Emission evaluation of carbon disulfide from rubber surfaces in small environmental chambers

Ligang Luo¹, Ronghui Yuan¹, Furong Liu¹, Huazhen Yao², Xiaoying Yan³ and Huihui He¹,₄

¹ Zhejiang Light Industrial Product Inspection and Research Institute, Hangzhou 310018, China;
² Hangzhou Wanxiang Polytechnic, Hangzhou 310023, China;
³ Zhejiang Quality and Environment Testing Technology Research Co., Ltd, Hangzhou 310030, China

Email: 729135152@qq.com

Abstract. Carbon disulfide (CS₂) emitted from rubber surfaces was determined by TD-GC-MS. Simulated with 60 L environmental chambers, the emission characteristics of CS₂ from rubber surfaces were investigated. The quantitative approach was confirmed using a dynamic recovery experiment. The emission factors of CS₂ presented a rapid increase especially in the inception phase, and an equilibrium status was obtained while the relative standard deviations were within 5% after 6 h. This method was quite appropriate for the emission characteristic research of sulfide, which provided a theoretical basis for the corresponding environmental supervision of rubber surfaces.

1. Introduction
Few dozen companies produce synthetic runways in China at the beginning of the 21st century, but there have been thousands of those companies so far. Synthetic surfaces are usually used for playground exercise, and together with stable physical performance, their appearance can give customers a sense of comfort [1]. They not only tidy up the environment but also allow activities in various weather conditions [2]. It’s worth noting that carbon disulfide (CS₂) emissions from rubbers are concerned as sources of pollution for outdoor ambient air, which may destroy the metabolism of cells as an enzyme inhibitor with cytotoxic effects [3-5]. In addition, CS₂ is widely utilized as a reaction solvent [6], and rubber polymers release sulfides in the production processes [7]. Rubbers need to be vulcanized for high elasticities. Despite the high vulcanization temperatures, CS₂ is still wrapped in the structure of rubbers in monomer form. During applications of rubber surfaces, natural (ultraviolet radiation) or man-made (material surface damage) conditions will lead to the emissions of free CS₂.

The emissions of detectable volatile sulfides can be measured to explore the current emission inventories entering the atmosphere [8]. Present employed methods for volatile compound tests include environmental chamber-thermal desorption-mass spectrometry, microchamber extractor-thermal desorption-mass spectrometry, and proton transfer reaction-mass spectrometry [9-12]. Harmful substances from rubber materials have received much attention of public opinion and media [13]. Inhalation of CS₂ from synthetic surfaces composed of rubber granules constitutes a hazard to humans [14], for example, students exercising on such surfaces. Children are more vulnerable to CS₂...
poisoning than adults due to their height and immature organs [15], and CS₂ emitted from rubber products into the atmosphere is an important factor influencing environmental quality.

It has been recognized that CS₂ affect health in the actual case of rubber production and usage due to possible acute symptoms to workers. Therefore, research on the CS₂ emission from rubber surfaces is desirable, and has social benefits. In this paper, CS₂ emissions were simulated with small environmental chambers, and then determined by thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS). The proposed quantitative approach was validated using a dynamic recovery experiment. Additionally, the typical curves of CS₂ emission factors (EF) were examined, and meaningful progress was made for the monitoring of CS₂ emissions from rubber surfaces.

2. Experimental section

2.1. Instruments and reagents
The instruments used included a H6L60 environmental test chamber (Qinpei, China), a Trace 1300 gas chromatograph connected to an ISQ 7000 mass spectrometer (Thermo Scientific, USA), a TD-100 thermal desorber (Markes International, UK), a TC-20 multi-tube aging device (Markes International), and a LSP01 micro-injection pump of flow rate within 5–800 µL h⁻¹ (Longer, China).

Ethanol and methanol of chromatographic grade were purchased from Macklin (China). 1000 mg L⁻¹ CS₂ in ethanol was purchased from Aoke (China), and the standards were diluted with relevant solvents. 18.2 MΩ cm water was prepared with a Smart-D water purifier (China).

2.2. Rubber surface preparation
Rubber surfaces of fifteen batches were selected from rubber companies in China, and stored at 23 ± 1 °C and 50 ± 5%RH of environmental norms. Before processing in chambers, the inner surfaces of the chamber were cleaned by ethanol and water. Each rubber surface was prepared in 14 × 15 cm size, and then sealed with aluminium tape at both the cutting faces and the bottom. Next, the surfaces composed of rubber granules were placed in chambers for emission measurement.

