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Review

Detection methods for the analysis of biogenic non-methane hydrocarbons in air

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Abstract

Volatile organic compounds in air, especially the reactive biogenic hydrocarbons (e.g., isoprene and monoterpenes), play important roles in the chemistry of the troposphere even at very low concentrations. Sensitive and reliable detection methods are required in order to determine their low concentrations in air and to estimate their emission fluxes from sources. The flame ionization detector and the mass spectrometer have been widely used for the quantitative and qualitative analysis of biogenic non-methane hydrocarbons in air but other detection systems are available. Both the sampling and analytical methods used for these measurements are summarized in this review. The possible applications of several potential detection methods and recent developments in the use of new methods are also discussed.

Contents

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1. Introduction

Although there are considerable uncertainties [1,2] in estimates of the emission rates of volatile organic compounds (VOCs) from the biosphere, it is believed that the majority of global VOC emissions are from biogenic, and not anthropogenic, sources [3]. The emission of VOCs from plant foliage to the atmosphere accounts for about half of the estimated total VOC emissions in the USA [4] and two-thirds of global VOC emissions [2]. Although they comprise less than 50% of the total VOC mass emitted from vegetation [3], the non-methane hydrocarbons (NMHCs), especially isoprene and monoterpenes, have received much more attention than other VOC species during the past two or three decades. The concentrations of NMHCs in ambient air, especially of the more reactive compounds, are very low, and their measurement is therefore difficult. However, even at low concentrations they play an important role in atmospheric chemistry at global, regional and local scales (i) by reacting rapidly with hydroxyl radicals and ozone, forming, among other products, carbon monoxide and thereby impacting directly on the oxidizing capacity of the atmosphere, (ii) by influencing the formation and removal of ozone, depending on the ambient hydrocarbon and nitrogen oxides mixing ratios, and hence influencing the photochemical oxidant loading of the troposphere, (iii) by contributing to the global carbon budget, (iv) by the production of organic acids, contributing to the deposition of acidity in remote areas. Thus, more and better measurements of their concentrations in air and of their rates of emission into the atmosphere are required in order to fully understand their role in tropospheric chemistry and in order to estimate their contributions to the global atmospheric carbon budget.

The low concentrations of hydrocarbons in ambient air and the lack of adequately sensitive detection methods means that preconcentration is required during the sampling of ambient air. This may result in artifact formation, possible destruction of analytes by reaction with O_3 and other oxidants, and loss (or gain) on contact with surfaces. By developing more sensitive detection methods, not only can these problems be minimized, but also development of automatic sampling and analytical systems may be possible.

Although many other gas chromatographic (GC) detection systems are available, only flame ionization detection (FID) and mass spectrometry (MS) have been used widely for the quantitative and qualitative analysis of biogenic NMHCs in air. In this paper, the sampling and analytical methods used for these measurements are summarised. The possible application of several potential detection methods in this area and recent developments of new methods are also discussed.

2. Measurements of hydrocarbons in air

2.1. Sampling methods

Several different sampling methods are available [5,6], each method has its own range of application, and suitable sampling techniques should be used in order to carry out accurate and reliable sampling. The most widely used methods for the sampling of NMHCs at low concentrations in air are grab sampling with Teflon bags or stainless-steel canisters, and the adsorptive sampling method.

2.1.1. Grab sampling

Grab sampling, which is also called whole-air sampling, involves the direct collection and isolation of the test atmosphere in an impermeable container, and generally requires relatively simple equipment. This technique is ideal for the light hydrocarbons, and has been widely used for the measurements of C_2–C_6 hydrocarbon concentrations in rural, remote and maritime atmospheres [7–14]. Although it is in general not applicable to less volatile compounds due to their possible adsorptive losses on the walls of the sample containers, this method has also been used occasionally for the measurements of biogenic hydrocarbons in air [15,16]. Because the concentrations of NMHCs in air are very low and the sensitivity of present detection methods

is not adequate, large volumes of sample, which must be preconcentrated prior to analysis, are required for analysis. Samples can be preconcentrated cryogenically on adsorbents, followed by thermal desorption [14], or by cryogenic on-column enrichment [12]. As the volume of sample containers is, for practical reasons, limited to a few litres, the total amount of air available for analysis is very low. Larger amounts of air can be collected by pressurizing the samples cryogenically, e.g., by immersing the container in liquid nitrogen.

