Review

Detection by ozone-induced chemiluminescence in chromatography

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Abstract

Gas phase ozone-induced chemiluminescence is reviewed in this work with the emphasis on its applications in analytical chemistry and in chromatography in particular. Background information on various types of ozone-induced chemiluminescent reactions is presented and the reaction mechanisms are discussed. These reactions are of great importance to academic researchers as well as application chemists, due to their unique properties. Although there are many direct ozone chemiluminescent reactions with various gaseous molecules, the incorporation of a conversion step to convert various non-chemiluminescent analytes to a species capable of reacting with ozone to produce chemiluminescence broadens the horizon of this technique tremendously. The conversion of nearly all nitrogen- and sulfur-containing compounds to their respective chemiluminescent species for universal nitrogen and sulfur detection has made nitrogen/sulfur chemiluminescence detection the most widely used analytical methods based upon ozone-induced chemiluminescence. In addition to non-chromatographic applications, nitrogen/sulfur chemiluminescence detection has been adapted to various chromatographic techniques from gas chromatography to liquid and supercritical fluid chromatography as specialized element-specific detectors. The characteristics of these detectors are evaluated and compared to other element-selective detection techniques. The unique features of the chemiluminescence detectors have made them powerful tools in many diverse fields of analytical chemistry.   © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chemiluminescence is defined as 'emission of light as a result of a chemical reaction without an apparent change in temperature' [1]. This phenomenon, along with bioluminescence, has been reviewed previously [2–13]. A broad spectrum of chemiluminescent reactions have been studied and reported. They have been covered by a number of excellent reviews, e.g. liquid phase chemiluminescence and bioluminescence by Kricka and Thorpe [10]. Among the various types of chemiluminescent reactions, gas phase chemiluminescent reactions, particularly those induced by a reaction with ozone, hold a prominent place in the literature. Its importance is manifested both in the academic studies on this subject, and in the commercial application of this unique technology to sensitive and selective detection of certain elements, notably nitrogen and sulfur, in a broad range of samples. Numerous research articles, technical presentations and patents have been added to the continuously growing body of literature on ozone-induced chemiluminescence. Several reviews and monographs on gas phase chemiluminescence or, specifically, on ozone-induced chemiluminescence have also been published [6,7,11,12,14,15]. However, in light of the continuing growth in this field, particularly the explosive growth in commercialization of the technology in the 1980s and 1990s, where much of it has been in the realm of chromatography, a new review on this topic is in order. Because the academic and commercial interest and recent advances have been focused on gas phase ozone chemiluminescence, so will the emphasis be in this review. Other types of chemiluminescent reactions (e.g. ozone-induced chemiluminescence in condensed phases, or gas phase chemiluminescent reactions not involving ozone) will only be treated briefly, with pertinent literature cited as appropriate. The focus of this review will be on the recent advances and analytical applications of ozone-induced chemiluminescence in various sub-fields of chromatography, particularly on those by commercial instruments for nitrogen and sulfur determinations. It is meant to be an addition to the previous reviews on this subject, with no attempt at exhaustive coverage.

2. Brief history and background

2.1. Early history

More than a hundred years ago, chemiluminescence from the reaction between ozone and ethanol was reported in 1896 [16]. Numerous more gas phase ozone-induced chemiluminescent reactions have been discovered since then, notably that with hydrogen sulfide [17,18]. In fact, almost all gas phase reactions involving ozone are chemiluminescent. The chemiluminescent reaction between nitric oxide (NO) and ozone is probably the most well known and has found the broadest applications.

2.2. Theoretical investigations

Extensive studies have been carried out on the important $NO+O_3$ chemiluminescence system [19–21]. In particular, the extensive theoretical work by Clyne et al. [20] and Clough and Thrush [21] laid a strong foundation of the understanding of this well-known ozone chemiluminescence system. Similar theoretical investigations of the chemiluminescent reaction between sulfur monoxide (SO) and ozone were also carried out by the same research group [22–24]. The $SO+O_3$ chemiluminescence system was studied in great detail both kinetically and spectroscopically. Further spectroscopic studies of ozone-induced sulfur chemiluminescent reactions [25–27] showed almost identical chemiluminescence spectra from several different sulfur species, indicating a common intermediate or precursor (likely to be SO). Glinski et al. [28–31] continued the spectroscopic work in the 1980s and early 1990s, concluding that the common chemiluminescent emitter was SO_2^*. They did, however, investigate the direct single-collision chemiluminescent reactions of ozone with H_2S and CH_3SH [32]. More recently, Benner and Stedman [33] and Burrow and Birks [34] carried out flow tube investigations to further study the detection mechanism in sulfur chemiluminescence. However, the sulfur chemiluminescence detection mechanism is not universally agreed and accepted. In fact, the disagreement over the mechanism prompted a recent exchange of correspondence [35,36]. A detailed discussion on the mechanism of sulfur

chemiluminescence detection is given below in Section 4.

2.3. Analytical applications

Many attempts at analytical applications of chemiluminescent reactions began to take place in the 1970s. The chemiluminescent reactions between ozone and various molecules have been exploited for detection of olefins, ozone, nitric oxide, other nitrogen oxides, organosulfur compounds, as well as a variety of other organic compounds. $NO+O_3$ chemiluminescence forms the basis of a large number of these applications. In the early stages, many of the applications were analyzers for a particular one or a particular type of analyte without chromatographic separation. Chromatographers then began to apply these techniques to the development of specialized (usually selective) detectors. These analytical applications have been reviewed by various authors [10,11,14,15,37–43]. However, the coverage of the subject is limited in some cases and, in others, they are limited to certain types of applications. This review surveys a broad range of applications and shows a comprehensive picture of the current status of the ozone-induced chemiluminescence in analytical chemistry.

2.4. Commercial development

The major advancement in the analytical applications of chemiluminescence detection made in the 1970s through to the 1990s has been the rapid commercialization of analyzers and chromatographic detectors based on ozone-induced chemiluminescence. Among the early commercial instruments is the thermal energy analyzer by Thermo Electron Corporation (Waltham, MA, USA), which was initially developed for the selective detection of N-nitroso compounds. Most notable and successful of the commercial applications of ozone-induced chemiluminescence detection have been the highly selective analyzers and chromatographic detectors for nitrogen and sulfur, such as those manufactured by Antek Instruments (Houston, TX, USA) and Sievers Instruments (Boulder, CO, USA). These analyzers and detectors offer very unique advantages in the determination of nitrogen and sulfur in a broad range of samples compared to other technologies.

3. Chemiluminescent reactions

3.1. Gas phase ozone chemiluminescent reactions

Chemiluminescent reactions can be classified according to their phase and reactants. This review is mostly concerned with the chemiluminescent reactions between ozone and another compound in the gas phase. The original sample may be in a different form or phase, but the ultimate detection always involves a gas phase reaction chamber in which the ozone-induced chemiluminescent reaction occurs. All of the applications discussed in Section 6 are of this type.

3.2. Other gas phase chemiluminescent reactions

As stated above, most gas phase chemiluminescent reactions employed in chromatography and other analytical methods involve ozone as one of the reactants. One major exception is fluorine-induced chemiluminescence for the detection of reduced sulfur compounds [44–51]. This technique was developed by Nelson et al. [44] and was first applied to GC. The detector monitors chemiluminescence from the reaction of the reduced sulfur analytes with molecular fluorine at reduced pressures. Vibrationally excited HF is generated and the red and near-infrared emission is detected. This detection method was subsequently adapted to liquid chromatography [45], as well as supercritical fluid chromatography (SFC) [47,48]. The fluorine-induced chemiluminescence detection was also extended to biologically mellylated tellurium and selenium in addition to sulfur [49], as well as to phosphine and its derivatives [50]. The same technology was also utilized to detect trace level dimethyl sulfide [51]. With limited space available, this technique will not be discussed further in this review and readers are encouraged to seek additional information directly from the above-cited references.

3.3. Condensed phase ozone chemiluminescent reactions

Compared to the almost ubiquitous ozone chemiluminescent reactions in the gas phase, chemiluminescent reactions of ozone in liquids and solids are much rarer. Early work on ozone- induced chemiluminescence in the liquid phase has been summarized by Bernanose and Rene [52].

Brief reviews on ozone chemiluminescent reactions in the liquid phase have been provided by Rauhut [3] and Toby [11]. Even less work on ozone chemiluminescent reactions in the solid phase has been reported. A brief summary has been given by Toby [11]. Since there have been few analytical applications of ozone-induced chemiluminescence in the condensed phases, it will not be discussed beyond this point.

3.4. Solution phase chemiluminescent reactions

Speaking of detection based on chemiluminescence in chromatography, one cannot ignore another important class of chemiluminescent reactions, the solution-based chemiluminescence systems. There is a considerable amount of literature published in this field, and it has been thoroughly reviewed by Nieman [53]. One of the most widely used chemiluminescent reactions is the luminol+peroxide system. Some applications of this detection scheme are for the determination of nitrogen dioxide [54,55] and quinone [56]. However, it is beyond the scope of this review, and readers are referred elsewhere for further information [53].

4. Reaction mechanisms

Although numerous direct gas-phase ozone chemiluminescent reactions have been studied and a large number of these reactions have been exploited analytically, even more applications of ozone-induced chemiluminescence involve analytes that do not react with ozone directly or produce sufficient chemiluminescence. Therefore, pretreatment of the original reactants is necessary to convert them into a species that is capable of reacting with ozone to produce analytically detectable chemiluminescence.

It is referred to as the 'chemiluminescent species' in this article. It is convenient then to differentiate and discuss two categories of chemical reactions in chemiluminescence detection. The first category is the direct gas phase chemiluminescent reaction with ozone or the chemiluminescent reactions of ozone with chemiluminescent species generated from another conversion reaction. The other type covers the various conversion reactions that generate chemiluminescent species (often involving pyrolysis or combustion).

4.1. Reactions between ozone and chemiluminescent species

4.1.1. NO + O₃ chemiluminescence

Undoubtedly, the chemiluminescent reaction between ozone and nitric oxide ($NO+O_3$ system) occupies a prominent place in analytical chemistry. This reaction produces a distinctive and broad near-infrared chemiluminescent emission centered around 1200 nm [19]. This bimolecular reaction was investigated quite extensively [19–21]. It has been established that the chemiluminescence is the result of the following reactions:

$$NO + O_3 \rightarrow NO_2^* + O_2 + 47.8 \text{ kcal/mole} \quad (1)$$

$$NO_2^* \rightarrow NO_2 + h\upsilon \quad (2)$$
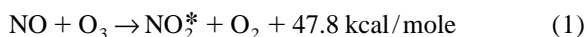
It has been shown by Clyne et al. [20] that the chemiluminescence intensity is given by

$$I = I_o \frac{[NO][O_3]}{[M]} \quad (i)$$

If one of the reactants NO or O_3 is in great excess, the reaction then becomes a pseudo first-order reaction for the other reactant and, hence, forms the basis for a linear analytical detection method for the reactant that is not in excess.

4.1.2. SO + O₃ chemiluminescence

Extensive studies on the similar gas-phase ozone chemiluminescent reaction with sulfur monoxide (SO) were carried out by Halstead, Thrush and co-workers [22–24]. The rapid bimolecular reaction between SO and O_3 has been shown to resemble that of the $NO+O_3$ system, but it is much more ex-

othermic. The reactions are very similar to reactions (1) and (2) above.

$$SO + O_3 \rightarrow SO_2^* + O_2 + 106 \, kcal/mole \qquad (3)$$

$$SO_2^* \rightarrow SO_2 + h\upsilon \qquad (4)$$
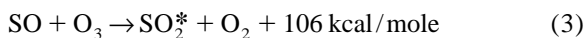
Due to the much higher energy in this case, the chemiluminescence emission spectrum extends from about 280 to 460 nm and is centered around 360 nm, with some discrete features between 380 and 450 nm. Electronically excited $^3B_1$ and $^1B_2$ were identified as being responsible for the chemiluminescence. [23]. The chemiluminescent emission intensity again is very similar to that of the $NO + O_3$ system:

$$I = I_o \frac{[SO][O_3]}{[M]} \qquad (ii)$$

Again, if the ozone concentration is in large excess, the reaction is pseudo first order for SO. This forms the basis of analytical methods for the detection of SO (if it could be sampled and brought into contact with ozone), or other reduced chemiluminescent sulfur species that can react with ozone and be converted to SO as an intermediate before the final elementary chemiluminescent reactions (3) and (4). Obviously, the reverse case of SO concentration being in excess is not realistic, due to the instability of SO.

Subsequent spectroscopic investigations on the chemiluminescent reactions of ozone with various sulfur compounds revealed striking similarity in the chemiluminescence spectra between these sulfides. Kummer et al. [25] first compared emission spectra of chemiluminescent reactions of ozone with dimethyl sulfide and hydrogen sulfide, respectively, and found them to be very similar. More detailed spectroscopic investigation by Akimoto et al. [26] showed almost identical emission spectra from ozone chemiluminescent reactions with hydrogen sulfide, methyl mercaptan, dimethyl sulfide and sulfur monoxide. Fig. 1 shows the chemiluminescent emission spectra from the reactions of ozone with these four sulfur compounds. It was postulated that all of these emission spectra were those of the excited state of SO_2, and the possible involvement of SO radical as a common intermediate was suggested. These findings

were later confirmed by Arora and Chatha [27] by ozone chemiluminescent reactions with more sulfur compounds. Again, SO was suggested as a precursor for the observed chemiluminescence. Glinski et al. [28,29,32] continued the spectroscopic investigations with a beam-gas apparatus at low pressures. Ozone reactions with small organosulfur compounds, such as methyl mercaptan, were investigated and chemiluminescent reaction mechanisms were proposed [28,32]. Direct single-collision chemiluminescent reactions of ozone with hydrogen sulfide and methyl mercaptan were investigated [32]. Chemiluminescence spectra were also obtained that were similar to those in the previous work. In this case, hydrogen sulfide reacts with ozone to form excited SO_2^* at a single collision. A corresponding reaction mechanism was proposed. More work along the same line was carried out on two slightly larger sulfur compounds: dimethyl sulfoxide and dimethyl disulfide [29]. The emission was found to be congruent to that observed in the reactions of ozone with hydrogen sulfide, methyl mercaptan and dimethyl sulfide under similar conditions. Mechanisms involving a HSO radical were proposed. In all of these cases, various sulfur compounds react with ozone to form SO_2^*, often involving a final intermediate SO. Martin and Glinski [31] continued this line of investigation and studied a sulfur-dioxide-containing hydrogen-rich flame from a commercial sulfur chemiluminescence detector (SCD) and proved that SO_2^* is the emitter of the chemiluminescence.

A separate line of investigation on the rate of reaction between hydrogen sulfide and ozone in air was carried out by Cadle and Ledford [57] and Hales et al. [58]. The rate of reaction was determined and the reaction

$$H_2S + O_3 \rightarrow SO_2 + H_2O \qquad (5)$$

was thought to represent true stoichiometry adequately under the experimental conditions.

4.1.3. Other ozone-induced gas phase chemiluminescence

Compared to the extensively investigated $NO + O_3$ and $SO + O_3$ systems, other gas-phase ozone chemiluminescent reactions received less attention. The chemiluminescent reactions between ozone and hydrocarbons are the next widely studied subject. A
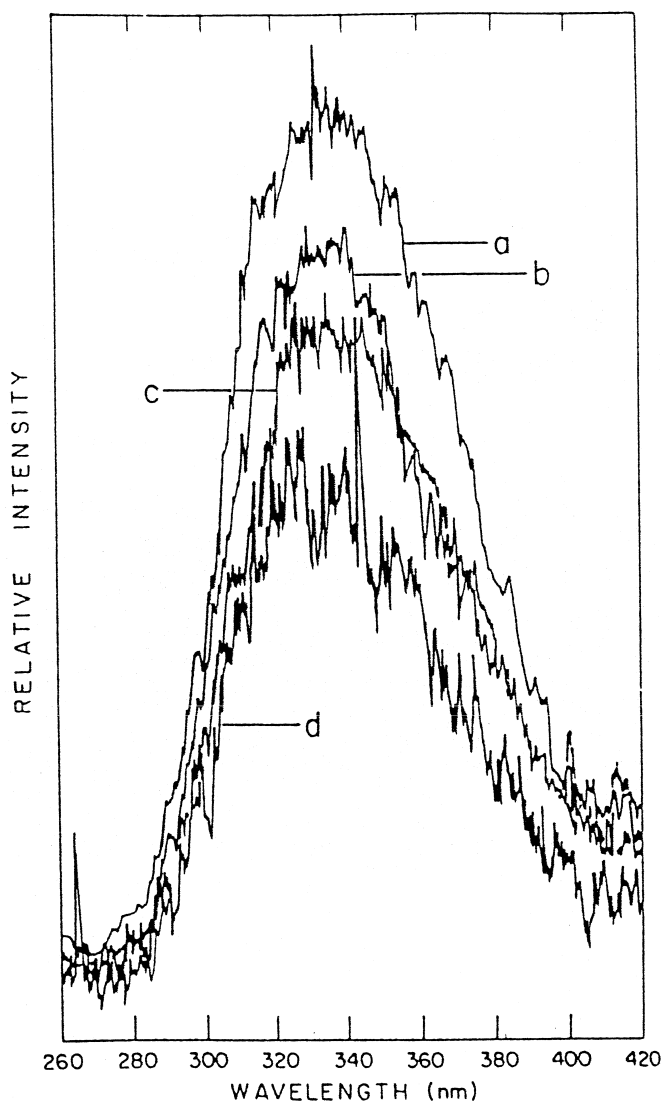
Fig. 1. Uncorrected chemiluminescent emission spectra at a total pressure of approximately 3 torr from the reaction of ozone with (a) SO, (b) CH_3SH, (c) CH_3SCH_3 and (d) H_2S (total pressure, 1 torr). Reprinted with permission from Ref. [26].

broad band chemiluminescence from the reaction of ozone and ethylene was observed with relatively weak intensity (compared to other olefins and sulfur compounds) by Kummer et al. [25]. Much stronger chemiluminescence was observed from the reaction of ozone with trimethylethylene and tetramethylethylene with narrow emission peaks within the approximate range of 500 to 570 nm. Kinetic studies on the gas-phase ozone–aromatic reactions was carried out by Toby et al. [59]. Similar, weak

chemiluminescence was observed for all of the aromatic compounds studied. The chemiluminescent reaction between ozone and methane was studied both kinetically and spectroscopically by the same research group [60]. Mechanisms were proposed to account for various experimental observations of the reaction. Recently, Toby and Toby [61] extended their kinetic investigation to the chemiluminescent reaction of ozone and ethane. The study suggested a chain reaction, and a 42-step mechanism was used to

simulate the system. A kinetic study by Mehrab-zadeh et al. [62], aimed at optimizing the response of chemiluminescence analyzers, was published. The behavior of chemiluminescence analyzers was discussed in terms of the response equations for exponential-dilution and plug-flow reactors. The response equations were tested experimentally with the ozone/ethylene chemiluminescent reaction.

There have been a few reports on gas-phase ozone oxidation of compounds of elements other than nitrogen and sulfur. Glinski et al. [63] also carried out a spectroscopic study of the oxidation processes in a gas-phase silane–ozone chemiluminescent reaction. The emission was thought to come from H_2SiO, based on ab initio molecular orbital calculations. In a separate study, chemiluminescence detection of arsine oxidation was discussed by Fraser et al. [64] in terms of reaction mechanism, rate of reaction and pressure dependence of the chemiluminescence intensity.

4.2. Reactions that produce chemiluminescent species

4.2.1. NO generation

Nitric oxide is a relatively stable compound, which allows its generation, storage and use for experimental studies. In fact, many applications utilizing $NO+O_3$ chemiluminescence are for detection of NO directly. However, the application of this unique chemiluminescent reaction can be expanded tremendously if the analyte can directly or indirectly generate NO. There are several means to generate NO for analytical detection and they are discussed below.

One important application is the detection of N-nitroso compounds (nitrosamines) by thermal cleavage of the nitrosyl radical group (NO) followed by chemiluminescence detection. This detection scheme forms the basis of the thermal energy analyzer (TEA) (manufactured by Thermo Electron Corporation). The principle of operation of the TEA was described by Fine et al. [65]. In TEA, N-nitroso compounds in the sample are pyrolyzed with or without a catalyst in a pyrolyzer at elevated temperatures. The N–NO bond in the N-nitroso compounds is usually the weakest in the molecule. Therefore, it may be selectively cleaved by thermal energy without break-

ing the moiety of the molecule apart. The pyrolysis temperature is very important to the selectivity of the detector. The released NO is stable enough to be transferred to the ozone reaction chamber and detected. The breakdown molecule and other species in the matrix usually do not react with ozone to produce significant chemiluminescence in the same spectral region as that of the $NO+O_3$ chemiluminescence and, therefore, they do not interfere with the detection of the N-nitroso compounds.

