

This article was downloaded by:

On: 17 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

Determination of Sulfur Compounds in Air by Chemiluminescence

G. Galán^a; M. J. Navas^a; A. M. Jiménez^a

^a Department of Analytical Chemistry, Faculty of Pharmacy, University of Sevilla, Sevilla, Spain

To cite this Article Galán, G. , Navas, M. J. and Jiménez, A. M.(1997) 'Determination of Sulfur Compounds in Air by Chemiluminescence', International Journal of Environmental Analytical Chemistry, 68: 4, 497 – 510

To link to this Article: DOI: 10.1080/03067319708030849

URL: <http://dx.doi.org/10.1080/03067319708030849>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

DETERMINATION OF SULFUR COMPOUNDS IN AIR BY CHEMILUMINESCENCE

G. GALÁN*, M. J. NAVAS and A. M. JIMÉNEZ

*Department of Analytical Chemistry, Faculty of Pharmacy, University of Sevilla,
Prof. Garcia Gonzalez s/n, 41012 Sevilla, Spain*

(Revised 15 March 1996; In final form 10 September 1997)

The present review is devoted to applications of chemiluminescence to the analysis of trace sulfur species in air. Determinations of oxidized (sulfur dioxide and sulfite), reduced (hydrogen sulfide, dimethyl sulfide, carbonyl sulfide, carbon disulfide and mercaptans) and/or sulfur compounds in general are described and some practical considerations are discussed. The development of detectors based on chemiluminescence in the approximately last fifteen years is also reviewed.

Keywords: Chemiluminescence; air analysis; sulfur compounds

INTRODUCTION

One of the most important problems in environmental protection is the determination of low levels of sulfur compounds such as hydrogen sulfide, thiols, organic sulfides and disulfides, sulfur containing pesticides and their metabolites in atmospheric gases, different waters, industrial wastes and effluents, particularly from the paper industry. The sensitive detection of low levels of sulfur-containing compounds is also important in the petrochemical and chemical industry, because they can produce unpleasant odours, catalyst poisoning or corrosion and general air pollution when fuel is burned^[1]. Therefore, the determination of total sulfur, both its compound types or classes and individual compounds, is of current concern in many fields.

*Corresponding author. Fax No.: +34-95-4556749. E-mail: galan@fafar.us.es

The gaseous compounds of sulfur which are of interest in air pollution studies fall into three main categories: oxides (SO_2 and SO_3), hydrides and organic compounds^[2].

Sulfur dioxide is one of the most common and harmful air pollutants and one of the main causes of acid rain generation which is widely believed to be responsible for acidifying soil and water. This compound is emitted primarily from combustion sources, with minor sources including metallurgical processes and miscellaneous chemical industries. Sulfur dioxide is released to the atmosphere in enormous quantities on combustion of fossil fuels^[3], and is responsible for injury to plants (trees in particular) and damage to building stone (particularly carbonates such as dolomite, limestone and marble). It is detectable by smell at levels above 1 mg/l and causes severe irritation of the nose and throat. Therefore, its determination at mg/l and lower concentrations has been the subject of much interest and the reduction in its emission is currently emphasized.

Reduced sulfur compounds such as hydrogen sulfide (H_2S), dimethyl sulfide (DMS)(CH_3SCH_3), carbonyl sulfide (COS), carbon disulfide (CS_2), mercaptans and disulfides are present in the atmosphere by the microbiological reduction of sulfate and organosulfur compounds^[4]. The odours of all these species are unpleasant even at very low concentrations, and the toxicity hazard of H_2S is enhanced by the ease with which the sense of smell becomes paralysed by its presence. Hydrogen sulfide is released mainly from pulp and paper manufacture and also from certain refining and cooking activities. It is oxidized rapidly to sulfuric acid in air and this, coupled with the odour, is the main concern from the air-pollution point of view^[2].

Emissions of organic sulfur compounds are relatively less important. The main sources are industries which process natural products, such as wood pulp, paper and animal offal, sewage treatment plants and other chemical processes^[3]. Many of these species also have natural sources, e.g. hydrogen sulfide from swamps, and organic sulfides from a variety of aerobic and anaerobic biological processes.

All these reduced compounds are subsequently oxidized in the troposphere to sulfur dioxide and sulfate, thus contributing to their natural occurrence.

While chemiluminescent reactions have been known for centuries, the analytical interest of Chemiluminescence (CL) has increased considerably over the last decade. This is especially clear from the abundance of books and articles that have appeared during this time^[5-17].

Chemiluminescence can be produced in the gas, liquid and solid phase. This review will deal with CL in gas and liquid phase. In this way, CL generally has

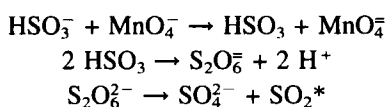
proven to be an extremely selective and sensitive method of detection for sulfur oxidized and reduced compounds and/or sulfur compounds in general.