2.3. Sampling and TD-GC-MS conditions

| Variables                        | Conditions          |
|----------------------------------|---------------------|
| Chamber volume (V_i)            | 60 L                |
| Sample area (S)                 | 0.021 m²            |
| Sorbent                          | Activated charcoal  |
| Air flow rate                    | 0.3 L min⁻¹         |
| Total sampling volume (V_s)     | 3 L                 |
| Air change rate (AC)            | 0.5 h⁻¹             |
| Sample loading factor (S/V_i)   | 0.35 m² m⁻³         |
| Surface velocity                 | 0.1 m s⁻¹           |
| Atmospheric pressure (P)        | 103.0 kPa           |
| Temperature (T)                 | 60 ± 1 °C           |
| Relative humidity               | 40 ± 2%             |
| Simulated emission time         | 8 h                 |
Sampling parameters including sample loading factor, temperature, relative humidity, and atmospheric pressure inside chambers were set in Table 1, and then the chamber air was gathered for CS\textsubscript{2} determination.

A liquid external standard method of CS\textsubscript{2} was established. Activated charcoal tubes were activated by aging device to minimize the coexistence interference; they were aged at 300 °C for 1 h. Liquid components were injected into the tubes. High purity nitrogen was kept constant through tubes at 100 mL min\textsuperscript{-1} for 5 min, and the tubes were sealed as standards. The TD-GC-MS conditions are presented in Table 2.

### Table 2. TD-GC-MS conditions.

| Parameters | Conditions |
|------------|------------|
| TD         | Cold trap temperature: -5 °C  
Desorption: 220 °C (15 min) |
| GC         | Column: TG-5MS (30 m × 0.25 mm × 0.25 µm)  
Carrier gas: He (99.999%) of 1.0 mL min\textsuperscript{-1} flow rate  
Temperature program: 40 °C (3 min) at 25 °C min\textsuperscript{-1} to 200 °C (2 min) |
| MS         | Ionization mode: EI  
Ionization energy: 70 eV  
\(m/z\) range: 33–90 amu  
Transmission line temperature: 280 °C  
Ion source temperature: 300 °C  
Solvent delay: 1.2 min |

### 3. Results and discussion

#### 3.1. Method validation

Outdoor conditions (temperature 60 °C, relative humidity 40%, surface velocity 0.1 m s\textsuperscript{-1}, etc.) in small chambers were set to evaluate the CS\textsubscript{2} emissions from rubber surfaces in hot weather, simulating the environmental norms of rubber surfaces in summer. Qualitative research was conducted combining both retention time and mass-to-charge ratio \(m/z\), and a chromatogram peak exhibited at around 1.8 min (Figure 1).

![Figure 1. GC-MS chromatogram of CS\textsubscript{2} in ethanol.](image-url)
It could be inferred that TG-5MS column combined with suitable temperature program facilitated the separability of ethanol and CS$_2$. Calibration curves were prepared with standards within 0.3–8.0 μg, and the chromatographic peak areas had good linear relation with the known amounts of standards (Figure 2). The correlation coefficient ($R$) was 0.998. For TD-GC-MS analysis of CS$_2$, the limit of detection was calculated as 0.01 mg m$^{-2}$ h$^{-1}$ based on S/N ratio of the low concentrations at 3:1.

![Figure 2](image-url) Linear regression relationship of CS$_2$ standards, and error bars represent standard deviations.

The standards of CS$_2$ were usually prepared in ethanol or methanol solvents. A bi-component solvent ($V_{\text{carbon disulfide}}/V_{\text{solvent}} = 1/30$) was adopted, and quantitative approach of CS$_2$ was validated using dynamic recovery. For flow-injection testing at flow rate ($\nu$) of 20 μL h$^{-1}$, the injection pump was utilized to diffuse solvent components to chambers till the concentrations eventually equilibrated. The recovery is calculated by Equation (1):

$$\text{Recovery} = \frac{30 \times m_s}{(\nu \times \tau \times \rho \times V_s)/60} \times 100\%$$

where $m_s$ is the amount (μg) of CS$_2$, for $m/z$ at 38.0, 44.0, 75.9 and 77.9 of mass spectrum in Figure 3, the $m/z$ of quantitation peak is 75.9, while the $m/z$ of confirming peak is 44.0. $\tau$ is the balance time (h), and $\rho$ is the density of CS$_2$ ($\rho = 1.26$ g mL$^{-1}$).

![Figure 3](image-url) Mass spectrum of CS$_2$ obtained from TD-GC-MS.
An unspiked-in specimen was used to determine the concentrations of CS$_2$ emitted from bicomponent solvent in environmental chambers. The spike-in specimen was a specific amount of CS$_2$ sequentially adding to mixture solvents. The mean recoveries of flow-injection analysis were 83.1%–87.4% for ethanol, and the mean recoveries for methanol were 79.7%–85.4% (Table 3). The relative standard deviations (RSD) ≤8.5% demonstrated that reproducible data could be generated, whose accuracy and reproducibility were relatively good. The results indicated that the proposed method had a great potential in terms of CS$_2$ monitoring.

