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## Review

# Air analysis by gas chromatography

Detlev Helmig\*

*Cooperative Institute for Research in Environmental Sciences (CIRES) and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0216, USA*

### Abstract

This review of gas chromatographic air analysis considers approximately 170 research articles published in the literature from 1995 to 1998. The focus is on sample collection, injection, separation and detection techniques, with special emphasis on capillary gas chromatography details. These parameters are summarized in two tables, the first one ordered by the chemical groups of compounds analyzed and the second by stationary phase. The reported techniques are analyzed and evident trends are summarized for the parameters and key words: Capillary Columns, Carrier Gas, Detection, Film Thickness, Injection, Liquid Stationary Phase, Multidimensional GC, Oven Programming, Packed Columns, PLOT Columns and Sampling Techniques. Furthermore, a brief summary of emerging alternative approaches replacing traditional GC methods is given. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Reviews; Air analysis

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\*Tel.: +1-303-492-2509; fax: +1-303-492-5894.

*E-mail address:* detlev@terra.colorado.edu (D. Helmig)

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## 1. Introduction

Analysis of the atmosphere is conducted using a wide variety of analytical approaches and techniques among which chromatography is one of the most commonly used. Important applications include the gas chromatographic analysis of hydrocarbons (HCs); volatile organic compounds (VOCs); halogenated compounds, such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs); peroxyacyl nitrates (PANs) and sulfur containing compounds, such as dimethyl sulfide (DMS) and sulfur hexafluoride ( $\text{SF}_6$ ). Another field where chromatography is an important component of the atmospheric analysis procedure is the measurement of carbonyls by liquid chromatography (LC) after derivatization, such as with dinitrophenylhydrazine (DNPH).

These analysis techniques are undergoing a steady evolution resulting in continuous improvements in areas such as sensitivity, accuracy, precision and ease of operation. Particular aspects that have been the focus of extended research are the sample collection, sample storage, preconcentration, interferences from other atmospheric gases (such as water and ozone), generation of calibration gases and detection. While these areas have been the context of many research articles, the chromatographic separation procedure itself is rarely the focus point. This neglect is addressed by this survey of the recent literature.

This article reviews and identifies the most common and popular gas chromatography (GC) techniques that are being used for air analysis. Thereby the emphasis is on the chromatography procedure and its details. The information given in this paper may help the reader put his or her work into perspective with the published literature, aid in choosing equipment, and quickly determine chromatographic parameters needed for successful analysis of a target compound or target compound class.

## 2. Approach

This review focuses on analytical applications in the field of “ambient air analysis”. The emphasis is

on the analysis techniques itself. No aspects of data analysis are discussed. Ice core analysis, chamber experiments, exhaust studies, biomass burning, workplace monitoring and indoor analysis, although related to ambient air analysis, were deliberately excluded from this review. Methodology used in these latter applications in some cases is quite specific and not applicable to general ambient air analysis because of the unique conditions or significantly higher concentration levels encountered in the experiment.

Only articles on gas phase analysis techniques were considered. Methods for the analysis of particles, aerosols and organic or inorganic aerosol constituents were not included in this review. Furthermore, only GC procedures were included in this review. Consequently, analysis of certain important gas-phase atmospheric constituents analyzed by non-gas chromatographic techniques, such as spectrometric, wet-chemical or LC procedures (e.g., carboxylic acids, light carbonyls, nitrogen oxides, hydrogen peroxide) were excluded. While this review centers on capillary column applications, citations of packed column use were included in order to allow a comparison and an evaluation of the relative significance of capillary column techniques in this field.

In order to identify the latest developments and trends, predominantly research literature from the period of 1995 to mid-1998 was reviewed. Only occasionally, a few significant and earlier references were included. Besides the authors personal literature archive, scientific journals that were specifically researched for this manuscript are:

- Analytical Chemistry
- Atmospheric Environment
- Chemosphere
- Chromatographia
- Environmental Science and Technology
- Fresenius Journal of Analytical Chemistry
- Journal of High Resolution Chromatography and Chromatographic Communications
- Journal of the Air and Waste Management Association
- Journal of Atmospheric Chemistry
- Journal of Chromatography
- Journal of Geophysical Research, Part D, Atmospheres

Articles were considered for this review when

analytical details on the chromatography process, column parameters and oven program conditions were given. In numerous publications, GC techniques were used for the measurements; however the procedure was referenced to earlier publications. In those cases, the paper was omitted because of the lack of analytical details.

This review certainly does not claim to be complete. Most likely, some significant research articles and other relevant references have been overlooked. One probable cause is that during the preparation of this review numerous issues of the considered journals were not available in any of the utilized libraries for extended periods because they had been sent to the bindery. However, approximately 300 articles underwent review and almost 2/3 of these were considered for this paper. This should allow a reasonable overview.

It was attempted to supplement, rather than to reiterate information given in other recent publications. Numerous other research and review articles have previously given comprehensive overviews of different aspects relating to air analysis by GC. These references are suggested resources for more elaborate information on selected issues related to this topic. A selection of these articles include:

- Hutte et al. [1] “Column Selection and Optimization for Sulfur Compound Analyses by Gas Chromatography”
- Des Tombe et al. [2] “Sampling and Analysis of Light Hydrocarbons (C<sub>1</sub>–C<sub>4</sub>) – A Review.”
- Clement et al. [3] “Environmental Analysis”
- Cicciooli and Cecinato [4] “Advanced Methods for the Evaluation of Atmospheric Pollutants Relevant to Photochemical Smog and Dry Acid Deposition”
- Fox [5] “Air Pollution”
- Westberg and Zimmerman [6] “Analytical Methods Used to Identify Nonmethane Organic Compounds in Ambient Atmospheres”
- Apel et al. [7] “The Nonmethane Hydrocarbon Intercomparison Experiment (NOMHICE): Tasks 1 and 2”
- Mukund et al. [8] “Status of Ambient Measurement Methods for Hazardous Air Pollutants”
- Kelly and Holdren [9] “Applicability of Canisters for Sample Storage in the Determination of Hazardous Air Pollutants”

- Larsen et al. [10] “Sampling and Analysis of Terpenes in Air: An Interlaboratory Comparison”
- Helmig [11] “Ozone Removal Techniques in the Sampling of Atmospheric Volatile Organic Trace Gases”
- Dewulf and Van Langenhove [12] “Analytical Techniques for the Determination and Measurement Data of 7 Chlorinated C1 and C2 Hydrocarbons and 6 Monocyclic Aromatic Hydrocarbons in Remote Air Masses: An Overview”
- Woolfenden [13] “Monitoring VOCs in air using sorbent tubes followed by thermal desorption–capillary GC analysis: Summary of data and practical guidelines”
- Clement et al. [14] “Environmental Analysis”
- Fox [15] “Air Pollution”
- Wardencki [16] “Problems with the Determination of Environmental Sulphur Compounds by Gas Chromatography”
- Dewulf and Van Langenhove [17] “Anthropogenic Volatile Organic Compounds in Ambient Air and Natural Waters: A Review on Recent Developments of Analytical Methodology, Performance and Interpretation of Field Measurements”

### 3. Results

The results of this review are summarized in two tables. Table 1 is organized by the chemical compound classes analyzed. Details on sampling, pre-concentration, injection technique, GC stationary phase, and detector used, are given, as far as they were detailed in the reference. Table 2 provides an overview of the chromatography column phases used. This table is divided into the sections Capillary Columns, PLOT Columns, Packed Columns and Multidimensional Techniques. Capillary column phases used are listed in the order of approximate increase of polarity. Details on the chromatography column and technique are listed, such as column dimensions, support material for packed columns (including mesh size where available), carrier gas and GC oven temperature details. Furthermore, a more specific description of the compound or group of compounds analyzed is given. Quotations are listed in order of increasing publication year within sections.

