Review

Sulfur and nitrogen chemiluminescence detection in gas chromatographic analysis

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Abstract

Sulfur and nitrogen compounds exist in a wide variety of analytical samples, from harmful contaminants in refinery streams to important ingredients in certain beverages, spices and condiments. Accurate determination of sulfur/nitrogen concentrations in these diverse samples is very important for process monitoring, quality control, product development, as well as basic research in these different industries. Due to the complex nature of the matrices, and the fact that the sulfur/nitrogen analytes usually exist at low concentrations, an element-selective detector for sulfur/nitrogen is indispensable to the GC analysis of these samples. To meet this challenge, sulfur and nitrogen chemiluminescence detectors for GC have become one of the most powerful tools available to analytical chemists, thanks to their high sensitivity, selectivity and equimolar detector response. In this brief review, an overview of the chemiluminescence detector operating principles, as well as the detector characteristics is presented. Examples of their applications in petroleum refinery, environmental analysis and food/flavor industry are presented. The two chemiluminescence detectors have also been combined into one convenient package and an example of applications of the simultaneous sulfur/nitrogen chemiluminescence detector is also provided. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Reviews; Chemiluminescence detection; Detection, GC; Sulfur compounds; Nitrogen compounds

Contents

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1. Introduction

Sulfur and nitrogen compounds exist in a wide variety of analytical samples. In refinery streams, they often represent harmful contaminants to the expensive catalysts used in refining processes, even at very low concentrations. At the other end of the spectrum, sulfur- and/or nitrogen-containing compounds sometimes are important ingredients in certain beverages, spices and condiments. Accurate determination of sulfur/nitrogen concentrations in these diverse samples is very important for process monitoring, quality control, product development, as well as basic research, in these different industries. Due to the complex nature of the matrices, and the fact that these sulfur/nitrogen analytes usually exist at low concentrations, an element-selective detection method for sulfur/nitrogen is indispensable to the GC analysis of these samples [1]. A number of such detection methods like flame photometric detection (FPD) have been used over the years. However, speciation and quantitation of sulfur and/or nitrogen is becoming increasingly more demanding. Detection limits required are decreasing while sample matrices are becoming more complex. Current detector technology is hard pressed to provide adequate results. To meet this challenge, a relatively new type of GC detectors based on ozone-induced chemiluminescence have become one of the most powerful tools available to analytical chemists, thanks to their unique characteristics. The topic has been covered previously [2,3]. This paper is intended to provide a focused and succinct overview of sulfur chemiluminescent detection (SCD) and chemiluminescence nitrogen detection (CLND) when interfaced with gas chromatography, with several examples of their applications using commercial chemiluminescence detectors produced by author's company to illustrate their utilities in a variety of analyses.

2. Mechanism and operating principles

2.1. Two-step universal elemental detection mechanisms

Although highly selective for two different elements, the nitrogen and sulfur chemiluminescence detectors have much in common in terms of their overall reaction mechanism and operating principles, and therefore it is convenient to discuss them together. Both of them follow a general two-step detection scheme as follows [2].

Step 1: universal conversion of nitrogen/sulfur analytes to their respective chemiluminescent species.

Step 2: detection of chemiluminescence from the reactions between ozone and the nitrogen/sulfur chemiluminescent species.

The ultimate detection of the nitrogen/sulfur analyte (in step 2) is achieved from the reaction between ozone and the nitrogen/sulfur species capable of producing chemiluminescence, which is referred to as the nitrogen/sulfur chemiluminescent species. For universal nitrogen/sulfur detection, another reaction, usually a high-temperature pyrolytic reaction (usually with oxidation and/or reduction), is needed to convert all or nearly all nitrogen/sulfur-containing compounds in the sample to their respective chemiluminescent species (in step 1).

