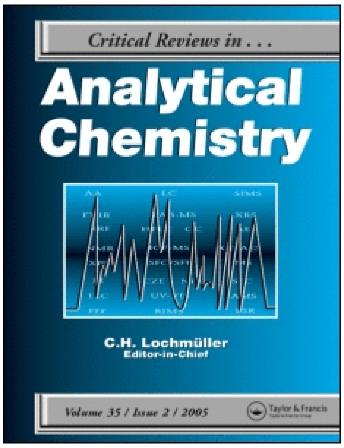

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# Chemiluminescent Methods in Petroleum Products Analysis

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**ABSTRACT:** This review focuses on the applications of chemiluminescence for the determination of petroleum products and covers the literature published in the last 5 years. The article has been divided into several sections, including specific applications to sulfur compounds, nitrogen compounds, polycyclic aromatic hydrocarbons, as well as a brief section dedicated to imaging analysis. The possibilities and limitations of the chemiluminescence detection systems for this purpose are evaluated.

**KEY WORDS:** chemiluminescence analysis, petroleum products analysis.

## I. INTRODUCTION

Chemiluminescence (CL) is one of the luminescent phenomena and it can be defined as the light emission (ultraviolet, visible or infra-red radiation) produced by a chemical reaction. It can occur in the gas, liquid, and solid phase. Chemiluminescence methods have been amply employed in the quantification of trace concentrations in many fields (per se, as well as detection systems in chromatographic techniques) due to its inherent advantages: high sensitivity, controllable emission rate, wide linear range, simple and inexpensive instrumentation, and considerable reduction of background noise. Coupled to separation methods, it constitutes an important tool for analytical applications, because high selectivity is achieved, offering excellent analytical sensitivity.

Environmental problems have determined to a certain extent the development of new, sensitive and selective methods of analysis. Petroleum and petroleum products are among the most important and widespread environmental pollutants. Fuel oil spills during transpotation, storage, etc., and unburned fuel residues in the exhaust gases from internal combustion engines can be sources of environmental pollution.[1] Crude oil (petroleum) consist of many thousands of components. It is largely composed of hydrocarbons, but there is an appreciable proportion of sulfur compounds. The catalytic oxidation of gasoline hydrocarbons generates heat within the catalytic converter that promotes other, environmentally unfavorable oxidations. Probably the most harmful of these is the increased conversion of $N_2$ to NO and $NO_2$[2]. Nitro-substituted polycyclic aromatic hydrocarbons are probably the most important class of mutagens identified as air pollutants in the last 15 years,[3] and they have been identified as components from diesel and gasoline engine exhaust emissions.

It is well established that a relatively important number of CL reactions constitute the basis for selective detection of environmental contaminants. Common applications of CL include the detection of sulfur compounds and nitrogen compounds[4] in gas chromatography, many of them making use of CL reactions that involve ozone.

The present review focuses on the application of chemiluminescence to the determination of the aforementioned compounds that are encountered during the refining processes of fuels or that are produced by combustion. Table 1 summarizes some applications of CL detectors to the determination of petroleum products.

## II. DETERMINATION OF SULFUR COMPOUNDS

There is a need for high-accuracy and high-sensitivity sulfur analysis in many industries.

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**TABLE 1**
**Cl Determination of Petroleum Products**

| CL Detector | Sample | Analite | Reference |
|---|---|---|---|
| SCD | Gasoline | Sulfur compounds | Di Sanzo et al.[8] (1994) |
| | Gasoline | Sulfur total content | Kubala et al.[9] (1995) |
| | Oil pollutions of marine environment | Sulfur compounds | Savchuk et al.[10] (1995) |
| Flameless SCD | Petroleum products | Sulfur compounds | Shearer et al.[12] (1993) |
| | Petroleum products | Sulfur compounds | Shearer and Skelton[6] (1994) |
| | Petroleum gases | Sulfur compounds | Larson and Haydt[13] (1995) |
| | Gasoline | Sulfur compounds | Chen and Lo[14] (1996) |
| | Diesel, gasoline and kerosene | Total sulfur compounds | Haydt[15] (1998) |
| SCLD | Petroleum products | Sulfur compounds | Shi et al.[16] (1997) |
| | Diesel fuel | Sulfur compounds | Shi et al.[17] (1998) |
| PFPD | Petrochemical fluids and gases | Sulfur compounds | Amirav et al.[19] (1998) |
| | Gasoline | Mn | Jing and Amirav[26] (1998) |
| CLND | Petroleum fractions | Nitrogen compounds | Young and Fujinary[20] (1994) |
| | Petroleum products | Nitrogen compounds | Tourres et al.[21](1995) |
| | Gasoline and diesel | Nitrogen compounds | Chawla[22] (1997) |
| Based on TCPO + $H_2O_2$ | Gasoline | Nitro PAHs | Li and Westerholm[23] (1994) |

