sulfur species. Also, combustion of a small amount (≤1% of the hydrogen) of introduced hydrocarbons cannot increase the temperature of the flame and thus reduce the sulfur response; moreover, it has a larger heat capacity than the flame gases. Thus only concepts based on collisional deactivation and chemical interactions between quencher and
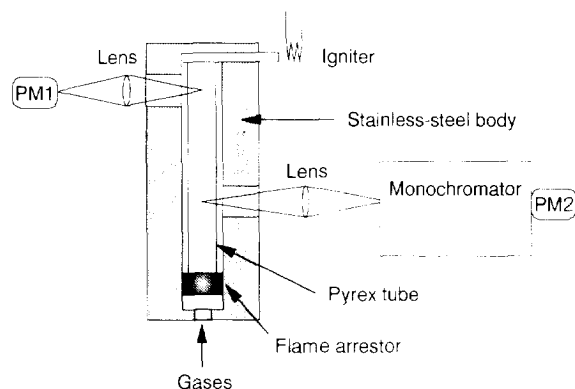

Fig. 1. Schematic diagram of the pulsed FPD instrument. PM1 and PM2 are photomultipliers.

sulfur and/or hydrogen atoms seem like likely candidates for S_2^* emission quenching in FPD.

Fig. 2 shows typical kinetic experimental curves of sulfur emission measured by PFPD as presented in Fig. 1 and its quenching time dependence. Note that similar results were obtained for all the quenchers studied (CH_4, CO_2 and CO) and we shall discuss them below. These curves illustrate the kinetics of the formation and consumption of S_2^* excited molecules after the flame front has passed the observation zone. As can be seen in Fig. 2, the addition of quencher can result in a total decrease in sulfur signal and a shift of the emission maximum to shorter times. Further, the decrease in the sulfur response is asymmetric in time. The signal at long times is more dramatically reduced than that at short times. The main conclusions emerging from Fig. 2 are that quenching becomes dominant at quencher concentrations of about 500–1000 ppm (0.4–0.8 Torr) and its kinetics exhibit
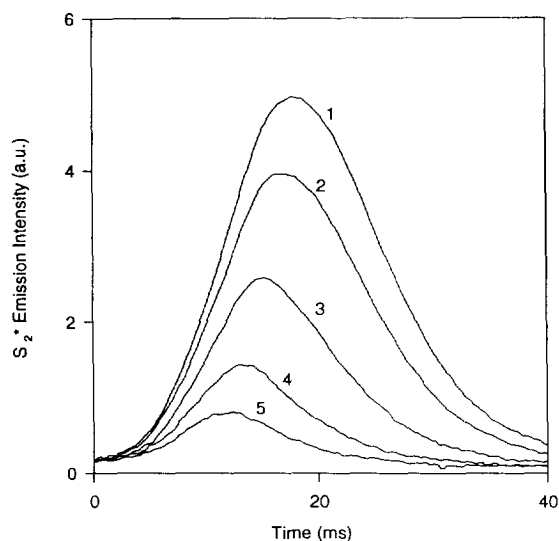

Fig. 2. Kinetic curves of sulfur emission in H_2–air pulsed flame at various concentrations of carbon dioxide obtained at 395 nm through a monochromator. Zero time corresponds to the beginning of the emission from the propagating flame front, which is caused mainly by OH^* molecules. Flow-rates were 65 and 55 ml/min for H_2 and air, respectively. The detector body temperature was 160°C. The CO_2 concentrations were (1) 0, (2) 650, (3) 1480, (4) 2800 and (5) 4600 ppm.

time asymmetry. We note that the first of these observations has been established in a large number of previous studies (e.g., Refs. [9] and [10] and references cited therein).

Note that the collisional quenching concept is in disagreement with this experimental evidence. Indeed, it is well established [21–23] that the radiative lifetimes of the $S_2^*(B^3\Sigma_u^-)$ excited state are in the region of 20–40 ns. The addition of quenching gases leads to complex fluorescence decay with a maximum lifetime of about 100–300 ns [23]. If we propose that collisional deactivation plays the dominant role in quenching, we have to draw the conclusion that it must not depend on the emission kinetics of sulfur because characteristic times of energy transfer (nanoseconds) are much shorter than those of the formation of S_2 (milliseconds in Fig. 2) unless the observed kinetics is of the quencher itself, which is highly unreasonable. This conclusion is in contradiction with the experimental asymmetry of quenching. Thus the time dependence of quenching shown in Fig. 2 serves as strong evidence both against the collisional quenching mechanism and in favour of the chemical nature of quenching. This conclusion seems true for other mechanisms of physical quenching, e.g., a diffusional model and deactivation of some other excited flame species. Since physical concepts are unable to explain the experimental observations, it is necessary to search for a quenching mechanism in the chemistry of the sulfur species involved.

