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Review

Transportable, fast and high sensitive near real-time analyzers: Formaldehyde detection

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ABSTRACT

Formaldehyde is a colorless gas emitted into the indoor environment by furniture and many other sources. In 2006, International Agency for Research on Cancer (IARC) classified formaldehyde as carcinogen to humans even at low concentrations. The World Health Organization (WHO) determined a guideline value of 82 ppb (parts per billion). Standard analysis based on sampling and then gas chromatography (GC) or high-performance liquid chromatography (HPLC) methods are off-line methods and are considered to be time-consuming and cumbersome, in addition to their large sizes, weights, high cost in terms of both equipment and consumables. This review reports the developments made over the last decade toward the realization of portable, high sensitive and real-time formaldehyde analyzers.

Contents

1. Introduction

Formaldehyde (HCHO) is a colorless gas that is readily soluble in water but not in most organic solvents, except alcohol and ether [1]. The human body consists of hydrocarbons among its components, and it requires formaldehyde to metabolize biochemical substances [2].

Formaldehyde constitutes a part of our general outdoor environment. It is released into the atmospheric air by means of automobile fumes, industrial facilities that burn fossil fuels, forest fires and the open burning of waste [3,4]. Because of its high water solubility, formaldehyde is contained in rain water, oceans and surface waters [1]. Formaldehyde is also highly present in human indoor environment. Formaldehyde resins are used in the production of plywood and particle board [5]. Paper products treated with formaldehyde include paper bags, waxed paper, paper towels and disposable sanitary products [6,7] which are usually used in human work environment. Formaldehyde also finds its way into the workplace through other textile products [8,9]. It has been stated that the concentration of formaldehyde in the indoor areas is usually 2–10 times higher than the outdoor concentration, and it is in the range of several tens of ppb [6,10–13]. The major anthropogenic sources that influence human health are found in the indoor environment where people spend more than 80% of their time.

OSHA (Occupational Safety and Health Administration) determined that formaldehyde is genotoxic, showing properties of

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both a cancer initiator and promoter. In 2006, the classification of formaldehyde was upgraded by the International Agency for Research on Cancer (IARC) from probably carcinogenic to carcinogenic to humans. The OSHA reported that people must not be exposed to airborne concentration of formaldehyde that exceeds 0.75 parts per million parts (0.75 ppm) as an 8-h work-time. WHO guideline determined that the concentration of formaldehyde in residential indoor areas must not exceed 82 ppb (parts per billion parts) for 30 min [14]. In France, this concentration limit will be decreased down to 10 $\mu g/m^3$ (~8 ppb) in indoor areas by 2022 [15] for a long time exposure.

Accurate measurement of formaldehyde concentration in indoor and outdoor areas and control of its indoor level can be effective approaches to reduce its effect on the human health. Since formaldehyde emission depends on temperature and humidity [16], indoor formaldehyde level exhibits large fluctuation throughout the day. Continuous monitoring of indoor formaldehyde level is therefore highly requested. The relation between indoor formaldehyde level and its effect on human health was investigated by the analysis of transported samples using high-performance liquid chromatography (HPLC) [17], gas chromatography (GC) [18] or other derivatization methods [19]. Although chromatographic apparatus provide detection limits of ppb to sub-ppb, they are time-consuming and not suitable for in-field measurements because of their weight and bulk. Semiconductor gas sensors based on gas-sensitive films [20–23] provide a good alternative in indoor formaldehyde monitoring for their stability and short response time. However, the selectivity is considered to be a great limitation of such sensors [24] and their detection limits are still to be very high (>300 ppb) compared to the formaldehyde concentrations encountered in indoor environments. On the other hand, enzyme-based biosensors, which provide excellent sensitivity and selectivity, are limited by their poor temporal stability [25]. Thus there still need for transportable, highly sensitive and fast formaldehyde analyzers.

In this study, we review the developed transportable formaldehyde analyzers for near real-time in-field monitoring. The detection principle is based on colorimetric and fluorescence methods. Portability, sensitivity and continuous near real-time analysis are considered to be the key comparison features of the presented analyzers.

2. Colorimetry and fluorescence-based formaldehyde analyzer

Formaldehyde analysis is basically performed on two consecutive stages: a concentration stage in order to increase the detected formaldehyde concentration and the detection stage by a colorimetric or fluorescence system. The concentration stage is the most controversial part. In the next two paragraphs two types of concentration stages are discussed: adsorption on a doped surface and uptake into aqueous reactant. A comparison among literature available analyzers based on these methods is reported in Table 1 in which, detection limit, resolution time and the trapping type are presented.

2.1. Adsorption on doped surfaces and direct analysis

In 1991, EPA's atmospheric research and exposure assessment laboratory announced the development of a real-time analyzer for gaseous formaldehyde [26]. They have used a spectroscopic method based on fluorescence detection for gaseous formaldehyde molecules excited by a UV light. The methods consisted of the modification of a commercially available SO_2 analyzer (Thermo Environmental Model 43-S [27]). They changed the optical filters in order to fit the appropriate wavelength for formaldehyde (260–350 nm for excitation and 380–550 nm for emission). The sensitivity of the apparatus was good and the detection limit was in the range of 30 ppb. However, a tank pressure was needed, calibration processes was complex and a vacuum stage was necessary.

Nakano and Nagashima [28] have realized a miniature and automatic monitor of formaldehyde based on the color change. The apparatus was composed of a trapping unit, a detection system and the flow systems (Fig. 1). The trapping unit is a porous cellulose

Table 1
Methods used for formaldehyde trapping and detection.

Method	Detection limit	Recovery time	Weight or dimensions of the device	References
Gaseous HCHO excitation by UV and fluorescence detection	30 ppb	–	>20 kg [24]	EPA 1991 [25]
Direct exposition of a doped with hydroxylamine sulfate surface to HCHO	80 ppb	30 min	106 mm × 78 mm × 141 mm	Nakano and Nagashima [26]
Porous cellulose paper containing silica-gel doped with 4-amino-4-phenylbut-3-en-2-one reagent	5 ppb	15 min	190 mm × 85 mm × –	Suzuki et al. [27]
Surface doped with AHMT (4-amino-hydrazine-5-mercapto-1,2,4 triazole) reagent	80 ppb	3 min	200 mm × 50 mm × 100	Kawamura et al. [28]
Surface doped with Schiff's reagent (reversible reaction)	10 ppb	1 h	–	Maruo et al. [29]
Porous glass impregnated in a solution of Beta-diketone and ammonium ions (reversible reaction)	10 ppb	30 min	–	Maruo et al. [30–32]
Sol–gel doped with Fluoral-P	30 ppb	3 min	350 mm × 250 mm × 200 mm	Descamps et al. [15]
Sol–gel doped with acetylacetone	30 ppb	~3 h	–	Bunkoed et al. [33]
Diffusion denuder + 2,4 pentandione solution + debubbler system	1.2 ppb	2.5 min	–	Motyka et al. [34]
Double diffusion scrubbers + AHMT reagent solution	0.08 ppb	5 min	8.5 kg	Toda et al. [35]
Shiff's reagent without concentration stage	200 ppb	–	150 mm × 110 mm × 50 mm	Gibson et al. [36]
Quenching of quantum dots	5 ppb	30 min	–	Ma et al. [23]
Honeycomb microfluidic scrubber + 2,4 pentandione reagent solution	0.01 ppb	~1 min	350 mm × 290 mm × 170 mm	Toda et al. [37]
Diffusion scrubber + Fluoral-P reagent solution	0.1 ppb	6–10 min	8 kg	Le Calvé et al. [38]