

Combined PFPD–FID assessment of sulfur in liquid fuels

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ARTICLE INFO

Article history:

Received 15 February 2011

Received in revised form 19 July 2011

Accepted 19 July 2011

Available online 27 August 2011

Keywords:

PFPD

Sulfur

Gasoline

Diesel

ABSTRACT

A pulsed flame photometric detector (PFPD) was calibrated using standard sulfur compounds present in gasoline and diesel fuels, in combination with a flame ionization detector (FID). Gasoline range standards were added to a hydrocarbon mixture simulating gasoline, with individual sulfur concentrations from 3 to 80 ppm. Diesel range standards were added to a low sulfur commercial diesel fuel, with sulfur concentrations from 10 to 100 ppm. In gasoline, both the chromatographic areas calculated with the linearized signal (data points elevated to a given power), and reported by the instrument were regressioned with the sulfur mass concentrations. In both cases the areas were normalized with the FID areas to reduce deviations. Results were better when using the linearized signal. Only the normalized areas calculated with the linearized signal can be used in the case of the diesel, due to significant peak coelution. Individual calibration coefficients were calculated for each standard, but overall coefficients can be used safely in each of the boiling ranges. The compliance of regulations about sulfur was verified in commercial fuels and the different sulfur compounds were inspected. The simultaneous combined FID–PFPD use allows adding the sulfur to the conventional analysis of liquid fuels (e.g. composition, simulated distillation).

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1. Introduction

The occurrence of sulfur in transportation liquid fuels is the one of the issues of highest impact in environmental care due to, among other reasons, the combustion of sulfur containing hydrocarbons that lead to sulfur oxides, considered precursors of acid rain. In the case of diesel fuels, also is the emission of particulate material an important problem, which is in direct relationship to the amount of sulfur in the fuel [1]. Particularly for high technology diesel motors, if sulfur exceeds certain concentration, it may originate filter plugging as well as corrosion in combustion chambers due to recirculation of discharge gasses. Sulfur is also a poison for catalytic converters.

Both gasoline and diesel fuels have amounts of sulfur compounds that vary widely, but there is a neat world trend to decrease them significantly. At present, in the average, stringent environmental regulations point to not more than 50 ppm of sulfur in gasoline and diesel. The process of catalytic cracking of hydrocarbons (FCC) is the main contributor to the gasoline pool, where its naphtha cut is the most important source of sulfur, and also supplies a highly aromatic, low quality cut with high sulfur content to the diesel pool. Ultra low sulfur liquid fuels are also an attractive option for automotive and portable fuel cells [2], but sulfur concentration should be even lower in these applications.

The analysis of sulfur in fuels is usually accomplished by energy dispersive X-ray fluorescence (ASTM D-2622), or UV fluorescence (ASTM D-5453), but these techniques do not identify particular sulfur compounds. However, for various reasons, it may be necessary to recognize individual compounds. Selective sulfur detection devices coupled with gas chromatographs exist that can accomplish such a task [3]; among them, the atomic emission detector (AED), the sulfur chemiluminescence detector (SCD) and the flame photometric detector (FPD) have all particular advantages and disadvantages, depending on the applications.

The pulsed flame photometric detector (PFPD [4]) introduced a new concept for the operation of FPDs, based on a pulsed flame instead of a continuous flame to generate the chemiluminescence emission. The new operation concept improved the performance of FPDs by adding the light emission time dimension and the ability to separate the emissions of the carbon species from those of the sulfur and phosphorus species. The PFPD has a low minimum detection level for sulfur of about 1 pg/s and equimolar response characteristics, and moderate cost. However, its response to the concentration of sulfur is not linear and a quenching effect (reduction of the sulfur signal) may exist in the coelution of sulfur compounds with hydrocarbons. Together with the inherent complexity of commercial fuel mixtures, these facts can make sulfur analysis a complicated matter. An extensive list of applications of the PFPD can be seen in [5] and a combined PFPD–PFID, which is a pulsed flame photometric ionization detector (PFPID) allowing the simultaneous selective detection of molecules containing carbon, sulfur, phosphorous or nitrogen atoms, has been described by Tzanani and Amirav [6]. Moreover, the PFPD has a carbon channel that allows for the

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simultaneous detection of carbon and sulfur, although the carbon sensitivity of the PFPD and the PFPID is smaller than that of the FID [6,7].

It is the objective of this work to report a new approach for the assessment of sulfur in mixtures of hydrocarbons (e.g. transportation fuels such as gasoline and diesel) by combined use of PFPD and FID detectors, and to illustrate the application of the procedure to some cases.

2. Experimental

A 5380 pulsed flame photometric detector (OI Analytical) was installed in an Agilent 6890+ gas chromatograph that also had a FID detector. The PFPD was used in the “sulfur” mode. A 30 m length, 0.25 mm i.d. and 0.25 μm phase thickness, HP-1 methyl silicone column was used. The end of the column was connected to a “Y” quartz splitter with equal length empty column branches leading to each detector with the same i.d. as the chromatographic column. Following this approach, similar sample sizes were expected. The injector was used in the split (120:1) mode. The possible quenching effect from the coelution of hydrocarbons was minimized by using a high air flow rate in the detector and an optimized chromatographic analysis method [8].