4. Chemistry of hydrogen–air flame seeded with hydrocarbons

In order to enhance our understanding of hydrocarbon chemistry in rich H_2–air flames, we carried out model calculations using the Chemkin code for a constant-pressure explosion problem [24]. To make this model more realistic we incorporated exponential heat losses into the model and fitted its time constant to provide the best agreement between the observed sulfur emission time domain and our model calculations [20]. The general scheme of flame calcula-

tions has been divided into two subsystems: one hydrogen–oxygen reaction as has been done by Kee et al. [24] and a methane combustion subsystem with rate constants according to Westbrook [25]. Because of the low concentration of carbon-containing molecules, we did not consider reactions including more than one such molecule. The analysis of the calculation results shows that methane and its products undergo strong atomic pyrolysis by hydrogen atoms in rich H_2–air flames. Reactions with OH radicals are responsible, converting virtually all the methane into CO and CO_2 where the CO/CO_2 ratio is governed by the fast equilibrium reaction $OH + CO = H + CO_2$.

Fig. 3 shows the results of our calculations when 5000 ppm of CH_4 was added to the hydrogen–air system. It is seen that during ca. 0.2 ms all the hydrocarbon molecules are converted into CO and CO_2 with negligibly small concentrations of other molecules. Similar calculated results were obtained when 5000 ppm of CO and CO_2 were added; after combustion, all three systems give almost the same amounts of CO and CO_2 in less than 1 ms. The similarity of the results is even more conclusive at lower

concentrations of quencher. Hence the results of our calculations show that any memory about the origin of the quencher is lost after a very short initial time and then all the processes in the system are determined by the equilibrium between CO and CO_2. A change in this equilibrium with decrease in temperature produces an increase in the CO_2/CO ratio, as can be seen in Fig. 3 at time 1–2 ms. The final CO_2/CO ratio strongly depends on an equivalence ratio defined as the molar ratio of fuel to oxidant divided by the stoichiometric ratio. Fig. 4 shows such a dependence as the fraction of final CO in comparison with the hydrocarbon concentration which was initially added to the system.

According to our calculations, the addition of CH_4, CO or CO_2 to the hydrogen–air flame at a concentration lower than 5000 ppm hardly affects the fuel–oxidant combustion during its first 5 ms (Fig. 5). However, at longer times the additive dramatically decreases the hydrogen atom concentration. Since the concentrations of other reactive species, such as O and OH, are connected by equilibrium reactions, their con-
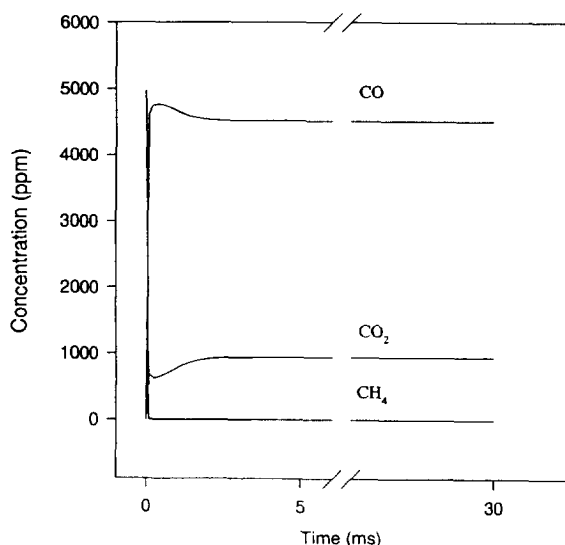

Fig. 3. Calculated kinetic curves of CH_4, CO and CO_2 concentrations during the pulsed flame combustion of 5000 ppm of methane in a hydrogen-rich H_2–air flame.
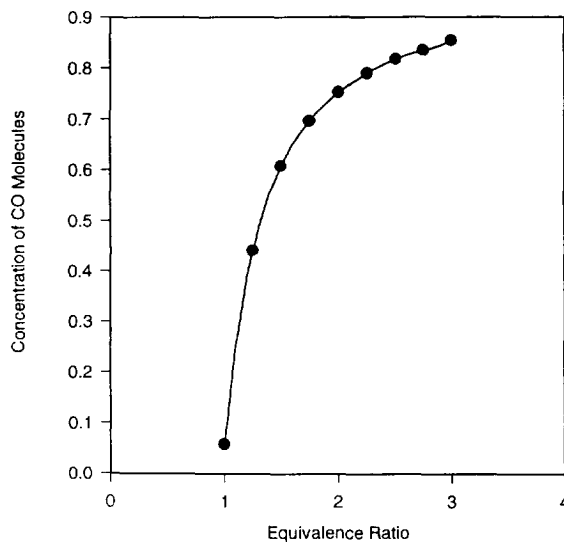