Table 1  
Atmospheric trace gases analyzed by GC with analytical parameters<sup>a</sup>

Sampling technique	Injection technique	GC stationary phase	Detection	Ref.
<i>CH<sub>4</sub></i>				
6 l SS canisters	3 ml sample injection	Carbosphere PC	FID	[63]
In-situ	Loop injection	Porapak Q/Molecular Sieve 5A PC	FID	[64]
<i>Light VOCs (≈C2–C5)</i>				
Cryogenic	Thermal evaporation	Alumina-GS PLOT	FID	[65]
3.2 l SS canisters	Cryo-focusing	OPN/Porasil C PC	FID	[66]
Cryogenic	Cryo-focusing	Phenyl isocyanate PC	FID	[42]
Cryogenic	Thermal evaporation	Al <sub>2</sub> O <sub>3</sub> /KCl PLOT	FID	[67]
Activated charcoal at –10°C	Thermal desorption (400°C)	Al <sub>2</sub> O <sub>3</sub> /Na <sub>2</sub> SO <sub>4</sub> PLOT, RTX-1	FID	[40]
HayeSep/activated charcoal at –45°C	Thermal desorption (145°C)	Al <sub>2</sub> O <sub>3</sub> /KCl	FID	[68]
Gas sampling valve	Direct injection	Unibeads IS/Molecular Sieve 5A PC	ECD	[30]
Glass syringe→Carbotrap C/Carbotrap/ Carbosieve S-III at 5°C	Thermal desorption/cryo-focusing	Al <sub>2</sub> O <sub>3</sub> /KCl PLOT	FID	[69]
2.8 l SS canister	One-step preconcentration	Al <sub>2</sub> O <sub>3</sub> /PLOT	FID	[70]
0.85 l SS flasks	Two-stage preconcentration	Al <sub>2</sub> O <sub>3</sub> /KCl PLOT	FID	[71]
6 l SS canister	Double-preconcentration, Tenax at –120°C	Al <sub>2</sub> O <sub>3</sub> /PLOT	FID	[63]
800 ml SS canisters	Two-stage cryogenic	Phenyl Isocyanate PC	FID	[72]
SS canisters	Two-stage preconcentration	Al <sub>2</sub> O <sub>3</sub> /KCl Plot	FID	[73]
Carboxen 569, Carbotrap/Carbotrap C	Thermal desorption (390°C)/solid adsorbent focusing	GS-Alumina, DB-1	FID/MS	[37]
CNH charcoal	Thermal desorption at 250°C	Porapak Q PC	FID	[74]
Glass wool/Carbopack BHT/ Carbosphere at –40 to –50°C	Thermal desorption	CP-Sil-5 CB/Poraplot U	FID	[39]
Carbopack B filled cryotrap	Thermal desorption onto column	Al <sub>2</sub> O <sub>3</sub> /Na <sub>2</sub> SO <sub>4</sub> PLOT	FID	[75]
Cryogenic (LN <sub>2</sub> ) on glass beads	Thermal evaporation at 100°C	Porapak QS/SE-54	FID	[76]
Carbosieve/Carbotrap/charcoal at –25°C	Thermal desorption/cryo-focusing	Al <sub>2</sub> O <sub>3</sub> /KCl PLOT	FID	[77]
Cryogenic (LN <sub>2</sub> ) on glass beads	Thermal evaporation	Porapak N/Alumina F-1	FID	[36]
0.8 l SS canisters	Cryogenic preconcentration (LAr)	Al <sub>2</sub> O <sub>3</sub> /KCl PLOT	FID	[78]
2 l SS canisters	Cryogenic preconcentration	Al <sub>2</sub> O <sub>3</sub> /KCl PLOT	FID	[79]
Active charcoal at –20°C	Thermal desorption (400°C)	Al <sub>2</sub> O <sub>3</sub> /Na <sub>2</sub> SO <sub>4</sub>	FID	[80]
1 l SS canister	Preconcentration trap at –120°C/thermal desorption (200°C)	GasPro GSC/CP-Sil 5CB	FID	[81]
Activated alumina/activated carbon at 0°C	Thermal desorption (250°C)	Activated Alumina PC	FID	[82]
3.2 l SS canister	Two-stage cryo-trapping	Al <sub>2</sub> O <sub>3</sub> /KCl PLOT	FID	[83]
<i>Mid-range VOCs (≈ C5–C12)</i>				
6 l SS canister	Cryogenic preconcentration	DB-1	FID	[84]
Cryogenic (LN <sub>2</sub> )	Thermal evaporation at 100°C	DB-5	FID	[85]
6 l SS canister	Cryogenic preconcentration	HP-1	MS	[86]
Charcoal passive samplers	CS <sub>2</sub> solvent extraction	DB-624	ECD/FID	[33]
Cryogenic	Cryo-focusing	DB-1	FID	[42]
Tenax TA, Tenax GR, Carbotrap C/ Carbotrap/Carbosieve S III	Thermal desorption (250–300°C)	DB-1, DB-5, DB-1701	MS	[87]
Tenax GR/Carbotrap/Carbosieve S-III at –20°C	Cryo-focusing	DB-1	FID	[38]
0.85–16 l SS canisters	Preconcentration on Carbotrap C/Carbotrap	DB-1	MS	[88]
SS canisters	Cryo-focusing at –180°C	HP-1	MS	[89]
SS canisters	Cryogenic preconcentration	HP-1	MS, FID	[90]
Cryogenic (LN <sub>2</sub> )	Thermal evaporation at 80°C	GS-Q	FID	[91]
100 ml sample loop transferred to graphitized Tenax/Carbotrap	Thermal desorption (240°C)	Al <sub>2</sub> O <sub>3</sub> /SE-54	FID	[92]
Canister	Cryogenic preconcentration (LN <sub>2</sub> )	Rtx-1	FID	[93]
6 l SS canister	Cryogenic preconcentration (LO <sub>2</sub> )	DB-1	FID	[94]
Tenax TA/Amborsorb/charcoal	Thermal desorption (300°C)	DB-1	MS	[94]
Cryogenic (LN <sub>2</sub> ) in Teflon sample loop	Direct thermal evaporation at 100°C	DB-5	FID	[95]
Carbotrap C/Carbotrap	Thermal desorption onto solid adsorbent focusing trap	DB-1	FID/MS	[37]
Carbotrap/Carbosieve S III	Thermal desorption	DB-5	FID	[96]
6 l Summa canisters	Cryogenic focusing	HP-1	MS	[77]

Table 1 (continued)