Petroleum refineries are required to reduce or control the amount of total sulfur present in their refined products for environmental reasons. These requirements have led many refineries to search for on-line instrumentation that can produce accurate and repeatable total sulfur measurements within allowed levels. Several analytical methods currently exist for the measurement of total sulfur content. We are going to describe some chemiluminescence detection systems most usually utilized in recent years and which we have classified in four groups.

## A. Sulfur Chemiluminescence Detection (SCD)

A universal sulfur detector capable of measuring both reduced and oxidized sulfur compounds in the low of picogram ranged has been described by Benner and Stedman.[5] Recently, the SCD has received much attention due to its linearity, selectivity, sensitivity, and equimolar response. In conventional SCD operation, sulfur compounds are combusted in a reductive flame in an ionization detector (FID) to form sulfur monoxide and other products. The combustion products are collected under vacuum by means of a ceramic probe and transferred to an ozone reaction cell where the luminescence resulting from the reaction of sulfur monoxide with ozone is measured.[6] The SCD produces a linear response to sulfur and does not suffer significantly from quenching or interferences. The absolute SCD response is dependent on the condition and positioning of the ceramic probe, however, and this has limited SCD use to skilled analyst and has prevented it from being used in process instruments. Gas chromatography with a sulfur chemiluminescence detector provides a rapid means to identify and quantify various sulfur compounds that may be present in petroleum feeds and products.[7]

A method using capillary column gas chromatography with sulfur chemiluminescence detector has been developed by Di Sanzo et al.[8] for the qualitative and quantitative determination of sulfur components in stabilized gasoline-range process streams, including blended gasolines containing between 1 and > 4000 ppm total sulfur. Several modifications were made to the SCD to improve its operation at the low ppm sulfur level. Operational reliability depends on such factors as prevention of moisture accumulating in the transfer line, proper alignment and depth of insertion of the probe in the FID flame, and precise control of gas flows. The authors have used zirconia probes, which could be inserted deeper into the flame, and, at times, this resulted in better detection limits than those obtained with aluminia probes (normally fabricated from aluminia), and a new method, using a hydrogen sulfide permeation tube, was developed for rapid alignment of the probe in the FID. Using on column injection, the method has excellent total sulfur linearity to at least 5 ppm total sulfur. The detection limit is approximately 50 ppb per compound. The method is applicable to total sulfur concentrations of > 4000 ppm if such samples are diluted accordingly. Improvements made to the SCD probe and its alignment procedure minimized down time and improved sensitivity.

Kubala et al.[9] have constructed a specially designed system to permit the determination of total sulfur content in gasoline. At the beginning of each analysis cycle, a small sample is injected by sampling valve and vaporized. Air carrier gas transports the vaporized sample through an inert column and into a dual-flame hydrogen/air burner. The hydrocarbon matrix is combusted into $CO_2$ and $H_2O$, while the sulfur in the sample is converted into sulfur oxides:

$$\mathrm{R\text{-}H + R\text{-}S + O_2 \rightarrow CO_2 + H_2O + SO_2 + SO}$$

where R-H is the hydrocarbon matrix and R-S is the sulfur component. The highly reactive sulfur monoxide (SO) can be reacted with ozone under reduced pressure to produce electronically excited $SO_2^*$:

$$\mathrm{SO + O_3 \rightarrow SO_2^* + O_2}$$
$$\mathrm{SO_2^* \rightarrow SO_2 + light}\,(\lambda_{\max} = 350\,\mathrm{nm})$$

The spectral emission produced as a result of the chemiluminescence is isolated, the emission intensity is converted into an electrical signal and data processing electronics amplify and integrate the signal. The detector is linear over 3 orders of magnitude with a minimum detectable level of approximately 0.1 ppm S. Repeatabilities of 1% are obtained for most sulfur concentration ranges. When the authors compared it with other techniques, the SCD provided well-correlated results. The SCD system can be easily adapted to the determination of total sulfur content in diesel, fuel gas, and other process streams.