For even broader applications, most nitrogen-containing compounds (with the exception of atmospheric diatomic nitrogen) can be converted by oxygen to NO at about 900 to 1100°C. A commercial total nitrogen analyzer and a nitrogen-specific GC detector, called a chemiluminescent nitrogen detector, or CLND (manufactured by Antek Instruments), are based upon this detection scheme. The entire detection process may be divided into two major steps: the conversion of nitrogen-containing compounds to NO and the chemiluminescence detection of NO. The former step is expressed by reaction (6), in addition to the latter step, which has been discussed earlier and is given in reactions (1) and (2).

$$R\text{–}N + O_2 \rightarrow CO_2 + H_2O + NO \qquad (6)$$
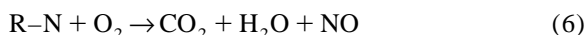
Since neither of combustion products CO_2 or H_2O reacts with ozone to produce any discernable chemiluminescence, it renders the detector or the analyzer transparent to the breakdown parts of the nitrogen-containing molecule and the sample matrix (such as the majority of hydrocarbon components or the solvents). The unique property of the high-temperature oxidative pyrolysis makes the analyzer or the detector highly selective for nitrogen.

Another analytical application utilizing the $NO+O_3$ chemiluminescent reaction is called redox chemiluminescence detection. It is the basis of a commercial redox chemiluminescence detector (RCD) (manufactured by Sievers Instruments). Again the method consists of two major steps, i.e., conversion to NO and chemiluminescence detection. The conversion step is based on the catalytic reduction of XNO_2-type compounds (where X denotes a radical group) to NO by certain oxidizable analytes (e.g., CO, H_2, H_2S, CS_2, SO_2 and various other organic compounds) with the use of a gold catalyst [66,67].

The thermochemical conversion can be described generically by reaction (7), in addition to the NO chemiluminescence detection step, which is shown in reactions (1) and (2).

$$XNO_2 + \text{oxidizable analyte} \rightarrow NO + \text{oxidized analyte} \tag{7}$$
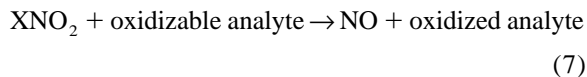
where X stands for a radical group (e.g. OH group in the case of HNO_3). The first step here is the rate-limiting step. Therefore, the degree of conversion is dependent on the type of surface, catalyst-bed temperature and the type of analyte compounds. These differences of reactivity account for the selectivity of the detector.

4.2.2. Generation of sulfur chemiluminescent species

Other than the applications involving the direct reaction of ozone with various sulfur compounds, the universal detection of sulfur requires a conversion step. Due to the complexity of the chemiluminescent reactions between ozone and various reduced sulfur species, investigations of the mechanisms of conversion of sulfur-containing compounds to chemiluminescent species as defined above is much more difficult, and often controversial. Although SO is believed to be the common intermediate species that reacts with ozone in a final elementary reaction to form SO_2^*, it is not necessarily the product of the first conversion step.

An early attempt by Parks [68,69] for universal sulfur detection is based on sequential oxidative and reductive pyrolysis of the sulfur analyte to convert it to a chemiluminescent species and resulted in two patents for chemiluminescent sulfur detection. The reaction chemistry is summarized in reactions (8), (9), (5) and (4).

$$R-S + O_2 \rightarrow SO_2 + CO_2 + H_2O \tag{8}$$

$$SO_2 + H_2 \rightarrow H_2S + H_2O \tag{9}$$
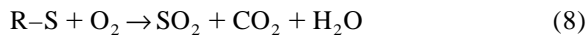
This method is similar to that for universal nitrogen detection discussed above. Both are composed of two major steps: (1) converting an element (nitrogen or sulfur) from all of the compounds possessing that element within a sample to a chemiluminescent species and (2) reacting with ozone to generate

chemiluminescence. However, the conversion step in the sulfur method is more complicated than that in the nitrogen method. The usual high-temperature oxidative pyrolysis (as used in the nitrogen method) produces SO_2 that is NOT a chemiluminescent species (in the sense of producing sufficient chemiluminescence for analytical detection under the experimental conditions). An additional reduction step is required to produce a (or several) reduced sulfur chemiluminescent species. Under the reductive conditions of the method, H_2S is formed whenever there is sulfur present in the original sample. The formation of H_2S is also consistent with basic inorganic chemistry principles. In fact, the reactions represented by reactions (8) and (9) form the basis of another sulfur detection method, i.e., hydrogenolysis followed by lead acetate detection of H_2S [70]. With the understanding of the above combustion chemistry, and knowledge of the $H_2S + O_3$ chemiluminescent reaction, it was natural for Parks to attribute the chemiluminescent species in this method to H_2S.

In 1989, Benner and Stedman [71] published an article describing the development of a universal sulfur detector based on production and detection of SO. A hydrogen-rich H_2/O_2 flame was utilized to break down the sulfur-containing compounds and any other combustible matrix molecules. Based on the authors' interpretation of the previous theoretical and experimental studies on sulfur species in a H_2/O_2 flame [72,73], and the theoretical work by Halstead and Thrush [23] on the $SO + O_3$ chemiluminescent reaction, they hypothesized that SO was produced in the flame and was subsequently transferred into an ozone reaction chamber and was detected by the $SO + O_3$ chemiluminescent reaction. However, the authors noted that, since H_2S was also formed in a hydrogen-rich flame, the possibility that a portion of the observed chemiluminescence was due to the more complex $H_2S + O_3$ reaction [57,58] could not be ruled out. This development work soon resulted in one commercial sulfur chemiluminescence detector (SCD) (manufactured by Sievers Instruments) commonly referred to as the flame SCD.

Later, Shearer [74] improved the performance of the SCD significantly by changing the means of sulfur chemiluminescent-species production from a hydrogen-rich flame to a closed hydrogen/air burner.

It was termed a 'flameless' SCD, apparently due to the change in conversion method. This new development eventually resulted in a new model of the SCD by Sievers Instruments. An even higher equivalence ratio (more hydrogen rich) was employed in this detector. The enhancement in sensitivity was partially attributed to the more reductive atmosphere based on the reaction equilibrium being shifted right.

$$SO_2 + H_2 \rightarrow SO + H_2O \quad (10)$$

Shearer [74] also noted that some reduced sulfur compounds might react directly with ozone to produce chemiluminescence, particularly because of the very highly reducing combustion environment used. However, he discounted a significant contribution to the observed chemiluminescence from H_2S by noting that hydrogen sulfide yielded a greater signal, of about 30 times, by passing it through the combustion assembly compared to directly reacting it with ozone.

In the meantime, a new SCD (originally termed chemiluminescent sulfur detector, or CLSD) based on sequential oxidative and reductive pyrolysis followed by chemiluminescence detection was developed by Yan [75] and was commercially introduced by Antek Instruments. The author based this development on Parks' patents [68,69] and the $H_2S + O_3$ reaction mechanism, with the acknowledgement of possible involvement of other reduced sulfur species. However, no experimental confirmation of any of the non-H_2S reduced sulfur species was carried out or observed.

The mechanism of sulfur chemiluminescence detection soon became a point of contention between the two rival SCD manufacturers, Sievers Instruments and Antek Instruments. To prove that SO was the only significant chemiluminescent species in the reaction chemistry of SCD, Benner and Stedman [33] then carried out a flow tube kinetics study on the mechanism of chemiluminescence detection with a flame SCD. They concluded that SO was identified as the precursor species produced in the SCD combustion based on four independent kinetic experiments, the emission spectrum, the chemical kinetic reaction rate with ozone, the gas-phase titration reaction with NO_2 and the direct addition of H_2S to the post-flame gas stream without measurable chemiluminescence.

A more comprehensive flow tube kinetics investigation on the SCD mechanism was carried out by Burrow and Birks [34]. Both flame and furnace versions of the SCD from Sievers Instruments as well as Antek instruments were tested. Rate constants and their temperature dependencies were measured for the chemiluminescent reaction of ozone. Various reduced sulfur species, including H_2S and SO as the chemiluminescent species, were considered and ruled out. An unknown reduced sulfur species, X, was believed to be formed in the combustion zone and/or transfer line of the instruments. The authors concluded that this key intermediate, X, was not SO but rather was a species that reacted rapidly with ozone to form SO:

$$X + O_3 \rightarrow SO + products \quad (11)$$
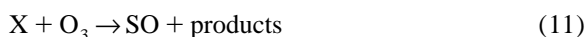
The authors further hypothesized that X was S_3, formed in the association reaction of S atoms with S_2 within the transfer line.

As mentioned above, the simple $SO + O_3$ mechanism was not universally agreed upon. Yan [75] proposed an updated $H_2S + O_3$ mechanism as follows:

$$R–S + O_2 \rightarrow SO_2 + CO_2 + H_2O \quad (8)$$

$$SO_2 + H_2 \rightarrow H_2S + \text{other reduced sulfur species}$$
$$(12)$$

$$H_2S + \text{other reduced sulfur species} + O_3 \rightarrow SO_2^*$$
$$(13)$$

$$SO_2^* \rightarrow SO_2 + h\nu \quad (4)$$
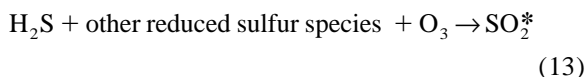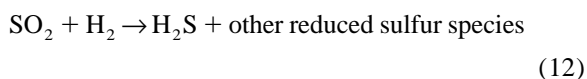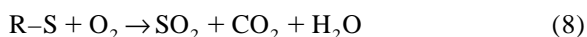
This mechanism acknowledges possible other chemiluminescent sulfur species that may be involved. The appearance of this mechanism in the published literature [76,77] prompted continued discussion and an exchange of correspondence [35,36]. Further discussion on the mechanism is likely to ensue [78].

In light of the confusion and disagreement regarding the sulfur chemiluminescence detection mechanism, suffice it to say that it is a far more complicated phenomenon than previously believed and much more research is needed to fully elucidate this subject. In the sections below, only general terms

such as 'chemiluminescent sulfur species' that are not in disagreement are used.

4.2.3. Generation of nitrogen and sulfur chemiluminescent species simultaneously

It has been discovered that, in oxidative/reductive pyrolysis, the nitric oxide generated in the combustion at least partially survives the reductive step. In addition, the conversion is found to be quantitative for analytical applications [79]. By detecting the NO chemiluminescence from the same stream, simultaneous nitrogen and sulfur chemiluminescence detection is achieved. This forms the basis of a commercial simultaneous nitrogen/sulfur chemiluminescence detector introduced by Antek Instruments recently.

5. Instrumentation and characteristics

As we will see in Section 6, the universal nitrogen and sulfur detection techniques are the most widely used ozone-induced chemiluminescence detection methods. The major commercially available instruments are the detectors based on these techniques. To assist readers who are not very familiar with ozone chemiluminescence to better understand the various applications presented below, a brief description of the detection system, a summary of some of the very unique features of ozone chemiluminescence detectors, and a quick comparison to other nitrogen/sulfur-selective detection methods are given in this section. Most of the discussion is with regard to the commercial GC (and sometimes SFC) detectors, unless LC is specifically mentioned.

5.1. Instrumentation

5.1.1. Ozone reaction chamber

The core of an ozone-induced chemiluminescence detection system is invariably a light-tight gas chamber where ozone and a chemiluminescent species mix and react to produce a metastable species that chemiluminesces. The emission is detected by a photon-sensing device, usually a photomultiplier tube (PMT). The basic design of the ozone reaction chamber is similar among all of the major manufacturers and research groups. The variations in

volume, shape and materials are based on considerations of residence time, efficiency of emission detection, chromatographic peak broadening and chemical inertness. Usually, an optical filter is placed in between the reaction chamber and the PMT to enhance selectivity for the desired chemiluminescence signal against unwanted light emission in other spectral regions.

Ozone is typically generated by a stream of oxygen (or air) flowing through a high voltage discharge.

Frequently, a vacuum is applied to the exit port of the reaction chamber to enhance chemiluminescence, because the chemiluminescence intensity is inversely related to the pressure of the chamber. The vacuum also serves an auxiliary function of keeping the water vapor pressure in the reaction chamber below the dew point, thus preventing condensation from happening in the chamber or the transfer lines leading to it. This function is particularly important in the case of the SCD where water is constantly generated from the conversion furnace (or the hydrogen/air flame) by oxygen/hydrogen reaction, and/or in the case of HPLC applications where water is a part of the chromatographic effluent, or is generated during the combustion of an organic effluent.

5.1.2. Conversion device

There are several variations in the conversion device that is used to convert the analyte to the chemiluminescent species. They range from a flame or furnace, catalyst beds to chemical solutions. However, for universal nitrogen/sulfur detection, usually it is a pyrolyzer (or furnace), or a hydrogen/air flame, which may be considered as an open pyrolyzer.

For nitrogen, either catalytic or non-catalytic combustion is used for the conversion step. At high temperatures, of around 1000°C or higher, almost all chemically bound nitrogen compounds are converted to NO by oxygen without the need for a catalyst. This type of non-catalytic high temperature furnace is employed in the commercial CLND. Another version of the nitrogen chemiluminescence detector, called NCD, employs a burner that is very similar to that used in the flameless SCD (discussed below).

For sulfur, however, simple oxidative combustion cannot produce the chemiluminescent species de-

sired. A reduction step or a reducing environment must be added. A number of seemingly very different devices have been used for this purpose. A hydrogen-rich flame was utilized when the original flame SCD was developed [71] and the commercial flame SCD utilizes a flame ionization detector (FID) as its flame source. Although a single device is used here, functionally two reaction steps take place. First, the analyte and the combustible sample matrix molecules are broken down in the hot oxygen/hydrogen reaction zone in the lower part of the flame. The sulfur chemiluminescent species is then generated in the reducing environment in the upper part of the flame and is subsequently transferred into the ozone reaction chamber by means of a sampling probe. One advantage of the flame SCD is that both the FID and

SCD responses can be obtained simultaneously. However, the conversion reaction requires much more hydrogen-rich conditions than those used for normal FID operation, hence, the FID response is not optimized.

In the flameless SCD, the flame is translated into an enclosed burner [74]. A schematic drawing of this type of burner assembly is shown in Fig. 2. The column effluent mixed with oxygen comes into the burner from the bottom and is oxidized before reaching the hottest zone in the middle, where the oxygen/hydrogen reaction takes place. More hydrogen-rich flow-rates are employed in this burner than in the flame version. When the combustion products leave the hot zone, they are in a very reductive environment, which facilitates the formation of the
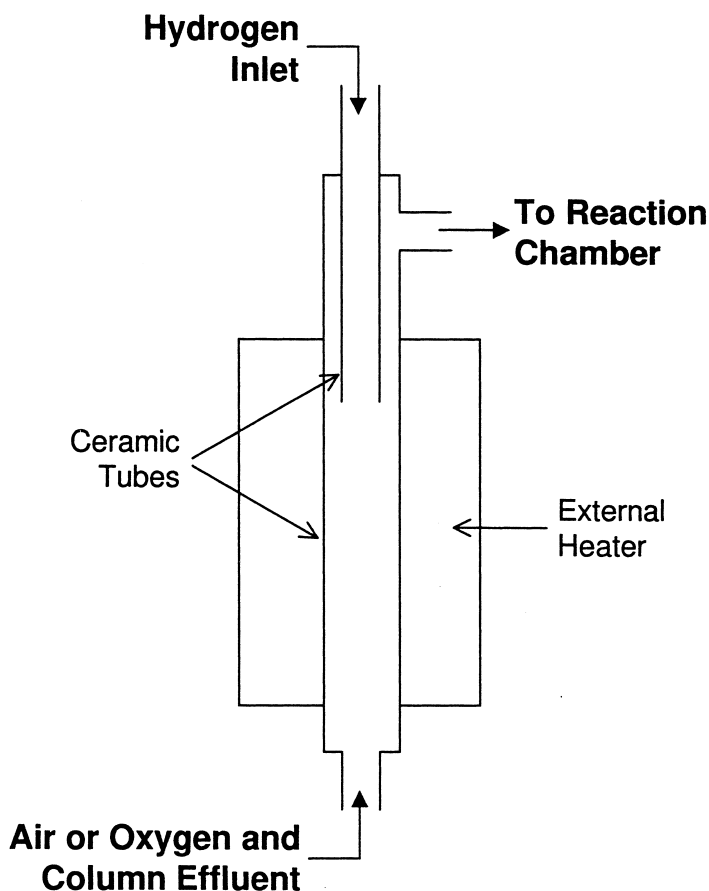
Fig. 2. Schematic diagrams of the burner assembly of the flameless SCD.

chemiluminescent sulfur species. No simultaneous FID signal is available from the standard configuration of the flameless SCD.

An FID adapter has been devised to allow the introduction of the flame gas from the FID to the flameless SCD burner, thus providing simultaneous FID/SCD detection. The drawback of this configuration is the loss of sensitivity by an order of magnitude due to the fact that only about 10% of the flame gas is transferred into the burner.

Alternatively, two physically separate oxidative and reductive furnaces have been employed [68,69] and a modified two-furnace configuration has been incorporated into a commercial total sulfur analyzer. Two-step oxidative/reductive pyrolysis can also be realized in a single furnace with two distinctive

zones, as employed in a different version of the SCD [75]. A schematic drawing of this configuration is shown in Fig. 3. In this case, oxidation of the column effluent takes place inside the inner ceramic tube at the lower part of the furnace and the subsequent reduction takes place in the outer ceramic tube at the upper part.

In any of the above configurations, the oxygen (or air) and hydrogen flow-rates are very critical in achieving the optimal conditions for complete combustion of the analyte molecules and any combustible matrix molecules (if present), as well as maximum generation of the sulfur chemiluminescent species. Evidence suggests that the ceramic probe (in the case of the flame SCD) and the high-purity alumina (ceramic) pyrolysis tubes (in the case of the
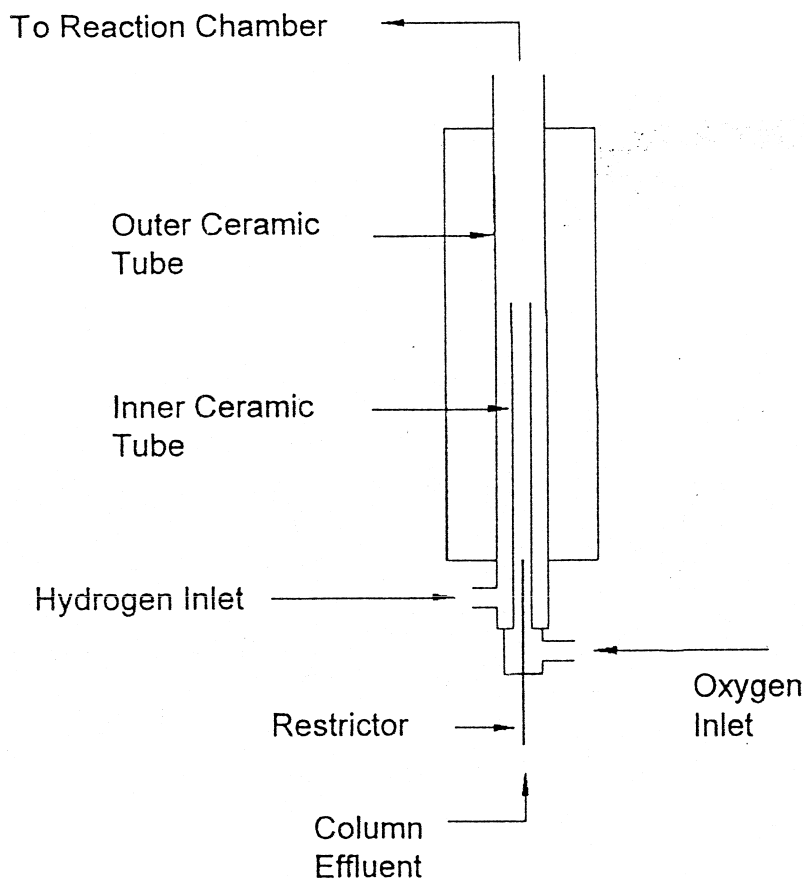
Fig. 3. Schematic diagram of the oxidative/reductive pyrolysis furnace of another non-flame SCD. Reprinted with permission from Ref. [76].

SCD with a furnace or a burner) have catalytic functions and their conditions sometimes significantly affect the SCD response. Therefore, conditioning or reconditioning of the probe or the pyrolysis tubes may be required from time to time.

For one version of the non-flame-based SCD, a much longer furnace has been introduced and has been claimed to significantly improve the overall performance, particularly the stability of the SCD [80]. The improvement has been attributed to the larger volume (thus longer residence time) and larger catalytic surface, for more complete combustion.

For HPLC applications, usually pre-combustion of the LC effluent with an additional large furnace and removal of water are required. These provisions are incorporated in a commercial HPLC chemiluminescence detector that is used in many of the applications discussed below.

5.2. Characteristics

A number of unique characteristics of nitrogen/sulfur chemiluminescence detection following the universal pyrolytic conversion reactions stem from the underlying principles (discussed in Section 4). These features set the nitrogen/sulfur chemiluminescence detection system apart from other element-selective detection methods.

5.2.1. Sensitivity

Unlike other luminescence methods, such as fluorescence measurements, light emission in chemiluminescence detection methods occurs in a dark background. Without interference from other light sources (apart from a little background chemiluminescence), the powerful gain of the PMT can be utilized to its fullest extent. Both nitrogen and sulfur chemiluminescence methods are among the most sensitive for these elements.

The detection limits for the nitrogen GC detector are typically in the low picogram of nitrogen range.

