

## **SUPPORTING INFORMATION**

### **Simple and Excellent Selective Chemiluminescence-Based CS<sub>2</sub> On-Line Detection System for Rapid Analysis of Sulphur-Containing Compounds in Complex Samples**

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**Reagents.** Ethylene thiourea, malathion, tolclofos-methyl, iprobenfos, chlorpyrifos-methyl, sulfathiazole, sulfamethizole, sulfachloropyridazine and sulfadiazine were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). L-methionine was purchased from Sinopharm. Chemical Reagent Co., Ltd. (Shanghai, China). L-cysteine was purchased from Shanghai Bio Science & Technology. Co., Ltd. (Shanghai, China). Methamidophos, phorate, demeton, phenthoate, dimethoate, simazine, atrazine, chlorothalonil, hexachlorobenzene and dichlorvos were supported by Agro-Environmental Protection Institute of Ministry of Agriculture.

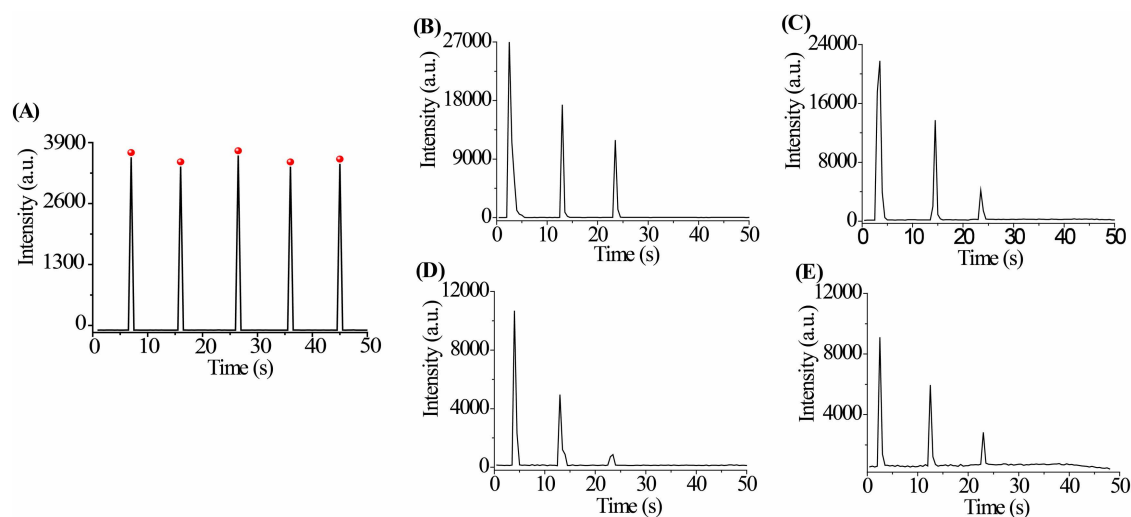
## Instrument Operating Parameters of GC-MS

**Table S1.** Instrument operating parameters of GC-MS

Items	Parameters
Column	HP-INNOWax column (30 m, 0.25 mm i.d., and 0.25 $\mu\text{m}$ film thickness)
Carrier gas	Helium
Oven temperature	120 °C
Injection temperature	220 °C
Injection mode	Splitless
Flow control mode	Linear velocity
Pressure	42.3 kpa
Total flow	11.8 mL min <sup>-1</sup>
Colum flow	0.80 mL min <sup>-1</sup>
Linear velocity	23.8 cm sec <sup>-1</sup>
Purge flow	3.0 mL min <sup>-1</sup>
Ion source temperature	200 °C
Interface temperature	230 °C
Electron energy	70 eV
Scan mod	Full scan
Mass range (m/z)	42-100

## The Results of Using Different Materials for Chemiluminescence (CL) Detection of Carbon Disulfide (CS<sub>2</sub>).

The results of using different materials for three parallel determinations of CS<sub>2</sub> are shown in Figure S1. The CL intensities of CS<sub>2</sub> on these catalyst surfaces decline significantly after exposing to CS<sub>2</sub>, indicating that the CS<sub>2</sub> cause the catalysts' deactivation.