The operation of the PFPD detector was optimized using parameters (relationship between hydrogen (18 ml/min) and air-1 and air-2 flows (16 and 7.5 ml/min, respectively)), position of the fine adjustment valve (open 3.5 turns), and temperature (300 °C) that were not exactly the same as those suggested by the manufacturer. The electrometer range was 100.

The volume of sample injected was 0.5 μl . In the case of gasoline boiling range analysis, the oven temperature program was started at 0 °C during 2 min, then a heating rate of 4 °C/min was applied up to 50 °C, then the heating rate was changed to 8 °C/min up to 135 °C, and finally changed to 30 °C/min up to a final temperature of 300 °C. In the case of diesel fuel boiling range analysis, the starting temperature was 40 °C during 0.5 min, and then a heating rate of 10 °C/min was applied up to a final temperature of 310 °C, that was kept during 3 min. The constant gas carrier flow (1.1 ml/min) was chosen so as to achieve maximum peak resolution and detector sensitivity. Under the conditions used, the detection limit for single compounds was determined to be 3 ppm of sulfur.

The identification of sulfur compounds in the commercial fuels was performed by comparing their retention times with those of Sigma-Aldrich standards and with elution orders published in the literature [9–11]. To calibrate the PFPD detector, solutions of sulfur compounds in a mixture of hydrocarbons in the range of gasoline boiling points (approximately 50% of xylenes, 30% of a mixture of hexane isomers and 20% of heptane simulating a commercial gasoline) were prepared by adding known amounts, from 3 to 80 ppm of sulfur, of thiophene (T, 99 wt.%), tetrahydrothiophene (THT, 99 wt.%), 2-methylthiophene (2MT, 97 wt.%), 2-ethylthiophene (2ET, 97 wt.%) and 2-propylthiophene (2PT, 97 wt.%). The validation of the quantification method was done against the analysis of a high sulfur standard gasoline (total 358 sulfur ppm, Accustandard ASTM-FUEL-QCS-02). Other solutions were prepared with the addition of known amounts, from 10 to 100 ppm of sulfur, of benzothiophene (BT, 99 wt.%), 3-methylbenzothiophene (MBT, 96 wt.%), dibenzothiophene (DBT, 98 wt.%) and 4,6 dimethyldibenzothiophene (DMDBT, 97 wt.%) to a sulfur commercial diesel fuel (360 ppm). In the analysis, the sulfur compounds are shown and considered either individually or grouped according to their family type and boiling point range, following a similar procedure to that of Deapuw and Froment [12]. The concentrations of the solutions prepared in both the gasoline and diesel fuel boiling ranges are shown in Table 1.

Samples of commercial gasoline and diesel fuels were purchased from gasoline stations in Santa Fe city, Argentina. The FID information was used for the ordinary analysis of the fuels (composition (ASTM D5134), fuel quality (cetane index or RON), simulated distillation, etc.). The research octane numbers RON were assessed with a

Table 1
Concentration (ppm S) of the solutions of sulfur compounds.

Boiling range	Compound	Concentration (ppm S)			
Gasoline	Thiophene (T)	11.9	26.0	39.7	76.9
	Tetrahydrothiophene (THT)	5.6	11.7	20.2	38.0
	2-Methylthiophene (2MT)	12.4	35.2	61.6	83.0
	2-Ethylthiophene (2ET)	4.0	25.0	47.1	63.1
	2-Propylthiophene (2PT)			11.4	31.2
Diesel	Benzothiophene (BT)	9.4	12.0	15.1	27.2
	3-Methylbenzothiophene (MBT)			13.0	24.3
	Dibenzothiophene (DBT)				35.4
	4,6-Dimethyldibenzothiophene (DMDBT)				64.1

modified Anderson's method [13]. The distillation properties were determined by simulated distillation ASTM D3710 (gasoline) and D2887 (diesel fuels). The cetane index of the diesel fuels was determined with ASTM D976, and the density by means of the assessment of weight and volume at 15 °C.

A study of reproducibility of the analysis was performed with 12 consecutive injections of solutions of 26 ppm of sulfur from 2-methylthiophene and tetrahydrothiophene added to the same mixture of hydrocarbons in the gasoline boiling range used to calibrate the PFPD detector.

3. Results and discussion

The PFPD operates using a propagating a flame that terminates within a quartz combustor, the combustion reaction producing a light emission with specific luminescent spectra and lifetimes. Lifetimes are different for different elements, and this can be used, e.g., to separate emissions from sulfur and hydrocarbons. As compared to the continuous flame FPD, the PFPD has equimolar response close to quadratic, no dependence of response on the type of sulfur compound, less quenching, and higher sensitivity and selectivity against hydrocarbons [5–8]. Its detection limit is similar to that of the sulfur chemiluminescence detector (SCD), but it is far simpler to operate and maintain, has inherently better long term stability, can be integrated in the GC without additional bench space and costs less to purchase. So far, the detector has been applied to many different analysis, including petrochemicals, sulfur and phosphorus pesticides, chemical warfare agents and drink aroma analysis, among others [14].

The chromatograms of a typical commercial gasoline obtained with both the FID and PFPD detectors are shown in Fig. 1. The main sulfur compounds are indicated and grouped according to their family type, as well as some of the most important hydrocarbons. It can be seen that the analytical conditions used lead to an elution of sulfur compounds and hydrocarbons in the mixtures which resulted proper to assess the quality of the fuels (refer to Section 3.3).