Sampling technique	Injection technique	GC stationary phase	Detection	Ref.
Tenax, Tenax/Poropak N, Tenax/Hayesep Q	Thermal desorption	SE-54, Al <sub>2</sub> O <sub>3</sub> /KCl	FID/NPD	[97]
Tenax TA/Chromosorb 102/ Carbosieve SIII	Thermal desorption (250°C)/focussing on Tenax TA at –30°C/thermal desorption (300°C)	RTX-1	MS	[98]
Activated charcoal at 5°C	Thermal desorption (400°C)	Methyl polysiloxane/ Al <sub>2</sub> O <sub>3</sub> /Na <sub>2</sub> SO <sub>4</sub>	FID	[99]
Carbotrap C/Carbotrap/Carbosieve at –20°C	Thermal desorption	Al <sub>2</sub> O <sub>3</sub> PLOT	FID	[36]
Carbotrap C/Carbotrap/Carbosieve at –20°C	Thermal desorption/cryo-focusing	SE-30	FID(80%)/ ECD(20%), MS	[36]
Carbotrap C/Carbotrap/Carbosieve-SIII	Thermal desorption (250°C)/cryo-focusing (–175°C)	DB-1	MS	[100]
850 ml SS canister	Cryogenic preconcentration (LO <sub>2</sub> )	DB-1	FID, MS	[101]
Tenax GC/Carboxen 1000 at 0°C	Thermal desorption	502.2 Quadrex	PID/ELCD	[34]
Carbotrap B/Carboxen 1000/ Carboxen 1001	Thermal desorption (280°C)	DB-624	PID/ELCD	[35]
Carbopack B/Carbosieve SIII	Focusing/thermal desorption (300°C)	Petrocol DH	FID	[102]
Poropak Super Q™	Thermal desorption (140°C)/cryo-focusing (5°C)	WCOT-CP-Wax-CB/ WCOT-CP-Sil-CB	FID	[103]
Graphisorb at 30°C	Thermal desorption (300°C)	DB-1	HID, FID	[104]
Tenax TA	Thermal desorption (300°C)	CP-Sil Pona CB	FID	[105]
Carbograph 1	Solvent extraction/liquid injection	Carbograph 1/Carbograph 1	MS	[106]
Tenax TA	Thermal desorption (200°C)/cryo-focusing	DB-1	FID	[107]
Carbopack BHT/Carbosphere at –40 to –50°C	Cryofocussing (LN <sub>2</sub> )	SP-Sil-5 CB/Poraplot U		[108]
Tenax TA	Thermal desorption/cryo-focusing	Al <sub>2</sub> O <sub>3</sub> PLOT	FID, MS	[109]
<i>Semi-volatile VOCs (≈&gt;C12)</i>				
PUF plugs	CO <sub>2</sub> supercritical fluid extraction/solid-phase solvent exchange	DB-5	MS	[110]
PUF plugs	Solvent extraction/liquid injection	DB-1301, HP-5	MS, ECD	[111]
PUF Plug/XAD-2/PUF plugs	Solvent extraction/liquid injection	Ultra-2	MS	[112]
PUF plugs	Solvent extraction/liquid injection	DB-1701	MS	[94]
PUF plugs	Toluene solvent extraction/liquid injection	DB-35	MS	[113]
Silica gel 60/ENVI-Carb/ ANGI-Sorb 5B/ANGI-Sorb 10B	Solvent extraction/solid-phase extraction/liquid injection	CP-Sil-2, HP Ultra-2, DB-1701	ECD, MS	[114]
PUF/XAD-2 resin plugs	Solvent extraction/derivatization/liquid injection	RTx-5	MS	[115]
PUF plugs	Solvent extraction/solid-phase extraction/liquid injection	Ultra-2	MS,	[116]
		NICI-MS		
PUF plugs/Tenax-GC	Solvent extraction/derivatization-solvent extraction/ liquid injection	DB-1301	MS	[117]
PUF plugs	Solvent extraction/liquid extraction/solid-phase extraction	CP-Sil-8 CB	ECD	[118]
XAD traps	Solvent extraction, fractionation, liquid injection	DB-5MS	MS	[119]
<i>Biogenic HC/Biogenic HC oxidation products</i>				
Tenax TA/Carbopack B	Thermal desorption/cryo-focusing	DB-5	MS	[120]
Cryogenic at –145°C	Direct injection by thermal evaporation	DB-5	MS	[121]
Cryogenic (LO <sub>2</sub> ) on silanized glass beads	Thermal evaporation	DB-1	FID	[122]
Tenax	Thermal desorption	Poraplot Q	MS	[123]
Tenax TA/Carbotrap	Thermal desorption/focusing on adsorbent microtrap	Ultra-2, Al <sub>2</sub> O <sub>3</sub> /KCl PLOT	FID	[124]
Carbotrap B	Thermal desorption	PLOT Al <sub>2</sub> O <sub>3</sub> /KCl/CP-Sil 8 (particle trap)	FID	[92]
Tenax TA/Carboxen 569 at 20°C	Thermal desorption (250°C)	Poraplot Q	MS	[125]
“Air Toxics”	Thermal desorption (300°C)/focusing on microtrap/ thermal desorption (325°C)	DB-1	MS, FID	[126]
<i>Halogenated HC/CFCs/HCFCs</i>				
1.5 l SS canister	Cryogenic focusing	DB-1	MS	[127]
2 l SS canister	Cryogenic focusing	SPB-1	ECD	[128]
20 l whole air cryo-samples	Cryogenic focusing	CP-Sil-13CB	MS	[129]

(continued on next page)

Table 1 (continued)

Sampling technique	Injection technique	GC stationary phase	Detection	Ref.
Carbotrap/Carboxen 1003/ Carboxen 1000 at –45 to –50°C	Thermal desorption (220°C)	Alumina/KCl PLOT, Poraplot Q, CP-Sil-5	MS	[130]
Aluminum cylinders	Cryo-focusing	Porapak Q PC	ECD	[131]
SS canisters, passivated aluminum cylinders	“Focusing”	WCOT CP-Sil-13CB	MS	[132]
Cryogenic (LAr) on glass beads	Thermal volatilization	DB-1	MS	[133]
Cryogenic	Thermal volatilization	GS-Q	FID	[133]
Cryogenic (LAr) on glass beads	Direct thermal volatilization (100°C)	CP-Sil-5	FID	[133]
Glass beads/Carbotrap B/Carbosieve S-III	Thermal desorption (250°C)	Supelcowax 10	FID	[134]
Tenax TA	Thermal desorption (230°C)/focusing on microtrap (0°C)/ thermal desorption (210°C)	Poraplot Q	MS	[135]
0.8/3.2 l SS canister	Cryogenic focusing	Al <sub>2</sub> O <sub>3</sub> /KCl PLOT	MS	[136]
Aluminum cylinders, SS canisters	Focusing on Al <sub>2</sub> O <sub>3</sub> /KCl PLOT trap at –80°C	DB-1, DB-1301, Al <sub>2</sub> O <sub>3</sub> /KCl PLOT	MS	[137]
Sample loop	Direct injection	3% OV-101 on Chromosorb, 20% OV-101 on Chromosorb	ECD	[30]
Cryo-cooled SS tubes	Cryo-focusing	DB-1	MS	[138]
Cryotrapped in “loop”		Porapak Q PC	ECD	[28]
Carbosieve S-III, Amberlite XAD-4	CS <sub>2</sub> liquid desorption/derivatization/liquid injection	DB-1	ECD	[139]
Silica gel/ENVI-Carb	Solvent extraction/solid extraction/liquid injection	CP-Sil 5–50% C18, CP-Sil 2, DB 1701	MS, ECD	[140]
Canisters	Cryogenic preconcentration		FID, ECD	[141]
Tenax TA	Thermal desorption/cryo-trapping at 0°C	Poraplot Q	MS	[142]
2 l SS canister	Cryogenic focusing	DB-624, Chromapak PLOT	ECD/FID	[143]
SS canisters	Cryogenic preconcentration on Porasil C/Porapak T at –50°C	Proasil C/Porasil C	ECD (O <sub>2</sub> -doped)	[29]
SS canisters	Cryogenic preconcentration on Porapak Q at –85°C	PoraPLOT Q	ECD (O <sub>2</sub> -doped)	[29]
Carboxen 1000/Carboxen 1003 at –50°C	Thermal desorption (235°C)	Methyl silicone	MS	[144]
0.7–1.0, 8 l SS canisters	Single stage and two-stage cryo-trapping	DB-1, CP-Sil-5	ECD, MS	[145]
<i>Alkyl nitrates</i>				
Silica gel, PUF	Solvent extraction/liquid injection	CP Sil-5, HP 5MS	ECD, MS	[146]
Tenax	Thermal desorption	DB-1701	ECD	[147]
Charcoal	Benzene extract/liquid injection	RTX-1701	Pyrolysis/ NO-CL	[148]
Cryogenic freezeout	Thermal evaporation at 70°C	OV-1701	Pyrolysis/ NO-CL	[149]
Tedlar bags	Cryogenic focusing at –180°C/thermal evaporation (30°C)	DB-1	ECD	[150]
Tenax TA	Thermal desorption	HP-VOC	ECD	[151]
Silica gel	Solvent extraction/liquid chromatography fractionation/ liquid injection	DB-1	ECD, MS, FID	[151]
<i>Peroxy acyl nitrates</i>				
7.5 ml sample loop	Direct injection	Rtx-1/Rtx-1701	ECD	[25]
6.7 ml sample loop	Direct injection	Carbowax 400/Chromosorb P	ECD	[152]
250 ml cryogenic preconcentration (–80°C)	Thermal evaporation at 20–25°C	10% Carbowax 600/ Chromosorb W-HP	ECD	[39]
0.5 ml loop injection	Direct injection	OV-1	ECD	[23]
1, 2, 5 ml sample loop	Direct injection	DB-1	Luminol Detection	[24]
1 ml sample loop	Direct injection	DB-210	ECD	[26]
	Direct injection	DB-210	ECD	[27]
250 ml cryogenic preconcentration (–80°C)	Thermal evaporation at 20–25°C	10% Carbowax 600/ Chromosorb W-HP	ECD	[108]
<i>Carbonyls</i>				
2,4,6-Trichlorophenylhydrazine-coated C <sub>18</sub> cartridges	2 µl of liquid extract	DB-5	ECD	[153]
Cryogenic preconcentration (–100°C)	Thermal evaporation at 80°C	Carbowax CP Wax 52 CB/CP Sil 5 CB/CP Sil 8 CB	FID/MS	[41]