**Figure S1.** The three parallel determinations of CS<sub>2</sub> on different materials. (A) Without catalyst, (B) MgO, (C) SrCO<sub>3</sub>, (D)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, (E) TiO<sub>2</sub>. Working temperature, 368 °C; wavelength, 380 nm; air flow rate, 150 mL min<sup>-1</sup>; concentrations of all compounds, 4 mg L<sup>-1</sup>; volumes of sample injection, 1 mL.

### Selectivity of the CL Detection.

To investigate the selectivity of the CL detection to CS<sub>2</sub>, the saturated vapors (at room temperature) of other 68 compounds, including *n*-pentane, *n*-hexane, *n*-octanol, *n*-nonane, 1,4-dioxane, tetrahydrofuran, ethylene, carbon dichloride, carbon trichloride, carbon tetrachloride, 1,2-dichloroethane, pyrrole, trichloroethylene, epichlorohydrin, *n*-butyl bromide, methanol, ethanol, *n*-propanol, *iso*-propanol, *n*-butanol, *iso*-butanol, *n*-hexanol, *n*-octanol, aniline, phenol, acetone, 2-pentanone, acetylacetone, cyclohexanone, acetophenone, *n*-butyric acid, methacrylic acid, acrylic acid, acrylonitrile, trimethylamine, triethylamine, *o*-toluidine, 2-aminoethanol, triethanolamine, formaldehyde, acetaldehyde, propionaldehyde, *n*-butanal, *n*-hexaldehyde, *n*-nonanal, terephthalaldehyde, benzene, *p*-xylene, *m*-xylene, *o*-xylene, benzoic acid, styrene, phenylacetaldehyde, formic acid, acetic acid, propionic acid, butyric acid, ethyl acetate, methyl propionate, methyl butyrate, ethyl propionate, methyl methacrylate, diallyl disulfide, dimethyltrisulfide, diallyl thioether, allyl methyl disulphide, dimethoxybenzoin and ammonia, as well as 1 mL of high purity nitrogen and carbon dioxide were injected into the system, no CL emission was observed. Moreover, we also could not detect the CL signal even when directly added 20  $\mu$ L of pure ethanol and acetone solutions on the stainless steel heating tube (SSHT) surface. These results indicated that this CL reaction system has an excellent selectivity to CS<sub>2</sub>.