Our purpose is to review the applications of CL for the determination of sulfur compounds in air analysis during over the last fifteen years.

Determination of sulfur dioxide

There are many analytical methods available for the determination of SO₂ in the atmosphere^[18]. One of the most frequently employed is the pararosaniline method proposed by West and Gaeke^[19]. This method presents several problems such as the use of toxic mercury and the long response times. Sulfur dioxide in the gas phase have been determined by flame photometric or fluorescence methods. On the other hand, CL techniques have received in the past much attention for sensitive and selective detection. The method developed by Meixner and Jaesche^[20] to determine atmospheric SO₂, uses disulfite mercurate complex which is oxidized in aqueous solutions with KMnO₄ under acid conditions. The detection limit is (10 to 1) parts/100/vol. SO₂.

Kato *et al.*[21] describe a CL method for direct continuous monitoring of SO₂ in the atmosphere. The method is based on the principle that the oxidation of sulfite in acidic permanganate solution is accompanied by a weak CL in the spectral region of 450-600 nm, which arises from excited SO₂^{*}, that is sensitized by flavin mononucleotide. The CL reaction scheme proposed would be:



and the overall reaction: $2 \text{HSO}_3^- + 2 \text{MnO}_4^- \rightarrow 2 \text{MnO}_4^{2-} + 2 \text{H}^+ + \text{SO}_4^{2-} + \text{SO}_2^*$ indicates that very acidic conditions are not desirable for the CL reaction. The sensitized emission is further enhanced by means of Tween surfactants micelles, Tween 85 (polyoxyethylene (20) sorbitan trioleate) providing the largest micellar enhanced signal of 25 times. The calibration curve exhibit a linear range up to 30 μg/l. Interferences by H₂S and O₃ can be negligible in practice because in the atmosphere hydrogen sulfide is generally present in concentrations less than ca. 10% that of SO₂ and ozone is present in concentration less than 0,1 mg/l.

Sulfur dioxide could be determined using the fact that SO₂ enhances the chemiluminescence produced by the reaction of luminol with NO₂^[22]. The enhanced signal is proportional to sulfur dioxide concentration at a fixed NO₂ concentration. According with the spectra, it seems likely the chemiluminescence of the SO₂/NO₂/luminol system is also produced from the excited state of

aminophthalate ion and sulfur dioxide probably acts as a catalyst. The authors have reported a 95% response within 2 min. Relative standard deviations for 10 $\mu\text{g/l}$ and 1 $\mu\text{g/l}$ of SO_2 are 0,9% and 10%, respectively, and the detection limit is approximately 0,3 $\mu\text{g/l}$. By this method, real-time determination of SO_2 in ambient air can be made. Further, Takenaka *et al.*[23], found that in a luminol CL system using H_2O_2 instead of NO_2 , the response time became shorter and the interference from other gases, especially from hydrogen sulfide, was reduced. This method is based on the fact that SO_2 enhances the chemiluminescence produced by the reaction of luminol with hydrogen peroxide. The calibration graph for SO_2 was linear in the 1 to 1000 $\mu\text{g/l}$ range. The detection limit was 0,6 $\mu\text{g/l}$ and the relative standard deviation for ten measurements of 10 $\mu\text{g/l}$ of SO_2 was 5,3%. The method suffers from interference by ozone and nitrogen dioxide but these compounds can be completely removed by using a tube packed with glass beads coated with FeSO_4 . Sulfur trioxide and the other gases except hydrogen sulfide did not interfere.

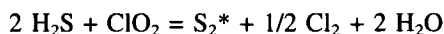
A simple continuous-flow method has been described by Koukli *et al.*[24], for the determination of sulfite and sulfur dioxide in air. These authors examine the CL produced by reduction of Ce(IV). The enhancing effect of 3-cyclohexylaminopropanesulfonic acid (CAPS), which acts as sensitizer, on the sulfite-cerium(IV) system is similar to that of the permanganate system^[25]. The calibration graph was rectilinear in the range of 1,0-20,0 $\mu\text{g/ml}$ of sulfite (equivalent to 0,80-16,0 $\mu\text{g/ml}$ of sulphur dioxide). The limit of detection was 0,80 $\mu\text{g/ml}$ of sulfite. In addition, the authors have compared the method with the spectrophotometric p-rosaniline method. The results obtained by both methods are in good agreement.

A comparison between the two sensitizers: 3-cyclohexylaminopropanesulfonic acid (CAPS) and cyclooctylamine has been carried out more recently by Paulls *et al.*[26]. They found that cyclooctylamine acted as a far superior sensitizer of the chemiluminescent oxidation of sulfite. A detection limit of $5.4 \cdot 10^{-7} \text{ mol.l}^{-1}$ sulfite was achieved. In another paper^[27], these authors try to explain why CAPS sensitized the chemiluminescent oxidation of sulfite. It was found that the sensitization was due to the presence of the cyclohexyl ring and that other cycloalkyl compounds also sensitized the reaction. Although the evidence is not conclusive, it is thought that the nature of the sensitization could be due to the formation of a β -sultine.