2.1.2. Adsorptive sampling

Sampling by pumping air through an adsorption tube packed with adsorbent(s), followed by thermal desorption, is the most widely used method for the sampling of less volatile NMHCs (C_5 and above) at low concentrations in air. Several different adsorbents can be used for this purpose, such as Tenax-TA, Tenax-GR, Carbotrap, Chromsorb, activated carbon, etc. Suitable adsorbents should be used for the sampling of different hydrocarbons to ensure not only the representative collection of the hydrocarbons of interests, but also their subsequent complete desorption for analysis. It has been found that some monoterpene compounds (e.g., α- and β-pinene) can be partly or completely decomposed, or transformed to other isomers, during thermal desorption on some adsorbents [17,18]. The most commonly used adsorbent for the sampling of monoterpenes is Tenax (GC or TA). Although it has the desired property of not retaining significant amounts of water, its adsorption capacity for the more volatile hydrocarbons is poor, and it also has the problem of artifact formation by reaction with oxidizing gases (e.g., O_3) in air. It has been observed that several new compounds appeared after Tenax polymer was exposed to the air containing ozone, with benzaldehyde and acetophenone being the most significant [19,20].

2.2. Analytical methods

Because of the complexity of the mixture of hydrocarbon compounds present in air, an analytical method that can resolve one compound from another is required. GC, particularly combined with the use of a high-resolution capillary column, offers excellent possibilities of speciation while the commonly used FID gives good sensitivity. However, there are also several other potential detection methods, some offering advantages over FID.

2.2.1. Flame ionization detection

FID is traditionally considered as a highly non-selective detector, and can respond to almost all VOCs. It has therefore been widely used for the determination of volatile organic compounds in air [7–17,21–33], and has undergone little change in the last two decades. Table 1 gives examples of the use of FID for the detection of biogenically-derived VOCs in ambient air.

Measurements of air concentrations of biogenic hydrocarbons (isoprene and monoterpenes) and their diurnal variations have been made at different forest and agricultural sites since the late 1970s [e.g., 16,21,25–27,30]. Different diurnal patterns have been observed for isoprene and monoterpenes. Generally, isoprene concentrations increase sharply in the early morning after sunrise with a maximum in the afternoon, while the air concentrations of monoterpenes during the diurnal cycle are the inverse of those observed for isoprene. This is due to the fact that emission of isoprene from vegetation is highly dependent on both temperature and light intensity, and is almost nil during the night. Monoterpenes are still emitted during the nighttime, since their emissions depend mainly on temperature, and are not very sensitive to light intensity. In a polluted area, isoprene and monoterpenes can be destroyed by reactions with ozone and the OH radical during the day, and during the night they can react with the NO_3 radical, in addition to ozone. Since some monoterpenes, especially α-pinene, can react more quickly with ozone and NO_3 than does isoprene, their concentrations during the day may reach a minimum even though their emissions are at maximum.

Concentrations of light hydrocarbons (C_2–C_6)