## Thermodynamic Energy of Related Species of Thermal Oxidation of CS<sub>2</sub>.

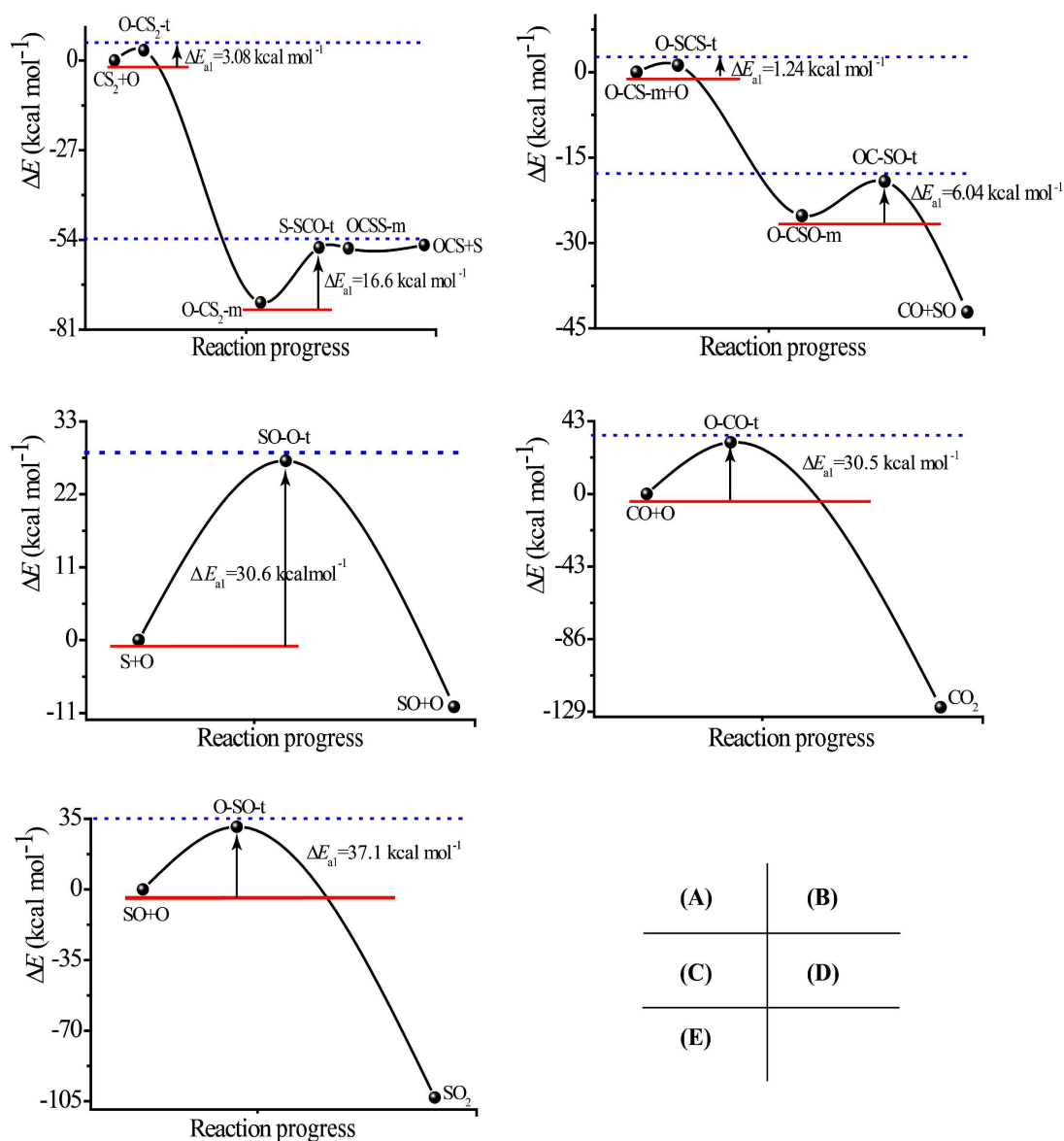
The thermodynamic energy of related species of the thermal oxidation of CS<sub>2</sub> is shown in Table S2.

**Table S2.** Thermodynamic energy (kCal/mol, 641 K) of related species of thermal oxidation of CS<sub>2</sub>

	<i>E</i> /Hartree/Particle	<i>H</i> /Hartree/Particle	<i>G</i>
S	-398.07	-398.07	-398.09
S-3	-398.13	-398.13	-398.15
O	-74.99	-74.99	-75.00
O-3	-75.09	-75.09	-75.10
CS <sub>2</sub>	-834.55	-834.54	-834.57
CO	-113.34	-113.34	-113.36
SO	-473.36	-473.36	-473.38
SO-3	-473.40	-473.40	—
CS <sub>2</sub> O-m	-909.68	-909.68	-909.71
O <sub>2</sub>	-150.31	-150.30	-150.32
O <sub>2</sub> -3	-150.37	-150.36	-150.39
SOO-m	-548.50	-548.50	-548.53
SOO-t	-548.39	-548.39	-548.42
S-CSO-t	-909.60	-909.59	-909.63
OCS <sub>2</sub> -t	-909.64	-909.64	-909.67
O-CSO-t	-586.52	-586.51	-586.55
OC-SO-t	-586.71	-586.71	-586.74
CSO	-511.36	-511.36	-511.39
O-CS <sub>2</sub> -t	-909.63	-909.63	-909.66
OCS <sub>2</sub> -m	-909.75	-909.75	-909.78
S-SCO-t	-909.72	-909.72	—
S-CSO-m	-909.73	-909.72	-909.75
OCS-m	-511.59	-511.59	-511.61
OCSS-m	-909.73	-909.73	-909.75
O-SCO-t	-586.68	-586.67	-586.71
OSCO-m	-586.72	-586.72	—
O-SO-t	-548.44	-548.44	—
SO <sub>2</sub>	-548.66	-548.65	-548.68
O-CO-t	-188.39	-188.38	—
CO <sub>2</sub>	-188.63	-188.63	-188.66

## The Energy Profiles

The energy profiles of the corresponding reaction are shown in Figure S2.

