analytical chemistry

Subscriber access provided by NEW YORK UNIV

Article

Simple and excellent selective chemiluminescence-based CS2 on-line detection system for rapid analysis of sulphur-containing compounds in complex samples

Runkun Zhang, Gongke Li, and Yufei Hu

Anal. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.analchem.5b00722 • Publication Date (Web): 27 Apr 2015

Downloaded from http://pubs.acs.org on April 27, 2015

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a free service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are accessible to all readers and citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

ACS Publications
High quality. High impact.

Analytical Chemistry is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Simple and Excellent Selective Chemiluminescence-Based CS_2 On-Line Detection System for Rapid Analysis of Sulphur-Containing Compounds in Complex Samples

Runkun Zhang, Gongke Li*, Yufei Hu*

School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, China

* Corresponding Authors: Gongke Li, Yufei Hu

Tel. : +86-20-84110922

Fax : +86-20-84115107

E-mail: cesgkl@mail.sysu.edu.cn

huyufei@mail.sysu.edu.cn

ABSTRACT: To study the interesting chemical reaction phenomenon can greatly contribute to the development of innovative analytical method. In this paper, a simple CL reaction cell was constructed to study the chemiluminescence (CL) emission from the thermal oxidation of carbon disulfide (CS_2). We found that the CL detection of CS_2 exhibits unique characteristics of excellent selectivity and rapid response capacity. Experimental investigations together with theoretical calculation were performed to study the mechanism behind the CL reaction. The results revealed that the main luminous intermediates generated during the thermal degradation of CS_2 are SO_2^* and CO_2^*. Significantly, this CL emission phenomenon has a wide application due to many sulphur-containing compounds can convert to CS_2 under special conditions. On the basis of this scheme, a CS_2-generating and detection system was developed for rapid measurement of CS_2 or other compounds that can convert to CS_2. The usefulness of the system was demonstrated by measuring dithiocarbamate (DTC) pesticides (selected mancozeb as representative analyte) based on the evolution of CS_2 in spiked agricultural products. Results showed that the system allows on-line and large volume detection of CS_2 under non-equilibrium condition, which greatly reduces the analytical time. The concentrations of mancozeb in the spiked samples were well quantified with satisfied recoveries of 76.9-97.3%. The system not only addresses the urgent need for rapid in-field screening of DTC residues in foodstuffs, but also opens a new opportunity for the fast, convenient, and cost-effective detection of CS_2 and sulfur-containing compounds in complex samples.

KEYWORDS: Chemiluminescence; Carbon disulfide; On-line detection; Sulphur-containing compound; Dithiocarbamates; Mancozeb; Complex sample.

INTRODUCTION

In the history of analytical chemistry, the research on chemical reaction plays an important role in the development of the innovative analytical methods or instruments. For example, a number of analytical methods are based on the four general reaction types, namely: acid-base,[1] redox,[2] complexation[3] and precipitation reactions.[4] More typically, the chemiluminescence (CL) emission from the reaction between ozone and nitric oxide (NO+O_3 system) occupies a prominent place in analytical chemistry.[5] The application of this light emission phenomenon is not limit to direct determine the concentration of NO, and has been expanded tremendously via directly or indirectly converting other nitrogen-containing compounds (e.g. NO_2 and N-nitroso compounds) to NO.[6-8] Significantly, the total nitrogen analyzer and nitrogen-specific gas chromatography (GC) detector were developed based on this detection scheme.[5, 9, 10]

Chemiluminescence (CL) has proved to be a powerful analysis method for rapid analysis due to its high sensitivity, wide dynamic range, simple instrumentation, and lack of background scattering light interference.[11-13] Many interesting CL phenomena have been developed into analytical methods for biological assays,[14] clinical diagnoses[15] and environmental analysis.[13, 16] However, to the best of our knowledge, methods characterized by coupling sample preparation with CL detection for on-line analysis of objects in complex samples are seldom reported, mainly due to the unsatisfying selectivity for the CL detection. In addition, the conventional CL analysis can only detect a limited number of analyses, and are virtually powerless against many organic gases. In recent years, the research on the CL produced during the oxidation processes of combustible compounds on nanomaterial surface—namely, cataluminescence (CTL)-which has greatly expanded the detectable analytes of CL analysis.[17-19] The luminescence efficiency can be improved greatly when different catalysts and diverse catalysis conditions were applied to CTL detection, resulting in many organic gases which were hardly detected previously and then can be detected successfully.[18] Unfortunately, although the selectivity can be improved by selected by appropriate catalyst, it still remains a major challenge to the CTL detection for the analysis of complex samples. In this regard, to explore CL reaction with intrinsical selectivity has promising applications in rapid analysis of complex sample.

As a highly volatile organic compound (VOC), carbon disulfide (CS_2, boiling point is 46.5 °C; saturated vapor pressure is 53.32 kPa at 28 °C) is a well-known occupational hazard in various industrial processes, such as vulcanizing rubber, oil extraction and viscose rayon fibres manufacturing.[21] It is also frequently used as an insecticide to protect fresh fruit and grains from insects and fungus during shipping, in adhesives for food packaging.[22] However, exposure to CS_2 may cause various health risks such as atherosclerosis, coronary artery disease, encephalopathy and nervous system diseases etc.[23, 24] Aparting from released by anthropogenic activities, CS_2 is also released naturally from volcanoes eruption, marshland, food wastes, coal and natural gas.[25, 26] Moreover, many sulphur-containing compounds also can quantitatively convert to CS_2 under special conditions. For example, CS_2 is one of the degradation products of methyl mercaptan (CH_3SH) in the plasma reactor;[27] the thermal decompositions of dimethyl sulfide ($CH_3S_2CH_3$)[28] and ammonium thiocyanate (NH_4SCN) will form CS_2;[29] Acid hydrolysis of xanthate and dithiocarbamates (DTCs) will release CS_2.[30, 31] Obviously, the development of a simple and miniaturized analytical system for rapid CS_2 detection will has wide applications in many fields.