Table 1
Sampling and analytical methods for the analysis of natural NMHCs in air

Ref.	Sampling methods	Analytical methods	Detection limit	Compounds	Sampling location	Concentration (average/range) (ppbv)	
14	Stainless-steel canisters	Cryogenic preconcentration on Tenax GC (−120°C) Thermal desorption GC–FID	1 l 2 pptv (6 pg)	Ethyne	Rural area France	1.674	
				Ethene		2.039	
				Ethane		2.418	
				Propane		2.302	
				Propene		0.535	
				1-Butene		0.055	
				n-Butane		0.352	
				Isoprene		0.088	
				1-Pentene		0.014	
				1-Hexene		0.011	
10	Stainless-steel canisters	On-column enrichment (−80°C) GC–FID	0.5 l 5–10 pptv (5–10 pg)	Ethyne	Antarctic troposphere	0.011 (0.01–0.024)	
				Ethene		0.36 (0.20–0.90)	
				Ethane		0.37 (0.30–0.45)	
				Propene		0.21 (0.01–0.05)	
				Propane		0.04–0.09	
12	Stainless-steel canisters	On-column enrichment (−80°C) GC–FID	0.5 l 30 pptv (30 pg)	Ethyne	North Atlantic	0.19 (0.08–0.40)	
				Ethene		0.18 (0.04–0.51)	
				Ethane		1.56 (1.0–3.3)	
				Propene		0.11 (0.04–0.20)	
				Propane		0.48 (0.13–2.5)	
				n-Butane		0.30 (0.03–1.3)	
				n-Pentane		0.22 (0.03–1.3)	
16	Stainless-steel canisters	GC–FID	1 l 2.5 pptv (14 pg)	Isoprene	Tropical atmosphere: Brazil	2.40 (1.00–5.24)	
				β-Pinene		0.27 (0.07–0.54)	
				Myrcene		0.19 (0.01–0.32)	
				α-Phellandrene		0.18 (0.11–0.28)	
				α-Terpinene		0.49 (0.12–0.81)	
				Δ^3-Carene		0.24 (0.05–0.62)	
				γ-Terpinene		0.11 (0.03–0.18)	
				α-Terpineol		0.76 (0.04–1.46)	
				Linalool		0.20 (0.11–0.30)	
						Aug./Sept. 1982	Nov. 1982
				Isoprene	Niwot Ridge forest USA	0.63 (0.22–1.76)	0.11 (0.03–0.16)
				α-Pinene		0.14 (0.01–0.66)	0.07 (0.03–0.11)
				β-Pinene		0.08 (0.01–0.39)	0.07 (0.01–0.11)
				Camphene		0.04 (0.01–0.11)	0.05 (0.03–0.11)
				Δ^3-Carene		0.05 (0.01–0.19)	0.03 (0.01–0.04)
				α-Terpinene		0.04 (0.01–0.05)	
26	Adsorption on Tenax GC	Thermal desorption GC–FID GC–MS (SIM mode, for identification)	1 l 1 pptv (6 pg)		Niwot Ridge forest USA	May–Oct. 1981, Jun.–Oct.1982	
				α-Pinene		0.054	
				β-Pinene		0.097	
				Δ^3-Carene		0.051	
				Camphene		0.038	
				Limonene		0.03	
17	Adsorption on Tenax GC or Carbochrome	Thermal desorption GC–MS GC–FID	not available	Σmonoterpenes	Conifer forests USSR	7.25 (0.5–26.8)[b]	
						47.3 (3.0–180.4)[B]	

Table 1 (*continued*)