The sensitivity of the SCD is generally better than that of its nitrogen counterpart. The non-flame version is typically an order of magnitude more sensitive than the flame version. An extremely low detection limit of 25 fg S/s was reported by Shearer [74]. However, most authors have observed minimum detection limits (MDLs) of between 0.1 and 1 pg S/s.

5.2.2. Selectivity

The unparalleled selectivity over hydrocarbons is probably the most unique advantage of chemiluminescence techniques compared to other element-selective detectors. In the literature, very often the term 'specific' detectors or analyzers is used. Strictly speaking, the term 'specific' can only be used when the selectivity is infinity. In reality, most (if not all) detectors or analyzers possess finite selectivity and, hence, scientifically speaking, they can only be called 'selective'. However, a selectivity of 10^6 or higher may be considered 'specific' enough for practical purposes, and the term 'specific' is liberally used in this review, maintaining consistency with many cited original references.

From the combustion step in the mechanisms, reactions (6) and (8), the hydrocarbon backbone or matrix is converted to water and carbon dioxide, provided the combustion is complete. Neither of these species reacts with ozone to produce any discernable chemiluminescence in the spectral region used for nitrogen or sulfur detection. In other words, the detector is transparent to the hydrocarbons.

5.2.3. Linearity

The chemiluminescence detectors exhibit a linear response corresponding to the amount of nitrogen or sulfur present in the sample. This is a direct consequence of Eqs. (i) and (ii) when ozone is in excess. Because of the high sensitivity of these detectors, the minimum detectable concentration of the analyte is usually orders of magnitude lower than the concentration of the ozone. Often, deviation from linearity is due to saturation of the PMT or the electronic amplifier, when the operating conditions are not set optimally. The reported linearity range is typically between 10^3 and 10^5.

5.2.4. Equimolarity

Probably the most important characteristic of the chemiluminescence method is its equimolar response to the element in question (nitrogen or sulfur). This characteristic also directly stems from the mechanisms discussed above. For both nitrogen and sulfur, the combustion step converts all of the analytes to a

chemiluminescent species that contains a single nitrogen or sulfur atom (regardless of which sulfur chemiluminescence mechanism is considered). The equimolarity means that the chemiluminescence detector response to the same number of nitrogen/sulfur atoms is the same, regardless of the molecular structure of the analytes or sample matrix. The importance of the equimolar response is manifested in the numerous applications where (theoretically) any single nitrogen or sulfur standard can be used to calibrate the detector for measurement of any other nitrogen/sulfur analyte, even unknown ones. Excellent equimolarity has been reported, with per mole nitrogen/sulfur relative response factors varying only by several percent for vastly different analyte types. In reality, however, many other factors, but mainly those in sampling, introduce discriminations causing the final system response (as opposed to the detector response) to deviate from equimolarity. This is particularly a problem in the case of sulfur determination due to the reactive nature of certain sulfur compounds, such as hydrogen sulfide and mercaptans.

5.2.5. Interference and quenching

Although some authors have claimed certain chemiluminescence detectors to be free from interference or quenching effects, no systematic research on this subject has been carried out to date. Interference refers to a detector's response to anything other than the nitrogen/sulfur analyte. Quenching (sometimes also called negative interference) refers to the reduction of the detector's response to nitrogen/sulfur due to the presence of other substances (usually the solvent or hydrocarbon matrix) at the same time.

As we will see in Section 6, in real world applications, there are no significant amounts of heteroatoms other than nitrogen or sulfur in petroleum products. No observation of significant nonhydrocarbon interferences has been reported for petroleum and various other applications. The interference described in some cases is still that from hydrocarbons. Even with an extremely high rejection ratio of 10^6 or 10^7, hydrocarbon interference still can be a problem for certain ultratrace analyses. As mentioned above, hydrocarbon interference is caused by incomplete combustion. This is the result of

instantaneous lack of oxygen when the peak concentration of the interfering hydrocarbon enters the combustion furnace. Careful optimization of various detector conditions (such as combustion-gas flow-rates, furnace temperature, etc.), and chromatographic conditions (such as the carrier flow-rate, column temperature, split ratio, etc.) can reduce this interference to its minimum. However, there are often practical limitations as to how much one can reduce the hydrocarbon interference due to conflicting performance requirements, such as high sensitivity, short analysis times and so on.

Slight quenching was observed in some cases and none in others. The cause of quenching in terms of the detector conditions is still not clear, but is believed to be related to the non-radiational collision deactivation of the chemiluminescence emitter. The fact that it can be reduced or eliminated in some cases suggests that it is a correctable problem. More research on quenching is needed and should further improve nitrogen/sulfur chemiluminescence technology.

5.2.6. Other characteristics in chromatography

When nitrogen/sulfur chemiluminescence detection is coupled with chromatography, questions of compatibility and how the two techniques affect each other arise. Again, only limited characterization of various chemiluminescence detectors has been reported.

One issue that concerns chromatographers, particularly for fast GC applications, is peak broadening. With a significant volume in the flow paths of these detectors, some band broadening is bound to happen. However, the use of a vacuum appears to alleviate this problem substantially. Shearer et al. [81] showed slight band broadening in their characterization of the flame-based SCD. To investigate the effect, the SCD peak of 8 ng ethyl disulfide was studied at an expanded time scale, as illustrated in Fig. 2 of Ref. [81]. The SCD exhibited a peak width (full width at half maximum) of approximately 2.4 s, as compared to the simultaneously obtained FID response with a peak width of approximately 1.5 s. A slight tailing in the SCD response was also observed. Band broadening and tailing in other chemiluminescence detectors are probably similar.

Another problem reported was the effect of col-

umn bleed on the SCD response [81]. It appears to affect both flame-based and flameless SCDs, presumably by altering the surface characteristics of the ceramic probe or pyrolysis tubes. This phenomenon indirectly supports the notion that these surfaces participate in the conversion reaction catalytically.

It is not uncommon to observe a baseline rise from a chemiluminescence detector when the column temperature is close to its upper limit. This phenomenon has often been attributed to column bleed. However, based on the author's observation that the baseline rise frequently can be reduced by baking out the column and the interface between the GC column and the detector furnace, it may be caused by desorbed contamination from the column and/or the surfaces of the interface. Also, because the chemiluminescence detector is flow- and pressure-sensitive, the baseline rise may also be the result of a change in the intensity of background chemiluminescence. Little research on these aspects of the chemiluminescence detectors has been reported. A better understanding of these issues will undoubtedly improve future chemiluminescence detectors.

5.3. Comparison to other techniques

The need for and the characteristics of selective chromatographic detectors have been discussed and reviewed by several authors [38,41–43,82,83]. Hav-

ing discussed the characteristics of nitrogen/sulfur chemiluminescence detection, we can compare them to some other methods for the selective detection of these two elements. Table 1 compares the various performance characteristics and other aspects of the nitrogen/sulfur chemiluminescence detectors to those of other major GC element-selective detectors. Some of these alternative detection methods are summarized below.

5.3.1. Thermionic nitrogen phosphorus detection

The thermionic nitrogen phosphorus detector (TID or NPD) [84] is the most widely used detector for nitrogen-selective detection. The sensitivity is over an order of magnitude higher than that of the nitrogen chemiluminescence detector and the cost is much lower. However, the TID is more sensitive to phosphorus by about an order of magnitude. For applications in areas such as tobacco or pesticides, there may be substantial phosphorus interference. If the analytical interest is specifically of nitrogen-containing compounds in such areas, a detector that is highly selective to nitrogen is advantageous. The TID is considered somewhat difficult to operate. It is prone to drift and maintaining stable operation can be a challenge.

5.3.2. Flame photometric detection

There are quite a few sulfur-selective detection

Table 1
Comparison of major commercially available element-selective GC detectors

Detector		CLND or NCD	Flame SCD	Non-flame SCD	TID or NPD	FPD	PFPD	AED	ELCD
Sensitivity (N)	(g N/s)	10^{-12}	–	–	10^{-13}	–	10^{-11}	10^{-12}	10^{-11}
Selectivity (N)	(N/C)	10^7	–	–	10^4–10^5	–	10^5–10^6	10^4–10^5	About 10^5
Sensitivity (S)	(g S/s)	–	10^{-12}	10^{-13}	–	10^{-11}	10^{-13}	10^{-13}	10^{-11}
Selectivity (S)	(S/C)	–	$>10^6$	$>10^7$	–	10^3–10^5	10^6	10^4–10^5	About 10^5
Linear response		Yes	Yes	Yes	Yes	No	No	Yes	Yes
Linear range		10^4–10^5	10^4–10^5	10^4–10^5	$>10^4$	10^{3a}	10^{3a}	10^4–10^5	10^4–10^5
Equimolarity		Yes	Yes	Yes	Yes	No	No	Yes	Yes
Interference		No[b]	No[b]	No[b]	P	P, X, etc.	P, X, etc.	No	X, P, etc.
Quenching		Limited[c]	Limited[c]	Limited[c]	No	Yes	Yes[d]	No	No
Ease of use		Simple	Moderate	Simple	Moderate	Simple	moderate	Difficult	Difficult
Cost		Medium	Medium	Medium	Low	Low	Medium low	High	Low

[a] After linearization.

[b] Only limited amount of data available, no significant interference reported in literature.

[c] Some quenching observed by some researchers, but no quenching reported by others.

[d] Less quenching reported than for the regular FPD.

techniques currently in use. Among them, flame photometric detection (FPD) [85] has been, and probably still is, the most widely used. A thorough review of FPD [86] and a comparison to SCD [38] were provided by Farwell and coworkers. The FPD is a relatively robust and low-cost GC detector. However, its sensitivity is about an order of magnitude or more lower than that of the SCD and it exhibits a quadratic detector response. Although the FPD is a fairly selective detector for sulfur, with a rejection ratio of about 10^5 over hydrocarbons, it is still not sufficient for many trace level applications. Significant quenching by the presence of hydrocarbon solvents is another problem reported.

5.3.3. Pulsed flame photometric detection

Recently, an improved FPD called a pulsed flame photometer detector (PFPD) was developed by Cheskis et al. [87]. The PFPD employs pulsed flame and time-resolved emission detection with gated electronics. The added time-domain information is used to enhance element-specific detection and increase selectivity over hydrocarbons. The PFPD has been reported to improve the overall performance of the regular FPD substantially. The improvements include one to two orders of magnitude sensitivity enhancement, about an order of magnitude of increased selectivity and reduced quenching effects. Although sulfur and phosphorus detection is still the main application of the PFPD, the time-dependent emission detection affords the detector increased versatility in multi-element detection. Detection of 28 different elements, including sulfur and nitrogen, has been reported [88].

The PFPD exhibits comparable sensitivity to that of the nitrogen/sulfur chemiluminescence detectors, with the versatility of multi-element detection beyond nitrogen and sulfur and at a lower cost. However, the selectivity for both sulfur and nitrogen over hydrocarbons is still much lower than that of the chemiluminescence detectors, which is crucial in ultratrace analysis or for complex samples. The nonlinear PFPD response and column flow effect are some of the other disadvantages.

5.3.4. Atomic emission detection

Another alternative for selective nitrogen and sulfur detection is atomic emission detection (AED) [89,90]. The AED is a very powerful all-around multi-element-selective detection tool for researchers. The technique has been reviewed [91] and compared to SCD in chromatographic detection [41,42]. The detector response is linear and equimolar. However, in the narrowly defined task of nitrogen/sulfur-selective detection, it has a number of disadvantages compared to the chemiluminescence detectors. The sensitivity of AED for nitrogen is no higher than that of the chemiluminescence detector and its selectivity is much lower. The sensitivity for sulfur is comparable to that of the SCD, but again the selectivity is not quite as good. In addition to that, the AED is much more expensive and requires skilled operators.

5.3.5. Electrolytic conductivity detection

The electrolytic conductivity detector (ELCD) developed by Hall [92] (hence also referred to as the Hall detector) is another commercially available detector. A comparison of the ELCD to other GC sulfur-selective detectors including SCD was also provided by Wardencki and Zygmunt [41]. Although ELCD is reasonably sensitive and less expensive, it suffers from disadvantages such as lower selectivity, greater operational complexity and the need for routine maintenance.

5.3.6. Other

Some other sulfur selective detection methods have been used, but with little or limited applications in chromatography. Pyro-fluorescence is a robust, simple, total sulfur detection method with modest sensitivity [93], but no chromatographic application has been reported. In this method, nearly all sulfur-containing compounds are converted to sulfur dioxide by oxidative combustion and subsequently detected by UV fluorescence.

Hydrogenolysis and lead acetate stain detection [70,94] is another sulfur-selective detection technique that operates by converting all sulfur-containing analytes to hydrogen sulfide with high-temperature oxygen/hydrogen combustion followed by specific optical detection of the staining of the lead acetate tape by hydrogen sulfide. This method is quite sensitive for sulfur, but again, application in chromatography has been very limited in the literature.

6. Analytical applications

6.1. Non-chromatographic applications

Although this review is primarily in the scope of chromatography, it is important to include non-chromatographic applications of ozone-induced chemiluminescence to get a complete picture of this extensively used technology. A large number of early applications were detection systems (analyzers) without any separation of the sample. Many of them have been further developed into chromatographic applications. A broad knowledge of all facets of the technology and applications of ozone-induced chemiluminescence is very helpful for future development and applications.

6.1.1. Detection of ozone, olefins and other organic compounds

Covered here are the analytical applications utilizing direct chemiluminescent reaction of ozone with another gaseous compound (often the target analyte). This type of direct reaction is often used in environmental air monitoring. Hills and Zimmerman [95] described an instrument for the continuous monitoring of gaseous isoprene. The isoprene/O_3 reaction produces electronically excited HCHO, the subsequent emission of which was detected. A MDL of 400 parts-per-trillion (vol.) at $S/N = 2$ and a linear detection range of over three orders of magnitude were achieved. Selectivities over various alkenes and other compounds are also discussed. The first real-time isoprene fluxes from oak leaves, using a single living leaf, were measured. Another example of environmental air monitoring is described in a report of an ambient ozone analyzer for use in eddy-correlation measurements by Pearson [96]. Based on a chemiluminescent reaction with NO, it was designed primarily for use on meteorological aircraft, but was also suitable for tower measurements. It was highly sensitive (<0.1 ppbv at a 12-Hz bandwidth) as well as highly selective for ozone. The only known interference was a slight quenching of the chemiluminescence by water vapor.

A very different application is ozone detection and measurement in the human respiratory system implemented by Ben-Jebria et al. [97] and MacDougal et al. [98]. A fast-responding ozone analyzer was developed to sample gases respired by human subjects [97]. It was necessary that the reacting species be nontoxic. Fortunately, there were a large number of choices, thanks to the almost ubiquitous gas phase chemiluminescent reactions of ozone with various classes of compounds. Out of the ten alkenes tested, 2-methyl-2-butene was selected. The analyzer exhibited a linear response with an ozone resolution of 20 ppb and a 90% step response time of 200 ms. The same research group improved the performance of the ozone analyzer recently with the use of ethylene as the reactant gas [98], and achieved a minimum ozone resolution of 6 ppb and a 90% step response time of 70 ms.

6.1.2. NO detection based on the $NO + O_3$ chemiluminescent reaction

Nitric oxide is one of the common air pollutants. In an early attempt by Fontijn et al. [99] to monitor NO in the ambient air, a homogeneous chemiluminescent detector based on the $NO + O_3$ chemiluminescent reaction was tested. Ambient air and ozone (as the second reactant) were continuously flowed through and mixed in a reaction chamber. A linear response range from about 4 ppbv NO to at least 100 ppmv NO was obtained. Other components in the ambient air, NO_2, CO_2, CO, C_2H_4, NH_3, SO_2 and H_2O, were found not to interfere with NO monitoring.

Nitric oxide also plays an important role in human central nervous system cells. In a medical application by Weikert et al. [100], sensitive ozone chemiluminescence detection was used to study certain neural biological activities. NO formation was observed upon stimulation with various reagents. NO is also found in other parts of the human body, such as in breath, and serves various important biological functions. A fast and sensitive detection method was proved to be very useful.

Direct measurement of dilute nitric oxide in solution with chemiluminescence detection was described by Beckman and Conger [101]. In a novel extraction device, the hydrophobic nitric oxide in the sample solution was allowed to diffuse through a hydrophobic membrane into the ozone chemiluminescence detector. The instrument was capable of measuring NO at as low as 10 nM in a steady flow with a response time of under 1 s. When the

collected NO was allowed to accumulate, the sensitivity of this method could be increased by one to two orders of magnitude.

6.1.3. Total nitrogen detection based on the NO + O₃ chemiluminescent reaction

As discussed in Section 4.2.1, the conversion of nitrogen-containing compounds to NO by high temperature pyrolysis followed by chemiluminescence detection with ozone opens up an enormous range of possibilities. Various nitrogen-containing analytes, not necessarily capable of chemiluminescent reactions with ozone themselves, may be converted to NO and are subsequently measured. Thanks to the high temperature (typically $>1000°C$) employed in the method, most materials can be pyrolyzed and, therefore, are suitable for total nitrogen measurement. Because the method does not convert atmospheric nitrogen to NO, total nitrogen determination is sometimes referred to as total chemically bound nitrogen determination.

The commercial total nitrogen analyzer employing this pyro-chemiluminescence technique by Antek Instruments was initially developed to monitor the stack gases. Because it is capable of analyzing gases, liquids and solids, when appropriate sample introduction and combustion methods are used, a broad spectrum of applications ensued.

The petroleum and petrochemical industry has long been one of the major markets for nitrogen determination. Organic nitrogen compounds in refinery feedstocks poison hydrocracking catalysts and have other adverse effects on the refinery processes. A fast and reliable method for measuring total nitrogen in a variety of petroleum samples can be a valuable asset to the petroleum industry. Traditionally, the Kjeldahl method [102] and microcoulometric methods are used for the determination of nitrogen. There are a number of disadvantages associated with these methods, including the fact that they are time-consuming, involve hazardous chemicals, lack sensitivity and have bias in nitrogen recovery. The pyro-chemiluminescence method, on the other hand, offers a fast, clean, sensitive and accurate instrumental alternative for total nitrogen determination, as described by Hernandez [103]. In addition to the lighter hydrocarbon streams, Dreshel [104] and Shay and Woodward [105] reported successful complete

combustion of the more difficult residual fuel and petroleum residua. Jones and Daughton [106] tested 56 various representative chemical compounds and obtained 90 to 110% recovery of the nitrogen contents, thus establishing quantitative nitrogen conversion of the chemiluminescence method.

A short laboratory note by Snodgrass [107] described the application of the pyro-chemiluminescence method to total nitrogen determination in wastewater and process gases. Good correlation was obtained between the chemiluminescence method and the combined results from total Kjeldahl nitrogen and nitrate nitrogen by the US EPA method 352.1.

Walsh [108] used the pyro-chemiluminescence method to measure total dissolved nitrogen in seawater. The method was found to have sensitivity below 1 ng N and have near complete recovery (94–102%) for all tested inorganic, organic and recalcitrant nitrogen compounds.

In a separate study by Merriam et al. [109], a high-temperature catalytic oxidation technique was used in conjunction with the chemiluminescent nitrogen analyzer for determination of total dissolved nitrogen. The aqueous sample was pyrolyzed in an oxygen environment at $680°C$, converting all forms of nitrogen to nitric oxide, which was subsequently detected by ozone chemiluminescence.

Because protein contains nitrogen, it allows the use of the highly sensitive and selective pyro-chemiluminescence method as a powerful tool in protein assays. A rapid protein determination using pyro-chemiluminescence by means of nitrogen content was described by Gorimar et al. [110]. As an excellent alternative to the traditional protein assay procedures, this method offers not only accuracy and precision, but also speed of analysis and small sample requirement. A similar assay for protein, peptides and amino acids was developed by Luli and Lee [111]. The method was compared to the traditional Lowry method and was found to have 200-fold higher sensitivity, a broader linear range, minimum interference from non-nitrogenous buffers and reagents and a much shorter analysis time.

In clinical nitrogen balance studies, urinary urea nitrogen (UUN) has been used to estimate total urinary nitrogen (TUN), largely due to the fact that the traditional TUN method, typically one of the

several variations of the Kjeldahl technique [102], is a time-consuming laborious assay. However, the validity of this practice has been questioned [112–120]. In these studies, a pyro-chemiluminescence total nitrogen determination method has been used successfully in place of the traditional Kjeldahl method to determine TUN directly [113–115]. The accurate and cost-effective pyro-chemiluminescence TUN determination revealed the inaccuracies in TUN estimation from UUN. Much lower UUN/TUN values and larger variations were observed by Grimble et al. [113] for postoperative or injured patients, compared to those from a healthy population. Skogerboe et al. [114] found that the nitrogen balance estimated from UUN data underestimated nitrogen excretion in both healthy and hospitalized populations. The group lead by Konstantinides carried out extensive nitrogen balance studies comparing the results between estimation by UUN and direct measurement of TUN. In one test on a general surgical/trauma patient population, although on average about 80 to 90% of the TUN was represented by UUN, the variability ranged from 12 to 112% [116]. The authors concluded that $1.25 \times UUN$ was not an acceptable substitute for TUN. In another case, the UUN and TUN of 27 patients with thermal injuries were measured and the results showed that the UUN only represented approximately 65% of the directly measured TUN [117]. These results and other nitrogen balance studies were summarized by Konstantinides [118]. A similar line of investigation was carried out by Helms et al. [119] and Boehm et al. [120] in another medical research group. Important information on urinary nitrogen constituents in a group of postsurgical preterm neonates was obtained by various analytical methods, including that of TUN by pyro-chemiluminescence [119]. The validity of adjusted UUN as an estimate of TUN in three pediatric populations was also assessed [120].