Fig. 4. Calculated dependence of the stationary long time concentration of carbon monoxide (expressed as a fraction of the initial methane concentration) on the equivalence ratio in a hydrogen–air flame after the combustion of 5000 ppm of CH_4.
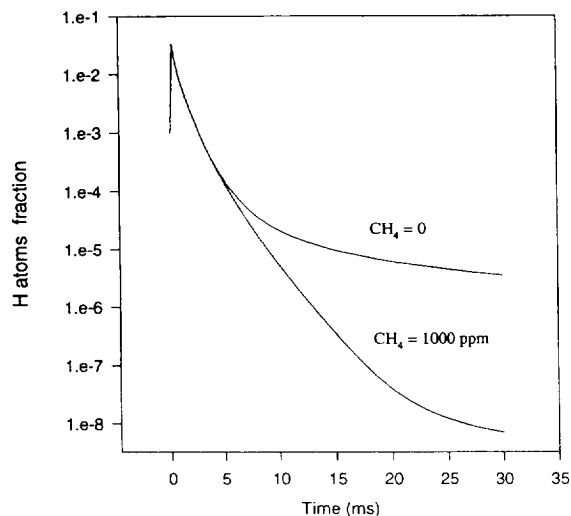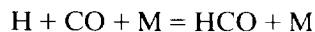
Fig. 5. Calculated kinetic curves of the concentration of hydrogen atoms in a hydrogen–air pulsed flame with and without the addition of methane.
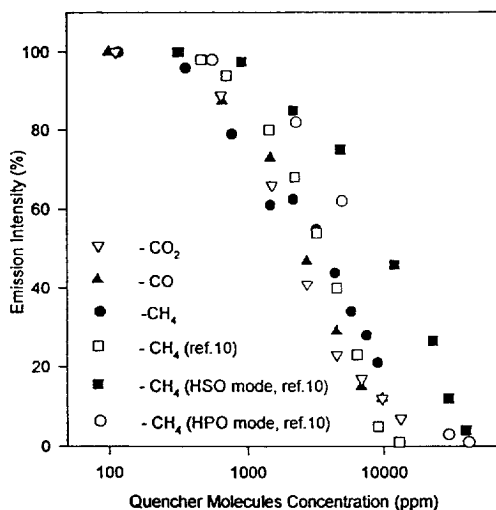

Fig. 6. Dependence of the relative sulfur emission intensity (expressed as a percentage relative to the emission intensity without quencher) on the concentration of quencher molecules. HSO and HPO emission dependences are added from Ref. [10].

centrations are also drastically reduced. The reason for such a decrease is the reaction

H + CO + M = HCO + M

followed by the fast reaction

H + HCO = H_2 + CO
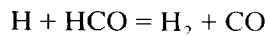
These two reactions produce a net effect of H atom recombination: H + H = H_2.

5. Results

Based on the conclusion regarding the chemical nature of quenching and computational results of hydrocarbon combustion, one of the principal questions is the type of molecule that is responsible for the quenching effect. There are three possibilities: (1) the hydrocarbons introduced into the flame; (2) their short-lived intermediate products of combustion and (3) the final products, mainly CO and CO_2. To clarify this problem, we measured the quenching efficiency of CH_4, CO and CO_2.

Fig. 6 shows the dependence of the sulfur response on quencher concentration. It also includes literature quenching data on the linear

sulfur detection via HSO emission [10] and phosphorus HPO quenching [10]. The sulfur response is defined as the ratio of the intensity of sulfur emission in the presence of quencher to that without quencher multiplied by 100. As can be seen, within the accuracy of our measurements and ability to regulate very small flows of gas-quencher (±20%) there is a universal dependence of the sulfur signal on the quencher concentration for CH_4, CO and CO_2 regardless of the chemical identity of the quencher. Moreover, the data on methane-induced quenching obtained in continuous GC–FPD by Aue and Sun [10] fit our quenching curve well. The latter testifies to the same nature of quenching for both types of detectors. Further, although the data on HSO and phosphorus quenching seem to indicate a lower degree of quenching, when these points are raised to the second power to simulate the sulfur quadratic response, they fall above but close to our points within the uncertainty of our accuracy.

It should be noted that the main kinetic regularities were also the same for all quenchers, i.e., the shift of the maximum of the kinetic curve to shorter times and more effective

quenching at the long time edge (Fig. 2) are characteristic for all quenching gases. The universal dependence of quenching efficiency and the similar kinetic phenomenology serve as strong evidence to support the idea that the final products of hydrocarbon combustion provide the main contribution to sulfur emission quenching. This conclusion is confirmed by the comparison of characteristic times for CH_4 combustion (Fig. 3) and sulfur formation (Fig. 2). Fig 3 shows that all intermediate processes of hydrocarbon combustion end after ca. 0.3 ms whereas the sulfur emission and its quenching begin at much longer times ($\geqslant 5$ ms) when only CO and CO_2 are present at the flame in noticeable amounts.

