

FLUE GAS MONITORING TECHNIQUES

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Manual Determination of Gaseous Pollutants

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PREFACE

The term *monitoring*, in this context, means to keep track of, but not necessarily on a continuous basis. The methods discussed in this book include "grab" and/or semicontinuous methods which usually involve taking a sample in the field and wet chemical or instrumental analysis in a laboratory.

The Environmental Protection Agency (EPA) and its predecessor agency, the National Air Pollution Control Administration (NAPCA), have sponsored considerable research and development oriented toward providing improved methods for sampling and analysis of gaseous pollutants in flue gases. Although this work is documented in government publications and is available through NTIS (National Technical Information Service) in Arlington, Virginia, a majority of the air pollution community is not familiar with this work. It is the purpose of this book to familiarize the readers with some of this pertinent material.

Major portions of various chapters were abstracted or re-written from the following NAPCA or EPA sponsored reports written by the author while at Walden Research Corporation:

"Improved Chemical Methods for Sampling and Analysis of Gaseous Pollutants from the Combustion of Fossil Fuels"

Volume I -- Sulfur Oxides, APTD 1106, PB 209-267 (1971).

Volume II-- Nitrogen Oxides, APTD 1108, PB 209-268 (1971).

Volume III--Carbon Monoxide, APTD 1109, PB 209-269 (1971).

"Validation of Improved Chemical Methods for Sulfur Oxide Measurements in Stationary Sources," EPA Report EPA R2-72-105 (November 1972).

"Monitoring Methods and Instrumentation for Carbon Monoxide and Hydrocarbons in Stationary Source Emissions," EPA Report EPA R2-72-106 (November 1972).

The material in these reports was updated and supplemented by a literature search in order to provide a detailed volume on gas sampling and analysis methods.

The burden of gaseous pollutant emissions from various man-made sources is detailed in Chapter 1. This is followed, in Chapter 2, by a description of the characteristics (pertaining to sampling) of industrial processes. The EPA standards are also included in this chapter. Chapter 3 reviews the many aspects of sampling gases including probes, sampling trains, and site selection. Techniques for measurement of sample gas volume and volumetric flow in ducts are covered in Chapter 4. Chapter 5 discusses some aspects of the sulfur oxides including the concentrations in industrial processes, the chemistry, the collection methods, the analytical methods and statistical analyses. Chapter 6 compiles the results of field testing wet chemical methods for SO_2 and SO_3 at five different types of stationary sources. Chapters 7 to 10 discuss nitrogen oxides, carbon monoxide, hydrocarbons, and hydrogen sulfide and other sulfur compounds, respectively. Each chapter is broken down into sections on concentrations in industrial processes, chemistry, and a review of sampling and analytical methods.

Evaluation of the material in this book should allow the selection of gas sampling procedures for those sources where EPA standards have not been promulgated or where alternate methods are desired.

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CHAPTER 1

SOURCES

1.1. INTRODUCTION

In this chapter, natural and manmade sources of sulfur oxides, nitrogen oxides, carbon monoxide, hydrocarbons, and hydrogen sulfide are discussed. The burden of these emissions on the atmosphere is detailed for the major stationary sources. Atmospheric chemical reactions and sinks for these pollutants are not discussed in this book. The reader is referred to Robinson and Robbins [1] for a detailed discussion on this subject.

1.2. SULFUR OXIDES

Emissions of sulfur compounds into the atmosphere occur from both natural and manmade sources. The natural sulfur is emitted from swamps as H_2S whereas sulfur compounds in the latter category are released predominantly as SO_2 . The worldwide emissions of SO_2 into the atmosphere from manmade sources have been estimated by Robinson and Robbins [1,2] and a summary of their data is given in Table 1.1. The primary source of SO_2 emissions is from the combustion of coal. Residual oil combustion, smelting, and petroleum refining are also major sources of SO_2 emissions.

The combustion of fossil fuels accounts for more than 85% of the worldwide SO_2 emissions. A detailed breakdown of fossil fuel combustion excluding direct-fired process emissions is shown in Table 1.2. The data in Table 1.2 indicate that 90% of the total (non-process) emissions are attributable to water-tube boilers which have a capacity of $\geq 25,000$ pounds of steam per hour. It

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Table 1.1
Worldwide Annual Emissions of Sulfur Dioxide in 1967*

<i>Source</i>	<i>Tons x 10⁶</i>	<i>% of Total</i>
Coal	102.0	70.00
Petroleum Combustion		
Gasoline	0.3	0.20
Kerosene	0.2	0.14
Distillate	2.0	1.37
Residual	20.3	13.88
Petroleum Refining	5.7	3.70
Smelting		
Copper	12.9	8.80
Lead	1.5	1.02
Zinc	1.3	0.89
TOTAL	146.2	100.0

*Taken from Robinson and Robbins [1].