Tscherwenka *et al.*[28] have applied the chemiluminescence reaction of dissolved SO_2 with Ce(IV) as an oxidant to the sulfur dioxide measurement at the Sonnblick Mountain in Austria and the results were compared with filter pack measurements^[29].

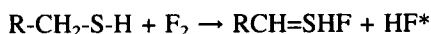
Determination of reduced sulfur compounds

The most frequently used analytical methods to determine this kind of compounds in air are: colorimetry, conversion to metal sulfides and subsequent photometry, gas chromatography with the flame photometric detector and ion selective electrodes^[30]. For low concentration levels, all these techniques require collecting the gas sample of interest over fairly long times and/or some chemical preparation. In addition to that, these methods suffer from interferences, analysis complexities, and/or lack on sufficient sensitivity to monitor reduced sulfur gases at the sub-part-per billion levels expected in ambient air^[4]. CL is an extremely sensitive method for compounds such as H₂S and CH₃SH. A method for real-time measurement of both species based on the chemiluminescent reaction with chlorine dioxide has been reported by Spurlin *et al.*[30]. The sulfur compounds react with ClO₂ to form excited S₂, which emits in the visible region of the spectrum (250 to 450 nm). The net reaction is probably:



These authors have reported a working on-line chemiluminescence detector for the continuous monitoring of low levels of H₂S and CH₃SH. The response of the detector for hydrogen sulfide is linear from 0.2 to 1300 mg/l, and other sulfur compounds, olefins, and other species present in ambient air (with the exception of nitric oxide) do not interfere. To minimize the effects of quenching, one must keep the reaction zone at reduced pressures. To maximize sensitivity despite the high-order reaction, one must keep the volume of the reaction zone small, and the reagent (ClO₂) must be in excess to produce complete reaction. The limit of detection is 3 μg/l with a response time of 1 s, by using photon counting techniques with a cooled photomultiplier. However, the ClO₂ reagent is not easily prepared or stored and formation of elemental sulfur can occur in the chemiluminescent reaction chamber, reducing the sensitivity. While this detector has been used for monitoring sulfur compounds in ambient air, the CL reaction could also become the basis for a GC detector^[31].

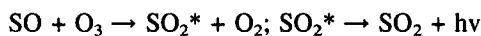
Nelson *et al.*[32] have described a new gas chromatographic detector with selectivity for reduced sulfur compounds, based on vibrational overtone emission of HF. The reaction of sulfur compounds with fluorine produces vibrationally excited HF whose emission is detected with a red sensitive photomultiplier tube at reduced pressures. The reaction that takes place is:



Many sulfides, thiols, disulfides and mercaptans have been found to chemiluminesce with fluorine, while sulfur dioxide, carbonyl sulfide, hydrogen sulfide, and carbon disulfide do not produce a response. The detection limits range from

24 pg for ethanethiol to 257 pg for 1-octanethiol, that compare favourably with other available sulfur-selective detectors. This detector presents a linear response to sulfur compounds over at least 3 orders of magnitude and a selectivity over normal hydrocarbons of greater than 10^7 .

For developing a simple, sensitive and selective real-time method for measurement of reduced sulfur gases, Kelly *et al.*[4] have investigated the chemiluminescent detection of hydrogen sulphide, DMS and other compounds by their oxidation with ozone as reagent. CL in the 300-400 nm region denotes the presence of electronically excited SO_2^* . If the ozone chemiluminescent method is used to ambient sulfide detection, it is important to determine the effect of NO_x in the air sample. The sensitivity of the detector can be increased by using air vs. oxygen for the generation of ozone and by operating the CL reaction chamber at elevated temperatures. The final steps in the mechanism of ozone/sulfide chemiluminescence are:



The differing response of the detector to different sulfur compounds might require a separation or derivatization step to assure unambiguous measurement. The authors have proposed ethyl iodide derivatization as one possibility in this field.

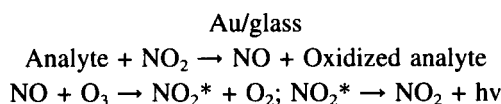
In the same way, Gaffney *et al.*[33] have studied the use of ozone chemiluminescent reactions with reduced sulfur compounds as a chromatographic detector and have compared this detection system with other ones for monitoring reduced sulfur compounds by gas chromatography. A strong temperature dependence was observed in the detection sensitivity for the reduced sulfur compounds, especially for the less reactive compounds. It was observed too, that increased sensitivity could be obtained if air was used instead of oxygen in the ozone source. This indicates that addition of trace levels of nitrogen oxides may accelerate the chemiluminescent reaction. The detection limits were a function of detector operating conditions and exhibited the following values, expressed as $\mu\text{l/l}$: 0,1-1 for methyl mercaptan; 0,1-2 for methyl disulfide; 1-6 for hydrogen sulfide and 1-6 for carbon disulfide. Olefins were the only compounds that interfere in the analysis.