Ref.	Sampling methods	Analytical methods	Detection limit	Compounds	Sampling location	Concentration (average/range) (ppbv)	
30	Adsorption on Tenax GC	Thermal desorption GC–FID GC–MS (for identification)	0.2 l 10pptv (10 pg)	Isoprene α-Pinene β-Pinene Camphene	Agricultural area Japan	Wet season 0.56 (0.10–4.0)[a] 2.0 (0.10–21.0)[a] 0.82 (0.10–6.1)[a] 0.77 (0.10–4.0)[a]	Dry season 1.9(0.12–4. 3.0(0.23–22 0.73(0.10–4 0.44(0.10–2
15	Teflon bags	GC–FID	1 l 5 pptv (28 pg)	Isoprene Σmonoterpenes Σalkanes Σalkenes Σaromatics	Forests	2.04 (1.14–2.72) 0.23 (0.12–0.34) 7.88 (6.0–15.1) 17.41 (12.6–22.0) 8.43 (3.7–26.2)	
31	Stainless-steel canisters cryogenic	GC–FID GC–PID	0.3 l 20 pptv 1 ml 20 pptv	Isoprene	Forests Amazon basin	1.6 (0.6–2.7)	
32	Adsorption on Tenax TA	Thermal desorption GC–MS (for idetification) GC–FID	not available	α-Pinene β-Pinene Δ^3-Carene Limonene + 1,8-Cineole	Landes forests France	1.3 (0.6–2.5) 1.7 (0.6–3.4) 0.6 (0.2–2.5) 1.1 (0.5–2.0)	
33	Adsorption on Tenax-TA + Carbotrap	Thermal desorption GC–FID GC–MS (SIM mode, for identification)	5 l 2–4 pptv (20 pg)	Isoprene α-Pinene β-Pinene Limonene Myrcene Sabinene	Sitka spruce forests SW Scotland	Fall daytime 0.59 0.027 0.012 0.016 0.021 0.008	Fall nighttii 0.302 0.025 0.015 0.015 0.027 0.008
36	Adsorption on Tenax GC	Thermal desorption GC–MS (SIM mode)	0.1 l 10 pptv (6 pg)	α-Pinene β-Pinene Δ^3-Carene	Forests USA	0.11 (<0.01–0.73) 0.09 (<0.01–0.46) 0.10 (<0.01–0.38)	
37	Adsorption on Tenax GC	Thermal desorption GC–MS (SIM mode)	0.1 ng	α-Pinene β-Pinene Myrcene Δ^3-Carene Limonene	Forests (Pine, Sugi, Hinoki) Japan	0.05–1.30 0.03–0.54 0.01–0.12 0.01–0.04 0.03–0.27	
40	Adsorption on Tenax TA	Thermal desorption GC–MS (ITD)	1 l 10 pptv (60 pg)	α-Pinene Camphene β-Pinene Δ^3-Carene Limonene	Scots pine forests Sweden	0.15–1.2 0.01–0.2 0.01–0.35 0.20–2.2 0.01–0.5	
42	Adsorption on Tenax TA	Thermal desorption GC–MS (ITD, full-scan mode)	30–60 pg	α-Pinene β-Pinene Δ^3-Carene Limonene	Pine forest Netherlands	0.56 (0.12–1.2)[b] 0.43 (0.10–1.0)[b] 0.19 (0.03–0.58)[b] 0.11 (0.03–0.25)[b]	

[a]Data are given as parts per billion carbon (ppbC).
[b]Data are given as $\mu g/m^3$.

have also been measured in different areas (rural area, oceanic atmosphere, etc.) (e.g., Refs. [7–14]). In general, the concentrations of less reactive hydrocarbons (e.g., alkanes) are higher than those of more reactive compounds (e.g., alkenes).

The detection limit for the GC–FID system, depending on the operation mode (split or split-

less) when thermal desorption system is used, generally ranges from 5–50 pg. Although FID has been used for the analysis of hydrocarbons in air at very low concentrations (sub part-per-billion levels) with difficulty, the accuracy and precision of the results at these levels become progressively worse, and further improvements to the sensitivity and detection limits of FID would be extremely beneficial. However, FID still remains by far the most commonly used detection system for the measurement of ambient VOCs.

2.2.2. Mass spectrometry

MS has been used extensively as a GC detection method for the identification of organic compounds, and it has made a significant contribution to the understanding of the emissions of VOCs from vegetation. Although isoprene and monoterpenes are the main compounds emitted from plants, many other oxygenated VOCs have also been observed. Isidorov et al. [17] investigated more than 20 plant species, mainly representatives of the forests of northern Europe and Asia, and about 60 compounds of various classes were identified (see Table 2). They included paraffins and unsaturated hydrocarbons, alcohols, esters and ethers, carbonyl compounds, furans, and halogenated compounds. The main VOC components from deciduous trees were light hydrocarbons and oxygenated compounds, while most of the compounds (80%) emitted from coniferous trees were terpenes. Some of the compounds (e.g., paraffin hydrocarbons) may also be from anthropogenic sources. Many agricultural species can also emit VOCs. In the work of Winer et al. [29], VOC emissions from more than 30 agricultural species (crops and fruits) and a few plants have been investigated, and over 50 individual organic compounds were identified or tentatively identified as emissions from these species (see Table 2). In addition to isoprene and the monoterpenes, a number of alcohols, acetates and other esters, aldehydes, ketones, ethers, alkanes, alkenes and aromatic hydrocarbons were observed. Among the monoterpenes, 2-carene, which has not previously been reported as a biogenic emission, was observed to be a principal emission, along with β-phellandrene, from tomatoes. Sesquiterpenes were also observed from a number of plants species and in some cases the emission rates of the sesquiterpenes exceeded the monoterpene emission rates. Among the oxygenated compounds observed, *cis*-3-hexen-1-ol and *cis*-3-hexenylacetate were the most dominant. In the work of Tanner and Zielinska [34], several oxygenated compounds (see Table 2) were identified in addition to α- and β-pinene and camphene from the tarweed species. It has been reported that 6,6-dimethylbicyclo[3.1.1]heptane-2-one is a major product from the β-pinene oxidation reactions [35].