Table 1.2
Nationwide (U.S.) Emissions of SO₂, 1967*

		<i>10⁶ tons/year</i>
Total from Fossil Fuel Combustion in Stationary Sources		18.63
By Fuel	Coal	15.60
	Residual Fuel Oil	2.76
	Distillate Fuel Oil	0.27
By Sector	Utilities	12.58
	Industrial	4.28
	Commercial	1.53
	Residential	0.24
By Boiler Category (excluding residential)		
	Watertube ≥ 500,000 pph	9.29
	Watertube ≤ 500,000 pph	6.50
	Firetube	0.88
	Cast Iron	0.72

*Taken from Ehrenfeld *et al.* [3].

is easy to see from Table 1.2 that the emphasis on emission testing has been, and will continue to be, centered on large sources since they account for the majority of the SO_2 emissions. Considering the data in Table 1.1, it is not surprising that a large portion of the analytical method development has in the past centered on fossil fuel-fired power plants.

1.3. NITROGEN OXIDES

The most abundant nitrogen compound in the atmosphere is nitrous oxide (N_2O) which is derived mainly from biological action in the soil [1,4]. Equilibrium calculations [5] indicate a significant amount of N_2O could be present in flue gases provided that there is a kinetic route to formation of N_2O . However, no measurements of this species have been found for flue gases.

Robinson and Robbins [4] estimate that natural sources, *i.e.*, bacterial action under anerobic conditions, produce significant quantities of nitric oxide. The estimate of NO produced by biological action is 501×10^6 tons compared to 52.9×10^6 tons from manmade sources. Thus, pollutant emissions appear to contribute only about 10% of the total NO_x emissions to the atmosphere.

A compilation of the worldwide emissions of nitrogen oxides ($\text{NO} + \text{NO}_2$) from manmade sources is given in Table 1.3, and the U.S. emissions of nitrogen oxides is shown in Table 1.4. NO_x emissions in the U.S. account for more than a third of the total worldwide emissions. It is interesting to compare some of the differences between Tables 1.3 and 1.4. Gasoline used for worldwide transportation is 7.5×10^6 tons of NO_x or 14.17% of total. In the U.S., however, 6.6 tons or 33% of the nitrogen oxides are from this source. Coal, on a worldwide basis, accounts for almost 51% of the total NO_x , but in the U.S. it is only 19% of the total. Note the large discrepancy in natural gas emissions, *i.e.*, 4.8×10^6 tons in Table 1.4 compared to 2.1×10^6 tons worldwide. This is due to the inclusion in Table 1.4 of fuel used to power the transmission of fluids through pipelines. Emission estimates for 22 U.S. cities indicate that 50% of the total NO_x can be attributed to stationary sources with a range from 10 to 79% [6].

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Table 1.3
Worldwide Urban Emissions of Nitrogen Oxides for 1967*

<i>Fuel</i>	<i>Source</i>	<i>NO_x Emission 10⁶ tons/year</i>	<i>% of Total</i>
Coal	Power Generation	12.2	23.06
	Industrial	13.7	25.89
	Domestic/Commercial	1.0	1.89
Petroleum	Refinery Production	0.7	1.32
	Gasoline	7.5	14.17
	Kerosene	1.3	2.46
	Fuel Oil	3.6	6.80
	Residual	9.2	17.39
Natural Gas	Power Generation	0.6	1.13
	Industrial	1.1	2.08
	Domestic/Commercial	0.4	0.8
Others	Incineration	0.5	0.9
	Wood	0.3	0.6
	Forest Fires	0.8	1.51
		<u>52.9</u>	<u>100.00</u>

*Taken from Robinson and Robbins [1].

Table 1.4
Summary of U.S. Emissions of Nitrogen Oxides in 1968*

	<i>NO_x Emissions 10⁶ tons/year</i>	<i>% of Total</i>
Transportation (total)	8.1	39.3
(Gasoline)	(6.6)	
Fossil Fuel Combustion		
Coal	4.0	19.4
Fuel Oil	1.0	4.8
Natural Gas	4.8	23.3
Wood	0.2	1.0
Industrial Sources	0.2	1.0
Miscellaneous		
Forest Fires	1.2	5.8
Structural Fires	-	-
Coal Refuse	0.2	1.0
Agriculture	0.3	1.5
	<u>20.6</u>	<u>100.0</u>

*Taken from "Air Quality Criteria for Nitrogen Oxides"[6].

1.4. CARBON MONOXIDE

Robinson and Robbins [1] indicated that manmade combustion sources accounted for essentially all the CO emissions into the atmosphere. Recent work [7] has shown that the ocean is a major sink for CO, reducing the estimated lifetime in the atmosphere to 0.1 years.

The estimated yearly worldwide emissions of CO from combustion sources is 232 million tons. A breakdown of these sources is tabulated in Table 1.5. The estimates of CO emissions in the U.S. in 1968 are given in Table 1.6 and total 101.6 million tons [8]. In both cases, automotive emissions account for the major portion. Note the large contribution of CO from residential heating in Table 1.5. In the U.S., large stationary sources which emit CO include industrial processes and solid waste disposal.