A procedure for determination of sulfur-containing compounds in oil pollutions of marine environments (in seawater and in recent sediments) is based on the applications of gas chromatography with open tubular columns and chemiluminescence detection.[10] The combustion of sulfur-containing compounds is performed in the hydrogen-rich flame of a flame-ionization detector operating in parallel with the recording of chemiluminescence and the detection limit was 0.1 ng/L.

## B. Flameless Sulfur Chemiluminescence Detection

A modified version of the SCD, termed "flameless" SCD because the detector utilizes a heated combustion assembly operated outside the flammability limits of hydrogen in air has been developed by Shearer[11] and applied to the analysis of petroleum products by Shearer et al.[6,12] The flameless SCD system was reported to exhibit operability, precision, and increased sensitivity by one order of magnitude. Shearer et al.[12] have applied gas chromatography using flameless sulfur chemiluminescence detection to the analysis of sulfur compounds in petroleum products. The method described improves on the previous method, e.g., the flameless SCD method exhibits greater precision than FPD method and conventional SCD. In addition, the flameless SCD analysis is quicker and less susceptible to the effects of hydrocarbon interferences, and it eliminated the need to recondition and reposition the probe. Precision of 1 to 2% RSD was typically obtained for replicates by the GC flameless.

Supercritical fluid chromatography using flameless sulfur chemiluminescence detection has been investigated by Shearer and Skelton[6] for the analysis of sulfur compounds in petroleum products. The chromatography and detection system was easy to implement and exhibited good precision, linearity, selectivity and sensitivity. A minimum detectable limit of 0.3 pg sulfur/s was obtained, and response to sulfur in different sulfur species was nearly equimolar.

Larson and Haydt[13] have developed a sulfur-specific analyzer based on sulfur chemiluminescence. The detector employs an externally heated combustion zone that eliminates the use of an open flame to form sulfur monoxide. Ozone is then reacted with the sulfur monoxide to produce an electronically excited form of sulfur dioxide which releases ultraviolet radiation after relaxation. The radiation is detected by a photomultiplier tube and is linearly proportional to the amount of sulfur present. This analyzer has a wide range of applications for on line sulfur analysis involving vapor phase samples. Sensitivity down to 5 ppb v/v and linearity up to 1000 ppm v/v was achieved and signal repeatability was found to be +/- 1 %. The authors have described applications to light petroleum gases.

Chen and Lo[14] have presented a method to detect sulfur compounds in gasoline. When a destructive detector such as the flame ionization detector (FID) is followed by the flameless sulfur chemiluminescence detector (SCD), they can be used to detect simultaneously carbon and sulfur. The authors have presented a method for dual-channel detection of hydrocarbon and sulfur compounds in three gasoline samples, using the coupling of FID and flameless SCD in series after gas chromatography. Optimum condition for flameless SCD were evaluated by altering the flow rates of hydrogen and air and the oxygen pressure to the ozone generator. Under optimal conditions, for example, 145 mL min$^{-1}$ $H_2$, 60 mL min$^{-1}$ air, the detection limit of the flameless SCD was 1.8 pg s$^{-1}$ for $H_2S$. The samples were identified by retention indices where the homologous *n*-alkylthiols are used as standards.