2.2. Nitrogen/sulfur chemiluminescence detection
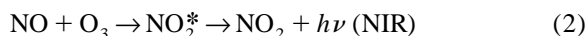
2.2.1. Nitrogen chemiluminescence detection

For CLND, the chemiluminescent nitrogen species is nitric oxide (NO) and the chemiluminescence is derived from the well-known $NO+O_3$ reaction [4–6]. Oxidative combustion at around $1000\,°C$ is required for complete conversion of chemically bound nitrogen contained in these GC amenable analytes to nitric oxide [7,8]. The detection mechanism of CLND, therefore, is simply the following.

Universal conversion to nitrogen chemiluminescent species:

$$R-N+O_2 \rightarrow CO_2+H_2O+NO \qquad (1)$$
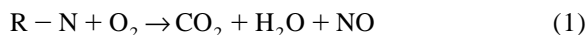
Detection of nitrogen chemiluminescence:

$$NO+O_3 \rightarrow NO_2^* \rightarrow NO_2+h\nu \text{ (NIR)} \qquad (2)$$

2.2.2. Sulfur chemiluminescence detection

For SCD, on the other hand, a simple oxidative combustion does not generate a sulfur chemiluminescent species (SO_2 does not chemiluminesce with ozone). High-temperature reduction by hydrogen is required after the oxidation step in order to produce the chemiluminescent species. The complete picture of the complex combustion reactions is still not thoroughly understood. Extensive discussion on the conversion process has taken place and the reader is referred elsewhere for further details [2,7–10]. However, it suffices to say that the high-temperature oxidation-reduction generates chemiluminescent species of sulfur which react with ozone to produce chemiluminescence.

Universal conversion to sulfur chemiluminescent species:

$$R-S+O_2 \rightarrow CO_2+H_2O+SO_2 \qquad (3)$$

$$SO_2+H_2 \rightarrow \text{Sulfur chemiluminescent species} \qquad (4)$$
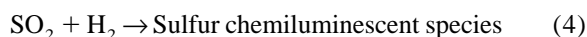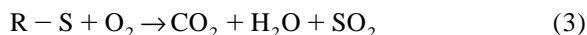
Detection of sulfur chemiluminescence:

Sulfur chemiluminescent species +

$$O_3 \rightarrow SO_2^* \rightarrow SO_2+h\nu \text{ (UV-Blue)} \qquad (5)$$
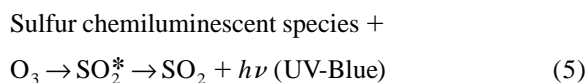
2.3. Characteristics of nitrogen/sulfur chemiluminescence detection

A number of unique characteristics of nitrogen/sulfur chemiluminescence detection stem from the underlying principles which set it apart from other element-selective detection methods.

2.3.1. Selectivity

In most applications, the CLND and SCD are used as a universal detector for nitrogen/sulfur, while at same time being a highly selective detector for these elements over matrices like hydrocarbons. This is because in the chemiluminescence detection methods, the sample matrix and other non-nitrogen/sulfur components are converted to non-chemiluminescent species (CO_2 and H_2O) in the first conversion step.

2.3.2. Sensitivity

Unlike other luminescence methods, light emission in chemiluminescence methods occurs in a dark background, without the interference from other light sources. This allows full sensitivity of the detection system to be realized, which renders the chemiluminescence methods among the most sensitive for nitrogen and sulfur.

2.3.3. Equimolarity

Probably the most important characteristic of the chemiluminescence methods is its equimolar response to the element in question (nitrogen or sulfur). The equimolar nitrogen/sulfur response refers to the equivalent total integrated detector response to the equivalent amount (total mass) of nitrogen/sulfur entering the detector, regardless of the molecular structure of the analytes or their chemical environment. This characteristic also stems from the fact that all nitrogen/sulfur compounds are converted into common intermediate chemiluminescent species. The equimolarity allows quantitation of various nitrogen/sulfur compounds without requiring authentic calibration standards of each and every analyte.

2.3.4. Linearity

When the ozone is in great excess in the detection step, the reaction is pseudo first-order, hence the detector response is linear to the nitrogen/sulfur concentration in the original sample.