The pyro-chemiluminescence technique was also used in similar medical research, such as metabolic rate and nitrogen balance measurements by Hyltander et al. [121].

6.1.4. Nitrate/nitrite and NO$_x$ detection based on the NO+O$_3$ chemiluminescent reaction

Another analytical method that takes advantage of the sensitive NO+O$_3$ chemiluminescence detection is the selective reduction of nitrate/nitrite to NO followed by ozone chemiluminescence detection. Determination of nitrate/nitrite at the parts-per-billion level by chemiluminescence was first reported by Cox [122]. Among the two anions, nitrites can be reduced under much milder conditions than those for nitrates. By carefully choosing appropriate reducing agents and conditions, only nitrites are reduced and selectively determined, while the total nitrate/nitrite content can be determined using stronger reducing conditions, and the nitrate concentration can be calculated by difference. Compared to the traditional colorimetric methods for nitrate/nitrite determination, the chemiluminescence method was found to have 10 to 100 times more sensitivity, as well as greater accuracy and precision. This method was later applied to the determination of nitrate/nitrite in seawater by Garside [123]. A precision of ± 2 nM was reported with analytical rates of 10–12 samples/ h. Braman and Hendrix [124] improved and simplified the analyses by using vanadium(III) as the reducing agent. Reduction of nitrite or nitrate+ nitrite was controlled by varying the reaction temperature. Much lower acidity was required, allowing a series of water samples to be analyzed sequentially, thus reducing the turn-around time. Again, nanogram detection limits were obtained. A variety of real-world samples were successfully analyzed. Further development based on these chemiluminescence methods resulted in the commercial nitrate/nitrite instrument reported by Boehm [125].

Delany et al. [126] and Dickerson et al. [127] described a modification of the commercial TEA instrument for ambient air monitoring. Changes including a larger gold-coated reaction chamber, increased ozone flow and a faster vacuum pump resulted in much higher sensitivity. An extremely low detection limit of about 10 part-per-trillion (ppt) with a 20-s response time, or about 45 ppt with a 1-s response time, was achieved. The incorporation of several converters to the enhanced detector allowed detection of a number of different nitrogen species.

6.1.5. Total sulfur detection based on ozone-induced chemiluminescent reactions

Total sulfur detection was achieved with the development of the universal sulfur chemiluminescence detector [71]. A field evaluation of this detector by Benner and Stedman [128] as a real-time total atmospheric sulfur detector, compared to a

flame photometric detector and a fluorescent SO_2 monitor, was carried out. The potential of this technology to be used as a sensitive yet interference-free ambient air monitor was shown.

Commercial development of sulfur chemiluminescence detection technology has resulted in total sulfur analyzers manufactured by both Antek Instruments and Sievers Instruments primarily for petroleum applications.

6.1.6. Detection of other elements based on ozone chemiluminescent reactions

Although most applications of gas-phase ozone-induced chemiluminescent reactions have focused on those involving nitrogen and sulfur, detection of other elements by ozone gas phase chemiluminescence has been reported [129–132].

Fujiwara et al. [129] first described ozone oxidation and chemiluminescence detection for determination of arsenic, antimony, tin and selenium. The procedure was based on the reactions between ozone and the hydrides of the analytes, and the detection limits were found to be 0.15 ng for As, 10 ng for Sb, 35 ng for Sn and 110 ng for Se. Matsumoto et al. [130] then reported phosphorus determination by continuous reduction of phosphorus-containing compounds to phosphine in a liquid sample by passing the sample mist through an incandescent carbon tube, followed by detection of the $PH_3 + O_3$ chemiluminescence. Ozone chemiluminescent reactions with arsenic and tellurium hydrides were also observed. Fujiwara et al. [131] continued this line of research and described the determination of phosphate by ozone–phosphine gas phase chemiluminescent reaction. The same research group subsequently reported the determination of silicate in natural waters by an ozone–silane gas phase chemiluminescent reaction [132]. Although phosphorus and arsenic gave positive interference, the existence of them in natural waters was usually negligible. River waters and seawaters were analyzed with this method and the results agreed with an independent method of molybdenum yellow colorimetry.

6.2. Gas chromatography

It is probably not surprising that gas-phase ozone-induced chemiluminescence has found the broadest applications in gas chromatography (GC), among the

various chromatographic techniques. The fact that the analyte is in the gaseous phase when entering the GC detector makes the two techniques intrinsically compatible. Numerous applications of this technology have been made. Only representative applications can be summarized here.

6.2.1. Detectors based on direct ozone chemiluminescent reactions with the analyte

Complex refinery samples from cracking processes usually contain large amounts of saturated and unsaturated hydrocarbons that are difficult to separate even with high-resolution GC. An olefin-selective detector can simplify the hydrocarbon analysis considerably. Bruening and Concha [133,134] described such an olefin-selective GC detector that made use of the chemiluminescent reactions of ozone with the various olefin compounds. The selectivity of the detector was based on the variation in reactivity towards ozone of different classes of compounds and it could be adjusted by varying the detector temperature, which was adjusted between 50 and 250°C. Extensive tests on a group of olefins for detector performance in terms of sensitivity, linearity and selectivity were carried out. The detector was found to be mass flow-rate-sensitive with detection limits frequently at the nanogram level and gave a linear response to various types of compounds tested over several orders of magnitude. The utility of this detector was demonstrated in hydrocarbon analysis as shown in Fig. 4. Considerably different chromatograms were obtained from the detector with different detector temperatures, which were compared to the chromatogram from an FID.

Direct ozone chemiluminescent reactions with a number of reduced sulfur compounds were used for sensitive detection of these compounds by Kelly et al. [135]. It was shown to be sensitive to low ppb and sub-ppb levels for the four reduced sulfur compounds, hydrogen sulfide, dimethyl sulfide, carbonyl sulfide and carbon disulfide. This method was later adapted to serve as a GC detector [136]. Detection limits for several reduced sulfur compounds ranged from sub-nanogram to low tens of nanograms of analyte. High selectivity was the strong point of this detector, over seven orders of magnitude for most of the compounds investigated. It still possessed about three orders of magnitude
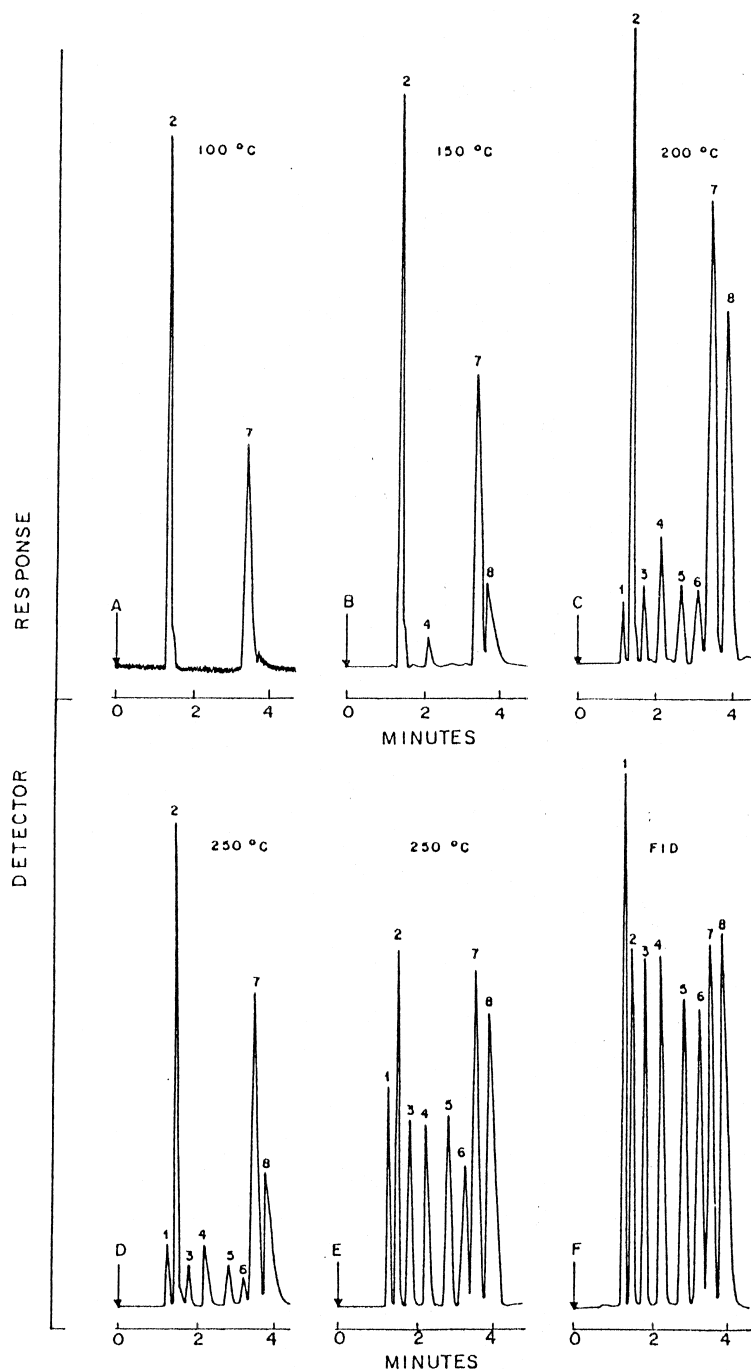
Fig. 4. Hydrocarbon analysis using a chemiluminescence detector with an ozone mixture flow-rate of 100 ml/min (A, B, C and E) and 300 ml/min (D), and using a commercial FID (F). Chromatographic conditions: column: 3 m, 5/64″ I.D.; packing: 10% diethylene glycol succinate on 100–150 mesh Porasil C; carrier gas: nitrogen at 60 ml/min; injector temperature: 200°C; column temperature: 127°C. Peaks: (1) cyclohexane; (2) hexane; (3) heptane; (4) benzene; (5) 1-octane; (6) 2,2,5-trimethylhexane; (7) octene and (8) toluene. Reprinted with permission from Ref. [134].

selectivity for the only significant interference, that from olefins.

6.2.2. Nitrosamine-selective detection based on the $NO + O_3$ chemiluminescent reaction

The selective thermal cleavage of the N–NO bond in nitrosamines, as discussed above in Section 4.2.1, gives rise to the possibility for a highly selective nitrosamine detector [65]. The first nitrosamine-selective instrument, the TEA, was developed by Fine and coworkers. The TEA had been shown to exhibit sub-ng/ml detection limits and was highly selective for N-nitroso compounds [137,138]. Application of this technology to GC [139,140] allowed speciation and the selective detection of a variety of nitrosamine compounds in complex samples. Thanks to the high sensitivity, and especially the high selectivity of TEA, little sample cleanup was required. Detailed characterization of the GC–TEA performance [140] showed a nearly equimolar response among various N-nitroso compounds, as reflected by the relative response factors at nitrosyl mole basis shown in Table 2. A list of non-interfering compounds for TEA and the relative response factors for various interfering species are also given in Tables 3 and 4, respectively.

This sensitive method was employed in the determination of N-nitrosodimethylamine (NDMA) at part-per-trillion levels in drinking waters and contaminated groundwaters by Tompkins et al. [141]. The aqueous sample was filtered and extracted using

dichloromethane, which was subsequently concentrated and absorbed on a carbon sorbent trap. The concentrated residues were then chromatographed and NDMA was selectively detected by a CLND in its nitrosamine-selective mode. An ultimate MDL of 2 ng of NDMA/l was achieved. This method, along with a modified, automated procedure, was successfully used to measure NDMA concentrations (spanning four orders of magnitude) in drinking water and groundwater samples routinely.

6.2.3. Nitrogen-specific detection based on the $NO + O_3$ chemiluminescent reaction

The successful application of $NO + O_3$ chemiluminescence detection to total nitrogen determinations was followed by its chromatographic applications. Kashihira et al. [142] constructed a nitrogen detector for GC by combining a commercial nitric oxide analyzer with a pyrolyzer catalyzed by a hot platinum catalyst. The detector was found to be quite sensitive and specific only to nitrogen. It was used to determine the collection ability of several adsorbents for ammonia and amines. Almost 100% recovery of nitrogen was observed.

The operating conditions of the TEA could also be modified to achieve nitrogen-specific detection. Yu et al. [143] reported the determination of nitrated polycyclic aromatic hydrocarbons (nitro-PAH) in diesel particulates by raising the operating temperature of the catalytic pyrolyzer above 800°C. The detection limit was determined to be 10–25 pg

Table 2
TEA response factors for different N-nitroso compounds[a]

N-Nitroso compound	Response per nitrosyl group	Relative response, nitrosyl mole basis
N-Nitrosodimethylamine	18.1	1.00
N-Nitrosodiethylamine	19.4	1.07
N-Nitrosodipropylamine	19.8	1.09
N-Nitrosodiphenylamine	20.1	1.11
N-Nitroso-N-ethylaniline	18.6	1.03
9-Nitrosocarbazole	17.6	1.03
N-Nitroso-N-methyl urethane	18.8	1.04
N-Nitroso-N-phenylbenzylamine	16.7	0.92
Ethyl-N-nitrososarcosinate	17.5	0.97
N-Methyl-N-Nitroso-N-nitroguanidine	18.4	1.02
N-Nitrosopiperidine	21.2	1.17
Dinitrosopiperazine	15.7	0.87

[a] Data from Ref. [140]

Table 3
Representative list of compounds that give no interference on the TEA[a]

Acetic acid	Ethyl carbamate	Oxalic acid
Acetone	Ethylene glycol	n-Pentane
Acetonitrile	Fluorobenzene	Phenyl hydrazine
Alizarin red	Gasoline	D,L-Phenylalanine
Ammonia (gas)	Glycerol	p-Phenylazoaniline
Benzene	D-Glucose	Phosphoric acid
Benzylsalicylate	Glutamic acid	Propane (gas)
2-Butoxy ethanol	n-Hexane	Pyridine
Carbon dioxide	Hydrogen (gas)	Quinine
Carbon disulfide	Hydroquione	Sodium acetazolamide
Carbon monoxide (gas)	8-Hydroxyquinoline	Sulfadiazine
Carbon tetrachloride	Inosine	Sulfanilic acid
Chloral hydrate	D,L-isoleucine	Tetrahydrofuran
Chlorobenzene	Methane (gas)	Theophylline
1-Chloropropane	Methyl acetate	Toluene
2-Chloropropane	N-Methyl bisacrylamide	2,4,6-Trichlorophenol
Cyclohexane	2-Methyl butane	2,2,4-Trimethylpentane
Cyclopentane	Methyl formamide	D,L-Tryptophan
1,2-Dichloroethane	Methyl isobutyl ketone	Urea
2,3-Dichloropropane	Methyl orange	Uric acid
Diethylether	Methyl red	Urethane
Dimethylamine (gas)	Naphthalene	Water
p-Dioxane	Nitrogen (gas)	Xylene
Diphenylamine	Nitrobenzene	
Ethyl acetate	o-Nitrotoluene	

[a] Reprinted with permission from Ref. [140].

Table 4
Mole basis response ratio for those compounds that give a detectable response on the TEA[a]

Compound	Response ratio (RR)
N-Nitroso compounds	1.0
2,2′,4,4′,6,6′-hexanitro-diphenylamine	1.4
Isopentylnitrite	1.0
D,L-Cyclohexylaminenitrite	1.0
Pentylnitrite	1.0
Sodium nitrite (in H_2O)	1.0
Sodium nitrate (in H_2O)	$\simeq 1.0$ (very slow response lasting from hours to days)
Nitric acid	$\simeq 1.0$ very slow response lasting from hours to days)
Dimethyl sulfoxide	0.03
Hydrazine (95%)	0.03
5-Nitrouracil	0.017
p-Nitrosodiphenylamine	0.0050
3-Nitrophthalidimide	0.0030
Nitromethane	0.0018
Ammonium hydroxide	0.0016
Dimethylglyoxime	0.0010
Dimethylamine hydrochloride	0.0009
Diphenyl carbazone	0.0007
Aniline	0.0003
2-Nitroso-1-naphthol	0.0002

[a] Reprinted with permission from Ref. [140].

injected on-column. 1-Nitronaphthalene, 2-nitronaphthalene, 2-nitrofluorene and 1-nitropyrene were found in the diesel particulate sample. The presence of these nitro-PAHs was confirmed by mass spectrometry.

A commercial nitrogen-specific GC detector called a chemiluminescent nitrogen detector (CLND) was introduced by Antek Instruments in 1986. It was basically a scaled-down version of the Antek total nitrogen analyzer to accommodate much smaller gas flow-rates and dead volume requirements [144]. Like the total nitrogen analyzer, it has found a broad range of applications primarily due to its universal response to almost all nitrogen-containing compounds. Britten [144] and Courthaudon and Fujinari [145] showed applications of this detector to a variety of fields from petroleum industry, agricultural/environmental studies, to pharmaceutical research. Some of these applications are illustrated by Figs. 5 and 6, respectively. To facilitate method development in agricultural/environmental studies, GC–CLND was used to detect five pesticides, acephate, dimethoate, parathion, chlorpyrifos and isazofos, as shown in Fig. 5. Fig. 6 illustrates the detection of the nitrogen-containing natural products enilconazole and azaconazole, which helps to provide additional confirmatory information to pharmaceutical development.
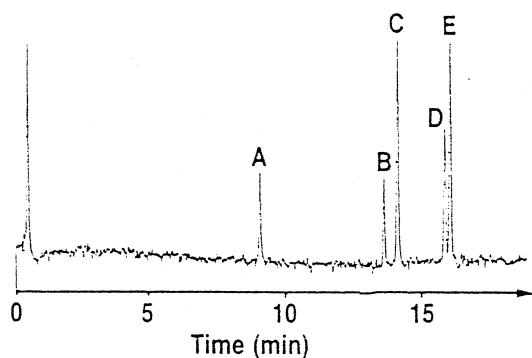

Fig. 5. GC–CLND analysis of a standard solution containing five pesticides. GC conditions: column: SPB-35, 30 m, 0.53 mm I.D., 1.0 μm film thickness; injector temperature: 220°C; column temperature program: 120°C for 1 min, 120–250°C at 5°C/min, 250°C for 5 min, 1 μl splitless injection. Peaks: (A) acephate (165 pg N); (B) dimethoate (128 pg N); (C) parathion (162 pg N); (D) chlorpyrifos (110 pg N); (E) isazofos (304 pg N). Reprinted with permission from Ref. [145].
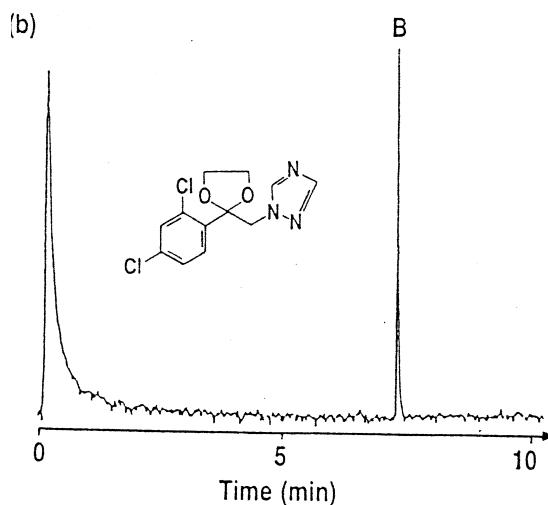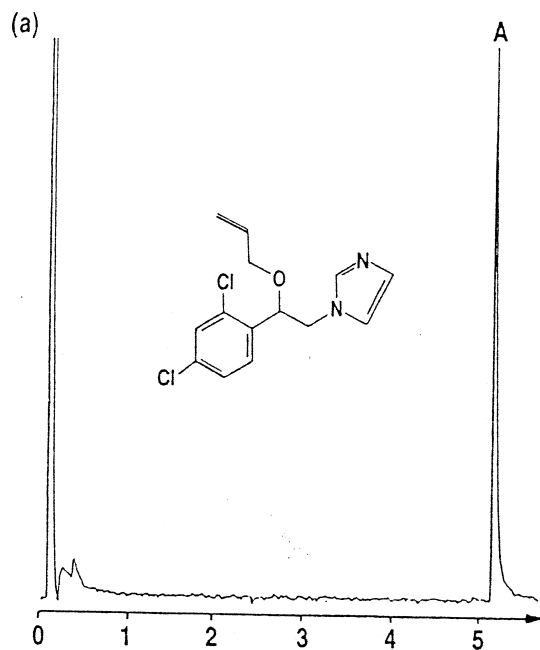

Fig. 6. GC–CLND analysis of extractions from natural products containing (a) enilconazole and (b) azaconazole. GC conditions: column: RSL-300 (polyphenylmethylsiloxane), 10 m, 0.32 mm I.D., 0.3 μm film thickness; injector temperature: 250°C; column temperature program: (a) 100–280°C at 30°C/min, (b) 100–280°C at 20°C/min; splitless injection. Peaks: (A) 9.97 ng of enilconazole and (B) 25 ng of azaconazole. Reprinted with permission from Ref. [145].