A sulfur-specific detection system based on sulfur chemiluminescence has been developed by Haydt[15] that is capable of measuring total sulfur in liquid samples. The analyzer is fully automated and is designed to measure sulfur on-line. The technology has been modified to handle liquid streams by the installation of an integrally heated liquid injection valve. A small sample of the liquid is injected directly to the detector and all sulfur-bearing compounds are detected simultaneously as a single peak representing total sulfur. The sulfur chemiluminescence analyzer offers several advantages over other technologies: (1) large linear range, (2) high sensitivity, (3) equimolar response to sulfur bearing compounds, and (4) high selectivity to sulfur. In this system, in the reaction furnace hydrogen, air and sample are combined at 750ºC under vacuum to produce sulfur monoxide among other combustion products. These reaction products are drawn under vacuum to the reaction cell where ozone is continuously added from an ozone generator. The ozone and sulfur monoxide combine to form an electronically excited state of sulfur dioxide that releases light after relaxation. The system was tested on diesel, gasoline, and kerosene samples. Very good linearity and repeatability were observed, and the system was found to be free of effects from significant changes in the hydrocarbon content of sample.

### C. Sulfur Chemiluminescence Detection (SCLD) with $H_2S/O_3$ Chemiluminescent Reaction

A new generation sulfur chemiluminescence detection (SCLD) system was studied by Shi et al.[16] and was interfaced and tested for supercritical fluid chromatography (SFC) with packed columns using 100% SF-$CO_2$ and methanol modified $CO_2$ as the mobile phase. The SCLD operation principle involves a post column two-step reaction process. Sulfur-containing analytes emerging from the chromatographic column are first oxidized to sulfur dioxide ($SO_2$), and subsequently the $SO_2$ is reduced to the hydrogen sulfide ($H_2S$) and possibly other reduced species by a large excess of hydrogen.

$$R_1 - S - R_2 + O_2 \rightarrow SO_2 + \text{other oxides}$$
$$SO_2 + H_2 \rightarrow H_2S + \text{other reduced sulfur species}$$

The $H_2S$, together with all other reduced products, are then draw into a reaction chamber where $H_2S$ is oxidized with ozone to sulfur dioxide ($SO_2^*$) in the excited electronic state.

$$H_2S + O_3 \rightarrow SO_2^*$$
$$SO_2^* \rightarrow SO_2 + \text{light}$$

The chemiluminescence of $SO_2^*$ is then measured by a photomultiplier tube. SCLD demonstrated high sensitivity, selectivity in a wide linear dynamic range, as well as equimolar responses to sulfur. The minimum detectable quantity was determined to 3 pg sulfur (0.2 pg S/s) at the detector. The applications and capabilities of SFC-SCLD system for sulfur speciation and detection are presented for petroleum product.

Shi et al.[17] have described a method that interfaces sulfur chemiluminescence detection with open-tubular column supercritical fluid chromatography (SFC) using 100% supercritical carbon dioxide as the mobile phase. With the high sensitivity and selectivity of sulfur chemiluminescence detection, it is possible to separate and detect sulfur-containing compounds in diesel fuel and other heavy refinery samples successfully by using SFC interfaced with chemiluminescence detection.

### D. Pulsed Flame Photometric Detector (PFPD)

The PFPD is based on a flame source and combustible gas flow rate that cannot sustain a continuous flame operation.[18] Thus, the ignited flame is propagated through the detector and self-terminates after the combustible gas mixture is burnt. Typically the combustible gases $H_2$ and air are mixed together in a small flame chamber and flow to a continuously heated Ni/Cr wire igniter. The ignited flame then propagates back to the gas source and is self-terminated once all of the combustible gas mixture present in the combustion path is consumed. The result of the gas phase reactions in the flame is that some molecular products emit light with specific spectral emission and emission lifetimes. The differences in the emission lifetimes of the emitting products combined with the propagation and termination properties of the flame permit both time and spectral information to be used to improve selectivity of the PFPD. Amirav et al.[19] have described possible applications of the PFPD to sulfur compounds in petrochemical fluids (fuels) and gases. This is the most widely used PFPD application. While the PFPD has equivalent performance to the SCD, it is far simpler to operate and maintain, has better long-term stability, is fully integrated with the GC without additional bench-space, and costs much less to purchase and maintain. The combination of PFPD-GC enable a fast (under one minute) total sulfur determination method that can be applied to petrochemical gases and fluids, including gasoline and diesel fuel. This method is based on the use of a short microbore column connected in series with a short megabore column that is coupled with the PFPD. Standard 0.5 microliter split injection is employed with column flow rate of 0.1 ml/min and split flow rate of 12 ml/min, resulting in 20 to 25 sec broad quasi-GC peak of unseparated matrix and sulfur compounds. The injector and column are maintained at a high temperature, typically 300ºC. No quenching is observed and the equimolar sulfur response ensures the accuracy of the method. Thus, the same GC-PFPD combination can be used for both fast total sulfur determination and sulfur compound speciation.