2.4. Nitrosamine-selective detection

Although the CLND is usually used as a universal detector for nitrogen, a special variation on the conversion step turns it into a highly selective detector for a particular class of nitrogen compounds, *N*-nitroso compounds, commonly known as nitrosamines [11]. Instead of the high-temperature oxidation, thermal cleavage of the nitrosamine molecules preferentially releases the nitrosyl radical group (NO), followed by the same nitrogen chemiluminescence detection. The following mechanism clearly shows the similarity and difference in the universal and nitrosamine-selective conversion.

Universal nitrogen conversion:

$$R - N = NO + O_2 \rightarrow CO_2 + H_2O + 2NO \qquad (6)$$

Nitrosamine selective conversion:

$$R - N = NO \rightarrow R - N + NO \qquad (7)$$
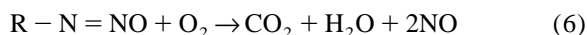
3. Applications

There have been many applications of SCD and CLND in a wide variety of industries. A few examples are given below to illustrate the utilities of the chemiluminescence detectors in each of the several different analytical tasks.

3.1. Monitoring desulfurization process of refinery streams by GC–sulfur chemiluminescence detection

One of the major applications of the chemiluminescence detectors is in the petroleum and petrochemical industry where sulfur/nitrogen components are often harmful contaminants in process or product streams. Even at low concentrations, these sulfur/nitrogen contaminants pose a serious threat to the expensive catalysts used in many of the processes in petroleum industry. Due to the almost ubiquitous presence of sulfur in petroleum streams and the ever-increasing sulfur content in the crude supply, desulfurization process like the hydrogenation process is routinely used in the refineries. As an example, the hydrogenation of C5 stream removes sulfur from the feed stock, yielding low-sulfur top reflux in the C5 product and concentrating the sulfur

in the bottom stream. GC–SCD provides an ideal tool for monitoring this process. Separation by a non-polar capillary column gives an approximate distribution of the streams by boiling points, where sulfur contaminants are monitored by SCD (as shown in Fig. 1) [12]. With the sensitivity and the equimolar response of SCD, the boiling range (and often the identities), as well as the quantities of the sulfur contaminants are readily determined with calibration by a sulfur standard. In this case, the hydrogenation process is quite effective in removing sulfur, particularly the heavier sulfur components, leaving only low concentrations of the volatile sulfur compounds in the top reflux stream. The less volatile sulfur contaminants, on the other hand, are concentrated in the bottom stream.

3.2. Boiling point distributions of sulfur/nitrogen by simulated distillation with GC–sulfur/nitrogen chemiluminescence detection

In a similar application, GC–SCD/CLND has been employed in boiling point distribution determination of sulfur and/or nitrogen in various petroleum streams. As a fast and more cost-effective method, simulated distillation (SimDis) by GC is gaining popularity in boiling point range determinations. In addition to the standard hydrocarbon boiling point distribution, analysts become more interested in the distribution of sulfur (and sometimes even nitrogen) compounds in these streams, which is of increasing
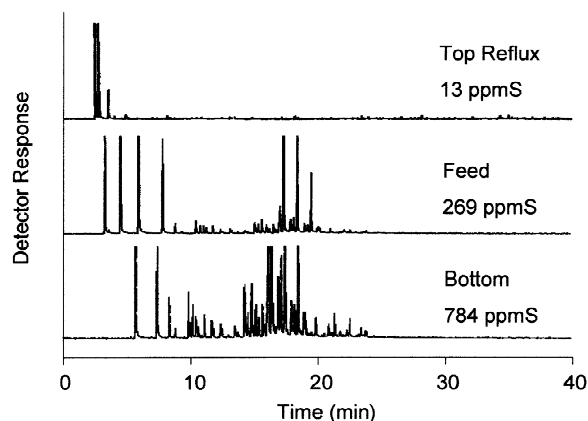

Fig. 1. Chromatograms of sulfur content in feed and product streams in C_5 hydrogenation process by GC–SCD.