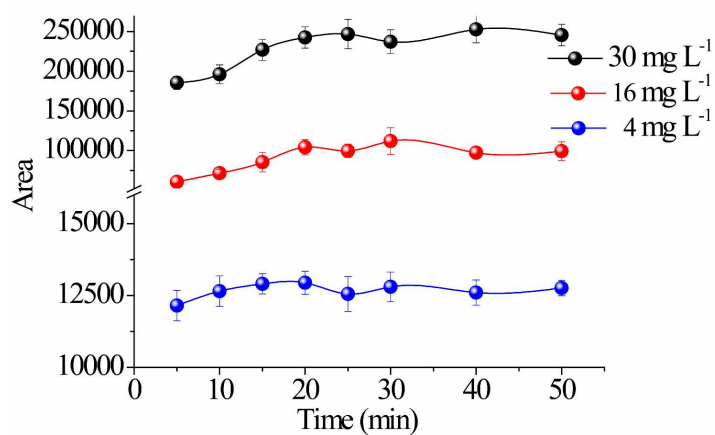


**Figure S2.** The energy profiles of different reaction paths. (A) path 2; (B) path 3a; (C) path 3b; (D) path 4a; (E) path 4b.



### Optimization of Acid Hydrolysis Time

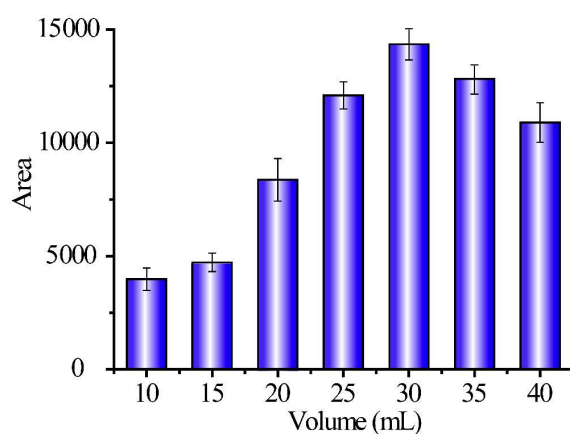
The effect of the time on the acid hydrolysis efficiency is shown in Figure S3, and 30 min was selected as the optimum time of acid hydrolysis for mancozeb.



**Figure S3.** The hydrolysis curves of mancozeb. Working emperature, 368 °C; wavelength, 380 nm; air flow rate, 150 mL min<sup>-1</sup>; 1 mL of CS<sub>2</sub> at a concentration of 4 mg L<sup>-1</sup> was added into the generator.

### Optimization of the volume of the Hydrolysis Reagent

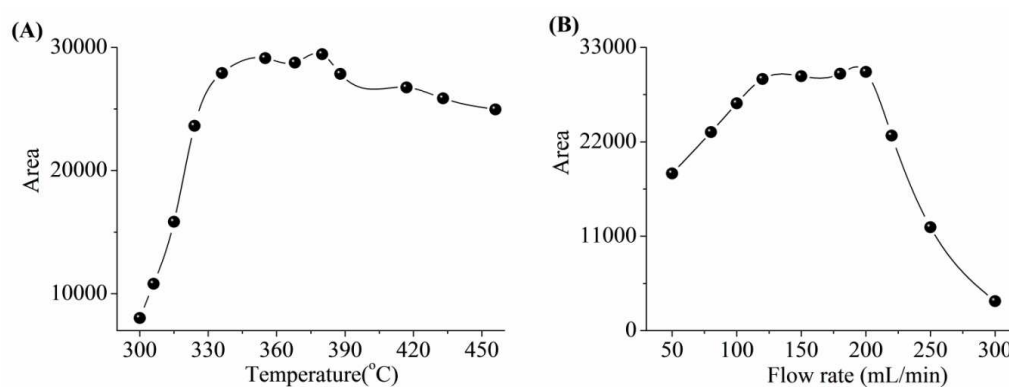
According to the results shown in Figure S4, 30 mL of 1.5%  $\text{SnCl}_2$ -4 mol/L HCl solution was selected as hydrolysis reagent for acid hydrolysis of mancozeb.