In the present work, we found that the CL emission from the thermal oxidation of CS_2 exhibits intrinsically selectivity for it does not require any catalyst to assist the light emission, which indicates that this CL reaction has a tremendous application in complex sample analysis. On the basis of this CL reaction, a CS_2-generating and detection system (CS_2-generating DS) characterized by coupling sample preparation device with CL reaction cell, was developed for on-line rapid determination of CS_2 or other compounds that can convert to CS_2. As a proof of-principle work, the system was applied to measure DTC pesticides. DTCs are the most frequently detected pesticides and they show the highest frequency in exceeding the maximum residue limits (MRLs). With the global trading of agricultural goods increases, fast and efficient methods for the monitoring of DTCs in imported/exported foods are urgently needed. Due to the they are practically insoluble in common organic and inorganic solvents, the common methods for measuring DTCs are based on the acid digest of the sample in the presence of stannous chloride ($SnCl_2$) to evolved CS_2, which is further analyzed by absorption spectrometry or gas chromatography (GC).[31-33] However, these methods are tedious and time-consuming, and have the potential to increase errors due to they require off-line complex operations. The CS_2-generating DS allows on-line measure CS_2 released by DTCs in real samples without separation or extraction operation for the excellent selectivity of the CL detection. In addition, the system also can realize large-volume detection of CS_2 under non-equilibrium condition for the rapid response speed of CL detection, resulting in its analysis speed is much faster than the previous methods for DTCs based on the evolution of CS_2. Our system not only addresses the unmet need for inexpensive and simple analytical instrumentations for rapid analysis of DTCs, but also provides an ingenious approach for rapid measure of CS_2 or sulfur-containing compounds that can convert to CS_2 in relative fields.

■ EXPERIMENTAL SECTION

Reagents. Standard solution of 100 μg/mL of mancozeb (chemical formula: $[C_4H_6MnN_2S_4]_xZn_y$, x:y = 1 : 0.091) dissolved in eathylene diamine tetraacetic acid (EDTA) was purchased from Center of Chinese Standard Material Information (Beijing, China). Carbon disulfide was purchased from Damao Chemical Reagent Factory (Tianjin, China). Tin (II) chloride ($SnCl_2$) was obtained from Xilong Chemical Ind., Co., Ltd (Shantou, China). The information of some other reagents can be seen in the Supporting Information.

Analysis System Fabrication. As shown in Figure 1, the CS_2-generating DS mainly comprises a CL reaction cell using a miniature stainless steel heating tube (SSHT, length =6 cm, diameter= 0.3 cm) as heating element, and a CS_2 generator (a polytetrafluoroethylene vessel of about 70 mL volume) with two check valves. The CL reaction cell was simply constructed by placing the miniature SSHT into a quartz tube (length=8 cm, diameter=0.6 cm) with a gas inlet and gas outlet. The temperature of the surface of the SSHT was controlled by a voltage regulator and monitored by a thermocouple. The inlet of the CS_2 generator was connected to a miniature air pump (Model: FAT200.8, Chengdu Xin Wei Cheng Technology Co. Ltd., Chengdu, China) by a polytetrafluoroethylene tube (inner diameter= 0.2 mm, outer diameter= 0.3 mm), and its outlet was connected to the inlet of the CL reaction cell. A computerized BPCL ultraweak luminescent analyzer with a photomultiplier (PMT) detector (Institute of Biophysics, Academia Sinica, Beijing, China) was used to measure the CL intensity. The luminescent analyzer can be easily miniaturized to a very compact one.[34, 35] A high voltage of 860 V was applied to the PMT and the data acquisition time for each signal point was set as 0.5 s. The detection wavelengths of the system could be selected by changing the interference optical filters.

Methods for Mechanism Study. An Agilent HP 6890 gas chromatography (GC)-973 mass spectra (MS) equipped with an HP-VOC fused silica capillary column (60 m length × 0.320 mm inner diameter× 1.80 μm film thickness) was used to identify the products from the thermal oxidation of CS_2. The instrument operating conditions were listed in Table S1 in the Supporting Information. The exhaust from thermal oxidation of CS_2 was collected into a sampling bag of 1 L, and 200 μL of the exhaust was injected into the GC-MS. A Shimadzu RF-5301PC spectrofluorophotometer (Shimadzu Company, Japan) was used to record the CL emission spectrum when the xenon lamp was turned off. CS_2 at the concentration of 4 mg L^{-1} was continuously introduced into the CL reaction cell by the air pump for spectrum scanning. The scanning range was 350 to 550 nm, and the scanning speed was set at super grade. In addition, the CL spectrum was also investigated by the BPCL luminescence analyzer through changing the bandpass filters of 350, 380, 400, 425, 440, 490, 535 and 555 nm.

The Gaussian's implementation of the B3LYP hybrid density functional method with the 6-311++G** basis set was adopted to calculate the optimized geometries of CS_2 and its decomposition species. Vibrational frequency were performed at the same theoretical level to verify reactants and intermediate at the minimum point on the potential energy surface by no imaginary frequency and the transition states at saddle point by only one imaginary frequency.

Sample Preparation and Measurement Procedure. Mung bean and barley were obtained from local market. Because DTC residues are typically located superficially, it is recommended that samples consisting of bigger units (e.g. apples, melons, tomato, iceberg lettuce) will require a comminution step, while for samples composed of small units or particle sizes (e.g. grain, nuts, dry pulses, raisins and even small berries), sample comminution can be typically omitted as long as the sample portion employed for analysis is large enough.[36] Therefore, 5.0 g of mung bean and barley were directly placed into the CS_2 generator, and then were spiked with mancozeb at three levels of 1.0, 5.0 and 8.0 mg/kg for the recovery studies. It was reported that heating, ultrasound or microwave etc. assisted technologies can effectively shorten the hydrolysis time of DTCs.[31] In the present work, ultrasonic bath was used to accelerate the hydrolysis speed of DTCs.