The application of GC–CLND in the food and flavor industry is best demonstrated by the work of Benn et al. [146]. This is well illustrated in Fig. 7 in the detection of galbanum oil adulteration. Root body (a material containing three nitrogenous isomers) was often added in small amounts to elude organoleptic examination of the galbanum oil. It would have been extremely difficult to detect this adulteration in an FID chromatogram (see Fig. 7a). Comparing the CLND chromatograms of the genuine galbanum oil (Fig. 7b) and a root body standard (Fig. 7d), the addition of root body in the oil was readily detected (Fig. 7c) and became the telltale sign of the adulteration. Nitrogen-specific detection was employed to pinpoint the nitrogen-containing compounds of interest, by rendering the very complex matrix transparent.

The petroleum and petrochemical industry is perhaps the most important market for GC nitrogen-specific detectors. The detrimental effects of nitrogen on certain refinery processes and the importance of nitrogen speciation have been increasingly recognized. One of the unique characteristics of the CLND, high selectivity for nitrogen, is a major advantage over other nitrogen-selective GC detectors. Chawla [147] described the development of a GC method with nitrogen chemiluminescence detection. The detector exhibited a uniform and linear response to different classes of nitrogen compounds and a MDL of 100 ppb nitrogen per component. The method was capable of quantitative nitrogen speciation for refinery streams ranging from gasoline to diesel fuel. In addition, the total nitrogen content of the sample could also be determined accurately.

6.2.4. Redox chemiluminescence detection based on the $NO + O_3$ chemiluminescent reaction

As mentioned above, the detection of $NO + O_3$ chemiluminescence may be exploited in a different way to detect certain compounds that are capable of reducing NO_2 to NO when passing through a heated gold catalyst bed [148–153]. This detection scheme, researched and developed by Sievers' group, resulted in a commercial detector called a redox chemiluminescence detector (RCD) manufactured by Sievers Instruments. The detector was described by Nyarady et al. [148]. The RCD was found to be sensitive to a number of compounds that were not

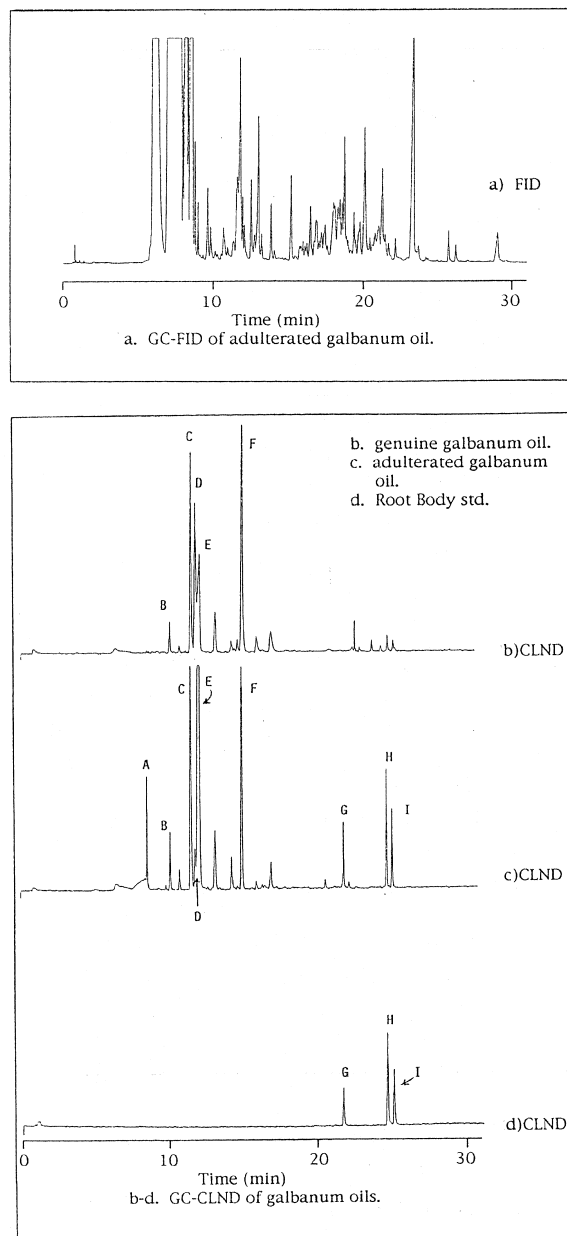a. GC-FID of adulterated galbanum oil.

b-d. GC-CLND of galbanum oils.

Fig. 7. Detection of adulteration of galbanum oil. (a) GC–FID chromatogram of adulterated galbanum oil; (b) GC–CLND chromatogram of genuine galbanum oil; (c) GC–CLND chromatogram of adulterated galbanum oil; (d) GC–CLND chromatogram of a root body standard. Peak A: 2,4,6-trimethylpyridine; Peaks B–F: naturally occurring pyrazine compounds in galbanum oil; Peaks G–I: root body isomers. Reprinted with permission from Ref. [146].

sensitively detected by an FID, such as ammonia and hydrogen sulfide. On the other hand, it did not respond to many compounds that form the bulk of the sample matrix, such as water and alkanes. The relative response factors were reported to vary over six orders of magnitude, depending on the analyte and detector temperature. A list of compounds that produced a response and another list of compounds that did not interfere significantly are given in Tables 5 and 6, respectively. The selectivity was further investigated by varying the active metal and the temperature of the catalyst [150]. The striking effects are illustrated in Fig. 8. The selectivity control permitted selective analysis for a wide range of sample types. This detector was used to measure trace level carbon monoxide in hydrocarbon matrices without any preconcentration [151]. Samples containing 0.2 ppmv of carbon monoxide in ethylene were readily quantitated. Further research on the catalyst was carried out [152,153]. A superconducting oxygen-deficient perovskite, $YBa_2Cu_3O_7$, was tested and was found to exhibit strong catalytic activity, especially for alcohols.

Table 5
Compounds that produce an RCD response[a]

C_1 to C_{10} 1-alcohols	1-Nitropropane
2-Pentanol	2-Nitropropane
2-Octanol	*tert.*-Butyl disulfide
4-Methyl-2-pentanol	1-Octanethiol
Benzyl alcohol	Tetrahydrothiophene
2-Phenylethanol	Benzene
3-Phenylpropanol	Toluene
C_1 to C_{10} *n*-aldehydes	Naphthalene
Benzaldehyde	1-Methylnaphthalene
p-Tolualdehyde	Indole
Anisaldehyde	Tetrahydrofurfuryl alcohol
Phenylacetaldehyde	Ammonia
C_1 to C_4 *n*-carboxylic acids	Carbon disulfide
Acetone	Hydrogen peroxide
Butanone	Hydrogen
4-Methyl-2-pentanone	Carbon monoxide
5-Nonanone	Sulfur dioxide
Aniline	Hydrogen sulfide
2,6-Dimethylaniline	Diethyl ethylphosphonate
N,N-Dimethylaniline	Triethyl phosphite
2,6-Dimethylphenol	Tri-*n*-butyl phosphite
Cyclohexene	Dibutyl phosphite
2-Hexene	Triethyl phosphate
1-Methylcyclohexene	

[a] Reprinted with permission from Ref. [148].

Table 6
Compounds that produce very low or no detectable RCD response with the catalyst bed at 350–400°C[a]

Compound	RRF
Water	$<1\times10^{-6}$
Dichloromethane	$<1\times10^{-6}$
Pentane	1×10^{-6}
Octane	$<1\times10^{-6}$
Hexane	2×10^{-6}
2,2,4-Trimethylpentane	1×10^{-6}
Cyclohexane	1×10^{-6}
Tetrahydrofuran	2×10^{-5}
2-Methyltetrahydrofuran	2×10^{-5}
C_7 and C_9 to C_{14} *n*-alkanes	N.D.[b]
1,2-Dichloroethane	N.D.
tetrachloroethylene	N.D.
oxygen	N.D.
nitrogen	N.D.
helium	N.D.
argon	N.D.
carbon dioxide	N.D.

[b] N.D., no detectable response was observed, and the RRF was not determined.
[a] Reprinted with permission from Ref. [148].

6.2.5. Sulfur-specific detection based on ozone-induced chemiluminescent reactions

The most widely used chemiluminescence detector in chromatography is undoubtedly the sulfur chemiluminescence detector (SCD). With the advent of commercial sulfur chemiluminescence detectors (manufactured by Sievers Instruments and Antek Instruments), there has been explosive growth of applications thanks to the unique features of this type of detector.

Column selection and SCD optimization were discussed by Hutte et al. [154]. The effects of stationary film thickness, column length and internal diameter for sulfur determination in hydrocarbon matrices were investigated. Non-polar methyl silicone columns with thick films were found to be suitable for the separation of most sulfur compounds. In addition, a sub-ambient starting column temperature was needed to separate sulfur gases with these columns.

The performance of the flame SCD interfaced to a capillary column GC was evaluated by Shearer et al. [81]. The detector was reportedly found to be at least one order of magnitude more sensitive than most flame photometric detectors (FPD), exhibited a
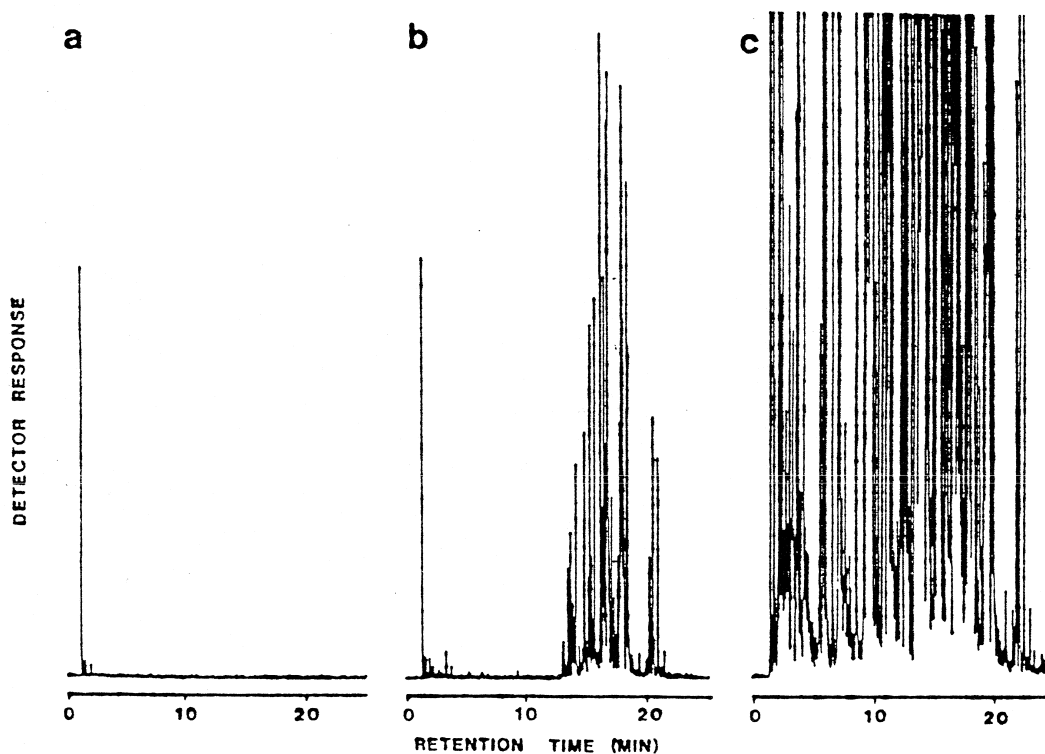
Fig. 8. Gasohol analysis by GC–RCD at different gold catalyst bed temperatures. (a) At 360°C, only methanol is detected; (b) at 390°C, methanol and the later eluted aromatic fraction components of gasoline are detected; (c) at 420°C, the analysis is even less selective, producing a chromatogram as complex as that of an FID. GC conditions: column: DB-1701, 25 m, 0.32 mm I.D., 0.25 μm film thickness; column temperature program: 30°C for 1 min, 30–250°C at 6°C/min, 1.4 μl 1:50 split injection. Reprinted with permission from Ref. [150].

sulfur-to-carbon selectivity greater than 10^6 and a linear and equimolar response. No appreciable quenching was observed.
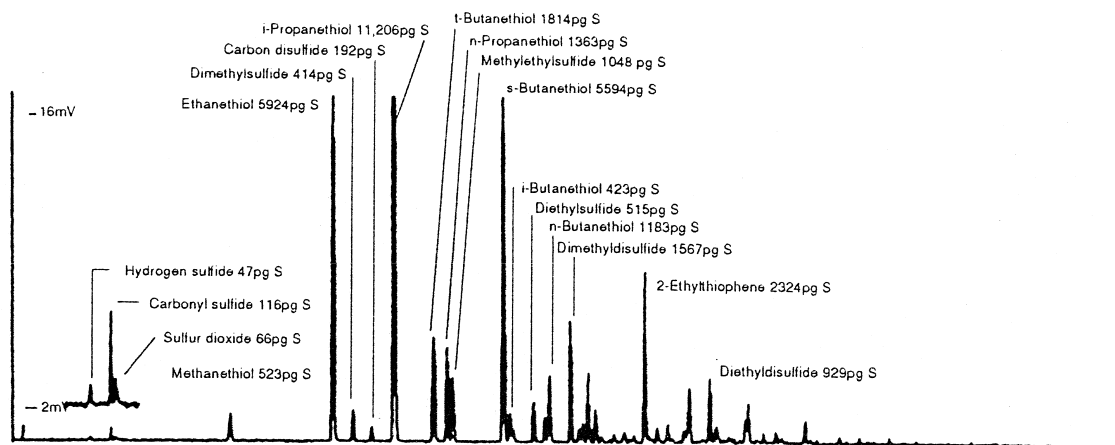
Sulfur determination by GC–SCD in difficult matrices was investigated by Johansen and Birks [155]. Trace level sulfur speciation and detection in refinery streams has always been difficult due to the complex hydrocarbon matrix. The SCD was shown to be able to selectively detect picogram levels of sulfur components in a natural gas stream, as shown in Fig. 9. Many other applications in the petroleum and petrochemical industry have been reported. Shearer et al. [156] described the gas chromatographic determination of sulfur in liquid petroleum gas (LPG) and gasoline samples with the flameless SCD. The detector was evaluated with an emphasis on practical applications in plant laboratories. In addition to the usual advantages, the flameless SCD

was found to be easier to use and more reliable than the flame SCD.

Application of the SCD to light hydrocarbon streams was also implemented by Chawla, Di Sanzo and co-workers [157,158]. Speciation and quantitation of the process streams containing 0.01–3.13% (w/w) of sulfur were achieved [157]. Further work from this group resulted in sensitive determination of sulfur in stabilized gasoline-range process streams with total sulfur ranging from 1 to over 4000 ppm [158]. The detection limit per sulfur component was found to be approximately 50 ppb.

The SCD has found many applications in the beer and wine industries. Johansen et al. [159] described the detection of sulfur compounds in hop oils using a flame-based SCD. The SCD was also used extensively in the measurement of flavor-active volatile sulfur compounds in beer. Development of techniques for

Sulfur Chemiluminescence Detector Response

i-Propanethiol 11,206pg S
Carbon disulfide 192pg S
Dimethylsulfide 414pg S
Ethanethiol 5924pg S
t-Butanethiol 1814pg S
n-Propanethiol 1363pg S
Methylethylsulfide 1048 pg S
s-Butanethiol 5594pg S

i-Butanethiol 423pg S
Diethylsulfide 515pg S
n-Butanethiol 1183pg S
Dimethyldisulfide 1567pg S
2-Ethylthiophene 2324pg S
Diethyldisulfide 929pg S

— 16mV

Hydrogen sulfide 47pg S
Carbonyl sulfide 116pg S
Sulfur dioxide 66pg S
Methanethiol 523pg S

— 2mV

Flame Ionization Detector Response

Propane
n-Butane
i-Pentane
n-Pentane

—1000mV

i-Butane

Ethane

2-Methylhexane
3-Methylpentane
n-Hexane

Methylcyclopentane
2-Methylpentane
n-Heptane
Methylcyclohexane
Toluene
n-Octane

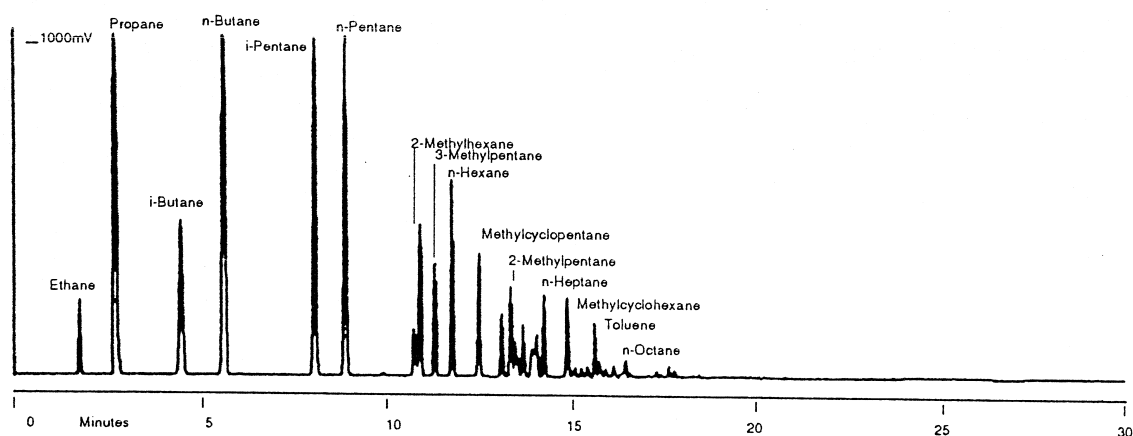0   Minutes   5   10   15   20   25   30

Fig. 9. Natural gas analysis by GC–SCD/FID. GC conditions: column: SPB-1 SULFUR, 30 m, 0.32 mm I.D., 4.0 μm film thickness; column temperature program: −10°C for 3 min, −10 to 300°C at 10°C/min, 10:1 split injection; sample: 0.5 ml natural gas condensate. Reprinted with permission from Ref. [155].

this application was reported by Burmeister et al. [160] and Dercksen et al. [161]. The SCD was found to be a more sensitive replacement of FPD. Volatile sulfur components in beers were readily detected. This technique was used to distinguish beers with different characteristics. Fig. 10 shows the SCD chromatograms of two distinctively different beers, one with sulfury character (Fig. 10A) and the other non-sulfury (Fig. 10B). This method was also com-

pared to flame ionization, flame photometry and mass spectrometry detection methods by Goldstein et al. [162].

Simultaneous nitrogen and sulfur detection has also been applied to the petroleum and petrochemical industry. Yan et al. used this technique to obtain simultaneous hydrocarbon, sulfur and nitrogen chromatograms of various refinery streams (an example is shown in Fig. 11) [79]. A post-column splitter was
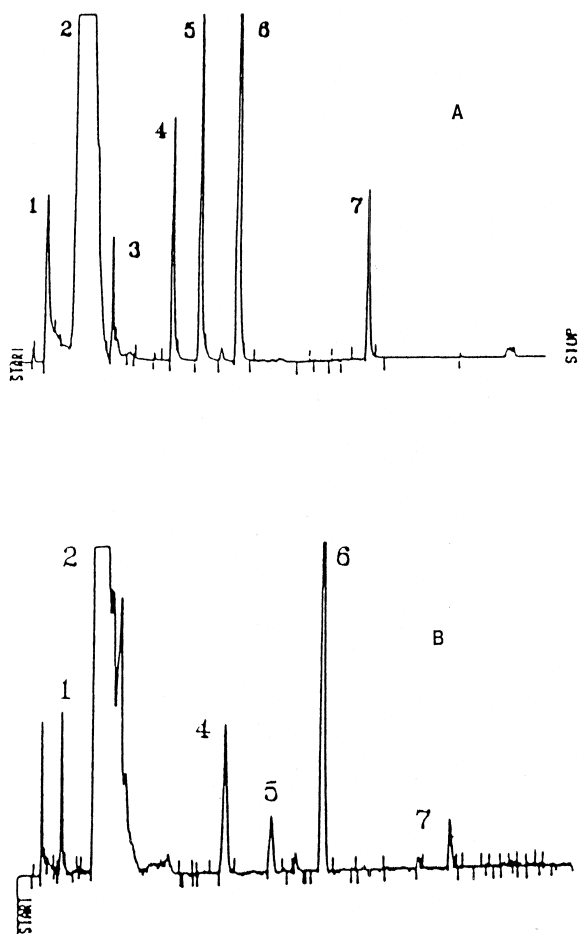
Fig. 10. GC–SCD chromatograms of (A) a beer with a sulfury character and (B) a non-sulfury beer. GC conditions: column: DB-5, 30 m, 0.53 mm I.D., 1.5 μm film thickness; injector temperature: 150°C; column temperature program: 20–50°C at 5°C/min, 50–180°C at 8°C/min, 10:1 split injection. Peaks: (1) methanethiol; (2) dimethyl sulfide; (3) ethylene sulfide; (4) diethyl disulfide; (5) dimethyl disulfide; (6) isopropyl sulfide (internal standard) and (7) dimethyl trisulfide. Reprinted with permission from Ref. [161].

employed to split to an FID and a simultaneous nitrogen/sulfur chemiluminescence detector, respectively. Very closely matched retention times between the nitrogen and sulfur channels were observed, as demonstrated in Fig. 12 by the simultaneous chromatograms in both nitrogen and sulfur channels of an analyte molecule, thiamorpholine, containing both nitrogen and sulfur.
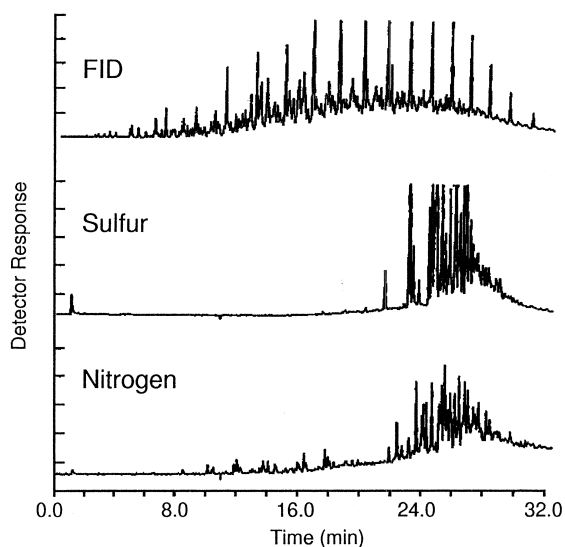

Fig. 11. Diesel fuel analysis by GC and simultaneous FID and nitrogen/sulfur chemiluminescence detection. The three-way (FID, sulfur and nitrogen) chromatograms of a heavy diesel fuel sample were obtained with a post-column split between the FID and the simultaneous nitrogen/sulfur chemiluminescence detector. GC conditions: column: SPB-1, 30 m, 0.32 mm I.D., 4.0 μm film thickness; injector temperature: 250°C; column temperature program: 40–300°C at 10°C/min, 300°C for 6 min, 1 μl splitless injection. Data from Ref. [79].

