



Gas analyzer for continuous monitoring of trace level methanethiol by microchannel collection and fluorescence detection



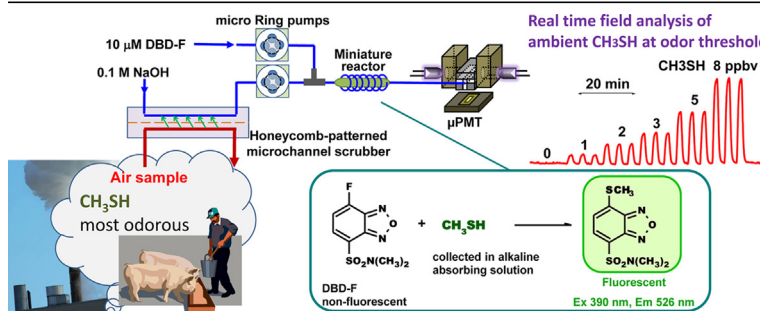
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HIGHLIGHTS

- An inexpensive and small system is developed for analysis of CH₃SH in ambient air.
- CH₃SH is collected by a microchannel scrubber and reacted with DBD-F.
- DBD-F reacts with CH₃SH to produce fluorescence for fluorometric analysis.
- With this method, CH₃SH can be detected at the odor threshold.
- CH₃SH emitted from pulping and a piggery could be monitored continuously.

GRAPHICAL ABSTRACT



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ABSTRACT

The highly odorous compound methanethiol, CH₃SH, is commonly produced in biodegradation of biomass and industrial processes, and is classed as 2000 times more odorous than NH₃. However, there is no simple analytical method for detecting low parts-per-billion in volume ratio (ppbv) levels of CH₃SH. In this study, a micro gas analysis system (μ GAS) was developed for continuous or near real time measurement of CH₃SH at ppbv levels. In addition to a commercial fluorescence detector, a miniature high sensitivity fluorescence detector was developed using a novel micro-photomultiplier tube device. CH₃SH was collected by absorption into an alkaline solution in a honeycomb-patterned microchannel scrubber and then mixed with the fluorescent reagent, 4-(*N,N*-dimethylaminosulfonyl)-7-fluoro-2,1,3-benzoxadiazole (DBD-F). Gaseous CH₃SH was measured without serious interference from other sulfur compounds or amines. The limits of detection were 0.2 ppbv with the commercial detector and 0.3 ppbv with the miniature detector. CH₃SH produced from a pulping process was monitored with the μ GAS system and the data agreed well with those obtained by collection with a silica gel tube followed by thermal desorption–gas chromatography–mass spectrometry. The portable system with the miniature fluorescence detector was used to monitor CH₃SH levels in near-real time in a stockyard and it was shown that the major odor component, CH₃SH, presented and its concentration varied dynamically with time.

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1. Introduction

Reduced sulfur compounds are highly odorous and are emitted naturally and anthropogenically from many sources. Among these compounds, methanethiol (CH₃SH, common name methyl mercaptan) is the most odorous and is naturally emitted with

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biological activity. Emission of methanethiol is high from anthropogenic sources such as landfill facilities [1], pit latrines [2] and pig farming [3]. Chemical production of methanethiol is also a problem in industries such as pulp and paper production [4]. The odor threshold for CH_3SH , 1.6 ppbv (parts-per-billion in volume ratio), is four orders of magnitude smaller than that for NH_3 (52 ppmv) [5]. Consequently, CH_3SH detection at low concentrations is required for odor control. However, measurement of CH_3SH is very difficult [6] and there are no reports of analytical methods for continuous CH_3SH detection at levels around the odor threshold. Pandey and Kim [7] and Ras et al. [8] reviewed the available methods for determination of reduced sulfur compounds. The most common method for trace level determination of CH_3SH involves collection into a stainless steel canister or a Tedlar bag in the field and subsequent laboratory analysis. In the laboratory, the gas is preconcentrated at liquid argon temperature, thermally desorbed to introduce into a gas chromatograph (GC) and detected by a flame photometric detector. Loss of CH_3SH through reaction and adsorption during transport and storage is of a concern in the conventional method. Deshmukh et al. determined the odor intensity in methyl mercaptan equivalents using an electric nose comprising an array of commercial gas sensors and a data processor [9]. The electric nose gave real time data but could only detect CH_3SH at concentrations down to the ppmv levels. Soft ionization mass spectrometry is an attractive real time method for CH_3SH detection [3] but it is extremely costly and too large for mobile monitoring. Kudryavtsev et al. demonstrated CH_3SH analysis with an original portable MS coupled with a preconcentration device [10]. The same inline preconcentration system was previously developed by our group for a field instrument called a single column trapping/separation–ozone-induced chemiluminescence measurement (SCTS-CL) [11,12]. The SCTS-CL was applied to monitoring of CH_3SH emitted from a pulp plant on the Lake Baikal shore [13] and indoor air monitoring at a pig farm [14]. Automated field monitoring on a ship and a car with the SCTS-CL instrument was successful, with sequential analyses conducted at 15 min intervals. We recently developed a micro gas analysis system (μGAS) to monitor atmospheric H_2S and SO_2 [15], HCHO in forests and city streets [16], and NO in exhaled breath [17]. The μGAS can also be used to measure unstable dissolved volatile compounds in natural water at trace levels (nanomoles per liter order) by coupling with a vapor generator [18]. A honeycomb-patterned microchannel scrubber, a key part of the μGAS , enables collection of gaseous CH_3SH , H_2S and SO_2 into an alkaline solution.