Table 1.5
Worldwide Annual CO Emissions for 1967*

<i>Source</i>	<i>CO Emissions 10⁶ tons/year</i>	<i>% of Total</i>
Gasoline	193	83.2
Coal		
Power	0.3	0.1
Industry	1.2	0.5
Residential	10.0	4.3
Coke & Gas Plants	0.1	0.1
Wood (fuel)	16.0	6.9
Forest Fires	11.3	4.9
	<hr/> 232	<hr/> 100.0

*Taken from Robinson and Robbins [1].

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Table 1.6

Carbon Monoxide Emission Estimates by Source Category U.S. - 1968*

Source	CO Emissions	
	10 ⁶ tons/year	% of Total
Transportation	63.8	62.8
Motor Vehicles	59.2	58.2
Gasoline	59.0	58.0
Diesel	0.2	0.2
Aircraft	2.4	2.4
Vessels	0.3	0.3
Railroads	0.1	0.1
Other Non-highway Use of Motor Fuels	1.8	1.8
Fuel Combustion in Stationary Sources	1.9	1.9
Coal	0.8	0.8
Fuel	0.1	0.1
Natural Gas	N	N
Wood	1.0	1.0
Industrial Processes	11.2	11.0
Solid Waste Disposal	7.8	7.7
Miscellaneous	16.9	16.6
Manmade	9.7	9.5
Forest Fires	<u>7.2</u>	<u>7.1</u>
Total	101.6	100.0

N = Negligible.

*Taken from "Air Quality Criteria for Carbon Monoxide" [8]

1.5. HYDROCARBONS

Methane is the major hydrocarbon emitted into the atmosphere from natural sources [1]. More than 300 million tons are emitted annually from bacterial decomposition in swamps and marshes. Other natural sources are terpenes from vegetation which are estimated to emit 170 million tons annually [1]. Manmade sources then account for only about 15% of the total quantity of hydrocarbons emitted to the atmosphere. Hydrocarbon emissions

are tabulated in Tables 1.7 and 1.8 for worldwide and U.S. estimates, respectively. We see several similarities to CO emissions with automotive emissions providing the major single source of hydrocarbons. The major stationary sources of hydrocarbon emissions both worldwide and U.S. are fossil fuel combustion, solid waste disposal, organic solvent evaporation, and industrial processes.

Table 1.7
Worldwide Hydrocarbon Emissions for 1967*

Source	Hydrocarbon Emissions	
	10 ⁶ tons/year	% of Total
Coal		
Power	0.2	0.2
Industrial	0.7	0.8
Domestic and Commercial	2.0	2.3
Petroleum		
Refining	6.3	7.1
Gasoline	34.0	38.4
Fuel Oil	0.1	0.1
Residual Oil	0.2	0.2
Evaporative and Transfer Losses	7.8	8.8
Miscellaneous		
Solvents	10.0	11.3
Incineration	25.0	28.2
Wood (Fuel)	0.7	0.8
Forest Fires	1.2	1.4
	88.2	100.0

*Taken from Robinson and Robbins [1].

1.6. HYDROGEN SULFIDE

Hydrogen sulfide is produced from anerobic oxidation of decaying organic matter. Robinson and Robbins [1] attribute the major source of hydrogen sulfide evolution to biological decay

Table 1.8

Estimates of U.S. Hydrocarbon Emissions by Source Category, 1968*

<i>Source</i>	<i>Hydrocarbon Emissions</i>	
	<i>10⁶ tons/year</i>	<i>% of Total</i>
Transportation	16.6	51.9
Motor Vehicles	15.6	48.7
Gasoline	15.2	47.5
Diesel	0.4	1.2
Aircraft	0.3	1.0
Railroads	0.3	1.0
Vessels	0.1	0.2
Other Nonhighway Use of Motor Fuels	0.3	1.0
Fuel Combustion in Stationary Sources	0.7	2.2
Coal	0.2	0.7
Fuel Oil	0.1	0.3
Natural Gas	N	N
Wood	0.4	1.2
Industrial Processes	4.6	14.4
Solid Waste Disposal	1.6	5.0
Miscellaneous	8.5	26.5
Forest Fires	2.2	6.9
Structural Fires	0.1	0.2
Coal Refuse	0.2	0.6
Organic Solvent Evaporation	3.1	9.7
Gasoline Marketing	1.2	3.8
Agricultural Burning	1.7	5.3
Total	32.0	100.0

*Taken from "Air Quality Criteria for Hydrocarbons" [9]

in the ocean and on land. The former source produces 30 million tons annually and the latter source emits 70 million tons annually. Industrial sources such as kraft mills and refining yield the relatively minor contribution of 3 tons per year.

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