Fig. 7 illustrates the above-mentioned kinetic asymmetry of sulfur quenching. The CO_2 concentration necessary for sulfur emission intensity is halved; $[Q]_{1/2}$ is 1200 ppm at $t = 25$ ms and 3400 ppm at $t = 12$ ms. In Fig. 7 the data are presented on semi-logarithmic coordinates [log-(sulfur signal) versus quencher concentration], showing an exponential decrease of the sulfur signal with rise in quencher concentration.

The results of octane-induced quenching studies by GC–PFPD are presented in Fig. 8. These plots also show that the S_2 emission

Fig. 8. Dependence of the relative sulfur emission intensity on the octane concentration. (1) Sulfur emission signal integrated over the whole kinetic curve of the sulfur emission (full gate) in a hydrogen-rich H_2–air pulsed flame; (2) sulfur signal measured at the short time edge of the kinetic curve (narrow gate) in a hydrogen-rich H_2–air pulsed flame; (3) sulfur signal measured with full time integral in a hydrogen medium-concentration H_2–air pulsed flame.

quenching by octane conform to the same regularities as quenching by CO, CO_2 and CH_4 studied spectroscopically. However, the quenching efficiency of octane is much higher, $[Q]_{1/2} = 110$ ppm for full gate and $[Q]_{1/2} = 240$ ppm for narrow gate observation. The full gate denotes that the sulfur signal was measured as the integral over the entire kinetic curve of the S_2 response and the narrow gate is the signal integrated at the short time edge. It is seen that octane-induced quenching is reduced upon transition to the field of short times. The higher quenching efficiency of octane is easily understandable in terms of the approach we presented. Indeed, the combustion of octane, whose molecule contains eight carbon atoms, results in the formation of eight molecules of CO or CO_2, whereas the combustion of the other quenchers gives only one molecule of CO or CO_2 per quencher molecule. Accordingly, the quenching efficiency of octane has to be higher by a factor of eight than that for CH_4, CO and CO_2. The observed disagreement by a factor of two
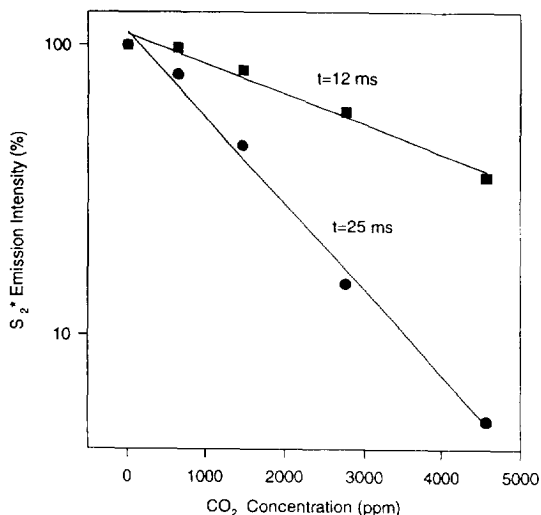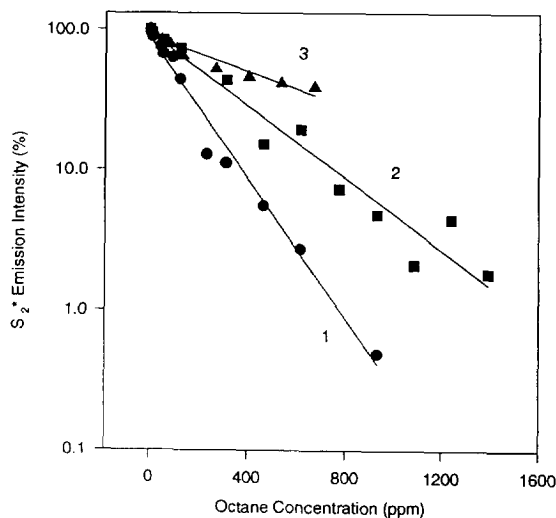

Fig. 7. Dependence of the relative S_2^* emission intensity on the carbon dioxide concentration measured at different times of the kinetic curve of sulfur emission.

($[Q]_{1/2} \approx 2000$ ppm for CO_2 and 1000 ppm for octane) is small considering the difference in the methods of registration of quenching and the use of two different experimental set-ups.