After the samples containing DTCs were placed into the generator, 30 mL of 1.5% $SnCl_2$-4 mol/L HCl (hydrolysis reagent recommended by EU reference laboratories and European commercial testing laboratories.) was added to digest DTCs.[36] Subsequently, the generator was placed into an ultrasonic bath for 30 min. At this stage, the valves of the generator were close. After finishing the acid hydrolysis, the valves were open immediately and a steady air stream was introduced into the generator to carry the generated CS_2 vapor passing through the CL reaction cell. The data was recorded by a computer and further processed with Origin 8.0. The CL kinetic curve showing the CL intensity versus time is used for the study of CL characteristics of CS_2, and peak area is used as the indicator for conditions optimization and quantization.

■ RESULTS AND DISCUSSION

CL Characteristics of CS_2. The CL Characteristics of CS_2 were investigated by off-line injection mode. It was reported that many organic gases can be oxidized on the heated catalysts to produce CL emission, but they cannot produce light emission without catalysts.[37, 38] Therefore, we first tried to use MgO, $SrCO_3$, γ-Al_2O_3 and TiO_2 as catalysts for CL detections of CS_2. As Figure S1 in the Supporting Information shows, the CL intensities of three continuous determinations of CS_2 on these catalyst surfaces decline significantly in sequence, indicating that CS_2 cause the deactivation of catalysts. Similar phenomenon was also observed during the synthesis process of ammonia and methanol etc, which was attributed to sulfur-poisoning.[39,40]

Unexpectedly but Fortunately, we found that strong CL signal also can be observed when CS_2 was heated in air without any catalysts. Therefore, we used a bare SSHT as heating element for CL detection of CS_2. As the Figure 2A shows, the use of SSHT for CL detection of CS_2 overcomes the adverse effect from catalyst poisoning, which also endows this CL system with excellent selectivity to CS_2. The selectivity of this CL system was evaluated by injecting in total of 70 compounds (listed in the Supporting Information) into the CL reaction cell, no CL emission was observed. Consequently, we employ the miniature SSHT to induce the CL emission of CS_2 for the subsequent experiments.

Figure 2A also shows that the response speed of the CL detection to CS_2 is very quick. It can be seen that each injection only acquire a single signal point, indicating that the CL signal of CS_2 vanishing just as suddenly as it appears. However, the signals of the previous reported CL reaction systems generally must spend several seconds to reach the maximum and dozens of seconds to decay to the background.[37,41] In order to give a more concrete comparison, the CL reactions of n-propanol and acetone on $SrCO_3$ surface were investigated under the same conditions. As Figure 2B shows, the CL signals of the two reaction systems last over twenty seconds, the recovery times are much longer than that of CS_2.

Mechanism Study. To study the mechanism behind the CL from the thermal oxidation of CS_2, the GC-MS experiment was performed to investigate the reaction products of the dissociation products of CS_2. As shown in Figure 3A, the thermal degradation of CS_2 yields carbon monoxide (CO), carbon dioxide (CO_2), sulfur dioxide (SO_2) and carbonyl sulfide (OCS). We also found that CL could not be observed when replaced clean air with high purity nitrogen, and no any other products were detected except original CS_2. These results fully demonstrate that oxidant is necessary for the CL emission during the thermal degradation of CS_2.

Gaseous CS_2/O_2 mixtures were observed to laser in flash photolysis and pulsed electrical discharge system.[42] It was reported that one of the possible channel reactions for the oxidation of of CS_2 is to yield the primary products of OCS and S. Subsequently, OCS reacts easily with oxygen atoms to form CO and SO radicals, and then SO radicals are immediately transformed to SO_2 at excited state (SO_2^*), the decay of SO_2^* to its ground state results in photoemissions.[43] The SO_2 afterglow is a strong CL continuum emission band which is reported in the literature to be extends from ultraviolet to blue wavelength with a maximum at about 365 nm, and with some discrete features between 380 and 469 nm.[44, 45] The emission spectrum of our study is given in Figure 3B, the broad band in the range 350 to 550 nm with a maximum at 368 nm matches well with the SO_2 afterglow spectrum. In addition, it was well known that CO also can react with oxygen atoms to form CO_2 at excited state (CO_2^*), accompanying with photoemission.[46, 47] The CO_2* feature which is reported in the literatures is particularly strong in the CS_2 thermal oxidation.

To further study the mechanism, calculations of reaction processes were performed by using the Gaussian 03 suite of programs. The optimized structures of reaction species were successfully obtained by Gaussian's implementation of the B3LYP hybrid density functional method using the 6-311++G** basis set for all atoms. The thermodynamic energies of the reactants, transition states, intermediate state and products are shown in Table S2 in the Supporting Information. It can be seen that the energy of the species in triplet state are lower than they in singlet state, indicating that the triplet species are more thermodynamically accessible during the reaction process. Therefore, according to our experimental results and the relevant data in the literatures, the thermal oxidation mechanism of CS_2 is suggested by reaction paths shown in the Figure 4, and the reactions of 4a and 4b are supposed to the mainly responsible for the CL emission. According to the suggested reaction paths, the total reaction of CS_2 decomposition can be expressed as:

$$\mathrm{CS_2} + 3\mathrm{O_2} = \mathrm{CO_2} + 2\mathrm{SO_2} + hv \qquad (1)$$

According to the Table S2, the enthalpy energy change ($\Delta_r H°$), and Gibbs free-energy change ($\Delta_r G°$) of the corresponding reactions can be obtained from the energy differences between the reactants and the products; the activation energy (ΔE_a) can be obtained from the energy difference between the reactants and the transition states. The $\Delta_r H°$, $\Delta_r G°$ and $\Delta_r E_a$ of the corresponding reaction are shown in Table 1, and the energy profiles are illustrated in Figure S2 in the Supporting Information. These results show the suggested reaction paths are thermodynamically accessible for their low activation energies. The path of oxygen dissociation to produce oxygen atoms requiring large amounts of energy of 79.6 kcal mol^{-1}, while the $\Delta_r H°$ and $\Delta_r G°$ of the other reaction paths are negative, indicating that these reactions are considerably exothermic and feasible from the thermodynamic point of view. The largest negative value of $\Delta_r H°$ and $\Delta_r G°$ of the total reaction are -193.4 kcal mol^{-1} and

-183.7 kcal mol^{-1}, respectively. For a CL reaction, the required energy (ΔE, kcal mol^{-1}) to produce the electronically excited state can be calculated using the following relation:[47]

$$\Delta E = \frac{hc}{4.18\,\lambda} N_A \qquad (2)$$

Where h is Planck's constant (6.626×10^{-34} J·s), c is the speed of light (3×10^{8} m s^{-1}), λ is the wavelength of the CL transition, and N_A is Avogadro's number (6.022×10^{23} mol^{-1}). Since the emission spectrum is present at wavelengths between 350 and 550 nm, an average wavelength 450 nm is used for the calculation. The ΔE is calculated to be 63.6 kcal mol^{-1}. The $\Delta_r H°$ (193.4 kcal mol^{-1}) of the reaction very much exceeds the ΔE, and it is then identified as energetic enough to produce excited state.