This selectivity is comparable to that obtained for the fluorine CL detection method^[32]. The chlorine dioxide chemiluminescent detector^[30] is very specific and shows better sensitivity for H_2S but not for other sulfur compounds. By other hand, the sensitivity was comparable to a flame photometric detector for reduced sulfur compounds.

Another method that involves oxidation of S or S^{2-} with O_3 in 98 to 100% H_2SO_4 (or 98% H_3PO_4) containing 0.1 mM- O_3 and 1 to 10 mM- UO_2^{2+} , as a

sensitizer, was used for the determination of elemental sulfur and sulfide^[34] and for the determination of hydrogen sulfide^[35]. The maximum intensity of green luminescence or the total luminescence produced by the oxidation of the hydrogen sulfide by the ozone is related to the concentration of S or S²⁻. The calibration curves were rectilinear from 0.1 to 100 μM of S or S⁼. The method is used for determining approximately 60 ng l⁻¹ of hydrogen sulfide in air. No interference was caused by large concentration of dichromate, Fe(II), Mn(II), Ru(II) or sulfur dioxide.

The redox CL detector is a post-column reaction chromatographic detector which provides a wide range of selectivity for a variety of compounds classes. The theory and operation of this detector have been described by Nyarady *et al.*[36]. The RCD combines new catalyzed post column redox reactions with sensitive CL detection of NO. Nitrogen dioxide is mixed with the analyte continuously in a post column gold catalyst bed, and NO is formed. This NO produced is subsequently detected upon reaction with ozone further downstream to produce a chemiluminescence signal. The mechanism of the reaction is as follows:



The RCD responds to compounds that are not sensitively detected by flame ionization detectors (FID) such as ammonia, hydrogen sulfide, carbon disulfide, sulfur dioxide, hydrogen peroxide, hydrogen, carbon monoxide, formaldehyde and formic acid. However is not sensitive to the major constituents in the matrices of many samples such as alkanes, chlorinated hydrocarbons, water, or the major constituents of air (nitrogen, oxygen and carbon dioxide). The selectivity of the detector can be controlled by changing certain detector parameters such as the operating temperature of the catalyst bed, the metal ion in the catalyst bed, the catalyst support material, and the reagent gas^[37].

More recently, an automated gas chromatograph has been developed for the analysis of the atmospheric concentrations of DMS and CS₂^[38]. The system comprises cryogenic concentration of DMS and CS₂ from 4 l. of air after oxidant and water removal, capillary gas chromatography, and sulfur chemiluminescence detection. Detection and quantitation of DMS and CS₂ in the range of 5 to 500 ng/m³ has been achieved. The detection limit was of 10 pg S per compound.

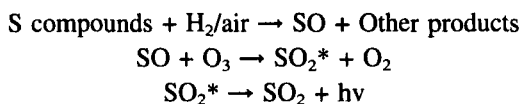
Universal sulfur detection

In the previous paragraph, we have seen several CL detection methods reported only for reduced sulfur species with O₃, ClO₂ and F₂. These detectors present

several problems like interferences, difficulties in handling reagents, drastic differences in sensitivity, or lack of detection for oxidized species.

The flame photometric detector (FPD) is the most commonly used in GC, due to its high selectivity, ease of operation, low maintenance, and relative low cost. The FPD is based on the S_2^* chemiluminescence emission bands at 384-394 nm.

Benner and Stedman[39] have developed a universal sulfur detector (USD) capable of measuring both reduced and oxidized sulfur compounds in the low picogram range. The USD is based on the formation of SO from sulfur compounds combusted in a reducing hydrogen/air flame. The combustion products are drawn through a critical orifice into a low pressure flow system and then mixed with ozone. Halstead and Trush[40] observed a strong blue chemiluminescence of SO_2^* from the reaction of ozone with SO. The produced SO_2^* emits light at 350 nm. The reaction mechanism can be summarized as follows:



The USD, which has been tested in the real time mode, exhibits identical molar response for the low molecular weight compounds tested (SO_2 , SF_6 , H_2S , CH_3SCH_3 and C_2H_5SH). The calibration graph was rectilinear from sub- $\mu\text{l/l}$ to sub- ml/l concentration of S and has a detection limit of about 0.13 $\mu\text{l/l}$ with a time constant of 2 s. This detector does not suffer interferences by water vapor or CO_2 and interferences from hydrocarbons can be minimized by varying the residence time of the sample in the flame. Thus, the SCD is warranted for applications that require accurate low level sulfur measurements and/or when known interfering species exist.