A comparison of curves 1 and 3 in Fig. 8 shows that the change in the stoichiometry of the flame gases (equivalence ratio) influences the quenching efficiency, i.e., under conditions of a leaner mixture the quenching becomes weaker. This indicates that carbon monoxide plays the dominant role in quenching, because the reduction of hydrogen in the flame leads to a shift of the CO_2/CO equilibrium to the predominant formation of carbon dioxide (Fig. 4). It should be noted that the transition to lean mixtures results not only in a decrease in quenching but also in a shift of the sulfur emission time response to short times and also in a reduced emission intensity which sharply decreases near the stoichiometric mixture.

6. Mechanism of quenching

The major conclusions emerging from the above results and discussion are that (1) the hydrocarbon-induced sulfur quenching takes place through the chemical interactions of the quencher with sulfur-related chemical species and (2) carbon monoxide, which is the principle product of hydrocarbon combustion in the rich flame, is the direct reason for quenching.

There are two main possibilities for the influence of carbon monoxide on sulfur-related chemistry in flames, depending on the mechanism of sulfur emission. If S_2^* excited dimers are formed through the following reaction [9]:

$$H + H + S_2 = H_2 + S_2^* \qquad (1)$$

CO can react with hydrogen atoms according to the scheme described in Section 4, and which would reduce the sulfur emission. In the case of sulfur atoms, recombination is a dominant mechanism of the formation of S_2^* [9]:

$$S + S + M \rightarrow S_2^* + M \qquad (2)$$

Both the reaction of CO with H atoms and the reaction between CO and S,

$$CO + S + M \rightarrow COS + M \qquad (3)$$

can cause the quenching effect. Indeed, the sulfur atom production includes many steps in which hydrogen atoms are involved. The most important steps are

$$H + H_2S \rightarrow SH + H_2$$
$$H + SH \rightarrow S + H_2$$
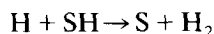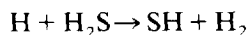
Hence the decrease in H atom concentration on addition of hydrocarbons to the flame (as seen in Fig. 5) will result in a decrease in sulfur atom production.

The proposed mechanism of sulfur emission [20] showed that reaction 2 describes the observed PFPD time delay of sulfur emission and its temporal profile much better. Therefore, to model quenching we carried out numerical calculations based on three subsystems. The first subsystem describes the basic hydrogen–oxygen flame reactions, the second is due to hydrocarbon combustion and the third is concerned with sulfur-related chemistry with the mechanism of sulfur-excited dimer formation according to reaction 2. To simulate the interaction between the sulfur and hydrocarbon subsystems, the following reactions were added to the flame:

$$S + CO = COS + M \qquad (4)$$
$$H + COS = CO + SH \qquad (5)$$

The rate constant for reaction 5 was used according to Lee et al. [26] [$k_5 = 9.06 \cdot 10^{-12} \exp(-3.85/RT)$ cm^3 molecule^{-1} s^{-1}]. Unfortunately, we could not find the rate constants for reaction 3, so we used the rate constant for the analogous reaction between oxygen and CO [27] [$1.7 \cdot 10^{-32} \exp(-4100/RT)$].

The calculated kinetic curves of sulfur emission with the addition of methane are shown in Fig. 9. There is excellent qualitative agreement between the calculated and measured experimental data (Fig. 2). Our calculations show that without reaction 3, quenching hardly occurs. This means that the CO–hydrogen interaction contributes minimally to the quenching process. This is not surprising because Fig. 5 shows that the number of hydrogen atoms begins to de-
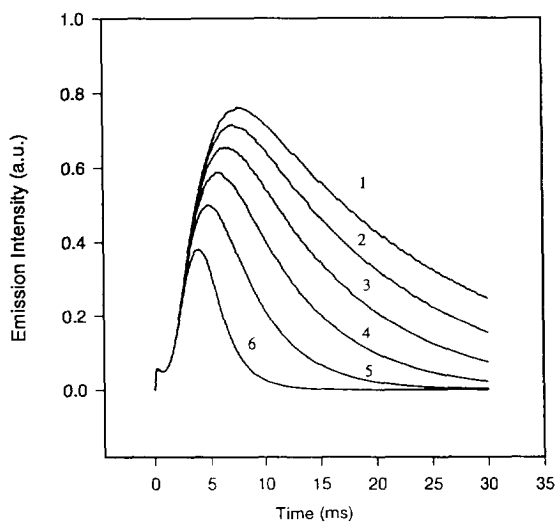
Fig. 9. Calculated kinetic curves of sulfur emission in a hydrogen–air rich pulsed flame at various concentrations of CH$_4$: (1) 0; (2) 200; (3) 500; (4) 1000; (5) 2000; (6) 5000 ppm.