Table 1 (continued)

Sampling technique	Injection technique	GC stationary phase	Detection	Ref.
<i>SF<sub>6</sub></i>				
Cryogenic whole air	Cryogenic preconcentration on SPEROSIL XOB	SPEROSIL XOB 075	MS	[154]
Porapak Q at -77°C	Thermal desorption (100°C)	Molecular Sieve 5A/ Molecular Sieve 5A	ECD	[155]
Sample loop	Direct injection	Porapak Q PC	ECD	[30]
Cryogenic whole air	Cryogenic (LN <sub>2</sub> ) preconcentration on GC Column	Porasil-L	ECD	[156]
10 ml sample	Direct injection	Porapak Q PC	ECD	[157]
<i>Sulfur containing organic compounds</i>				
Cryogenic trap	Thermal evaporation	DB-1	SCD	[158]
Tenax TA at -117°C	Thermal desorption (100°C)	Chromosil 330 PC	FPD	[159]
Molecular Sieve 5A at -15°C	Thermal desorption	Carbopack B/1.5% XE-60/1.0% H <sub>3</sub> PO <sub>4</sub>	FPD	[160]
Cryogenic on glass fiber wool (LAr)	Thermal evaporation	Chromosil 330 PC	[162]	
Molecular Sieve 5A	Thermal desorption (280°C)	Chromosil 330 PC	FPD	[162]
Activated charcoal	Thermal desorption (400°C)	Methyl polysiloxane/Al <sub>2</sub> O <sub>3</sub> /NaSO <sub>4</sub>	FID	[99]
Molecular Sieve 5A	Thermal desorption		FPD	[164]
Tenax at -25°C	Thermal desorption	DB-1	SCD	[164]
Gold-coated glass wool	Thermal desorption (450°C)	Porapak QS	FPD	[165]
Gold wool		Chromosil 330 PC	FPD	[166]
<i>CO</i>				
Tedlar bags	5 ml loop injection	Molecular Sieve PC	HgO RGD	[167]
1 ml loop	Direct injection	Carbosphere	Methanizer/FID	[168]
SS sample loop	1 ml loop injection	Molecular Sieve 5A PC	HgO RGD	[42]
3 ml sample loop	Loop injection	Molecular Sieve 5A PC	HgO RGD	[169]
1.9 l titanium flasks	5 ml loop injection	Silica Gel/TritonX-305/Molecular Sieve 5A PC	Methanizer/FID	[170]
0.5, 2.5, 3 l glass flasks	2 ml loop injection	Unibeads 1S/Molecular Sieve 5A PC	HgO RGD	[171,172]
<i>Fatty acids</i>				
Sr(OH) <sub>2</sub> -coated glass beads	Formic acid extraction/ GC injection	0.3% FFAP/0.3% H <sub>3</sub> PO <sub>4</sub> on Carbopack B PC	FID	[173]
<i>N<sub>2</sub>O</i>				
Polyethylene sample bag	Loop injection	Hayesep N	ECD	[18]
Sample loop	Direct injection	Porapak Q PC	ECD	[30]
10 ml sample	Direct injection	Porapak Q PC	ECD	[158]
<i>H<sub>2</sub></i>				
Sample loop	Direct injection	Molecular Sieve 5A PC	ECD	[30]
<i>NO<sub>2</sub></i>				
1, 2, 5 ml sample loop	Direct injection	DB-1	Luminol Detection	[24]

<sup>a</sup> Abbreviations: CFC=chlorofluorocarbon, DMS=dimethylsulfide, ECD=electron capture detection, ELCD=electrolytic conductivity detection, FID=flame ionization detection, FPD=flame photometric detection, HC=hydrocarbon, HCFC=hydrochlorofluorocarbon, HID=helium ionization detection, LAr=liquid argon, LN<sub>2</sub>=liquid nitrogen, LO<sub>2</sub>=liquid oxygen, MS=mass spectrometry, NICI-MS=negative ion chemical ionization MS, NO-CL=nitrogen oxide/chemiluminescence, PAN=peroxyacetylnitrate, PC=packed column, PID=photoionization detection, PPN=Peroxypropyl nitrate, PLOT=porous-layer open tubular, PUF=polyurethane foam, RGD=reduction gas detection, SCD=sulfur chemiluminescence detection, VOC=volatile organic compound.

GC column manufacturers use different names for their stationary liquid phases. While many of these phases chemically may be identical, subtle differences in the preparation technique and properties may exist. Generally, column description, terminology and significant figures for dimensions given in Tables 1 and 2 are those given in the references.

Rather than attempting to make uniform this information for better comparison, it was chosen to keep the original terminology in order to avoid possible misinterpretations. In some cases, this may lead to the use of different terms describing very similar analytical steps or procedures. The use of a slash (“/”) between terms means that adsorbents,

Table 2

Stationary phases used in chromatography air analysis, chromatography parameters and applications (abbreviations as in Table 1)

