

# Guided episodic sampling for capturing and characterizing industrial plumes

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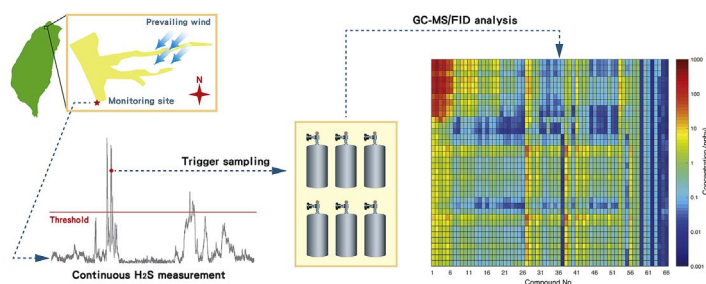
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## GRAPHICAL ABSTRACT



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## ABSTRACT

An integrated sampling technique, dubbed trigger sampling, was developed to capture characteristic industrial emissions or plumes. In the field experiment, a hydrogen sulfide ( $\text{H}_2\text{S}$ ) analyzer was used as the triggering instrument at the boundary of a refinery plant due to frequent complaints of foul smell from local residents. Ten episodic samples were captured when the  $\text{H}_2\text{S}$  level surpassed the prescribed trigger level of 8.5 ppbv over a three-day period. Three non-episodic (blank) samples and 23 road-side samples were also collected for comparison. All the 36 flask samples were analyzed by gas chromatography–mass spectrometry/flame ionization detection (GC–MS/FID) for 108 volatile organic compounds (VOCs). The total VOC abundance of the event samples was exceedingly higher than the non-episodic samples by over 80 times in the extreme case. Alkanes were found to be the dominant constituents in the event samples, amounting to over 90% of the total VOC concentrations vs. only 30–40% for the blank and metropolitan samples. In addition, light alkanes in the event samples were highly correlated with the trigger species  $\text{H}_2\text{S}$  ( $R^2 = 0.82$ ), implying their common origin. The matrix of chemical composition vs. sample types permitted easy visualization of the dominance of light alkanes for the event samples compared to other types of samples. Principle component analysis (PCA) identified two major contributors to cover 93% of the total variance arising from the 36 samples, further quantifying the distinction of the triggered episodic samples from the contrast samples. The proposed trigger sampling is a coupling of fast-and-slow measurement techniques. In this example, the fast-response  $\text{H}_2\text{S}$  analyzer served to “guide” sampling to capture industrial plumes which were then characterized by a relatively slow method of GC–MS/FID for detailed chemical composition representative of the prominent sources.

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## 1. Introduction

In recent decades the pursuit of high economic growth with brisk industrial activities creates an unprecedented burden on the environment and public hygiene. The impact is even more acute in regions where land is scarce and the boundaries between industrial and residential areas become blurry over time. Residential housing is often in the proximity of the factories by only crossing a street. In Taiwan, residential complaints of industrial pollutants from the peripheral communities often rank the highest among various forms of pollution on the island. Intuitively, pollution from the industrial sources is often subjectively perceived as toxic, arousing health concerns and thus creating political pressure for the governmental agency to act and provide solutions. Although industrial emissions can be persistent in some cases, it is often elusive and intermittent due either to the nature of industrial activities or to local meteorology, rendering source investigation challenging. As a result, devising techniques that can produce robust chemical evidence to hold emitters accountable would aid regulatory agencies in effectively curbing pollution and ultimately improving air quality.

In light of the elusive nature of industrial pollution episodes, on-site monitoring in residential areas with fast response and sufficient selectivity and sensitivity to key compounds is a necessity. However, instruments that can analyze a wide variety of volatile organic compounds (VOCs) of interest because of their odor or toxicity with sufficient speed and sensitivity, such as proton-transfer-reaction mass spectrometry (PTR-MS) (Lindinger et al., 1998; Blake et al., 2009), atmospheric pressure chemical ionization mass spectrometry (APCI-MS) (Mulligan et al., 2006; Badjagbo et al., 2009), and differential optical absorption spectrometer (DOAS) (Skov et al., 2001; Chiu et al., 2005; Lee et al., 2005) are either rare or costly. On the other hand, flask sampling is a mature and cost-effective means to analyze a full spectrum of VOCs in plumes. However, it is not only laborious but also more subject to sampling biases for field personnel when attempting to collect plume samples, and sometimes can even be misleading if samples are not representative of the sources. Information resulting from unreliable sampling could further cloud judgments and decision making.