6.2.6. Elemental boiling point distributions in simulated distillation

Simulated distillation (SimDis) is a technique used in the refinery industry to estimate the hydrocarbon boiling range distribution of various petroleum fractions for process control, quality assurance and product specification purposes. There is a growing need to measure the boiling point range distribution of heteroatoms (mainly sulfur and nitrogen) in these petroleum fractions to further improve the process and quality. Naturally, sulfur and nitrogen chemiluminescence detectors have been interfaced to SimDis systems to meet this challenge. Young and Fujinari [163] reported the SimDis application of the CLND to various refinery streams. Fig. 13 shows simulated distillation results from a nitrogen-spiked (about 90–100 ppm N) gasoline sample (Fig. 13A) and a 95–105 ppm N reference gas oil (RGO) sample (Fig. 13B) with separate AED or CLND detection. A good nitrogen boiling point distribution
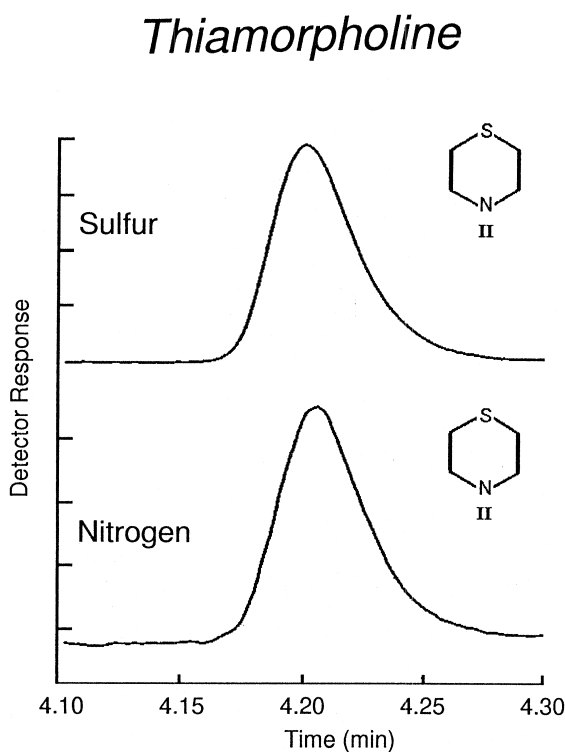
Thiamorpholine

Fig. 12. Simultaneous detection of nitrogen and sulfur. Virtually the same retention times and peak shapes in both the nitrogen and sulfur channels are shown in the simultaneous chromatograms of a thiamorpholine standard on an expanded time scale. Data from Ref. [79].

(171–349°C) was obtained from the gasoline sample. As an important feature for SimDis application, the CLND exhibited an equimolar response (the authors mistakenly referred to it as 'linearity') with a 4% R.S.D. for the eight-nitrogen-component standard. Along with the high selectivity and sensitivity, this enabled the CLND to be a powerful tool for nitrogen measurement in refinery feedstocks. However, no nitrogen signal was observed from the RGO sample in the normal elution range (up to 522°C, or C_{40}), although carbon, hydrogen and sulfur elutions were practically complete, as detected by the corresponding AED channels under similar SimDis conditions. Further investigation revealed that the nitrogenous compounds in the RGO sample were believed to have much higher boiling points and could only be eluted with a much shorter column.

Likewise, the SCD has been used for sulfur boiling point range determination in SimDis. Shearer and Meyer [164] reported sulfur SimDis results commensurate with those obtained by standard hydrocarbon SimDis using an FID. A very good sulfur SimDis chromatogram was obtained considering the fact that typical sulfur levels in petroleum streams are several orders of magnitude lower than the hydrocarbon levels. With a different SCD, Yan and Borny [165] showed successful simultaneous FID/SCD SimDis based on ASTM 2887 with a post-column splitter, as shown in Fig. 14. Validation of hydrocarbon SimDis and excellent precision of both FID and SCD channels were demonstrated. The same methodology was extended to the simultaneous nitrogen/sulfur chemiluminescence detector, and simultaneous C, S, N SimDis data was also obtained as shown by Borny [166] in Fig. 15.

6.3. Supercritical fluid chromatography

Due to the similarity between gas chromatography and supercritical fluid chromatography (SFC) in many aspects, it is relative easy to adapt the ozone chemiluminescent detection technology (primarily that of universal nitrogen and sulfur chemiluminescence detection) from GC to SFC. One research group in this field, lead by Taylor, has single-handedly made significant contributions to the applications of both nitrogen and sulfur chemiluminescence detection methods to SFC.

6.3.1. Sulfur-specific detection based on ozone-induced chemiluminescent reactions

Determination of sulfur-containing compounds by SFC is of great interest because many sulfur-containing compounds are either thermally labile or non-volatile and, therefore, are not suitable for analysis by GC. Soon after the introduction of SCD as a GC detector, Chang and Taylor [167] and Howard and Taylor [168] started to investigate the possibility of interfacing the SCD to SFC. The SCD was found to be compatible for use in capillary SFC without any modification [167]. An example of SFC determination of some thermally labile sulfur-containing pesticides is shown in Fig. 16. The use of packed column SFC coupled with SCD was also investigated [168]. As low as 1 pgS/s detection limit
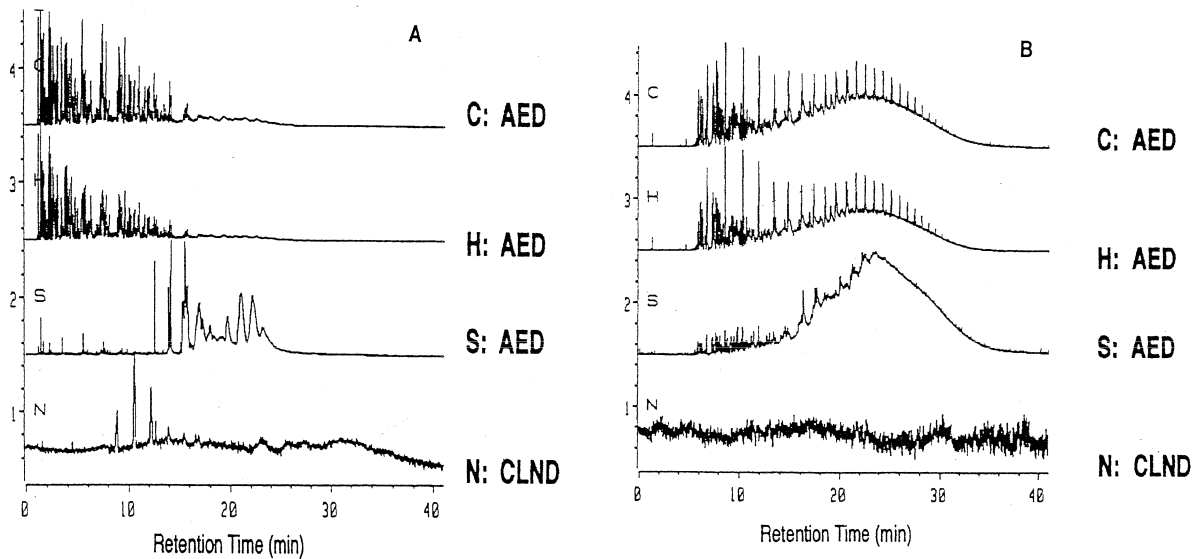
Fig. 13. Simulated distillation of (A) a nitrogen-fortified (about 90–100 ppm N) gasoline sample and (B) a 95–105 ppm N reference gas oil sample. Cool-on-column injections were made onto two matched injectors and columns interfaced to an AED and a CLND, respectively. The simultaneous chromatograms of C, H, S channels are obtained by means of a multielement SimDis software package. GC conditions: columns: HP-1, 25 m, 0.53 mm I.D., 1.05 μm film thickness; injector temperature: 35°C; column temperature program: 35°C, hold 1 min, 35–350°C at 10°C/min, 350°C, hold 7.5 min; 0.1 μl cool-on-column injections, detector base temperatures: 350°C. Reprinted with permission from Ref. [163].
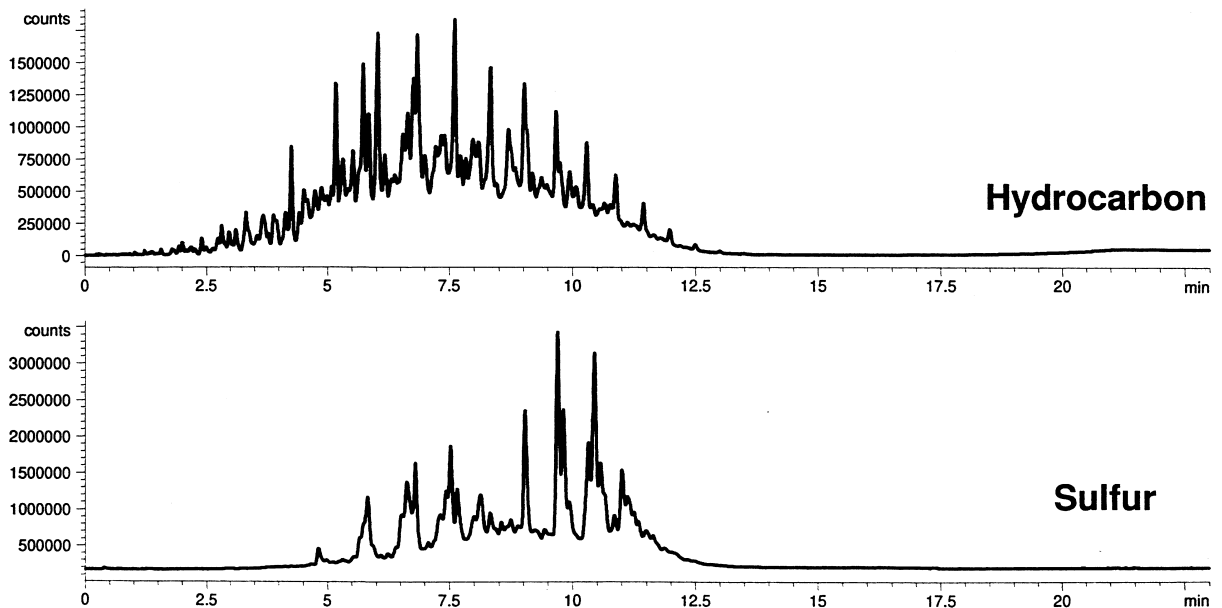

Fig. 14. Example of sulfur SimDis. The SimDis–FID/SCD simultaneous chromatograms of the NIST Standard 1624b. Data from Ref. [165].
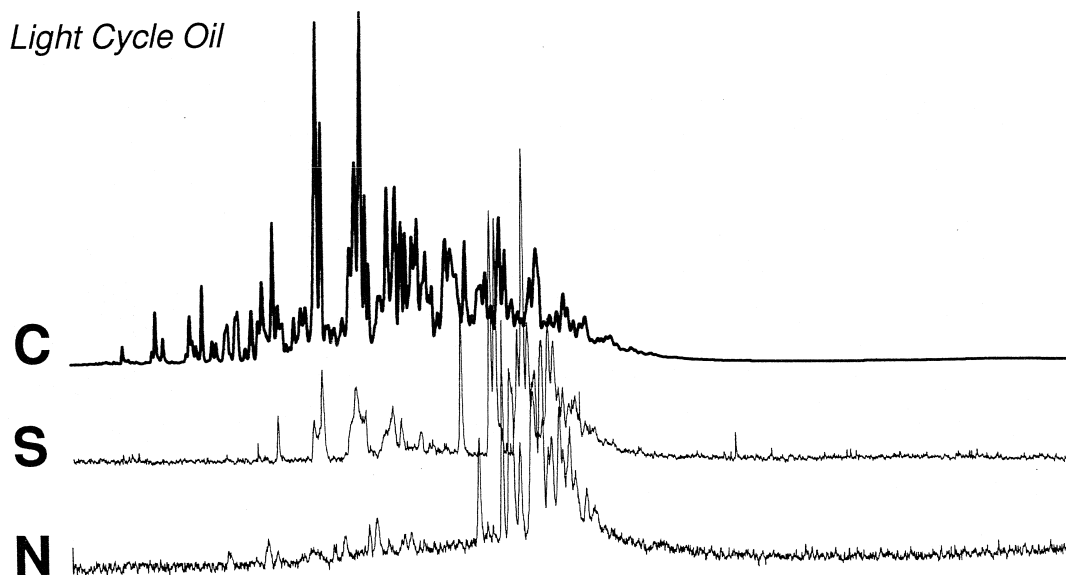
Fig. 15. Example of simultaneous hydrocarbon, sulfur and nitrogen SimDis. The simultaneous C, S and N chromatograms of a light cycle oil sample were obtained with post-column split to an FID and a simultaneous nitrogen/sulfur chemiluminescence detector. Data from Ref. [166].

was obtained. Applications to the analysis of PAHs, diesel fuels and sulfonylurea herbicides were also explored. Further investigations by the same research group were carried out with a different version of the SCD [76,77]. The detector was successfully interfaced with packed column SFC using 100% SF–CO$_2$ and methanol-modified CO$_2$ as the mobile phase. The minimum detectable quantity was determined to be 3 pg of sulfur or 0.2 pg S/s. SFC–SCD was also evaluated by Pekay and Olesik [169]. The SCD was optimized and used for the determination of several three-ring organosulfur compounds. Shearer and Skelton [170] investigated coupling of the SCD to a packed column SFC system using 100% SF–CO$_2$ as the mobile phase. Minimum detection of 0.3 pg S/s, a sulfur-to-carbon selectivity of 10^6 and a linearity of nearly 10^3 were reported along with an approximately equimolar response of the detector.

6.3.2. Nitrogen-specific detection based on the NO + O$_3$ chemiluminescent reaction

Successful adaptation of nitrogen chemiluminescence detection to SFC similar to that of SCD was also achieved by Taylor's group. The CLND was interfaced with capillary SFC by Shi et al. [171]. In addition to an equimolar nitrogen response, the detector exhibited high nitrogen selectivity, sensitivity (minimum detectable quantity, 60 pg N) and linearity. Flavor samples were analyzed by SFC–CLND as its applications. The SFC–CLND studies were further expanded to packed-column and methanol-modified CO$_2$ as the mobile phase by the same research group [172,173]. To handle the continuous flow of an increasingly more combustible carrier stream, a much larger pyrolysis system was employed. To ensure nitrogen chemiluminescence detection without interference from hydrocarbons, complete combustion must be maintained according to reaction (6) in the universal nitrogen detection mechanism. Simultaneous UV detection was also incorporated, which was particularly amenable for analyses of pharmaceuticals. Fig. 17 shows the simultaneous chromatograms of five sedatives obtained by Shi et al. [172]. Lacking chromophores, meprobamate could not be detected by the UV detector, whereas it was easily detected by the CLND. Further optimization of this system by Combs et al. [173] lowered the minimum detectable quantity to 0.1 ng N, with an analytical column, and 0.025 ngN, with a microbore column.
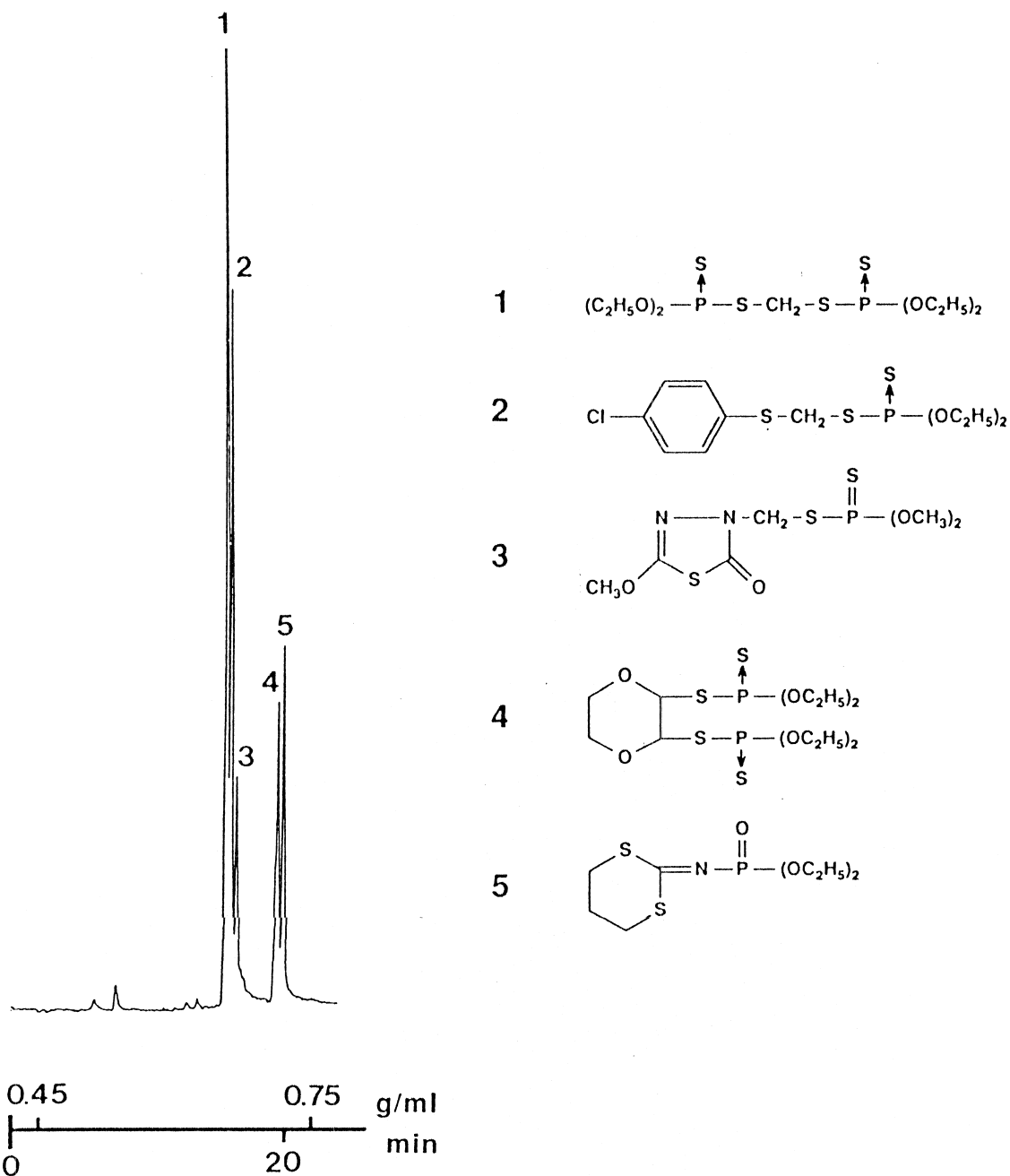
Fig. 16. Separation and detection of five thermally labile sulfur-containing pesticides by SFC–SCD. Chromatographic conditions: packed-capillary column: 250 μm I.D.; packing: 5 μm Deltabond-CN; mobile phase: 2% (w/w) methanol-modified CO_2; oven temperature: 50°C; density program: 0.45 g/ml for 3 min, 0.45–0.75 g/ml at 0.015 g/ml/min. Peaks: (1) ethion; (2) carbophenothion; (3) methidathion; (4) dioxathion and (5) phosfolan. Reprinted with permission from Ref. [167].
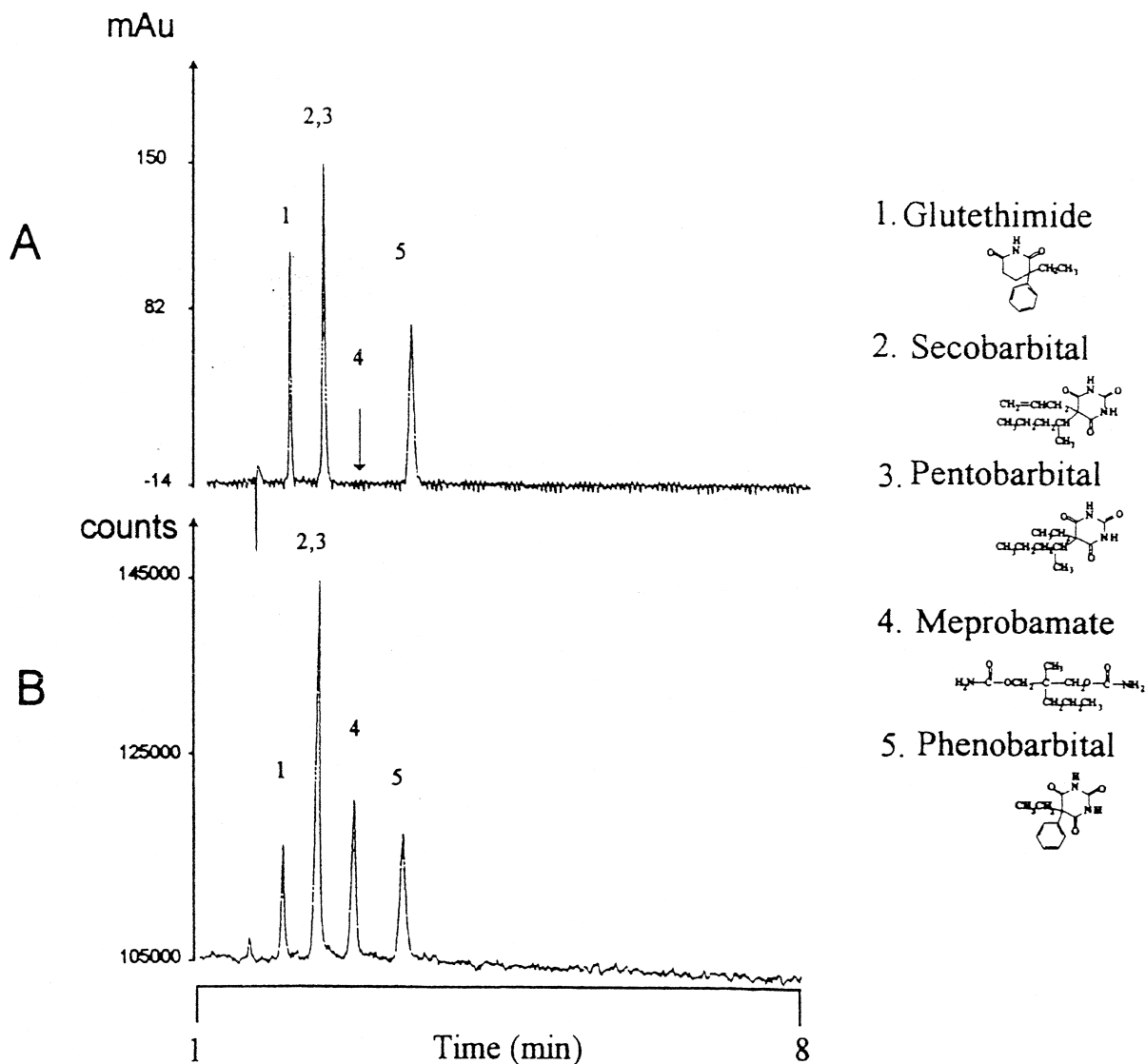
Fig. 17. Separation and detection of five sedatives by packed-column SFC–UV/CLND. Simultaneous (A) UV chromatogram at 219 nm and (B) CLND chromatogram were obtained via a post-column splitter. Chromatographic conditions: packed column: 150 mm, 4.6 mm I.D.; packing: Amino 1, 5 μm particle size; mobile phase: 15% (v/v) methanol-modified CO_2; oven temperature: 50°C; pressure: 250 atm; 5 μl injection loop; liquid CO_2 flow-rate: 2.5 ml/min; decompressed CO_2 flow-rate: 1300 ml/min at UV and 120 ml/min at CLND. Reprinted with permission from Ref. [172].