GC stationary phase	Column <sup>a</sup> (I.D.×length×film)	Carrier gas	Temperature program (all temperatures in °C)	Compound/approximate range of compounds analyzed	Ref.
<b>Liquid film capillary columns</b>					
<i>Dimethylpolysiloxane</i>					
DB-1	0.25×100×0.5		−50(3)/6/175(0)/25/250 <sup>b</sup>	C2–C10 HC	[84]
DB-1	0.25×30×1.0		−65(1)/4/45	HCFC 141b	[127]
CP-Sil-5	0.32×100×5	He	30(12)/10/100(40)	HCFCs	[130]
HP-1	0.32×50×1.0		−60(3)/8/250	Benzene	[86]
SPB-1	0.75×60	N <sub>2</sub>		Tetrachloroethene	[128]
DB-1	0.32×30×1.0	He	−50(0)/4/200	C3–C10 HC	[42]
DB-1	0.25×30×1.0	He	−50(0)/6/180	C3–C12 HC, CFCs, oxygenated HC	[87]
DB-1	0.25×30×1.0		−65(2)/4/175	Methyl halides	[133]
DB-1	0.32×60×5.0	He	30(6)/6/240(7)	C2–C11 HC	[38]
DB-1	0.25×30×1.0		“Subambient”	HCFC-134a	[137]
DB-1	30 m length		−50(0)/4/80	Isoprene	[122]
DB-1	0.32×60×0.25			C3–C13 VOC	[88]
RTX-1	0.53×60×3	He	5(1)/3/130(0)/15/220	C5–C10 HC	[40]
HP-1	0.32×50		−40(1)/10/150(7)	C3–C10 HC	[89]
HP-1	0.31×50×1.0	He	−60(3)/8/280(5)	C3–C8 HC, isoprene, monoterpenes	[90]
CP Sil-5	0.25×10×0.25	H <sub>2</sub>	40(1)/6/250(5)	C6–C17 Alkyl nitrates	[146]
DB-1	0.32×60×1.0		−60(5)/4/200	C2–C10 HC	[94]
DB-1	0.25×60×1.0		−60(5)/4/200	C2–C13 HC	[94]
DB-1	0.32×60×1	He	30(4)/3/280	C5–C13	[37]
Rtx-1	60 m length, 1.5 μm film		35(5)/5/180	C3–C11 VOC	[98]
Rtx-1	0.32×105×1		−50(2)/8/230	C2–C10 Alkanes/alkenes, aromatics	[93]
HP-1	0.32×50×1.0		−60(3)/8/250	C3–C12	[77]
CP-Sil-5	0.32×50×1.2		−40(2)/15/40(0)/10/200	Halogenated anisoles, benzenes	[114]
SE-30				C6–C16 HC	[36]
DB-1	0.53×30×1.5	N <sub>2</sub>	32(7)/5/92(0)/15/200	C6–C10 HC	[107]
DB-1	0.25×60×1.0		−60(5)/4/200	Ethanol, methyl- <i>tert</i> .-butyl ether	[101]
DB-1	0.53		50 isothermal	DMS	[165]
DB-1	0.53×3×3.00	He	“Room temperature”	PAN, PPN, PBN, NO <sub>2</sub>	[24]
DB-1	0.32×30×1.0	He	−60(3)/6/150	C3–C11 HC, CFCs, oxygenated HC	[100]
DB-1	0.32×20×1	He	30(6.6)/10/46(1.6)/10/54	PAN, PPN, alkyl nitrates, CFCs	[150]
DB-1			−25 to 150	Halons (CBrF <sub>3</sub> , CBrClF <sub>2</sub> , CBr <sub>2</sub> F <sub>4</sub> )	[145]
Methyl silicone	100 m length, 5 μm film			HCFC-134a, HCFC-141b, HCFC-142b	[144]
OV-1	0.53×10×1	95% Ar/5% CH <sub>4</sub>	45 isothermal	PAN, PPN	[23]
Petrocol DH	0.25×100×0.5		30(25)/3/200	C6–C9 HC/aromatics	[102]
CP-Sil-5 CB	0.32×50×1.2	He	50 to 150 temperature programmed	C3–C10 HC	[108]
CP-Sil-5			−65 to 200	Halons (CBrF <sub>3</sub> , CBrClF <sub>2</sub> , CBr <sub>2</sub> F <sub>4</sub> )	[145]
DB-1	0.25×60×0.25		40(3)/3/250	C1–C14 alkyl nitrates	[151]
<i>(5%-Phenyl)-methylpolysiloxane</i>					
DB-5	0.25×60×1	H <sub>2</sub>	−50(0)/16/200	Alkanes, oxygenated HC, aromatics, alkenes, monoterpenes, cyclic HC	[85]
DB-5	60 m length, 1 μm film			3-Methylfuran, methyl vinyl ketone, methacrolein	[121]
DB-5	0.32×50			Isoprene, monoterpenes, sesquiterpenes	[120]
DB-5	0.25×30×0.25	H <sub>2</sub>	40(1)/30/140(0)/0.8/230(0)/30/280(30)	PCBs/endsulfan	[110]
HP-5	0.25×25			PCBs	[111]
DB-5	0.33×60×0.25	He	−50(0)/6/180	C3–C12 HC, CFCs, oxygenated HC	[87]
DB-5	0.30×30×1	He	140(0)/5/250(2–10)	Carbonyl derivatives	[153]
HP-5MS	0.25×5×0.25	H <sub>2</sub>	40(1)/6/250(5)	C6–C17 alkyl nitrates	[146]
Ultra-2	0.20×25×0.1	He	70(1)/5/300	PAH	[112]
DB-5	0.25×60×1	H <sub>2</sub>	−50/13/200	C3–C10 HC, oxygenated HC, aromatics, monoterpenes	[95]
DB-5	0.25×9			C5–C8 HC	[96]
Ultra-2	0.22×50×1.05	He	30(1)/4/150(0)/45/250(5)	Monoterpenes	[124]
SE-54	0.32×50×1	He	40(2)/10/220(5)	Alkylated benzenes	[97]
Rtx-5	0.25×30×0.25	He	100(1)/20/220(0)/5/300(5)	Pentachlorophenol	[115]
DB-5MS	0.25×30×0.25			PCBs, PAHs	[119]



Table 2 (continued)

GC stationary phase	Column <sup>a</sup> (I.D.×length×film)	Carrier gas	Temperature program (all temperatures in °C)	Compound/approximate range of compounds analyzed	Ref.
Ultra-2	0.2×25×0.11	He	60(2)/20/150(0)/4/280(10)	PCBs, chlordanes, DDT compounds, γ-hexachlorocyclohexane	[116]
HP-5	0.32×30×0.25	He	−60(3)/4/125(0)/40/250(10)	Aromatics, biogenic HC, oxygenated HC	[126]
<i>(6%-Cyanopropyl-phenyl)-methylpolysiloxane</i>					
DB-1301	0.25×30×0.25			PAHs	[111]
DB-1301	0.25×30×0.25	He	90(1)/6/260	PAHs, chlorinated phenols, chlorinated guaiacols, chlorinated benzenes	[117]
<i>(14%-Cyanopropyl-phenyl)-methylpolysiloxane</i>					
DB-1701	0.33×60×0.25	He	−50(0)/6/180	C3–C12 HC, CFCs, oxygenated HC	[87]
DB-1701	0.25×30×0.25	N <sub>2</sub>	40(3)/20/80(0)/2/240(30)	Halogenated methyl-phenyl ethers	[140]
DB-1701	0.32×30×0.25		40(x)/4/100(0)/10/275(17.5)	C14–C28 alkanes	[94]
RTX-1701	0.53×30		Alkyl Nitrates		[148]
OV-1701	0.53×25×2	N <sub>2</sub>	30(2)/2.4/80(40)	Alkyl nitrates	[149]
<i>Other</i>					
DB-624	0.53×105×3	He	35(5)/4/150(0)/7/240(30)	Aromatic and chlorinated HC	[33]
CP-Sil-13CB	0.53×50×2.0		−20 to 120	HCFC-141b/HCFC-142b	[129]
Supelcowax 10	0.75×30×1.0		35(5)/30/250	Vinyl chloride	[134]
CP-Sil-5-50% C18	0.32×100×0.1	N <sub>2</sub>	40(3)/2/240(30)	Halogenated methyl-phenyl ethers	[140]
CP-Sil-2	0.25×55×0.25	N <sub>2</sub>	40(3)/20/80(0)/2/240(45)	Halogenated methyl-phenyl ethers	[140]
CP-Sil 2	0.25×55×0.25	N <sub>2</sub>	40(0.5)/100/100(0)/4/240(30)	Halogenated anisoles and benzenes	[114]
DB-35MS	0.25×30×0.25	He	75(1.5)/15/200(0)/2/250(0)/10/290	PAH	[113]
DB-624	0.53×75×3	He	40(5)/6/200(10)	C1–C10 VOC, halogenated VOC	[35]
CP-Sil Pona CB	0.32×100×1.12	He	40(5)/5/250(10)	C7–C8 HC	[105]
DB-210	0.53	He	20 isothermal	PAN, peroxypropylnitrate, peroxymethacryloylnitrate	[26]
DB-210	0.53×15×0.1	He		Peroxyacetyl nitrates	[27]
502.2 Quadrex	0.53×75×1.5	He	35(10)/5/230(2)	C1–C9 VOC	[34]
RTx-2330	0.25×30×0.10		60(2)/20/170(1)/3/213(0)/20/270	PCBs, chlordanes, DDT compounds, γ-hexachlorocyclohexane	[116]
HP-VOC	0.32×60×1.8		45(2)/3/250	C3–C5 alkyl nitrates	[151]
<b>PLOT columns</b>					
Alumina-GS	0.53×30	He	35(4)/12/100(0)/9/200(15.6)	C2–C6 HC	[65]
Al <sub>2</sub> O <sub>3</sub> /KCl	0.32×50			C2–C6 HC	[67]
Al <sub>2</sub> O <sub>3</sub> /KCl	0.53×50	He	30(1)/10/150	HCFC-134a	[136]
Al <sub>2</sub> O <sub>3</sub> /KCl				C2–C5 HC	[71]
Al <sub>2</sub> O <sub>3</sub> /KCl			−80 to 120	C2–C5 HC	[63]
Al <sub>2</sub> O <sub>3</sub> /KCl	0.53×50		40(5)/4/190(10)/15/200(15)	C2–C7 HC	[68]
GS-Q	0.35×30	H <sub>2</sub>	30(2)/10/150(0)/35/220(5)	Methyl halides	[133]
GS-Q	30 m length	H <sub>2</sub>	40(0)/10/200	Benzene, toluene	[91]
Al <sub>2</sub> O <sub>3</sub> /Na <sub>2</sub> SO <sub>4</sub>	0.53×50×10	He	5(1)/3/130(0)/15/220	C2–C6 HC	[40]
Poraplot Q	0.32×10	He		Halocarbons	[135]
Al <sub>2</sub> O <sub>3</sub> /KCl	0.32×30		50 to 200 temp. programmed	C2–C6 HC	[77]
Al <sub>2</sub> O <sub>3</sub> /KCl	0.33×25		80(0)/8/200(10)	Isoprene	[92]
Al <sub>2</sub> O <sub>3</sub> /KCl				C2–C6 HC	[71]
Al <sub>2</sub> O <sub>3</sub> /KCl	0.32×50	He	120(1)/3/165(0)/40/200(10)	Isoprene	[124]
Al <sub>2</sub> O <sub>3</sub> /KCl	0.32×50	He	100(2)/10/200(5)	Alkylated benzenes	[97]
Al <sub>2</sub> O <sub>3</sub> /KCl	0.32×50×5	He	35(2)/7/220(30)	C2–C7 HC	[73]
Al <sub>2</sub> O <sub>3</sub> /KCl	0.32×25	N <sub>2</sub>		C3–C9 HC	[36]
Al <sub>2</sub> O <sub>3</sub> /Na <sub>2</sub> SO <sub>4</sub>	50 m length	He	60(3)/3/200(30)	C2–C7 HC	[75]
Poraplot Q	0.32×10	He	40(10)/15/220	Isoprene, MVK, MAC	[123]
Poraplot Q	0.32×10	He		CH <sub>3</sub> I, C <sub>2</sub> H <sub>5</sub> I, CH <sub>3</sub> Br, CH <sub>2</sub> Br <sub>2</sub>	[142]
GS-Q	0.53×30			C2 HC	[77]