analytical and commercial importance. However, there remain considerable challenges in sulfur/nitrogen SimDis. First, the sulfur/nitrogen components are only minor components in these streams, representing at most low percentage levels of the total mass, and often much lower. Secondly, these contaminants tend to spread out over the entire boiling range, and are overlapped with the hydrocarbon matrices. The task poses very stringent requirements on the SimDis system requiring high sensitivity to detect the minute amount of the sulfur/nitrogen components, whereas at the same time to discriminate the coeluting hydrocarbon matrix. The chemiluminescence detectors again are ideal for this task. Employed in conjunction with a flame ionization detection (FID) system for the standard hydrocarbon SimDis of a diesel fuel sample, SCD/CLND provides the sulfur/nitrogen boiling point distribution, respectively, as shown in Fig. 2 [13]. The boiling point distribution data are collected in Table 1. Assuming all the sulfur/nitrogen compounds are eluted under the GC program (a reasonable approximation for SimDis analysis), total sulfur/nitrogen concentrations can also be determined from the SimDis data. Typical of heavy hydrocarbon fuels, this diesel sample exhibits fairly broad sulfur distribution situated slightly higher than the main
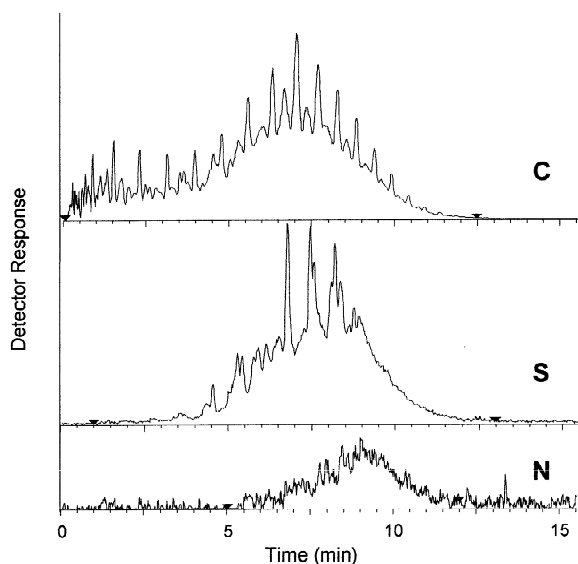
Table 1
Boiling point distributions of carbon, sulfur and nitrogen of a diesel sample by SimDis GC–FID/SCD/CLND

% Mass eluted	Temperature (°C)		
	Carbon	Sulfur	Nitrogen
IBP	115.5±1.1	205.7±3.4	274.5±0.8
10	197.6±0.2	271.4±1.6	312.1±3.1
20	239.5±0.2	289.1±0.8	326.2±2.3
30	265.3±0.2	299.9±0.4	336.4±1.1
40	281.4±0.2	311.5±0.4	343.0±0.5
50	294.9±0.2	318.6±0.3	349.7±0.2
60	305.6±0.1	328.9±0.1	355.0±0.6
70	317.9±0.1	336.9±0.1	361.5±1.0
80	331.7±0.1	347.7±0.1	368.4±1.6
90	349.9±0.0	361.5±0.4	379.1±2.8
FBP	396.0±0.1	402.6±0.5	409.0±3.2

IBP, initial boiling point, 0.5% mass eluted; FBP, final boiling point, 99.5% mass eluted.

hydrocarbon distribution with a relatively high concentration (4067 mg S/L), as well as a nitrogen distribution at even slightly higher boiling range with a much lower level (68 mg N/L). The data provide a fairly clear picture of the distribution and quantity of the sulfur/nitrogen components in this diesel sample.

