

# Contents

<i>Chapter 1</i>	
Introduction . . . . .	1
References . . . . .	3
<i>Chapter 2</i>	
Air as an object of analysis . . . . .	4
2.1. Atmospheric air and sources of atmospheric pollution . . . . .	4
2.2. General characteristics of air pollutants . . . . .	5
2.3. Specific features of air as an object of analysis . . . . .	8
References . . . . .	9
<i>Chapter 3</i>	
Gas chromatography in the analysis of air pollutants . . . . .	10
3.1. General considerations . . . . .	10
3.2. Peculiarities of the gas chromatographic analysis of impurities . . . . .	20
References . . . . .	23
<i>Chapter 4</i>	
Detectors for the gas chromatographic determination of impurities . . . . .	25
4.1. Principal characteristics of detectors for gas chromatography . . . . .	25
4.2. Flame ionization detector . . . . .	28
4.3. Thermionic detector . . . . .	28
4.4. Photoionization detector . . . . .	29
4.5. Electron-capture detector . . . . .	30
4.6. Flame photometric detector . . . . .	30
4.7. The thermal energy analyser (TEA) detector . . . . .	31
4.8. Detectors for direct identification of impurities . . . . .	31
4.9. Hall electrolytic detector . . . . .	31
References . . . . .	33
<i>Chapter 5</i>	
Collection and pretreatment of samples for chromatographic analysis . . . . .	35
5.1. Sampling into containers . . . . .	35
5.2. Use of absorption of contaminants in sample collection . . . . .	37
5.3. Cryogenic concentration of contaminants . . . . .	40
5.4. Use of adsorption for contaminant concentration . . . . .	46
5.4.1. Activated coal and carbon adsorbents . . . . .	48
5.4.2. Porous polymer adsorbents . . . . .	50
5.4.3. Sorbents used in gas-liquid chromatography . . . . .	55
5.4.4. Silica gel . . . . .	57

5.4.5.	Molecular sieves . . . . .	58
5.4.6.	Aluminium oxide . . . . .	58
5.5.	Multilayer sorption traps . . . . .	59
5.6.	Sorbents for passive sampling . . . . .	59
5.7.	Chemisorbents . . . . .	62
5.8.	Trapping of solid particles and aerosols . . . . .	65
5.9.	Preparation of concentration tubes containing solid sorbent . . . . .	67
5.10.	Influence of sampling conditions on the efficiency of sorption of pollutants . . . . .	70
5.10.1.	Properties of analysed compounds . . . . .	71
5.10.2.	Properties of the sorbent used . . . . .	72
5.10.3.	Air flow-rate . . . . .	78
5.10.4.	Air sample volume . . . . .	78
5.10.5.	Concentration temperature . . . . .	80
5.10.6.	Air humidity . . . . .	80
5.10.7.	Coadsorption . . . . .	80
5.10.8.	Concentration in the flow . . . . .	81
5.11.	Desorption of pollutants from the sorbent . . . . .	83
5.11.1.	Solvent extraction . . . . .	83
5.11.2.	Extraction in Soxhlet apparatus and ultrasonic field . . . . .	85
5.11.3.	Thermal desorption . . . . .	86
5.12.	Influence of experimental conditions on the completeness of recovery of pollutants . . . . .	91
5.12.1.	Temperature . . . . .	96
5.12.2.	Humidity . . . . .	96
5.12.3.	Coadsorption . . . . .	97
5.12.4.	Desorption duration . . . . .	98
5.12.5.	Choice of solvent . . . . .	98
5.13.	Increase in desorption efficiency . . . . .	100
5.13.1.	Solvent mixture . . . . .	100
5.13.2.	Two-phase desorption systems . . . . .	100
5.13.3.	Desorption methods . . . . .	102
5.14.	Choice of sampling method . . . . .	103
5.15.	Metrological aspects of air pollutant determination by gas chromatography . . . . .	108
	References . . . . .	113

## Chapter 6

	The reactive-sorption method and its application for concentrating pollutants . . . . .	119
6.1.	Concentration of pollutants on solid adsorbents . . . . .	119
6.2.	Reactive-sorption concentration . . . . .	121
6.3.	Use of the reactive-sorption method to enhance the reliability of the determination of pollutants . . . . .	123
6.3.1.	Determination of aggressive gases . . . . .	123
6.3.2.	Determination of nitrogen oxides . . . . .	124
6.3.3.	Determination of sulphur fluorides . . . . .	125
6.3.4.	Determination of hydrocarbons . . . . .	126
6.4.	Diminution of coadsorption of pollutants . . . . .	127
6.4.1.	Dynamics of sorption and coadsorption . . . . .	127
6.4.2.	Diminution of coadsorption . . . . .	130
6.5.	Improvement of chromatographic separation . . . . .	133
6.6.	Moisture removal . . . . .	134
6.7.	Identification of pollutants . . . . .	135
6.7.1.	Determination of hydrocarbons . . . . .	135

6.7.2.	Determination of oxygen-containing compounds	137
6.7.3.	Determination of halogen-containing compounds	139
6.7.4.	Determination of sulphur-containing compounds	143
6.7.5.	Determination of nitrogen-containing compounds	144
6.7.6.	Determination of inorganic compounds	145
6.8.	Conclusion	146
	References	147

### Chapter 7

	Quantitative methods for the determination of impurities	150
7.1.	Preparation of standard mixtures	150
7.1.1.	Static methods	150
7.1.2.	Dynamic methods	151
7.1.2.1.	Methods used to dilute (mix) streams	151
7.1.2.2.	Diffusion method (use of diffusion cells)	152
7.1.2.3.	Exponential dilution flask method	152
7.1.2.4.	Diffusion method using permeation tubes (ampoules)	153
7.1.2.5.	Other methods	157
7.1.2.6.	Preparation of standard aerosol mixtures	159
7.2.	Detector calibration	161
7.3.	Calculation of impurity concentrations	161
7.4.	Detection limits for air contaminants	162
	References	163

### Chapter 8

	Practical application of gas chromatography to the determination of air pollutants	165
8.1.	Carbon oxides	165
8.2.	Halides and their derivatives	167
8.3.	Nitrogen-containing compounds	170
8.4.	Sulphur- and phosphorus-containing compounds	172
8.5.	Metals and their derivatives	176
8.6.	Low-boiling hydrocarbons	178
8.7.	Aromatic hydrocarbons	179
8.8.	Polyaromatic compounds	180
8.9.	Organic oxy compounds	186
8.10.	Amines and nitro compounds	190
8.11.	Odorants	194
8.12.	Halogenated hydrocarbons	195
8.13.	Freons	196
8.14.	Chlorine-containing pesticides, polychlorobiphenyls and dioxins	197
8.15.	Bis(chloromethyl) ether	198
8.16.	Vinyl chloride	199
	References	203

	Conclusion	208
	Subject Index	209