(continued on next page)

Table 2 (continued)

GC stationary phase	Column <sup>a</sup> (I.D.×length×film)	Carrier gas	Temperature program (all temperatures in °C)	Compound/approximate range of compounds analyzed	Ref.
GS-Alumina	0.53×30	He	30(3.5)/4/200	C1–C7 HC	[37]
Al <sub>2</sub> O <sub>3</sub> /KCl	0.32×50		40(0)/5/70(0)/25/130(0)/7/200(15)	C2–C8 HC	[83]
Al <sub>2</sub> O <sub>3</sub> /KCl	0.53×50×0.10		–10(0.5)/5/50(0)/10/200(17.5)	C2–C6 HC	[79]
Al <sub>2</sub> O <sub>3</sub> /Na <sub>2</sub> SO <sub>4</sub>	0.53×50		50(3)/8/195(5)	C2–C6 HC	[80]
Al <sub>2</sub> O <sub>3</sub> /KCl	0.52×50			C2–C8 HC	[78]
Poraplot Q	0.32×30	He	20 to 200 Temp. Programmed	Isoprene, MVK, MAC	[125]
Poraplot U	0.32×7	He	55 isothermal	C2 HC	[108]
Al <sub>2</sub> O <sub>3</sub>	0.53×50	He	100(15)/5/180(20)/5/200(20)	Aromatic HC	[109]
<b>Packed columns</b>					
0.3% FFAP/0.3% H <sub>3</sub> PO <sub>4</sub> / Carbopack B (60–80°)	3 mm I.D.×1.5 m	N <sub>2</sub>	110(0)/8/240	Fatty acids	[173]
OPN/Porasil	3 m×2 mm I.D.	He		C1–C6 HC	[66]
Porapak Q	1.8 m×3.2 mm		70 isothermal	CH <sub>3</sub> Br	[131]
Hayesep N	2 m×3.2 mm O.D.	5% CH <sub>4</sub> /95% Ar		N <sub>2</sub> O	[18]
Phenylisocyanate/Poracil C (80/100)	6 m×0.76 mm I.D.	He	40 isothermal	C2–C4 HC	[42]
Carbosphere (80/100)	2 m×1/16 in. diameter	He	160 isothermal	Methane	[63]
Chromosil 330				DMS, CS <sub>2</sub> , methyl mercaptan	[161]
10% Carbowax 400/ Chromosorb P(60/80)	3 mm×0.8 m	N <sub>2</sub>	36 isothermal	PAN, PPN	[152]
Chromosil 300	3.6 m×3.2 mm	N <sub>2</sub>	40(1.5)/10/65	COS, DMS	[159]
SPEROSIL XOB075	3 m length		–50(0)/10/80(0)/15/175	SF <sub>6</sub> , CF <sub>4</sub> , C <sub>2</sub> F <sub>6</sub>	[154]
Carbopack B/1.5% XE-60/1.0 H <sub>3</sub> PO <sub>4</sub>	3 m length		Temperature programming	DMS	[160]
Phenyl Isocyanate/Porasil C			50 isothermal	C1–C5 HC	[72]
Porasil-L (80/100)	4 m×3.2 mm O.D.		–50 to 200	SF <sub>6</sub>	[156]
Porapak N (80–100)	0.2 m×1/8 in. O.D.	He	130 isothermal	C1–C5 HC	[36]
Alumina F-1 (60–80)	4 m×1/8 in. O.D.	He	130 isothermal	C1–C5 HC	[36]
10% Carbowax 600/ Chromosorb W-HP (60–80)	6 m×1.5 mm I.D.	N <sub>2</sub>	35 isothermal	PAN	[39]
Alumina (60–80)	2 m×2 mm I.D.,	N <sub>2</sub>	50(4)/7/180	C2–C5 HC	[82]
10% Carbowax 600/ Chromosorb W-HP (60–80)	6 m×1.5 mm I.D.	N <sub>2</sub>	35 isothermal	PAN	[108]
Porapak Q (80–100)	1.2 m×3 mm I.D.		145 isothermal	Methanol, ethanol, acetone, pentane	[74]
Molecular Sieve 5A (60–80)		He		CO	[169]
Chromosil 330				DMS	[166]
<b>Multi-dimensional</b>					
Rtx-1/ Rtx-1701	0.53×3 0.53×3	N <sub>2</sub>	26 isothermal	PAN	[25]
DB-1/ DB-1	0.53×30×5 0.32×50×1		45(5)/25/160	Sulfur compounds	[158]
Molecular Sieve 5A (60–80)/ Molecular Sieve 5A (60–80)	0.3 m×2 mm I.D. 1.8 m×2 mm I.D.	Zero air	100 isothermal	CO	[42]
Molecular Sieve 5A (80–100)/ Molecular Sieve 5A 80–100)	0.3 m×2.4 mm I.D. 3 m×2.4 mm I.D.	N <sub>2</sub>	65 isothermal	SF <sub>6</sub>	[155]
3% OV-101 on Chromosorb/ 3% OV-101 on Chromosorb	1.2 m×2.2 mm I.D. 3.2 m×2.2 mm I.D.	N <sub>2</sub>	45 isothermal	CFCs	[30]
Porapak Q/ Porapak Q	2 m×3.8 mm I.D. 3 m×3.8 mm I.D.	5% CH <sub>4</sub> / 95% Ar	95 isothermal	N <sub>2</sub> O, SF <sub>6</sub>	[30]
Porasil B/ 30% OV-101 on Chromosorb	0.3 m×3.8 mm I.D. 4 m×3.8 mm I.D.	N <sub>2</sub>	45 isothermal	CFCs	[29]
Unibeads 1S/ Molecular Sieve 5A	2 m×3.8 mm I.D. 3.3 m×3.8 mm I.D.	N <sub>2</sub>	140 isothermal	H <sub>2</sub> , CH <sub>4</sub>	[29]
PorapakQ (100/200)/ HayesepQ (80/100)	1 m×3.18 mm O.D. 2 m×3.18 mm O.D.	N <sub>2</sub> (O <sub>2</sub> -doped)	140 isothermal	Methyl bromide	[28]
Methyl polysiloxane/ Al <sub>2</sub> O <sub>3</sub> /Na <sub>2</sub> SO <sub>4</sub>	0.32×100×5 0.53×15×10	N <sub>2</sub>	55 isothermal 85 isothermal	Isoprene, DMS	[99]
Porapak Q/ Porapak Q	2 m×4.8 mm I.D. 3 m×4.8 mm I.D.	5% CH <sub>4</sub> / 95% Ar	80 isothermal	SF <sub>6</sub> , N <sub>2</sub> O	[157]