Although MS is used mainly for the identification of organic compounds, it has also been used occasionally for quantitative analysis [e.g., 36–42]. The detection limits of a GC–MS system depend on the split ratio, when the thermal desorption system is used, and also its operation mode, that is, full-scan mode and selected ion monitoring (SIM) mode. By choosing only a few selected ions, instead of full-scan, that are characteristic of the analyte(s), much lower detection limits (up to 100 times lower) are obtained with SIM, as a result of the increased time spent by the detector on the chosen ions. Generally, the detection limit of a GC–MS system in SIM mode is slightly lower than that of GC–FID.

2.2.3. Photoionization detection

Photoionization detection (PID) can almost be considered as a non-destructive detection system, since the ionization efficiency is about 0.1%. It is highly sensitive to most organic compounds, and the detection limits are typically 10 to 50 times lower than those of FID for the same compounds, due to a larger response and a lower signal noise [43,44]. Since a response is obtained only from compounds which have an ionization potential below the energy of the UV photons generated by the lamp, PID is a highly selective detection system, especially for alkenes, aromatic and other reactive hydrocarbons which have lower ionization potentials. This is very advantageous for atmospheric monitoring pro-

Table 2
Volatile organic compounds identified as emissions from vegetation

Sources						
38 agricultural (crops and fruits) and plant species [29]		22 species of plants [17]		Scots pine Norwegian spruce [41]	Monterey pine [28]	Tarweed species [34]
Isoprene	Bornylacetate	Propylene	Santene	α-Pinene	α-Pinene	6,6-Dimethylbicyclo[3.1.1]-heptane-2-one
Camphene	Butylacetate	Butylene	Cyclofenchene	β-Pinene	β-Pinene	Borneol
2-Carene	*cis*-3-Hexenylacetate	Isoprene	Bornilene	Camphene	Limonene	6,6-Dimethylbicyclo[3.1.1]-heptane-2-carboxaldehyde
Δ^3-Carene	*n*-Hexanal	2-Methylbutane	Tricylene	Sabinene	Myrcene	6-C_5H_{11}-tetrahydro-pyrane-2-one
Limonene	*trans*-2-Hexenal	2,3-Dimethyl butadiene	α-Thujene	Δ^3-Carene	Δ^3-Carene	
Myrcene	2-Heptanone	Methanol	α-Pinene	Myrcene	Camphene	
cis-Ocimene	2-Methyl-6-methylene-1,7-octadien-3-one	Ethanol	δ-Fenchene	β-Phellandrene		
trans-Ocimene	Pinocarvone	3-Hexene-1-ol	ϵ-Fenchene	Limonene		
α-Phellandrene	Verbennone	Propanal	α-Fenchene			
β-Phellandrene	1,8-Cineole	Isobutanal	Camphene			
α-Pinene	*p*-Dimethoxybenzene	Crotonal	Sabinene			
β-Pinene	Estragole	Acetone	β-Pinene			
Sabinene	*p*-Methylanisole	Butanone-2	Myrcene			
α-Terpinene	Methylsalicylate	Methyl vinyl ketone	Δ^3-Carene			
γ-Terpinene	*n*-Hexane	Pentanone-2	α-Phellandrene			
Terpinolene	1-Decene	Pentanone-3	β-Phellandrene			
Tricyclene	1-Dodecene	Furan	α-Terpinene			
or α-thujene	1-Hexadecene	2-Methyl furan	β-Terpinene			
β-Caryophyllene	*p*-Mentha-1,3,8-triene	3-Methyl furan	γ-Terpinene			
Cyoerene	1-Pentadecene	Ethyl furan	Limonene			
α-Humulene	1-Tetradecene	Vinyl furan	Terpinolene			
p-Cymen-8-ol	*p*-Cymene	3-Hexene-1-ol acetate	1,8-Cineole			
cis-3-Hexen-1-ol		Methyl chloride	Fenchone			
Linalool		Chloroform	Thujone			
		Dimethyl sulfide	*p*-Cymene			