This USD, has subsequently been named as SCD (Sulfur Chemiluminescence Detector). A field evaluation of this SCD have been reported by the same authors^[41]. The SCD was installed in a monitoring trailer along with a flame photometric detector (FPD) and a fluorescent SO_2 monitor (Fluor), in order to evaluate sensitivity, stability, and interferences and quantify the differences between the three designed analyzers. The SCD showed no ambient temperature dependence on either the baseline or sensitivity, and no interference effects, but had a drift in sensitivity larger than the other analyzers.

GC coupled with sulfur selective detectors is frequently used for analysis of individual sulfur compounds in complex matrices. The most common detectors used are the flame photometric detector (FPD), the Hall electrolytic conductivity detector (ELCD), the atomic emission detector (AED), the electron capture

detector, and various chemiluminescence-based detectors proposed previously for the determination of reduced sulfur compounds.

The SCD developed by Benner and Stedman^[39], when operating at real time is an almost ideal sulfur selective detector. But despite offering many advantages over other sulfur selective detectors, the GC-SCD has some limitations. Many authors have tried to optimize the conditions for a correct use of the SCD^[42-44].

A commercial version of the SCD (Sievers Research, Inc.; SCD Model 350)^[45] has also been evaluated as a GC detector by Shearer *et al.*^[44] The GC version of the SCD uses a flame ionization detector (FID) as the hydrogen flame, but operates on the same detection principle as the real-time analyzer. The authors have applied the SCD to the determination of organic sulfur compounds separated by GC. Detector response is rectilinear over the three to four orders of magnitude. A modification of this SCD has been developed by Shearer^[46]. The manner in which sulfur monoxide was generated is the only part of the detector that was modified. The modification makes use of an externally heated ceramic combustion assembly that is operated at low pressure and under fuel-rich conditions outside of the flammability limits of hydrogen in air. Hence, this detector is named the flameless SCD. One of the biggest advantages of flameless SCD is that it makes the detector easier to operate and the modification of SCD also results in improved detector precision.

The flameless SCD described by the author is more sensitive than the conventional SCD by at least 1 order of magnitude in most cases (25-50 fg/s vs 400-1000 fg/s for sulfur). This enhances selectivity of the detector, since smaller sample sizes may be used for analysis. Precision was tested with standards of eight sulfur compounds, iso-propyl mercaptan (iPSH), ethyl methyl sulfide (EMS), thiophene (THIOP), methyl disulfide (MDS), 3-methylthiophene (3-MTHIOP), 3-chlorothiophene (3CLTHIOP), benzothiophene (BENZO), and phenyl sulfide (PHS) in n-hexane at concentrations levels of nominally 20 $\mu\text{g}/\text{Kg}$ to 3 mg/Kg.

Therefore, the flameless SCD, as report the author, is the most sensitive GC detector^[47] that produces a nearly equimolar response to sulfur containing compounds.

Matsukami *et. al.*^[48] have applied this flameless-SCD detector to the determination of the total sulfur content. All S compounds (aliphatic sulfides, cyclic sulfides, inorganic sulfides and mercaptans) could be plotted on the same calibration graph, which was linear for up to ~ 14 pg of S. To determine total S contents, a non-stationary phase column was used. Co-existing air gave a positive, correctable bias. Using methane and propane containing 20 mg/l of COS as model hydrocarbons. The interference from the latter was minimized by

setting the FID H₂/air flow rate ratio at about 11:20. The dynamic range of the method was >10⁵ and the detection limit was 31 pg of S.

Other authors^[49] have analyzed volatile sulfur compounds such as H₂S, COS and SO₂, in air samples using the flame photometric detector (FPD) and either the redox CL detector (RCD) and two sulfur CL detectors (SCD 300 and SCD 350). The FPD is the most commonly used detector in the analysis of sulfur compounds that typically responds to 40-430 μg/l of analyte. The RCD is selective for compounds capable of reducing NO₂. Detection limits are generally in the low mg/l range. The SCD 300 is selective for mercaptans, sulfides and disulfides, with detection limits of less than 10 mg/l. The SCD is a general sulfur detector with detection limits of 10 to 90 μg/l. This latter detector demonstrated characteristics of high sensitivity, linearity and insensitivity to matrix effects; these characteristics are highly desirable for the analysis of environmental air samples. This detector for GC is more versatile than the SCD 300 which has greater sensitivity to selected compounds. The RCD is limited due to relatively high detection limits for sulfur compounds.

An evaluation of an electrolytic conductivity (Hall) detector (ELCD), a sulfur chemiluminescence detector (SCD) and the FPD, has been presented by Dominguez *et al.*^[50], for the analysis of sulfur compounds in gaseous matrices. This evaluation includes detection limit determinations, linearity studies and matrix effects on the response. The ELCD demonstrates sensitivity comparable to that of the SCD for mercaptans, sulfides, disulfides and hydrogen sulfide. Linearity for this system is maintained over approximately one order of magnitude. Matrix effects are significant in FPD and ELCD analysis of samples with high hydrocarbon contents.