# III. DETERMINATION OF NITROGEN COMPOUNDS

When a simulated distillation system is coupled with a chemiluminescent nitrogen detector (SimDis-CLND), the nitrogen boiling point distribution of refinery streams and crude oils can be studied to improve the production of the various petrochemicals and fuels. A simulated distillation technique was then developed by Young and Fujinari[20] using the CLND with matched capillary columns placed in a single GC oven for the analyses of nitrogen-containing components in petroleum fractions. The detection mechanism is shown below:

$$R_3N + O_2 \xrightarrow{>1000°C} H_2O + NO + \text{other oxides}$$

$$NO + O_3 \rightarrow NO_2^* + O_2$$

$$NO_2^* \rightarrow NO_2 + \text{light}$$

Each nitrogen-containing compound entering the CLND undergoes high-temperature (>1000ºC) oxidation with oxygen ($O_2$). The nitrogen-containing compounds are converted to nitric oxide (NO). The resulting gases are dried, then mixed with ozone in the reaction chamber. This yields nitrogen dioxide ($NO_2^*$) in excited state. Light emitted by this chemical reaction is detected by a PMT. Chemically bound nitrogen in the sample is detected with a sensitivity of 12 pg N. The GC-CLND, unlike the nitrogen-selective detector, has high sensitivity, nitrogen specificity, and the ability to see through nonnitrogenous components in very complex sample matrices.

Tourres et al.[21] have studied the CLND detector coupled with GC, and they concluded that the system brings results never obtained with other detectors (e.g., thermo-ionic), but it presents some defects, for example, their not equivalent response for all nitrogen-molecules, their instability through the time, and the problem of the basic line to take down and this reduces the clarity of the results. The authors have studied the applications of CLND to petroleum products.

It is know that nitrogen compounds cause color and gum formation and are responsible for catalyst poisoning during catalytic hydrotreating/hydrocracking process. In order to obtain the desired product quality and also to understand the effect of nitrogen compounds during catalytic processes, it is beneficial to speciate nitrogen compounds that are present in various process streams. Chawla[22] describes the development of a gas chromatographic method that uses nitrogen-specific detection based on chemiluminescence (CLND) and optimized to speciate nitrogen compounds in gasoline and diesel range process streams. Under optimized conditions, the nitrogen-to-carbon selectivity is greater than $10^6$. It is possible to detect concentration of individual components down to 100 ppb nitrogen. The detector's linear response in a range of 0.2 to 54 ppb nitrogen for an individual nitrogen component is established using several aliphatic and aromatic nitrogen-containing compounds. Gasoline and diesel range streams containing any level of total nitrogen can be analyzed after appropriate dilution so that each nitrogen component is below 50 ppm. In addition to the nitrogen speciation, total nitrogen can simultaneously be determined with reasonable accuracy using the system. The repeatability and accuracy of the nitrogen quantitation is found to be within 7 at the 95% confidence level based on six to seven measurements.