| Solvent   | Detected (µg) | Added (µg) | Found (µg) | Recovery (%) | RSD (%) |
|-----------|---------------|------------|------------|--------------|---------|
| Ethanol   | 38.7          | 160.0      | 168.2      | 84.6         | 8.3     |
|           | 20.0          | 98.6       | 83.1       | 7.8          |         |
|           | 160.0         | 169.3      | 85.4       | 7.3          |         |
| Methanol  | 38.2          | 80.0       | 98.0       | 82.9         | 7.6     |
|           | 20.0          | 46.4       | 79.7       | 8.5          |         |

3.2. Emission characteristics of CS$_2$ from rubber surfaces

The CS$_2$ concentration ($C_j$) and the CS$_2$ concentration in the standard state ($C_{si}$) were examined in six small chambers using different sequence numbers. $C_j$ can be calculated by Equation (2):

$$C_j = \frac{m_j-m_0}{V_S}$$

(2)

where $m_j$ is the amount of component, and $m_0$ is the amount of blank sample. $C_{si}$ and EF are calculated by Equation (3) and (4):

$$C_{si} = C_j \times \frac{101.3}{p} \times \frac{T+273.1}{273.1}$$

(3)

$$EF = \frac{C_{si} \times V_j \times AC}{S}$$

(4)

| No. | $m_0$ (µg) | $m_j$ (µg) | $T$ (°C) | $C_j$ (mg m$^{-3}$) | $C_{si}$ (mg m$^{-3}$) | EF (mg m$^{-2}$ h$^{-1}$) |
|-----|------------|------------|----------|---------------------|------------------------|--------------------------|
| 1   | 0.07       | 1.36       | 60.1     | 0.43                | 0.52                   | 0.74                     |
| 2   | 0.15       | 1.99       | 60.7     | 0.61                | 0.74                   | 1.05                     |
| 3   | 0.11       | 4.63       | 60.8     | 1.51                | 1.81                   | 2.59                     |
| 4   | 0.14       | 1.68       | 59.5     | 0.51                | 0.61                   | 0.88                     |
| 5   | 0.09       | 0.11       | 60.0     | ND$^a$              | ND                     | ND                       |
| 6   | 0.13       | 5.07       | 59.4     | 1.65                | 1.97                   | 2.82                     |
| 7   | 0.18       | 2.06       | 60.1     | 0.63                | 0.75                   | 1.07                     |
| 8   | 0.12       | 3.58       | 60.5     | 1.15                | 1.39                   | 1.98                     |
| 9   | 0.16       | 5.88       | 60.8     | 1.91                | 2.29                   | 3.28                     |
| 10  | 0.17       | 1.83       | 60.9     | 0.55                | 0.67                   | 0.95                     |
| 11  | 0.15       | 3.02       | 60.2     | 0.96                | 1.15                   | 1.64                     |
| 12  | 0.10       | 0.13       | 59.3     | ND                  | ND                     | ND                       |
| 13  | 0.14       | 9.51       | 59.7     | 3.12                | 3.74                   | 5.35                     |
| 14  | 0.09       | 1.50       | 60.6     | 0.47                | 0.56                   | 0.81                     |
| 15  | 0.13       | 3.95       | 60.3     | 1.27                | 1.53                   | 2.18                     |

$^a$ ND = Not detected.
Four batches were >2.5 mg m\(^{-2}\) h\(^{-1}\), which were associated with No. 3, No. 6, No. 9 and No. 13, respectively (Table 4). Furthermore, the $EF$ curves of No. 3, No. 6 and No. 9 were screened. The CS\(_2\) concentrations of positive CS\(_2\) specimens were detected periodically. The GC-MS chromatograms were gathered from chamber air of representative rubbers. We considered it to be the steady-state emission of CS\(_2\) after long-term emissions, which meant it was time to end measurement. The $EF$ increased quickly during the inception phase, revealing that the $EF$ peaks of positive specimens appeared at around 2 h (Figure 4). Subsequently, the typical curves decreased in a nonlinear way, and the $EF$ values were steady with minor changes when prolonging to 6 h. Hence, the evaluation of CS\(_2\) emissions from rubber surfaces was helpful for enterprises to promote the quality of rubber products.

![Figure 4. Typical curves of CS\(_2\) emissions from positive specimens.](image)

4. Conclusions
Environmental chamber combined with TD-GC-MS was utilized to preliminarily assess the $EF$ of CS\(_2\) form rubbers. A case study of rubber surfaces had illustrated the methodological applicability. For evaluation of CS\(_2\) emission characteristics, $EF$ values of representative surfaces were studied. The $EF$ peaks of positive specimens occurred near 2 h, and a steady state for CS\(_2\) emissions was finally obtained. 26.7% of $EF$ derived from the rubber selections were >2.5 mg m\(^{-2}\) h\(^{-1}\). Hence, rubber material is an important source of reactive CS\(_2\) and should be considered in the emission inventories of air pollutants. It will be beneficial for future revision of CS\(_2\) emission limits of rubber materials, and proposing a simple route to establish appropriate sulfide supervision.

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