Another comparison of SCD with a commercially available microwave-induced plasma atomic emission spectroscopic detector (AED) has been reported by Eckert-Tilotta *et al.*^[51]. The two detectors were compared for ten aliphatic and aromatic sulfur-containing organic compounds. This study showed that both instruments have sulfur detection limits in the low picogram range (6-10 pg injected sulfur) with the AED exhibiting slightly better sensitivity. The linear dynamic range for AED was independent of sulfur species at 10⁵, whereas the LDR for the SCD was generally 10⁴. The results of this comparison demonstrate that the selection of AED or SCD for sulfur detection is dependent on cost and whether the need is for a sulfur-only detector or a multielement detector.

A model 350 SCD has been compared, as well, with the standard or 19256 A FPD for the detection of various S gases in air by high-reduction GC analysis (HRGC)^[52]. The SCD showed enhanced sulfur selectivity, greater linear dynamic ranges and lower detection limits than the FPD, while the FPD gave more symmetrical peaks and higher resolution.

Several authors have applied the conventional SCD to chromatography^[53-55]. The application to gas, supercritical fluid and liquid chromatography has been reviewed^[56]. Detection limits, linearity, response factors and selectivity were discussed by the authors for each of these techniques and a brief performance comparison with other selective detectors has been carried out. The flameless SCD is expected to provide advantages when it is applied to supercritical fluid and liquid chromatography. Supercritical fluid chromatography (SFC)^[57-63] offers some advantages over GC for analytical problem solving. For example, analysis of thermally unstable and relatively non-volatile compounds which cannot be achieved in GC has been performed by SFC, because relatively mild temperatures (30-100°C) are employed to achieve their separation.

Applications of the SFC-SCD to the analysis of thermally labile pesticides, sulfur-containing surfactant, polycyclic aromatic sulfur containing hydrocarbons (PASH), diesel fuel, and sulfonyleurea herbicides have been developed.

Ryerson *et al.*^[64] have recently reported the development of a sensitive sulfur-selective detector that can be used at liquid flow rates (ca. 1 ml/min.) characteristic of analytical-scale HPLC, Ion chromatography, and flow injection analysis, employing gas-phase CL for selective detection of liquid-phase sulfur compounds. This detector operates by converting sulfur-containing compounds in the liquid phase, under pressure and elevated temperatures, into sulfur monoxide. Furthermore, once formed, the SO must be allowed to react rapidly with ozone for detection before undesirable side reactions consume it.

Actually, several authors are interested in developing new sulfur CL detection methods, all of them based in the reaction between sulfur monoxide and O₃ to produce SO₂*^[65-69], and its application to the determination of sulfur^[70] and sulfur containing compounds^[71], preferably at trace levels or above, particularly in the fields of environment, biological and medical analysis.

CONCLUSIONS

This paper tries to review the CL techniques used for atmospheric sulfur measurements which have a great interest in air analysis due to the toxicity and low concentrations of species involved.

CL offers several potential advantages for analytical applications. Because of its inherent sensitivity, low detection limits are possible. In addition, instrumentation is relatively simple and inexpensive.

There are many analytical methods available for the determination of SO₂ and SO₃ in the atmosphere which are based in the oxidation of sulfite with MnO₄⁻ or Ce(IV) to SO₂*. The sensitized emission is further enhanced by means of

surfactant micelles, CAPS or cyclooctilamine. However, sulfur dioxide can also be determined using the fact that SO₂ enhances the chemiluminescence produced by the reactions of luminol with NO₂ or H₂O₂.

Several other CL reactions with ClO₂, F₂ or redox schemes have been employed for reduced sulfur compounds detection, but they present many problems, like interferences and difficulties in handling reagents.

The SCD is an Universal sulfur detector based on the reaction between sulfur monoxide and ozone to produce chemiluminescent SO₂*. GC coupled with SCD is frequently used for analysis of individual sulfur compounds in complex matrices, especially in air. A modification of this, the flameless SCD, is more sensitive than the conventional SCD in most cases, and detection limits of 10 to 90 µg/l can be achieved. The high sensitivity, linearity and insensitivity to the matrix effects are highly desirable for the analysis of environmental air samples. Moreover, the flameless SCD compares favorably with other several detectors for sulfur compounds. So, we can conclude that flameless SCD is an alternative and reliable detector for determining atmospheric sulfur compounds.