Since the primary response of the sulfur selective PFPD is quadratic in theory [15], it could be linearized by extracting the square root of all data points from the recordings and then peak areas could be assessed subsequently. This method was also designated as “direct linearization” [15]. However, some facts such as the detector's operational conditions, the type of matrix where the sulfur compounds are present, and their nature [2,16], can influence the response of the detector, making it not to be purely quadratic.

In this way, the mass concentration of sulfur could be related to the n th power of the signal:

$$w_i \propto \sum_k S_{i,k}^n \Delta t_k \quad (1)$$

where w_i is the sulfur mass concentration of the compound i , $S_{i,k}$ is the intensity of the detector output signal recorded in the data acquisition

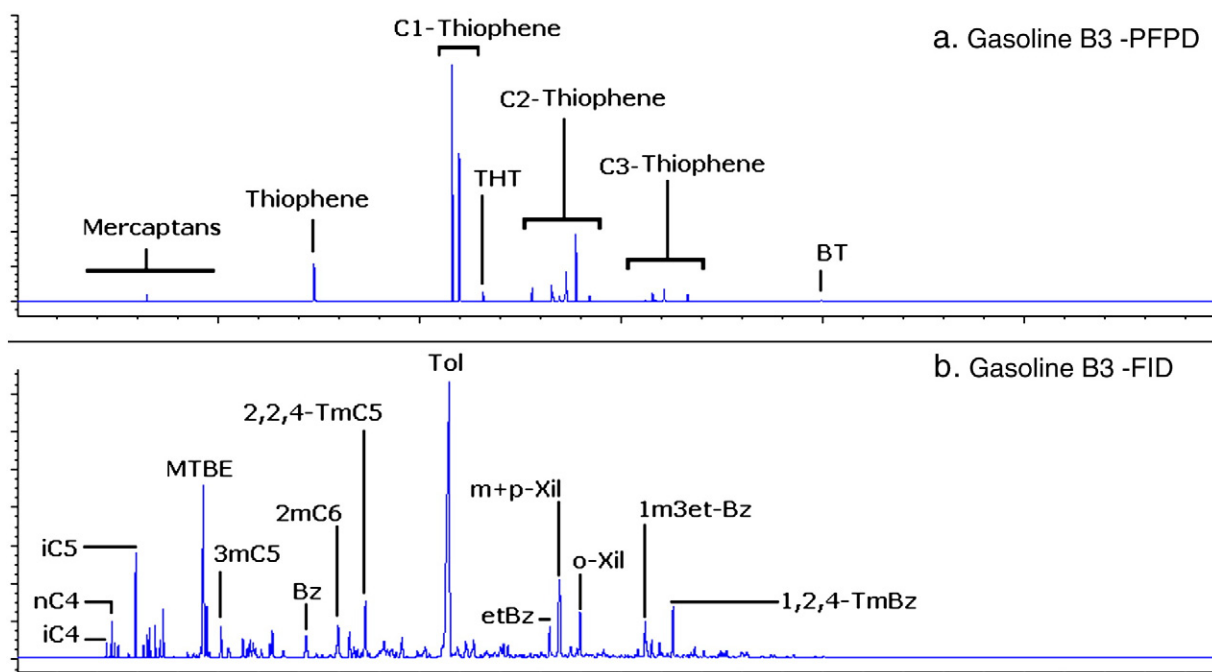


Fig. 1. Chromatograms of a commercial gasoline. a) FID; b) PFPD.

device, which is emitted during the elution of the corresponding peak at the time interval k , and Δt is the length of the sampling time interval in the data acquisition software (1/20 s in this case).

Alternatively, the areas reported by the instrument, A_i , could be considered the response of the detector and correlated to the sulfur amount as shown in Eq. (2) (see, e.g., [2]). However, unfortunately, peak width and shape, or variations of these as a function of sulfur amount or peak height affect the relationships between areas and sulfur amount. For example, it can be verified that the area of a broad peak is smaller than the area of a narrow peak when the amount of sulfur is the same and when the signal is the square of the instantaneous sulfur amount in the detector [15].

The correlation between the mass concentration of sulfur and the reported area would be then

$$w_i \propto \left(\sum_k S_{i,k} \Delta t_k \right)^m \quad (2)$$

or

$$w_i \propto A_i^m \quad (3)$$

Exploratory injections showed an important dependency on variations of the amount of sample injected due to the nonlinear response and, in order to minimize this effect, the areas calculated with the linearized signal (Eq. (1)), or reported by the PFPD (Eq. (3)) were normalized with the total area obtained in the FID detector, since it is linearly proportional to the mass of sample injected. In this way it is possible to set the following relationships, according to either the treatment of the signal (Eq. (4)), or the area reported (Eq. (5)):

$$\frac{\sum_k S_{i,k} \Delta t_k}{A_{total,FID}} = \frac{A_i^*}{A_{total,FID}} = f w_i \quad (4)$$

$$\frac{\left(\sum_k S_{i,k} \Delta t_k \right)^m}{A_{total,FID}} = \frac{A_i^m}{A_{total,FID}} = g w_i \quad (5)$$

where A_i^* is the area calculated with the linearized signal and $A_{total,FID}$ is the total area reported by the FID. Another positive effect of the area

normalization can be observed in the results of the repeatability study, where the variability coefficient decreased from 3.7 to 3.1%. Fig. 2 helps to recognize these two signal treatments.

