Monitoring VOCs in atmospheric air I. On-line gas analyzers

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This article reviews the literature on analytical instruments routinely used for monitoring volatile organic compounds in atmospheric air. We classify the analyzers as stationary or mobile, according to their ease of transport. We describe a stationary differential optical absorption spectroscopy analyzer, and membrane-introduction mass spectrometry (MS), membrane extraction with sorbent interface, ionization at atmospheric pressure or low pressure coupled with tandem MS instruments, into which air samples can be injected directly. We also describe mobile instruments (e.g., automatic analyzers for benzene, toluene, ethylobenzene, and xylenes, portable mass spectrometers and a mobile monitoring system).

Keywords: Air monitoring; Atmospheric air pollutant; Atmospheric pressure ionization; BTEX analyzer; Differential optical absorption spectroscopy analyzer; Low-pressure ionization; Membrane extraction with sorbent interface; Membrane-introduction mass spectrometry; VOC analyzer; Volatile organic compound

Abbreviations: APCI-MS^2, Atmospheric pressure chemical ionization with tandem mass spectrometry; APPI, Atmospheric pressure photoionization; ATSDR, Agency for Toxic Substances and Disease Registry; BTEX, Benzene, toluene, ethylbenzene, xylenes; CCN, Cloud-condensation nuclei; CFC, Chlorofluorocarbon; CIT, Capture ion trap; DOAS, Differential optical absorption spectroscopy; DS-MS, Direct sample-mass spectrometry; ECD, Electron-capture detector; EEA, European Environment Agency; EPA, Environmental Protection Agency (USA); FID, Flame ionization detector; GC, Gas chromatography; HAP, Hazardous Air Pollutant; LPCI-MS^2, Low pressure chemical ionization with tandem mass spectrometry; MESI, Membrane extraction with sorbent interface; MIMS, Membrane-introduction mass spectrometry; MS, Mass spectrometry; MMS, Mobile monitoring system; NMVOC, Non-methane volatile organic compound; POM, Particulate organic matter; PTR-MS, Proton-transfer mass spectrometry; PUF, Polyurethane foam sampler; SOA, Secondary organic aerosol; SVOC, Semi-volatile organic compound; VOC, Volatile organic compound; VVOC, Very volatile organic compound; WHO, World Health Organization

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1. Introduction

Volatile organic compounds (VOCs) comprise a large group of pollutants that occur in atmospheric air mainly in gaseous form. More than 500 compounds have been classified as VOCs [1]. They include alkanes, alkenes, aromatic hydrocarbons, chlorinated aromatic hydrocarbons, saturated and unsaturated aldehydes, ketones, esters, alkyl halides and alcohols [2]. Most of the generally accepted classifications of VOCs are based on their physicochemical properties (e.g., boiling point and vapor pressure). The World Health Organization (WHO) suggested that the term ''volatile organic compounds'' should cover only compounds adsorbed on a solid sorbent and whose boiling points lie in the range 50–260°C. By contrast, the US Environmental Protection Agency (EPA) definition of VOCs includes polar and non-polar C_2–C_{10} compounds, whose vapor pressure at 25°C exceeds 13.33 Pa [3].

According to the provisions of the Geneva Convention on Long-Distance Cross-Border Air Pollution (1991), VOCs do not include methane (CH_4). Methane, an alkane, is present in atmospheric air at levels far in excess of those of the other VOCs, so it has become commonplace to divide VOCs into non-methane VOCs (NMVOCs) and methane [4]. VOCs are subdivided in accordance with a number of their properties {e.g., degree of volatility (Table 1), ozone-forming potential [5], polarity [3], and their effects on particular ecosystems (Table 2) [6]}.

The VOCs present in atmospheric air may be natural or man-made. The principal natural sources of VOC emissions are the growth processes of plants [7], which release them into the atmosphere (e.g., isoprene, pentanols, pentanones, pentanals, hexanols and hexanals) [8]. It has also been observed that selected VOCs get into the atmosphere along with the characteristic scents of flowers [9]. Results of

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Table 1. Classification of organic compounds according to their volatility

Name	Abbreviation	Boiling-point range [°C]
Very volatile organic compounds	VVOCs	<0–100
Volatile organic compounds	VOCs	50–100 to 240–260
Semi-volatile organic compounds	SVOCs	240–260 to 380–400
Non-volatile organic compounds associated with particulate matter	POM	>380

Table 2. Classification of volatile organic compounds (VOCs) with respect to their action on ecosystems and human health [6]

Abbreviation	Characteristics	Examples
VOC-OX	High potential for generating photochemical oxidants (O_3, PAN)	Alkanes C_2–C_8, Alkenes C_2–C_8, Alkynes C_2–C_8, Xylenes, Arenes, Terpenes, Tetramethylbenzenes
VOC-TOX	Highly toxic to living organisms	Chlorinated hydrocarbons, Oxygenated hydrocarbons
SVOC	Adversely affect human health (skin lesions, allergies)	PCB PAH Phthalic-acid esters
VOC-FORM	Secondary pollution of atmospheric air as a result of photochemical oxidation	Free fatty acids Aldehydes, Esters, Ketones
VOC-STRAT	Highly capable of destroying the stratospheric ozone layer	Chlorofluorocarbons, Halocarbons, Chlorinated hydrocarbons
VOC-CLAIM	High positive or negative global warming potential	DMS Methane

soil and waste-sample analyses prove that soil microorganisms are, besides herbaceous plants, the chief natural producers of VOCs [10]. As a result of the decomposition of wastes in landfills, fermentation products – principally alkanes, alkenes, aromatic hydrocarbons, terpenoids, furfurals, organic acids, aldehydes and ketones – enter the atmospheric air [9,11]. Other natural sources of VOC emissions into atmospheric air include:

- volcanic processes;
- combustion of organic matter and biomass; and,
- forest fires [3].

Some VOCs can occur naturally in the environment. These include the benzene, toluene, ethylbenzene and xylenes (BTEX), hydrocarbons that are constituents of crude oil, and toluene, which is present in the tolu tree [12].

Anthropogenic VOC emissions to atmospheric air can be divided into two basic groups:

- stationary; and,
- mobile.

Nowadays, large amounts of VOCs in the atmosphere come from the different forms of transportation. The quantities of VOCs emitted from motor vehicles depend on the type of vehicle, the weather and ambient temperature, as well as the time of day, week and year [13]. Other anthropogenic VOCs, especially BTEX and chlorinated aromatic hydrocarbons, are emitted from stationary sources as a result of:

- crude-oil refining and spills from tankers;
- combustion of fossil fuels in heat and power plants;
- utilization of solvents (carbon tetrachloride, dichloromethane, chloroform, and BTEX compounds); and,
- production of synthetic materials, including synthetic fibers (nylon), resins, paints, solvents, dyes and pesticides [14–16].

2. The adverse effects of VOCs on human health

The results of investigations into the properties and the behavior of VOCs in atmospheric air are grounds enough for declaring their negative effects on human health [17]. The extent of the threat from exposure to these compounds is reflected by the list of harmful substances compiled by EPA experts. This list contains more than