crease after 5 ms, when the accumulation of sulfur is already finished (Fig. 9). Fig. 10 presents the calculated and experimental dependences of the sulfur response on the quencher concentration at long times of the kinetic curves.
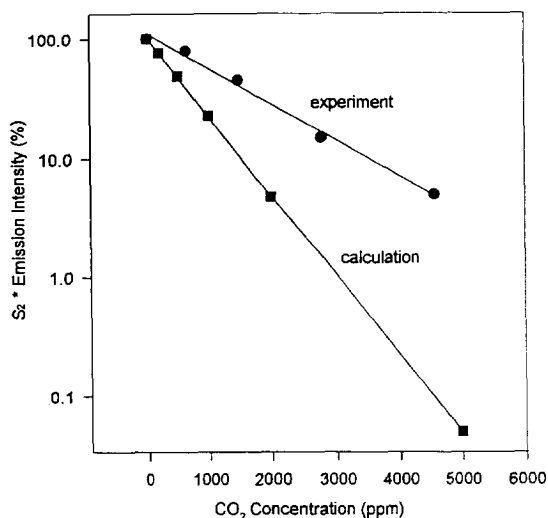

Fig. 10. Dependence of the relative sulfur emission intensity on the carbon dioxide concentration measured at long times of the kinetic curves of sulfur emission. Experimental data are taken from Fig. 2 and calculation results from Fig. 9.

The slope of the calculated line is twice that of the experimental line and full coincidence can be obtained with a halved rate constant for reaction 3. Taking into account the large uncertainty in our knowledge of this rate constant, the obtained agreement of experimental and calculated results seems adequate. In its turn, such agreement serves as indirect evidence for the rationality of the previously developed mechanism of sulfur emission [20].

While our study indicates reaction 4 as the most important sulfur-scavenging reaction, the catalytic destruction of atomic hydrogen by CO will result in a universal response change (usually quenching) of all elements in all the flame and combustion-based chemical detectors. This mechanism is expected to be important at hydrocarbon concentrations above 1000 ppm.

7. Quenching and its reduction using the pulsed FPD with gas chromatography

The emerging general conclusion from this study and based on Fig. 6 is that response quenching is a general phenomenon that exists in all the flame photometers as it depends on basic combustion and flame chemical reactions. This conjectured conclusion can be further generalized into claiming that quenching is a universal phenomenon in the detection of any element in all types of detectors that employ flame and combustion. Note that 1% CH$_4$ in a 50% air flame can lower the available relative amount of oxygen by 40% through its combustion, whereas octane at this level can extinguish the flame itself.

While quenching is well established in sulfur detection with FPD, it also exists in several other elements in FPD [10]. In addition, it also seems to exist in the flame chemiluminescence detector [28], where a massive decrease in response is observed (Ref. [28], Fig. 4) at the time of solvent elution. Based on this paper, it is clear that the scavenging reaction CO + S = COS is a universal sulfur-quenching mechanism which affects its detection through S$_2$ emission or HSO emission [10,13] or SO plus ozone chemi-

lumenescence [28]. CO can also affect other species such as ozone decomposition or induce hydrogen recombination. Thus, in attempting to assess a quantitative factor that will specify quenching, one should establish an acceptable parameter that will quantify the effect of quenching.

We have shown above that the degree of response quenching depends only on the final carbon concentration in the flame and on its stoichiometry. Thus quenching exists in all FPD instruments and its magnitude is similar if it is normalized to the total gas flow-rate. Accordingly, dual FPD is the least subjected to quenching among the various FPD designs, not because of its dual flame design [16,17] but rather owing to its highest total flow, which dilutes the CO and sulfur species (also owing to its wide flame nozzle, which dilutes the flame species). It was shown above that the prior combustion of hydrocarbons into CO_2 in the first flame has virtually no effect on quenching as the quenching induced by CO_2 is identical with that induced by CH_4. On the other hand, different FPD designs result in different detection sensitivities. Lower detection limits permit the injection of smaller sample amounts into the GC column and thus results in decreased quenching. We define here a new term to quantify quenching, namely the "quenching free dynamic range (QFDR)", which is the ratio of maximum allowed amount of co-eluting hydrocarbon that results in response quenching of less than 10% divided by the minimum detected amount of sulfur in that particular detector.

The PFPD instrument has a QFDR of 10^5 as the onset of 10% quenching under normal conditions is at 20 ng C/s, while its sulfur MDA is 0.2 pg S/s [13]. In comparison, the dual FPD instrument [16,17] has a higher overall gas flow-rate by a factor of 20 and MDA [13] by a factor of 100. Thus the PFPD instrument is assumed to have a higher QFDR by a factor of 5 than the dual FPD instrument. Note, however, that the dual FPD instrument can accept 0.4 μg C/s without quenching, and this level is beyond the level that is normally encountered in capillary GC and so it can be considered as a quenching-

free FPD system for practical applications, while care should be exercised when using PFPD although it has a higher QFDR.