The power coefficients n and m and the slope coefficients f and g can be estimated in each case by linear data fitting, as shown below.

3.1. PFPD calibration in the gasoline boiling range

Both approaches (Eqs. (4) and (5)) were used in the calibration procedure of the PFPD in the gasoline boiling range, for all the sulfur standards. When a particular software allowing the treatment of the detector signal is not available, the treatment by means of the reported areas is usual. The values of m and g (coefficients in the area treatment approach) corresponding to each sulfur standard are shown in Table 2;

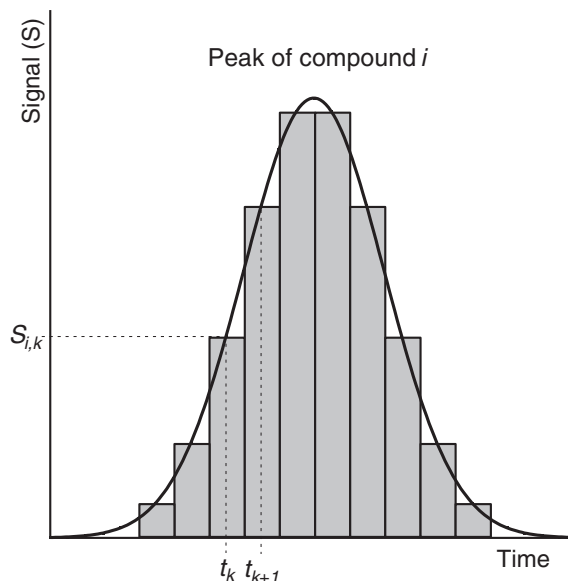


Fig. 2. Schematic representation of a chromatographic peak and information necessary for the proposed data treatments.

Table 2
Individual coefficients in Eqs. (4) and (5) for sulfur compounds in the gasoline boiling range.

Compound	Treatment	Coefficients		
		m	$10^4 g$	R^2
Thiophene	Area	0.4201	1.2228	0.9997
Tetrahydrothiophene	Area	0.4277	1.4421	0.9961
2-Methylthiophene	Area	0.5108	3.3186	0.9967
2-Ethylthiophene	Area	0.3891	0.9610	0.9950
2-Propylthiophene	Area	0.4876	2.8516	0.9997
All standards	Area	0.4604	2.0188	0.9596
All standards	Area	0.5000*	3.3421	0.9567
		n	$10^4 f$	R^2
All standards	Signal	0.3900	2.1669	0.9958
All standards	Signal	0.5000*	7.1066	0.9804

* Power coefficient in the theoretical relationship.

they were obtained from the optimization (maximum linear regression coefficient R^2 , with R from the Pearson's correlation, performed with a commercial spreadsheet) of the relationships between reported areas and sulfur concentrations shown in Eq. (5). The resulting m power coefficients are all dissimilar and diverge somewhat from a quadratic relationship, with the exception of 2-methylthiophene and 2-propylthiophene. These results are shown in Fig. 3, where it can be seen that all the particular linear data fittings are very good, extending up to approximately 80 ppm.

The analytical information from all the standards was also treated as a single data set, that is, considering all the areas vs. sulfur concentration data, according to Eq. (5). The optimization to a linear relationship leads to values of m and g that are also shown in Table 2; again the overall m power (0.4604) differed from 0.5, and the graphical comparison (see Fig. 4) shows that the differences between experimental data points and predictions are negligible in the range from 10 and 40 ppm. At higher sulfur concentrations, the error increases up to 20%. Essentially the same result was observed if the exercise of imposing the theoretical $m = 0.5$ value is performed (see Table 2).

Indeed, what is expected to be related to the sulfur concentration through a theoretical 0.5 power is the detector response (signal intensity). Even though individual f slope and n power coefficients could be obtained from Eq. (4) (it is to be noted that the calibration performed with each of the standards following this approach lead to results that were qualitatively similar to those obtained with the

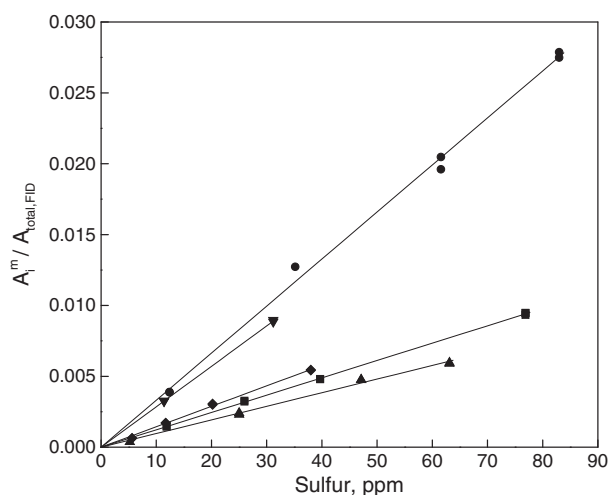


Fig. 3. Relationships between areas and sulfur concentrations for standards in the gasoline boiling range. Individual linear regressions according to Eq. (5). Symbols: ■, Thiophene; ●, Methylthiophene; ▲, Ethylthiophene; ▼, Propylthiophene; ◆, Tetrahydrothiophene.