References

- [1] W. Wardencki and B. Zygmunt, *Anal. Chim. Acta.*, **255**, 1-13 (1991).
- [2] I. Shanahan, in: *Chemical Analysis in complex matrices* (M. R. Smyth Ed., Ellis Horwood Ltd., London, 1992), 1st ed., pp. 192-240.
- [3] I. L. Marr and M. S. Cresser, *Environmental Chemical Analysis* (Blackie & Son Ltd., London, 1983), 1st. ed., p. 94.
- [4] T. J. Kelly, J. S. Gaffney, M. F. Phillips and R. L. Tanner, *Anal. Chem.*, **55**, 138-140 (1983).
- [5] E. L. Wehry, *Anal. Chem.*, **58**, 13-33R (1986).
- [6] D. H. Stedman and M. E. Fraser in: *Chemiluminescence and Bioluminescence* (J. G. Burr ed., Marcel Dekker Inc., New York, 1985), pp. 439-468.
- [7] A. Townshend, *Anal. Proc.*, **22**, 370-371 (1985).
- [8] K. Van Dyke, *Bioluminescence and Chemiluminescence. Instruments and Applications* (CRC Press, Cleveland, 1985), Vol. I and II.
- [9] M. L. Grayeski, *Anal. Chem.*, **59**, 1243A-1256A (1987).
- [10] A. K. Campbell, *Chemiluminescence, Principles and Applications in Biology and Medicine* (Ellis Horwood/VCH, Chichester, 1988).
- [11] J. S. Lancaster and P. J. Worsfold, *Anal. Proc.*, **26**, 362-363 (1989).
- [12] A. Townshend, *Analyst*, **115**, 495-500 (1990).
- [13] K. Robards and P. J. Worsfold, *Anal. Chim. Acta.*, **266**, 147-173 (1992).
- [14] S. A. Soper, L. B. McGown and I. M. Warner, *Anal. Chem.*, **66**, 428-444R (1994).
- [15] M. J. Navas and A. M. Jimenez, *Food Chem.*, **55**, 7-15 (1996).
- [16] A. M. Jimenez, M. J. Navas and G. Galán, *Applied Spectroscopy Reviews*, **32**, 141-149 (1997).
- [17] M. J. Navas, A. M. Jimenez and G. Galán, *Atmos. Environ.*, **31** (1997) in press.
- [18] J.-P. Aittola, M. Hahkala and A. Laukkanen, *Kem.-Kemi*, **15**, 18-21 (1988). *A.A.* **50**, 7H3 (1988).
- [19] P. W. West and G. C. Gaeke, *Anal. Chem.*, **28**, 1816-19 (1956). *C.A.* **51**, 11930h (1957).
- [20] F. X. Meixner and W. A. Jeaschke, *Intern. J. Environ. Anal. Chem.*, **10**, 51 (1981).
- [21] M. Kato, M. Yamada and S. Suzuki, *Anal. Chem.*, **56**, 2529-2534 (1984).