As described above, many sulphur-containing compounds can release CS_2, and hence we can make full use of the CL emission of CS_2 to indirect detect these compounds. The work mechanism of the methodology can be described as:

$$\text{Sulphur-containing compound} \xrightarrow{\text{Release}} CS_2 \xrightarrow{[O]} CO_2 + SO_2 + h\nu \qquad (3)$$

Application. Obliviously, this interesting light emission not only is able to direct determine the concentration of CS_2, but also can be expanded to other sulfur-containing compounds via converting them to CS_2. We coupled the CL reaction cell to a CS_2 generator to construct CS_2-generating DS for the demonstration of the methodology in this dimension. In such system, CS_2 is first released by certain process occurred in the generator, and then is introduced into the CL cell for further analysis. As a proof of-principle work, mancozeb, one of the most widely used DTC pesticides in agriculture, was selected as representative analyte. Headspace-gas chromatography (HS-GC) is one of the most commonly used methods for the determination of the DTC residues.[31,33] It involves acid hydrolysis of DTCs to release CS_2, and then a certain volume of CS_2 is injected into the instrument after vapor-liquid equilibrium. However, such method is time-consuming because of it takes a long time to establish vapor-liquid equilibrium, and requires separation procedure for subsequent analysis. Moreover, they are prone to errors due to the off-line incomplete operations. We expect that the system shown in Figure 1 can realize on-line and large-volume detection of CS_2 released by DTCs under non-equilibrium condition, and thereby to effectively reduce the analysis time.

1. Feasibility. The precondition of the CS_2-generating DS to realize on-line and large-volume detection is that serious trailing in CL response curve must be avoided. In order to demonstrate the feasibility, 1 mL of CS_2 at 4 mg L^{-1} was added into the generator, and then was pretreated as the procedure described in sample preparation section. The results of three parallel determinations are shown in Figure 5A, we were pleased to find that the CL response curves show no signs of peak tailing, the signals decay to background within 15 s. In order to further accentuate the unique CL response characteristics of CS_2, the CL response curves of n-propanol and acetone on $SrCO_3$ surface were investigated under the same conditions. As shown in Figure 5B, serious tailing in peak on CL response curves of the two reaction systems are observed, which will affect the quantitative accuracy. This is the rapid response speed of the CL detection of CS_2 enables the realization of the non-equilibrium and large-volume detection. The CS_2-generating DS allows the whole CS_2 in the generator to be transferred into the CL cell under non-equilibrium condition, the analysis time is therefore reduced greatly. In addition, the on-line detection also reduce errors because of it avoids the volatilization loss of CS_2.

2. Conditions Optimization. First, the effect of the time on the acid hydrolysis efficiency of mancozeb was investigated. As Figure S3 in the Supporting Information shows, the decomposition of mancozeb can finish in 30 min under ultrasonic bath condition, while above this value the signal remains constant. Therefore, 30 min was selected as the optimum time of acid hydrolysis.

Next, the volume of the hydrolysis reagent was optimized. As shown in Figure S4 in the Supporting Information, the peak area increases with the increase of volume of the hydrolysis reagent and reaches its maximum at 30 mL. However, the peak area decreases significantly when the volume is above 30 mL, possibly due to the headspace of the vessel decreases with the increase of volume of the hydrolysis reagent.

Finally, the working temperature and flow rate were optimized. The results are shown in Figure S5 in the Supporting Information. It can be seen that the optimum working temperature and flow rate are 368 °C and 150 mL min^{-1}, respectively.

Analytical characteristics. Under the optimal detection condition, calibration curves for CS_2 and mancozeb were prepared by plotting the area versus their concentrations, the results are shown in Figure S6. The linear range of CS_2 and mancozeb are 0.32-82 mg L^{-1} and 1.2-120 mg L^{-1}, and the detection limits are 0.24 and 0.8 mg L^{-1} for CS_2

and mancozeb, respectively. These results fully demonstrate the CS_2-generating DS is able to quantify CS_2 and other sulphur-containing compounds that can convert to CS_2. The relative standard deviations (RSDs) for peak height and peak area of five replicate determinations of 4 mg L^{-1} of CS_2 are 3.3% and 1.4%, and are 4.3% and 2.8% for five replicate determinations of 4 mg L^{-1} of mancozeb, respectively. Obviously, the peak area is more reproducible than peak height, which is the reason of the peak area is used for quantization purpose.

It is worth pointing out that the signal of CS_2 evolved from DTCs is not equal to the same amount of the pure CS_2, leading to the regression equation constructed by the pure CS_2 standards is not the same as that constructed by CS_2 evolved from DTCs standards.[31,48] In addition, DTCs with different polymeric structures evolve different stoichiometric amount of CS_2 for the different sulphur groups in their chemical structures (the more detailed state can be seen in the Supporting Information).[31,48] Because the current legislation for routine enforcement at international levels is based on the determination of DTCs as CS_2, and the existing maximum residue level for DTC residues specified worldwide as mg CS_2/kg food.[31,48,49] Similar with other reported methods, when we cannot ascertain the identities of DTCs or several kinds of DTCs coexist in the samples, CS_2 standards are preferable for the compliance with MRLs;[31,36] however, it is recommend to use the specific DTCs suitable to be present in the samples as standard when only one pesticide will be determined and its identity is well known.[48]

