Atmospheric Environment 82 (2014) 401–409

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Quantitative determination of pulp and paper industry emissions and associated odor intensity in methyl mercaptan equivalent using electronic nose

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HIGHLIGHTS

- Electronic nose designed to assess obnoxious emissions from pulp and paper industries.
- E-nose is trained to accurately determine odorant concentration and odor intensity.
- Concentrations of $(CH_3)_2S$, $(CH_3)_2S_2$, CH_3SH and H_2S were predicted rapidly by e-nose.
- Odor intensity of emissions is determined by e-nose in methyl mercaptan equivalent.
- Results indicate potential of e-nose for onsite industrial emissions measurement.

ARTICLE INFO

Article history:
Received 14 March 2013
Received in revised form
1 October 2013
Accepted 17 October 2013

Keywords:
Electronic nose
Reduced sulfur compounds
Principal component analysis
Response surface methodology
Odor intensity
Singular value decomposition

ABSTRACT

The obnoxious odors generated from pulp and paper industries have been the cause of nuisance since the instigation of these industries. The objective of the study was to develop a metal oxide sensor based electronic nose for rapid measurement of odorant concentration and associated odor intensity of major reduced sulfur compounds emitted from different sources of these pulp and paper mills. The gas samples collected from the surroundings of major source points of industry were exposed to sensor array of the electronic nose and the change in voltage was measured and taken to PC through data acquisition cards. The same sets of samples were also tested with gas chromatography. The results of electronic nose and GC-FPD were correlated using response surface methodology to know the odorant concentration. The model fed with unknown industrial samples had more than 95% prediction capability. To determine odor intensity by electronic nose firstly a collective index was generated using SVD based 2-norm method (e-nose index) proportional to the sensors response relative to reference gas, methyl mercaptan. Secondly the e-nose index was associated with human expert evaluations. The training of the electronic nose enabled it to predict odorant concentration found at the industrial site and associated odor intensity in methyl mercaptan equivalent. The overall results of the experiments carried out suggest the potential of electronic nose as a device for on or off line measurement of odorant concentration and odor intensity.

1. Introduction

Industrial obnoxious odors produced due to the gaseous emissions have been a cause of concern; as they are one of the foremost contributors to the increase in the levels of environmental pollution The various process industries such as petrochemical, pharmaceutical, pulp and paper, tanneries, etc though are major contributors to economy of the country, have a disadvantage of emitting highly obnoxious odors. These airborne gaseous emissions are of main concern due to their high mobility, since such shifty pollution causes losses, as public places cannot be developed in the affinity of such plants (Schlegelmilch et al., 2005; Francesco et al., 2001; Bourgeois et al., 2003). One such key process industry manufacturing one of the most useful and valuable commodities in the form of paper is pulp and paper industry, the per capita

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http://dx.doi.org/10.1016/j.atmosenv.2013.10.041

Nomenclature

DMS	dimethyl sulphide
DMDS	dimethyl disulphide
MM	methyl mercaptan
H_2S	hydrogen sulphide
PCA	principal component analysis
RSM	response surface methodology
RSC	reduced sulfur compounds
MOS	metal oxide sensors
GC	gas chromatography
FPD	flame photometric detector
OSHA	occupational safety and health administration
TWA	time weighted average
VOCs	volatile organic compounds
SVD	singular value decomposition
ANOVA	analysis of variance
PRESS	predictive error sum of squares
OIRS	odor intensity reference scale
MME	methyl mercaptan equivalent

consumption of which is increasing exponentially. The high degree of obnoxiousness associated with the gaseous emissions from these industries is due to the presence of reduced sulfur compounds (RSCs) viz., dimethyl sulphide [$(CH_3)_2S$], dimethyl disulphide [$(CH_3)_2S_2$], methyl mercaptan [(CH_3SH)] and hydrogen sulphide [(H_2S)] (Giri et al., 2010). All the above gases have very low odor threshold and can cause serious problems if exposed above OSHA TWA limits (Table 1). Further, as can be observed from Table 1, all the four compounds have very low boiling points with the exception of dimethyl disulphide. Due to very low boiling point they are highly volatile this in turn makes them difficult to control.