3.3. Detecting food/flavor adulteration by GC–chemiluminescence nitrogen detection

The utility of the chemiluminescence detectors is not limited to the petroleum industry. There have been many applications in various biological analyses. Food and flavor samples are typically very complex in nature. They usually consist of hundreds, if not more, compounds. Often nitrogen and/or sulfur containing compounds play an important role, either as central ingredients, or being an integral part of some biological processes. Conventional GC analysis of these samples is often difficult due to the fact that it is practically impossible to separate all the nitrogen and/or sulfur compounds of interest from the sample matrix. An element-selective detector like chemiluminescence detectors can significantly simplify the analysis by selectively seeing nitrogen/sulfur components with the coeluting matrix. This is best demonstrated by the detection of galbanum oil adulteration [14]. Root body (a material containing three nitrogenous isomers) is often added in small quantities to elude organoleptic examination of the

Fig. 2. Boiling point distributions of carbon, sulfur and nitrogen of a diesel sample by SimDis GC–FID/SCD/CLND.
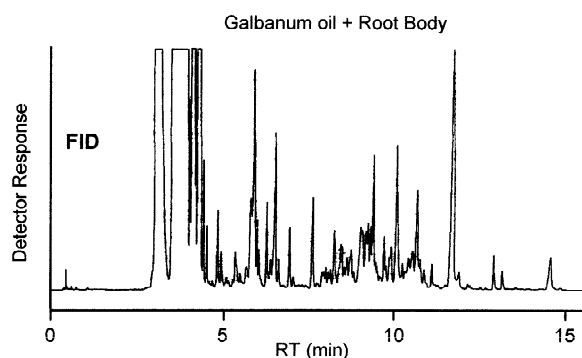
Galbanum oil + Root Body

Fig. 3. GC–FID chromatogram of an adulterated galbanum oil sample with added root body. RT, retention time. Data from Ref. [14]. Reprinted with permission from Ref. [14], Copyright 1993, Elsevier Science.

galbanum oil. It would be extremely difficult to detect the adulteration with a GC–FID chromatogram (as shown in Fig. 3). However, comparing the GC–CLND chromatogram of the genuine galbanum oil (Fig. 4a) and those of the adulterated oil sample and a root body standard (Fig. 4b,c), the addition of root body in the oil is readily apparent. The adulteration is hence revealed by the telltale sign of the addition of the root body. CLND pinpoints the nitrogen-containing compounds of interest, by rendering other matrix compounds transparent to the detector.

3.4. Detecting ultratrace level nitrosamines in groundwater by GC–chemiluminescence nitrogen detection

As mentioned in Section 2, the CLND system can operate in a special mode for selective nitrosamine detection. A typical application of the nitrosamine detection is found in tobacco industry. However, there are many other fields in which selective nitrosamine detection is crucial. A method of determination of carcinogen *N*-nitrosodimethylamine (NDMA) at ultratrace level (ppt) in groundwater by GC–CLND has been developed [15]. The aqueous sample is filtered and extracted by dichloromethane, which is then concentrated to 1 ml, and loaded onto a sorbent trap. The desorbed sample is analyzed by GC with CLND nitrosamine-selective detection. A two-tiered method is developed to cover a 4-order-of-magnitude detection range. The automated "high-level" protocol is used for fast screening, with method detection limit (MDL) at 110 ng/l, while the "low-level" protocol is capable of detecting minute amounts of NDMA, with the MDL at 2 ng/l. Fig. 5 shows the chromatograms of two groundwater extract samples with different amounts of NDMA, as compared to a synthetic groundwater blank. This method provides much higher selectivity for nitro-