Table 2 (continued)

GC stationary phase	Column <sup>a</sup> (I.D.×length×film)	Carrier gas	Temperature program (all temperatures in °C)	Compound/approximate range of compounds analyzed	Ref.
CP-Sil-5 CB/	0.32×50×1.2	He	30-150	C3–C7 HC	[39]
Poraplot U	0.32×7	He	55 isothermal	C2 HC fraction	
Porapak QS (100/120)/	3 m×1/8 in.			C2–C5 HC	[76]
SE-54	0.32×60				
Carbowax CP Wax 52 CB/	0.53×10×2.0	He	35 isothermal	C2–C5 carbonyls, C1–C2	[41]
CP Sil 5 CB/	0.32×50×1.2		35(9)/30/75(0)/5/87(0)/30/150(5)	alcohols, C5–C8 HC	
CP Sil 8 CB	0.32×50×1.2		35(9)/30/75(0)/5/87(0)/30/150(5)		
Al <sub>2</sub> O <sub>3</sub> /	0.32×50		70(0)/10/130(0)/20/220	VOCs	[92]
SE-54	25 m length				
Porapak Q (60/80)/	2 m×3.2 mm O.D.			Methane	[64]
Molecular Sieve 5A (80/100)	2 m×3.2 mm O.D.				
Silica gel/TritonX-305/		N <sub>2</sub>	65 isothermal	CO	[170]
Molecular Sieve 5A					
Porasil C/	0.3 m×2.1 mm I.D.	N <sub>2</sub> (O <sub>2</sub> -doped)	70 isothermal	HCFC-22	[29]
Porasil C	6.1 m×2.1 mm I.D.				
PoraPLOT Q/	0.53×2.5	He	90 isothermal	HCFC-22	[29]
PoraPLOT Q	0.53×22.5				
Unibeads 1S/				CO	[171,172]
Molecular Sieve 5A					
GasPro GSC/	0.32x 15	He	−30(2.5)/3.5/−13(0)/20/8(0)/5/70(0)/10/ 240(12.2)	C2–C9 HC	[81]
CP-Sil 5CB	0.25×50×1		−30(2)/4/160(0)/20/200(15)		
Carbograph 1/	0.25×30	He	40(3)/12/200	Aromatics, oxygenates	[106]
Carbograph 1	0.25×30				
WCOT-CP-Wax-B/	0.25×25×0.2	N <sub>2</sub>	50(9)/7/75(0)/4/90(0)/10/145	C4–C12	[103]
WCOT-CP-Sil-CB	0.32×25×1.2		45(0)/7/120(0)		
Chrompak PLOT/	0.53×50		−10(0)/7.6/200(17.5)	CFCs (+HC)	[143]
DB-624	0.53×75×3				

<sup>a</sup> Capillary column parameters are given in inner diameter (I.D.) in mm×length in m×film thickness in μm. Packed column parameters given are inner diameter (units as indicated)×length (in m).

<sup>b</sup> Numbers are temperatures in °C, numbers in parentheses are isothermic times in min, numbers between two “/” are oven program rates, for example: −50(3)/6/175(0)/25/250 means −50°C for 3 min, 6°C min<sup>−1</sup> to 175°C, 25°C min<sup>−1</sup> to 250°C.

<sup>c</sup> Grain size in mesh.

columns or detectors were used in series or simultaneously during one analysis, whereas terms listed and separated by comma (“,”) indicate that different adsorbents, columns or detectors were used in an alternate or sequential fashion. Multidimensional techniques include the use of GC columns in series or in a backflush or heart-cut arrangement, respectively.

#### 4. Conclusions

In the following some trends deduced from the literature review are summarized in alphabetical order of selected keywords.

##### 4.1. Capillary columns

Most commonly used columns are 0.23 to 0.53

mm I.D. capillaries. Selection of column diameter mainly depends on the interfacing to the injection system and the detector. For mass spectrometric detection, diameters of 0.32 mm or less are preferred to accommodate a flow into the analyzer of no more than 2–3 ml min<sup>−1</sup>. On the other side, wider capillaries have the advantage of possible higher flow-rates which facilitates sample transfer from a focusing trap or a thermodesorption cartridge. Overall, capillary column applications make up approximately 74% of all GC analysis methods considered in this review and therefore clearly are the dominant chromatographic technique.

PANs have been recognized as intermediate reaction products in atmospheric hydrocarbon oxidation and as important components in smog for almost four decades [19,20]. After more than 25 years of measurements exclusively by packed column GC, first reports on PANs capillary column GC analysis

were published in 1989 and 1991 [21,22]. It now appears that liquid film capillary column techniques are gradually becoming the method of choice for PANs analysis. Successful analysis has been achieved on non-polar phases [23,24] as well as on moderately polar phases [25–27].

#### 4.2. Carrier gas

Helium is the most commonly carrier gas used, followed second by nitrogen. Despite the chromatographic advantages of hydrogen, it is rarely used as carrier gas in air analysis applications. It is common to purify the carrier gas by flowing it through a combination of oxygen, moisture of hydrocarbon purifier traps or by cryogenic trapping to reduce contaminant concentrations. This is particularly critical when components of the analytical systems containing adsorbent or cryogenic traps are purged by the carrier gas in order to minimize contaminant enrichment during these steps.

#### 4.3. Detection

Ten different GC detection methods were used in the reviewed literature. Detector selection depends on the target compound, concentration range and whether qualitative identification or quantitative analysis is desired. The most popular detection methods are FID, MS and ECD, with approximate %-age uses of 37%, 27% and 21%, respectively. FID is the predominant method for light hydrocarbon analysis. While traditionally ECD has been the method of choice for halogenated compounds, improved overall sensitivity and ease of operation has lead to a gradual increase of MS detection in this field.

Some novel approaches have been developed to enhance the sensitivity of ECD detection to meet sensitivity requirements of trace gas analysis at low parts-per-trillion levels. By either doping carrier gas [28] or make-up gas [29] with oxygen, the detector sensitivity for halogenated VOC, CFC and HCFC analysis was improved. Elkins et al. [30] doped the ECD make-up gas with  $\approx 15$  ppm  $N_2O$  to enhance response for  $H_2$  and  $CH_4$ . Cao and Hewitt [31] applied on-column bromination for the ECD of alkenes.

GC/ion mobility detection was used by Simpson et al. [32] for measuring chlorinated and aromatic compounds. Multi-detection with either sequential detector arrangement [33–35] or by splitting the column flow [36,37] were used by several groups. These techniques allow powerful analysis of both hydrocarbons (FID) and halogenated VOCs (ECD, PID) or aromatic compounds (PID) in one sample run. It is remarkable that two rather novel and powerful detection methods, atomic emission detection (AED) and Fourier-transform infrared detection (FT-IR), while commercially available for several years, have scarcely been applied so far.

#### 4.4. Film thickness

In the analysis of light hydrocarbons and halogenated hydrocarbons, GC columns with relatively thick liquid films are being preferred to achieve better retention of these highly volatile compounds and to reduce or even possibly avoid the use of oven cryogen. Film thicknesses between 1 to 5  $\mu m$  are common. With the use of a 5  $\mu m$  film, analysis of compounds down to the volatility of the  $C_2$ -hydrocarbons at oven program start temperatures slightly above ambient ( $30^\circ C$ ) was reported [38]. For analysis of heavier organic compounds, such as the semivolatile fraction, thinner films ( $< 1 \mu m$ ) are used more preferably.

#### 4.5. Injection

Direct loop injection is primarily used for gases present in the 100 ppbv to ppmv concentration range, such as methane,  $N_2O$  and carbon monoxide. It is also the most common injection technique in the analysis of PANs. Cryogenic freezeout techniques are frequently used for sample concentration from flasks and canisters during VOC analysis. In the thermal desorption of solid adsorption cartridges, early techniques relied mainly on the direct sample transfer onto the column head with possible focusing on the column stationary phase. It becomes apparent that more researchers are now using a pre-focusing step, where the sample volume is reduced in a micro-trap which subsequently is rapidly heated and injected onto the GC column for separation. The focusing step particularly improves resolution for the

more volatile VOC fraction, which may not be efficiently focused on the column head at oven program start temperatures. Injection of liquid extracts is used where analyte recovery by solvent extraction and possible subsequent fractionation and solvent concentration is performed, such as in the analysis of semivolatile compounds.