Air analysis by gas chromatography–mass spectrometry (GC–MS) is a mature and effective tool for VOC analysis, which can either be placed in the field (on-line) (Su et al., 2008; Wang et al., 2012; Ou-Yang et al., 2016) or in the laboratory (off-line) (Chang et al., 2010, 2014) to monitor ambient VOCs. However, the low-speed analysis with GC, requiring minutes to tens of minutes for each cycle of analysis, makes it unsuitable as a frontline tool to capture elusive pollution episodes. Fast detection of molecular ions by mass spectrometry can meet the requirements of speed and compound range (de Gouw and Warneke, 2007); however, the overall cost of operation is high. In light of the aforementioned drawbacks, a method was sought that involves a simple and inexpensive approach targeting a single key compound to “guide” sampling at the moment of plume occurrence. The much needed chemical composition representative of the episodic air can be subsequently obtained in the laboratory by slow but more available and robust analytical techniques such as GC or GC–MS to analyze the

triggered samples. The fast-and-slow complementary approach that combines both speed and chemical composition can provide robust knowledge of plume characteristics, which is pivotal to pollution investigation and thus control measures (Zhou et al., 2007).

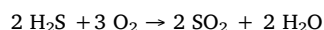
In this work, a major refinery complex situated on the rim of a heavily populated city (approximately 410 k residents) was suspected to be the major source of public complaints in the region. Due to perennial complaints of foul odor from residents, both the local government and the refinery were under pressure to find solutions to unambiguously determine the source of the episodes in the region. As a demonstration, the fast-and-slow complementary approach was adopted by configuring a hydrogen sulfide ( $\text{H}_2\text{S}$ ) analyzer as the fast-response monitoring unit to capture plumes and trigger sampling instantaneously due to its strong linkage to the characteristic emission from the refinery. Subsequently, the triggered samples were then analyzed by an in-laboratory GC–MS as the slow analytical technique to obtain chemical composition to facilitate source identification. For instance, previous efforts have employed a cavity ring-down spectrometer for guided sampling to investigate methane source apportionment in a hydraulic fracturing region near Fort Worth (Townsend-Small et al., 2015). Although both analytical methods are conventional, the method of trigger-sampling to unambiguously capture plumes for detailed compositional analysis provides an integrated approach to secure fingerprinting evidence for further source identification.

## 2. Experimental

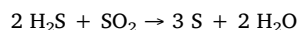
### 2.1. Background description

The demonstration site was a refinery complex, which was established decades ago, and produced premium gasoline and jet fuel for the island. In earlier years, the surrounding areas were mostly rural with a limited population. Throughout the years of rapid urbanization, residential and business establishments sprouted and diminished the buffer zone adjacent to the complex (see Fig. 1 for the terrain of the plant and its surroundings). Complaints of emissions from local residents mainly to the west were frequent over the years. For instance, the number of complaints received during the period from 2006 to 2010 was 52 per year on average, mainly occurring in the fall (September–October).

$\text{H}_2\text{S}$  was one of the characteristic pollutants from the refinery due to its distinct smell. The hydro-desulfurization process converting sulfur compounds in crude oil to  $\text{H}_2\text{S}$  via reaction with hydrogen to lower the sulfur content in gasoline to less than 20 ppm was required to meet the Taiwan EPA regulations. A fraction of  $\text{H}_2\text{S}$  was oxidized to sulfur dioxide ( $\text{SO}_2$ ):



Subsequently, the resulting  $\text{SO}_2$  reacted with the remaining  $\text{H}_2\text{S}$  to form elementary sulfur via the Claus reaction:



The unreacted  $\text{H}_2\text{S}$  along with other waste products of refinery were



Fig. 1. Location and terrain of the refinery and the monitoring site. The boundary of the refinery plant is indicated by the yellow line on the right panel. The satellite images were acquired by the FORMOSAT-2. The Taiwan's National Space Organization retains the copyright of the imagery products. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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