A: 2,4,6-trimethyl pyridine

B–F: Naturally occurring pyrazine compounds found and identified in galbanum oil

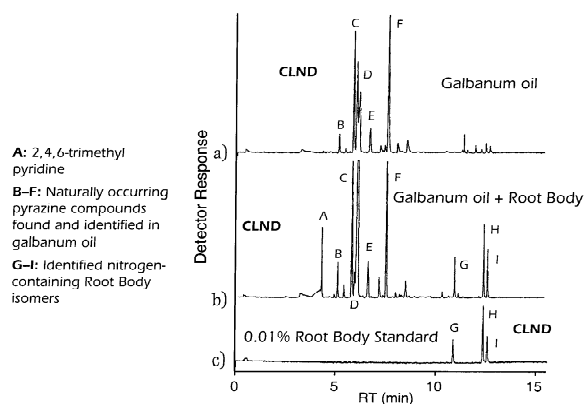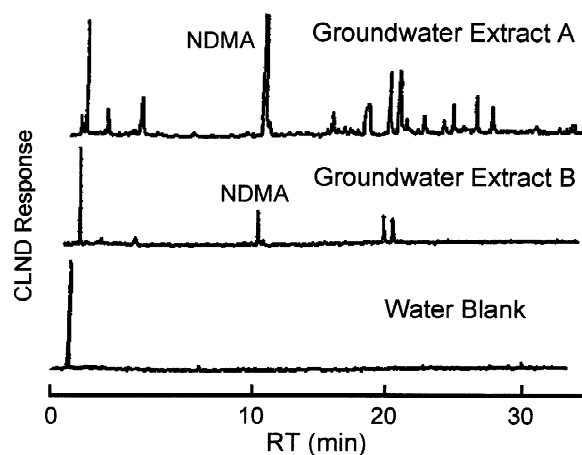G–I: Identified nitrogen-containing Root Body isomers

Fig. 4. GC–CLND chromatograms of a genuine galbanum oil sample (a) and an adulterated galbanum oil sample with added root body (b), as compared to a root body standard (c). Data from Ref. [14]. Reprinted with permission from Ref. [14], Copyright 1993, Elsevier Science.
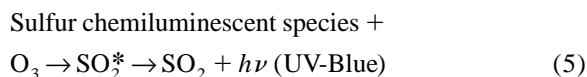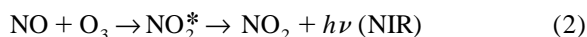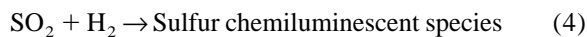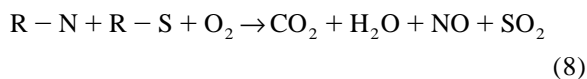

Fig. 5. Representative chromatograms of NDMA determination of groundwater samples by a method utilizing GC analysis with nitrosamine selective CLND detection. Data from Ref. [15]. Reprinted with permission from Ref. [15], Copyright 1995, American Chemical Society.

samines as compared to the alternative method employing the more commonly used NPD detector.

3.5. Sulfur/nitrogen, two results with one injection by GC–simultaneous sulfur/nitrogen chemiluminescence detection

As shown in the above examples and numerous other applications of SCD and CLND, the chemiluminescence detection of sulfur and nitrogen, separately, is a well-established technology for GC. Considering the similarities between the two detectors, it is natural to combine them into one flow path. Earlier investigations have shown that the nitric oxide generated in the oxidation step of SCD can survive quantitatively in the hydrogen reduction, allowing simultaneous quantitative detection of sulfur and nitrogen [16,17]. The mechanism can be summarized as follows.

$$R-N + R-S + O_2 \rightarrow CO_2 + H_2O + NO + SO_2 \tag{8}$$

$$SO_2 + H_2 \rightarrow \text{Sulfur chemiluminescent species} \tag{4}$$

$$NO + O_3 \rightarrow NO_2^* \rightarrow NO_2 + h\nu \text{ (NIR)} \tag{2}$$

$$\text{Sulfur chemiluminescent species} + O_3 \rightarrow SO_2^* \rightarrow SO_2 + h\nu \text{ (UV-Blue)} \tag{5}$$

With simultaneous sulfur/nitrogen detection, one achieves the effect of "one injection, two results", realizing cost and time savings. By splitting the column effluent to an FID system, one in fact achieves "one injection, three results", obtaining simultaneous chromatograms of hydrocarbons, sulfur and nitrogen. An example of such analysis, C, S and N simultaneous chromatograms of a regular unleaded gasoline sample [18], is shown in Fig. 6. One cannot obtain any information on sulfur/nitrogen quantity or distribution directly from the FID chromatogram, since the existence of minor sulfur/nitrogen components is overwhelmed by the hydrocarbon matrix response. However, with simultaneous SCD/CLND, distinctive sulfur and nitrogen chromatograms are obtained showing not only the distribution, but also the quantities of various sulfur/nitrogen components.