# IV. DETERMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS

Diesel and gasoline engine exhaust emissions are complex mixtures containing some nitrated polycyclic aromatic hydrocarbons (nitro PAHs), and they have been identified as mutagens and possible carcinogens.[23] Nitro PAHs have been estimated to be responsible for up to 40% of the total mutagenic activity determined in diesel particulate extracts. The determination of nitro PAHs in complex sample matrices is usually carried out using analytical methods, such as gas chromatography with some detectors as mass spectrometry, or high-performance liquid chromatography (HPLC) with fluorescence or electrochemical detection. Li and Westerholm[23] have developed a sensitive and routine analytical method for determining mono- and di-nitro PAHs in engine exhaust emission. The determination was accomplished by on-line reduction of nitro PAHs to amino PAHs using a catalyst column, the amino PAHs is then separated and detected using HPLC and chemiluminescence detection. The peroxyoxalate chemiluminescence reaction is used for the detection of fluorescent compounds such as amino PAHs. Peroxyoxalate chemiluminescence involves the oxidation, usually with hydrogen peroxide, of various aryll oxalate esters.[24] The reaction is suggested to proceed via a cyclic intermediate with then interacts with the sensitizer (fluorophore) to excite it and liberate carbon dioxide.[25] *Bis*(2,4,6-trichlorophenyl) oxalate (TCPO) and hydrogen peroxide was used as the chemiluminescent reagent to determine 1.8-dinitropyrene, 2-nitroanthracene, 1-nitropyrene, 6-nitrochrysene, 3-nitroperylene, and 1-nitroperylene, and the detector used is usually a photo multiplier tube without a light source that gives an improved signal-to-noise ratio when compared with conventional fluorescence detection. The major advantages of this approach are (1) the catalyst column shows enough reduction capacity and life time, (2) Both mono- and di-nitro PAHs can be quantified, and (3) the detection limits are in the range of 1 to 10 picograms of the standard compounds injected.

## V. DETERMINATION OF MN

Pulsed flame photometric detector (PFPD) is characterized by the added information available from flame chemiluminescence emission time dependence. Jing and Amirav[26] have found that many elements posses unique delayed emission, whose time dependence can serve for their identification. The authors have shown the PFPD analysis of methylcyclopentadienyl manganese tricarbonyl (MMT) at sub-ppm levels (far below the 80 ppm allowed in Canada) as Mn additive in gasoline. Manganese can be selectively detected with the PFPD with high selectivity against hydrocarbons.

## VI. CHEMILUMINESCENCE IMAGING ANALYSIS

In terms of bulk emissions, by far the greatest sources of atmospheric pollutants are combustion sources.[27] For engines, considering the fact that combustion is the chemical process converting fuel into heat energy, water, and $CO_2$ (one of major greenhouse gases) improvement in thermal efficiency provides the only viable means to combat the global problems of greenhouse warning and oil resource depletion.[28] In the future, designers of diesel engines will be challenged by the need to meet more stringent emission standards while improving fuel consumption.[29] Several papers have demonstrated that chemiluminescence imaging constitutes an important tool for examining autoignition in diesel combustion, and it has been applied to the understanding of the diesel combustion process. CL constitutes one of the components of natural emission of diesel combustion and it arises from combustion radicals that are raised to an excited state by energetic chemical reactions and then subsequently decay back to equilibrium enegy levels by emitting a photon. Chemiluminescent emission occurs in specific wavelength bands located mainly in the near ultraviolet, blue and blue-green parts of the spectrum for OH, CH, and $C_2$, respectively. CL will occur throughout the combustion heat release, but is a relatively weak signal.[30]

Kuwahara and Ando[31] have studied the postflame reaction zone structure of a lean-burn flame by two-dimensional consecutive imaging of flame chemiluminescence using an image intensifier with a sub-microsecond-decay phosphor. Quantitative and statistical analysis of the recorded images are employed to elucidate the effects of tumble and charge stratification on flame structure. In order to eliminate the solid emission from soot and the thermal emission from the reactions produced in the burned gas zone, wavelength range from 450 to 550 nanometers is selected. The authors concluded that in the early stage of combustion, significant air entrainment enhancement was realized by tumble, having a small effect on eddy burning. However, after the completion of flame propagation, tumble activated the last process. Charge stratification realized by concept of “barrel stratification” activated both air entrainment and eddy burning. Under uniform mixing conditions, no reaction-zone structure was observed. When charge was stratified, an annular postflame reaction zone was observed behind the flame front.