PFPD offers two additional advantages in comparison with FPD in attempt to reduce the effects of response quenching on quantitative measurements: (a) the time gating of sulfur emission eliminates the hydrocarbon contribution to the flame emission through increased selectivity; and (b) the existence of quenching can be observed, identified and corrected for through its unique effect on the sulfur emission time response.

This identification can be achieved by the observation of the pulsed flame emission on an oscilloscope. Alternatively, we have used a double-gated amplifier for automatic quenching identification and correction. One gate was used to collect and time integrate all the sulfur-emitted light and the other gate was time delayed by 10 ms to amplify the effect of quenching as shown in Fig. 2. The gas chromatogram of sulfur compounds was then monitored with the two gates simultaneously using a double-gated amplifier. From the two chromatograms obtained, the various sulfur compound responses of the delayed gate chromatogram were divided by that of the normal gate chromatogram to obtain the gate response ratio (GRR). The gate response ratio was normalized to 1 for a sulfur compound peak that has no quenching. Any decrease in the GRR now automatically indicated response quenching, and the GRR was monotonically decreased with increased degree of quenching. Fig. 11 shows a calibration graph for the GRR plotted against the degree of quenching in the normal gate. The plot depends on the gate delays and width and also on the H_2–air stoichiometry, but once these parameters are fixed, Fig. 11 can be very useful for introducing correction factors to correct for quenching. The data in Fig. 11 were obtained by measurement of the effect of hydrocarbon elution from the GC column on a background of sulfur in the PFPD instrument. Note that the magnitude of quenching is independent of the amount of sulfur (pseudo-first-order kinetics). The data in Fig. 11
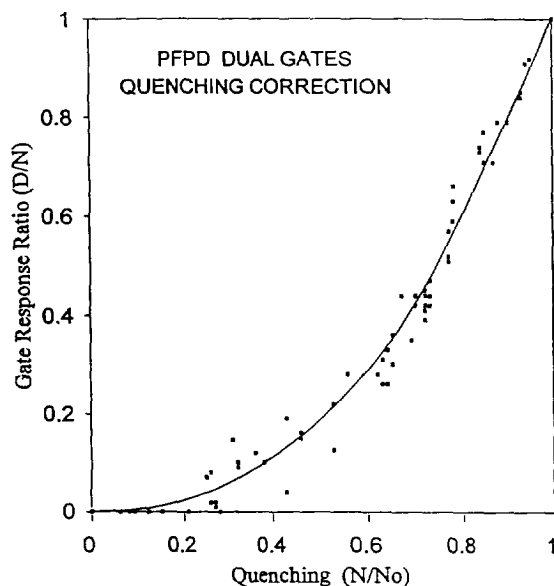
Fig. 11. Calibration graph of the gate response ratio (GRR) versus the degree of quenching at fixed gate delay and H₂-air stoichiometry. The gate response ratio is normalized to unity for a compound that has no quenching.
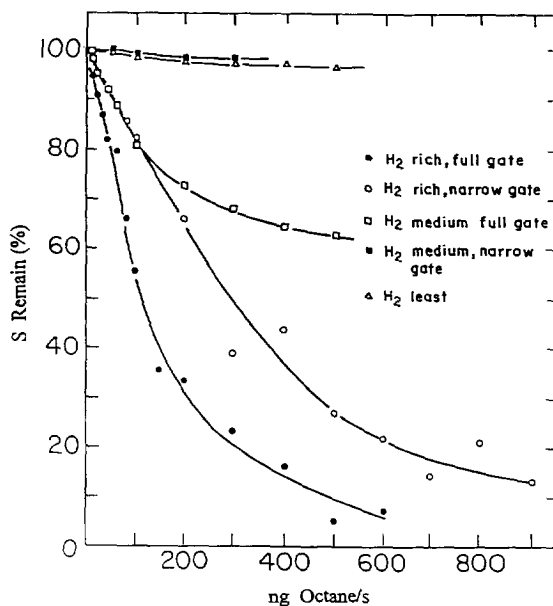

Fig. 12. Dependence of the sulfur response quenching on the amount of co-eluting octane. A PFPD instrument mounted on a gas chromatograph was continuously fed with tetrahydrothiophene and its response under octane elution was measured. The remaining sulfur is defined here as the square root of the sulfur signal to indicate the effective reduction in the extrapolated amount of sulfur. The relative hydrogen concentrations are as follows: H_2 rich is 2.7 equivalence ratio, H_2 medium is 2.1 equivalence ratio and H_2 least is 1.7 equivalence ratio.

can also be obtained by other standard GC methods for the creation of overlapping hydrocarbon and sulfur compound peaks [29].