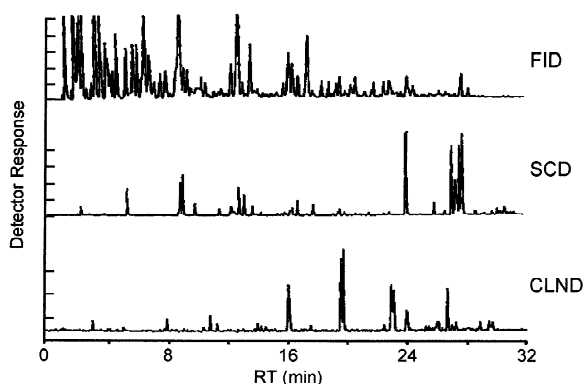The convenience and cost savings of the simulta-

Fig. 6. Simultaneous chromatograms of hydrocarbon, sulfur and nitrogen of a regular unleaded gasoline sample by GC–FID/SCD/CLND.

neous SCD/CLND do come with some compromises. Performance of the simultaneous detector tends to be less than the individual chemiluminescence detectors, particularly in sensitivity. Typically the sulfur and nitrogen channels are optimized with different gas flow conditions, so compromises in performance have to be made when simultaneous detection is used. An alternative operating procedure is to use the detector for one element (sulfur or nitrogen) at one time, with gas flow conditions optimized for its performance. This is sometimes referred to as the "single channel mode". Although no longer detecting simultaneously, the combined detector retains much versatility. Both elements can be determined separately, but conveniently with a simple adjustment of operating conditions, without physically exchanging the individual sulfur and nitrogen detectors.

4. Conclusion

SCD and CLND are powerful analytical tools in GC analysis, thanks to their unique and beneficial characteristics including the extremely high selectivity and their equimolar response. They have found a broad range of applications in diverse industries in which they provide analytical solutions not available with conventional methods.

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References

[1] H.V. Drushel, J. Chromatogr. Sci. 21 (1983) 375.
[2] X. Yan, J. Chromatogr. 842 (1999) 267.
[3] R.E. Sievers (Ed.), Selective Detectors, Environmental, Industrial, and Biomedical Applications, Wiley, New York, 1995.
[4] J.C. Greaves, D. Garvin, J. Chem. Phys. 30 (1959) 348.
[5] M.A.A. Clyne, B.A. Thrush, R.P. Wayne, Trans. Faraday Soc. 60 (1964) 359.
[6] P.N. Clough, B.A. Thrush, Trans. Faraday Soc. 63 (1967) 915.
[7] R.E. Parks, R L. Marietta, US Pat. 4,018,562 (1977).
[8] R.E. Parks, US Pat. 4,352,779 (1982).
[9] R.L. Benner, D.H. Stedman, Anal. Chem. 61 (1989) 1266.
[10] P.L. Burrow, J.W. Birks, Anal. Chem. 69 (1997) 1299.
[11] D.H. Fine, D. Lieb, F. Rufeh, J. Chromatogr. 107 (1975) 351.
[12] J.-F.A. Borny, in: Presented at the 2001 Pittsburgh Conference, New Orleans, LA, 2001.
[13] X. Yan, J.J. Werner, in: Presented at the 1999 Gulf Coast Conference, Galveston, TX, 1999.
[14] S.M. Benn, K. Myung, E.M. Fujinari, in: G. Charalambous (Ed.), Food Flavors, Ingredients and Composition, 1993, p. 65.
[15] B.A. Tomkins, W.H. Griest, C.E. Higgins, Anal. Chem. 67 (1995) 4387.
[16] X. Yan, E.M. Fujinari, US Pat. 5,916,523 (1999).
[17] X. Yan, E.M. Fujinari, US Pat. 6,143,245 (2000).
[18] X. Yan, J.-F.A. Borny, in: Presented at the 1997 Gulf Coast Conference, Galveston, TX, 1997.