grammes focusing on photochemical ozone production in which the priority is the speciation and quantification of the more reactive hydrocarbons. PID may also give a less complex chromatogram than FID, and thus simplify peak identification.

Improvements to the design of PID systems with capillary GC are still in progress [45], and despite its advantages mentioned above, PID has only been used occasionally for the analysis of hydrocarbons in ambient air [46–48]. This may be due partly to its major disadvantage, that its response is compound specific, making its general application tedious. It has been recently used for the determination of trace quantities of isoprene and monoterpenes in the atmosphere [49]. Since it is a highly sensitive and selective detector and is very suitable for the reactive hydrocarbons, it is suggested that efforts should be made in the future to use PID with capillary GC for the determination of low concentrations of reactive hydrocarbons, especially biogenic hydrocarbons, in air.

2.2.4. Electron-capture detection

After FID, electron-capture detection (ECD) is most commonly used for GC. The sensitivity of the detector is extremely high, and the detection limits can be 10^4 times lower than with FID. It is also extremely selective, and it has been widely used for the analysis of organic compounds in the atmosphere having strong electron affinity, such as chlorofluorocarbon (CFC) compounds. Its response to hydrocarbons is very low. However, if highly electronegative atoms, such as halogens, can be added to the hydrocarbon molecule, then use of ECD, with much higher sensitivity than FID, should be possible.

Efforts have been recently made to use the GC–ECD for the analysis of volatile alkenes via on-column bromine addition reactions [50,51]. In the work of Cao and Hewitt [50], pyridinium bromide perbromide (PBPB) was used as the Br_2 source, and the excess Br_2 remaining after bromine addition to alkenes removed by a methanol treated cholesterol–glass bead mixture. This mixture also provides suitable polar conditions for the bromine addition reactions with the alkenes in the gas-phase. The conversion efficiencies of the individual alkenes to their brominated products is very low for ethene, but increase with carbon number, reaching 74% for 1-butene. The sensitivity of ECD to brominated C_3–C_5 alkenes is about 200–300 times higher than conventional FID, but poor peak shapes limits its applicability at present. Further work is planned to improve the chromatograms, and thus the detection limits of the brominated compounds, by using a two-oven system which allows the temperatures for the brominating phase and the GC column to be maintained independently.

In the work of Trigg et al. [51], copper(II) bromide coated onto a solid support was used as the Br_2 source. Because of the low bleed of Br_2 from $CuBr_2$, higher temperatures (up to 140°C) could be used, and a bromine bleed scrubbing phase was not required. In addition, the Cu^{2+} ion in $CuBr_2$ may have a catalytic effect on the bromination of alkenes, but at higher temperatures (above 80°C), substitution reaction may occur. The conversion rates for C_2–C_4 alkenes were normally greater than 80%, and the detection limits of the GC–bromination–ECD system for alkenes (C_2–C_5) less than 5 pg.

2.2.5. Reduction gas detection

Reduction gas detection (RGD) was originally developed for detecting the reducing inorganic gases, particularly CO and H_2 [52,53]. However, since the principle of detection relies only on the reduction of HgO to Hg vapour:

$$HgO(s) + X \rightarrow Hg(vapour) + products \quad (1)$$

any reducing species (X) will, in principle, be detected, including organic molecules containing unsaturated bonds. O'Hara and Singh [54] used RGD to measure acetaldehyde and acetone concentrations in air, and Greenberg et al. have used it to determine isoprene concentrations at sub-ppbv levels in air [55]. The responses of RGD to C_2–C_6 alkenes, C_2–C_6 alkanes, isoprene and benzene have been investigated under different conditions using packed column GC [56]. RGD is considerably (about 200–300 times)

more sensitive to alkenes than is FID, and it has much greater sensitivity to alkenes than to alkanes. Its sensitivity increases with increasing HgO bed temperature, but its selectivity towards alkenes decreases at the same time. An additional positive feature of this detector is that it does not require flammable support gases (hydrogen and oxygen).