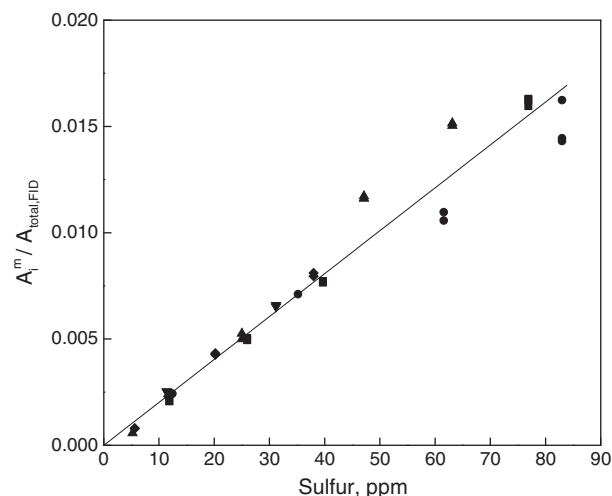


Fig. 4. Relationships between areas and sulfur concentrations for standards in the gasoline boiling range. Overall linear regression (single m and g coefficients) according to Eq. (5). Symbols as Fig. 3.

areas), it is convenient for the sake of simplicity to assess overall coefficients for the range, that is, single n and f coefficients. Therefore, the analytical information from all the standards was judged as a single data set, that is, considering the totality of area and sulfur concentration data. The normalized areas calculated with the linearized signal (Eq. (4)) were then regressed linearly with the sulfur mass concentrations, searching for the best value of the power n that yielded the maximum linear regression coefficient R^2 . This optimization process (n and f coefficients from overall data) lead to results that were better than those obtained with the area approach (Eq. (5), see Table 2), with a linear range extending up to approximately 80 ppm, as confirmed in Fig. 5. In case the n power coefficient is assigned the theoretical value of 0.5, the results are similar in a smaller range (30 to 80 ppm) although of slightly inferior quality (see Table 2 and Fig. 6).

A comparison was established among the errors resulting from the quantification of the different injections using the various approaches (conventional n , $m = 0.5$; area optimization (total) $m = 0.4691$; and signal optimization (total) $n = 0.3900$), which is shown in Fig. 6. Errors were defined as the relative difference between the known sulfur concentrations and those assessed with the PFPD, according to the various methods. It can be seen that the errors were significantly

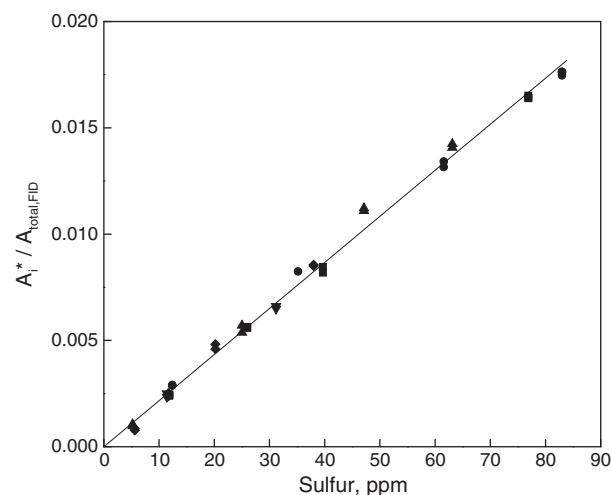


Fig. 5. Relationships between areas and sulfur concentrations for standards in the gasoline boiling range. Overall linear regression (single n and f coefficients) according to Eq. (4). Symbols as Fig. 2.

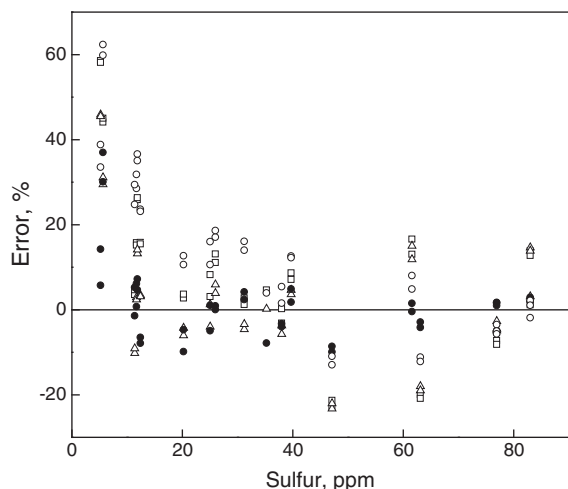


Fig. 6. Errors in the analysis of sulfur according to the various approaches. Standards in the gasoline boiling range. Symbols: \square , $m=0.5$; \circ , $n=0.5$; \triangle , $m=0.4691$; \bullet , $n=0.3900$.

lower when using the signal optimization approach ($n=0.3900$). Moreover, in this case, the distribution of errors showed homocedasticity, thus confirming linearity in this range of concentrations.

From the above discussion, it is clear that sulfur compounds in hydrocarbon mixtures in the gasoline boiling range can be analyzed more safely if the signal optimization approach is followed, with an optimized power coefficient (n close to but different from 0.5) that diverged somewhat from the theoretical quadratic response of the PFPD detector. The repeatability study under these conditions indicated that the variability coefficient was 2.6%.