**Figure S4.** The effect of the volume of hydrolysis reagent on decomposition efficiency of mancozeb. Working emperature, 368 °C ; wavelength, 380 nm; air flow rate, 150 mL min<sup>-1</sup>. 1 mL of CS<sub>2</sub> at a concentration of 4 mg L<sup>-1</sup> was added into the generator.

### Optimization of Working Temperature and Flow Rate.

Because the current legislation for routine enforcement in many countries is based on the determination of DTCs as CS<sub>2</sub>, and the existing maximum residue level for DTC residues specified worldwide as mg CS<sub>2</sub>/kg food.<sup>1,2</sup> Moreover, the standard methods in many countries for the determination of DTCs also use CS<sub>2</sub> to construct calibration curve.<sup>3</sup> Therefore, working temperature and flow rate were optimized by measuring CS<sub>2</sub> as the same procedure as Figure 5A in the manuscript. As Figure S5 shows, the optimum working temperature and flow rate are 368 °C and 150 mL min<sup>-1</sup>, respectively.

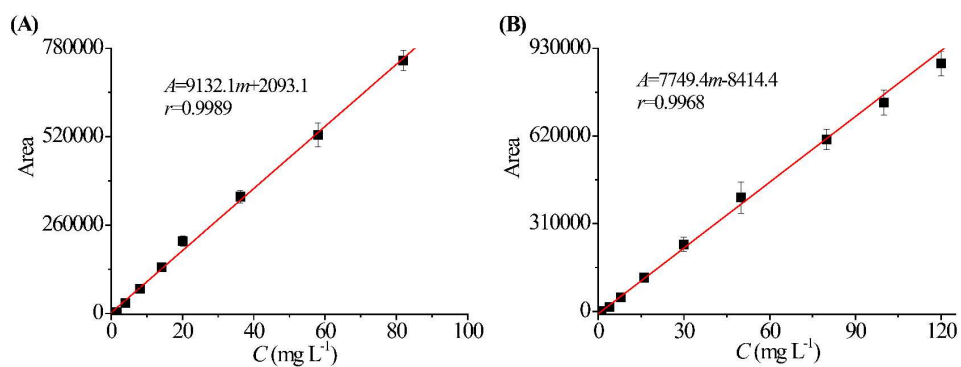


**Figure S5.** (A) The optimization of reaction temperature. (B) The optimization of flow rate.

The wavelength for both (A) and (B) is 380 nm; air flow rate for (A) is 150 mL min<sup>-1</sup>; working temperature for (B) is 368 °C; 1 mL of CS<sub>2</sub> at a concentration of 4 mg L<sup>-1</sup> was added into the generator.

## Calibration Curves.

Under the optimal conditions, the calibration curves of CS<sub>2</sub> and mancozeb are shown in Figure S6, respectively.



**Figure S6.** (A) Calibration curve of CS<sub>2</sub>. (B) Calibration curve of mancozeb. Working temperature, 368 °C ; wavelength, 380 nm; air flow rate, 150 mL min<sup>-1</sup>.

## The Influence of the Polymeric Structure of DTCs

DTC pesticides such as mancozeb, propineb, zineb, and metiram etc. are mainly complexed with transition metals such as Mn, Zn, Cu, Fe and so on, Since the different polymeric structures contain different sulphur groups, for example, mancozeb ( $[\text{C}_4\text{H}_6\text{MnN}_2\text{S}_4]_x\text{Zn}_y$ ,  $x:y = 1 : 0.091$ ), and metiram  $(\text{C}_4\text{H}_7\text{N}_3\text{S}_4\text{Zn})_3(\text{C}_4\text{H}_6\text{N}_2\text{S}_4)_x$ , the number of sulphur atom in the two polymeric DTCs are different, which affects the yield of  $\text{CS}_2$  and will further affect the CL response of the analytical method.<sup>2,4</sup> Because the polymeric structure has relation to the polymer metal, in this regard, the kinds of polymer metal also has an influence on the CL response, and then further affects the sensitivity of the method.

## REFERENCE:

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