Although RGD was engineered for use with packed GC columns, an interfaced capillary GC–RGD system has also been developed, and used for environmental analysis [57,58]. The detection limit of this system for hydrocarbons is still not adequate for this purpose, being about 10 pg, due to peak tailing. It should be possible to improve the detection limit by heating the transfer line between the GC column and the detector. However, the peak tailing problem may be mainly due to the dynamic equilibrium process (adsorption–desorption) between the mercury vapour and the wall of the detection cell. Thus, more inert materials towards mercury should be used to reduce this effect.

2.2.6. Combustion–isotope ratio mass spectrometry

Since the isotopic abundances of carbon may be different according to origin (natural and anthropogenic), it may be possible to establish the origin of a chemical compound in air and to evaluate the relative importance of different sources by measurement of the $^{13}C/^{12}C$ ratio of that compound. Isotopic data may also facilitate an understanding of the mechanisms of the production and consumption of compounds. GC–combustion–isotope ratio mass spectrometry (C–IRMS) has been widely used for the determination of the $^{13}C/^{12}C$ ratios for CO_2 and CH_4 in the atmosphere [59–61]. It has also been recently used for studying the biosynthetic pathway of isoprene by measuring the fractionation between stable carbon isotopes during biosynthesis [62]. At present, GC–C–IRMS has rather high detection limits of about 50 ng for isoprene. Because hydrocarbons eluted from the GC column have to be converted to carbon dioxide prior to MS analysis for carbon isotope measurement by passing through an electrically heated combustion oven containing copper(II) oxide, the detection limits of this method for hydrocarbons are also dependent on the combustion efficiency of each organic compound. These can be improved by increasing the oven temperature. Growing interest in isotopic studies of the biogenic emission of hydrocarbons, for which the present detection limits are a limiting factor, necessitates improvements to the sensitivity of the GC–C–IRMS method.

2.2.7. Ozone chemiluminescence detection

The reactions between alkenes and ozone produce electronically excited formaldehyde which subsequently chemiluminesces:

$$\text{alkenes} + O_3 \rightarrow HCHO^* + \text{products} \quad (2)$$

$$HCHO^* \rightarrow HCHO + h\nu \quad (3)$$

Emission from $HCHO^*$ occurs in the region 450–550 nm, and this light can be measured and related to the concentrations of alkenes.

The chemiluminescence of alkene–ozone reactions was first explored as a possible method of detecting ozone by Nederbragt et al. [63], and as a selective GC detector for hydrocarbon gas analysis by Bruening and Concha [64]. It is selective, owing to the relatively small number of compounds that chemiluminesce upon reaction with a given reactant, and very sensitive since the chemiluminescence appears out of a near zero light background. In principle, a single photon generated from a chemiluminescent reaction can be detected. Its selectivity depends very much on the detector temperature: at lower temperatures (100°C), only alkenes can be detected; at higher temperatures (250°C), alkanes can also be detected. The detection limit is frequently at the nanogram level and is temperature dependent. This detection method has the advantage of being based on a very fast, non-catalytic and flameless reaction, but the foremost advantage is that it is possible to monitor certain atmospheric species in real-time.

Hills and Zimmerman [65] constructed a continuous isoprene monitor, based on its reaction with ozone. It has a response time of 0.1 s, is linear over 3 orders of magnitude, and has a

detection limit of 400 pptv and no baseline drift. Its application resulted in the first continuous measurements of single-leaf isoprene fluxes from white oak, aspen, and cottonwood trees, as well as fluxes from blue spruce. In general, one would expect discrimination between isoprene and other alkenes to be poor since all alkenes react to some extent with ozone to produce $HCHO^{*}$, but the rapid reaction of isoprene with ozone and the use of selected wavebands does allow discrimination of isoprene. Interference from propene is the major problem as responses to these two compounds are roughly the same, and if comparable amounts of each were present, the chemiluminescent signals could not be distinguished. Fortunately, this is rarely the case since the isoprene–propene ratio in air is usually > 10 in regions where biogenic isoprene fluxes are significant. Interferences from monoterpene compounds are also slight. Thus, the instrument has the rapid response necessary to measure isoprene fluxes using the micrometeorological eddy correlation technique.