The use of PFPD also offers other ways to overcome quenching at the expense of a lower detection sensitivity. Fig. 12 shows the sulfur response quenching versus the amount of co-eluting octane under different conditions: (a) normal operation conditions; (b) normal hydrogen-rich conditions as in (a), but using a shorter gate; the sulfur response was decreased 3.3-fold but the quenching level was also decreased; note that decrease in response by a factor of 3.3 means that the MDA increase by a factor of less than 1.8 owing to the sulfur quadratic response, and a lower noise level with a shorter gate; (c) the amount of air was increased and even though a full gate was used, the response was decreased by a factor of 14 and the MDA was increased by a factor of 3.7; (d) stoichiometry as in (c), but with a short gate; under these conditions,

quenching was eliminated in the range of practical applicability of using capillary GC; the trade-off is a factor of 30 in the sulfur response and an increase by a factor of ca. 5.5 in the MDA to the level of about 1–2 pg S/s; (e) a further increase in the air level eliminates quenching even with full gate but the MDA is reduced by a factor 9; we note that while the same trade-off of sensitivity-reduced quenching can be achieved with continuous FPD, the penalty of a further reduction in selectivity by one or two orders of magnitude seems unacceptable with FPD, in contrast to PFPD.

In conclusion, either the use of the gate response ratio for quenching identification and correction or the use of increased air and a

shorter gate can decrease, eliminate or correct the sulfur response quenching and increase its QFDR by another order of magnitude to 10^6.

References

[1] D. Weber, K.B. Olsen and J.D. Ludwick, Talanta, 27 (1980) 665.

[2] W.E. Rupprecht and T.R. Phillips, Anal. Chim. Acta, 47 (1969) 439.

[3] S. Fredriksson and A. Cedergren, Anal. Chem., 53 (1981) 614.

[4] S. Fredriksson and A. Cedergren, Anal. Chim. Acta, 100 (1978) 429.

[5] D.A. Clay, C.H. Rogers and R.H. Jungers, Anal. Chem., 49 (1977) 126.

[6] D.A. Ferguson and L.A. Luke, Chromatographia, 12 (1979) 197.

[7] E. Mangani, F. Bruner and N. Penna, Anal. Chem., 55 (1983) 2193.

[8] T. Sugiyama, Y. Suzuki and T. Takeuchi, J. Chromatogr., 80 (1973) 61.

[9] S.O. Farwell and C.J. Barinaga, J. Chromatogr. Sci., 24 (1986) 483.

[10] W.A. Aue and X.-Y. Sun, J. Chromatogr., 641 (1993) 291.

[11] M. Maruyama and M. Kakemoto, J. Chromatogr. Sci., 16 (1978) 1.

[12] S.V. Olesik, L.A. Pekay and E.A. Paliwoda, Anal. Chem., 61 (1989) 58.

[13] S. Cheskis, E. Atar and A. Amirav, Anal. Chem., 65 (1993) 539.

[14] A. Amirav, Isr. Pat., 95617 (1990); US Pat., 5153673 (1992).

[15] E. Atar, S. Cheskis and A. Amirav, Anal. Chem., 63 (1991) 2061.

[16] P.L. Patterson, R.L. Howe and A. Abu-Shumays, Anal. Chem., 50 (1978) 339.

[17] P.L. Patterson, Anal. Chem., 50 (1978) 345.

[18] R. Buffington and M.K. Wilson, Detectors for Gas Chromatography—A Practical Primer, Hewlett-Packard, Palo Alto, CA, 1987.

[19] V.L. McGuffin and M. Novotny, Anal. Chem., 53 (1981) 946.

[20] S. Cheskis, Combust. Flame, in press.

[21] K.A. Meyer and D.R. Crosley, J. Chem. Phys., 59 (1973) 1933.

[22] T.H. McGee and R.E. Weston, Chem. Phys. Lett., 47 (1977) 352.

[23] T.H. McGee and R.E. Weston, J. Chem. Phys., 68 (1978) 1736.

[24] R.J. Kee, F.M. Rupley and J.A. Miller, Sandia National Laboratory Report, SAND89-8009, 1991.

[25] C.K. Westbrook, Combust. Sci. Technol., 20 (1979) 5.

[26] J.H. Lee, L.J. Stief and R.B. Timmons, J. Chem. Phys., 67 (1977) 1705.

[27] B. Lewis and G. Elbe, Combustion, Flames and Explosions of Gases, Academic Press, New York, 1987, p. 102.

[28] R.L. Stearer, Anal. Chem., 64 (1992) 2192.

[29] J. Efer, T. Maurer and W. Engewald, Chromatographia, 29 (1990) 115.