3.2. PFPD calibration in the diesel fuel range

The chromatograms of a typical commercial diesel fuel obtained with both the FID and PFPD detectors are shown in Fig. 7. The higher

amount of sulfur compounds of heavier molecular weight than those in gasoline makes their identification more complex, but still families can be defined. The main sulfur compounds in the range and some of the most important hydrocarbons are indicated. It can be seen in the PFPD chromatogram that the coelution of sulfur compounds in some regions is significant, thus impeding in most of the cases the resolution of peaks and the assessment of individual areas. If two co-eluting compounds have areas that partially overlap, it is obvious from Eq. (5) that the total amount of sulfur quantified is different if the peaks are divided and then the individual amounts added, or taken as a single peak. This does not occur if Eq. (4) is used. In this boiling range, then, it is not possible to use the area optimization approach (Eq. (5)), and signal data points must be used following the signal optimization approach given by Eq. (4). The PFPD A_i^* areas calculated with the linearized signal were normalized with the total FID area and regressed linearly with the sulfur mass concentrations, searching for the best value of the power n that yielded the maximum linear regression coefficient R^2 .

In this case the analytical information from all the standards was also treated as a single data set, the optimum values being $n=0.4853$ and $f=7.3556 \times 10^{-4}$ ($R^2=0.9957$). This is an example of how deviations can be decreased by normalizing the peak areas with the total FID area, because otherwise a $R^2=0.93$ coefficient would be obtained. The quality of data fitting is shown in Fig. 8, where it can be seen that the linear relationship extends appropriately up to 100 ppm.

Other calibrations of PFPD detectors were reported with, e.g., directly the square root of the signal at very low sulfur concentrations [17] in injections with either constant sample size or constant concentration, but different slope coefficients (similar to our f and g coefficients) were observed for each standard. Ma et al. [2], compared the responses of FPD and PFPD detectors, observing that under their operational conditions, the linear range between reported areas to a power $n=0.5$ and sulfur concentrations was conserved only up to 32 ppm.

In summary, the comparison between these overall results with gasoline and diesel fuels and previous reports (e.g. [18,19]) confirms that the response of the PFPD depends on the operational conditions of the detector. However, it is possible to optimize it, e.g. extending the range of linearity, by a proper data treatment.

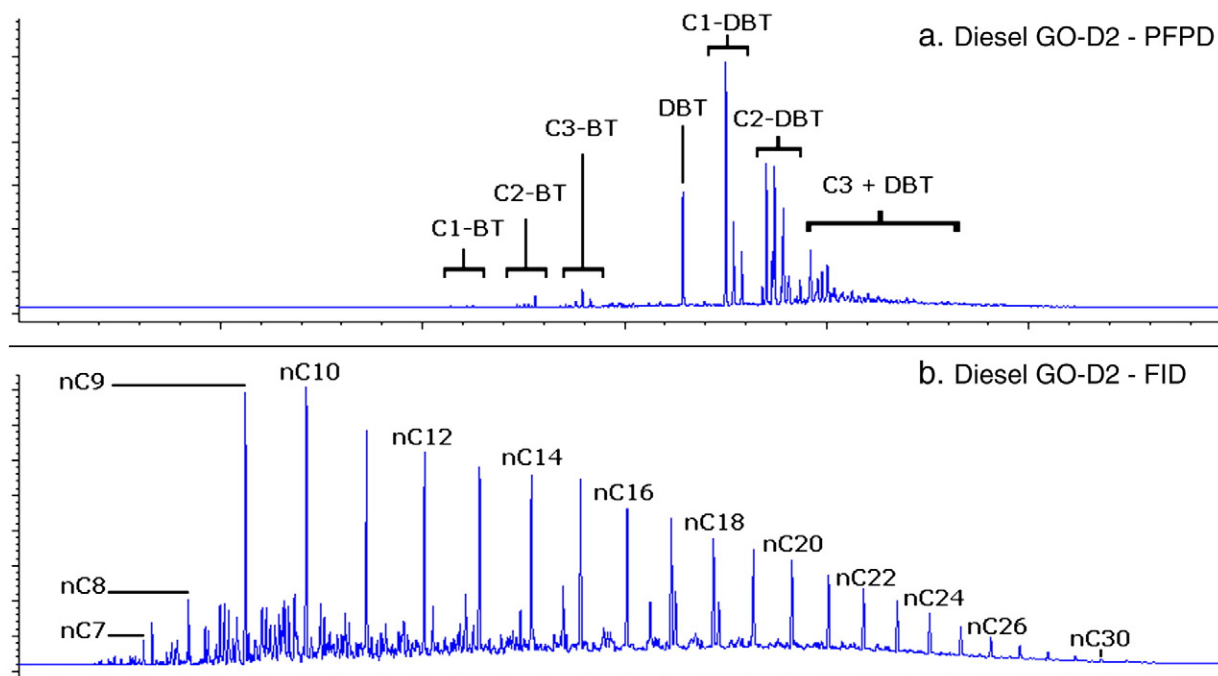


Fig. 7. Chromatograms of a commercial diesel fuel. a) FID; b) PFPD.