There are various environmental gaseous measurement methods based on different principles viz., colorimetery, and chromatography (Environment Agency Technical Guidance Note M13, 2001). These analytical methods are cost intensive and have limitations for onsite analysis. Sophisticated analytical instruments such as gas chromatography needs to be coupled with cryogenic system for preconcentration of gaseous compounds having boiling point less than 0 °C, for example hydrogen sulphide (boiling point −60 °C). This further limits the use of such analytical instruments at industrial level. Moreover, while using such analytical instruments the odor perceived is not depicted. Till date, electronic nose developed for measurement of gaseous emissions generated from various industrial sites has found its application limited to the monitoring of VOCs (Pearce et al., 2003; Polikar et al., 2006) and for detection of singular compounds such as H_2S, NH_3, etc (Bockreis and Jager, 1999; Xu et al., 2000). The electronic nose has not been explored for measurement of reduced sulfur compounds generated from pulp and paper industries and the odor intensity associated with these compounds. Therefore, keeping in view the global importance of pulp and paper industries, the inherent environmental pollution problem associated and considering the limitation offered by present analytical techniques it is necessary to investigate and develop a measurement system for rapid qualitative and quantitative analyses of such emissions as well as the odor intensity associated. Eventually this will lead to better control and regulation of these unwanted emissions.

In the present investigation an attempt has been made to develop an electronic nose to characterize, measure live gases emissions containing obnoxious sulfurous odorants by correlating the quantitative data generated through GC-FPD and sensor array using response surface methodology. Further, a collective index of sensors' response (e-nose index) was generated using SVD based 2-norm method proportional to reference gas methyl mercaptan. This e-nose index was then associated with human olfaction. The developed prototype was pre-trained to determine the odor intensity associated with these odorants in terms of methyl mercaptan equivalent (MME). The results on these aspects are presented and discussed in this paper.

Table 2
Normal targeted compounds of the sensors used in the study.

Sensor type	Sensor's application (as specified by manufacturer)
TGS 823	Detection of organic solvent
TGS 825	Special sensor for hydrogen sulfide
TGS 826	Detection of ammonia
TGS 832	Detection of chlorofluorocarbons (CFC's)
TGS 2602	Detection of air contaminants
TGS 2610	Detection of LP gas
TGS 2620	Detection of solvent vapors
MICS 5525	Detection of carbon monoxide

2. Materials and methods

2.1. Sensors for electronic nose

The most important component of any artificial olfaction system is the sensor array. The signature of sensor array is interpreted using some computational method to present the results to the users. In many application of electronic nose, the sensors selected are metal oxide type due to their long-term stability to environmental application (Romain and Nicolas, 2010; Yu and Wang, 2007). Screening of different commercially available metal oxide sensors (MOS) was done to select sensors sensitive enough to targeted compounds; however, detailed description of sensor selection process is out of scope of the present study. An array consisting of 7 different nonspecific commercial tin oxide sensors from Figaro, Japan and a CO sensor from e2v technologies, UK (TGS 823, TGS 825, TGS 2610, TGS 2602, TGS 826, TGS 832, TGS 2620 and MICS 5525) which were found adequately sensitive to the odorants

Table 1
Physical characteristics of the reduced sulfur compounds emitted from pulp and paper industries.

Compound	Characteristic odor	OSHA	Odor threshold (ppm)	Molecular weight (g mol^{-1})	Boiling weight (°C)	pH dependency	Water solubility (at room temperature)
[a]Dimethyl sulphide	Garlic like odor	10 ppm OSHA TWA	0.0025	62.13	36–39.3	Yes	Slightly soluble
[a]Dimethyl disulphide	Strong garlic odor	0.5 ppm OSHA TWA	0.008–0.01	94.2	110	Yes	Insoluble
Hydrogen sulphide	Rotten egg odor	10 ppm OSHA TWA. 20 ppm OSHA ceiling	0.13	34.08	−61 to −60.3	No	2.6%
Methyl mercaptan	Garlic like odor	0.5 ppm OSHA TWA. 10 ppm OSHA ceiling	0.0021	48.11	6.2	No	2.4%

[a] OSHA ceiling limit for these compounds is not given.