Although the CL detection exhibits excellent selectivity, the presence of CS_2 not related to the use of the DTC fungicides will cause positive interference in the evaluation of DTC residues using the method based on the evolution of CS_2. L-methionine and L-cysteine are important amino acids containing sulphur in foodstuffs, and ethylene thiourea is the main metabolites of ethylene-bis-dithiocarbamates. Interferences from these compounds were investigated by adding 1 mL of these compounds at 100 mg L^{-1} into the generator, and then was analyzed as the same procedure as mancozeb. In addition, interferences from some organosulfur, organophosphorous and organochlorine pesticides (1 mL of 100 mg L^{-1}), including malathion, tolclofos-methyl, iprobenfos, chlorpyrifos-methyl, sulfathiazole, sulfamethizole, sulfachloropyridazine, sulfadiazine, methamidophos, phorate, demeton, phenthoate, dimethoate, simazine, atrazine, chlorothalonil, hexachlorobenzene and dichlorvos were also investigated. The results show that all of these compounds cannot produce CL signal for they cannot decompose into CS_2, which can be possibly attributed to the lack of sulphur–carbon–sulphur bond in their chemical structure.

Recently, methods based on UV/vis spectroscopy[50] and surface enhanced Raman spectroscopy (SERS)[51] were developed for the rapid detection of DTCs. These methods have advantages of simple instrument, high sensitivity and in-field application. However, the uses of gold nanomaterials as colorimetric probes or SERS substrates require expensive and tedious synthetic process to prepare nanomaterials. Especially, the gold nanomaterials are disposable during the analytical processes, which against the reduction of the analytical price. CL methods with lower limits of detection were also developed,[52,53] but they are the same as the SERS methods that only for the detections of some specific DTCs, but not a generic method for total DTCs analysis. Our work provides a robust, reversible and inexpensive method for total DTCs analysis, due to it without using nanometer catalyst, and only consumes the sample and oxygen from the air during the CL detection process.

Samples Analysis. In real sample analysis, a lot of water together with other matrix components will interfere with the detection of CS_2. In this account, separation or extraction steps are necessary for the traditional methods, which leads to these methods are complex and time-consuming. The excellent selectivity of the CL detection suggests that the developed method might be directly applied for detecting DTC residues in real samples. Considering the MRLs for total DTCs (expressed as CS_2) in mung bean and barley were established at 5.0 mg kg^{-1} and 2.0 mg kg^{-1} in EU, respectively. Therefore, recovery studies were carried out at levels of 1.0, 5.0 and 8.0 mg kg^{-1} for mancozeb in mung bean and barley to investigate whether our method could be utilized to analysis the residues of DTCs in real samples. The results are shown in Table 2, satisfactory recoveries ranging from 76.9 to 97.3% were obtained, which is an indicator of its good accuracy and practicability for use with real samples.

Significantly, through preparing the 30 samples (two types of crops × three levels of spiked concentration × five replicate detections) in different generators, the acid hydrolysis of the samples can be performed as planned in an ultrasonic bath, and then these samples were analyzed in sequence after 30 min ultrasonic treatment. The analytical time of each CL detection is about 15 s (Figure 5A), the batch processing of sample enables the analysis of 30 samples to be finished in about 45 min, indicating that our method is particularly promising for customs inspection in where a lot of agricultural products need analyzing for the evaluation of the residual level of DTCs.

CONCLUSION

In conclusion, we have studied the CL phenomenon from the thermal oxidation of CS_2 to exploit its analytical application. Experimental investigations together with theoretical calculation were performed to reveal the mechanism behind the CL reaction. On the basis of this light emission, a CS_2-generating DS was developed for rapid measurement of CS_2 or other sulphur-containing compounds that can convert to CS_2. The usefulness of the system was demonstrated by measuring DTC pesticides based on the evolution of CS_2 in spiked agricultural products. Although further development is still needed to miniaturize and integrate the system for the better in-field application, at this stage it could be used as a rapid screening tool in laboratories to evaluate the need for more detailed analysis of DTCs. In addition, it also has promising applications in other related fields such as direct monitoring CS_2 in air, monitoring natural process accompanying with CS_2 release, or indirectly determinate xanthate in sulfide ore flotation etc.

■ ASSOCIATED CONTENT

Supporting Information

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: cesgkl@mail.sysu.edu.cn

*E-mail: huyufei@mail.sysu.edu.cn

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to thank the National Natural Science Foundation of China for financially supporting this research under grant numbers 21475153, 21127008 and 21105133, and Major National Scientific Instrument and Equipment Development Project (2011YQ03012409), respectively. We thank Dr. Shen Wei at Southwest University for the great help of the theoretical calculation.

REFERENCE

(1) Tajima, T.; Kishi, Y.; Nakajima, A. *Electrochim. Acta* 2009, *54*, 5959−5963.

(2) Noguerol-Arias, J.; Rodríguez-Abalde, A.; Romero-Merino, E.; Flotats, X. *Anal. Chem.* 2012, *84*, 5548−5555.

(3) Sierra, I.; Pérez-Quintanilla, D. *Chem. Soc. Rev.* 2013, *42*, 3792−3807.

(4) Akter, R.; Rahman, M. A.; Rhee, C. K. *Anal. Chem.* 2012, *84*, 6407−6415.

(5) Yan, X. W.; *J. Chromatogr. A* 1999, *842*, 267−308.

(6) Hunter, R. A.; Storm, W. L.; Coneski, P. N.; Schoenfisch, M. H. *Anal. Chem.* 2013, *85*, 1957−1963.

(7) Coneski, P. N.; Schoenfisch, M. H. *Chem. Soc. Rev.* 2012, *41*, 3753−3758.

(8) Liu, M. L; Zhen, L.; Lin, J. M. *Anal. Chim. Acta* 2010, *670*, 1−10.

(9) Soto, R. J.; Privett, B. J.; Schoenfisch, M. H. *Anal. Chem.* 2014, *86*, 7141−7149.

(10) Kocak, D.; Ozel, M. Z.; Gogus, F.; Hamilton, J. F.; Lewis, A. C. *Food chem.* 2012, *135*, 2215−2220.