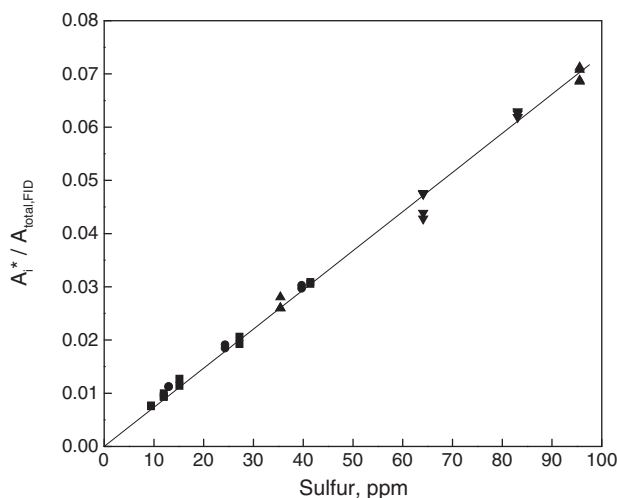


Fig. 8. Relationships between areas and sulfur concentrations for standards in the diesel fuel boiling range. Overall linear regression (single n and f coefficients) according to Eq. (4). Symbols: ■, Benzothiophene; ●, Methylbenzothiophene; ▲, Dibenzothiophene; ▼, Dimethylidibenzothiophene.

3.3. Analysis of commercial gasolines

The signal optimization method was applied to the quantification of sulfur compounds in commercial gasolines and the ASTM high sulfur standard gasoline. The corresponding results are shown in Table 3, together with additional characterization data gathered simultaneously with the FID detector (aromatic hydrocarbons, oxygenated compounds, distillation, overall composition, etc.), and product specifications from national regulations. All the samples satisfied the regulations concerning distillation, and MTBE, oxygen and sulfur contents. Only one sample did not satisfy the limit of total aromatics. According to the RON values, the samples belonged to either Grade 2 (Super) or Grade 3 (Ultra) types. In relation to sulfur, all the samples satisfied the limit of 300 ppm (Grade 2).

The distribution of sulfur compounds was different in the various gasoline samples, as shown in Table 4. However, alkylthiophenes were prevailing, particularly C1- and C2-species, that in the average represented approximately 62% of the sulfur compounds; if C3- and C4-species were included, the proportion increased to approximately 73.5%. Thiophene was always present in significant amounts (average 12%). Mercaptans, benzothiophene and tetrahydrothiophene were present in smaller amounts. Particularly, mercaptans showed more significant changes in their proportion.

Table 3

Gasoline specifications and values observed in commercial samples.

Type or sample	Distillation (T, °C)			Final point (°C)	Aromatics (%v)	MTBE (%v)	Oxygen (%p)	RON	Sulfur (ppm)
	10%v	50%v	90%v						
Grade 1 (Common)	70 Max	120 Max	190 Max	225 Max	40.0 Max	15 Max	2.7 Max	83 Min	500 Max
Grade 2 (Super)	70 Max	120 Max	190 Max	225 Max	40.0 Max	15 Max	2.7 Max	93 Min	300 Max
Grade 3 (Ultra)	70 Max	120 Max	190 Max	225 Max	40.0 Max	15 Max	2.7 Max	97 Min	150 Max
A2-1	31	98	171	<225	30.3	3.28	0.90	95.6	211
A2-2	31	98	171	<225	31.7	2.20	0.70	95.1	233
B2	30	97	151	<225	27.4	4.72	0.90	95.9	71
C2	30	101	165	<225	33.1	2.29	0.42	95.0	67
D2	31	101	161	<225	37.9	2.90	0.53	95.6	166
A3	31	97	165	<225	30.8	7.09	1.30	98.2	240
B3	58	110	170	<225	36.1	11.05	2.00	99.1	170
C3	30	98	165	<225	32.6	9.18	1.67	96.4	43
D3	34	110	161	<225	43.1	7.65	1.40	101.4	90
BB2	30	108	170	<225	37.4	3.60	0.65	95.8	71
ASTM standard	31	92	181	<225	33.7	0.48	0.09	88.7	352

Table 4

Proportions of sulfur compounds in commercial gasolines.

Sample	Sulfur compound or family (%)								
	Mercaptans	T	Dialkyl sulfides	C1-T	THT	C2-T	C3-T	C4-T	BT
A2-1	0.0	12.3	0.0	23.7	1.5	32.4	15.2	8.4	6.6
A2-2	3.8	15.0	0.0	26.2	2.2	30.0	13.2	4.4	5.3
B2	11.6	15.1	0.0	48.2	0.0	25.1	0.0	0.0	0.0
C2	12.0	10.6	0.0	34.7	1.5	32.4	7.6	0.4	0.8
D2	7.6	12.1	0.0	25.6	2.6	31.2	12.6	0.2	8.0
A3	4.6	14.5	0.0	26.9	1.7	32.1	12.0	3.1	5.1
B3	5.1	11.2	0.0	26.3	4.6	38.9	13.9	0.0	0.0
C3	16.1	12.8	0.0	30.2	0.0	35.4	5.4	0.0	0.0
D3	0.0	7.3	10.1	27.5	2.5	31.7	10.3	0.2	10.4
BB2	9.4	10.3	0.0	32.8	0.5	28.5	8.0	0.0	10.6
ASTM standard	1.0	17.9	0.0	31.0	2.9	31.4	10.2	5.8	0.0

Table 5

Diesel fuel specifications and values observed in commercial samples.