John E. Dec and co-workers have published several papers in relation to imaging diagnostic, including Cl imaging, in direct-injection (DI) diesel engines. A combination of optical imaging diagnostics (Natural Flame Emission, Laser-Induced Incandescence and Elastic [Rayleigh] Scattering) has been applied by Dec and Espey[30] to the fuel jet of a DI diesel engine to study the ignition and early soot formation processes. Measurements were made in a single cylinder optically accesible diesel of the "heavy-duty" size class, at a representative medium speed (1200 rpm) operating conditions. They used two diesel fuels, a 42.5 cetane number mixture of the diesel reference fuels (*n*-hexadecane and heptamethynonane) and a new low-sooting fuel consisting of 70% tetraethoxipropane and 30% heptamethylnonane, by volume. Semiquantitative imaging of natural CL is used to investigate the onset of combustion via an intensified video camera. By synchronizing the camera-intensifier gate with the engine, these images provided time-resolved measurements of the spatial distribution of the CL, with the limitation that the signal was integrated along the line of sight. The results obtained by the authors showed that a weak Cl was detected as early as 3.5º ASI (after the start of injection) that occurs throughout the downstream portion of all eight jets. From 3.5º to 5.0º ASI, the emission intensity increases progressively but remains almost uniformly distributed throughout the downstream portion of all jets. The main area of this emission coincides with the vapor-fuel region in the leading portion of the jets. Finally, a very strong randomly occurring emission was detected beginning at 5.0º ASI. From these studies, the authors concluded that the ignition occurred at multiple points across the dowstream region of all the fuel jets prior to the first apparent heat release and well before any soot luminosity occurred.

In a later paper,[32] one of the authors has presented a compilation of data obtained in previous laser imaging and CL imaging investigations, as soon as new results on the onset of PAH formation and soot distribution under higher fuel load. A section that reviews selected literature describing the old picture of diesel combustion is included in order to contrast with previous and recent investigations of the author and co-workers, concluding that the conceptual model of DI diesel combustion presented differs significantly from what had been thought prior to the laser-sheet imaging investigations, although some limitations are mentioned such as the fact that the model is based on detailed imaging data taken primarily at one typical operating condition with idealized fuels.

CL imaging of diesel autoignition studies have been extended by Dec and Spey[33] to earlier crankangles. They compare the evolution of the CL in the differents fuel jets for a variety of operating conditions The authors used the same reference fuel and similar engine operating conditions as in Reference 30. A range of top dead center (TDC) temperatures from 900 to 1100 K at constant density, and TDC density from 11.1 to 24.9 kg/m$^3$ at constant temperature are used for parametry study. The paper included an ample section of summary and conclusions that show that CL imaging constitutes a useful tool for investigating the timing and location of the early reactions that occur during diesel autoignition.The images obtained show that CL is detected shortly after the start of the injection for all the conditions studied, and it grows brighter and shifts downstream as the jet penetrates across the chamber, until soot luminosity dominates the emission. For changes in either TDC temperature or density, changes in the chemical-kinetic rates of the processes were observed. They inform that spectral data show that CL arises mainly from formaldehyde and CH emission, with no OH emission detected. The last appeared in the sooting combustion spectra after the diffusion flame had formed.

## CONCLUSIONS

This paper has examined the possibilities of several chemiluminescence detection systems in the determination of petroleum products that have shown an increasing interest in recent years. From the literature reviewed, it can said that sulfur compounds determination can be carried out satisfactorily, making use of chemiluminescent deterctors (SCD, "flameless" SCD, SCLD, and PFPD) coupled to chromatographic techniques

(GC and SFC). In general, they do not suffer significantly from quenching or interferences, response to sulfur is nearly equimolar and the detection limits can be improved with the modifications investigated and introduced by the authors. The chemiluminescent reaction of nitrogen monoxide with ozone constitutes the basis of CL detectors mainly applied to the determination of nitrogen-containing compounds in petroleum fractions, gasoline, and diesel. Some inconveniences with GC-CLND have been pointed out such as no equivalent response for all nitrogen compounds or instability through the time. However, the system presents high sensitivity and nitrogen specificity.

On the other hand, the HPLC separation with peroxyoxalate chemiluminescence detection supplies a viable alternative for the determination of mono- and di-nitro PAHs, providing high sensitivity. Finally, imaging analysis based on natural chemiluminescence of the autoignition allows a better comprenhesion of this process.

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