6.3.3. Redox chemiluminescence detection based on the $NO+O_3$ chemiluminescent reaction

Efforts were also made by Foreman et al. [174] to extend the utility of the RCD from GC to SFC. The commercial RCD was interfaced to a capillary column SFC with minor modifications. The system's capability was demonstrated by successful separation

and detection of two antioxidant isomers and other biologically relevant samples. Mobile phase compatibility and signal quenching were also discussed.

6.4. Liquid chromatography

Interfacing LC with gas-phase ozone-induced

chemiluminescence detection is considerably more difficult because of the introduction of a continuous stream of liquid (often incompatible with gas-phase ozone chemiluminescent reactions and sometimes variable in composition).

6.4.1. Direct ozone chemiluminescence detection

An early attempt to utilize chemiluminescence technology in conjunction with LC was reported by Birks and Kuge [175]. In this detector, the LC effluent was nebulized by a high velocity stream of O_3/O_2 gas. The chemiluminescence produced from the direct reaction of ozone with any chemiluminescent species present in the aerosol spray of the sample solution was then detected. This detector was shown to be selective to a variety of highly fluorescent compounds including olefins, divalent sulfur compounds, hydrazines, azides and nitrogen heterocycles. A series of improvements was made to this detector later [176], which made it more versatile and practical to use. The dead volumes were reduced significantly to rival those in a standard UV detector. However, due to the large variation in response factors to many different types of compounds, the detector based on direct ozone chemiluminescent reactions only finds limited utility.

6.4.2. Nitrogen-specific detection based on the NO + O3 chemiluminescent reaction

The marriage of the analytical power of high-performance liquid chromatography (HPLC) and highly selective universal nitrogen/sulfur chemiluminescence detection proves to be a powerful combination. From the detection mechanisms, reactions (6) and (8), it is obvious that the key to the successful interface of HPLC and chemiluminescence detectors is complete combustion of the LC mobile phase to produce only non-interfering CO_2 and H_2O. It is a similar, but stronger, challenge than that encountered in SFC with modified mobile phases. A commercial HPLC nitrogen-specific detector (HPLC–CLND) was developed and manufactured by Antek Instruments, which employs a large pyrolysis furnace to handle the increased task of sample combustion and a membrane dryer for water removal. With the help of HPLC–CLND, Fujinari and co-workers [177–182] reported a number of HPLC analyses utilizing this unique technology. The first application of

HPLC–CLND was for the detection and quantitation of ammonium nitrogen in metropolitan wastewater and the detector was found to be a sensitive tool for routine and continuous operation [177]. The unique properties of the CLND proved to be a very powerful tool in peptide research by Manes' group in collaboration with Fujinari [178–180]. Nitrogen-containing analytes without UV chromophores were easily detected without the need for any pre- or post-column derivatization, due to the high sensitivity of the detector for nitrogen. Of further significance, the non-nitrogenous compounds in the sample matrix were rendered transparent, thanks to the extremely high selectivity for nitrogen. Quantitation of the peptides was facilitated by the equimolar response of the detector. The CLND revealed the existence of a nitrogenous impurity without chromophores, as illustrated in Fig. 18. The CLND was also used in conjunction with size-exclusion chromatography (SEC) to estimate the molecular mass distribution of food-grade protein hydrolyzates [181]. The CLND provided an accurate peptide content profile. The CLND was also found to be very helpful in synthetic organic chemistry by Fitch et al. [182]. The equimolar response of the detector for nitrogen eliminated the need for authentic reference standards for every nitrogen-containing synthetic chemical. This unique advantage was illustrated with the synthesis of diketopiperazine.

Recently, an improved version of the CLND for HPLC was introduced by Antek Instruments with the use of a nebulizer to ensure complete and uniform combustion of column effluent. Flow injection analysis (FIA) or reversed-phase (RP) chromatography was employed by Taylor et al. [183] in conjunction with UV, CLND and MS detection to characterize small organic molecules derived from combinatorial libraries. The CLND was demonstrated to be a universal quantitative detector for compounds that contain nitrogen, down to low-picomole levels.

There is tremendous potential for HPLC–CLND in a variety of pharmaceutical and biological applications such as those carried out by Homan and Borny [184,185]. Again, one of the major advantages of this method is the elimination of the need for high purity standards for each target compound, thanks to the equimolar response of the detector. Antibiotics, liver extracts, polyamino acids, proteins and peptides in biological samples were analyzed as examples.
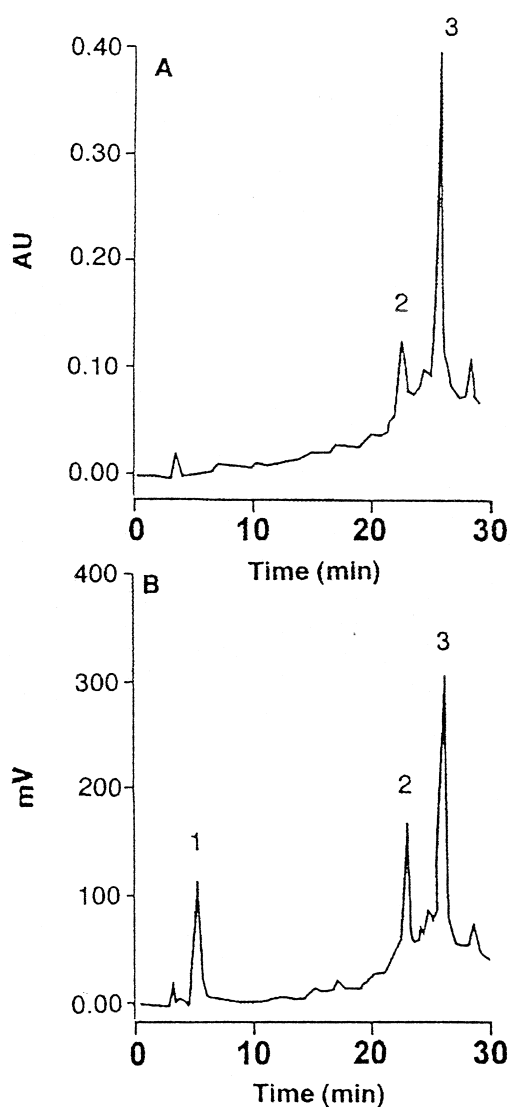
Fig. 18. HPLC profiles of 20 μl of 1 mg/ml crude synthetic C-peptide in 0.05% trifluoroacetic acid (TFA) buffer by HPLC–UV/CLND. Simultaneous UV chromatogram at 220 nm (A) and a CLND chromatogram were obtained via a post-column splitter. Peaks: (1) impurity without chromophores; (2) unknown peptide; (3) C-peptide. Reprinted with permission from Ref. [180].

6.4.3. Redox chemiluminescence detection based on the $NO + O_3$ chemiluminescent reaction

The application of the RCD to LC was implemented by DeAngelis et al. [186]. Certain organic compounds, such as sugars, and inorganic reducing agents, such as iron(II), were detected by reacting them with dilute nitric acid at an elevated tempera-

ture and pressure to produce a NO pulse for subsequent chemiluminescence detection. UV irradiation could alternatively be used to initiate the reaction at room temperature. The characteristics of the redox reactions of potential analytes with aqueous nitric acid and other reagents were discussed. Measurement of sugars at ppm levels was presented.

6.4.4. Nitrite detection based on the $NO + O_3$ chemiluminescent reaction

Another way to exploit the high sensitivity and selectivity of the $NO + O_3$ chemiluminescence detection method was reported by Dunham et al. [187] for aqueous nitrite ion determination. The nitrite ion in a flow injection sample was converted to nitric oxide by aqueous iodide in acid. The resulting NO was then transported into the gas phase through a semipermeable membrane and was subsequently detected by ozone chemiluminescence. A detection limit of 0.04 ppb of nitrite ion was achieved. The method was highly selective and free from sample coloration or turbidity interference because all three steps involved (the reduction of nitrite ion, the volatilization of NO and $NO + O_3$ chemiluminescence detection) were highly selective.

6.4.5. Sulfur-specific detection based on ozone-induced chemiluminescent reactions

Attempts were also made to interface sulfur chemiluminescence detection to LC [188,189]. Chang and Taylor [188] reported successful coupling of a flame-based SCD to packed-capillary-column HPLC. The optimum flame gas composition was found to strongly depend on the mobile-phase composition and flow-rate, and quenching of the SCD signal resulting from the liquid mobile phase was discussed. A detection limit of 4 pg S/s, linearity of three orders of magnitude and a selectivity of at least 10^6 were achieved. Thermally labile thiocarbamates, phenylthiohydantoin–amino acids, and nonvolatile alkyl sulfonates were analyzed as applications. The chromatogram of seven thiocarbamates is shown in Fig. 19 as an example. The same research group also described an optimization process to interface the flame-based SCD to a microcolumn HPLC [189]. System performance was evaluated under various reversed-phase conditions, and the best detection limit achieved was determined to be 600 fg S/s.

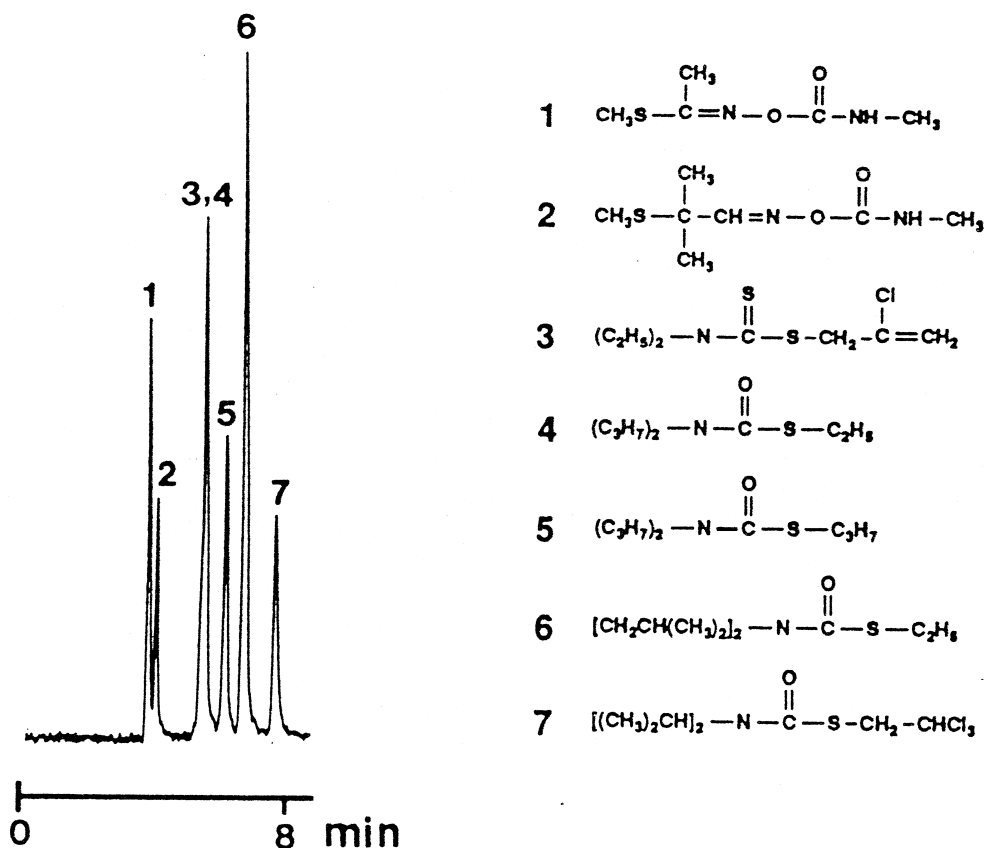For general application of the SCD in LC, addi-

Fig. 19. Separation and detection of seven thiocarbamates by packed-capillary-column HPLC–SCD. Chromatographic conditions: packed-capillary column: 150 mm, 320 μm I.D.; packing: 3 μm Fusica, RP-18; mobile phase: water–methanol (10:90, v/v); sample: 3–7 ng of each compound. Peaks: (1) methomyl; (2) aldicarb; (3) sulfallate; (4) eptam; (5) vernolate; (6) butylate and (7) triallate. Reprinted with permission from Ref. [188].

tional pre-combustion of the column effluent and water removal have been incorporated in the development of a sulfur HPLC chemiluminescence detector. Preliminary data on sulfur determination in grease and kerosine were reported by Homan and Borny [190].

A novel LC detector based on the $SO + O_3$ chemiluminescent reaction was described by Ryerson et al. [191]. Sulfur monoxide was reported to be generated from sulfur-containing compounds in the liquid phase, under pressure and at an elevated temperature. The SO was then allowed to permeate through a membrane, into the ozone reaction chamber to be detected. The applications presented included the detection of sulfur-containing compounds in pesticides, proteins and blood plasma.

7. Conclusion

Among the various chemiluminescent reactions, those of ozone in the gas phase hold a prominent place in analytical chemistry. These reactions are of great importance to academic researchers as well as application chemists due to their unique properties. Although there are many direct ozone chemiluminescent reactions with various gaseous molecules, the incorporation of a conversion step to convert various non-chemiluminescent analytes to a species capable of reacting with ozone to produce chemiluminescence broadens the horizon of this technique tremendously. The conversion of nearly all nitrogen- and sulfur-containing compounds to their respective chemiluminescent species for universal nitrogen and

sulfur detection has made nitrogen/sulfur chemiluminescence detection the most widely used analytical method based upon ozone-induced chemiluminescence. The popularity of these methods also stems from the very unique and beneficial features of these techniques, including extremely high selectivity, an equimolar response, as well as high sensitivity and linearity. These characteristics have also made them suitable for chromatographic applications. Nitrogen/sulfur chemiluminescence detection has been adapted to various chromatographic techniques from gas chromatography to liquid and supercritical fluid chromatography as specialized element-specific detectors. The continuing research and development in this field, particularly that in nitrogen/sulfur chemiluminescence detection, is poised to lead us to further refinement of the techniques and an even broader range of applications.

Acknowledgements

References

[1] McGraw-Hill Dictionary of Scientific and Technical Terms, 5th Ed, McGraw-Hill, New York, 1994.
[2] F. McCapra, Q. Rev., Chem. Soc. 20 (1966) 485.
[3] M.M. Rauhut, Ace. Chem. Res. 2 (1969) 80.
[4] M.J. Cormier, D.M. Hercules, J. Lee (Eds.), Chemiluminescence and Bioluminescence, Plenum Press, New York, 1973.
[5] W.R. Seitz, M.P. Neary, Anal. Chem. 46 (1974) 188A.
[6] A. Fontijn, in: E.L. Wehry (Ed.), Modern Fluorescence Spectroscopy, Vol. 1, Heyden, London, 1976, p. 159.
[7] I.M. Campbell, D.L. Baulch, Gas Kinet. Energy Transfer 3 (1978) 42.
[8] W.R. Seitz, CRC Crit. Rev. Anal. Chem. 13 (1981) 1.
[9] W. Adam, W. Cilento (Eds.), Chemical and Biological Generation of Excited States, Academic Press, New York, 1982.
[10] L.J. Kricka, G.H.G. Thorpe, Analyst 108 (1982) 1274.
[11] S. Toby, Chem. Rev. 84 (1984) 277.
[12] R.D. Kenner, E.A. Ogryzlo, in: J.G. Burr (Ed.), Chemi- and Bioluminescence, Dekker Press, New York, 1985, p. 45.
[13] F. McCapra, J. Photochem. Photobiol. A 51 (1990) 21.
[14] A.A. Turnipseed, J.W. Birks, in: J.W. Birks (Ed.), Chemiluminescence and Photochemical Reaction Detection in Chromatography, VCH, New York, 1989, p. 39.