(11) Tsogas, G. Z.; Giokas, D. L.; Vlessidis, A. G. *Anal. Chem.* 2014, *86*, 3484−3492.

(12) Chen, L. L.; Zhang, Z. J.; Zhang, X. M.; Fu, A. H.; Xue, P.; Yan, R. F. *Food Chem.*2012, *135*, 208−212.

(13) Chen, H.; Li, H. F.; Lin, J. M. *Anal. Chem.* 2012, *84*, 8871−8879.

(14) Li, Q. Q.; Zhang, L. J.; Li, J. G.; Lu, C. *Trends Anal.Chem.*2011, *30*, 401−413.

(15) Powe, A. M.; Das, S.; Lowry, M.; El-Zahab, B.; Fakayode, S. O.; Geng, M. L.; Baker, G. A.; Wang, L.; McCarroll, M. E.; Patonay, G. *Anal. Chem.* 2010, *82*, 4865−4894.

(16) Tang, Y. R.; Su, Y. Y.; Yang, N.; Zhang, L. C.; Lv, Y. *Anal. Chem.* 2014, *86*, 4528−4535.

(17) He, Y. H.; Lv, Y.; Li, Y. M.; Tang, H.; R. Tang, L.; Wu, X.; Hou, X. D. *Anal. Chem.* 2007, *79*, 4674−4680.

(18) Zhu, Y. F.; Shi, J. J.; Zhang, Z. Y.; Zhang, C.; Zhang, X. R. *Anal. Chem.* 2002, 74, 120−124.

(19) Zhang, R. K.; Cao, X. A.; Liu, Y. H.; Chang, X. Y. *Anal. Chem.* 2013, *85*, 3802−3806.

(20) Niu, W. F.; Kong, H.; Wang, H.; Zhang, Y. T.; Zhang, S. C.; Zhang, X. R. *Anal. Bioanal. Chem.* 2012, *402*, 389−395.

(21) Sun, Y. A.; Dai, B. Q.; Wu, Y. L.; Yang, L.; Liu, P.; Wang, Z. P. *Chem. Biol. Interact.* 2013, *206*, 126−133.

(22) Carbon disulfide: Production, import/export, use and disposal. http://www.atsdr.cdc.gov/toxprofiles/tp82-c4.pdf.

(23) Chuang, W. L.; Huang, C. C.; Chen, C. J.; Hsieh, Y. C.; Kuo, H. C.; Shih, T. S. *Neurotoxicology* 2007, *28*, 387−393.

(24) Zhang, B. Z.; Shen, C. Z.; Yang, L.; Li, C. H.; Yi, A. J.; Wang, Z. P. *Toxicol. Appl. Pharma.*2013, *273*, 381−389.

(25) Wu, T.; Wang, X. M.; Li, D. J.; Yi, Z. G. *Atmos. Environ.*2010, *44*, 5065−5071.

(26) Yi, H. H.; Zhao, S. Z.; Tang, X. L.; Song, C. Y.; Gao, F. Y.; Zhang, B. W.; Wang, Z. X.; Zuo, Y. R. *Fuel* 2014, *128*, 268−273.

(27) Tsai, C. H.; Lee, W. J.; Chen, C. Y.; Liao, W. T. *Ind. Eng. Chem. Res.*2001, *40*, 2384−2395.

(28) Vandeputte, A. G.; Reyniers, M.; Marin, G. B. *J. Phys. Chem. A* 2010, *114*, 10531−10549.

(29) Ohta, M.; Hirai, S.; Kato, H.; Sokolov, V. V.; Bakovets, V. V. *Mater. Trans.* 2009, *50*, 1885−1889.

(30) Cordeiro, T. G.; Hidalgo, P.; Gutz, I. G.; Pedrotti, J. J. *Talanta* 2010, *82*, 790−795.

(31) Crnogorac, G.; Schwack, W. *Trends Anal. Chem.* 2009, *28*, 40−50.

(32) Perz, R. C.; Van Lishaut, H.; Schwack, W. *J. Agric. Food Chem.*2000, *48*, 792−796.

(33) Royer, A.; Ménand, M.; Grimault, A.; Communal, P. Y. *J. Agric. Food Chem.* 2001, *49*, 2152−2158.

(34) Hu, J.; Xu, K. L.; Jia, Y. Z.; Lv, Y.; Li, Y. B.; Hou, X. D. *Anal. Chem.* 2008, *80*, 7964−7969.

(35) Kang, C.; Tang, F.; Liu, Y.; Wu, Y.; Wang, X. *Luminescence* 2013, *28*, 313−317.

(36) Analysis of dithiocarbamate residues in foods of plant origin involving cleavage into carbon disulfide, partitioning into isooctane and determinative analysis by GC-ECD. http://www.crl-pesticides.eu/library/docs/srm/meth_DithiocarbamatesCS2_EurlSrm.PDF.

(37) Na, N.; Zhang, S. C.; Wang, S.; Zhang, X. R. *J. Am. Chem. Soc.* 2006, *128*, 14420−14421.

(38) Zhang, R. K; Hu, Y. F; Li, G. K. *Anal. Chem.* 2014, *86*, 6080−6087.

(39) Li, W.; Diyong, W. U.; Wang, S. D.; Yuan, Q. *J. Environ. Sci.* 2008, *20*, 436−440.

(40) Wu, Z. J.; Zhang, M. H.; Li, W.; Mu, S. C.; Tao, K. Y. *J. Mol. Catal. A: Chem.* 2007, *273*, 277−283.

(41) Tao, Y.; Cao, X. A; Peng, Y.; Liu, Y. H. ; Zhang, R. K. *Microchim. Acta* 2012, *176*, 485−491.

(42) Hudgens, J. W.; Gleaves, J. T.; McDonald, J. D. *J. Chem. Phys.* 1976, *64*, 2528−2532.

(43) Sharma, A.; Padur, J. P.; Warneck, P. *J. Chem. Phys.* 1967, *71*, 1602−1607.

(44) Hatem, S.; A., A. S.; Ashwani, G.; 2011, 49th AIAA Aerospace Sciences Meeting including the New Horizons Forum and Aerospace Exposition, Orlando, Florida.