2.2.8. Other detection methods

Gas chromatography combined with atomic spectroscopic detection methods has been extensively used for the determination of organic species in air, and only a few representative examples are quoted here. Often several organic species based on the same element will co-exist in air, for example tetraethyl lead and tetramethyl lead, and GC–atomic spectroscopic detection offers the advantages of chromatographic separation, element specific detection and excellent sensitivity. Atomic absorption, with prior GC separation, has been used to determine individual tetraalkyl lead and ionic alkyllead species in air, with detection limits as low as 20 pg (Pb) [66,67]. Flame photometry has been used with GC separation to determine organosulfur species in air including dimethylsulfide, produced by marine phytoplankton [68]. Atomic fluorescence has been used for a range of organometallic compounds, including simultaneous detection of alkyllead, alkyltin and alkylselenide compounds [69]. Microwave-induced electrical discharge plasma has been used with GC for a wide range of organic and inorganic molecules, for example in gasoline samples [70]. Atomic emission spectroscopy with GC has been used to detect organomercury compounds [71].

Although not a chromatographic method, it should be noted that differential optical absorption spectroscopy (DOAS), which is based on the fact that all chemical compounds absorb light at specific wavelengths, was introduced for real-time monitoring of formaldehyde, ozone and nitrogen dioxide in air more than ten years ago [72]. Lofgren [73] recently used this technique to monitor benzene and toluene in urban air continuously. It has also recently been used to determine biogenic methane flux rates. Further instrumental development may extend the applications of DOAS to lower concentrations.

3. Requirement for continuous and fast-response detectors for hydrocarbons

Although chromatographic analysis can provide detailed information on the complex composition of the atmosphere, it is relatively labour intensive, costly and slow, usually requiring several hours from sample introduction to final tabulation. Thus only a limited number of samples can be collected and analyzed per day. This low sampling frequency makes detailed characterization of spatial and temporal variability difficult. One of the greatest uncertainties in the understanding of the mechanisms that control the chemical composition of the atmosphere concerns the exchange of trace species between the atmosphere and the surface. To investigate surface exchange, measurements of emission and deposition fluxes must be made over selected representative sites. Several techniques to measure these chemical fluxes have been developed, the most direct being that of eddy correlation. This micro-meteorological method is a fundamentally direct technique that has the advantage of not disturbing the nature of the surface. However, it relies on the use of a

continuous fast response detector and so has not been successfully applied to the measurement of hydrocarbon emission fluxes.

In order to continuously monitor individual hydrocarbons in the atmosphere, a separation step as in GC must be excluded. Thus any detector developed for this purpose must be selective and specific to the individual hydrocarbon of interest according to its unique characteristics (e.g., light absorption at specific wavelengths) with minimum interferences under specific conditions.

4. Summary

Although several potential detection methods are available, FID is still the most widely used method for the measurements of VOCs at low concentrations in air. By preconcentrating large sample volumes, concentrations of hydrocarbon in air as low as a few pptv (10^{-12} v/v) can be measured. However, the accuracy and precision of the results at these levels become progressively worse. Moreover, some compounds may be lost or formed by reaction with oxidizing gases (e.g., ozone) during the preconcentration process, making the results unrepresentative. Thus, increased sensitivity is required if the composition of the unpolluted atmosphere is to be better understood. Automation of sampling and analytical methods will allow temporal and spatial variations to be quantified and the development of detectors for specific compounds will allow particular research issues in atmospheric chemistry to be addressed. Finally, the development of continuous fast-response methods will allow measurement of hydrocarbon fluxes by micrometeorological techniques.

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