Type or sample	Distillation (Tmax, °C)			Density (g/cm ³)		Cetane index Min.	Sulfur (ppm)
	10%v	50%v	90%v	Min.	Max.		
Grade 1 (agrodiesel)	–	–	370	0.800	0.870	44	3000 Max.
Grade 2 (common)	235	300	360	0.800	0.870	45	1500 Max.
Grade 3 (ultra)	235	300	360	0.800	0.870	47	50 Max.
GO-A2	198	268	365	0.8410		49.8	1218
GO-B2	195	266	357	0.8432		48.6	1228
GO-B3	206	263	332	0.8453		47.7	360
GO-C2	230	289	370	0.8497		51.7	919
GO-D2	182	266	375	0.8302		52.5	1308
GO-BB1	158	270	397	0.8150		57.8	334
GO-BB2	197	267	357	0.8327		52.6	1481
GO-BB3	182	260	364	0.8269		52.8	1373
GO-BB4	228	283	362	0.8529		49.7	939
GO-BB5	180	270	374	0.8290		53.8	1488
GO-BB6	220	284	357	0.8484		51.0	1007
GO-BB7	209	266	338	0.8396		50.4	406

3.4. Analysis of commercial diesel fuels

The quantification of sulfur compounds in commercial diesel fuels according to the signal optimization method described above are shown in Table 5, together with additional characterization data and product specifications from national regulations. An important amount of samples did not satisfy the limit of maximum temperature to recover 90% of distilled volume. Density and minimum Cetane Index for all the

Table 6
Proportions of sulfur compounds in commercial diesel fuels.

Sample	Sulfur compound or family (%)							
	BT	C1-BT	C2-BT	C3-BT	DBT	C1-DBT	C2-DBT	C3-DBT
GO-A2	1.5	2.7	4.2	6.3	7.1	10.9	11.7	55.7
GO-B2	0.6	2.6	4.6	5.1	7.2	12.7	15.8	51.4
GO-B3	4.6	3.2	3.3	2.4	2.5	6.8	25.5	51.7
GO-C2	0.0	0.4	1.5	3.9	7.6	13.2	16.7	56.7
GO-D2	0.1	0.2	1.3	2.9	6.3	11.9	15.4	61.9
GO-BB1	0.0	0.0	0.5	0.6	2.9	10.4	16.7	68.8
GO-BB2	0.5	1.1	2.8	5.3	7.5	13.1	15.2	54.6
GO-BB3	0.8	0.6	1.2	2.7	6.2	11.3	14.2	63.0
GO-BB4	0.4	0.3	1.4	3.6	7.1	13.0	17.2	56.9
GO-BB5	0.0	0.5	1.4	2.9	5.8	10.1	12.6	66.7
GO-BB6	1.3	3.5	5.5	4.9	5.9	11.1	14.4	53.3
GO-BB7	0.5	1.8	3.5	5.1	4.4	13.8	23.5	47.2

grades were satisfied. It can be observed that considering the Cetane Index of the various samples, the fuel quality of commercial diesel fuels is well above the minimum required by regulations. Concerning sulfur, all the samples satisfied the requirements of Grade 2 (less than 1500 ppm).

The distribution of sulfur compounds in the diesel fuel samples is shown in Table 6. Distributions in the various samples were different, with predominant alkyl dibenzothiophene compounds, particularly C3-species or heavier, that showed to be usually above 50% of the total sulfur compounds present. Alkyl benzothiophene compounds were present in lower amounts (average usually less than 10%).

4. Conclusions

A PFPD detector was used to analyze the sulfur content—the type of compounds present and the corresponding amounts, in liquid fuels such as gasoline and diesel. Particular detector responses were observed in the calibration of the instrument that diverged somewhat from the theoretical quadratic relationship with the sulfur amount. If necessary, the power coefficient could be assumed to be the theoretical one (0.5), but errors at low sulfur concentration can be significant.

In the boiling range of gasoline, both the chromatographic areas calculated with the linearized signal (indeed data points elevated to a given power) and the chromatographic areas reported by the instrument (also elevated to a particular power) were regressed linearly with the sulfur mass concentrations, leading to better results in the first case. In both cases, the normalization of the areas with the FID area in each injection helped to decrease deviations. In the case of the diesel fuels, only the normalized areas calculated with the linearized signal can be used, due to significant peak coelution. Even though individual calibrations can be performed for each sulfur compound, all the compounds in the gasoline or diesel boiling ranges can be considered together, and more usefully, unique coefficients can be assessed, thus simplifying the analysis.

It was shown that the theoretical quadratic response of sulfur in this detector is influenced by the operational conditions and by the hydrocarbon matrix analyzed.

The simultaneous use of FID and PFPD detectors allows improving the analysis of liquid fuels, since sulfur analysis can be added to the

standard hydrocarbon analysis (e.g. composition and simulated distillation) without additional working time. Moreover, FID reported chromatographic areas can be used as a parameter for normalization to enhance the quality of sulfur analysis. If needed, the sensitivity of the detector can be increased by decreasing the electrometer's range.

Acknowledgments

This work was performed with the financial assistance of the National University of Litoral, Secretary of Science and Technology (Santa Fe, Argentina) CAI+D 2009, Proj. 60-297; National Council for Scientific and Technical Research (CONICET) PIP 1257/09, and National Agency for Scientific and Technological Promotion PICT 2005 14-32930.

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