#### 4.6. Liquid stationary phase

Non-polar liquids are the preferred stationary phases for GC air analysis. Dimethylpolysiloxane is the standard non-polar stationary phase. Dimethylpolysiloxane-coated columns were used in 52% of all liquid film capillary column applications, followed by (5%-phenyl)-methylpolysiloxane with 23%. Clearly, these popular phases exhibit properties that are favorable for air analysis, such as good separation of the target compounds, robustness against possible remaining oxidants and water in the sample concentrate and durability. Among the more polar phases, (14%-cyanopropyl-phenyl)-methylpolysiloxane appears to be the one most frequently used.

#### 4.7. Multidimensional GC

Multidimensional GC analysis techniques involving the use of 2–3 columns and column-switching during the separation of one sample are increasing in the air analysis field. These methods offer several advantages. A wider range of VOCs can be analyzed by directing the more volatile and less volatile portion of the sample onto two column phases with different retention strength. Combination of a PLOT and a liquid phase capillary column is becoming more and more popular to facilitate analysis of the light ( $\approx C_2$ – $C_6$ ) and heavier ( $\approx C_6$ – $C_{12}$ ) VOC fraction in one run and possibly without use of cryogenic oven programming [39–41]. Furthermore, water vapor, a common interference for the separation and detection process, can be eliminated by a column backflush. This can be a substantial advantage in PAN [30] or CO analysis [42]. A more general review of two-dimensional GC was recently given by Schomburg [43].

#### 4.8. Oven programming

Sub-ambient oven programming is frequently used in VOC analysis. The most commonly used oven coolant is liquid nitrogen. Oven program start temperatures in the  $-60^\circ\text{C}$  to  $-50^\circ\text{C}$  range are typical when cryogenic oven cooling is applied. Oven program rates usually are in the 2 to  $6^\circ\text{C min}^{-1}$  range. In order to reduce or prevent the liquid nitrogen consumption, stronger retaining column phases, such as PLOT columns, which allow separation of lighter VOCs at ambient and above ambient temperatures, are increasingly used. A different alternative to cryogenic oven cooling is the use of Vortex Tube cooling, which has been shown to allow cyro-focusing/cryo-trapping to  $-40^\circ\text{C}$  [44] and sub-ambient oven programming [45] and may be a viable alternative where supply of liquid cryogen is difficult and expensive, such as at remote field study sites.

#### 4.9. Packed columns

The use of packed columns in air analysis appears to be declining, in particular for light hydrocarbon and PANs analysis. For the reviewed time period, packed column techniques were used in 26% of the considered air analysis publications. However, for GC analysis of CO and DMS, packed columns are still the method of choice. For analysis of PANs, a gradual move from packed columns to capillary columns is being observed (see above).

#### 4.10. PLOT columns

PLOT (porous-layer open-tubular) columns have experienced a remarkable application increase over the last few years. PLOT columns were used in 21% of GC air analysis methods for the reviewed time period. PLOT columns exhibit stronger retention of volatile gases (permanent gases and light hydrocarbons) than liquid film columns and therefore allow separation of highly volatile gases without use of sub-ambient oven programming techniques. For these reasons, PLOT columns are on their way to becoming the predominant column type used for analysis of light hydrocarbons in the  $\approx C_2$  to  $C_7$  range. The most commonly used columns are 0.32 and 0.53 mm internal diameter capillaries. Some of

the earlier reported problems of PLOT columns, such as, particle release, dehydrogenation of certain HCFCs, strong (irreversible) retention of higher boiling and polar VOCs, shifting retention times and problems from the sample humidity, do not seem to have prohibited its widespread use. Improvements in the column preparation or column use have also helped to overcome some of the above listed problems. The most commonly used stationary phase is deactivated  $\text{Al}_2\text{O}_3$ . Some additional, newly developed and released phases, such as GS-Q, MolesievePLOT and CarbonPLOT will certainly enhance the PLOT column applicability. The higher temperature limits of the later columns reduce some of the drawbacks mentioned above. It is remarkable, that so far, PLOT columns have not found their way into some other traditional packed column analysis fields, such as the analysis of DMS, CO or PANs. Comprehensive overviews of PLOT column techniques and PLOT column use have been published recently [46,47].

#### 4.11. Sampling techniques

The three most common sampling techniques are (1) collection into stainless steel canisters, (2) collection onto solid adsorbents with subsequent thermal desorption and (3) in-situ sampling with either cryogenic freezeout or solid adsorbent trapping. While 1 and 2 are methods of choice where sampling and analysis are performed in different locations, in-situ sampling requires the deployment of the analytical instrument at the sampling site. Both 1 and 2 have received extensive research attention for compound storage, recovery and interferences. In both, whole air and adsorbent sampling methods, increased efforts have gone towards extending the range of compounds to the more polar VOC fraction.

Overall, in the area of volatile organic compound analysis ( $\text{CH}_4$ , light VOC, mid-range VOCs, halogenated compounds), adsorbent sampling techniques were used slightly more frequently than canister (including “flasks” and “cylinders”) sampling with a ratio of adsorbent/canister of approximately 1.25:1.

Sophisticated canister treatment and coating techniques have widened the volatility and polarity range of compounds that can be recovered and analyzed.

Multi-bed solid adsorbent cartridges, which contain a series of adsorbents, are being used increasingly in thermal desorption techniques. These cartridges allow a wider range of compounds to be collected and thermally released. While earlier applications of solid adsorbents were mainly of the mid-volatile fraction of VOCs, more and more applications for the lighter VOCs down to  $\text{C}_2$  hydrocarbons have been accomplished. Although passive sampling techniques are a common procedure for work place monitoring they are seldom used in ambient air analysis.

### 5. New alternatives to GC air analysis techniques

While in many cases, GC is the only viable method for the trace analysis of certain atmospheric constituents, it has also been recognized that atmospheric chromatography methods suffer from a number of limitations and constraints. Today's research and monitoring tasks increasingly ask for in-situ analysis, high spatial and temporal resolution, automated data processing, remote instrument and data access and low-maintenance operation. These requirements are difficult to meet with GC techniques. Therefore, increasing efforts are being observed in the development and applications of alternative techniques for analysis of atmospheric gases which traditionally have been analyzed by chromatography techniques. As new detection techniques are giving increasingly more sensitive and more selective response to compounds of interest, the GC separation step can be omitted.

In some cases viable alternatives allowing in-situ analysis have been developed. It is anticipated that in the future these methods will increasingly replace GC analysis. Some of the most promising universal techniques developed and applied to date include mass spectrometry techniques, such as membrane-inlet mass spectrometry (MIMS) [48–51] atmospheric pressure ionization tandem mass spectrometry (API-MS-MS) [52,53], ion mobility detection [54], direct inlet MS-MS ion trap detection [55,56] and ion storage/time-of-flight MS [57].

Other techniques specific for individual gas species are, for instance, ozone chemiluminescence

for the measurement of isoprene [58] and fluorine-induced chemiluminescence for the fast measurements of dimethyl sulfide [59]. Tunable diode laser (TDL) absorption spectrometry [60–62] has been used for several gases, such as formaldehyde, CO<sub>2</sub> and N<sub>2</sub>O. All of these methods are specifically suited for the fast time resolution required in Eddy-correlation flux measurements.

## 6. Summary

The most popular applications of capillary GC in air analysis are for ozone precursor compounds such as hydrocarbons, anthropogenic VOCs and biogenic VOCs. Another important field is analysis of ozone-layer depleting compounds, such as CFCs and HCFCs. Major advances in the past three years have been in the application of PLOT columns, mass spectrometry detection, GC separation without cryogenic oven programming, focusing steps and solid adsorbent use. It should be noted that in the literature referenced in this paper gases such as PAN, DMS, H<sub>2</sub>, CO and CO<sub>2</sub>, which frequently are analyzed by GC, probably are underrepresented because many of the recent articles do not detail the analytical procedure but rather refer to established procedures detailed in earlier work and therefore were not included in this review.

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