(45) Gaydon, A. G. *Proc. Roy. Soc. A,* 1934, *146*, 901−910.

(46) Lauer, M.; Sattelmayer, T. *J. Eng. Gas Turb. Power* 2010, *132*, 61502−61510.

(47) Kopp, M.; Brower, M.; Mathieu, O.; Petersen, E.; Güthe, F. *Appl. Phys. B* 2012, *107*, 529−538.

(48) Gonzálvez, A.; Garrigues, S.; Armenta, S.; de la Guardia, M. *Anal. Chim. Acta* 2011, *688*, 191-196.

(49) Caldas, E. D.; Miranda, M. C. C.; Conceição, M. H.; de Souza, L. C. K. R. *Food Chem. Toxicol.* 2004, *42*, 1877-1883.

(50) Giannoulis, K. M.; Giokas, D. L.; Tsogas, G. Z.; Vlessidis, A. G. *Talanta*, 2014, *119*, 276-283.

(51) Saute, B.; Premasiri, R.; Ziegler, L.; Narayanan, R. *Analyst*, 2012, *137*, 5082-5087.

(52) Kubo, H.; Tsuda, Y.; Yoshimura, Y.; Homma, H.; Nakazawa, H. *Anal. Chim. Acta*, 2003, 494, 49-53.

(53) Paz, J. L.; Catalá-Icardo, M. *Anal. Chim. Acta*, 2008, 625, 173-179.

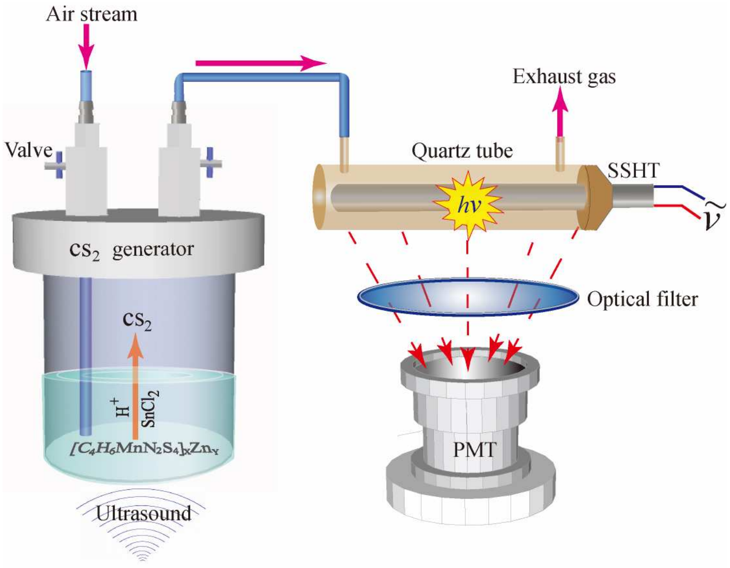


Figure 1. The schematic diagram of the CS_2-generating and detection system.

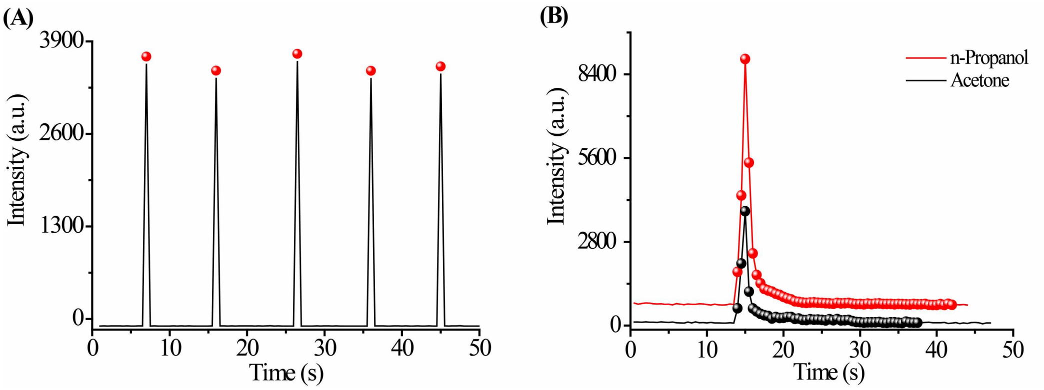


Figure 2. (A) The CL kinetic curves of CS_2 under off-line injection mode using bare SSHT to induce light emission. (B) The CL kinetic curves of n-propanol and acetone under off-line injection mode using $SrCO_3$ to assist the light emission. Working temperature, 368 °C; wavelength, 380 nm; air flow rate, 150 mL min^{-1}; concentrations of CS_2, n-propanol and acetone, 4 mg L^{-1}; volumes of sample injection, 1 mL.

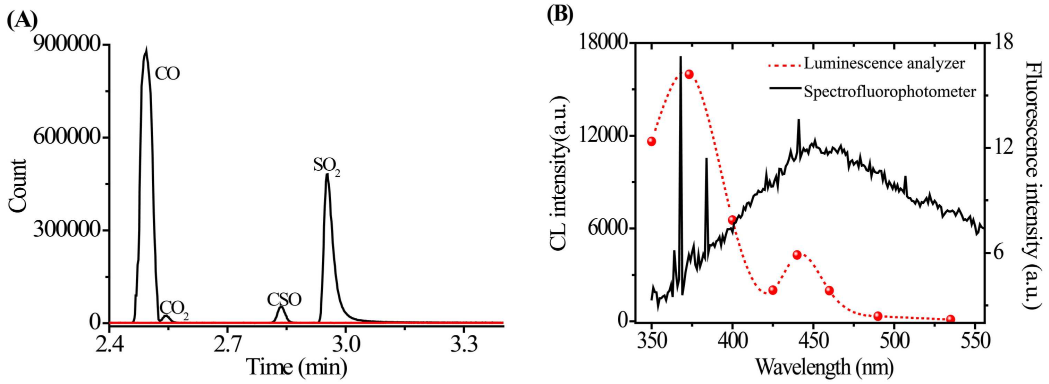


Figure 3. (A) The GC-MS chromatogram of reaction products from the thermal oxidation of CS_2. The red line stands for the result when using high purity nitrogen as carrier gas, no new product was produced. The black line stands for the result when using high purity oxygen as carrier gas. (B) The CL spectra of the thermal oxidation of CS_2 measured with spectrofluorophotometer and BPCL ultraweak luminescence analyzer. The two CL spectra were similar, but the spectrum obtained with the spectrofluorophotometer showed higher spectral resolution, since only several optical filters instead of a monochromator were used in the BPCL luminescence analyzer for the CL analysis. CL reaction condition: working temperature, 368 °C; air flow rate, 150 mL min^{-1}; concentrations of carbon disulfide, 4 mg L^{-1}.