The fluorescent reagent, 4-(*N,N*-dimethylaminosulfonyl)-7-fluoro-2,1,3-benzoxadiazole (DBD-F) [19], is commercially available for derivatization of amino [20] and thiol compounds [21] for their HPLC analysis. We tested this reagent for gaseous CH_3SH analysis and found that gaseous CH_3SH could be analyzed without interference from coexisting gases. DBD-F is a non-fluorescent

benzoxadiazole compound, and its fluoro functional group is exchanged with $-\text{SCH}_3$ of CH_3SH to produce a highly fluorescent derivative, DBD- SCH_3 (Scheme 1). In this work, the system and absorbing/reagent solutions were optimized for CH_3SH analysis. Unfortunately, the miniature fluorescence (FL) detector previously developed for the μGAS [15] was not sufficiently sensitive to detect DBD- SCH_3 FL. Therefore, a high performance miniature FL detector was developed using a novel micro-photomultiplier tube (μPMT) for field monitoring. The performance of the method was evaluated by comparison of the obtained data with those from thermal-desorption gas chromatograph–mass spectrometry (TD-GC-MS). The system was used to measure CH_3SH emissions from a laboratory-scale pulping process and in the field beside a piggery enclosure.

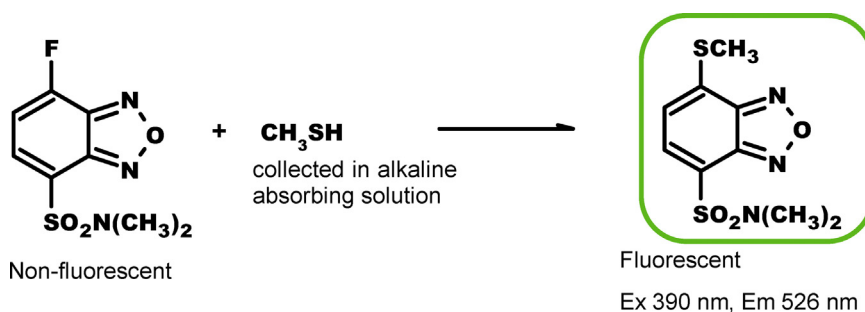
2. Experimental

2.1. Chemicals

DBD-F was obtained from Tokyo Kasei (Tokyo, Japan). A 1 mmol L^{-1} DBD-F stock solution was prepared by dissolving DBD-F in acetonitrile (ACN) and was stored in a refrigerator. A working reagent solution was prepared by diluting the DBD-F stock solution 100 times with purified water. The final composition of the working reagent solution was $10 \mu\text{mol L}^{-1}$ DBD-F in an aqueous 1% ACN solution. The absorbing solution for collection of CH_3SH was 0.1 mol L^{-1} NaOH.

The following chemicals were used to investigate interference in the aqueous phase: sodium methanethiol (CH_3SNa) and anhydrous sodium sulfide from Sigma–Aldrich (St. Louis, MO), dimethyl sulfide (DMS) from Wako Pure Chemical Industries (Osaka, Japan), and 1-propanethiol from Kanto Chemical (Tokyo, Japan). Each of these compounds was dissolved in 0.3 mol L^{-1} NaOH. For amine compounds, ammonium chloride from Wako Pure Chemical Industries and *L*-cysteine and histamine from Nacalai Tesuque (Kyoto, Japan) were dissolved in purified water.

For gas tests, the following standard gases were used: CH_3SH , H_2S , DMS, SO_2 , CS_2 , and NH_3 . The gas concentration in each cylinder was 100 ppmv with the balance as nitrogen gas. Ethanethiol and trimethylamine gases were prepared using permeation tubes P-72-H ($0.90 \mu\text{g min}^{-1}$ at 20°C) and P-180-H ($13 \mu\text{g min}^{-1}$ at 20°C) (Gastec, Kanagawa, Japan), respectively. 1-Propanethiol gas was prepared by placing liquid 1-propanethiol in a diffusion tube (D-01, 1.6 mm i.d. \times 60 mm, Gastec) to obtain a vaporization rate of $0.83 \mu\text{g min}^{-1}$. All gases were diluted with Peltier-cooler dried air purified with columns packed with silica gel and soda lime/activated carbon. The gas concentration was adjusted by controlling the flow rates of the cylinder gas and the purified air using mass flow controllers (Models 3600 and 3666A, Kofloc, Kyoto, Japan). Low concentrations (ppbv) of gases were prepared by diluting twice with the purified air.



Scheme 1. Reaction of CH_3SH with DBD-F.

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