[15] R.L. Shearer, R.E. Sievers, in: J.W. Birks (Ed.), Chemiluminescence and Photochemical Reaction Detection in Chromatography, VCH, New York, 1989, p. 71.
[16] M. Otto, C.R. Hebd. Seances Acad. Sci. 123 (1896) 1005.
[17] U. Bresciani, Am. Chem. Appl. 4 (1915) 343.
[18] K. Jablczynski, W. Orlowski, Rocz. Chem. 16 (1936) 406.
[19] J.C. Greaves, D. Garvin, J. Chem. Phys. 30 (1959) 348.
[20] M.A.A. Clyne, B.A. Thrush, R.P. Wayne, Trans. Faraday Soc. 60 (1964) 359.
[21] P.N. Clough, B.A. Thrush, Trans. Faraday Soc. 63 (1967) 915.
[22] C.J. Halstead, B.A. Thrush, Photochem. Photobiol. 4 (1965) 1007.
[23] C.J. Halstead, B.A. Thrush, Proc. R. Soc. Lond. 295 (1966) 380.
[24] B.A. Thrush, C.J. Halstead, A. McKenzie, J. Phys. Chem. 72 (1968) 3711.
[25] W.A. Kummer, J.N. Pitts Jr., R.P. Steer, Environ. Sci. Technol. 5 (1971) 1045.
[26] H. Akimoto, B.J. Finlayson, J.N. Pitts Jr., Chem. Phys. Lett. 12 (1971) 199.
[27] P.K. Arora, J.P.S. Chatha, Can. J. Chem. 62 (1984) 417.
[28] R.J. Glinski, J.A. Sedarski, D.A. Dixon, J. Phys. Chem. 85 (1981) 2440.
[29] R.J. Glinski, D.A. Dixon, J. Phys. Chem. 89 (1985) 33.
[30] R.J. Glinski, D.A. Dixon, J. Phys. Chem. 90 (1986) 3346.
[31] H.R. Martin, R.J. Glinski, Appl. Spectrosc. 6 (1992) 948.
[32] R.J. Glinski, J.A. Sedarski, D.A. Dixon, J. Am. Chem. Soc. 104 (1982) 1126.
[33] R.L. Benner, D.H. Stedman, Appl. Spectrosc. 48 (1994) 848.
[34] P.L. Burrow, J.W. Birks, Anal. Chem. 69 (1997) 1299.
[35] R.L. Shearer, LC·GC 16 (1998) 895.
[36] X. Yan, LC·GC 16 (1998) 896.
[37] R.S. Hutte, R.E. Sievers, J.W. Birks, J. Chromatogr. Sci. 24 (1986) 499.
[38] K.K. Gaines, W.H. Chatham, S.O. Farwell, J. High Resolut. Chromatogr. 13 (1990) 489.
[39] A.L. Howard, L.T. Taylor, J. High Resolut. Chromatogr. 14 (1991) 785.
[40] J.W. Drummond, L.A. Topham, G.I. Mackay, H.L. Schiff, Proc. SPIE-Int. Soc. Opt. Eng. 1433 (1991) 224.
[41] W. Wardencki, B. Zygmunt, Anal. Chim. Acta 255 (1991) 1.
[42] S.E. Eckert-Tilotta, S.B. Hawthorne, D.J. Miller, J. Chromatogr. 591 (1992) 313.
[43] R.E. Sievers (Ed.), Selective Detectors: Environmental, Industrial, and Biomedical Applications, John Wiley and Sons, New York, 1995.
[44] J.K. Nelson, R.H. Getty, J.W. Birks, Anal. Chem. 55 (1983) 1767.
[45] E.A. Mishalanie, J.W. Birks, Anal. Chem. 58 (1986) 918.
[46] R.J. Glinski, E.A. Mishalanie, J.W. Birks, J. Photochem. 37 (1987) 217.
[47] W.T. Foreman, C.L. Shellum, J.W. Birks, R.E. Sievers, J. Chromatogr. 465 (1989) 23.
[48] D.J. Bornhop, B.J. Murphy, L. Krieger-Jones, Anal. Chem. 61 (1989) 797.
[49] T.G. Chasteen, G.M. Silver, J.W. Birks, R. Fall, Chromatographia 30 (1990) 181.

[50] T.G. Chasteen, R. Fall, J.W. Birks, H.R. Martin, R.J. Glinski, Chromatographia 31 (1991) 342.

[51] A.J. Hills, D.H. Lenschow, J.W. Birks, Anal. Chem. 70 (1998) 1735.

[52] A.J. Bernanose, M.G. Rene, in: Ozone Chemistry and Technology, American Chemical Society, Washington, DC, 1959, p. 7.

[53] T.A. Nieman, in: J.W. Birks (Ed.), Chemiluminescence and Photochemical Reaction Detection in Chromatography, VCH, New York, 1989, p. 99.

[54] Y. Maeda, K. Aoki, M. Munemori, Anal. Chem. 50 (1980) 307.

[55] P. Mikuska, Z. Vecera, Anal. Chem. 64 (1992) 2187.

[56] J.R. Poulsen, J.W. Birks, Anal. Chem. 62 (1990) 1242.

[57] R.D. Cadle, M. Ledford, Int. J. Air Water Pollut. 10 (1966) 25.

[58] J.M. Hales, J.O. Wilkes, J.L. York, Atmos. Environ. 3 (1969) 657.

[59] S. Toby, L.J. Van de Burgt, F.S. Toby, J. Phys. Chem. 89 (1985) 1982.

[60] S. Toby, F.S. Toby, J. Phys. Chem. 93 (1989) 2453.

[61] S. Toby, F.S. Toby, J. Phys. Chem. A 102 (1998) 4527.

[62] A.A. Mehrabzadeh, R.J. O'Brien, T.M. Hard, Anal. Chem. 55 (1983) 1660.

[63] R.J. Glinski, J.L. Gole, D.A. Dixon, J. Am. Chem. Soc. 107 (1985) 5891.

[64] M.E. Fraser, D.H. Stedman, M. Nazeeri, M. Nelson, Anal. Chem. 55 (1983) 1809.

[65] D.H. Fine, D. Lieb, F. Rufeh, J. Chromatogr. 107 (1975) 351.

[66] M.J. Bollinger, R.E. Sievers, D.W. Fahey, F.C. Fehsenfeld, Anal. Chem. 55 (1983) 1980.

[67] N. Pourreza, S.A. Montzka, R.M. Barkley, R.E. Sievers, J. Chromatogr. 399 (1987) 165.

[68] R.E. Parks, US Pat. 4, 352 779, 1982.

[69] R.E. Parks, US Pat. 4, 678 756, 1987.

[70] H.V. Dreshel, Anal. Chem. 50 (1978) 76.

[71] R.L. Benner, D.H. Stedman, Anal. Chem. 61 (1989) 1266.

[72] C.H. Muller III, K. Schofield, M. Steinberg, H.P. Broida, Int. Symp. Combust. 17 (1979) 867.

[73] M.R. Zachariah, O.I. Smith, Combust. Flame 69 (1987) 125.

[74] R.L. Shearer, Anal. Chem. 64 (1992) 2192.

[75] X. Yan, Sulfur Selective GC Detection by Oxidative/Reductive Pyrolysis and Chemiluminescence, paper presented at the 47th Gulf Coast Conference, Galveston, TX, 1993.

[76] H. Shi, L.T. Taylor, E.M. Fujinari, X. Yan, J. Chromatogr. A 779 (1997) 307.

[77] H. Shi, L.T. Taylor, E.M. Fujinari, X. Yan, LC·GC 16 (1998) 276.

[78] X. Yan, Manuscript in preparation.

[79] X. Yan, J.-F. A. Borny, Petroleum Refining Applications of Simultaneous Selective Sulfur and Nitrogen Detection for Gas Chromatography, paper presented at the 51st Gulf Coast Conference, Galveston, TX, 1997.

[80] X. Yan, E.M. Fujinari, A New and Improved Gas Chromatography Sulfur Chemiluminescence Detector, paper presented at the 1996 Pittsburgh Conference, Chicago, IL, 1996.

[81] R.L. Shearer, D.L. O'Neal, R. Rios, M.D. Baker, J. Chromatogr. Sci. 28 (1990) 24.

[82] H.V. Dreshel, J. Chromatogr. Sci. 21 (1983) 375.

[83] M. Dressler, Selective Gas Chromatographic Detectors, Elsevier, Amsterdam, 1986.

[84] L. Giuffrinda, J. Assoc. Off. Agr. Chem. 47 (1964) 293.

[85] S.S. Brody, J.E. Chaney, J. Gas Chromatogr. 4 (1966) 42.

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

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

[88] H. Jing, A. Amirav, J. Chromatogr. A 805 (1998) 177.

[89] B.D. Quimby, J.J. Sullivan, Anal. Chem. 62 (1990) 1027.

[90] J.J. Sullivan, B.D. Quimby, Anal. Chem. 62 (1990) 1034.

[91] P.C. Uden, T. Wang, Z. Cheng, J. Chromatogr. 468 (1989) 319.

[92] R.C. Hall, J. Chromatogr. Sci. 12 (1974) 152.

[93] H. Hernandez, R. McGreger, Int. Labmate 12 (3) (1987) 33.

[94] P.J. Moore, Int. Labmate 15 (3) (1990) 43.

[95] A.J. Hills, P.R. Zimmerman, Anal. Chem. 62 (1990) 1055.

[96] R. Pearson Jr., Rev. Sci. Instrum. 61 (1990) 907.

[97] A. Ben-Jebria, S.C. Hu, J.S. Ultman, Rev. Sci. Instrum. 61 (1990) 3435.

[98] C.S. MacDougal, M.L. Rigas, A. Ben-Jebria, J.S. Ultman, Arch. Environ. Health 53 (1998) 161.

[99] A. Fontijn, A.J. Sabadell, R.J. Ronco, Anal. Chem. 42 (1970) 575.

[100] S. Weikert, D. Freyer, M. Weih, N. Isaev, C. Busch, J. Schultze, D. Megow, U. Dirnagl, Brain Res. 748 (1997) 1.

[101] J.S. Beckman, K.A. Conger, Methods (Companion publication to Methods in Enzymology) 7 (1995) 35.

[102] R.B. Bradstreet, The Kjeldahl Method for Organic Nitrogen, Academic Press, New York, 1965.

[103] H.A. Hernandez, Am. Lab. 13 (6) (1981) 72.

[104] H.V. Dreshel, Anal. Chem. 49 (1977) 932.

[105] J.Y. Shay, P.W. Woodward, Am. Lab. 18 (10) (1986) 114.

[106] B.M. Jones, C.G. Daughton, Anal. Chem. 57 (1985) 2320.

[107] W.M. Snodgrass, Am. Lab. 16 (3) (1984) 138.

[108] T.W. Walsh, Mar. Chem. 26 (1989) 295.

[109] J. Merriam, W.H. McDowell, W.S. Currie, Soil Sci. Soc. Am. J. 60 (1996) 1050.

[110] T.S. Gorimar, H.A. Hernandez, M.W. Polczynski, Am. Clin. Products Rev. 3 (11) (1984) 46.

[111] G.W. Luli, S. Lee, Am. Biol. Lab. 7 (2) (1989) 20.

[112] P.B. Loder, A.J. Kee, R. Horsburgh, M. Jones, R.C. Smith, Crit. Care Med. 17 (1989) 309.

[113] G.K. Grimble, M.F.E. West, A.B.C. Acuti, R.G. Rees, M.K. Hunjan, J.D. Webster, P.G. Frost, D.B.A. Silk, J. Parenter. Enteral Nutr. 12 (1988) 100.

[114] K.J. Skogerboe, R.F. Labbe, R.L. Rettmer, J.P. Sundquist, A.M. Gargett, Clin. Chem. 36 (1990) 752.

[115] F.N. Konstantinides, K.A. Boehm, W.J. Radmer, M.C. Storm, J.T. Adderly, S.A. Weisdorf, F.B. Cerra, Clin. Chem. 34 (1988) 2518.

[116] F.N. Konstantinides, N.N. Konstantinides, J.C. Li, M.E. Myaya, F.B. Cerra, J. Parenter. Enteral Nutr. 15 (1991) 189.

[117] F.N. Konstantinides, W.J. Radmer, W.K. Becker, V.K. Herman, W.E. Warren, L.D. Solem, J.B. Williams II, F.B. Cerra, J. Burn Care Rehab. 13 (1992) 254.

[118] F.N. Konstantinides, Nutr. Clin. Pract. 7 (1992) 231.

[119] R.A. Helms, C.A. Mowatt-Larssen, K.A. Boehm, M.L. Christensen, M.A. Hughes, E.T. Fernandes, M.C. Storm, J. Parenter. Enteral Nutr. 17 (1993) 68.

[120] K.A. Boehm, R.A. Helms, M.C. Storm, J. Parenter. Enteral Nutr. 18 (1994) 172.

[121] A. Hyltander, B. Arfvidsson, U. Korner, R. Sandstrom, K. Lundholm, J. Parenter. Enteral Nutr. 17 (1993) 158.

[122] R.D. Cox, Anal. Chem. 52 (1980) 332.

[123] C. Garside, Mar. Chem. 11 (1982) 159.

[124] R.S. Braman, S.A. Hendrix, Anal. Chem. 61 (1989) 2715.

[125] K.A. Boehm, An Improved Method for the Rapid Quantitation of Nitrate in Petrochemical and Aqueous Samples, paper presented at the 51st Gulf Coast Conference, Galveston, TX, 1997.

[126] A.C. Delany, R.R. Dickerson, F.L. Melchior, A.F. Wartburg, Rev. Sci. Instrum. 53 (1982) 1899.

[127] R.R. Dickerson, A.C. Delany, A.F. Wartburg, Rev. Sci. Instrum. 55 (1984) 1995.

[128] R.L. Benner, D.H. Stedman, Environ. Sci. Technol. 24 (1990) 1592.

[129] K. Fujiwara, Y. Watanabe, K. Fuwa, J.D. Winefordner, Anal. Chem. 54 (1982) 125.

[130] K. Matsumoto, K. Fujiwara, K. Fuwa, Anal. Chem. 55 (1983) 1665.

[131] K. Fujiwara, T. Kanchi, S. Tsumura, T. Kumamaru, Anal. Chem. 61 (1989) 2699.

[132] K. Fujiwara, M. Uchida, M. Chen, Y. Kumamoto, T. Kumamaru, Anal. Chem. 65 (1993) 1814.

[133] W. Bruening, F.J.M. Concha, J. Chromatogr. 112 (1975) 253.

[134] W. Bruening, F.J.M. Concha, J. Chromatogr. 142 (1977) 191.

[135] T.J. Kelly, J.S. Gaffney, M.F. Phillips, R.L. Tanner, Anal. Chem. 55 (1983) 135.

[136] J.S. Gaffney, D.J. Spandau, T.J. Kelly, R.L. Tanner, J. Chromatogr. 347 (1985) 121.

[137] D.H. Fine, F. Rufeh, B. Gunther, Anal. Lett. 6 (1973) 731.

[138] D.H. Fine, F. Rufeh, D. Lieb, Nature (London) 247 (1974) 309.

[139] D.H. Fine, D.P. Rounbehler, J. Chromatogr. 109 (1975) 271.

[140] D.H. Fine, F. Rufeh, D. Lieb, D.P. Rounbehler, Anal. Chem. 47 (1975) 1188.

[141] B.A. Tompkins, W.H. Griest, C.E. Higgins, Anal. Chem. 67 (1995) 4387.

[142] N. Kashihira, K. Makino, K. Kirita, Y. Watanabe, J. Chromatogr. 239 (1982) 617.

[143] W.C. Yu, D.H. Fine, K.S. Chiu, K. Biemann, Anal. Chem. 56 (1984) 1158.

[144] A.J. Britten, R & D 31 (1989) 76.

[145] L.O. Courthaudon, E.M. Fujinari, LC·GC 9 (1991) 732.

[146] S.M. Benn, K. Myung, E.M. Fujinari, in: G. Charalambous (Ed.), Food Flavors, Ingredients and Composition, Elsevier Science, Amsterdam, 1993, p. 65.

[147] B. Chawla, J. Chromatogr. Sci. 35 (1997) 97.

[148] S.A. Nyarady, R.M. Barkley, R.E. Sievers, Anal. Chem. 57 (1985) 2074.

[149] S.A. Nyarady, R.E. Sievers, J. Am. Chem. Soc. 107 (1985) 3726.

[150] R.E. Sievers, S.A. Nyarady, R.L. Shearer, J.J. DeAngelis, R.M. Barkley, R.S. Hutte, J. Chromatogr. 349 (1985) 395.

[151] R.E. Sievers, R.L. Shearer, R.M. Barkley, J. Chromatogr. 395 (1987) 9.

[152] E.A. McNamara, S.A. Montzka, R.M. Barkley, R.E. Sievers, J. Chromatogr. 452 (1988) 75.

[153] S.A. Montzka, R.M. Barkley, R.E. Sievers, S. Afr. J. Chem. 42 (1989) 81.

[154] R.S. Hutte, N.G. Johansen, M.F. Legier, J. High Resolut. Chromatogr. 13 (1990) 421.

[155] N.G. Johansen, J.W. Birks, Am. Lab. 23 (3) (1991) 112.

[156] R.L. Shearer, E.B. Poole, J.B. Nowalk, J. Chromatogr. Sci. 31 (1993) 82.

[157] B. Chawla, F. Di Sanzo, J. Chromatogr. 589 (1992) 271.

[158] F.P. Di Sanzo, W. Bray, B. Chawla, J. High Resolut. Chromatogr. 17 (1994) 255.

[159] N. Johansen, M. Plam, M. Legier, Brew. Dig. 65 (4) (1990) 37.

[160] M.S. Burmeister, C.J. Drummond, E.A. Pfisterer, D.W. Hysert, Y.O. Sin, K.J. Sime, D.B. Hawthorne, J. Am. Soc. Brew. Chem. 50 (1992) 53.

[161] A.W. Dercksen, I. Meijering, B. Axcell, J. Am. Soc. Brew. Chem. 50 (1992) 93.

[162] H. Goldstein, S. Rader, A.A. Murakami, J. Am. Soc. Brew. Chem. 51 (1993) 70.

[163] R.J. Young, E.M. Fujinari, Am. Lab. 26 (15) (1994) 38.

[164] R.L. Shearer, L.B. Meyer, Sulfur Simulated Distillation by Chemiluminescence, paper presented at 1998 Pittsburgh Conference, New Orleans, LA, 1998.

[165] X. Yan, J.-F.A. Borny, Sulfur Determination in Simulated Distillation of Petroleum Products Based on ASTM D2887, paper presented at the 52nd Gulf Coast Conference, Galveston, TX, 1998.

[166] J.-F.A. Borny, Simultaneous Nitrogen and Sulfur SimDis: Two Elements with One Detector, paper presented at the 52nd Gulf Coast Conference, Galveston, TX, 1998.

[167] H.-C.K. Chang, L.T. Taylor, J. Chromatogr. 517 (1990) 491.

[168] A.L. Howard, L.T. Taylor, Anal. Chem. 65 (1993) 724.

[169] L.A. Pekay, S.V. Olesik, J. Microcol. Sep. 2 (1990) 270.

[170] R.L. Shearer, R.J. Skelton, J. High Resolut. Chromatogr. 17 (1994) 251.

[171] H. Shi, J.T.B. Strode, L.T. Taylor, E.M. Fujinari, J. Chromatogr. A 734 (1996) 303.

[172] H. Shi, L.T. Taylor, E.M. Fujinari, J. Chromatogr. A 757 (1997) 183.

[173] M.T. Combs, M. Ashraf-Khorassani, L.T. Taylor, E.M. Fujinari, Anal. Chem. 69 (1997) 3044.

[174] W.T. Foreman, R.E. Sievers, B.W. Wenclawiak, Fresenius' Z. Anal. Chem. 330 (1988) 231.

[175] J.W. Birks, M.C. Kuge, Anal. Chem. 52 (1980) 897.

[176] B. Shoemaker, J.W. Birks, J. Chromatogr. 209 (1981) 251.

[177] E.M. Fujinari, L.O. Courthaudon, J. Chromatogr. 592 (1992) 209.

[178] E.M. Fujinari, J.D. Manes, J. Chromatogr. A 676 (1994) 113.

[179] E.M. Fujinari, J.D. Manes, R. Bizanek, J. Chromatogr. A 743 (1996) 85.

[180] R. Bizanek, J.D. Manes, E.M. Fujinari, Pept. Res. 9 (1996) 40.

[181] E.M. Fujinari, J.D. Manes, J. Chromatogr. A 763 (1997) 323.

[182] W.L. Fitch, A.K. Szardenings, E.M. Fujinari, Tetrahedron Lett. 38 (1997) 1689.

[183] E.W. Taylor, M.G. Qian, G.D. Dollinger, Anal. Chem. 70 (1998) 3339.

[184] M.E. Homan, J.-F.A. Borny, The Quantitation of Nitrogen in Biological Samples by HPLC–Chemiluminescent nitrogen Detection (CLND) and HPLC–MS–CLND, paper presented at the 22nd International Symposium on Chromatography, Rome, Italy, 1998.

[185] M.E. Homan, J.-F.A. Borny, Applications of a Nitrogen Specific Chemiluminescent Detector for HPLC, paper presented at the 37th Eastern Analytical Symposium, Somerset, NJ, 1998.

[186] J.J. DeAngelis, R.M. Barkley, R.E. Sievers, J. Chromatogr. 441 (1988) 125.

[187] A.J. Dunham, R.M. Barkley, R.E. Sievers, Anal. Chem. 67 (1995) 220.

[188] H.-C.K. Chang, L.T. Taylor, Anal. Chem. 63 (1991) 486.

[189] A.L. Howard, C.L.B. Thomas, L.T. Taylor, Anal. Chem. 66 (1994) 1432.

[190] M.E. Homan, J.-F.A. Borny, The analysis of Sulfur Containing Compounds in Heavy Oil Samples by HPLC–SCLD, paper presented at the 52nd Gulf Coast Conference, Galveston, TX, 1998.

[191] T.B. Ryerson, A.J. Dunham, R.M. Barkley, R.E. Sievers, Anal. Chem. 66 (1994) 2841.