- [22] D. Zhang, Y. Maeda and M. Munemori, *Anal. Chem.*, **57**, 2552-2555 (1985).
- [23] N. Takenaka, Y. Maeda, M. Munemori and D. Zhang, *Analyst*, **113**, 139-143 (1988).
- [24] I. I. Koukli, E. G. Sarantonis and A. C. Calokerinos, *Analyst*, **113**, 603-608 (1988).
- [25] S. A. Al-tamrah, A. Townshend and A. R. Wheatley, *Analyst*, **112**, 883 (1987).
- [26] D. A. Paulls and A. Townshend, *Analyst*, **120**, 467-469 (1995).
- [27] D. A. Paulls and A. Townshend, *Analyst*, **121**, 831-834 (1996).
- [28] W. Tschervenka, A. Kasper, P. Seibert and H. Puxbaum, *Transp. Chem. Transform. Pollut. Troposphere*, **1**, 118-123 (1997).
- [29] D. E. Schorran and R. E. Keislar, *Proc., Annu. Meet.—Air Waste Manage. Assoc.*, **88th (Vol. 3B)**, 95-WP96.05, 17 pp. (1995).
- [30] S. R. Spurlin and E. S. Yeung, *Anal. Chem.*, **54**, 318-320 (1982).
- [31] R. S. Hutte, R. E. Sievers and J. W. Birks, *J. Chromatogr. Sci.*, **24**, 499-505 (1986).
- [32] J. K. Nelson, R. H. Getty and J. W. Birks, *Anal. Chem.*, **55**, 1767-1770 (1983).
- [33] J. S. Gaffney, D. J. Spandau, T. J. Kelly and R. L. Tanner, *J. Chromatogr.*, **347**, 121-127 (1985). *C.A.* **104**, 14310d (1986).
- [34] A. T. Bikkulova, V. V. Yankovenko, V. A. Antipin, S. N. Zagidullin and V. P. Kazakov, *Zh. Anal. Khim.*, **41**, 486-489 (1986).
- [35] A. T. Bikkulova, V. V. Yankovenko and V. P. Kazakov, *Zavod. Lab.*, **52**, 19 (1986).
- [36] S. A. Nyarady, R. M. Barkley and R. E. Sievers, *Anal. Chem.*, **57**, 2074-2079 (1985).
- [37] R. E. Sievers, S. A. Nyarady, R. L. Shearer, J. J. DeAngelis, R. M. Barkley and R. Hutte, *J. Chromatogr.*, **349**, 395-403 (1985).
- [38] J. P. Ivey and H. B. Swan, *Anal. Chim. Acta*, **306**, 259-266 (1995).
- [39] R. L. Benner and D. H. Stedman, *Anal. Chem.*, **61**, 1268-1271 (1989).
- [40] C. J. Halstead and B. A. Thrush, *Proc. R. Soc. London*, **295**, 380-398 (1966).
- [41] R. L. Benner and D. H. Stedman, *Environ. Sci. Technol.*, **24**, 1592-1596 (1990).
- [42] N. G. Johansen and J. W. Birks, *American Laboratory*, **23**, 112, 114-119 (1991).
- [43] R. S. Hutte, N. G. Johansen and M. F. Legier, *J. High Resolut. Chromatogr.*, **13**, 421-426 (1990).
- [44] R. L. Shearer, D. L. O'neal, R. Rios and M. D. Baker, *J. Chromatogr. Sci.*, **28**, 24-28 (1990).
- [45] M. Dyson, *Anal. Proc.*, **30**, 79-86 (1993).
- [46] R. L. Shearer, *Anal. Chem.*, **64**, 2192-2196 (1992).
- [47] R. L. Shearer, *Chem. Anal.*, **131**, 35-69 (1995).
- [48] T. Matsukami, A. Machino and H. Sugimoto, *Anal. Sci.*, **10**, 453-456 (1994).
- [49] R. Jr. Dominguez and M. W. Wadley in: *Sampling Anal. Airborne Pollut.* (E. D. Vinegar and L. H. Keith, eds., Boca Raton, Fla, 1993) pp. 117-31.
- [50] R. Jr. Dominguez, C. B. Choa and M. W. Wadley, *Applied Science & Technology Division*, An air quality report, October (1991).
- [51] S. E. Eckert-Tilotta, S. B. Hawthorne and D. J. Miller, *J. Chromatogr.*, **591**, 313-323 (1992).
- [52] K. K. Gaines, W. H. Chatham and S. O. Farwell, *J. High Resolut. Chromatogr.*, **13**, 489-493 (1990).
- [53] T. B. Ryerson and R. E. Sievers, *Chem. Anal.*, **131**, 1-33 (1995).
- [54] Y. C. Chen and J. G. Lo, *Chromatographia*, **43**, 522-526 (1996).
- [55] H. Tang, P. Heaton and M. Hadley, *Intern. J. Environ. Anal. Chem.*, **64**, 59-69 (1996).
- [56] A. L. Howard and L. T. Taylor, *J. High Resolut. Chromatogr.*, **14**, 785-794 (1991).
- [57] H.-C. K. Chang and L. T. Taylor, *J. Chromatogr.*, **517**, 491-501 (1990).
- [58] L. A. Pekay and S. B. Olesik, *Journal of Microcolumn Separations*, **2**, 270-277 (1990).
- [59] W. F. Sye, Z. X. Zhao and M. L. Lee, *Chromatographia*, **33**, 507-513 (1992).
- [60] A. L. Howard and L. T. Taylor, *Anal. Chem.*, **65**, 724-729 (1993).
- [61] W. T. Foreman, C. L. Shellum, J. W. Birks and R. E. Sievers, *J. Chromatogr.*, **465**, 23-33 (1989).
- [62] H.-C. K. Chang and L. T. Taylor, *Anal. Chem.*, **63**, 486-490 (1991).
- [63] D. J. Bornhop, B. J. Murphy and L. Krieger-Jones, *Anal. Chem.*, **61**, 797-800 (1989).
- [64] T. B. Ryerson, A. J. Dunham, R. M. Barkley and R. E. Sievers, *Anal. Chem.*, **66**, 2841-2851 (1994).
- [65] J. D. Ray and N. Johansen, (Sievers Instruments, Inc. USA). Patent, U.S. US 5501281 A 26 Mar 1996, 9pp. *C.A.*, **124**, 305911 (1996).

- [66] M. Kozakura (Shimadzu Corp., Japan), Patent, *Jpn. Kokai Tokkyo JP 09021753 A2* 21 Jan 1997, 4pp. *C.A.*, **126**, 220069 (1997).
- [67] P. L. Burrow and J. W. Birks, *Anal. Chem.*, **69**, 1299-1306 (1997).
- [68] T. Aki, H. Namba, K. Nakajima, A. Mega, A. Seidoh, M. Kozakura, S. Sumi, T. Nonaka and H. Noda, *Shimadzu hyoron*, **53**, 241-255 (1997).
- [69] S. W. Kubala, D. N. Campbell and R. D. Pearson, Patent, U.S. US 5614417 A 25 Mar 1997, 12 pp. *C.A.*, **126**, 258191 (1997).
- [70] B. A. Larson and D. D. Haydt, *Adv. Instrum. Control*, **50**, 249-258 (1995).
- [71] T. J. Christie, A. Townshend and A. N. Trethewey, Patent, PCT Int. Appl. WO 9610169 A1 4 Apr 1996, 29 pp. *C.A.*, **125**, 25217 (1996).