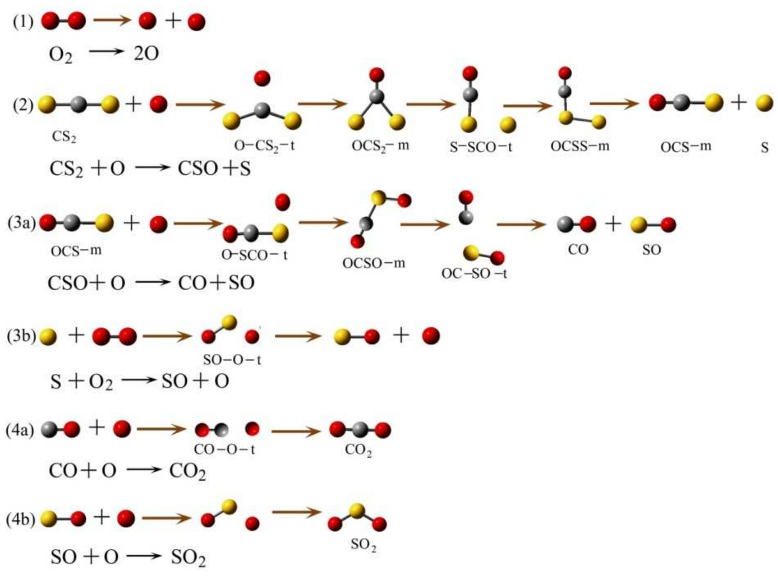


Figure 4. Possible reaction processes for thermal oxidation of carbon disulfide.

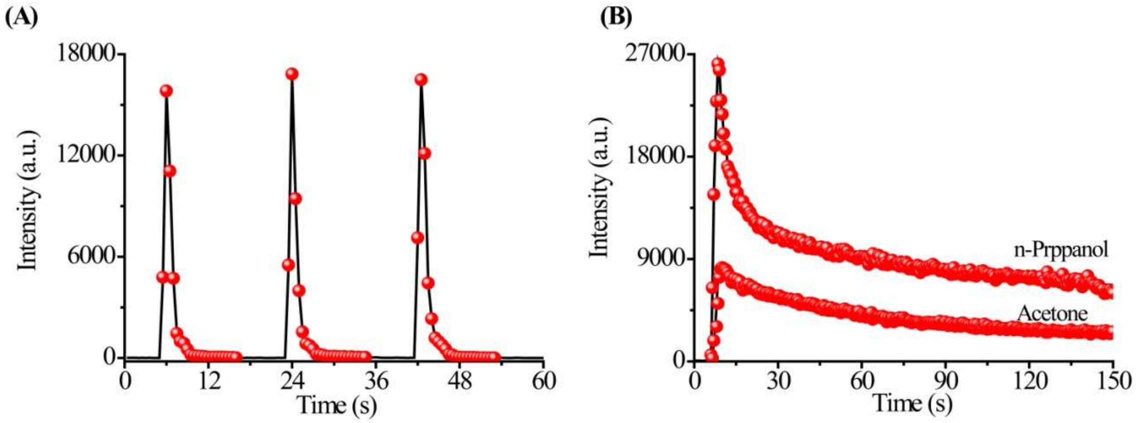


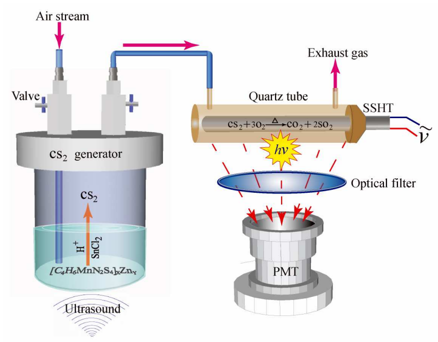
Figure 5. (A) The on-line and large-volume detection of CS_2 under non-equilibrium condition. (B) The on-line and large-volume detection n-propanol and acetone under non-equilibrium condition. Working temperature, 368 °C; wavelength, 380 nm; air flow rate, 150 mL min^{-1}; concentrations of CS_2, n-propanol and acetone, 4 mg L^{-1}; volumes of the three compounds added into the generator, 1mL.

Table 1. Thermodynamic energy (kCal mol^{-1}, 641 K) of possible reactions

Reactions	$\Delta_r H°$	$\Delta_r G°$	$\Delta_r E_{a1}$	$\Delta_r E_{a2}$
1	79.6	71.9	—	—
2	-55.7	-55.9	3.1	16.6
3a	-13.5	-15.4	1.2	6.0
3b	-6.5	-7.1	30.6	—
4a	-127.7	-118.4	30.5	—
4b	-132.5	-124.2	37.1	—
Total	-193.4	-183.7	—	—

Table 2. Recovery of mancozeb from spiked samples (*n*=5)

Samples	1.0 mg kg^{-1}		5.0 mg kg^{-1}		8.0 mg kg^{-1}	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Mung bean	94.7	11.9	92.5	8.5	97.3	5.4
Barley	76.9	14.4	79.3	8.7	86.4	7.7


Air stream
Exhaust gas
Valve
Quartz tube
SSHT
$CS_2+3O_2 \xrightarrow{\Delta} CO_2+2SO_2$
$\tilde{\nu}$
CS_2 generator
hv
Optical filter
CS_2
H^+
$SnCl_2$
$[C_4H_6MnN_2S_4]_xZn_Y$
PMT
Ultrasound

For TOC only